



Seasonal and diurnal variations of BTEX compounds in the semi-urban environment of Orleans, France



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HIGHLIGHTS

- The ambient levels and possible source of atmospheric BTEX in Orleans are reported for the first time.
- The order of the seasonal variation of the mean BTEX concentration was: winter > spring > autumn > summer.
- Vehicular exhaust might be the primary source of BTEX.
- There was an irregular emission source of benzene other than traffic-related emissions.

GRAPHICAL ABSTRACT



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ABSTRACT

Atmospheric concentrations of BTEX (benzene, toluene, ethylbenzene and xylene) were measured at a semi-urban site in Orleans, France, from October 2010 to August 2011. Air samples were collected by multi-bed adsorbent tubes. The BTEX concentrations were determined by thermal desorption–gas chromatography–mass spectrometry detector (TD–GC–MSD) technique. The average concentrations of the total measured BTEX during spring, summer, autumn and winter were 724.2, 337.4, 682.3, 823.0 ppt, respectively. Maximal values for their diurnal variations usually happened during rush hours in the morning and late afternoon, and the minimal values in the daytime usually happened in around noontime. The diurnal variation of BTEX in four seasons and the correlations between BTEX and NO indicated that vehicular exhaust might be the primary source of BTEX. Benzene was found in relatively high levels and the B/T ratio was significant high in spring, indicating an irregular emission source of benzene other than traffic-related emissions.

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1. Introduction

In semi-urban areas, atmospheric VOCs are from both anthropogenic and biogenic emissions. Major anthropogenic sources include vehicle

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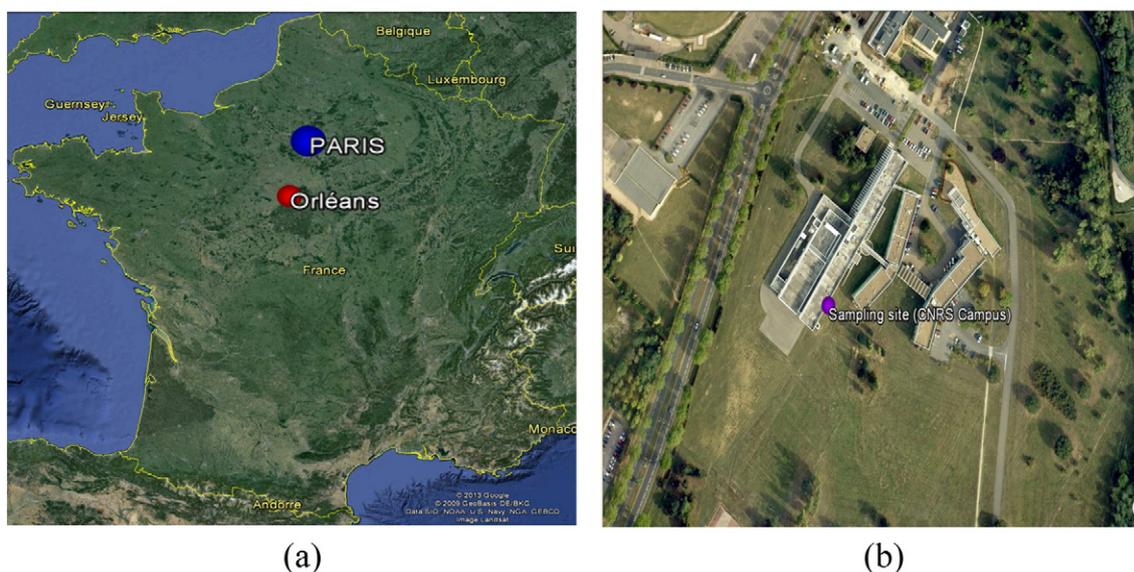


Fig. 1. The sketch map of sampling site. (a) The location of Orleans in France. (b) The sampling sites in CNRS-campus.

exhausts, gasoline evaporation, solvent use, natural gas emissions, and industrial processes (Friedrich and Obermeier, 1999). Among them, most of the aromatic compounds are listed as toxic air contaminants (e.g. benzene) or potential toxic air contaminants (e.g. toluene, xylenes) (Hanson, 1996). During daytime hours, once released into the atmosphere, aromatic components undergo OH oxidation, and thus participate in the formation of urban and suburban photochemical smog. Aromatic compounds are also the important precursors for the formation of secondary organic aerosols (e.g. Grosjean, 1992; Odum et al., 1997; Wang et al., 2002; Na et al., 2003; Barletta et al., 2008; Xie et al., 2008; Henze et al., 2008). In many nations, there have been various studies about ambient concentrations of the aromatic hydrocarbons to evaluate their impacts of on air quality (Grosjean, 1992; Bowman et al., 1995; Brocco et al., 1997; Fraser et al., 1998; Grosjean et al., 1999; Skov et al., 2001; Ho et al., 2004; Liu et al., 2005; Song et al., 2007; Lu et al., 2007; Gros et al., 2007; Barletta et al., 2008; Xie et al., 2008). These measurements provide useful information about the spatial and temporal variations of these compounds, and the ratios of benzene/toluene (B/T) and ethylbenzene/*m,p*-xylene (E/X) are recognized as useful indicators of atmospheric photochemical activity as well as the sources origination etc. (Nelson and Quigley, 1983; Roberts et al., 1984; Nutmagul and Cronn, 1985). However, information on ambient levels of aromatic hydrocarbons in France is scarce and has only been focused on large urban areas like Paris (Gros et al., 2007).

