Characterization of volatile organic compounds in the urban area of Beijing from 2000 to 2007

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Abstract

Beijing is one of the most polluted cities in the world. In this study, the long-term and continuous measurements of volatile organic compounds (VOCs) in the urban area of Beijing, specifically at Beijing 325 m Meteorological Tower, were conducted from 2000 to 2007. The annual record of VOC trends exhibited in two different phases was separated in 2003. Records show that VOC concentrations increased from 2000 to 2003 due to the abrupt increase in vehicle number. Contrarily, since 2003, there had been a decrease in VOCs concentrations as the policy on gasoline and air pollution was implemented. Toluene, benzene, and i-pentane are the chemicals that abound in and are directly related to vehicle activity, such as in vehicle exhaust and gasoline evaporation. Furthermore, records indicate that there had been seasonal variation in VOCs levels in that VOCs level in summer is higher than that in winter. As such, temperature is considered to significantly contribute to VOCs in Beijing. Records also show that VOCs level was high in the morning and during rush hours in the evening. In contrast, VOCs level was low during midday due to photochemical destruction with OH radical and dilution effect. In this study, a particular benzene to toluene ratio range (0.4–1.0) was used as the indicator of air propelled by vehicular exhaust. We also applied the correlation coefficients between BTEX and i-pentane to evaluate evaporation influence to ambient BTEX in the Beijing urban area.

Key words: VOCs; air pollution; continuous measurements; variations; BTEX; benzene to toluene ratio

DOI: 10.1016/S1001-0742(11)60732-8

Introduction

Volatile organic compounds (VOCs) significantly contribute to the photochemical reactions in the atmosphere. Their reaction with NOx in the presence of sunlight generates secondary pollutants and photochemical smog such as OH radical and ozone (Atkinson, 2000). Moreover, most aromatic compounds (except benzene) break down into fine particles and form secondary organic aerosols. Halocarbons also release the Cl atom, which can harm the ozone in the stratosphere (Molina and Rowland, 1974).

VOCs in the atmosphere are emitted by various sources. Such sources can either be mobile or stationary, and examples of which are vehicle exhaust, gasoline evaporation, solvent usage, industrial emission, and combustion (Na et al., 2004). Similarly, biogenic emission from vegetables, like isoprene, can not remain negligible. Isoprene is considered to be the most abundant compound emitted from vegetables and records an annual emission of approximately 500–750 Tg depending on the leading variables (Guenther et al., 2006). However, in urban areas, biogenic VOCs are recorded to have minimal contribution compared with anthropogenic VOCs emissions.

Beijing is the capital city of China and is one of the biggest cities in the country. It spans 16,410 km^2 and

contains more than 15.8 million inhabitants. Located in the northern part of the North China Plain, Beijing is surrounded by mountains at the north, west, and northeast, while on its southeast is a plain facing the Bohai Sea. During summer monsoon season, the mountains are faced with amassing air pollutants. In the same way, three populated, urbanized, and industrialized provinces surrounding Beijing–Hebei, Shangdong, and Shanxi–contribute to the increasing pollution as the pollutant emissions from these provinces are carried to the city by prevailing winds (Streets et al., 2007).

Beijing has experienced rapid economic growth in the past two decades. The city's GDP increased from 28.49 billion CNY in 1986 to 787 billion CNY at the end of 2006. As such, vehicle population also increased, with the number of vehicles reaching 2.75 million in 2006 (Beijing Municipal Bureau of Statistics, 2007). Consequently, air pollution, which is basically caused by the two principal pollutants in the air such as ozone and particulate matter (PM), has become a very important issue in Beijing. To reduce the ozone in urban areas, VOCs are considered as one of the important precursors in a typical urban VOC-sensitive area (Sillman, 1999). Although Beijing is considered as one of the most polluted cities in the world, its air quality was somehow improved in recent years. In reference to the national air quality grade II standard,

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the attainment days has increased from 177 days in 2000 to 246 days in 2007 (Beijing Environmental Protection Bureau, 2007).

