Atmospheric Research 196 (2017) 53–61

Contents lists available at ScienceDirect

Atmospheric Research

journal homepage: www.elsevier.com/locate/atmosres

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

Xue Yang[a], Likun Xue[a,*], Lan Yao[a,d], Qinyi Li[b], Liang Wen[a], Yanhong Zhu[a], Tianshu Chen[a], Xinfeng Wang[a], Lingxiao Yang[a,c], Tao Wang[a,b], Shuncheng Lee[b], Jianmin Chen[a,c,d], Wenxing Wang[a]

[a] *Environment Research Institute, Shandong University, Ji'nan 250100, China*
[b] *Department of Civil and Environmental Engineering, Hong Kong Polytechnic University, Hong Kong, China*
[c] *School of Environmental Science and Engineering, Shandong University, Ji'nan 250100, China*
[d] *Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention (LAP3), Fudan Tyndall Centre, Department of Environmental Science and Engineering, Fudan University, Shanghai 200433, China*

ARTICLE INFO

Keywords:
Carbonyls
Secondary formation
Regional transport
OH reactivity
Ozone formation
Multiple linear regression model

ABSTRACT

Carbonyl compounds, an important category of volatile organic compounds (VOCs), play important roles in ozone (O_3) formation and atmospheric chemistry. To better understand the characteristics and sources of carbonyl compounds and their effects on O_3 formation, C_1-C_8 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_3 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_3 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_2 and RO_2) and initiates the atmospheric oxidation (Volkamer et al., 2010; Xue et al., 2016). Meanwhile, when undergone photochemical degradation by reactions with OH and NO_3 radicals, the carbonyls will facilitate the production of ozone (O_3) 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_3/O_3/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

---

* Corresponding author.
E-mail address: xuelikun@sdu.edu.cn (L. Xue).

http://dx.doi.org/10.1016/j.atmosres.2017.06.005
Received 20 February 2017; Received in revised form 22 May 2017; Accepted 4 June 2017
0169-8095/

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_3-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_3 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_3 formation have also been evaluated by both observation-based models and estimations of OH reactivity and O_3 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_3 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_3 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_3 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_3 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^{-1} 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_3. 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_1-C_8 carbonyl species including formaldehyde (HCHO), acetaldehyde (CH_3CHO), acetone, methyl ethyl ketone, iso + n-butyraldehyde, benzaldehyde, isovaleraldehyde and m-tolualdehyde were quantified with a detection limit of 0.02 μg m^{-3}.

Meanwhile, O_3, carbon monoxide (CO), sulfur dioxide (SO_2) and nitrogen oxides (NO_X) 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_2 (J_{NO2}) 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 (HYSPLIT) model (Draxler and Hess, 1998), to investigate the transport characteristics of air masses that arrived at the receptor site during the sampling period. The HYSPLIT 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).

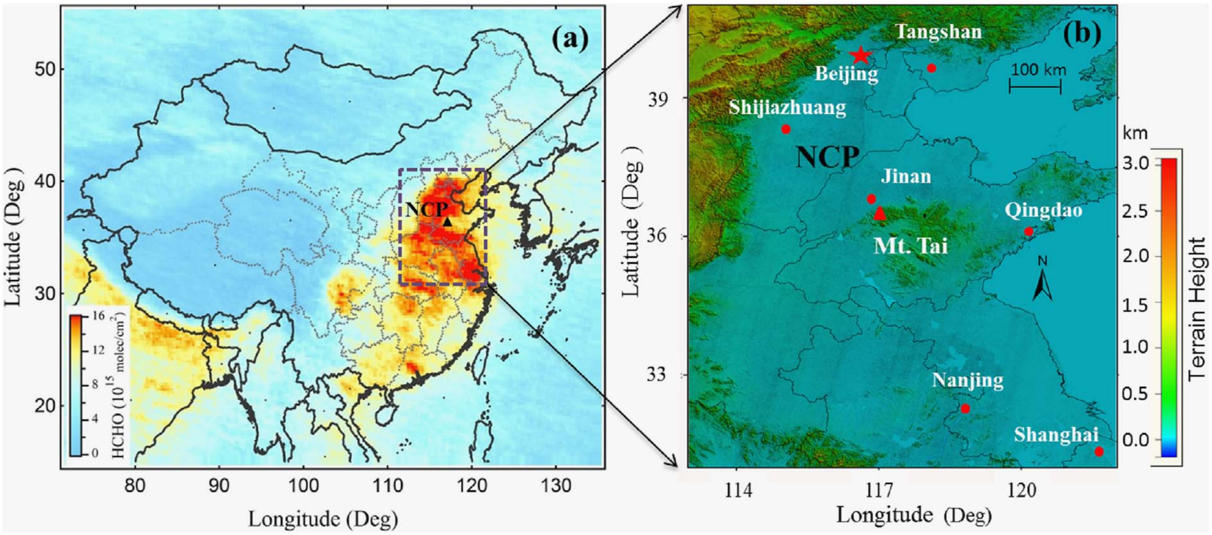

Fig. 1. Map showing the locations of the NCP region and Mount Tai. The left map is color-coded with the satellite (i.e., SCIAMACHY and GOME-2(B)) retrieved formaldehyde column, and the right one is color-coded by surface elevation height.

3. Results and discussion

3.1. Overall characteristics

Fig. 2 shows the overall time series of averaged 3-h concentrations of major carbonyl compounds together with O_3, CO, SO_2, NO_2, J_{NO2} and meteorological parameters at Mount Tai. Severe O_3 pollution was encountered during the sampling period with hourly average and 8-h average O_3 mixing ratios exceeding the national ambient air quality standards (Class II: 93 ppbv for hourly average and 75 ppbv for 8-h average) on 18 days (65% in frequency) and 22 days (85%), respectively. Higher levels of carbonyls were observed during the former period of the campaign, e.g., on 27–28 July and 4 August. The meteorological condition during this period was featured by relatively high temperature, low RH, high J_{NO2} and low wind speeds, suggesting the potential role of secondary photochemical sources for carbonyls. The highest concentration of carbonyls (13.70 ppbv; 3-h average) was recorded in the early afternoon (13:00 LT) of 27 July 2014, with O_3 reaching the maximum hourly value of 124 ppbv a few hours later. In comparison, relatively low carbonyl levels were observed during the later period of the campaign accompanied with relatively lower temperature. The lowest carbonyl concentration (5.17 ppbv; 3-h average) was observed in the evening of 10 August 2014. Overall, these observations reveal the severe photochemical air pollution in the NCP region in summer.