In this study, benzene, toluene, ethylbenzene and xylene (BTEX) have been measured in the atmosphere of a semi-urban site in Orleans, France, from October 2010 to August 2011. The major objectives were to determine their levels and variation character as well as possible sources at the semi-urban site.

2. Experimental

2.1. Sampling site

The map given in Fig. 1 shows the Orleans city site where the measurements were performed. Orleans city (47° 59' 12" N, 01° 44' 54" E) is located in the central part of France. In this study, a semi-urban site was selected as the sampling site, and it is positioned within the CNRS-campus (Centre National de la Recherche Scientifique) about 9.6 km away from Orleans city center. The site is close to a forest belt and farm. Air sampling for carbonyls (Jiang et al., 2016) and BTEX was performed on a rooftop of the ICARE laboratory (about 10 m above ground) from October 2010 to July 2011. Representative sampling time was chosen in different seasons according to temperature and weather with sunny or cloudy day. The detailed meteorological conditions and sampling dates are listed in Table 1.

2.2. BTEX sampling and analysis

The whole method was based on EPA method TO-17 (US EPA, 1999). Sample collection was carried out on stainless-steel adsorbent tubes Air Toxics (Perkin-Elmer, USA) filled with a combination of 2 adsorbent beds, Carboxpack B and Carboxieve S-III, what makes these tubes selective to the sampling of a wide range of VOC, from C3 to C12. Prior to first use, purchased Air toxics tubes were conditioned for 30 min at 350 °C in a pure Helium flow of 50 mL min⁻¹. However, for second and subsequent uses, tubes were reconditioned in the same way, but for only for 15 min. We used the STS25 sampler (Sequential Tube Sampler, Perkin Elmer, USA) a transportable device that allows the automatic collection of 25 thermodesorption tubes. The flow rate and sampling

Table 1
Meteorological parameters in the sampling periods at the semi-urban site in Orléans, France.

Sampling seasons	Sampling date	Temperature (°C)	Pressure (hPa)	Wind speed (km/h)	Weather condition
Spring	19–29 April 2011	15.1 ± 5.55	1013.1 ± 3.08	9.62 ± 3.14	Cloudy, sunny
Summer	28 June–2 July 2011	20.56 ± 6.17	1021 ± 4.65	13.32 ± 4.67	Sunny
Autumn	5–7 October 2010	16.7 ± 2.54	1011.6 ± 3.74	11.54 ± 3.21	Sunny
Winter	17–21 January 2011	3.73 ± 3.7	1030.77 ± 3.83	19.48 ± 5.25	Cloudy, sunny

