



## Variation of ambient carbonyl levels in urban Beijing between 2005 and 2012



Wentai Chen<sup>a</sup>, Min Shao<sup>a,\*</sup>, Ming Wang<sup>a,1</sup>, Sihua Lu<sup>a</sup>, Ying Liu<sup>a,b</sup>, Bin Yuan<sup>a,2</sup>, Yudong Yang<sup>a</sup>, Limin Zeng<sup>a</sup>, Zhongming Chen<sup>a</sup>, Chih-Chung Chang<sup>c</sup>, Qian Zhang<sup>a</sup>, Min Hu<sup>a</sup>

<sup>a</sup> State Joint Key Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing, China

<sup>b</sup> Chinese Research Academy of Environmental Sciences, Beijing, China

<sup>c</sup> Research Center for Environmental Change, Academia Sinica, Taipei, Taiwan

### HIGHLIGHTS

- Formaldehyde levels in Beijing decreased during summers of 2005–2012.
- Annual variations of carbonyl levels were related to changes of primary emissions.
- Attention should be paid to use of NG, LPG, and solvents to reduce carbonyls.

### ARTICLE INFO

#### Article history:

Received 21 May 2015

Received in revised form

24 December 2015

Accepted 28 December 2015

Available online 7 January 2016

#### Keywords:

Carbonyls

Trend analysis

Emission ratio

Photochemistry

### ABSTRACT

Carbonyl compounds are important precursors of secondary air pollutants. With the rapid economic development and the implementation of stricter control measures in Beijing, the sources of carbonyls possibly changed. Based on measurement data obtained at an urban site in Beijing between 2005 and 2012, we investigated annual variations in carbonyl levels and sources during these years. In summer, formaldehyde and acetaldehyde levels decreased significantly at a rate of 9.1%/year and 7.2%/year, respectively, while acetone levels increased at a rate of 4.3%/year. In winter, formaldehyde levels increased and acetaldehyde levels decreased. We also investigated the factors driving the variation in carbonyls levels during summer by determination of emission ratios for carbonyls and their precursors, and calculation of photochemical formation of carbonyls. The relative declines for primary formaldehyde and acetaldehyde levels were larger than those for secondary formation. This is possibly due to the increasing usage of natural gas and liquefied petroleum gas which could result in the rise of carbonyl precursor emission ratios. The increase in acetone levels might be related to the rising solvent usage in Beijing during these years. The influences of these sources should be paid more attention in future research.

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## 1. Introduction

Carbonyls are ubiquitous components of the urban atmosphere,

and play an important role in atmospheric chemistry. Carbonyls are not only important sources of free radicals but also potential precursors for ozone, peroxyacyl nitrates, and secondary organic aerosols (Liggio et al., 2005; Singh et al., 1995). In addition, some carbonyls are harmful to human health, causing irritation to human skin, eyes, and respiratory system. Formaldehyde and acetaldehyde have been listed in the National-Scale Air Toxics Assessment by the US-EPA (<http://www.epa.gov/ttn/atw/nata1999/177poll.html>).

Ambient levels and sources of carbonyl have been of great concern in recent years. High levels of carbonyls have been reported by several studies, and the highest mixing ratio of

\* Corresponding author.

E-mail address: [mshao@pku.edu.cn](mailto:mshao@pku.edu.cn) (M. Shao).

<sup>1</sup> now at: Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control, School of Environmental Science and Engineering, Nanjing University of Information Science & Technology, Nanjing, China.

<sup>2</sup> now at: NOAA Earth System Research Laboratory and Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO, USA.

formaldehyde exceeded 50 ppb (Duan et al., 2012; Pang and Mu, 2006; Zhang et al., 2012c). Carbonyls accounted for 37% of the measured volatile organic compound (VOCs) mixing ratios and 38% of the OH radical loss rate of VOCs in Beijing (Shao et al., 2009). Formaldehyde, acetaldehyde, and acetone were the three major carbonyl compounds, and contributed more than 80% of the total carbonyl levels (Chen et al., 2014; Shao et al., 2009). Formaldehyde photolysis was the dominant source of OH radicals (HOx) during daytime, with contributions larger than 60% in the period of 11:00–16:00 (An et al., 2009).

Due to the rapid development of Beijing, the number of vehicles in the city has increased rapidly, and a series of long-term clean air policies were adopted by the Beijing Government. As a result, sources of air pollutants possibly changed. The mixing ratios of NMHCs exhibited a decreasing trend since 2003 (Wang et al., 2015, 2012). In August, daytime NMHC mixing ratios decreased by 7%/year between 2005 and 2011 (Zhang et al., 2014). Similarly, NOx levels began to decrease from 1998 (Zhang et al., 2011). Although ambient levels of these primary pollutants have decreased in Beijing, ozone levels showed an obvious increase at a rate of 1 ppb/year between 1995 and 2005, especially for O<sub>3</sub> levels measured in summer afternoon, with an increasing rate of 3 ppb/year (Ding et al., 2008; Zhang et al., 2014).

As important intermediates in atmospheric photochemical reactions, carbonyl levels can be used to evaluate changes in air pollution levels in Beijing. Several studies reported annual variations of carbonyl levels based on field measurements and satellite observations. Zhang et al. (2012c) compared ambient levels of carbonyls offline measured during 2008–2010 with 2005. Ambient levels of formaldehyde were found to decrease by more than 50% in spring, summer, and autumn, but increased slightly in winter, whereas acetaldehyde levels decreased significantly in all four seasons. Acetone levels varied greatly among different seasons and did not show a clear trend (Zhang et al., 2012c). In contrast to the annual variations of carbonyl levels based on ground-based observations, satellite measurements indicated that formaldehyde columns in the Beijing-Tianjin-Hebei area showed an increasing trend. The rate of increase in the formaldehyde vertical column density (VCD) was 4%/year from 1997 to 2009 (De Smedt et al., 2010). In addition, another study based on satellite observations found that the formaldehyde VCD in summer increased by the rate of 7.8%/year from 2005 to 2011 in Beijing (Zhang et al., 2012a). Due to the limitation of ground-based carbonyl measurement data in Beijing and the discrepancy of carbonyl trends between ground-based and satellite-based observations, the trends in carbonyl levels in Beijing were still unclear.

