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The pollution levels, variation characteristics, sources and implications of atmospheric carbonyls in a typical rural area of North China Plain during winter

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ARTICLE INFO

Article history:

Received 1 October 2019

Revised 30 April 2020

Accepted 2 May 2020

Available online 28 June 2020

Keywords:

Carbonyl compounds

Pollution characteristics

Source apportionment

Ozone formation

Environmental implication

ABSTRACT

Atmospheric carbonyls were measured at a typical rural area of the North China Plain (NCP) from November 13 to December 24, 2017 to investigate the pollution characteristics, sources and environmental implications. Fifteen carbonyls were detected, and formaldehyde, acetaldehyde and acetone accounted for about 81% at most. The concentration of the total carbonyls in heavily polluted days was twice more than that in clean days. In contrast to other carbonyls, *m*-tolualdehyde exhibited relatively high concentrations in the clean days in comparison with the polluted days. The ratios of three principal carbonyls to CO showed similar daily variations at different pollution levels with significant daytime peaks. Multiple linear regression analysis revealed that the contributions of background, primary and secondary sources to three principal carbonyls showed similar variation trends from the clean level to the heavily polluted level. The OH formation rate of formaldehyde showed a similar variation trend to its photodegradation rate, reaching the peak value at noon, which is important to maintain relatively high OH levels to initiate the oxidation of various gas-phase pollutants for secondary pollutant formation at the rural site. OH radical consumption rate and ozone formation potential (OFP) calculations showed that formaldehyde and acetaldehyde were the dominant oxidative species among measured carbonyls. As for OH radical consumption, *n*-butyraldehyde and *m*-tolualdehyde were important contributors, while for ozone formation potential, *n*-butyraldehyde and propionaldehyde made significant contri-

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butions. In addition, the contribution of carbonyl compounds to secondary organic aerosol (SOA) formation was also important and needs further investigation.

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Introduction

Atmospheric carbonyl compounds are a group of oxygenated volatile organic compounds (OVOCs) and distributed widely in the troposphere (Atkinson, 2000; Atkinson and Arey, 2003). There are two sources for the tropospheric carbonyls, one is directly emitted from anthropogenic activities and natural sources, such as incomplete combustion of fossil fuels, biomass burning, vegetation emissions, adhesives and coatings releases and etc. (Edwards et al., 2013, 2014; Mellouki et al., 2015), the other is secondary formation during the oxidation process of volatile organic compounds which are released from human activities and the nature (Liu et al., 2015; Mellouki et al., 2015). Although the concentration of carbonyls in the troposphere is very low and the volume mixing ratio is generally at ppbV level (Ho et al., 2015), it plays an important role in tropospheric atmospheric chemistry. The carbonyl compounds can be dissociated by ultraviolet radiation and produce RO_x ($RO_x = OH + HO_2 + RO_2$), for example, the photolysis of formaldehyde alone can contribute about 10%–16% to RO_x radical in Hong Kong and the Pearl River Delta (PRD) region (Xue et al., 2016). The OH or NO_3 -initiated degradation of carbonyl compounds generates peroxy radicals (RO_2 and HO_2) which can oxidize NO to NO_2 and thus lead to ozone formation (Rao et al., 2016). Furthermore, recent studies have shown that carbonyl compounds can react with ammonia, organic amines and SO_2 in the liquid film of particles to produce low volatile organic compounds, which is a significant formation pathway for secondary organic aerosols (SOA) (Moch et al., 2018). Moreover, carbonyl compounds are harmful to human health. Formaldehyde has a strong stimulating effect on human respiratory tract and has been proved to be carcinogenic to human body by the International Agency for Research on Cancer (IARC, 2006). In particular, studies have shown that formaldehyde concentration in some cities of China has exceeded its cancer risk threshold (Gong et al., 2017; Pang et al., 2007; Zhang et al., 2012).

In order to scientifically assess the environmental impacts and health hazards of atmospheric carbonyls, a number of observational studies on atmospheric carbonyls have been conducted (Chen et al., 2014; Cheng et al., 2014; Dai et al., 2012; Edwards et al., 2014; Guo et al., 2014; Ho et al., 2015; Huang et al., 2008; Lv et al., 2009; Mu et al., 2007; Wang et al., 2020). Compared with developed countries, the concentration of atmospheric carbonyls is high in most parts of China with large spatial and temporal variations. In general, the concentration of carbonyls in economically developed urban areas is significantly higher than that in underdeveloped urban areas and coastal areas. For example, in other winter observations, atmospheric formaldehyde concentrations in Beijing, Shanghai and Xi'an city sites were as high as 5.51 ppbV (Rao et al., 2016), 10.45 ppbV (Huang et al., 2008) and 4.46 ppbV (Dai et al., 2012), respectively, while that in Qinghai (background site) and Yantai (coastal site) were 1.48 ppbV (Mu et al., 2007) and 1.17 ppbV (Ho et al., 2015), respectively. The concentration of carbonyls generally showed a pattern of summer > spring/autumn > winter, daytime higher than night, and traffic peaks higher than other periods (Cheng et al., 2014; Guo et al., 2014). In addition, the concentration levels of carbonyl compounds vary significantly at different air pollution levels, it was reported that the carbonyl concentration under

polluted weather conditions in Guangzhou went up to about three times as high as that under non-polluted conditions (Lv et al., 2009).