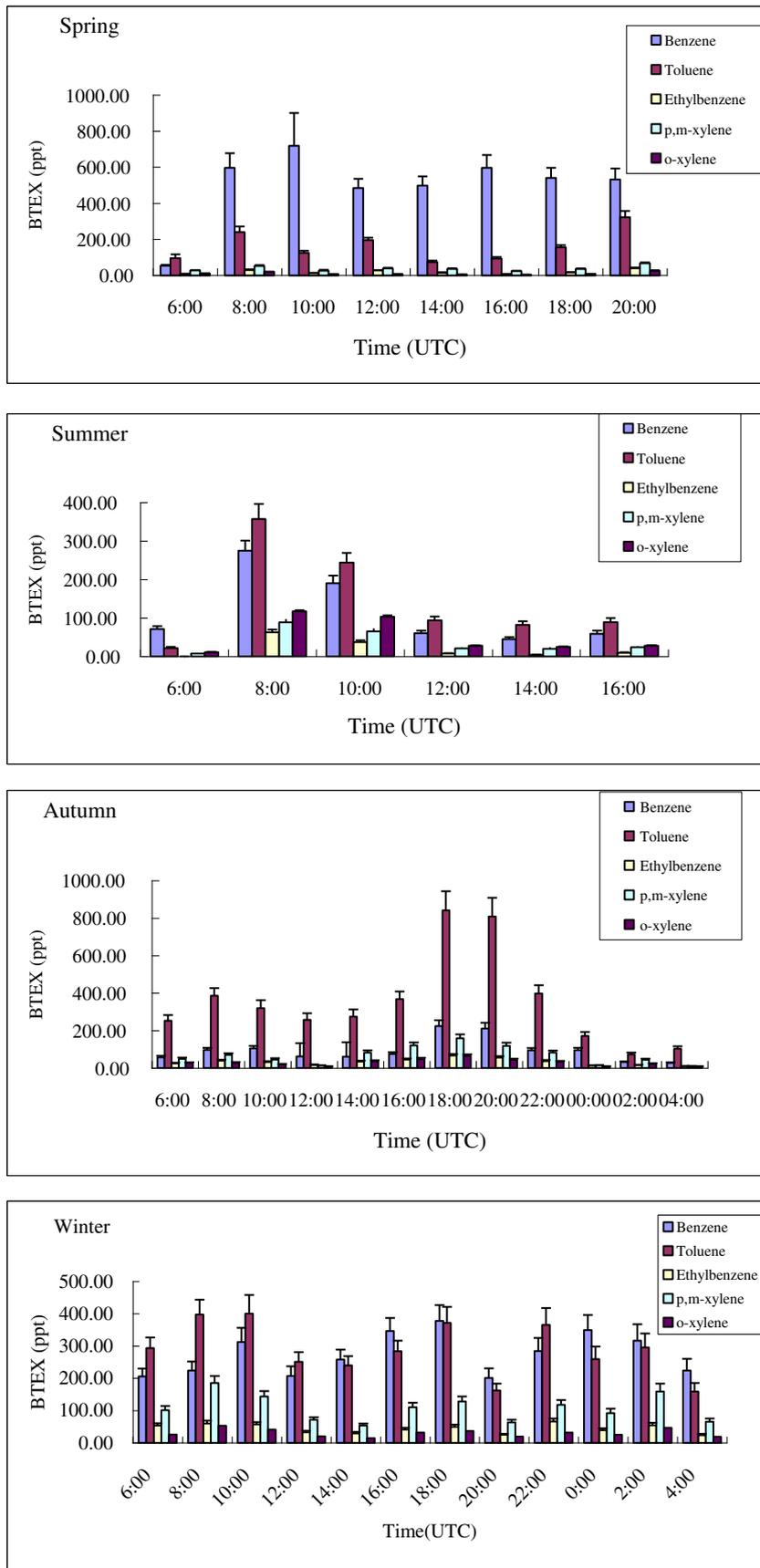


Fig. 2. Average daily variations of BTEX in each season in semi-urban site, Orleans.

Table 2
Average concentration (ppt) of BTEX in each season in semi-urban site, Orleans.

	Spring		Summer		Autumn		Winter	
	Mean \pm SD	Rang	Mean \pm SD	Rang	Mean \pm SD	Rang	Mean \pm SD	Rang
Sampling times	$n = 49$		$n = 30$		$n = 30$		$n = 56$	
Benzene	502.5 ± 629.2	16.8–2296	116.8 ± 153	16.6–674.4	111.21 ± 102.7	14.6–431.5	294.8 ± 170.1	49.8–1163.3
Toluene	156.0 ± 155.8	14–679.1	148.1 ± 159.1	15.1–595.7	420.14 ± 457.5	72.8–1887.1	326.02 ± 284.9	42.6–2007.2
Ethylbenzene	18.92 ± 23.1	2.5–100.6	20.2 ± 32.1	3.25–116.4	37.7 ± 37.4	6.3–143.1	48.1 ± 39.4	3.9–248.9
<i>m,p</i> -Xylene	37.3 ± 29.7	6.6–106.6	37.9 ± 42.6	5.3–187.2	80.1 ± 98.0	8–339	120.2 ± 120.1	3.78–801.5
<i>o</i> -Xylene	9.61 ± 10.6	3.1–47.5	14.3 ± 25.5	3.87–135.7	33.23 ± 36.3	5.2–134.6	34.0 ± 34.3	3.63–225.1
Total BTEX	724.2		337.4		682.3		823.0	

times were set to 100 mL min^{-1} and 2 h, respectively, which corresponds to the sampling of 12 L of air under standard conditions of temperature and pressure ($25 \text{ }^\circ\text{C}$ and $101,325 \text{ Pa}$). A digital flow meter (DEFENDER, Bios Corp., USA) was used to measure and control the sampling flow rate, which showed a very good stability over time with different batch tubes (variation lower than 2% between different adsorbent tubes for 48 h sampling), probably due to the use of a rugged flow-controlled sampling pump (LFS-113, Gilian, USA). At least one field blank should be used for each day of field sampling, shipped and analyzed with each group of samples. The field blank is treated identically to the samples except that no air is drawn through the tubes. Two field samples tubes were collocated with back-up tube to evaluate breakthrough. Recap the sampling tubes with Swagelok® fittings using PTFE ferrules and store them in a refrigerator for less than a week prior to analysis in laboratory.