Furthermore, there have been a number of publication that focused on air pollution in the Beijing urban area, but most of these concentrated on atmospheric aerosols only (Chan and Yao, 2008; Okuda et al., 2008). Only a few reports about surrounding VOCs in Beijing's urban area were published until recent years. For instance, Barletta et al. (2005) measured C2–C10 non-methane hydrocarbons (NMHCs) in the urban atmospheres of 43 different cities in China, but among the samples, only two ambient samples and one roadside sample were collected in Beijing. Liu et al. (2005) also investigated the temporal and spatial variations and sources of VOCs in the six monitoring sites in Beijing. Additionally, in 2008, the study of Song et al. (2008) and Duan et al. (2008) measured the NMHCs in different university campuses in August 2005 and 2006 during the ozone episode, respectively. To date, however, there have been no comprehensive reports on long-term VOC monitoring. This is despite the fact that long-term and continuous measurements of VOCs are necessary in order to estimate the impact of population explosion and extensive vehicle activity. The measurements should also be done to evaluate the effect of the atmospheric pollutant policy implemented by the Beijing municipal government. The Beijing government has been carrying out a series of measures since 1998 to ensure that air pollution be lessened and controlled as 2008 Olympic Games held in Beijing. However, despite the measures to control emission sources, in recent years, there are still no regulations for VOCs in China (except for some toxic hazards pollutants only in the workplace). For this reason, this research is conducted to discuss the characteristics and trends of VOCs in Beijing from the period of 2000 to 2007.

1 Experiments

1.1 Site description

We determined the measurements from our observations of air pollutant in the 325 m Beijing Meteorological Tower in the Institute of Atmospheric Physics of the Chinese Academy of Sciences. The tower is located at the north of Beijing at about 2 km away southwest of the Olympic Sports Centre. The sampling site, surrounded by residential areas, is between the 3rd and 4th ring roads of the city and approximately 1 km away from a highway. No direct industrial sources of atmospheric pollutants are located near the site. Therefore, this sampling site can represent Beijing urban ambient atmosphere. In addition, the height of the tower is advantageous in monitoring atmospheric pollution.

1.2 Sampling and analysis

Since year 2000, the ambient air samples were collected at 14:00 every Thursday, excluding strong wind and rain, using a Teflon tube (OD: 1/4″). The sample inlet was placed at the third floor of the tower (32 m above the ground). The collected air samples were drawn using a bypass pump (GAST Inc., USA), and then pressurized into a 1-L pre-cleaned and evacuated electropolished canister at a flow rate of 3 L/min. Prior to the sampling, the pump was turned on to draw ambient air and clear it in the tube for 3 min. A stainless steel bellows valve (Swagelok Inc., USA) of each canister was opened to be filled with air until the pressure reached 60 psi each. To avoid leakage and contamination, an identical sample was collected. The intensive daily collection of samples was done once a month in 2005 and 2006 when the weather was fair (that is, the day is sunny, and the wind speed les than 3.0 m/sec). During the sampling period, the automatic accumulative sampling system (custom manufactured by IAP) was used. There were 12 samples collected every time and the procedure started at 00:00 with 2 hr interval.

The details of the analytical procedure have been reported by Mao et al. (2008); nonetheless, minor differences in some parameters were considered in this study. The procedure is presented as follows. Based on EPA method TO-14, air sample was measured using a three-stage pre-concentration (7100A concentrator, Entech Inc., USA), followed by GC-MS analysis (Finnigan trace 2000-DSQ, Thermo Inc., USA). Air sample of 500 mL was drawn into the first cold trap at 150 mL/min using a vacuum pump. The VOCs and other trace gases were frozen at the glass beads in the trap at –16°C using liquid nitrogen. The other trace gases such as nitrogen and oxygen that have a boiling point lower than –165°C were removed. Next, the trap was heated at 20°C, and the frozen samples were transferred into the second trap filled with Tenax at –50°C at a flow rate of 10 mL/min for 4 min. The condensed water was left in the first trap, and the unadsorbed CO_2 passed through the Tenax trap at the same temperature. After the third trap was cooled at –150°C, the second trap was heated at 180°C and the VOCs components were transferred into the next trap for 4 min. Finally, the desorbed compounds were cryo-focused on the top of the column (third trap) and were thermally removed at 60°C using the heated nitrogen gas which could be adequate for the entire desorption of the VOCs and their infusion to the GC/MS column.

The chromatographic conditions are as follows: a DB-5MS fused-silica capillary column (60 m × 0.25 mm × 0.25 μm, Agilent Technologies Inc., USA) was used with GC temperature program: –35 to 15°C (5 min), –35 to 35°C at a rate of 15 °C/min, 35°C (1 min), 35–250°C at a rate of 10 °C/min. The carrier gas was heliumat at a constant pressure of 137 kPa. Mass range m/z from 20 to 200 was used for quantitative determination with full scan mode. The source temperature was 200°C. The electron multiplier voltage was 1187 eV (autotune).