North China Plain (NCP) has been experiencing serious air pollution due to rapid economic development and industrialization (Liu et al., 2015; Rao et al., 2016). Observations by Rao et al. (2016) showed that the average concentration of atmospheric carbonyls in Beijing was 16.05 ppbV in winter and 25.97 ppbV in summer, which was much higher than the concentrations in other regions of China. Moreover, it has been reported that the air pollution problems caused by residential household coal combustion for winter heating in rural areas of NCP were even more serious than that in urban areas (Liu et al., 2017b). This serious pollution may be accompanied by significant increase of atmospheric carbonyls. However, current studies on atmospheric carbonyls in China have been mainly concentrated in urbanized regions, and the observation of atmospheric carbonyls in vast rural areas of NCP has not been reported yet.

In order to investigate the pollution levels, variation characteristics, sources and environmental implications of atmospheric carbonyls in typical rural areas of NCP in winter, field measurement has been conducted at a typical rural site from November 13 to December 24, 2017 within the winter heating period during which coal burning was the main heat source. The characteristics of atmospheric carbonyls were analyzed under different air pollution levels. The environmental implications of carbonyls on atmospheric radical budget, SOA formation and so on were investigated by a variety of methods.

1. Materials and methods

1.1. Site description

The field measurement was carried out at the Station of Rural Environment, Chinese Academy of Sciences (SRE-CAS) (Xue et al., 2019), which locates in the farmland of Wangdu County, Baoding City, Hebei Province of China (115.25°E, 38.67°N) (Fig. 1), 270 km from Beijing, 100 km from Shijiazhuang (capital city of Hebei province), and 40 km from Baoding (the nearest large industrial city). This station is a typical rural site in the crop field (mainly wheat) in NCP region. The surrounding area is dominated by agriculture and there are no typical industrial emission sources. The nearest main road (Beijing-Hong Kong-Macau Expressway) is about one kilometer to the north and the traffic flow is heavy.

1.2. Sampling and analysis

The measurement was carried out from November 13 to December 24, 2017. The sampling and analysis of atmospheric carbonyls were conducted strictly following the USEPA Method TO-11A (USEPA, 1999). The air samples were collected by 2,4-dinitrophenylhydrazine (DNPH) coated cartridges (Sep-Pak, Waters, USA) with front-set ozone scrubber to eliminate O_3 interference. Samples were continuously collected every 2 hours per day with sampling flow of 1.2 L/min, meanwhile one laboratory blank and one field blank were collected each day. Samples were sealed and stored at 4°C in refrigerator, and then analyzed by high performance liquid chromatography (HPLC). The HPLC was calibrated using a mixture of carbonyl standards at concentration range of 0.025 - 1.50 µg/mL, covering

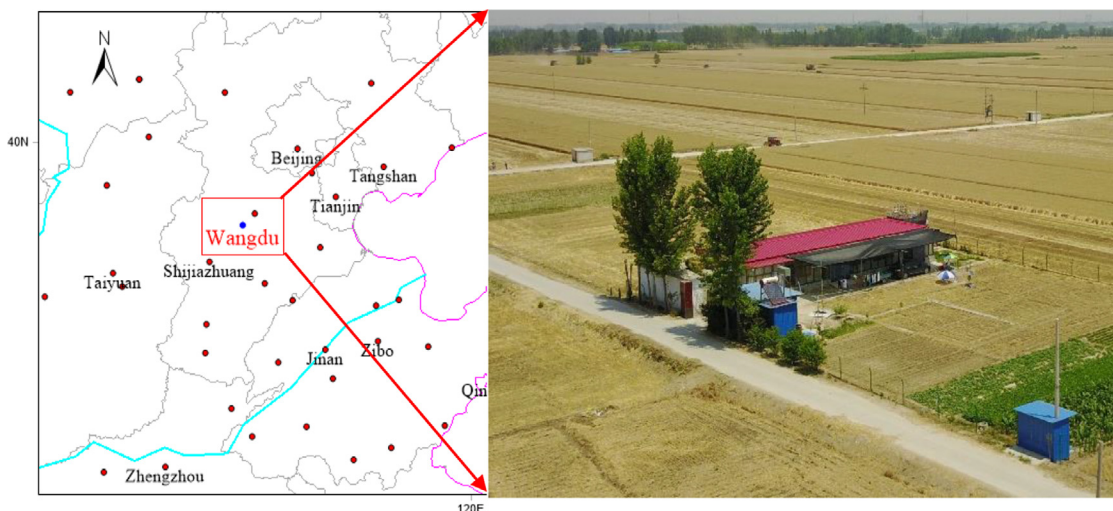


Fig. 1. – Location of measurement site in the rural area of Wangdu County.

the actual concentration range of carbonyl compounds in the atmosphere.

Concentrations of NO_x , SO_2 , O_3 and $\text{PM}_{2.5}$ were simultaneously measured using a set of commercial instruments, including a NO - NO_2 - NO_x chemiluminescence analyzer (Model 42i, Thermo Scientific (TS), USA), a pulsed fluorescence SO_2 analyzer (Model 43i, TS, USA), an ozone analyzer (Model 49i, TS, USA) and a tapered element oscillating microbalance (Model 1400A, TS, USA). These instruments were maintained and operated properly to ensure data accuracy. Scheduled quality control procedures were regularly performed, including daily zero and span checks, biweekly precision checks, quarterly multiple-point calibrations, and data validations as well. The acetonitrile (ACN) measurement was conducted online by a gas chromatography-mass spectrometry/flame ionization detector (GC-MS/FID) (ZF-PKU-VOC1007, Beijing Pengyuchangya, China) with a time resolution of 1 hr (Li et al., 2014, 2015), more detailed information about the instruments was described in previous studies (Yuan et al., 2013). Photolysis frequency of NO_2 (J_{NO_2}) was measured by 4- π - J_{NO_2} -Filter radiometer (Meteorologie Consult GmbH, Germany).

