Science of the Total Environment 490 (2014) 391–396

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

The pollution levels of BTEX and carbonyls under haze and non-haze days in Beijing, China

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HIGHLIGHTS

- Remarkable accumulation of carbonyls and BTEX was found under haze days.
- Photochemical reactivity exhibited to be stronger under haze days.
- Local emissions depressed by haze resulted to the higher ratios in winter.

ARTICLE INFO

Article history:
Received 24 October 2013
Received in revised form 27 April 2014
Accepted 6 May 2014
Available online xxxx

Editor: Xuexi Tie

Keywords:
Carbonyls
BTEX
Haze
Photochemical reaction
Local emission

ABSTRACT

The North China Plain including Beijing is frequently suffering from serious haze days in recent years. To best recognize the influence of haze days on regional air quality, the pollution levels of deleterious gases of BTEX (benzene, toluene, ethylbenzene, m,p-xylene and o-xylene) and carbonyls (formaldehyde, acetaldehyde and acetone) under haze and non-haze days were contrastively investigated during the period of September 2008–August 2010 in Beijing. In comparison with non-haze days, remarkable enhancement of BTEX and the carbonyls under haze days in winter was found, with enhancement factors of 1.9–5.7 for BTEX and of 1.5–4.2 for the carbonyls. Whereas the enhancement factors for both BTEX (1.0–3.0) and the carbonyls (1.2–1.9) under haze days in summer were relatively small. The ratios of each BTEX to CO under both haze days and non-haze days exhibited a minimal value in the afternoon, whereas maximal values for the ratios of the carbonyls to CO were usually found in the afternoon. The ratios of each BTEX to CO were extremely greater under haze days than those under non-haze days in winter, but no evident difference was found in summer. The ratios of each carbonyl under both haze days and non-haze days in summer were at least a factor of 2 greater than those in winter and only enhancement of the ratios under haze days was found in winter. The remarkably higher ratios of ethylbenzene to m,p-xylene under haze days than non-haze days in both winter and summer revealed high reactivity of photochemical reactions initiated by OH radicals under haze days.

1. Introduction

Carbonyl and BTEX (benzene, toluene, ethylbenzene, *m,p*-xylene and *o*-xylene) compounds are receiving increasing attention as the key participants in photochemical reactions and their adverse effect on human health (Haagen-Smit and Fox, 1956; Committee on Toxicology and Environmental Health Hazards, 1981; Carlier et al., 1986; Atkinson, 1997; Hoque et al., 2008). They are both recognized as important photochemical precursors for tropospheric ozone and second organic aerosols (Wang et al., 2002; Barletta et al., 2008). Besides, photolysis of the carbonyls is an important source for atmospheric hydroxyl radical (OH) and peroxy radicals (HO_2, RO_2), which are further involved in photochemical reactions (Carlier et al., 1986; Atkinson and Arey, 2003). BTEX and a number of carbonyl compounds are well-known toxic air pollutants (TAPs). Benzene, formaldehyde and acetaldehyde are even considered as human carcinogens (Stupfel, 1976; Crump, 1994; Carlier et al., 1986; Baez et al., 2003; Dutta et al., 2009).

It is well known that the concentrations of atmospheric pollutants near the earth surface are strongly affected by their sources' strength (local or transported), atmospheric chemical processes (production/removal) and meteorological conditions (wind, precipitation, the

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http://dx.doi.org/10.1016/j.scitotenv.2014.05.025
0048-9697/

Planetary Boundary Layer (PBL), etc.). Remarkable accumulation of atmospheric pollutants usually occurs under stagnant air condition (slow wind speed and low PBL), which has caused serious atmospheric environmental problems, e.g. haze is frequently raiding on vast areas of China in recent years. Most Chinese studies are focusing on measurements of particle matter to reveal the deterioration of air quality under haze days, but few studies are concerning the influence of haze on the deleterious gases of BTEX and carbonyls. Lü et al. (2009) found that the average total concentration of carbonyls in Guangzhou under hazy days in winter was a factor of 1.0–4.0 higher than those under clear days. Liu et al. (2009a) studied the influence of haze on levels of atmospheric BTEX and ratios of ethylbenzene/benzene (E/X) in summer of 2008 in Beijing and reported that both the concentrations and the ratio increased under haze days. Mao et al. (2008) investigated the vertical distributions of volatile organic compounds (including aromatic hydrocarbons) in the atmosphere of Beijing under haze and clear days, and they reported that the average concentrations of total volatile organic compounds under hazy days were greater by 7.6% to 89% than those under clear days. All above studies well revealed that remarkable enhancement of the deleterious gases under haze days. However, the above studies mainly focused on the influence of haze on atmospheric levels of carbonyls or BTEX during only one season by investigating a very short period (1–3 clear days in comparison with 1–3 haze days).

In this study, the atmospheric BTEX and carbonyls in Beijing were analyzed in-depth with the data measured during the period of September 2008–August 2010 to reveal the influence of haze on their levels and ratios during different seasons.

2. Materials and methods

2.1. Sampling site

Air samples were collected on a rooftop (20 m above the ground level) in the Research Center for Eco-Environmental Sciences (RCEES) which lies in the north of Beijing city (39.8°N, 116.5°E) between the 4th and 5th rings roads. The detail information about the sampling site was described in our previous studies (Pang and Mu, 2006; Liu et al., 2009a).

