



## Carbonyl compounds at Mount Tai in the North China Plain: Characteristics, sources, and effects on ozone formation



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### ABSTRACT

Carbonyl compounds, an important category of volatile organic compounds (VOCs), play important roles in ozone (O<sub>3</sub>) formation and atmospheric chemistry. To better understand the characteristics and sources of carbonyl compounds and their effects on O<sub>3</sub> formation, C<sub>1</sub>-C<sub>8</sub> carbonyls were measured at Mount Tai, the highest mountain in the North China Plain (NCP), in summer 2014. Acetone (3.57 ± 0.55 ppbv), formaldehyde (3.48 ± 0.98 ppbv) and acetaldehyde (1.27 ± 0.78 ppbv) are the three most abundant species, comprising as high as 90% of the total observed compounds. Isovaleraldehyde (0.37 ± 0.17 ppbv) presents another important carbonyl compound despite its high reactivity. Comparison with the observations available in China highlights the serious situation of carbonyls pollution in the NCP region. The sources of carbonyls are dominated by photo-oxidation of VOCs during the daytime and regional transport at night. Secondary sources from oxidation of hydrocarbons contribute on average 44% of formaldehyde, 31% of acetone, 85% of acetaldehyde, 78% of benzaldehyde, and 84% of isovaleraldehyde, demonstrating the dominant role of secondary formation in the ambient carbonyl levels. Formaldehyde, acetaldehyde and isovaleraldehyde are the most important contributors to the OH reactivity and O<sub>3</sub> production among the measured carbonyls. This study shows that carbonyl compounds contribute significantly to the photochemical pollution in the NCP region and hence understanding their sources and characteristics is essential for developing the science-based O<sub>3</sub> pollution control strategies.

### 1. Introduction

Carbonyl compounds, mainly composed of aldehydes and ketones, are an important class of volatile organic compounds (VOCs). They are ubiquitous in the troposphere and play critical roles in atmospheric chemistry (Atkinson, 2000). In the lower troposphere, photolysis of carbonyl compounds presents a significant primary source of the hydroxyl radical (OH) and peroxy radicals (i.e., HO<sub>2</sub> and RO<sub>2</sub>) and initiates the atmospheric oxidation (Volkamer et al., 2010; Xue et al., 2016). Meanwhile, when undergone photochemical degradation by reactions with OH and NO<sub>3</sub> radicals, the carbonyls will facilitate the production of ozone (O<sub>3</sub>) and secondary organic aerosols (SOA) (Atkinson and Arey, 2003; Li et al., 2011; Xue et al., 2016). Besides, carbonyls at high concentration levels can pose a direct threat to the human health because of their carcinogenic posing risks (Huang et al.,

2011). Kanjanasiranont et al. (2016) indicated that the formaldehyde posed high cancer risk to outdoor workers from the health risk assessment of related air pollutants. Therefore, it is of great significance to explore the characteristics and sources of carbonyls pollution from both points of atmospheric chemistry and regional air quality views.

In the troposphere, carbonyl compounds are either emitted directly from various primary sources including anthropogenic activities (e.g., traffic and industrial emissions) as well as natural and biomass burning sources (Guo et al., 2009; Liu et al., 2009; Pinto et al., 2014), or formed through the atmospheric oxidation of hydrocarbons (Atkinson, 2000; Atkinson and Arey, 2003; Menchaca-Torre et al., 2015). These secondary sources include the OH/NO<sub>3</sub>/O<sub>3</sub>/Cl atom-initiated degradation of a multitude of hydrocarbons such as alkenes, aromatics and alkanes (Atkinson and Arey, 2003; Liu et al., 2015; Xue et al., 2015). Consequently, the mixed primary and secondary sources result in the

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complexity in establishing a source-oriented control policy of carbonyls pollution. The source apportionment of carbonyls to primary emissions and secondary formation is an essential prerequisite for making effective control measures to mitigate photochemical air pollution.

Previous work has reported the serious carbonyls pollution in China (Li et al., 2010; Liu et al., 2009; Ling et al., 2016). Several studies have attempted to apportion the relative contributions of primary and secondary sources to the observed carbonyls in a few polluted regions. For instance, Wang et al. (2015) reported that photochemical production accounted for 34.9% of the measured HCHO in the Yangtze River Delta (YRD), eastern China. In comparison, about 48% of HCHO was attributed to secondary formation, with 54% of secondary HCHO producing from oxidation of alkenes in Beijing (Liu et al., 2009; Liu et al., 2015). However, these efforts mainly emphasized on the source apportionment of HCHO, with less attention being paid to the higher aldehydes which generally show higher photochemical reactivity. Further studies are required to estimate the source contributions for a wide variety of carbonyls to obtain a more comprehensive view on the cause of regional carbonyl pollution.

The wide-spread serious ozone air pollution in China have also been reported in the past three decades (Duan et al., 2008; Guo et al., 2017; Wang et al., 2016a; Wang et al., 2016b; Xue et al., 2014b). A number of studies have been conducted to assess the O<sub>3</sub>-precursor relationships to support the establishment of anti-pollution policy (An et al., 2015; Chou et al., 2011; Xue et al., 2014a; Xue et al., 2014b). In urban atmospheres, the O<sub>3</sub> production is more generally controlled by VOCs (Cheng et al., 2010; Xue et al., 2014a; Zhang et al., 2007). The contributions of different VOC groups to O<sub>3</sub> formation have also been evaluated by both observation-based models and estimations of OH reactivity and O<sub>3</sub> formational potential (OFP) of major VOCs (Kanaya et al., 2009; Xue et al., 2014a). However, most of these studies primarily focused on the hydrocarbons, and the contributions of carbonyls to the OH reactivity and O<sub>3</sub> formation have been rarely evaluated, due in part to the lack of observations. Indeed, limited studies have indicated the dominant fraction of oxygenated VOCs in the OH reactivity in the polluted Pearl River Delta region of China (Xue et al., 2016). Obviously, more efforts are needed to quantify the effects of carbonyls on the atmospheric oxidation and O<sub>3</sub> formation in other regions.