2. Results and discussion

2.1. Time series of atmospheric carbonyls

Fifteen carbonyl compounds in the air samples collected in the cartridge were identified with quantification and the time series of the carbonyls as well as meteorological parameters and related pollutants during the observation period are illustrated in Fig. 2. High concentration level of carbonyls appeared on 19–20 and 27 November, 1–3, 14–15, and 22–23 December, with the highest concentration of total carbonyls at 35.07 ppbV (18:00, December 23, 2017). It is evident that the concentrations of all the pollutants including the carbonyls exhibited significant fluctuations, with the difference between the highest and lowest concentrations of each species being 1–2 orders of magnitude. The lowest concentrations of the pollutants other than O_3 usually appeared under the condition with relatively high wind speed, revealing the dominant role of wind speed at the ground in the dispersion of atmospheric pollutants. The concentration of $\text{PM}_{2.5}$ frequently exceeded $150 \mu\text{g}/\text{m}^3$ and its maximal concentration could reach $600 \mu\text{g}/\text{m}^3$, revealing that the air pollution at this rural site was very serious. The variation trends of CO and $\text{PM}_{2.5}$ concen-

trations were very similar, suggesting that primary emission from incomplete combustion, such as household coal burning for heating by rural residents in winter, might be the dominant source for atmospheric $\text{PM}_{2.5}$ (Liu et al., 2017b). The atmospheric SO_2 at the rural site might also be affected by transportation from coal-fired power plants or industries besides the contribution of residential coal combustion, e.g., the occasional peaks of SO_2 concentration were not in line with those of CO and $\text{PM}_{2.5}$. The distinct difference between the variations of NO_2 and CO as well as SO_2 indicated different sources for them, e.g., NO_2 might be dominated by vehicle emission from the nearby highway, rather than the emission from the residential coal combustion. Biomass burning might be also an important source for atmospheric CO and $\text{PM}_{2.5}$ because the concentration of acetonitrile, the typical tracer of biomass burning, was relatively high (exceeding 0.6 ppbV during all pollution events with $\text{PM}_{2.5}$ greater than $150 \mu\text{g}/\text{m}^3$) and its variation trend was similar to those of $\text{PM}_{2.5}$ and CO. O_3 was mainly from the secondary formation through photochemical reactions, resulting in the distinct peak value around each noontime. Both the primary emissions from various sources mentioned above and the secondary formation like the case for O_3 were the sources for atmospheric carbonyls, and thus the variation trends of the carbonyls were distinctly different from those of above atmospheric pollutants. Nevertheless, high levels of atmospheric carbonyls were in line with the serious $\text{PM}_{2.5}$ pollution events, indicating that the primary emissions from the sources mentioned above for $\text{PM}_{2.5}$ might also made significant contribution to the atmospheric carbonyls.

In order to better understand the relationship between the concentrations of carbonyls and $\text{PM}_{2.5}$, the observation period was classified into three different air quality levels by referring to China's National Ambient Air Quality Standards (GB 3095-2012), which were clean level with $\text{PM}_{2.5} < 75 \mu\text{g}/\text{m}^3$, moderately polluted level with $\text{PM}_{2.5}$ in the range of 75 – $150 \mu\text{g}/\text{m}^3$ and heavily polluted level with $\text{PM}_{2.5} > 150 \mu\text{g}/\text{m}^3$. The concentrations of the total carbonyl compounds at three types of $\text{PM}_{2.5}$ levels were 8.07 ± 3.68 , 13.38 ± 85.77 and 16.93 ± 6.05 ppbV, respectively. The remarkable increase of atmospheric carbonyls from the clean level to the heavily polluted level was in agreement with the study of Rao et al. (2016) in Beijing.

2.2. Sources for atmospheric carbonyls

To recognize the sources of atmospheric carbonyls at the rural area, the composition proportions of the carbonyls, the diurnal variations for the ratios of three principle carbonyls to