The adsorbent tubes were analyzed with a thermal desorption instrument (TurboMatrix ATD 150 -Perkin Elmer) coupled with a gas chromatography and mass spectrometry detector (Clarus 600, Perkin Elmer). The tubes were thermally desorbed at $330 \text{ }^\circ\text{C}$ for 5 min onto a focusing tube named “cold trap” at a temperature of $-30 \text{ }^\circ\text{C}$. The second stage desorption, a flash heating ($40 \text{ }^\circ\text{C/s}$ to $350 \text{ }^\circ\text{C}$, and temperature hold for 10 min), focuses the analytes injection to the GC for better resolution. The transfer line (deactivated fused silica column) is heated at $225 \text{ }^\circ\text{C}$ and conducts to the GC oven which contains the analytical column ($30 \text{ m} \times 0.25 \text{ mm I.D.}$ and $0.25 \text{ }\mu\text{m}$ film thickness of 5%-diphenyl-95% methylpolysiloxane, Elite-5MS Perkin Elmer). The temperature program was initiated at $40 \text{ }^\circ\text{C}$ (15 min) with a ramp rate of $7 \text{ }^\circ\text{C min}^{-1}$ to $120 \text{ }^\circ\text{C}$ which was remained for 3 min. The head pressure of helium at 10.2 psi produced a carrier gas flow rate of approximately 1 mL min^{-1} . Quantification was achieved with six-point calibration using liquid standards in methanol solutions. Standard solutions were injected onto adsorbent tubes followed by a 50 mL min^{-1} nitrogen

flow for 5 min (temperature $80 \text{ }^\circ\text{C}$). Compounds were identified by their retention times and their mass spectra. *P*-xylene and *m*-xylene co-eluted in the GC columns in this study, and their concentrations were reported as their total as most of previous researches have done. The relative standard deviations (RSD) of each calibration level (10 replicates) did not exceed 7% for BTEX. The limits of detection (LOD) of BTEX were dependent upon the variability of the background contamination in each tube. The LOD of present study were found to range from 8.3 to 41.7 ng m^{-3} for various BTEX for 12 liters sampling volume.

O_3 was measured using a commercial UV photometric analyzer (Thermo Environmental Instruments (TEI), model 49C). NO_x (NO and NO_2) were detected using a chemiluminescence $\text{NO-NO}_2\text{-NO}_x$ analyzer (Thermo Electron Corporation, Model 42i trace level). Several meteorological parameters were monitored by an integrated sensor suite (Vantage Pro TM & Vantage Pro 2 Plus TM Weather Stations, Davis Instruments), including wind speed, temperature and relative humidity.

3. Results and discussion

3.1. Average diurnal variations of BTEX in each season

The average diurnal variations of BTEX in each season in semi-urban ambient site are presented in Fig. 2. Ambient BTEX concentrations are greatly influenced by many factors such as sources (mainly from vehicular exhaust, gasoline and solvent evaporation), and meteorological conditions, and their sinks. To some extent, the diurnal variation could reflect the influence of these multiple factors on the measured BTEX concentrations. It is evident that the measured BTEX exhibited distinct seasonal and diurnal variations.

The concentrations of BTEX in daytime were higher than those in nighttime. Maximal values usually happened during rush hours in the morning (8:00 h, Coordinated Universal time, UTC) and late afternoon

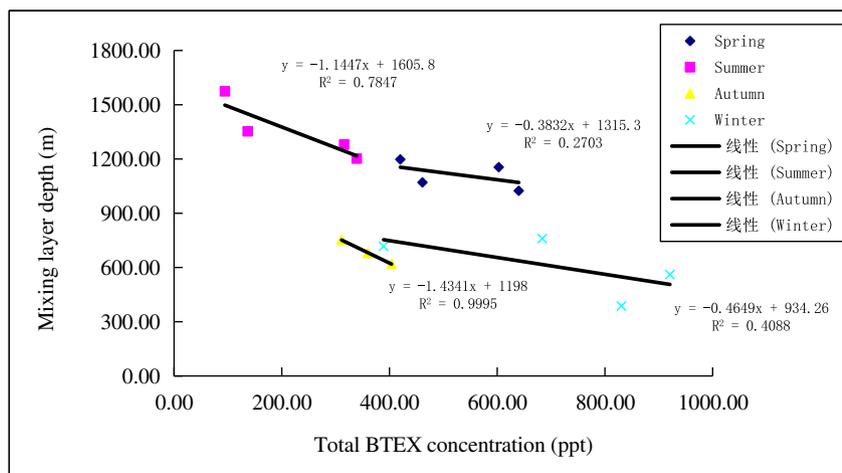


Fig. 3. The correlation between BTEX concentration and mixing layer depth at 12:00 (UTC) in each season in semi-urban site, Orleans from October 2010 to July 2011. The data of mixing layer depth obtained from the HYSPLIT website.