2.2. Sampling and analysis

Carbonyls and BTEX were simultaneously sampled at least 4 days per month from September 2008 to August 2010, with carbonyls' samples collected at 2 hr interval and BTEX at 1 hr interval. Nearly all kinds of weather were tried to be covered each month to collected samples, excepting raining day: at least one clear day, one cloudy day, one haze day with average wind speed lower than 3 m s^{-1}, and one wind day with hourly average wind speed higher than 5 m s^{-1}.

The sampling process and analysis procedure of atmospheric carbonyls were mainly based on the EPA TO-11A method (EPA, 1999), and the details have been described in our previous publications (Pang and Mu, 2006, 2007). Briefly, ambient air was drawn through a 2,4-dinitrophenylhydrazine (DNPH)-coated silica gel cartridge (Waters, United States) by a mini-pump (NMP 830 KNDC, Germany) at a flow rate of 800 Ml min^{-1} for 2 h, and the corresponding DNPH hydrazones of carbonyls were separated by a Thermo ODS Hypersil reverse phase column (5 μm, 250 mm × 4.6 mm) and automatically analyzed by an photodiode array UV detector (at 360 nm) in an Alliance 2695 HPLC system (Waters, USA). The detected limit ($S/N = 3$) by this method was in the range of 80–200 ng m^{-3} for various carbonyls of 96 L sampling volume.

As for BTEX, they were sampled by drawing air through an absorption tube (15 cm long, 4 mm ID) filled with Tenax-TA (80–100 mesh, 100 mg) at a flow rate of 350 m min^{-1} for 1 hr, and analyzed by a gas chromatography equipped with a Photo Ionization Detector (GC-PID, GC4400, East & West Analytical Instruments, Inc.) after thermal desorption. The method detection limit (with a signal-to-noise ratio of 2) for the benzene, toluene, ethylbenzene, *m,p*-xylene and *o*-xylene was 0.01, 0.02, 0.06, 0.07 and 0.07 μg m^{-3}, respectively. One blank sample was analyzed for each day, and found that the concentrations of BTEX in the blank tube were less than 3% of those in the ambient air samples. Distinct breakthrough for benzene was found when the absorption tube was kept under ambient air temperature, but greatly improved when the tube was kept in a bath of ice-salt bag. Therefore, all samples were collected under the bath of ice-salt bag, and the collection efficiencies for benzene, toluene, ethylbenzene, *m,p*-xylene and *o*-xylene were (81.5 ± 5.6)%, (93.6 ± 2.2)%, (95.8 ± 0.8)%, (96.5 ± 2.4)% and (91.5 ± 4.6)% (the result of 10 reduplicate experiments with two absorption tubes in series), respectively. The recovery ratios for benzene, toluene, ethylbenzene, *m,p*-xylene and *o*-xylene were (95.7 ± 3.1)%, (99.2 ±2.6)%, (98.6 ± 2.4)%, (98.1 ± 2.4)% and (96.2 ± 2.2)% (the result of 22 reduplicate experiments), respectively. The details about preparation of the absorption tube, sampling and analyzing procedures have been described in our previous publication (Liu et al., 2009a).

Meteorological conditions (temperature, wind speed, atmospheric pressure and precipitation) during the investigated years were recorded by an automatic meteorological station (the Beijing Urban Ecosystem Research Station, RCEES) located at the same site. Ozone concentrations in summers and winter of 2008 to 2010 were provided by the Chinese Research Academy of Environmental Science (CRAES) which lies in the north of Beijing city (40°2′N, 116°24′E)between 5th and 6th ring roads.

3. Results and discussion

3.1. The influence of haze days on the atmospheric BTEX

The identification of haze days was based on the visibility (<5 km) and relative humidity (<80%). Because haze days usually occur under stagnant air condition, to eliminate the influence of strong wind and precipitation for comparison, only the days with wind speed less than 3 m s^{-1} and without precipitation were selected for comparison of the pollutants between haze days and non-haze days. Among the 30 sampling days during the two winter seasons, there were 7 typical haze days, 2 snowy days, 6 windy days and 15 remaining days classified as non-haze days. During the two summer seasons, there were 15 haze days, 2 windy days and 16 non-haze days.

Fig. 1 illustrates the average diurnal variations of BTEX under haze days and non-haze days in winter and summer. It is evident that the hourly average concentrations of each BTEX compound under haze days were much higher than those under non-haze days both in winter and summer. The hourly average concentrations of benzene, toluene, ethylbenzene, *m,p*-xylene and *o*-xylene were about factors of 1.9–4.0, 2.3–5.7, 2.4–4.6, 2.2–4.0, and 2.2–3.6 respectively greater under haze days than those under non-haze days in winter, whereas were factors of 1.2–3.0, 1.1–2.5, 1.1–2.4, 1.0–2.4, and 1.0–2.4 respectively greater under haze days than those under non-haze days in summer. The enhancement of BTEX under haze days was mainly ascribed to the evolution of the PBL which was strongly depressed and weakened the diffusion of pollutants (Quan et al., 2013). In comparison with winter, the remarkable small enhancement of BTEX under haze days in summer indicated less BTEX sources, greater BTEX consumption through photochemical reactions and higher height of PBL in summer than in winter.

The ratios of the hourly averaged concentrations of each BTEX compound to CO under haze days and non-haze days in winter and summer is listed in Table 1. As the BTEX compounds and CO are mainly from the same primary sources in the urban area and CO is a relative chemical inert pollutant, the ratios of BTEX to CO would be useful indicators for photochemical reactivity, because the ratios could partly counteract the influence of diffusion (Satsumabayashi et al., 1995; Possanzini et al., 2002). As it could be seen from Table 1, the ratios of each BTEX