1.3 Quality control

Each target compound was identified by its retention time and fragmentation pattern. The quantification of target VOCs was accomplished using multi-point external standard curves and modified using relative response factors. The calibration curves were prepared using 100 ppb external standard gases (Scott Specialty, TO14 standard;

alkane and alkene) and 100 ppb internal standard gases of dibromomethane at five different diluted concentrations plus N_2 (0–100 ppb). Internal standard gas was added to each sample to trace the instrument change. Five sets of duplicate samples were collected to check the precision and reliability of the sampling and analyzing method. It was found that the relative standard deviation was better than 8% for the target compounds in all five duplicates and the method detection limit of the VOCs ranges from 7 to 40 ppt for all measured VOCs.

2 Results and discussion

2.1 General characterizations

Figure 1 summarizes the average mixing ratios and standard derivations of the total VOCs measured from 2000 to 2007. It can be noted that it was only in 2003 the average mixing ratios of the total VOCs exceeded 200 ppbC as the concentration recorded was 262.6 ppbC. The annual variations in total VOCs from 2000 to 2007 have two different trends particularly evident in 2003. From 2000 to 2002, the VOCs demonstrated an increasing trend with 12.4 ppbC per year and peaked in 2003, but the mixing ratios of VOCs illustrated a decreasing trend since 2003. Similarly, in 2006 and 2007, an instant decrease of 26.5% in the concentration was recorded. These two different trends could be explained by increase in the number of vehicles as well as the implementation of air pollution control policies. The vehicle population in Beijing has been steadily increasing, and the average rate of vehicle population increase per year was about 11.5% since 1997 (Hao and Wang, 2005). Moreover, in 2003, the increase rate of motor vehicle population reached 20.5%. Since 2004 the Beijing municipal government began the implementation of the 11th comprehensive control measures, along with the introduction to the city of the Euro-III standard for gasoline and diesel. In addition, about 3800 buses and 20,000 old taxies were updated in 2005. Although the number of motor vehicles are increasing, the concentration of VOC decreased and gradually stabilized. Meanwhile, the decreasing level of VOCs in 2006 and

2007 is directly related to the implementation of the atmospheric pollution control policy in Beijing. On the contrary, Tang et al. (2008) attributed the increase in VOC emissions from vehicular exhaust not to the number of vehicles but to the strict compliance to emission standards and to improved road conditions. On the contrary, Tang et al. (2008) attributed the increase in VOC emissions from vehicular exhaust not to the number of vehicles but to the strict compliance to emission standards and to improved road conditions.

As illustrated in Fig. 1, VOCs in summer and fall increased dramatically from 2000 to 2003, and then decreased from 2004 to 2007. Such VOC variations in summer and fall are recorded to have the largest contribution to the atmospheric VOC level in Beijing. During winter and spring, VOCs are recorded to have minimal difference in each year.

Moreover, the fractional contribution of the four different classes of compounds remains analogous from 2000 to 2007. In addition, alkanes were found to be the dominant components in all years except in 2003 when it has about 31% to 60% of all VOCs quantified on the ppbC basis. The aromatic compounds fraction was moderately constant at about 35% of the VOC concentrations, while alkenes and halogenated VOCs shared the other fraction. Similarly, in 2006, the northwest part of Beijing recorded the presence of 55% alkanes, 29% aromatic hydrocarbons, and 13% alkenes (Duan et al., 2008).

Among identified compounds, toluene is recorded the highest with an average mixing ratio of 18.3 ppbC, followed by benzene with 17.3 ppbC, and *i*-pentane with 16.2 ppbC. As such, these compounds are mainly attributed to vehicular exhaust and gasoline evaporation. Furthermore, the *i*-pentane compound is the prevalent compound in gasoline evaporation, while benzene and toluene exist in vehicular exhaust and gasoline evaporation. Thus, on-road vehicles were estimated to constitute approximately 60% of benzene emissions (Austin, 2003). In the urban area of Beijing, VOCs emission from vehicle-related sources such as gasoline evaporation and gasoline exhaust contribute about 52% of the total emission (Song et al., 2007).

