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Variations and sources of ambient formaldehyde for the 2008 Beijing Olympic games

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ABSTRACT

As the host city of the 2008 Olympic games, Beijing implemented a series of air pollution control measures before and during the Olympic games. Ambient formaldehyde (HCHO) concentrations were measured using a fluorometric instrument based on a diffusion scrubber and the Hantzsch reaction; hydrocarbons were simultaneously measured using gas chromatography–mass spectrometry (GC–MS). Meteorological parameters, CO, O_3, and NO_2 concentrations were measured by standard commercial instrumentation. In four separate periods: (a) before the vehicle plate number control (3–19 July); (b) during the Olympic Games (8–24 August); (c) during the Paralympic Games (6–17 September) and (d) after the vehicle control was ceased (21–28 September), the average HCHO mixing ratios were 7.31 ± 2.67 ppbv, 5.54 ± 2.41 ppbv, 8.72 ± 2.48 ppbv, and 6.42 ± 2.79 ppbv, while the total non-methane hydrocarbons (NMHCs) measured were 30.41 ± 18.08 ppbv, 18.12 ± 9.38 ppbv, 30.50 ± 13.37 ppbv, and 33.33 ± 15.85 ppbv, respectively. Both HCHO and NMHC levels were the lowest during the Olympic games, and increased again during the Paralympic games even with the same vehicle control measures operative. Similar diurnal HCHO and O_3 patterns indicated that photo-oxidation of NMHCs may be the major source of HCHO. The diurnal profile of total NMHCs was very similar to that of NO_2 and CO: morning and evening peaks appeared in rush hours, indicating even after strict vehicle control, automobile emission may still be the dominant source of the HCHO precursors. The contributions of HCHO, alkanes, alkenes, and aromatics to OH loss rates were also calculated. HCHO contributed 22 ± 3% to the total VOCs and 24 ± 1% to the total OH loss rate. HCHO was not only important in term of abundance, but also important in chemical reactivity in the air.

1. Introduction

Formaldehyde (HCHO) is ubiquitous and the most abundant carbonyl compound in the atmosphere (Seco et al., 2007). Ambient formaldehyde can influence the atmospheric OH budget (Grosjean, 1982; Ren et al., 2003) and enhance O_3 production (Lei et al., 2009). It is a known human carcinogen (Cavalcante et al., 2006). The lifetime of HCHO in the sunlit troposphere is limited to 2–4 h, indicating that the observed levels are largely produced in situ (De Smedt et al., 2008; Wert et al., 2003).

Ambient HCHO has been studied in some megacities in China, such as Beijing, Guangzhou, and Hong Kong (Feng et al., 2005; Ho et al., 2002; Lee et al., 2001; Pang and Mu, 2006; Sin et al., 2001): these are all economically important industrialized regions. Beijing and Guangzhou were shown to have relatively high HCHO levels (>10 ppbv, Feng et al., 2005; Pang and Mu, 2006). Ascertaining HCHO sources are important for adopting effective air quality mitigation and control policies in these megacities.

HCHO is the intermediate photochemical reaction product of a large array of volatile organic compounds (Atkinson, 2000; Wert et al., 2003). The principal source of HCHO in the atmosphere is the photochemical oxidation of methane and non-methane hydrocarbons (NMHCs) (Miller et al., 2008; Singh et al., 2000). In the polluted boundary layer, terminal alkenes such as isoprene, ethene, and propene are generally the most important HCHO precursors (Dodge, 1990; Goldan et al., 2000). In Beijing, the photo-oxidation of volatile organic compounds (VOCs) is a significant source of HCHO in summer, and also in spring and autumn (Pang and Mu, 2006). HCHO is also emitted directly into the atmosphere by incomplete fossil fuel combustion (Anderson et al., 1996; Corrêa and Arbilla, 2005), biomass burning (Lee et al., 1997), industrial processes, and natural emissions. The most recent estimate for the

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national emission of HCHO in China was 0.14 Tg, with transportation contributing 72% and the incomplete combustion of biomass and commercial energy ~25% (Wei et al., 2008).

Since 1998, a plethora of measures have been implemented to plan for improving air quality during the Beijing 2008 Olympic games, including relocation of industrial plants with large emissions out of Beijing, and utilizing cleaner production techniques wherever possible to reduce industrial emissions, implementing new standards to reduce vehicular emissions etc. All of these were expected to contribute to the decrease of NMHCs as well as those of NO_x, SO_2, CO, and O_3 in Beijing (Chan and Yao, 2008). For the sake of "Green Olympics," the city government further adopted vehicle control measures from 20 July to 20 September 2008, including odd/even plate number control, another 40% of government owned vehicles were stopped from using, and Cargo trucks were not allowed to run inside the 6th ring road of the city, to reduce mobile source emissions and in turn to minimize ozone levels during the games. A large difference in air quality of Beijing city was expected for the summer of 2008, offering an excellent opportunity to evaluate any changes in diurnal patterns and to ascertain sources of reactive compounds, such as HCHO, in the ambient air.

The levels and diurnal patterns before, during, and after the Olympic games of HCHO and NMHCs were measured in the summer of 2008 from July to September at an observatory on the campus of Peking University, together with measurements of SO_2, CO, O_3, NO, NO_2, and meteorological parameters. This manuscript presents the differences of the variations of HCHO and NMHCs during these periods, and attempts to estimate the contributions of primary and secondary sources of atmospheric HCHO in Beijing under the different vehicle control conditions.