Average concentrations (± standard deviations) of major carbonyl

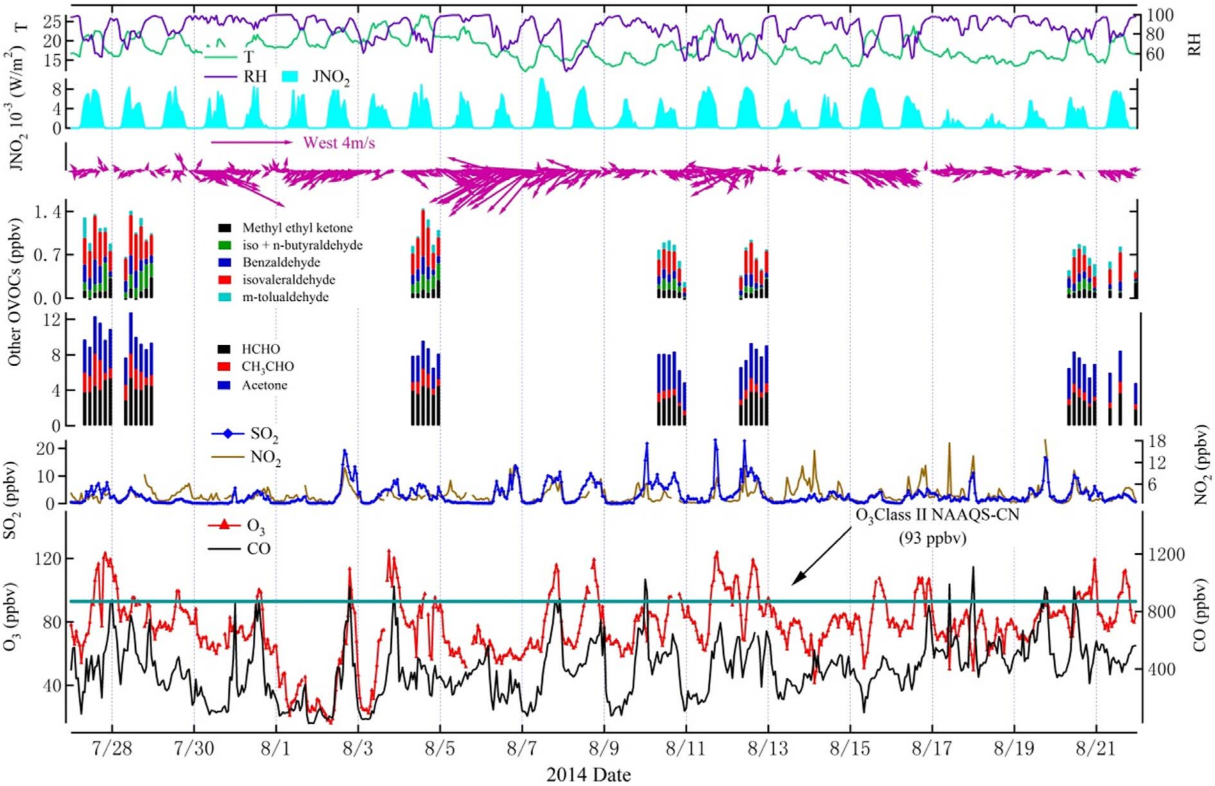

Fig. 2. Time series of major carbonyl compounds, related trace gases and meteorological parameters at Mount Tai from 24 July to 26 August 2014.

Table 1
Descriptive statistics of concentration levels and photochemical properties of the measured carbonyls at Mount Tai.

Compound	Mean ± SD (ppbv)	Range[a] (ppbv)	K_{OH}[b] (cm^3 $molecule^{-1}$ s^{-1})	L_{OH} (s^{-1})	MIR[c] (g O_3/g VOCs)	OFP (μg m^{-3})
HCHO	3.48 ± 0.98	1.15–5.36	$9.37 * 10^{-12}$	0.80	7.20	26.43
CH_3CHO	1.27 ± 0.78	0.37–3.68	$1.50 * 10^{-11}$	0.47	5.50	10.80
Acetone	3.57 ± 0.55	2.37–4.67	$1.70 * 10^{-13}$	0.01	0.56	4.07
Methyl ethyl ketone	0.12 ± 0.08	BDL–0.34	$3.00 * 10^{-14}$	0.00	–	–
Iso + n-butyraldehyde	0.13 ± 0.11	BDL–0.46	$2.40 * 10^{-11}$	0.08	5.28	1.72
Benzaldehyde	0.16 ± 0.08	0.06–0.40	$1.26 * 10^{-11}$	0.05	− 0.57	− 0.34
Isovaleraldehyde	0.37 ± 0.17	BDL–0.75	$2.80 * 10^{-11}$	0.25	4.42	4.89
m-Tolualdehyde	0.08 ± 0.07	BDL–0.33	$1.75 * 10^{-11}$	0.04	–	–

[a] BDL is "below detection limit".
[b] K_{OH} is the rate constant of carbonyls react with OH at 298 K (cm^3 $molecule^{-1}$ s^{-1}). The data are taken from Atkinson and Arey (2003) and Master Chemical Mechanism (*v3.3*; http://mcm.leeds.ac.uk/MCM/).
[c] MIR denotes the maximum incremental reactivity (unit: gram of ozone formed per gram of VOCs) (Carter, 1994).

species are summarized in Table 1. Of the eight measured carbonyls, acetone was the most abundant species, with an average value of 3.57 ± 0.55 ppbv and a maximum of 4.67 ppbv. Formaldehyde was the second abundant carbonyl species and its average concentration was 3.48 ± 0.98 ppbv with a maximum value of 5.36 ppbv, followed by acetaldehyde (1.27 ± 0.78 ppbv). Acetone, formaldehyde and acetaldehyde totally accounted for ~90% of the observed carbonyl compounds. The other five species showed relatively low concentrations, generally below 1 ppbv. Nevertheless, it is worth noting that isovaleraldehyde presented a considerably abundant level (0.37 ± 0.17 ppbv) compared to the other four compounds despite its high reactivity. Isovaleraldehyde, a high carbon carbonyl, is primarily produced from the chemical degradation of 3-methyl-1-butene, which is mainly used as raw materials for organic synthesis and high performance fuel manufacturing. The calculated lifetimes of isovaleraldehyde and 3-methyl-1-butene against OH oxidation are 8.3 and 7.3 h, with an assumed average OH concentration of ~1.2×10^6 molecules/cm^3 (Atkinson and Arey, 2003). Such relatively short chemical lifetimes of isovaleraldehyde and its parent hydrocarbon imply the presence of local emission source of 3-methyl-1-butene around the study region.

The formaldehyde/acetaldehyde ratio (F/A) has been widely adopted as an indicator to diagnose the possible sources of carbonyls in many previous studies. Generally, there is higher F/A ratio (up to 10) in the forested rural areas due to the fact that natural hydrocarbons, such as isoprene, produce more formaldehyde than acetaldehyde through photochemical reactions (Shepson et al., 1991). In comparison, the F/A ratios in polluted urban areas are much lower (generally ranging from 1 to 2), which should be attributed to the large amount of anthropogenic hydrocarbons and different meteorological conditions (Atkinson and Arey, 2003; Shepson et al., 1991). In the present study, the average F/A ratio at Mount Tai was 2.74, which was much smaller than those determined in the forest rural areas despite its high vegetation coverage fraction, but was comparable or a little higher than the ratios in urban atmospheres (see Table 2), elucidating the combined contributions of both natural sources and anthropogenic emissions to the atmospheric carbonyls at Mount Tai.