2.2 Seasonal variations

The seasonal cycles of total volatile organic compounds (total VOCs or the sum of the all quantified VOCs) in Beijing from 2000 to 2007 are illustrated in Fig. 2. In this research, we define spring season from March to May, summer from June to August, fall from September to November, and winter from December to February. The highest TVOC concentration was observed in summer, while the lowest was in spring, with a ratio of about 2:1 (can be seen both in Figs. 1 and 2). Correspondingly, in Guangzhou, one of the biggest cities in South China, the VOC level is similar (Zou et al., 2003). In the metropolitan area of Tokyo, the highest hydrocarbon concentrations were also observed in summer and fall from 2003 to 2004 (Hoshi et al., 2008). Nevertheless, the varying seasonal trends of VOC concentrations were observed in some other cities in the world (Na and Kim,
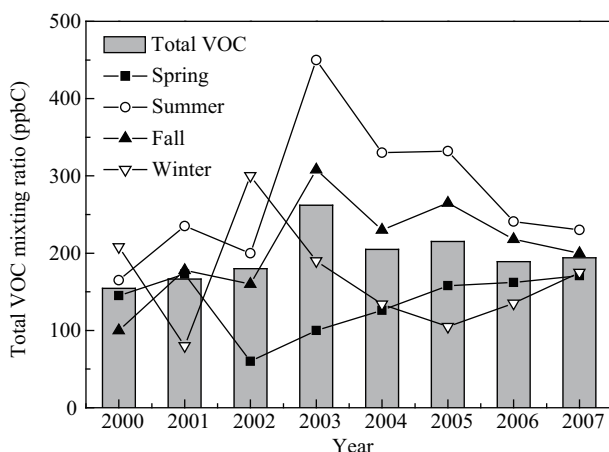

Fig. 1 Annual chart of the total VOCs from 2000 to 2007 and annual variations of total VOCs in each season in Beijing from 2000 to 2007.
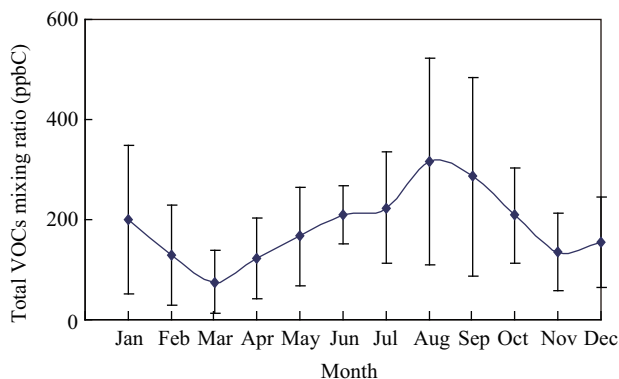
Fig. 2 Average TVOC concentrations for each month from 2000 to 2007. The error bars reflect the relative standard deviation in the average total VOCs mixing ratio.

Fig. 3 Diurnal VOC average concentration from 2000 to 2007.

2001; Borbon et al., 2002; Guo et al., 2007). The higher level of VOCs in summer suggests that temperature greatly affects the varying levels of VOC in Beijing's urban area. In Beijing from 2000 to 2006, the lowest temperature was recorded in January at –4°C, while the highest was in July at 26°C (Beijing Statistical Year Book 2001–2007). Additionally, in August, the maximum concentration is related to the higher temperature in July, thus, it is in the former that gasoline or solvent evaporation is increased. Starting mid-November up to the next mid-March is the period of domestic heating supply in Beijing, and the main energy source is coal and natural gas. In recent years, large amounts of VOCs are emitted from coal combustion and natural gas leakage, such as aromatic compounds (Garcia et al., 1992) and C2–C5 VOCs (Na and Kim, 2001). In this case of November and March, two extreme values of VOC concentration were studied for the interactive effects of ambient temperature and energy usage. Gasoline and sol-vent evaporation decreases as the temperature lowers from August to November, but the domestic heating supply in Beijing starts in mid-November, therefore VOC emission will increase with energy usage. On the contrary, the lowest VOC concentrations in the atmosphere were observed in March and were found to increase with the temperature elevated gradually since March.