2. Experimental

2.1. Sampling sites

The air quality observatory was located at the top of the Science and Technology Building of Peking University (39°59′20″N, 116°18′26″E), ~23 m above ground. It is located near the Zhongguancun area, the national innovation center for high-tech development, with heavy traffic flow on the north, south, and east side of the observatory. The Peking University campus lies to the west of it. This observatory has been used as a monitoring site for ozone and related precursors since 1987 (Shao et al., 2006). It is about 7 km aerial distance from the Bird's Nest (the National Olympic Center), and is located directly on the 2008 Olympic Marathon route; air quality measured at this site was considered representative of those experienced outdoors during the Olympics.

2.2. Measurements of HCHO and NMHCs

Ambient HCHO concentrations were measured from 3 July to 28 September 2008 with an instrument based on diffusion scrubber collection and online fluorometric Hantzsch reaction (Li et al., 2005). The Hantzsch reaction involves the solution phase cyclization of two molecules of 2,4-pentanedione and one molecule of formaldehyde in an ammonium acetate buffer to form fluorescent 3,5-diacetyl-1,4-dihydrolutidine detected by a flow-through fluorescence detector. The limit of detection (LOD, S/N = 3) of the instrument is <100 ppt for a 2 min sample, the instrument was operated with 2 min sample and 8 min zero cycles, resulting in a time resolution of 10 min.

The sampler inlet was downward pointing and ~1.5 m above the shelter of the roof; a 46.2 mm ϕ Poly (tetrafluoroethylene) (PTFE) filter (2 μm pore size, Pall R2PJ047) was placed in front of the sampler inlet to remove particles. Samples were drawn at 1 L min^{-1} through a 3 mm i.d. PTFE tube, covered with an opaque thermally insulating jacket to eliminate further photochemistry and maintain the original sample temperature and passed on to the diffusion scrubber collector.

The instrument uses an on-board gravimetrically calibrated paraformaldehyde filled permeation tube, maintained at 60 °C (permeation rate 70.1 ± 10.9 ng min^{-1}). High purity N_2 was used to dilute the HCHO output from the permeation tube during automated calibration. Five-point calibration, including a zero concentration point, was performed once a week and the instrument was calibrated daily with a two-point calibration with a calibrant concentration of 6.8 ppb (a value that is around half of the daily maximum) including zero air. Based on the calibration data for the entire period, we estimate that the maximum errors in HCHO measurements were <20%.

Two different approaches were used to quantify NMHC species. In an offline method, air was sampled into pre-cleaned evacuated stainless steel canisters (8 July to 28 September 2008), and analyzed by a capillary gas chromatography–flame ionization detection–mass spectrometry (GC–FID/MS) system that utilized a cryogenic pre-concentrator coupled to a gas chromatograph (Agilent 5973, USA) with two columns and two detectors. The C_2–C_4 alkanes, alkenes, and acetylene were separated on a non-polar capillary column (HP-1, 50 m × 0.32 mm i.d. × 1.05 μm) and quantified by FID. The C_4–C_{12} alkanes, C_4–C_{11} alkenes, and C_6–C_{10} aromatics were separated on a semi-polar column (DB-624, 60 m × 0.32 mm i.d. × 1.8 μm) and quantified using a quadrupole mass spectrometer (Agilent 6890). Method detection limits (MDLs) for most VOC species were below 0.1 ppbv, ranging from 0.01 to 0.35 ppbv (Liu et al., 2005). In the other approach, NMHC was measured continuously by online GC–MS with a time resolution of 1 h by the Research Center for Environmental Changes (RCEC) of Academia Sinica, Taiwan (24 July to 30 August 2008). The online automated GC/MS/FID (Varian CP-3800 and Saturn 2200 MS) system used dual-columns and dual-detectors to simultaneously analyze both low- and high-boiling NMHCs with each injection. The fundamental framework and analytical procedures are the same as the in-lab GC/MS/FID system developed by RCEC (Chang et al., 2003). A built-in cryotrap, packed with fine glass beads, was cooled with liquid nitrogen to −170 °C for trapping. Air was drawn from the air inlet through the cryotrap at a rate of 11 mL min^{-1} for 20 min, giving a 220-mL air sample for each analysis. Desorption occurred by flash heating of the trap to 85 °C, and a stream of ultra-high purity helium (99.9999% He) was used to flush the trapped hydrocarbons onto the columns. A glass Y-splitter divided the flow to two columns: a PLOT column (Chrompack; 30 m × 0.32 mm; $d_f = 5.0$ μm) connected to a FID system for the separation and detection of C_2–C_4 compounds, and a DB-1 column (J&W; 60 m × 0.32 mm; $d_f = 1.0$ μm) connected to a high-sensitivity ion-trap MS system for the separation and detection of C_5–C_{11} compounds. Two standard gas cylinders (68 C_2–C_{11} NMHCs, Scott Marrin, Inc., USA; 57 C_2–C_{12} NMHCs, Spectra Gases, Inc., USA) were used for calibration and quality control. Calibrant concentrations in the gas standard mixtures ranged from 0.05 to 15 ppbv. For all target species blank responses were below the detection limits. Precision for measured species was evaluated by seven repeat analyses of a standard mixture of known concentration (around 1 ppbv). Analytical precision (1σ) of most species was 0.5–2%, and the detection limit of the 66 target species ranged from 0.003 to 0.039 ppbv. To test the consistency of NMHC data from the RCEC and PKU laboratories, an interlaboratory comparison was carried out during the 2004 Pearl River Delta (PRD) air quality experiment (Liu et al., 2008). For the majority of the NMHC data, the linear regression slopes for the PKU vs RCEC measurements fell between