The North China Plain (NCP), owing to its fast expansion of economy and urbanization, has been undoubtedly experiencing severe photochemical air pollution (Liu et al., 2015; Rao et al., 2016). As an independent peak located in the center of the region, Mount Tai has been widely used to capture the “regional air pollution” in the NCP (Kanaya et al., 2013). Sun et al. (2016) have analyzed the climatological air mass transport pattern at Mount Tai in summer and indicated the dominant role of southerly and easterly air flows. To understand the characteristics and sources of the carbonyls, intensive field observations were conducted at this mountain site in the summer of 2014. In the following sections, we will first describe the concentration levels and chemical compositions of the measured carbonyls. We then explore the processes affecting the carbonyls by examining the diurnal variations and air mass transport histories. The relative contributions of primary and secondary sources are estimated with the aid of the multiple linear regression analysis, and finally the effects of carbonyls on O<sub>3</sub> formation are assessed by calculating the OH loss rates ( $L_{OH}$ ) and ozone formation potential (OFP) of individual VOCs.

## 2. Materials and methods

### 2.1. Experiments

The field campaign was conducted at the top of Mount Tai from 24 July to 26 August 2014. Mount Tai is situated in the center of the densely populated NCP region, and is also the highest mountain over the region (36.25°N, 117.10°E, 1534 m above sea level (a.s.l.); see Fig. 1). The measurement site was located approximately 1 km to the

north of the peak, the major tourism spot, with an altitude of 1465 m a.s.l., and there is little local emission nearby. During the measurement period, the southerly and southeasterly winds prevailed under the influence of the summertime Asian monsoon. The diurnal evolution of planetary boundary layer (PBL) makes the measurement site either in the upper PBL during the daytime on sunny days or in the free troposphere at night (Kanaya et al., 2013). Briefly, the study site is believed to be able to capture the regional air masses of the NCP region. Details of the study site have been described elsewhere (Gao et al., 2005; Sun et al., 2016).

Ambient carbonyl measurements were taken on seven potentially high O<sub>3</sub> days (i.e., 27 and 28 July, 4, 10, 12, 20 and 21 August). Specifically, air samples were collected into a 2,4-dinitrophenylhydrazine (DNPH) coated silica cartridge (Waters Sep-Pak DNPH-silica) at a flow rate of 1 L min<sup>-1</sup> every 3 h from 7:00 to 22:00 local time (LT; normally a total of 6 samples per day). An ozone scrubber coated with potassium iodide was connected in front of the cartridge to avoid the interference of O<sub>3</sub>. A total of 39 valid samples were taken during the campaign. After sampling, the samples were shipped to the air laboratory of the Hong Kong Polytechnic University for analysis using high-performance liquid chromatography (HPLC) based on the EPA TO-11a method (USEPA, 1999). The analysis procedures, quality assurance and quality control methods can be found elsewhere (Cheng et al., 2014; Ling et al., 2016). In the present study, selected C<sub>1</sub>-C<sub>8</sub> carbonyl species including formaldehyde (HCHO), acetaldehyde (CH<sub>3</sub>CHO), acetone, methyl ethyl ketone, iso + n-butyraldehyde, benzaldehyde, isovaleraldehyde and m-tolualdehyde were quantified with a detection limit of 0.02 μg m<sup>-3</sup>.

Meanwhile, O<sub>3</sub>, carbon monoxide (CO), sulfur dioxide (SO<sub>2</sub>) and nitrogen oxides (NO<sub>x</sub>) were continuously measured with a set of well-qualified commercial techniques, which have been extensively described in our previous publications (e.g., (Sun et al., 2016)). Several meteorological parameters were simultaneously recorded by an automatic weather station (PC-4, JZYG, China), including temperature, relative humidity (RH), wind speed and direction. Photolysis frequency of NO<sub>2</sub> ( $J_{NO_2}$ ) was monitored with a filter radiometer (Meteorologie Consult gmbh, Germany). Only data from 7:00–22:00 LT was analyzed in the present study considering the sampling time of carbonyls.

### 2.2. Meteorological and lagrangian particle dispersion model (LPDM)

The Weather Research and Forecasting model (WRF) was utilized to provide the meteorological fields in this study. Four domains, covering China, northern China, the North China Plain, and Mount Tai and its adjacent area, were used for the WRF model, with the grid resolution being 27, 9, 3 and 1 km, respectively. High spatial resolution was adopted to represent the complex terrain in this mountainous region. The parameterization options of the WRF model follow those in Tham et al. (2016) and Wang et al. (2016a).

The hourly meteorological simulation results from WRF was used to drive a Lagrangian particle dispersion model, the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) model (Draxler and Hess, 1998), to investigate the transport characteristics of air masses that arrived at the receptor site during the sampling period. The HYSPPLIT model calculated the spatiotemporal distributions of 2500 particles after they were released at Mount Tai for 12-h backward runs. Note that the model calculations were performed for the total 7 carbonyls sampling days, with 13:00 and 22:00 LT as the starting time and representing day and night, respectively. Detailed description and operating conditions of the LPDM can be found in our previous studies (Tham et al., 2016; Wang et al., 2016a).

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