2.3 Diurnal variations

The diurnal variation of VOCs from 2000 to 2007 is shown in Fig. 3. In Beijing, two peaks of VOC concentration were observed in the morning and in the evening. The maximum concentration was recorded from 8:00 to 10:00 in the morning, and then decreased at around 14:00. Thereafter, the concentration increased again until 20:00 when the second VOC peak occurred. This trend is very similar to the diurnal trends found in other urban areas (Ho et al., 2004; Yang et al., 2005; Filella and Peñuelas, 2006; Tang et al., 2007). The regular daily variation of VOCs from 2000 to 2007 in Beijing can be considered as the result of emission sources, meteorological conditions, and photochemical activity (Filella and Peñuelas, 2006). In Beijing, a high volume of traffic occurs, in the morning and in the evening, so during these periods, the VOC emissions from vehicle-related sources were likely to be high (Song et al., 2008). Moreover, photochemical reactivity and at-
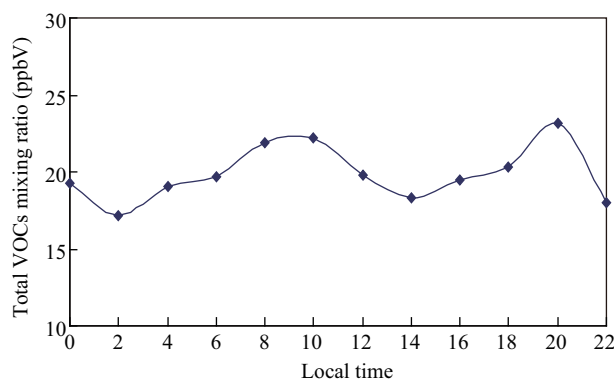
mospheric dispersion and advection are very weak, and because of this, urban boundary layer vertical extension becomes significant starting at 10:00 in the morning when the sun rises and reaches the maximum at about 15:00 (Guinot et al., 2006). During midday, VOCs decrease, which could be interpreted as a photochemical reaction (Warneke et al., 2004), and it also increases in the mixing depth (Yang et al., 2005). At this time, solar radiation becomes strongest in the day, and the urban boundary layer reaches higher values up to 3000 m (Guinot et al., 2006). Moreover, the atmospheric stability is in the lowest level at around 13:00, and because of this, the diurnal variation of pollutants usually lags stability by 1 to 2 hr (Zhou et al., 2005). In addition, vehicle activity in the afternoon decreases, and this commences low contributions from vehicle-related sources at around 14:00. Such increase in vehicle activity during the rush hour and the decrease in photochemical reactivity and atmospheric mixing depth may be interpreted as the increase in VOC concentration from 14:00 to 20:00. The emissions decreased in mid-night and led to the low level of pollutants until 2:00 the next day.

2.4 BTEX in the Beijing urban area

2.4.1 BTEX concentrations

In the urban area of Beijing, toluene and benzene were the two most abundant compounds of BTEX from 2000 to 2007 as discussed in Section 2.1. Toluene and benzene are considered to be emitted from vehicle-related activity, including vehicular exhaust and gasoline evaporation. In different cities, various BTEX compounds were found in the atmosphere. Kumar and Víden (2007) reviewed a number of published studies that delved on the levels of BTEX in major cities of the world. In general, the BTEX level in Beijing was much lower as compared to that of other developing countries. However, Beijing had a higher BTEX level as compared to the result obtained from major cities of developed countries, such as the USA (Aronian et al., 1989). Since 2000 most cars in China are equipped with a catalytic converter to reduce VOC and NOx emissions. This is true in Beijing, and this is done to improve the city's air quality. Despite this, the VOC standard in the atmosphere has not been carried out in China. In fact, the concentration of benzene in Beijing's urban area has exceeded the standard required by the European Union, which is 5 μg/m^3 (World Health Organization, 2000).
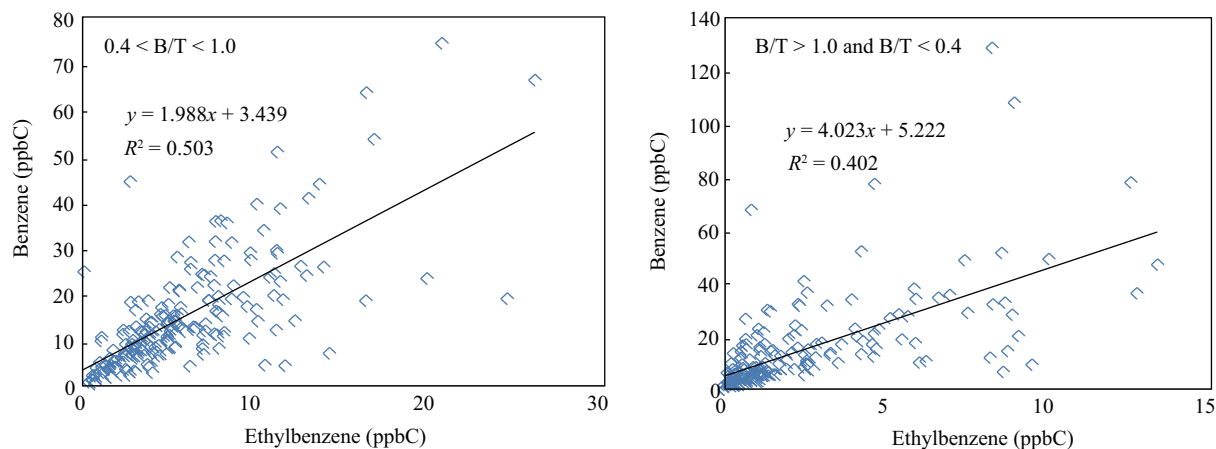
Fig. 4 Correlation between benzene and ethylbenzene for all the samples during 2000–2007. Samples separated by the B/T ratio. B/T: benzene to toluene.