The study on annual variations of carbonyl levels and their sources can help us to better understand changes in VOC emissions and sources, and oxidative capacity of atmosphere. In this study, we investigated changes in carbonyl levels and sources in Beijing based on VOC measurements conducted at an urban site from 2005 to 2012. We analyzed trend of carbonyl levels during summer and winter. Then variations in carbonyls levels from anthropogenic emissions and secondary sources were investigated based on emission ratios (ERs) of carbonyls and the photochemical formation of carbonyls from oxidation of their precursors to identify main driving factors for these carbonyl trends.

## 2. Experimental

Online measurements of NMHCs and carbonyls were conducted during 2005–2012 on the top of a six-floor building in the Peking University (PKU, 40.00° E, 116.31° E) campus. This sampling location was in northwest of Beijing city, about 500 m north of the Fourth Ring Road, and 10 km northwest of the center of Beijing (Liu

et al., 2009). In order to check the spatial representation of VOCs measurements at the PKU site for entire Beijing, regional VOCs measurements were conducted at 27 sites across the whole city from September 2009 to January 2011. Detailed descriptions on these regional sites and sampling strategies were provided by Wang et al. (2014a). The emission ratios for most VOC species showed good agreements between the PKU site and the 27 regional sites in Beijing, with  $r$  of 0.99 and linear regression slope of  $0.91 \pm 0.02$  (Wang et al., 2014a), indicating that the composition of VOCs determined at the PKU site could represent the urban mixture of anthropogenic emissions in Beijing. A summary of the analytical methods used to determine VOC levels in this work is listed in Table 1. The main VOC compounds of concern in this study were formaldehyde, acetaldehyde, and acetone and their precursors.

In summer 2005, NMHCs and carbonyls (with the exception of formaldehyde) were measured using an online gas chromatography-mass spectrometry/flame ionization detector system (GC-MS/FID), developed by the Earth System Research Laboratory (ESRL) of NOAA, USA. Detailed descriptions about this system were provided by Goldan et al. (2004). Briefly, air samples were cryocollected for 5 min in two parallel channels every 30 min. After separation by gas chromatography, one channel was connected to an FID to analyze C<sub>2</sub>–C<sub>5</sub> alkanes, C<sub>2</sub>–C<sub>4</sub> alkenes, and ethyne, and the other was connected to a mass spectrometry (MS) to quantify C<sub>5</sub>–C<sub>10</sub> alkanes, C<sub>5</sub>–C<sub>9</sub> alkenes, C<sub>6</sub>–C<sub>9</sub> aromatics, C<sub>2</sub>–C<sub>7</sub> aldehydes, and ketones. The detection limits for most of the target compounds were ca. 0.5 ppt (Goldan et al., 2004).

In summer 2006 and 2007, carbonyls were sampled with DNPH (2,4-dinitrophenyl hydrazine) cartridges and analyzed by HPLC (high-pressure liquid chromatography), using the US-EPA recommended TO-11A method (Yuan et al., 2012a). Samples were taken every 3 h (6 h at night) by pumping ambient air through cartridges at a flow rate of 1 L/min. After derivatization, the sampled cartridges were eluted with 5 mL of acetonitrile and analyzed by HPLC with a UV detector at 360 nm. The detection limits were below 0.01 ppb at a sampling volume of 180 L (Xie et al., 2008).

In summer 2008, formaldehyde was measured using an online instrument based on the Hantzsch reaction. The instrument was developed by Texas Tech University, U.S. (Li et al., 2005). Formaldehyde reacts with 2,4-pentanedione and ammonia in a slightly acid solution to form a fluorescent derivative, and is then quantified by a fluorescence detector. The detection limit of this instrument was less than 0.01 ppb (Li et al., 2010). Acetaldehyde and acetone were analyzed using a commercial high-sensitivity proton-transfer-reaction mass spectrometry (PTR-MS) (Ionicon Analytik, Innsbruck, Austria), with a time resolution of ca. 2.5 min (Liu et al., 2014). The detection limits of acetaldehyde and acetone were 0.043 and 0.148 ppb, respectively. NMHCs were measured using an online GC-MS/FID, developed by the RCEC (Research Center for Environmental Changes) of Academia Sinica, Taiwan, with a time resolution of 1 h. This system also analyzed low- and high-boiling point NMHCs using two separate channels. The detection limits of target species ranged from 0.003 to 0.039 ppb, and the analytical precision of most species was 0.5–2% (Li et al., 2010; Su et al., 2008).

In summer 2011 and 2012, and winter 2012, NMHCs and C<sub>3</sub>–C<sub>6</sub> carbonyls were analyzed using an online GC-MS/FID developed by PKU. This system collected samples for 5 min every 1 h using an electrical cryogenic device. The detection limits varied from 0.002 to 0.026 ppb (Wang et al., 2014b). C<sub>1</sub>–C<sub>3</sub> carbonyls were analyzed simultaneously by a commercial PTR-MS, with a time resolution of ca. 30 s. The detection limits of acetaldehyde and acetone were 0.20 and 0.15 ppb, respectively. Due to the influence of ambient humidity, the formaldehyde detection limit ranged from 0.22 to 0.34 ppb in winter, and 0.45–0.80 ppb in summer (Chen et al., 2014).

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