



# Carbonyl compounds over urban Beijing: Concentrations on haze and non-haze days and effects on radical chemistry



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## HIGHLIGHTS

- Haze reduced carbonyl compound level in summer but increased their level in winter.
- Carbonyl compound level on winter haze days approached their level on summer days.
- Both biogenic and anthropogenic sources contributed carbonyl compounds in summer.
- Yield of RO<sub>x</sub> radicals from carbonyl compound reactions was high on winter haze days.

## ARTICLE INFO

### Article history:

Received 15 February 2015

Received in revised form

23 June 2015

Accepted 27 June 2015

Available online 2 July 2015

### Keywords:

Carbonyl compound

Haze

Source

Radical cycling

## ABSTRACT

Carbonyl compounds play an important role in the formation of secondary aerosols and the cycling of free radicals in the atmosphere. We measured carbonyl compounds over urban Beijing, a megacity in the North China Plain, in summer and winter to investigate the relation of carbonyl compounds with haze and the interaction between carbonyl compounds and atmospheric radical cycling. We also determined carbonyl compounds in summer rainwater. Data of carbonyl compounds were analyzed in four cases, i.e., summer haze days (SHD), summer non-haze days (SND), winter haze days (WHD), and winter non-haze days (WND). Interestingly, the level of carbonyl compounds during WHD approached that of summer days. The results of the principal component analysis showed that there was no obvious source difference between SHD and SND. On WHD, however, more carbonyl compounds originated from the “diesel engine exhaust emission” than those on WND. We evaluated the effect of carbonyl compounds on the free radical cycling and the NO consumption potential for OH formation in the photochemical reactions using a novel ratio method. It was found that the production rate of RO<sub>x</sub> (the sum of OH, HO<sub>2</sub> and RO<sub>2</sub> radicals) was highest on SND, while the yield of RO<sub>x</sub> radicals from the reactions of carbonyl compounds was highest on WHD. Further, carbonyl compounds consumed more NO to produce OH radicals on WHD compared to the other three cases.

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## 1. Introduction

China has been suffering frequent haze pollution. The occurrence of haze brings serious adverse health effects to the public and greatly impairs the visibility. Understanding the cause of haze pollution therefore becomes an unprecedented challenge for researchers and policy makers. A number of studies have been focused on the haze pollution in China through monitoring and

modeling the variability of gaseous pollutants and particles on haze days (e.g., Sun et al., 2006; Wang et al., 2006; Zhang et al., 2013). These studies have made great contributions to the understanding of the cause of haze. Considering the complexity of this issue, however, the current knowledge about the formation of secondary aerosols is far from sufficient to understand the formation and duration of haze in China.

Haze is an aggregation of aerosols, majorly secondary aerosols in the case of Beijing. The level of secondary aerosols is known to be majorly determined by both the concentrations of gaseous precursors, such as SO<sub>2</sub> and VOCs (volatile organic compounds), and the atmospheric oxidizing capacity. It is noteworthy that VOCs,

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among the gaseous pollutants, play a dual role in the formation of secondary aerosols. Firstly, VOCs are important precursors to secondary organic aerosols (SOAs) (Claeys et al., 2004; Atkinson et al., 2008; Kroll and Seinfeld, 2008). Secondly, VOCs, especially the oxygenated volatile organic compounds (OVOCs), greatly affect the atmospheric oxidizing capacity by participating in the cycling of free radicals (Atkinson, 2000; Lelieveld et al., 2008). Liu et al. (2012) suggested that the photolysis of OVOCs, majorly carbonyl compounds, was the most important primary source of RO<sub>x</sub> (OH, HO<sub>2</sub> and RO<sub>2</sub> radicals) radicals, the most important oxidants in the atmosphere, in urban Beijing.

The interaction between carbonyl compounds and haze, however, is extremely complicated. First, the attenuated solar radiation by the high aerosol loading on haze days can directly decrease the photolysis frequency of carbonyl compounds and consequently affect the RO<sub>x</sub> chemistry. Second, the intensively produced aerosol particles and special meteorological conditions on haze days may influence the generation and removal of carbonyl compounds via heterogeneous reactions (Shen et al., 2013). A number of recent field studies have been performed to investigate the impact of haze on atmospheric carbonyl compounds in China. For example, Lü et al. (2009) compared the diurnal variation and the distribution of carbonyl concentrations between clear and haze days in Guangzhou and suggested that the meteorological condition was an important factor influencing the level and diurnal pattern of carbonyl compounds; Duan et al. (2012) suggested photochemical formation is the major source of carbonyl compounds on haze days in Beijing.

In the present study, we measured the concentrations of atmospheric carbonyl compounds in Beijing, on both haze and non-haze days. Through the analysis of chemical mechanisms and meteorological factors, we pointed out the major impact of haze on the distribution of carbonyl compounds and the different sources of carbonyl compounds over urban Beijing. With the aid of atmospheric models, we conducted a preliminary analysis on the interaction between carbonyl compounds and radical cycling.

