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Characteristics of atmospheric carbonyls during haze days in Beijing, China

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ABSTRACT

Characteristics of atmospheric carbonyls during haze days in Beijing were studied in August 2006. Formaldehyde (35.65 ± 14.74 μg/m^3), acetaldehyde (15.65 ± 12.37 μg/m^3) and acetone (8.83 ± 5.23 μg/m^3) are three most abundant carbonyls, accounting for ~75% of total carbonyls. Their levels and O_3 clearly peaked in the afternoon (especially for formaldehyde), implying photochemical formation. The observed C_1/C_2 (2.69 ± 0.78) and C_2/C_3 (6.29 ± 2.87) ratios indicated the important influence of anthropogenic source on carbonyls, and the higher C_1/C_2 (2.69) ratio in haze days also implied photochemical formation of carbonyls. Correlation coefficient (R^2) among formaldehyde, acetaldehyde, acetone and total carbonyls were 0.66–0.95 together with C_1/C_2 ratio analysis and diurnal variations of carbonyls and O_3, indicating ambient carbonyls in haze days of Beijing are mainly dominated by photochemical formation.

1. Introduction

As ubiquitous components in the atmosphere, carbonyl compounds have received increasing concern due to their adverse health effects on humans (Andreini et al., 2000; Guo et al., 2009; Lü et al., 2010) and to their roles as the major contributors to urban photochemical smog (Haagen-Smit, 1952; Bakeas et al., 2003; Ras et al., 2009). Generally, exhausts of motor vehicles and incomplete combustion of fuels in industrial processes are their primary sources in urban areas (Perry and Gee, 1995; Kean et al., 2001; Guo et al., 2007; Lü et al., 2010), and formations in photochemical oxidations of atmospheric hydrocarbons are their secondary sources (Atkinson, 2000; Sin et al., 2001; Grosjean et al., 2002; Atkinson and Arey, 2003). Moreover, their environmental toxicity has been a primary scientific subject, especially, short chain aldehydes (e.g., formaldehyde) have been long known to exert a great impact on human health because of their potentially carcinogenic and mutagenic properties (McLaughlin, 1994; Seco et al., 2007; Pal et al., 2008).

Considering the critical importance in atmospheric photochemistry and environmental toxicity of carbonyl compounds, many efforts have been conducted to accurately evaluate their environmental behaviors in urban and rural areas (Feng et al., 2005; Seco et al., 2007; Pal et al., 2008; Guo et al., 2009; Lü et al., 2010). Until now, however, very limited research aimed at characteristics of carbonyls in urban air under conditions of special pollutant episodes, e.g., haze (Lü et al., 2009; Tan et al., 2009), which could provide us for comprehensive insights into their behaviors in the atmosphere. Haze, defined as a weather phenomenon that leads to visibility of less than 10 km in China (CMA, 2003) as well as poor air quality in polluted cities (Chang et al., 2009; Tan et al., 2009), is formed from moisture, dust and vapor in the atmosphere. Now, haze pollution has attracted much interest among the public, scientific and governmental organizations due to its negative impact on visibility, human health, agriculture and even the global climate (Chameides et al., 1999; Okada et al., 2001; Chen et al., 2003; Schichtel et al., 2001; Yadav et al., 2003; Kang et al., 2004). Especially, meteorological conditions in haze days are different from those in normal days, which can lead to special characteristics of pollutants differing from that in normal days (Sun et al., 2006; Lü et al., 2009; Tan et al., 2009).

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Beijing (39.8°N, 116.5°E) is the political and cultural capital of China, which has been suffering from weak air quality including that caused by carbonyls due to rapid economic growth and a drastic increase of the number of vehicles in the past several decades (Wang et al., 2006; Chan and Yao, 2008; Mao et al., 2008; Fang et al., 2009; Li et al., 2010). Recent studies have shown that volatile organic compounds including carbonyls often present in ambient air of Beijing (Sun et al., 2006; Mao et al., 2008; Li et al., 2010), also haze has been observed frequently in Beijing, especially in summer (Sun et al., 2006; Wang et al., 2006; Pang et al., 2009). Our previous study studies showed that total concentration of carbonyls in haze days was higher than those in normal days (Lü et al., 2009). Especially, levels of atmospheric carbonyls can be largely evaluated in photochemical polluted areas, usually accompanying with high O_3 production. Considering (1) levels of carbonyls in haze days are higher and (2) study on carbonyls in haze days very limited up to now, it is important to investigate diurnal characteristics of carbonyls in haze days together with O_3 monitoring, which will be valuable for insight into the impacts of carbonyls on the air quality in Beijing.