(18:00 h, UTC), which suggested that automobile exhaust was an important source for atmospheric BTEX in Orleans. The results were in agreement with Liu et al. (2009), Zhang et al. (2012), Na et al. (2003) and Ho et al. (2004). The minimal values in the daytime usually happened in around noontime (12:00–14:00 h, UTC), which was probably due to the relative low traffic flow, the meteorological condition (such as the elevation of the boundary layer etc.), and the photochemical consumption of BTEX etc. However, high BTEX concentration was also observed during 22:00–2:00 in winter, it indicates there must be some other sources of BTEX in Orleans.

The ranges and arithmetic mean concentrations of BTEX in each season are listed in Table 2. In general, the mean concentrations of BTEX were very low. The order of the seasonal variation of the mean BTEX concentration was: winter (823 ppt) > spring (724 ppt) > autumn (682 ppt) > summer (337 ppt). Besides sources' strength, the seasonal and diurnal variations of atmospheric BTEX in urban areas also strongly depend on meteorological conditions and photochemical activity. The frequent inverse temperature layer during winter season hindered the dilution of the pollutants, and thus led to higher concentrations of BTEX in the atmosphere. Strong photochemical activity and dilution due to the increase in the mixing layer depth in summer (Fig. 3) accounted for the low concentration of the observed BTEX. The concentration of benzene in spring was very high and SD was also very high, meaning an irregular emission source of benzene in the season, as mentioned in Section 3.3.

3.2. The correlations among BTEX and other parameters

Correlation analysis among different pollutants can provide useful information about the sources origination, the correlations among the BTEX, O₃, NO, NO₂ and meteorological factors in summer were analyzed (Table 3). Ethylbenzene and *m,p*-xylenes had the highest correlation coefficient of 0.986, suggesting that they came from the same sources. In urban air, BTEX, especially ethylbenzene and xylenes, are typically related to emissions from gasoline vehicles and gasoline stations (Cohen et al., 1991; Jose et al., 1998). Significant positive correlations among the BTEX and NO were also found, but no significant correlations among BTEX, O₃ and meteorological factors. Because NO is usually considered as a typical indicator for the vehicle exhaust in urban areas, the good mutual correlations between each BTEX compound and NO suggested traffic emission was the dominant sources of the atmospheric BTEX in Orleans. Careful examination revealed that benzene showed lower correlation with NO with a significance level of 0.05 compared with TEX. Moreover, benzene was found in relatively high levels in two samples collected the same day at one site, indicating an irregular emission source of benzene other than traffic-related emissions.

3.3. The ratios among BTEX

The ratio of benzene to toluene (B/T) has been widely used as an indicator for distinguishing their various sources from vehicle emission.

Table 4

Comparison of Benzene/Toluene (B/T) and Ethylbenzene/*m* + *p*-Xylene (E/X) concentration ratios (ppb/ppb) in Orleans and in other areas.

Locations	B/T	E/X	Reference
Orleans, France (Autumn)	0.26	0.47	This work
Orleans, France (Winter)	0.90	0.40	This work
Orleans, France (Spring)	3.09	0.51	This work
Orleans, France (Summer)	0.79	0.53	This work
Guangzhou	0.35	0.81	Barletta et al. (2008)
Hong Kong	0.13	0.80	Ho et al. (2004)
Helsinki	0.36	0.36	Hellén et al. (2003)
Munich	0.53	0.41	Rappenglück and Fabian (1999)
St. Louis	0.93	0.60	Singh et al. (1985)
Paris	0.15	0.32	Gros et al. (2007)
London	0.65	0.29	Derwent et al. (1995)
Seoul	0.13	0.49	Na et al. (2003)
Beijing	0.71	0.55	Liu et al. (2009)
Beijing	0.87	0.70	Xie et al. (2008)

Benzene and toluene have been shown to be emitted by automobiles in a ratio of approximately 0.50 (Perry and Gee, 1995; Brocco et al., 1997; Monod et al., 2001; Barletta et al., 2005) depending on the motor type and the technology applied (Gros et al., 2007). The average ratios of B/T measured in Orleans autumn, winter and summer were 0.26, 0.90 and 0.79, respectively. These values were within the reported range (0.13–0.93) (as shown in Table 4), and close to 0.5, indicating vehicular emission as the main source of benzene and toluene in Orleans in seasons other than spring. Compared with autumn, winter and summer, the B/T ratio was significant high in spring of 3.09. Although either reduced toluene or enhanced benzene can lead to a high B/T ratio, the abundance of benzene in spring (Table 2) suggests that high ratio was caused by additional sources of benzene.