Table 2 compares the carbonyls pollution situations observed in recent years in four major domestic regions of China, i.e., NCP, YRD, Pearl River Delta (PRD), western China. Note the unit has been converted from μg m^{-3} to ppbv for comparisons. Compared with the other three regions, the NCP region clearly shows the most serious carbonyls pollution. Specifically, the concentrations of several major carbonyls, i.e. formaldehyde, acetaldehyde and acetone, at Mount Tai were even higher than those measured in urban/suburban areas of Hong Kong (Cheng et al., 2014; Ling et al., 2016), Guiyang (Pang and Lee, 2010), although they were as expected much lower than those in the metropolitan areas, such as Beijing (Duan et al., 2008; Rao et al., 2016), Shanghai (Huang et al., 2008), Xi'an (Dai et al., 2012; Wang et al., 2007), where anthropogenic emissions and photochemical oxidation functioned together as the sources of high levels of carbonyls. Overall, the comparison highlights the severity of carbonyls (and hence photochemical) pollution over the NCP region, not only in urban areas but also in background mountainous regions where rare investigations have been conducted previously.

3.2. Factors affecting the carbonyl variations

Diurnal variations of major carbonyls and O_3 on the individual sampling days are plotted in Fig. 3. These profiles clearly illustrate the daytime evolution characteristics of major carbonyls in this human-affected mountainous area. Formaldehyde, acetone and O_3 showed typical concentration peaks in the afternoon, which then decreased in the late afternoon, but increased again in the evening (19:00 LT) and remained at high levels at night (e.g., at 22:00 LT). The afternoon peaks reflect the significant contribution of photo-oxidation of VOCs to the observed concentrations of carbonyls and O_3 in the daytime. In addition, the uplift of PBL may also contribute to the increased concentrations in the afternoon. The high nighttime levels should be the result of transport of regional photochemically aged plumes to the mountain-top site. Indeed, high O_3 levels related to regional transport has been previously reported at Mount Tai (Sun et al., 2016). In comparison, acetaldehyde, isovaleraldehyde and benzaldehyde showed a different diurnal profile with a single concentration peak in the early afternoon (~13:00 LT) but low levels at night. The low nighttime levels of these reactive aldehydes are likely the result of more rapid loss during the transport considering their higher reactivity. The well-defined diurnal variation patterns evidence that the high carbonyl levels at Mount Tai are dominated by photochemical formation during the daytime and regional transport at night.

The aforementioned analysis reveals the remarkable effects of regional transport of polluted plumes on the observed high carbonyl levels at Mount Tai. To further understand the origin of air masses during the sampling period, we assessed the 12-h history of air masses arriving at the measurement site at 13:00 LT and 22:00 LT when major carbonyls showed the peak values for all sampling days by the LPDM (see Section 2). The calculated backward particle dispersion trajectories can be divided into two types according to the origins of air mass: one is originated from the south of Mt. Tai with higher carbonyl levels and the other is from the north with relatively lower carbonyl levels. Fig. 4 illustrates the backward particle dispersion simulations for the highest and lowest carbonyl pollution cases (i.e., 28 July and 10 August). It is clearly shown that on 28 July the air masses originated from the southeast sector at both 13:00 LT and 22:00 LT. There are many pollution sources nearby Mount Tai, including many power plants, steel plants and chemical plants which are situated ~30/40 km to the south (figures not shown). Therefore, the air masses mostly passed over the industrial zones in the southeast region before arriving at Mt. Tai, resulting in the observed high levels of carbonyls. On the contrary, on 10

Table 2
Comparison of major carbonyls and F/A ratio at Mount Tai with other locations in China.[a]

Region	Concrete locate	Type of sites	Time resolution	Formaldehyde	Acetaldehyde	Acetone	F/A	Period	Reference
North China Plain (NCP)	Mount Tai	Mountain	3-h	3.48	1.27	3.57	2.74	Jun.–Aug. 2014	This study
	Beijing (PKU)	Urban	24-h	11.39	4.75	5.65	2.40	21–30 Jul. 2013	Rao et al. (2016)
	Beijing (RCEES)	Urban	1-h	14.56	7.18	7.99	2.03	Jun.–Aug. 2005	Pang and Mu (2006)
	Beijing (PKU)	Urban	24-h	21.88	13.80	–	1.59	Jul. 4–Oct. 31 2008	Altemose et al. (2015)
	Beijing (THU)	Urban	3-h	26.82	11.16	10.05	2.40	16–19 Aug. 2006	Duan et al. (2008)
Yangtze River Delta (YRD)	Nangjing	Urban	2-h	5.07	8.05	2.10	0.63	Oct. 2011–Jul. 2012	Guo et al. (2016)
	Shanghai	Urban	2/3-h	14.49	8.10	4.58	1.79	Jan.–Oct. 2007	Huang et al. (2008)
Pearl River Delta (PRD)	Hong Kong (TW)	Urban	2-h	2.90	2.20	–	1.32	Sep.–Nov. 2010	Ling et al. (2016)
	Hong Kong (UST)	Suburban	24-h	1.97	0.46	–	4.28	Summer 2011	Cheng et al. (2014)
	Mount Tai Mo Shan	Mountain	2-h	3.32	1.24	3.71	2.68	Sep.–Nov. 2010	Ling et al. (2014)
	Guangzhou	Urban	–	10.90	8.45	5.95	1.29	Nov.–Dec. 2006	Lü et al. (2009)
	Mt. Dinghu	Mountain	–	2.7	2.2	–	1.23	Dec. 2006	Chi et al. (2008)
Northwest China	Xi'an	Urban	3-h	7.39	6.41	–	1.15	Jun.–Aug. 2004	Wang et al. (2007)
	Xi'an (IEECAS)	Urban	12-h	5.91	1.88	2.48	3.14	14–24 Jun. 2009	Dai et al. (2012)
	Guiyang	Urban	2-h	3.58	2.90	1.97	1.24	Dec. 2008–Aug. 2009	Pang and Lee (2010)

[a] The unit is ppbv except for F/A ratio which is ppbv/ppbv.

August the air mass transport route changed from the north/northwest directions at 13:00 LT to a prevailing westerly direction at 22:00 LT. These air masses mainly originated from the northern areas including some forest farms and the western areas including less developed and relatively clean suburbs at 13:00 and 22:00 LT, respectively. Furthermore, the weakened concentrations of CO, SO_2 and NO_2 at 22:00 LT on 10 August (see Fig. 2) are consistent with the switch of air masses. Statistically, the sampling site was dominated by southerly winds on 6 out of 7 sampling days, which is the typical summer condition in the NCP, highlighting the contribution of regional transport to the carbonyl levels at Mount Tai.

3.3. Contributions of primary and secondary sources

3.3.1. Formaldehyde

Ambient carbonyl concentrations are the result of both primary sources including traffic and fugitive industrial emissions and secondary formation from photochemical oxidation of the parent hydrocarbons. To evaluate the relative contributions of both primary and secondary sources to the observed carbonyls at Mount Tai, we used a tracer-based source apportionment approach that has been deployed in previous studies (Garcia et al., 2006; Li et al., 2010; Wang et al., 2015). Here acetylene (C_2H_2) and O_3 were selected as the specific tracers for primary and secondary sources, respectively. Generally, C_2H_2 is among the longest lived hydrocarbon species with a dominant source from the combustion emissions (Kanakidou et al., 1988), so the statistical analogy of carbonyls to acetylene can represent the primary contribution to the measured carbonyl concentrations. As an indicator of photochemical smog, O_3 is regarded as a typical secondary compound in the atmosphere. Hence, statistical analogies of carbonyls to O_3 were used to estimate the secondary contribution to the carbonyl concentrations. The contributions of both primary and secondary sources to the measured carbonyls can be estimated using the multiple linear regression model, as described as follows.