2.4.2 Source identification

Studies have shown that the major source of aromatic hydrocarbons included gasoline evaporation, solvent evaporation and diffuse emissions and vehicular emissions (Heeb et al., 2000). The ratio of benzene to toluene (B/T) is commonly used to identify the VOC emission sources. A B/T value of around 0.5 (wt./wt.) is found to be characteristic of vehicular emission in many urban areas worldwide, including many Chinese cities (Perry and Gee 1995; Brocco et al., 1997; Monod et al., 2001). In previous studies, the B/T ratio in Beijing's urban area ranged from 0.6 to 0.8 (Barletta et al., 2005; Liu et al., 2005; Song et al., 2008). In this study, the B/T ratio, which is 0.95, from 2000 to 2007 is actually a little higher than what is recorded by previous studies. We noted the value of B/T in 2000 is particularly high (3.54), excluding 2000 and the average ratio of B/T between 2001 and 2007 only was 0.87. This result was close to the study of Song et al. (2008), who suggested vehicular emissions as the main source of BTEX

The B/T ratio in this study ranged from 0.05 to 4.2. To further identify the source the samples were divided into two parts: other samples (B/T > 0.1 and B/T < 0.4), and traffic samples (0.4 < B/T < 1.0). In a previous study benzene versus ethylbenzene had a very good correlation in biomass combustion samples with a slope significantly higher than for vehicular traffic (Monod et al., 2001). Our benzene versus ethylbenzene plot has a slope of 4.0 (R^2 = 0.402) for other samples, and a slope of 1.9 (R^2 = 0.503) for the traffic related samples (Fig. 4). The findings actually indicated that there is a good correlation between benzene and ethylbenzene, and that they were caused by vehicular emissions, as revealed by the B/T ratio between 0.4 and 1.0. In addition, a weak correlation was found with the other B/T ratio, and such findings were consistent with other sources. The findings also show that the slope between benzene and ethylbenzene is significantly higher than that in vehicle-related air samples. The finding indicates that there might be an exit for the extra sources of benzene in Beijing, such as evaporation and other forms of combustion (Monod et al., 2001; Barletta et al., 2005).

In typical urban areas, BTEX constitutes up to 60% of the total VOCs identified. Also, BTEX mainly comes from

mobile sources (Lee et al., 2002), but evaporation cannot remain negligible since gasoline evaporation contributes about 10% to the VOCs in Beijing (Song et al., 2007). To evaluate the impact of evaporation-related sources, i-pentane is used as it is a good marker for solvent evaporation. The correlation coefficients between BTEX and i-pentane are shown in Fig. 4. Based on the findings, the correlations between BTEX and i-pentane were very low (benzene 0.131; toluene 0.073; ethylbenzene 0.049; m/p-Xylene 0.038; o-xylene 0.059) in the urban area of Beijing from 2000 to 2007. The low correlation coefficients indicate that gasoline evaporation is a minor emission source.

Moreover, C2 alkylbenzene is considered to be emitted from vehicular exhaust (Monod et al., 2001). However, benzene and toluene take off from other sources in the urban area, and this can be seen in Fig. 4. Despite the low correlation between BTEX and i-pentane, benzene and toluene have better correlation as compared to C2 alkylbenzene. This finding simply indicates that C2 alkylbenzene is mainly sourced from vehicles.

3 Conclusions

In this study, we present the data on long-term measurements of VOCs in Beijing's urban area over the period of 2000 to 2007. The average VOC level in 2003 was the highest and was mainly attributed to local vehicle-related activity, such as vehicular exhaust and gasoline evaporation. The anthropogenic sources and atmospheric pollutant control policy carried out by the Beijing municipal government were the two most important factors that contributed to the level of annual VOCs in the city. It was found that toluene, benzene, and i-pentane were the most abundant chemicals in Beijing's urban area. Similar to other urban areas in the world, alkanes were also found to be a dominant component with about 31% to 60% of all quantified VOCs. The findings further show that there was an observable seasonal variation that affect VOC levels, such that the VOC level was high during summer and was low during winter. This variation can be further explained by the effect of evaporation from the gasoline station and solvent usage. In addition to the seasonal variation,

diurnal variation of VOCs was also indicated. A high concentration of VOC was noted during rush hours, while a low concentration was recorded during the daytime; this was attributed to vehicular exhaust and photochemical reaction with OH in the atmosphere.