The ratio of ethylbenzene/*m,p*-Xylene (E/X) is usually used as the photochemical reactivity indicator, because the rate constant of *m,p*-Xylene with OH radicals is faster than that of ethylbenzene (Atkinson, 1990). The average ratios of E/X measured in Orleans autumn, winter, spring and summer were 0.47, 0.40, 0.51 and 0.53, respectively, which were similar to the ratio of B/T. These values were within the reported range (Table 4). The E/X ratio obtained in winter was the lowest, and the E/X ratio obtained in summer was the highest, because there was stronger photochemical activity in summer than in winter and the rate constants (K_{OH}) for the gas-phase reaction of OH radical with ethylbenzene, *m*-xylene and *p*-xylene are 7.1×10^{-12} , 23.6×10^{-12} and $14.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively (Yassaa et al., 2006). The distinct diurnal variations of E/X ratio (Fig. 4) evidently revealed that E/X ratio had a peak value at noon, which suggested the contribution of photochemical reactions to E/X ratio, due to the higher OH radical concentration, sunlight and higher temperature at noon.

Table 3

Correlation coefficients between BTEX, O₃, NO, NO₂ and meteorology factors in Orleans semi-urban ambient air in summer, 2011 (N = 30).

	1	2	3	4	5	6	7	8	9	10	11
Benzene (1)	1										
Toluene (2)	0.823**	1									
Ethylbenzene (3)	0.67**	0.875**	1								
<i>m,p</i> -Xylene (4)	0.609**	0.832**	0.986**	1							
<i>o</i> -Xylene (5)	0.453*	0.607**	0.845**	0.898**	1						
O ₃ (6)	−0.349	−0.265	−0.311	−0.272	−0.285	1					
NO (7)	0.442*	0.479**	0.573**	0.57*	0.472**	−0.667**	1				
NO ₂ (8)	0.358	0.274	0.397*	0.363*	0.327	−0.737**	0.842**	1			
Humidity (9)	0.297	0.213	0.257	0.192	0.156	−0.899**	0.568**	0.727**	1		
Temperature (10)	−0.172	−0.08	−0.135	−0.075	−0.056	0.851**	−0.457*	−0.588**	−0.915**	1	
Wind (11)	−0.068	0.124	−0.026	−0.015	−0.074	0.264	−0.249	−0.35	−0.27	0.214	1

** Correlation is significant at the 0.01 levels.

* Correlation is significant at the 0.05 levels.

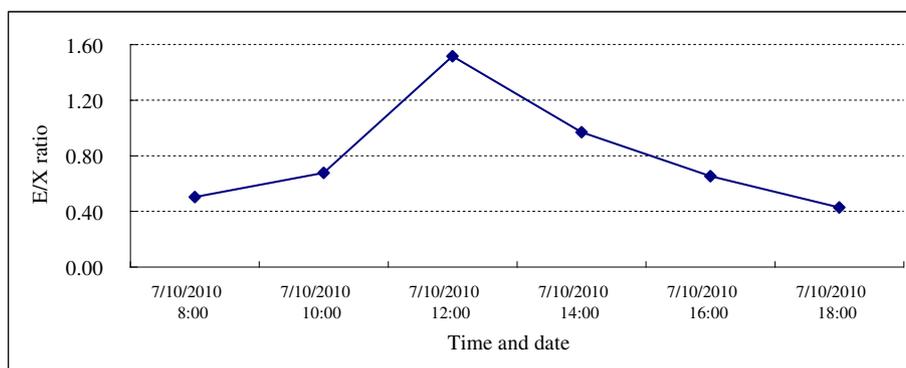


Fig. 4. Diurnal concentration ratio variations of Ethylbenzene/*m* + *p*-Xylene (E/X) measured on 7 October 2010, in Orleans semi-urban ambient air.

4. Conclusions

The ambient levels and possible source of atmospheric BTEX in Orleans are reported for the first time in this study. In general, the mean concentrations of BTEX were very low. The diurnal variation of BTEX in four seasons and the correlations between BTEX and NO indicated that vehicular exhaust might be the primary source of BTEX. The order of the seasonal variation of the mean BTEX concentration was: winter > spring > autumn > summer, suggesting that besides sources' strength, the seasonal and diurnal variations of atmospheric BTEX in urban areas also strongly depend on meteorological conditions and photochemical activity. Benzene was found in relatively high levels and the B/T ratio was significant high in spring, indicating an irregular emission source of benzene other than traffic-related emissions. The distinct diurnal variations of E/X ratio evidently revealed that the contribution of photochemical reactions to E/X ratio.