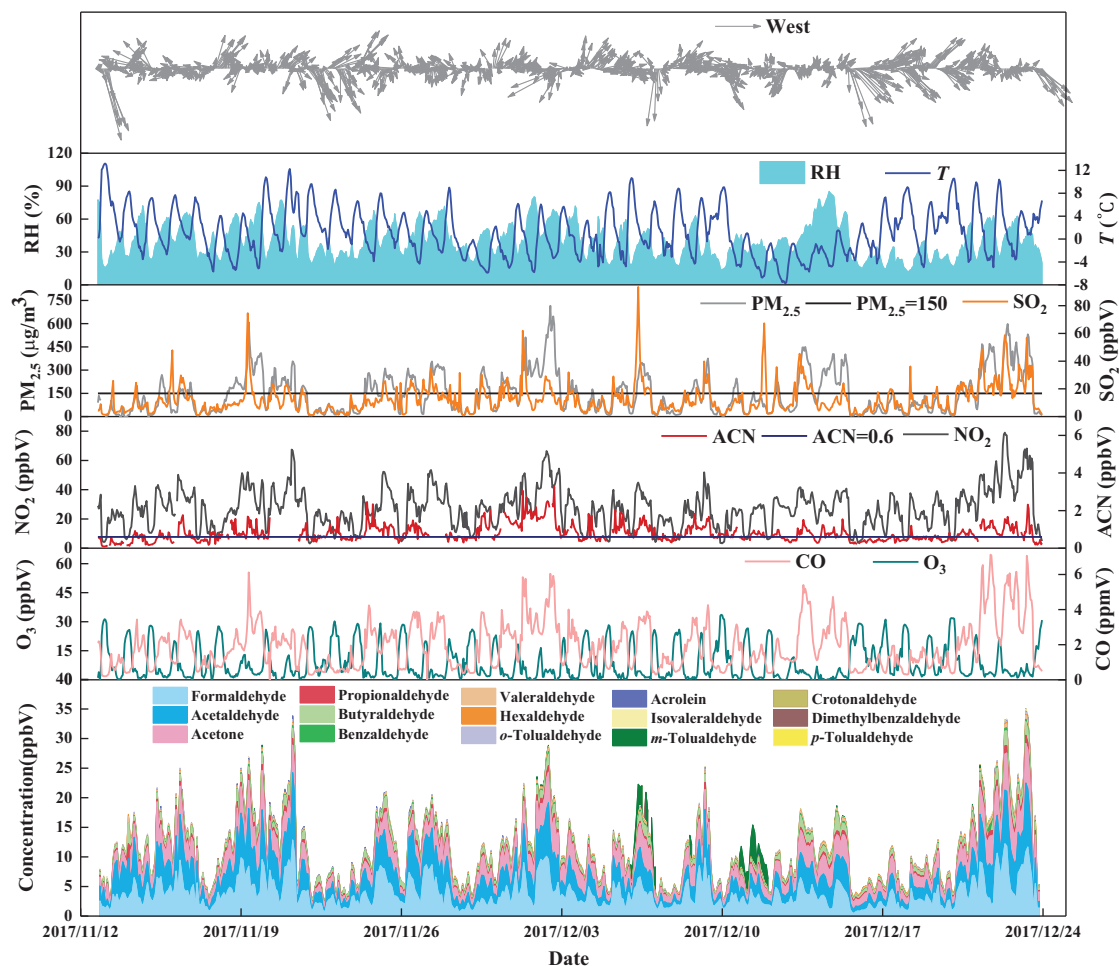


Fig. 2. – Time series of measured carbonyls, related pollutants and meteorological parameters during the observation period. ACN: acetonitrile; RH: relative humidity; T: temperature.

CO, and multiple linear regressions among the measured carbonyls, CO and O₃ were analyzed in this section.

2.2.1. Composition proportions of carbonyls

The composition proportions of atmospheric carbonyls measured at three types of PM_{2.5} levels are shown in Fig. 3. With only exception for the clean level, formaldehyde, acetaldehyde and acetone were found to be the most abundant, accounting for about 61%, 71% and 81% of the total carbonyls at the clean, moderately polluted and heavily polluted levels, respectively. The significant increase of their proportion from the clean level to heavily polluted level was mainly ascribed to the remarkable decrease of the *m*-tolualdehyde proportion. *m*-Tolualdehyde was the second largest carbonyl species with a proportion of 23.6% at the clean level, whereas became the fourth one (12.8%) at the moderately polluted level and the smallest one (1%) at the heavily polluted level. The opposite variation trends of the proportions between *m*-tolualdehyde and the three principal carbonyls indicated that the sources for *m*-tolualdehyde were evidently different from those for the three principal carbonyls. The clean level of PM_{2.5} in winter of the NCP usually occurred when wind direction was from the north (Liu et al., 2017b), and the Beijing-Hong Kong-Macao expressway is about 1 km to the north of the rural site. Therefore, it can be inferred that the relatively high concentration of *m*-tolualdehyde in clean days was very likely from the direct discharge of exhaust from high-speed motor vehicles and through the photooxidation of large amount of *m*-xylene emitted by those vehicles as well. The above deduction could

be supported by the frequent appearance of relatively high concentrations of *m*-tolualdehyde under the condition with wind from the north directions (Fig. 3). Additionally, previous study has shown that the combustion of residential household coal stoves mainly discharges formaldehyde, acetaldehyde and acetone, and the emission of *m*-tolualdehyde could even be ignored (Liu et al., 2017a). The heavy pollution of PM_{2.5} usually occurred when southerly winds were prevailing, while the south region of the observation station distributes high density of villages where farmers mainly depend on coal burning for winter heating. Therefore, the residential household coal combustion may be the main source for atmospheric carbonyl compounds in the rural area.

2.2.2. Diurnal variations for the ratios of three principal carbonyls to CO

In order to characterize the contribution of daytime photochemical reactions to atmospheric carbonyls, the diurnal variations of the ratios of three major carbonyls to CO were analyzed (offsetting the influence of meteorological factors). As shown in Fig. 4, FA/CO (formaldehyde/CO), AA/CO (acetaldehyde/CO), and AC/CO (acetone/CO) all exhibited distinct diurnal variations with minimal values at night, high values in daytime and maximal values around noontime, which was basically in line with the diurnal variation of O₃, indicating atmospheric photochemical reactions made significant contribution to the carbonyls. Although the O₃ peak concentration around noontime remarkably decreased from the clean level to the heavily polluted level, the peak values of the ratios espe-