Furthermore, the BTEX level in Beijing was much lower as compared to that of other developing countries, but compared to cities in developed countries, Beijing's BTEX level was higher. The ratio of B/T and correlation coefficients between BTEX and *i*-pentane was used to evaluate the impact of vehicular exhaust and evaporation. A B/T ratio between 0.4 and 1.0 was useful in identifying the VOCs that resulted from vehicular exhaust. Finally, poor correlation was identified for BTEX and *i*-pentane, indicating that gasoline evaporation is an insignificant source of BTEX. Comparing benzene and toluene with C2 alkylbenzene emitted from vehicle exhaust, the two formerly mentioned came from other sources such as evaporation from gasoline and solvent usage.

Acknowledgments

References

Aronian P F, Scheff P A, Richard A W, 1989. Wintertime source-reconciliation of ambient organics. *Atmospheric Environment*, 23(5): 911–920.

Atkinson R 2000. Atmospheric chemistry of VOCs and NO*x*. *Atmospheric Environment*, 34(12-14): 2063–2101.

Austin J 2003. Day-of-week patterns in toxic air contaminants in southern California. *Journal of the Air & Waste Management Association*, 53: 889–896.

Barletta B, Meinardi S, Rowland F S, Chan C Y, Wang C Y, Zou S C et al., 2005. Volatile organic compounds in 43 Chinese cities. *Atmospheric Environment*, 39(32): 5979–5990.

Beijing Municipal Bureau of Statistics 2007. Beijing Statistical Year Book 2007. China Statistics Press, Beijing.

Borbon A, Locoge N, Veillerot M, Galloo J C, Guillermo R, 2002. Characterisation of NMHCs in a French urban atmosphere: overview of the main sources. *Science of the Total Environment*, 292(3): 177–191.

Brocco D, Fratarcangeli R, Lepore L, Petricca M, Ventrone I, 1997. Determination of aromatic hydrocarbons in urban air of Rome. *Atmospheric Environment*, 31(4): 557–566.

Chan C K, Yao X H, 2008. Air pollution in mega cities in China. *Atmospheric Environment*, 42(1): 1–42.

Duan J C, Tan J H, Yang L, Wu S, Hao J M, 2008. Concentration, sources and ozone formation potential of volatile organic compounds (VOCs) during ozone episode in Beijing. *Atmospheric Research*, 88(1): 25–35.

Filella I, Peñuelas J, 2006. Daily, weekly and seasonal relationships among VOCs, NO*x* and O₃ in a semi-urban area near Barcelona. *Journal of Atmospheric Chemistry*, 54(2): 189–201.

Garcia J P, Beyne-Masclet S, Mouvier G, Masclet P, 1992. Emissions of volatile organic compounds by coal-fired power stations. *Atmospheric Environment*, 26(9): 1589–1597.

Guenther A, Karl T, Harley P, Wiedinmyer C, Palmer P I, Geron C, 2006. Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). *Atmospheric Chemistry and Physics*, 6(11): 3181–3210.

Guinot B, Roger J C, Cachier H, Wang P C, Bai J H, Tong Y, 2006. Impact of vertical atmospheric structure on Beijing aerosol distribution. *Atmospheric Environment*, 40(27): 5167–5180.

Guo H, So K L, Simpson I J, Barletta B, Meinardi S, Blake D R, 2007. C1–C8 volatile organic compounds in the atmosphere of Hong Kong: Overview of atmospheric processing and source apportionment. *Atmospheric Environment*, 41(7): 1456–1472.

Hao J M, Wang L T, 2005. Improving urban air quality in China: Beijing case study. *Journal of the Air & Waste Management Association*, 55(9): 1298–1305.

Heeb N V, Forss A M, Bach C, Reimann S, Herzog A, Jäckle H W, 2000. A comparison of benzene, toluene and C₂-benzenes mixing ratios in automotive exhaust and in the suburban atmosphere during the introduction of catalytic converter technology to the Swiss Car Fleet. *Atmospheric Environment*, 34(19): 3103–3116.

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. *Science of the Total Environment*, 322(1-3): 155–166.

Hoshi J Y, Amano S, Sasaki Y, Korenaga T, 2008. Investigation and estimation of emission sources of 54 volatile organic compounds in ambient air in Tokyo. *Atmospheric Environment*, 42(10): 2383–2393.

Kumar A, Víden I, 2007. Volatile organic compounds: Sampling methods and their worldwide profile in ambient air. *Environmental Monitoring and Assessment*, 131(1-3): 301–321.