2. Materials and methods

2.1. Experimental

2.1.1. Sampling

Beijing is located at temperate zone with half-moist continent monsoon climate. It is hot and humid in summer (e.g., August), especially, haze days in August with high relative humidity and high air temperature often occur. Field sampling was conducted on the ground level of 1.5 m on the campus of Tsinghua University in Beijing (Fig. 1). It is surrounded by several institutes, campuses, residential buildings and two side roads. No industrial emissions of carbonyls were found near the site.

Fig. 2 shows daily mean values of visibility in August 2006 in Beijing. As can be seen, mean values of visibility reached the lower levels (≤5.5 km) in the continuous three days (16–18th August). In our previous study, haze days are characterized by low visibility (≤10 km), low wind speed and high relative humidity and temperature (Tan et al., 2009). Fig. 2 shows diurnal values of visibility, wind speed, relative humidity and temperature on 16–18th August (these data were collected from http://www.wunderground.com). In this study, mean values of visibility, wind speed, relative humidity and temperature in haze days are 4.6 km, 2.2 m/s, 83.4% and 27.3 °C, respectively (Fig. 2). In China, haze days are defined as a weather phenomenon that leads to visibility of less than 10 km (CMA, 2003). Therefore, 16–18th August are selected out to be as haze days in this study.

Air samples were collected each day (16–18th August) (Beijing time) at 0:00, 3:00, 6:00, 9:00, 12:00, 15:00, 18:00 and 21:00 to observe carbonyls. Total 24 carbonyl samples were obtained during sampling periods. Briefly, samples were collected by drawing the air with a sampling pump (Gast, USA) through the 2,4-dinitrophenylhydrazine (DNPH)-coated cartridges (a Sep-Pak Silica Gel Cartridge: Waters, Millipore Co.). A potassium iodide (KI) denuder was connected to the upstream of the cartridge to prevent the interference of ozone. Before sampling, a breakthrough experiment was carried out by connecting two cartridges in series. The results indicated that no carbonyls were detected in the back cartridge when the sampling duration was 2 h at a flow rate of 2 l/min. Each sampling duration was 2 h and the flow rate was set at 2 l/min. To compare gas sampling data collected in various ambient conditions, we have specified that all gas volumes must be corrected to a set of predetermined standard conditions. After sampling, each cartridge was firstly wrapped in a Teflon bag

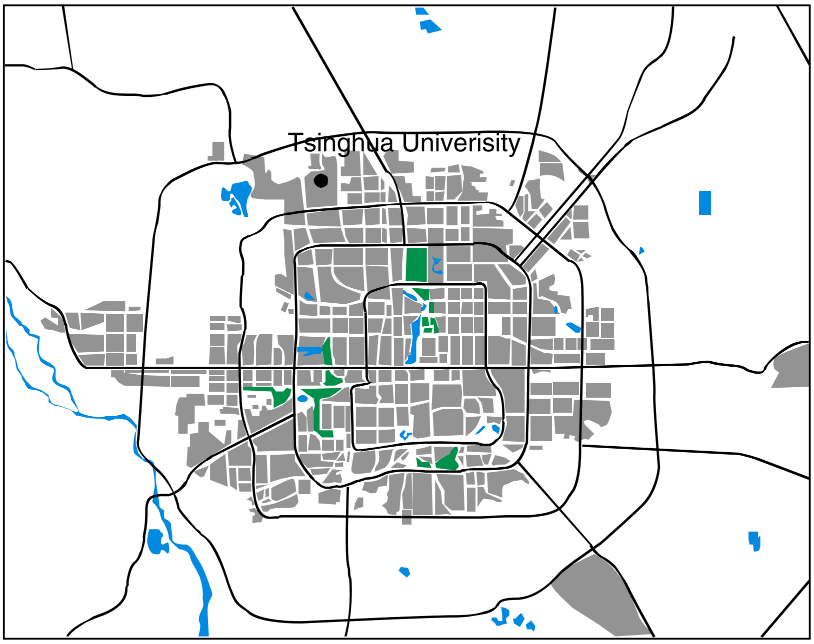

Fig. 1. Location of the sampling site in Beijing, China.