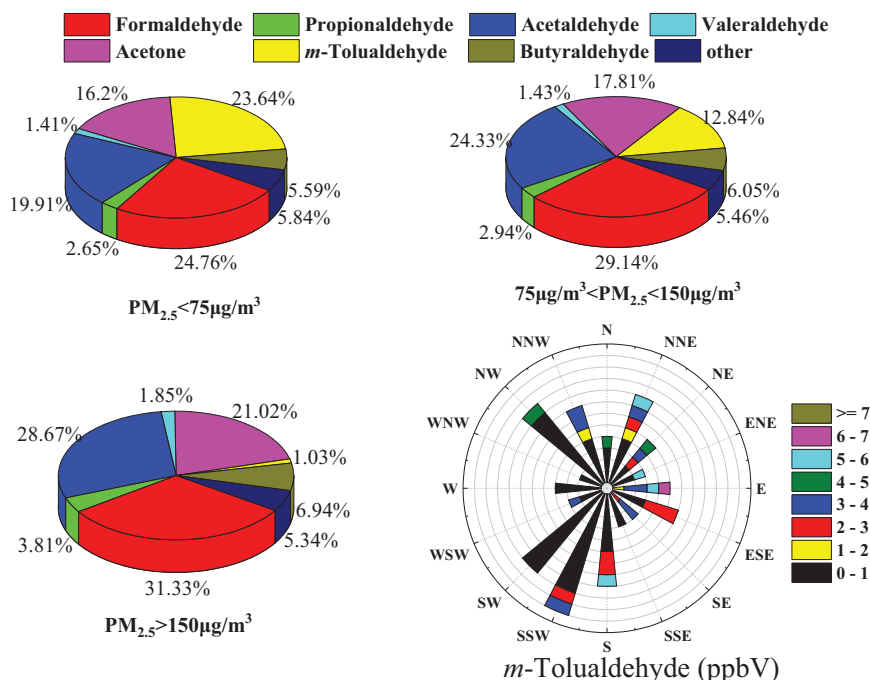


Fig. 3. – Compositions of carbonyl compounds at different air pollution levels and the wind rose of *m*-tolualdehyde with concentration.

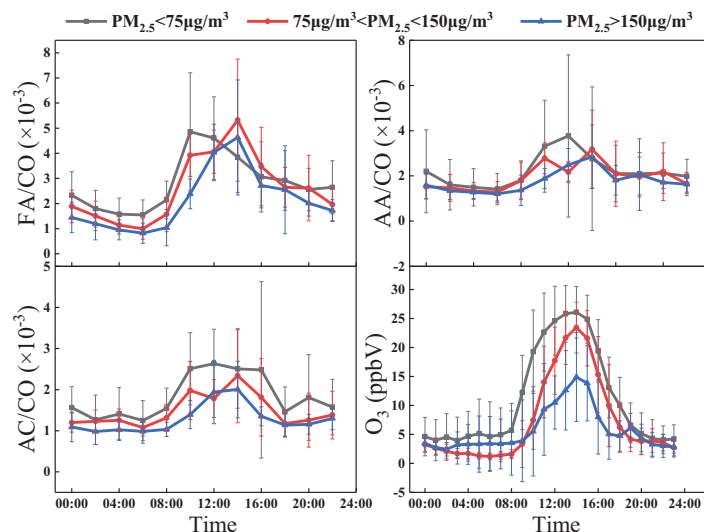


Fig. 4. – Diurnal variations of FA/CO, AA/CO, AC/CO and O₃ at different air pollution levels. FA: formaldehyde; AA: acetaldehyde; AC: acetone; CO: carbon monoxide.

cially for FA/CO decreased slightly, implying the photochemical reactions at the rural site even under the heavily polluted conditions with evident reduction of sunlight intensity were still very strong. Compared with the AA/CO and AC/CO, the much less reduction of FA/CO peak values around noontime from the clean level to the heavily polluted level might be ascribed to the decrease of formaldehyde photolysis, which is the dominant loss pathway for it, due to significant reduction of sunlight at the heavily polluted level.

2.2.3. Estimating the contributions of primary and secondary sources to atmospheric carbonyls

In order to quantitatively estimate the contributions of primary and secondary sources to atmospheric carbonyl compounds, multiple linear regression model was implemented

based on the typical tracers of these two sources, which have been used in previous studies (Li et al., 2010; Yang et al., 2017). Coal and biomass combustion as well as vehicle emissions were potential sources for the carbonyls and CO at the rural site, and hence CO was selected as the tracer for emission of carbonyls from the primary sources. O₃ was selected as the tracer for secondary sources because tropospheric O₃ is mainly produced from photochemical reactions. The linear regression model is shown in Eq. (1):

$$[\text{Carbonyl}] = \beta_0 + \beta_1[\text{CO}] + \beta_2[\text{O}_3] \quad (1)$$

where [Carbonyl], [CO] and [O₃] represent the concentrations of target carbonyl species, CO and O₃, respectively, and β_0 , β_1 , and β_2 are correlation coefficients obtained from multiple linear regression models. The sources of atmospheric carbonyls

Table 1 – Linear regression coefficients and relative contributions of sources to carbonyl compounds at different air pollution levels.

		Linear regression coefficients				Relative contributions of sources			
		β_0	β_1	β_2	Sig.	Background	Primary	Secondary	R
PM _{2.5} < 75 $\mu\text{g}/\text{m}^3$	Formaldehyde	1.086	1.151	0.020	0.00	41.1%	50.6%	8.4%	0.576
	Acetaldehyde	0.663	1.126	0.003	0.00	33.1%	65.3%	1.7%	0.699
	Acetone	0.779	0.746	0.005	0.00	45.8%	50.9%	3.3%	0.689
75 $\mu\text{g}/\text{m}^3$ < PM _{2.5} < 150 $\mu\text{g}/\text{m}^3$	Formaldehyde	1.354	0.980	0.069	0.00	34.0%	53.2%	12.8%	0.473
	Acetaldehyde	1.300	0.982	0.007	0.00	37.4%	61.1%	1.5%	0.638
	Acetone	0.722	0.931	0.005	0.00	26.0%	72.6%	1.3%	0.848
PM _{2.5} > 150 $\mu\text{g}/\text{m}^3$	Formaldehyde	3.270	0.398	0.333	0.00	56.8%	14.9%	28.3%	0.509
	Acetaldehyde	2.606	0.950	0.112	0.00	50.1%	39.4%	10.5%	0.647
	Acetone	2.165	0.654	0.049	0.00	56.7%	37.0%	6.3%	0.669

Sig. indicates that the coefficients on the regression are acceptable at the 95% confidence interval. β_0 , β_1 , and β_2 : correlation coefficients obtained from multiple linear regression models.