Lee S C, Chiu M Y, Ho K F, Zou S C, Wang X M, 2002. Volatile organic compounds (VOCs) in urban atmosphere of Hong Kong. *Chemosphere*, 48(3): 375–382.

Liu Y, Shao M, Zhang J, Fu L L, Lu S H, 2005. Distributions and source apportionment of ambient volatile organic compounds in Beijing City, China. *Journal of Environmental Science and Health Part A-Toxic/Hazardous Substances & Environmental Engineering*, 40(10): 1843–1860.

Mao T, Wang Y S, Jiang J, Wu F K, Wang M X, 2008. The vertical distributions of VOCs in the atmosphere of Beijing in autumn. *Science of the Total Environment*, 390(1): 97–108.

Molina M J, Rowland F S, 1974. Stratospheric sink for chlorofluoromethanes: chlorine atomcatalysed destruction of ozone. *Nature*, 249(5460): 810–812.

Monod A, Sive B C, Avino P, Chen T, Blake D R, Sherwood R F 2001. Monoaromatic compounds in ambient air of various cities: a focus on correlations between the xylenes and ethylbenzene. *Atmospheric Environment*, 35(1): 135–149.

Na K, Kim Y P, 2001. Seasonal characteristics of ambient volatile organic compounds in Seoul, Korea. *Atmospheric Environment*, 35(15): 2603–2614.

Na K, Kim Y P, Moon I, Moon K C, 2004. Chemical composition of major VOC emission sources in the Seoul atmosphere. *Chemosphere*, 55(4): 585–594.

Okuda T, Katsuno M, Naoi D, Nakao S, Tanaka S, He K B, et

al., 2008. Trends in hazardous trace metal concentrations in aerosols collected in Beijing, China from 2001 to 2006. *Chemosphere*, 72(6): 917–924.

Perry R, Gee I L, 1995. Vehicle emissions in relation to fuel composition. *Science of the Total Environment*, 169(1-3): 149–156.

Sillman S, 1999. The relation between ozone, NO*x*, and hydrocarbons in urban and polluted rural environments. *Atmospheric Environment*, 33(12): 1821–1845.

Song Y, Dai W, Shao M, Liu Y, Lu S H, Kuster W et al., 2008. Comparison of receptor models for source apportionment of volatile organic compounds in Beijing, China. *Environment Pollution*, 156(1): 174–183.

Song Y, Shao M, Liu Y, Lu S H, Kuster W, Goldan P et al., 2007. Source apportionment of ambient volatile organic compounds in Beijing. *Environmental Science & Technology*, 41(12): 4348–4353.

Streets D G, Fu J S, Jang C J, Hao J M, He K B, Tang X Y et al., 2007. Air quality during the 2008 Beijing Olympic Games. *Atmospheric Environment*, 41(3): 480–492.

Tang J H, Chan L Y, Chan C Y, Li Y S, Chang C C, Liu S C et al., 2007. Characteristics and diurnal variations of NMHCs at urban, suburban and rural sites in the Pearl River Delta and a remote site in South China. *Atmospheric Environment*, 41(38): 8620–8632.

Tang J H, Chan L Y, Chan C Y, Li Y S, Chang C C, Wang X M et al., 2008. Implications of changing urban and rural emissions on non-methane hydrocarbons in the Pearl River Delta region of China. *Atmospheric Environment*, 42(16): 3780–3794.

Warneke C, de Gouw J A, Goldan P D, Kuster W C, Williams E J, Lerner B M et al., 2004. Comparison of daytime and nighttime oxidation of biogenic and anthropogenic VOCs along the New England coast in summer during New England Air Quality Study 2002. *Journal of Geophysical Research*, 109: 10309–10309.

World Health Organization, 2000. Air Quality Guidelines for Europe (2nd ed.). Copenhagen.

Yang K L, Ting C C, Wang J L, Wingenter O W, Chan C C, 2005. Diurnal and seasonal cycles of ozone precursors observed from continuous measurement at an urban site in Taiwan. *Atmospheric Environment*, 39(18): 3221–3230.

Zhou L, Xu X D, Ding G A, Zhou M Y, Cheng X H, 2005. Diurnal variations of air pollution and atmospheric boundary layer structure in Beijing during winter 2000/2001. *Advances in Atmospheric Sciences*, 22(1): 126–132.

Zou S C, Lee S C, Chan C Y, Ho K F, Wang X M, Chan L Y et al., 2003. Characterization of ambient volatile organic compounds at a landfill site in Guangzhou, South China. *Chemosphere*, 51(9): 1015–1022.