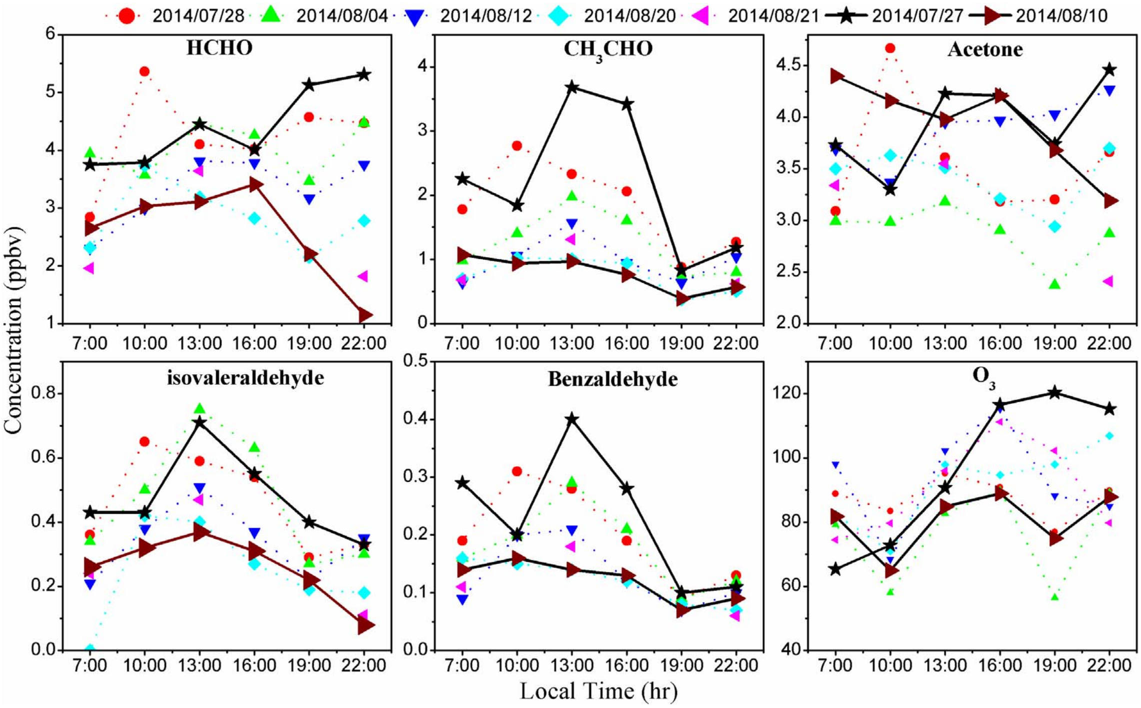

Fig. 3. Diurnal variation patterns of the measured major carbonyl compounds and O_3 on individual sampling days at Mount Tai.

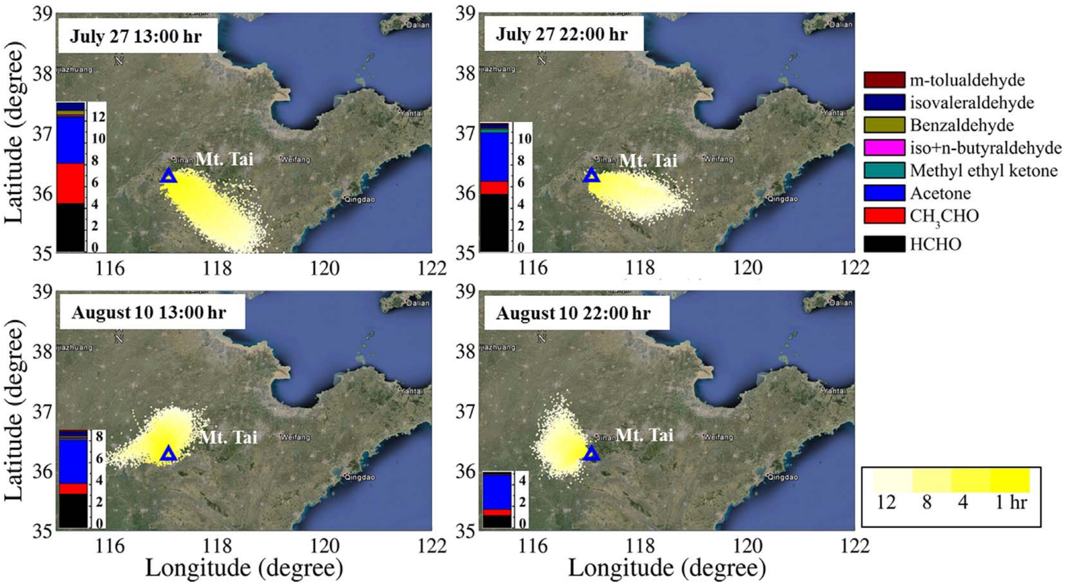

Fig. 4. The LPDM simulated 12-h history of air masses arriving at Mount Tai and the corresponding carbonyls concentrations (unit: ppbv) at 13:00 and 22:00 LT on 27 July and 10 August 2014.

$$[\text{carbonyl}] = \beta_0 + \beta_1 [C_2H_2] + \beta_2 [O_3] \tag{1}$$

where [carbonyl], $[C_2H_2]$ and $[O_3]$ represent the concentrations of the target carbonyl, C_2H_2 and O_3, respectively, and β_0, β_1, β_2 are correlation coefficients obtained from the multiple linear regression model. Based on Eq. (1), the carbonyl concentration can be apportioned to three parts: background concentration (β_0), primary source contribution (β_1 $[C_2H_2]$), and secondary production (β_2 $[O_3]$). It is noteworthy that the background concentration here represents the regional residual carbonyls, which may be attributed to either primary or secondary sources and not discriminated by the statistical analysis (Garcia et al., 2006).

The linear regression results including fitting parameters, the correlation coefficients (R) between calculated and measured concentrations, and the allocation to the three fractions of HCHO are summarized in Table 3. The significant value for the whole measurement period was determined as 0.00, indicating that the results obtained by Eq. (1) are statistically reliable. The calculated and measured concentrations during the sampling period showed excellent agreement with a correlation coefficient of 0.91. Secondary formation contributed on average nearly half of the measured HCHO (44%). The background value of HCHO was 1.20 ppbv, accounting for about 34% of the measured HCHO levels. Primary emissions contributed to the remaining 22%. Such source apportionment results for HCHO are comparable to those measured in Wenling, a rural site in the YRD, with primary and secondary sources accounting for 19% and 35%, respectively (Wang et al., 2015). A different result was obtained at an urban site in Beijing by Li et al. (2010), who showed a higher contribution from primary sources (48%) and a lower portion of secondary formation (23%). This can be explained by the difference between the study sites: the urban site of Beijing is surrounded by large amount of emission sources such as vehicles, whilst Mt. Tai is in a rural mountainous area and hence relatively remote from fresh primary emissions.