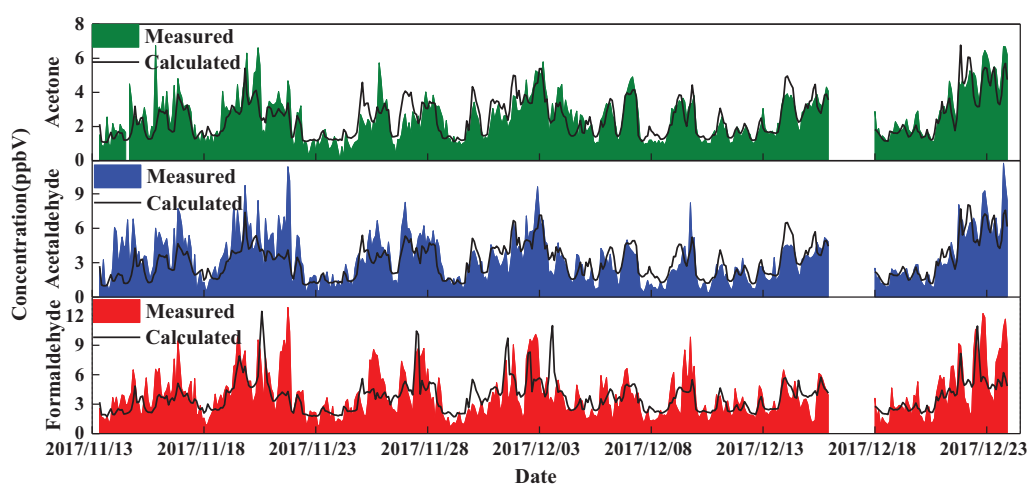


Fig. 5. – Time series of measured and calculated formaldehyde, acetaldehyde and acetone.

are usually divided into three sectors in the model, including background concentration (β_0), primary source contribution ($\beta_1[\text{CO}]$), and secondary source contribution ($\beta_2[\text{O}_3]$). It is worth noting that the background concentration for each carbonyl represents its concentration evenly distributed in the atmosphere over a region, without differentiating its primary sources from secondary sources (Garcia et al., 2006; Yang et al., 2017).

The regression coefficients and the relative contributions of these three source sectors from the model results are listed in Table 1 and the time series of carbonyls measured and modeled are illustrated in Fig. 5. The model regression significance (Sig.) of 0.00 for each carbonyl meant the regression analysis is statistically reliable (Yang et al., 2017). The regression coefficients of β_0 significantly increased from the clean level to the heavily polluted level, with contributions of the background sector increasing from 41.1% to 56.8% for formaldehyde, from 33.1% to 50.1% for acetaldehyde, and from 45.8% to 56.7% for acetone. The significant increase of the contributions from the background sector at the heavily polluted level was mainly attributed to remarkable elevation of the regional carbonyls because serious air pollution events usually occur in the whole region of the NCP, rather than being confined to the rural site. In contrast to the contributions from the background sector, the contributions from the primary sector to the three major carbonyls evidently decreased from the clean level to the heavily polluted level, with contributions decreasing from 50.6% to 14.9% for formaldehyde, from 65.3% to 39.4% for acetaldehyde, and from 50.9% to 37% for acetone. The remarkable reduction of the contributions from the primary sec-

tor at the heavily polluted level was ascribed to the significant increase of the contributions from both the background sector and the secondary sector. Although sunlight irradiation was usually significantly reduced at the heavily polluted level in comparison with the clean level, the contributions of the secondary sector to the three major carbonyls at the heavily polluted level increased by a factor of 2-5, verifying that the photochemical reactivity at the heavily polluted level was still very strong due to significant elevation of VOCs and OH precursors (such as HONO). For formaldehyde at clean level and moderated polluted level, the contribution of the primary source sector estimated by this study were in agreement with the results of Li et al. (2010) who reported a value of about 48% in Beijing city, whereas the contribution of the secondary source sector at the rural site were less than those estimated by previous studies, e.g., 23% in Beijing city (Li et al., 2010), 34.9% in a rural area of the Yangtze River Delta (Wang et al., 2015) and 44% at the summit of Mount Taishan (Yang et al., 2017).

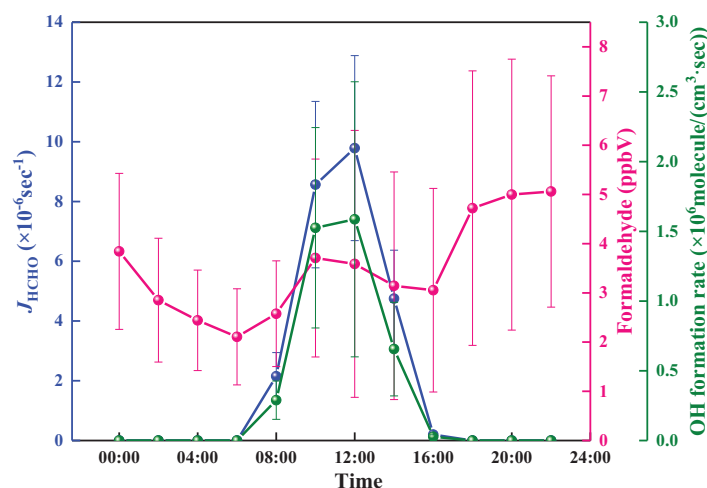
2.3. Comparisons with previous studies about carbonyls' levels at different places of NCP

The average concentrations of the three principal carbonyls are listed in Table 2 for comparison with those measured at different places in winter of the NCP by previous studies. Obviously, the average concentrations of formaldehyde, acetaldehyde and acetone at the rural site were comparable to those measured in urban Beijing from December 2004 to February 2005 (Pang and Mu, 2006) and in the winter

Table 2 – Comparisons of formaldehyde (FA), acetaldehyde (AA) and acetone (AC) levels between the rural site and urban Beijing.