## 2. Experimental methods

### 2.1. Site description

Our sampling site was located on the campus of Peking University (PKU, 39°59'20"N, 116°18'26"E), in northwest urban Beijing. The sampler was placed on top of the six-story teaching building, approximately 26 m above the ground.

### 2.2. Measurement methods

#### 2.2.1. Chemicals

The chemical reagents include ultrapure water (Milli-Q), 2,4-dinitrobenzene hydrazine (DNPH) (30 wt.%, TCI), acetonitrile (HPLC purity, MERCK), formaldehyde (35–38%, Sigma–Aldrich), acetaldehyde (≥99.7%, Fluka), acetone (≥96%, Fluka), propionaldehyde (≥96%, Fluka), methacrolein (≥95%, Sigma–Aldrich), methyl vinyl ketone (≥95%, Avocado), butaldehyde (≥99%, Alfa-Asia), benzaldehyde (≥99%, Alfa-Asia), glyoxal (40–45%, Sigma–Aldrich) and methyl glyoxal (~40%, Avocado).

#### 2.2.2. Determination method for carbonyl compounds

We used adsorption-reaction cartridges to collect samples and analyzed the samples using the high-performance liquid chromatography (HPLC) method. Air samples passed through an ozone scrubber (Waters Corp.) and a Sep-Pak DNPH-Silica Cartridge (Waters Corp.) successively and were trapped by DNPH cartridges. The ozone scrubber is filled with potassium iodide to avoid the

interference of ozone on analysis of carbonyl compounds. When relative humidity was high, potassium iodide would deliquesce and block the ozone scrubber. A novel method was used to solve this problem. When the ambient air was pumped into the sampling tubing, ultrapure nitrogen was simultaneously driven into the tubing and mixed with the sampled air. After mixing, the relative humidity was reduced. After the air sample was trapped, the DNPH cartridge was brought for elution (using 5 mL acetonitrile as eluent). The eluent sample was injected into HPLC for separation and ultraviolet (UV) detection. The eluent samples were calibrated by the standard solution of carbonyl compounds in acetonitrile with a concentration range of 0.25–10 μM, and the coefficient of determination ( $R^2$ ) of the calibrating curve was greater than 0.999. The HPLC analysis method was described in detail in our previous study (Wang et al., 2009).

The investigated periods were summer 2013 (21–30 July) and winter 2014 (4–13 and 16 January and 21 February to 1 March). Air was sampled continuously for 24 h at a total air flow rate of 0.8 standard L min<sup>-1</sup>. The cartridge was replaced every 3 h in daytime (07:20–22:20) and 9 h in nighttime (22:20–07:20). Every 3 days, a blank sample was determined to assure quality.

It should be noted that we measured the sum of the carbonyl compounds in both the gas- and particulate-phases. The additionally experimental results, however, showed that the ratio of carbonyl compound on PM<sub>2.5</sub> versus the total observed carbonyl compound was <1% for FA, AA and AC, and <7% for GL and MG (see the [supplementary materials](#)). This indicates that it is reasonable to represent the gaseous carbonyl compound using the total observed carbonyl compound.

#### 2.2.3. Determination method for common trace gases and particles

At the sampling site, a series of online monitors measured the concentrations of some common trace gases in the atmosphere, including CO, NO–NO<sub>2</sub>–NO<sub>x</sub>, O<sub>3</sub> and SO<sub>2</sub>. These gases were measured by Thermo 48i, 42i, 49i and 43i, respectively. Meanwhile, the mass concentration of PM<sub>2.5</sub> was measured by TEOM 1400A. The time resolution for all of the above data was 1 min.

#### 2.2.4. Meteorological conditions

At the sampling site, a meteorological station recorded real-time meteorological parameters continuously, including ambient temperature, relative humidity, wind speed, wind direction and barometric pressure. In general, the average temperature for the summer sampling period was 29.3 ± 4.0 °C (20.2–39.5 °C), the average relative humidity was 59 ± 16% (23–87%), the average barometric pressure was 993.6 ± 2.2 hPa (998.0–988.4 hPa), the average wind speed was 1.7 ± 1.2 m s<sup>-1</sup> (0.4–16.3 m s<sup>-1</sup>), and the dominant wind directions were southwest and northwest. The average temperature for the winter sampling period was 4.8 ± 2.7 °C (–1.1 to 13 °C), the average relative humidity was 45.2 ± 15.3% (3.7–71.5%), the average barometric pressure was 1020.2 ± 3.0 hPa (1012.5–1031.5 hPa), the average wind speed was 1.6 ± 1.2 m s<sup>-1</sup> (0.5–9.5 m s<sup>-1</sup>), and the dominant wind directions were southwest and northwest.

### 2.3. Modeling method

The photolysis frequencies of carbonyl compounds were calculated with a Tropospheric Ultraviolet and Visible (TUV, version 5.0; Madronich, 2002) radiation model. The model calculates the solar short-wave radiation between 120 and 735 nm in Earth's atmosphere. In this model, the radiation is affected by numerous factors, such as the column of ozone, sulfur dioxide and nitrogen dioxide, aerosol optical depth. In this study, the various variables involved were set at default values with the exception of the aerosol optical

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