The time series of the calculated HCHO from primary and secondary sources together with the measured concentrations are depicted in Fig. 5. As expected, secondary formation generally showed higher contributions in the early afternoon when the photochemistry is most intensive. Meanwhile, it's also noteworthy that the estimated HCHO of secondary origin also showed high levels at night, which can be explained by the transport of regional aged plumes containing photochemically produced HCHO from the southeast sector of the NCP region (see Fig. 4). Overall, our results point to the significant photochemical sources of HCHO on a reginal scale over NCP.

3.3.2. Other carbonyls

Similar analyses were also performed for the other four carbonyls, namely, acetone, acetaldehyde, isovaleraldehyde and benzaldehyde,

Table 3
Linear regression coefficients and relative contributions of primary, secondary and background sources to the major carbonyls.

Linear regression coefficients	β_0	β_1	β_2	Sig.[a]
HCHO	1.2	0.83	0.025	0
CH_3CHO	− 1.01	0.54	0.02	0
Acetone	1.99	0.47	0.013	0
Benzaldehyde	− 0.05	0.062	0.0017	0
Isovaleraldehyde	− 0.32	0.2	0.0045	0

Relative contributions of sources (%)	Background	Primary	Secondary	R
HCHO	34%	22%	44%	0.91
CH_3CHO	–	15%	85%	0.66
Acetone	56%	13%	31%	0.86
Benzaldehyde	–	22%	78%	0.67
Isovaleraldehyde	–	16%	84%	0.74

[a] The term Sig. shows that the regression coefficients are acceptable at the 95% confidence interval.

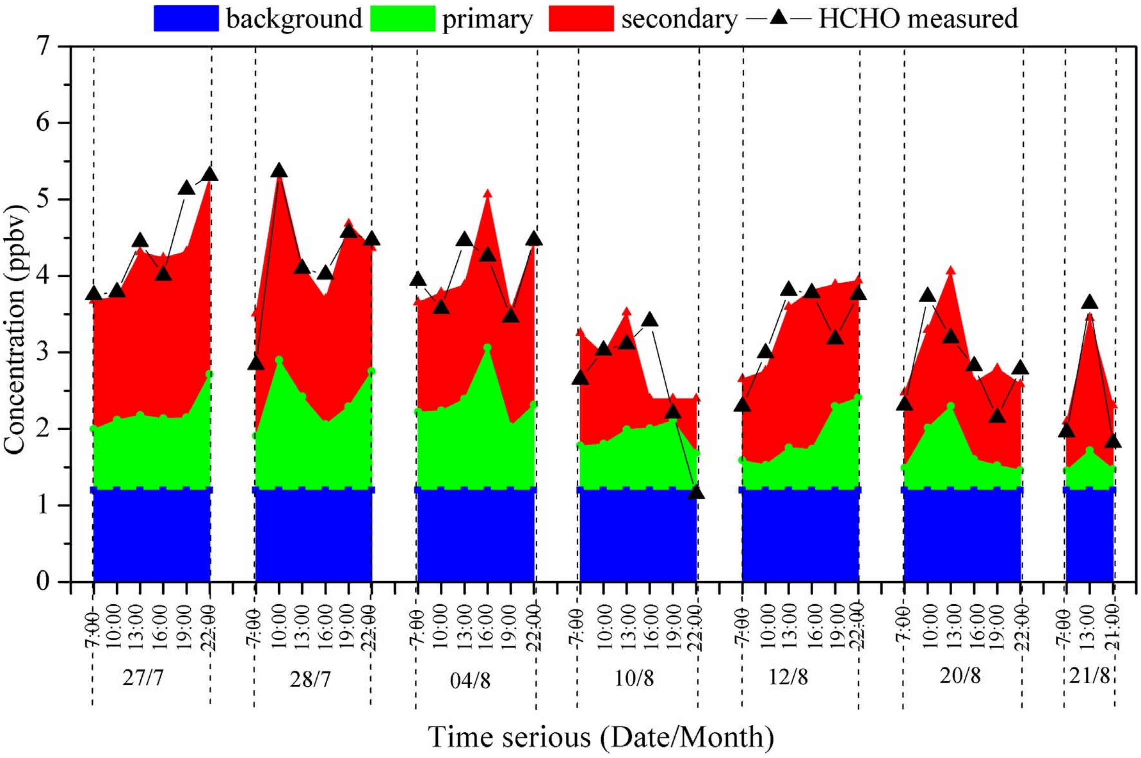

Fig. 5. The reconstructed time series of HCHO from the multiple linear regression model and comparison with the measured concentrations at Mount Tai.

and the results are documented in Table 3. The significant values determined for these four carbonyls are also 0.00, indicating the reliability of the statistical results. For acetone, a species with a low reactivity, secondary formation explained on average 31% of the measurements, with primary sources and regional background accounting for 13% and 56% respectively. For the other three highly reactive carbonyl species, in comparison, secondary production clearly played a dominant role and explained 85%, 84% and 78% of the measured acetaldehyde, isovaleraldehyde and benzaldehyde levels. This is in line with the fact that these higher carbon compounds in the atmosphere are mainly of photochemical origin (Atkinson, 2000; Atkinson and Arey, 2003; Yuan et al., 2012).

We also examined the diurnal variations of the calculated four carbonyls of both primary and secondary origins, as shown in Fig. 6. For the highly reactive compounds, i.e., acetaldehyde, isovaleraldehyde and benzaldehyde, the contributions of secondary sources generally showed a prominent noontime peak, consistent with the diurnal profiles discussed in Section 3.2. The small negative contributions from regional background suggest the minor negative effect of mixing with the background air on the concentration accumulation of these reactive carbonyls. For the less reactive acetone, in comparison, the regional background contributed to the majority of the measured concentrations (56%). These results indicate that the secondary sources dominate the variations of the highly reactive carbonyls, while for the less reactive carbonyls such as acetone, the residue concentration in the regional background air also plays a considerable role.

3.4. Effects on OH loss and O_3 formation

It is well known that O_3 is produced from the chemical reactions of nitrogen oxides ($NO_X = NO + NO_2$) and VOCs in the presence of sunlight in the troposphere (Crutzen, 1973). As mentioned above, markedly severe O_3 pollution was observed at Mount Tai during the sampling period. Individual carbonyl compounds have different photochemical reactivities and O_3 formation capacity. Therefore, it is of great importance to assess the contributions of individual carbonyl compounds to O_3 pollution at Mount Tai for developing science-based ozone pollution control measures. In the present study, the L_{OH} and OFP were calculated to evaluate the contributions of the individual measured carbonyls to ozone production. The L_{OH} of a particular compound was calculated as the product of its concentration multiplying its rate constant for reaction with OH (Li et al., 2010; Xue et al., 2014b). The OFP of VOC species is defined by $OFP_i = [VOC_i] \times MIR_i$, where $[VOC_i]$ is the concentration of VOC specie i expressed in μg m^{-3} and MIR_i is the maximum incremental reactivity coefficient for the VOC species i taking from literatures (Carter, 1994; Guo et al., 2016; Khwaja and Narang, 2008). The calculated results are summarized in Table 1.