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References

Atkinson, R., 1990. Gas-phase tropospheric chemistry of organic chemistry: a review. *Atmos. Environ.* 24A, 1–41.

Barletta, B., Meinardi, S., Rowland, F.S., Chan, C.Y., Wang, X.M., Zou, S.C., 2005. Volatile organic compounds in 43 Chinese cities. *Atmos. Environ.* 39, 5979–5990.

Barletta, B., Meinardi, S., Simpson, I.J., Zou, S.C., Rowland, F.S., Blake, D.R., 2008. Ambient mixing ratios of nonmethane hydrocarbons (NMHCs) in two major urban centers of the Pearl River Delta (PRD) region: Guangzhou and Dongguan. *Atmos. Environ.* 42, 4393–4408.

Bowman, F.M., Pilinis, C., Seinfeld, J.H., 1995. Ozone and aerosol productivity of reactive organics. *Atmos. Environ.* 29, 579–589.

Brocco, D., Fratracangeli, R., Lepore, L., Lepore, L., Petricea, M., Ventrone, I., 1997. Determination of aromatic hydrocarbons in urban air Rome. *Atmos. Environ.* 31, 557–566.

Cohen, M.A., Ryan, P.B., Spengler, J.D., Ozkaynak, H., Hayes, C., 1991. Source-receptor study of volatile organic compounds and particulate matter in the Kanawha Valley-II. Analysis of factors contributing to VOC and particle exposures. *Atmos. Environ.* 25B, 95–107.

Derwent, R.G., Middleton, D.R., Field, R.A., Goldstone, M.E., Lester, J.N., Perry, R., 1995. Analysis and interpretation of air quality data from an urban roadside location in Central London over the period from July 1991 to July 1992. *Atmos. Environ.* 29, 923–946.

Fraser, M.P., Cass, G.R., Simoneit, B.R.T., Rasmussen, R.A., 1998. Air quality model evaluation data for organics. 5. C₆–C₂₂ nonpolar and semipolar aromatic compounds. *Environ. Sci. Technol.* 32, 1760–1770.

Friedrich, R., Obermeier, A., 1999. Anthropogenic emissions of VOCs. In: Hewitt, C.N. (Ed.), *Reactive Hydrocarbons in the Atmosphere*. Academic Press, San Diego, CA, pp. 1–39.

Gros, V., Sciare, J., Yu, T., 2007. Air-quality measurements in megacities: focus on gaseous organic and particulate pollutants and comparison between two contrasted cities, Paris and Beijing. *Compt. Rendus Geosci.* 339, 764–774.

Grosjean, D., 1992. In situ organic aerosol formation during a smog episode: estimated production and chemical functionality. *Atmos. Environ.* 26A, 953–963.

Grosjean, E., Rasmussen, R.A., Grosjean, D., 1999. Toxic air contaminants in Porto Alegre, Brazil. *Environ. Sci. Technol.* 33, 1970–1978.

Hanson, D.J., 1996. Toxics release inventory report shows chemical emissions continuing to fall. *Chem. Eng. News* July 15, 29–30.

Hellén, H., Hakola, H., Laurila, T., 2003. Determination of source contributions of NMHCs in Helsinki (60°N, 25°E) using chemical mass balance and the Unmix multivariate receptor models. *Atmos. Environ.* 37, 1413–1424.

Henze, D.K., Seinfeld, J.H., Ng, N.L., Kroll, J.H., Fu, T.M., Jacob, D.J., 2008. Global modeling of secondary organic aerosol formation from aromatic hydrocarbons: high- vs. low-yield pathways. *Atmos. Chem. Phys.* 8, 2405–2421.

Ho, K.F., Lee, S.C., Guo, H., Tsai, W.Y., 2004. Seasonal and diurnal variations of volatile organic compounds (VOCs) in the atmosphere of Hong Kong. *Sci. Total Environ.* 322, 155–166.

Jiang, Z.H., Grosselin, B., Daële, V., Mellouki, A., Mu, Y.J., 2016. Seasonal, diurnal and nocturnal variations of carbonyl compounds in the semi-urban environment of Orleans, France. *J. Environ. Sci.* 40, 84–91.

Jose, M.B., Rose, D., Josep, C., 1998. Applying receptor models to analyze urban/suburban VOCs air quality in Martorell (Spain). *Environ. Sci. Technol.* 32, 405–412.