Location	FA (ppbV)	AA (ppbV)	AC (ppbV)	F/A	Period	References
Wangdu	3.73	3.19	2.46	1.17	November-December, 2017	This study
	5.43	4.96	3.66	1.09	November-December, 2017, haze	
	4.42	3.69	2.77	1.20	November-December, 2017, moderate	
	2.65	2.13	1.73	1.24	November-December, 2017, clean	
Beijing (RCEES)	3.13	3.86	3.01	0.81	December, 2004- February, 2005	Pang and Mu, 2006
	7.47	6.11	6.95	1.22	2008-2010, winter	
Beijing (PKU)	10.33	4.27	5.89	2.42	2013, summer haze	Rao et al., 2016
	12.17	5.11	5.46	2.38	2013, summer clean	
Beijing (BAAFS)	7.65	5.89	5.83	1.30	2013, winter haze	Sheng et al., 2018
	3.49	2.36	2.69	1.48	2014, winter clean	
	41.65	15.81	7.92	2.63	2016, winter haze	
Beijing (BAAFS)	18.32	4.37	2.22	4.19	2016, winter clean	
Wangdu	/	2.39	4.78	/	June 7-July 6, 2014	Han et al., 2019

RCEES: the campus of Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences; PKU: the campus of Peking University; BAAFS: the campus of Beijing Academy of Agriculture and Forestry Sciences; F/A: formaldehyde to acetaldehyde concentration ratio.

**Fig. 6. – Diurnal variations for the photolysis frequency of HCHO (J_{HCHO}), its concentration and the OH radical formation rate.**

of 2014 (Rao et al., 2016), but were about half of those reported in winter of Beijing city during years of 2008-2010 (Zhang et al., 2014) and 2013 (Rao et al., 2016). The most recent study of Sheng et al. (2018) reported that the formaldehyde concentrations in urban Beijing were 41.65 ppbV in winter haze and 18.32 ppbV in winter clean days, which were about a factor of 5-13 higher than most reported levels. The improper calibration of the proton transfer reaction-time of flight-mass spectrometer (PTR-TOF-MS, 8000, Ionicon Analytik GmbH Innsbruck, Austria) was suspected to be the possible reason for the abnormal high formaldehyde concentrations reported by Sheng et al. (2018). The ratios of formaldehyde to acetaldehyde (F/A) at the rural site were slightly less than those in urban Beijing for all studies with only exception of Sheng et al. (2018) whose F/A ratios were about a factor of 2-3 higher than others. The slight difference of the F/A ratios between the rural site and urban Beijing was ascribed to the different dominant primary sources, e.g., domestic coal combustion at the rural site, whereas vehicle emission in Beijing city.

2.4. Atmospheric implications

The photolysis of tropospheric carbonyls especially for HCHO in polluted areas is an important primary source for atmospheric OH radicals which initiate oxidation of various

gaseous species leading to formation of secondary pollutants, such as O_3 and secondary fine particles. To reveal the role of HCHO in atmospheric chemistry at the rural site, the photolysis frequency of HCHO was simulated by a box model (AtChem2) (Sommariva et al., 2020) with Master Chemical Mechanism (MCM v3.3.1, <http://mcm.leeds.ac.uk/MCM/>) during the period from 3 to 23 December, 2017.

The photolysis frequencies of HCHO under clear sky conditions were first obtained by the model (Jenkin et al., 1997; Saunders et al., 2003). Then we used the measured $J(\text{NO}_2)$ to calibrate the modeled photolysis frequencies by the following equation (Lee et al., 2016) to get the hourly photolysis frequencies under real weather conditions:

$$J(\text{HCHO}) = J(\text{HCHO})_{\text{modeled}} \times \frac{J(\text{NO}_2)_{\text{measured}}}{J(\text{NO}_2)_{\text{modeled}}} \quad (2)$$

where $J(\text{HCHO})$ and $J(\text{HCHO})_{\text{modeled}}$ refer to the calculated and simulated photolysis frequencies of HCHO, respectively; $J(\text{NO}_2)_{\text{modeled}}$ and $J(\text{NO}_2)_{\text{measured}}$ refer to the simulated and measured photolysis frequencies of NO_2 , respectively.

As shown in Fig. 6, the photolysis frequency of HCHO increased quickly with increasing sunlight intensity and HCHO concentration from early morning to noontime, resulting in the increase of OH radical formation rate accordingly. The major products of H and HCO produced from photolysis of HCHO

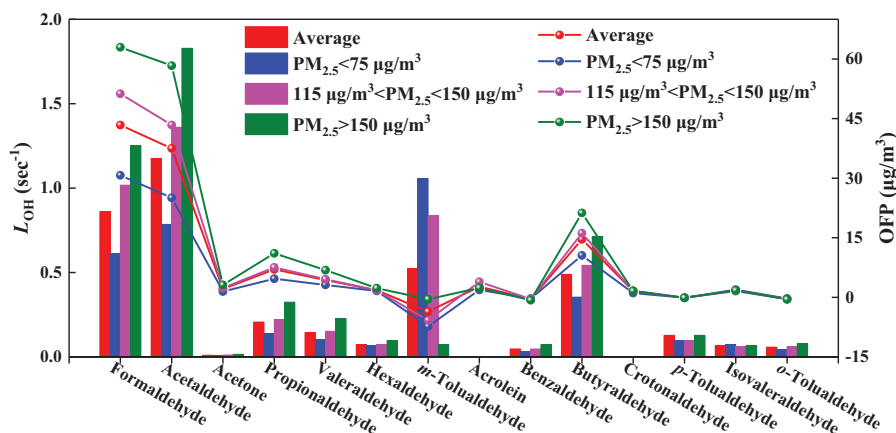


Fig. 7. – L_{OH} (column) and OFP (dot) of the measured carbonyl compounds at different air pollution levels. L_{OH} : OH radical consumption rate; OFP: ozone formation potential.