HCHO showed the highest L_{OH} value with an average of 0.80 s^{-1}, followed by CH_3CHO (0.47 s^{-1}) and isovaleraldehyde (0.25 s^{-1}). These three carbonyls altogether accounted for 90% of the total L_{OH} by carbonyls. It is interesting to note that isovaleraldehyde play an important role in the hydrocarbon reactivity despite its moderately low concentration. In comparison, the L_{OH} of other measured carbonyls were almost negligible ($<$ 0.05 s^{-1}). In terms of OFP, HCHO clearly dominated the ozone formation of all measured carbonyls at Mount Tai with an average OFP value of 26.43 μg m^{-3}. The CH_3CHO ranked secondly with a mean value of 10.80 μg m^{-3}. Isovaleraldehyde and acetone also presented considerable contributions to O_3 formation with average OFPs of 4.89 and 4.07 μg m^{-3}, respectively. In contrast, benzaldehyde showed a small negative OFP value ($-$ 0.34 μg m^{-3}) due to its significant role in NOx sinks, reflecting its minor negative effect on ozone formation (Carter, 1994). Obviously, HCHO, CH_3CHO, and isovaleraldehyde are the most important reactive carbonyls at Mount Tai in terms of not only OH reactivity but also O_3 formation potential.

Moreover, the L_{OH} and OFP values of the primary carbonyls, including HCHO, CH_3CHO, acetone, isovaleraldehyde and benzaldehyde, were also calculated based on the source apportionment results as described in Section 3.3. Such information is highly relevant to policy making as primary emissions can be directly controlled. The primary HCHO contributed on average 0.18 s^{-1} of OH sink and 5.81 μg m^{-3} of ozone formation potential. Primary CH_3CHO showed L_{OH} and OFP values of 0.07 s^{-1} and 1.62 μg m^{-3}, respectively. Clearly, secondary

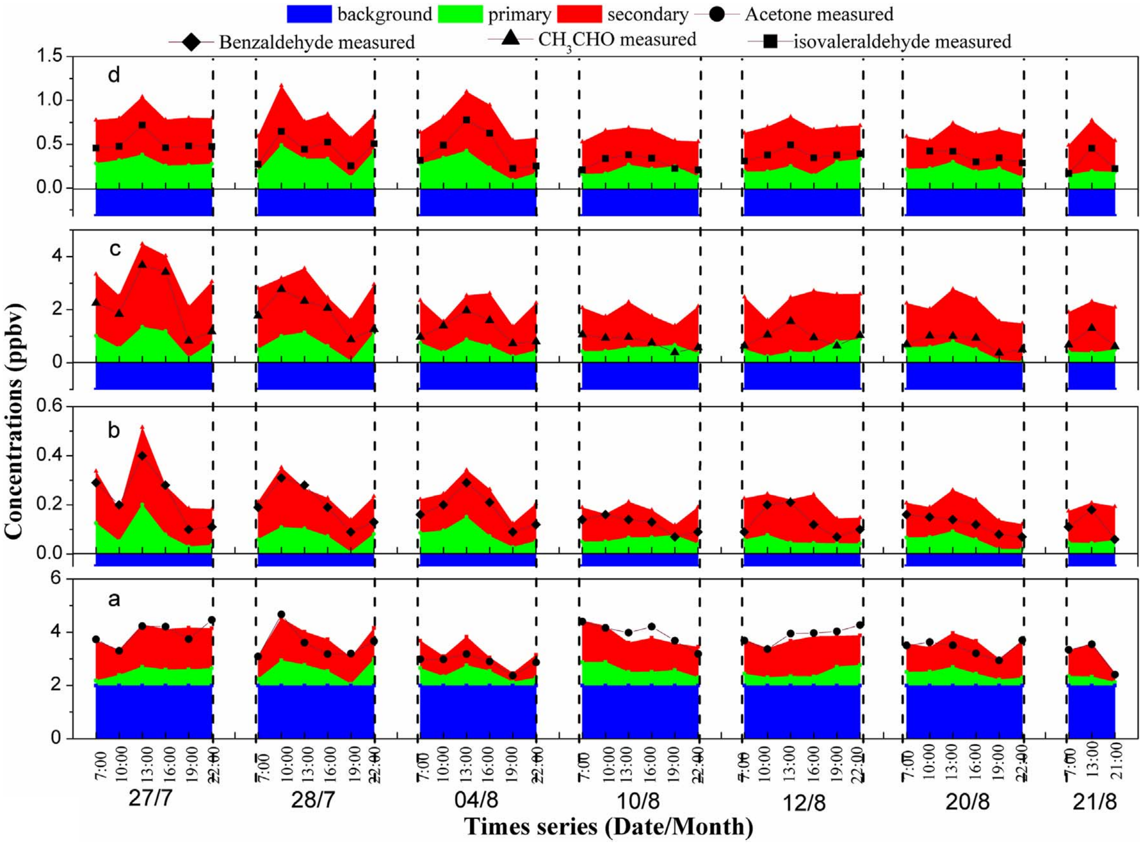

Fig. 6. The same as Fig. 5 but for (a) Acetone, (b) Benzaldehyde (c) CH_3CHO and (d) isovaleraldehyde.

carbonyls from photochemical formation of hydrocarbons contributed to the majority of the total OH sink and O_3 formation of measured carbonyls at Mount Tai. Overall, these above analyses reveal the important contributions of carbonyls and their parent hydrocarbons to the atmospheric chemistry and O_3 formation in the background atmosphere of the NCP region.

4. Conclusions

Ambient C_1-C_8 carbonyls and related trace gases were measured at the summit of Mount Tai from 24 July to 26 August 2014. Acetone, formaldehyde and acetaldehyde were the most three abundant carbonyls, while formaldehyde, acetaldehyde and isovaleraldehyde were the most reactive species. Secondary formation from photochemical degradation of parent VOCs and regional transport are the two major factors influencing the carbonyls pollution at Mount Tai. Secondary formation contributed to the majority of the ambient carbonyls, especially for the higher carbon compounds, with average contributions of 44%, 31%, 85%, 84% and 78% for formaldehyde, acetone, acetaldehyde, isovaleraldehyde and benzaldehyde, respectively. Formaldehyde, acetaldehyde and isovaleraldehyde played important roles in OH removal as well as ozone formation, and hence should be paid much attention for the future control of O_3 pollution. In sum, this study highlights the considerable impacts of carbonyls on the photochemical air pollution in the NCP region. In view of the relatively limited knowledge on the carbonyl pollution in China, it is recommended that more efforts are needed to better understand the characteristics, sources and impacts of carbonyl compounds in the polluted regions of China.

Acknowledgements

The authors thank Hao Wang, Weihao Wang and Caihong Xu for their help during the field measurements. We are grateful to NOAA Air Resources Laboratory for providing the HYSPLIT model. This study is supported by the National Natural Science Foundation of China (grant numbers 41275123, 91544213); the National Key Research and Development Programme of the Ministry of Science of Technology of China (grant number 2016YFC0200503); and the Qilu Youth Talent Program of Shandong University.

References

Altemose, B., Gong, J., Zhu, T., Hu, M., Zhang, L., Cheng, H., Zhang, L., Tong, J., Kipen, H.M., Strickland, P.O., Meng, Q., Robson, M.G., Zhang, J., 2015. Aldehydes in relation to air pollution sources: a case study around the Beijing Olympics. Atmos. Environ. 109, 61–69.