Liu, Y., Shao, M., Zhang, J., Fu, L., Lu, S., 2005. Distributions and source apportionment of ambient volatile organic compounds in Beijing city, China. *J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng.* 40, 1843–1860.

Liu, J.F., Mu, Y.J., Zhang, Y.J., Zhang, Z.M., Wang, X.K., 2009. Atmospheric levels of BTEX compounds during the 2008 Olympic Games in the urban area of Beijing. *Sci. Total Environ.* 408, 109–116.

Lu, S.H., Liu, Y., Shao, M., Huang, S., 2007. Chemical speciation and anthropogenic sources of ambient volatile organic compounds (VOCs) during summer in Beijing, 2004. *Front. Environ. Sci. Eng. China* 1, 147–152.

Monod, A., Sive, B.C., Avino, P., Chen, T., Blake, D.R., Rowland, F.S., 2001. Monoaromatic compounds in ambient air of various cities: a focus on correlations between the xylenes and ethylbenzene. *Atmos. Environ.* 35, 135–149.

Na, K., Kim, Y.P., Moon, K.C., 2003. Diurnal characteristics of volatile organic compounds in the Seoul atmosphere. *Atmos. Environ.* 37, 733–742.

Nelson, P.F., Quigley, S.M., 1983. The *m*, *p*-xylenes: ethylbenzene ratio, a technique for estimating hydrocarbon age in ambient atmospheres. *Atmos. Environ.* 17, 659–662.

Nutmagul, W., Cronn, D.R., 1985. Determination of selected atmospheric aromatic hydrocarbons at remote continental and oceanic locations using photoionization/flame-ionization detection. *J. Atmos. Chem.* 2, 415–433.

Odum, J.R., Jungkamp, T.P.W., Griffin, R.J., Forstner, H.J.L., Flagan, R.C., Seinfeld, J.H., 1997. Aromatics, reformulated gasoline and atmospheric organic aerosol formation. *Environ. Sci. Technol.* 31, 1890–1897.

Perry, R., Gee, I.L., 1995. Vehicle emissions in relation to fuel composition. *Sci. Total Environ.* 169, 149–156.

Rappenglück, B., Fabian, P., 1999. Nonmethane hydrocarbons (NMHC) in the Greater Munich Area/Germany. *Atmos. Environ.* 33, 3843–3857.

Roberts, J.M., Fehsenfeld, F.C., Liu, S.C., Bollinger, M.J., Hahn, C., Albritton, D.L., 1984. Measurements of aromatic hydrocarbon ratios and NO_x concentrations in the rural troposphere: observation of air mass photochemical aging and NO_x removal. *Atmos. Environ.* 18, 2421–2432.

Singh, H.B., Salas, J.L., Cantrell, B.K., Redmond, R.M., 1985. Distribution of aromatic hydrocarbons in the ambient air. *Atmos. Environ.* 11, 1911–1919.

Skov, H., Hansen, A.B., Lorenzen, G., Andersen, H.V., Lffstrfm, P., Christensen, C.S., 2001. Benzene exposure and the effect of traffic pollution in Copenhagen, Denmark. *Atmos. Environ.* 35, 2463–2471.

Song, Y., Shao, M., Liu, Y., Lu, S.H., Kuster, W., Goldan, P., 2007. Source apportionment of ambient volatile organic compounds in Beijing. *Environ. Sci. Technol.* 41 (12), 4348–4353.

US EPA (US Environmental Protection Agency), 1999. Method TO-17. Determination of volatile organic compounds in ambient air using active sampling onto sorbent tubes. Research Triangle Park, NC, USA.

Wang, X.M., Sheng, G.Y., Fu, J.M., Chan, C.Y., Lee, S.C., Chan, L.Y., 2002. Urban roadside aromatic hydrocarbons in three cities of the Pearl River Delta, People's Republic of China. *Atmos. Environ.* 36 (33), 5141–5148.

Xie, X., Shao, M., Liu, Y., Lu, S.H., Chang, C.C., Chen, Z.M., 2008. Estimate of initial isoprene contribution to ozone formation potential in Beijing, China. *Atmos. Environ.* 42, 6000–6010.

Yassaa, N., Brancaloni, E., Frattoni, M., Ciccioli, P., 2006. Isomeric analysis of BTEXs in the atmosphere using β-cyclodextrin capillary chromatography coupled with thermal desorption and mass spectrometry. *Chemosphere* 63, 502–508.

Zhang, Y.J., Mu, Y.J., Liu, J.F., Mellouki, A., 2012. Levels, sources and health risks of carbonyls and BTEX in the ambient air of Beijing, China. *J. Environ. Sci.* 24, 124–130.