An, J., Zou, J., Wang, J., Lin, X., Zhu, B., 2015. Differences in ozone photochemical characteristics between the megacity Nanjing and its suburban surroundings, Yangtze River Delta, China. Environ. Sci. Pollut. Res. Int. 22, 19607–19617.

Atkinson, R., 2000. Atmospheric chemistry of VOCs and NOx. Atmos. Environ. 34, 2063–2101.

Atkinson, R., Arey, J., 2003. Atmospheric degradation of volatile organic compounds. Chem. Rev. 103, 4605–4638.

Carter, W.P.L., 1994. Development of ozone reactivity scales for volatile organic compounds. J. Air Waste Manage. Assoc. 44, 881–899.

Cheng, H., Guo, H., Wang, X., Saunders, S.M., Lam, S.H., Jiang, F., Wang, T., Ding, A., Lee, S., Ho, K.F., 2010. On the relationship between ozone and its precursors in the Pearl River Delta: application of an observation-based model (OBM). Environ. Sci. Pollut. Res. Int. 17, 547–560.

Cheng, Y., Lee, S.C., Huang, Y., Ho, K.F., Ho, S.S.H., Yau, P.S., Louie, P.K.K., Zhang, R.J., 2014. Diurnal and seasonal trends of carbonyl compounds in roadside, urban, and suburban environment of Hong Kong. Atmos. Environ. 89, 43–51.

Chi, Y., Li, Z., Feng, Y., Wen, S., Yu, Z., Sheng, G., Fu, J., 2008. Carbonyl compound concentrations in the air at Dinghu Mountain, Guangdong Province. Acta Sci. Circumst. 28, 2347–2353.

Chou, C.C.K., Tsai, C.Y., Chang, C.C., Lin, P.H., Liu, S.C., Zhu, T., 2011. Photochemical production of ozone in Beijing during the 2008 Olympic Games. Atmos. Chem. Phys. 11, 9825–9837.

Crutzen, P., 1973. A discussion of the chemistry of some minor constituents in the stratosphere and troposphere. Pure Appl. Geophys. 106, 1385–1399.

Dai, W.T., Ho, S.S.H., Ho, K.F., Liu, W.D., Cao, J.J., Lee, S.C., 2012. Seasonal and diurnal variations of mono- and di-carbonyls in Xi'an, China. Atmos. Res. 113, 102–112.

Draxler, R.R., Hess, G., 1998. An overview of the HYSPLIT_4 modelling system for trajectories, diepersion, and deposition. Aust. Meteorol. Mag. 47, 295–308.

Duan, J., Tan, J., Yang, L., Wu, S., Hao, J., 2008. Concentration, sources and ozone formation potential of volatile organic compounds (VOCs) during ozone episode in Beijing. Atmos. Res. 88, 25–35.

Gao, J., Wang, T., Ding, A., Liu, C., 2005. Observational study of ozone and carbon monoxide at the summit of mount Tai (1534 m a.s.l.) in central-eastern China. Atmos. Environ. 39, 4779–4791.

Garcia, A., Volkamer, R., Molina, L., Molina, M., Samuelson, J., Mellqvist, J., Galle, B., Herndon, S., Kolb, C., 2006. Separation of emitted and photochemical formaldehyde in Mexico City using a statistical analysis and a new pair of gas-phase tracers. Atmos. Chem. Phys. 6, 4545–4557.

Guo, S., Wen, S., Wang, X., Sheng, G., Fu, J., Hu, P., Yu, Y., 2009. Carbon isotope analysis for source identification of atmospheric formaldehyde and acetaldehyde in Dinghushan Biosphere Reserve in South China. Atmos. Environ. 43, 3489–3495.

Guo, S., Chen, M., Tan, J., 2016. Seasonal and diurnal characteristics of atmospheric carbonyls in Nanning, China. Atmos. Res. 169, 46–53.

Guo, H., Ling, Z.H., Cheng, H.R., Simpson, I.J., Lyu, X.P., Wang, X.M., Shao, M., Lu, H.X., Ayoko, G., Zhang, Y.L., Saunders, S.M., Lam, S.H., Wang, J.L., Blake, D.R., 2017. Tropospheric volatile organic compounds in China. Sci. Total Environ. 574, 1021–1043.

Huang, J., Feng, Y., Li, J., Xiong, B., Feng, J., Wen, S., Sheng, G., Fu, J., Wu, M., 2008. Characteristics of carbonyl compounds in ambient air of Shanghai, China. J. Atmos. Chem. 61, 1–20.

Huang, Y., Ho, S.S., Ho, K.F., Lee, S.C., Yu, J.Z., Louie, P.K., 2011. Characteristics and health impacts of VOCs and carbonyls associated with residential cooking activities in Hong Kong. J. Hazard. Mater. 186, 344–351.

Kanakidou, M., Bonsang, B., Le Roulley, J., Lambert, G., Martin, D., Sennequier, G., 1988. Marine source of atmospheric acetylene. Nature 333, 51–52.

Kanaya, Y., Pochanart, P., Liu, Y., Li, J., Tanimoto, H., Kato, S., Suthawaree, J., Inomata, S., Taketani, F., Okuzawa, K., 2009. Rates and regimes of photochemical ozone production over Central East China in June 2006: a box model analysis using comprehensive measurements of ozone precursors. Atmos. Chem. Phys. 9, 7711–7723.

Kanaya, Y., Akimoto, H., Wang, Z.F., Pochanart, P., Kawamura, K., Liu, Y., Li, J., Komazaki, Y., Irie, H., Pan, X.L., Taketani, F., Yamaji, K., Tanimoto, H., Inomata, S., Kato, S., Suthawaree, J., Okuzawa, K., Wang, G., Aggarwal, S.G., Fu, P.Q., Wang, T., Gao, J., Wang, Y., Zhuang, G., 2013. Overview of the Mount Tai experiment (MTX2006) in central East China in June 2006: studies of significant regional air pollution. Atmos. Chem. Phys. 13, 8265–8283.

Kanjanasiranont, N., Prueksasit, T., Morknoy, D., Tunsaringkarn, T., Sematong, S., Siriwong, W., Zapaung, K., Rungsiyothin, A., 2016. Determination of ambient air concentrations and personal exposure risk levels of outdoor workers to carbonyl compounds and BTEX in the inner city of Bangkok, Thailand. Atmos. Pollut. Res. 7, 268–277.

Khwaja, H.A., Narang, A., 2008. Carbonyls and non-methane hydrocarbons at a rural mountain site in northeastern United States. Chemosphere 71, 2030–2043.

Li, Y., Shao, M., Lu, S., Chang, C.-C., Dasgupta, P.K., 2010. Variations and sources of ambient formaldehyde for the 2008 Beijing Olympic games. Atmos. Environ. 44, 2632–2639.

Li, Z., Schwier, A.N., Sareen, N., McNeill, V.F., 2011. Reactive processing of formaldehyde and acetaldehyde in aqueous aerosol mimics: surface tension depression and secondary organic products. Atmos. Chem. Phys. 11, 11617–11629.

Ling, Z., Guo, H., Lam, S., Saunders, S., Wang, T., 2014. Atmospheric photochemical reactivity and ozone production at two sites in Hong Kong: application of a master chemical mechanism–photochemical box model. J. Geophys. Res.-Atmos. 119, 10567–10582.

Ling, Z., Guo, H., Chen, G., Lam, S.H.M., Fan, S., 2016. Formaldehyde and acetaldehyde at different elevations in mountainous areas in Hong Kong. Aerosol Air Qual. Res. 16, 1868–1878.

Liu, Y., Shao, M., Kuster, W.C., Goldan, P.D., Li, X., Lu, S., Gouw, J.A.d., 2009. Source identification of reactive hydrocarbons and oxygenated VOCs in the summertime in Beijing. Environ. Sci. Technol. 43, 75–81.

Liu, Y., Yuan, B., Li, X., Shao, M., Lu, S., Li, Y., Chang, C.C., Wang, Z., Hu, W., Huang, X., He, L., Zeng, L., Hu, M., Zhu, T., 2015. Impact of pollution controls in Beijing on atmospheric oxygenated volatile organic compounds (OVOCs) during the 2008 Olympic Games: observation and modeling implications. Atmos. Chem. Phys. 15, 3045–3062.

Lü, H., Cai, Q.-Y., Wen, S., Chi, Y., Guo, S., Sheng, G., Fu, J., Antizar-Ladislao, B., 2009. Carbonyl compounds in the ambient air of hazy days and clear days in Guangzhou, China. Atmos. Res. 94, 363–372.

Menchaca-Torre, H.L., Mercado-Hernández, R., Mendoza-Domínguez, A., 2015. Diurnal and seasonal variation of volatile organic compounds in the atmosphere of Monterrey, Mexico. Atmos. Pollut. Res. 6, 1073–1081.

Pang, X., Lee, X., 2010. Temporal variations of atmospheric carbonyls in urban ambient air and street canyons of a Mountainous city in Southwest China. Atmos. Environ. 44, 2098–2106.

Pang, X., Mu, Y., 2006. Seasonal and diurnal variations of carbonyl compounds in Beijing ambient air. Atmos. Environ. 40, 6313–6320.

Pinto, J.P., Martins, L.D., da Silva Junior, C.R., Sabino, F.C., Amador, I.R., Solci, M.C., 2014. Carbonyl concentrations from sites affected by emission from different fuels and vehicles. Atmos. Pollut. Res. 5, 404–410.

Rao, Z., Chen, Z., Liang, H., Huang, L., Huang, D., 2016. Carbonyl compounds over urban Beijing: concentrations on haze and non-haze days and effects on radical chemistry. Atmos. Environ. 124, 207–216.

Shepson, P., Hastie, D., Schiff, H., Polizzi, M., Bottenheim, J., Anlauf, K., Mackay, G., Karecki, D., 1991. Atmospheric concentrations and temporal variations of C1-C3 carbonyl compounds at two rural sites in central Ontario. Atmos. Environ. 25, 2001–2015.

Sun, L., Xue, L., Wang, T., Gao, J., Ding, A., Cooper, O.R., Xu, P., Wang, Z., Wang, X., Wen, L., Zhu, Y., Chen, T., Yang, L., Wang, Y., Chen, J., Wang, W., 2016. Significant increase of summertime ozone at Mount Tai in Central Eastern China. Atmos. Chem. Phys. 16, 10637–10650.

Tham, Y.J., Wang, Z., Li, Q., Yun, H., Wang, W., Wang, X., Xue, L., Lu, K., Ma, N., Bohn, B., Li, X., Kecorius, S., Größ, J., Shao, M., Wiedensohler, A., Zhang, Y., Wang, T., 2016. Significant concentrations of nitryl chloride sustained in the morning: investigations of the causes and impacts on ozone production in a polluted region of northern China. Atmos. Chem. Phys. 1-34.

USEPA, 1999. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air Second Edition: Compendium Method TO-11A Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC). (Active Sampling Methodology).

Volkamer, R., Sheehy, P., Molina, L.T., Molina, M.J., 2010. Oxidative capacity of the Mexico City atmosphere – part 1: a radical source perspective. Atmos. Chem. Phys. 10, 6969–6991.

Wang, B., Lee, S.C., Ho, K.F., 2007. Characteristics of carbonyls: concentrations and source strengths for indoor and outdoor residential microenvironments in China. Atmos. Environ. 41, 2851–2861.

Wang, M., Chen, W., Shao, M., Lu, S., Zeng, L., Hu, M., 2015. Investigation of carbonyl compound sources at a rural site in the Yangtze River Delta region of China. J. Environ. Sci. (China) 28, 128–136.

Wang, T., Tham, Y.J., Xue, L., Li, Q., Zha, Q., Wang, Z., Poon, S.C., Dubé, W.P., Blake, D.R., Louie, P.K., 2016a. Observations of nitryl chloride and modeling its source and effect on ozone in the planetary boundary layer of southern China. J. Geophys. Res.-Atmos. 121, 2476–2589.

Wang, T., Xue, L., Brimblecombe, P., Lam, Y.F., Li, L., Zhang, L., 2016b. Ozone pollution in China: a review of concentrations, meteorological influences, chemical precursors, and effects. Sci. Total Environ. 575, 1582–1596.

Xue, L.K., Wang, T., Louie, P.K., Luk, C.W., Blake, D.R., Xu, Z., 2014a. Increasing external effects negate local efforts to control ozone air pollution: a case study of Hong Kong and implications for other Chinese cities. Environ. Sci. Technol. 48, 10769–10775.

Xue, L.K., Wang, T., Gao, J., Ding, A.J., Zhou, X.H., Blake, D.R., Wang, X.F., Saunders, S.M., Fan, S.J., Zuo, H.C., Zhang, Q.Z., Wang, W.X., 2014b. Ground-level ozone in four Chinese cities: precursors, regional transport and heterogeneous processes. Atmos. Chem. Phys. 14, 13175–13188.

Xue, L.K., Saunders, S.M., Wang, T., Gao, R., Wang, X.F., Zhang, Q.Z., Wang, W.X., 2015. Development of a chlorine chemistry module for the master chemical mechanism. Geosci. Model Dev. 8, 3151–3162.

Xue, L.K., Gu, R.R., Wang, T., Wang, X.F., Saunders, S., Blake, D., Louie, P.K.K., Luk, C.W.Y., Simpson, I., Xu, Z., Wang, Z., Gao, Y., Lee, S., Mellouki, A., Wang, W., 2016. Oxidative capacity and radical chemistry in the polluted atmosphere of Hong Kong and Pearl River Delta region: analysis of a severe photochemical smog episode. Atmos. Chem. Phys. 16, 9891–9903.

Yuan, B., Shao, M., de Gouw, J., Parrish, D.D., Lu, S., Wang, M., Zeng, L., Zhang, Q., Song, Y., Zhang, J., Hu, M., 2012. Volatile organic compounds (VOCs) in urban air: How chemistry affects the interpretation of positive matrix factorization (PMF) analysis. J. Geophys. Res. 117, D24302. http://dx.doi.org/10.21029/22012JD018236.

Zhang, J., Wang, T., Chameides, W., Cardelino, C., Kwok, J., Blake, D., Ding, A., So, K., 2007. Ozone production and hydrocarbon reactivity in Hong Kong, Southern China. Atmos. Chem. Phys. 7, 557–573.