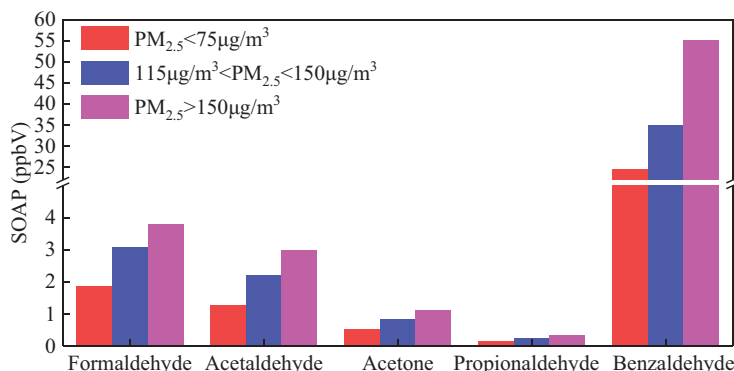


Fig. 8. – Secondary organic aerosol potential coefficients (SOAPs) of major carbonyl compounds at different air pollution levels.

can quickly react with O_2 to form HO_2 radicals which are finally converted into OH through reaction with NO in the polluted areas. The average peak OH formation rate around noon-time was 1.59×10^6 molecule/($cm^3 \cdot sec$), and the maximum value can reach 4.13×10^6 molecule/($cm^3 \cdot sec$) during the simulation period. Such high OH formation rate from photolysis of HCHO could maintain relatively high OH levels to initiate oxidation of various gas-phase pollutants for secondary pollutants formation at the rural site.

Atmospheric carbonyls not only produce OH radical through photolysis but also react with OH radical. In order to evaluate the photochemical reactivities of different carbonyls and their contributions to ozone formation, the calculations of OH radical consumption rate (L_{OH}) and ozone formation potential (OFP) were performed on the measured carbonyls by the following formulas.

$$L_{OH} = [VOC]_i \times K_i^{OH} \quad (3)$$

where $[VOC]_i$ (molecule/ cm^3) denotes the molecule concentration of VOC species i and K_i^{OH} (cm^3 /(molecule \cdot sec)) denotes the rate constant of $[VOC]_i$ reacting with OH radical at 298 K (Atkinson and Arey, 2003; Li et al., 2010).

$$OFP = [VOC]_i \times MIR_i \quad (4)$$

where MIR_i denotes the maximum incremental reactivity (g O_3 /g VOCs) of VOC species i (Carter, 1994, 2009; Duan et al., 2008).

During the observation period, acetaldehyde had the highest OH radical consumption rate, 1.18 sec^{-1} , which was much higher than other carbonyl compounds, accounting for 33% of the total L_{OH} of measured carbonyls, followed by formaldehyde, 0.86 sec^{-1} , accounting for 24% of the total L_{OH} . The contributions of n -butyraldehyde and m -tolualdehyde to L_{OH} were similar, namely 14% and 15%, respectively. The L_{OH} of propionaldehyde and n -valeraldehyde were 0.21 and 0.14 sec^{-1} , respectively, together accounting for 10% of the total L_{OH} . The total L_{OH} of remaining carbonyl compounds is 0.15 sec^{-1} , accounting for only 4% of the total L_{OH} . Among the ozone formation potentials of measured carbonyls, the most important species contributing to near-surface ozone formation was formaldehyde, which had an OFP of 43.32 µg/m^3 and contributed to 39% of total ozone formation potential of all measured carbonyls, which was mainly ascribed to its relative high concentration and high MIR coefficient. The OFP of acetaldehyde was 37.47 µg/m^3 , and its contribution to total OFP was 34%. The OFP of n -butyraldehyde and propionaldehyde was 12.88 and 7.04 µg/m^3 , contributing 12% and 6% to total OFP, respectively. As L_{OH} and OFP were directly obtained by the product of some specific carbonyl's concentration times its coefficient (Eqs. (3) and (4)), the variation trends of measured carbonyls' L_{OH} and OFP were similar to their concentrations' variation at different pollution levels (Fig. 7). In heavily polluted days, the total L_{OH} and OFP of carbonyls reached their peak values at 4.87 sec^{-1} and 169.80 µg/m^3 , respectively, and formaldehyde and acetaldehyde always remained the two principal species contributing to total L_{OH} and OFP. Through the above analysis, formaldehyde and

acetaldehyde were the dominant carbonyl compounds contributing to atmospheric oxidation capacity (AOC) at the rural site. In addition, in terms of L_{OH} , the contribution of *n*-butyraldehyde and *m*-tolualdehyde cannot be ignored, while for OFP, *n*-butyraldehyde and propionaldehyde also had significant contributions.

The carbonyl compounds are important precursors of secondary organic aerosol (SOA) (Hui et al., 2019). In particular, dicarbonyl compounds, due to their strong polarity and water solubility, can be actively absorbed into cloud, mist and aqueous-phase aerosols, undergoing photolysis or reacting with OH radical to form oligomers, which make an important contribution to SOA formation and growth (Fu et al., 2008). Studies also found that formaldehyde is an important influencing factor during haze events (Moch et al., 2018). The contributions of carbonyl compounds to SOA were calculated using the secondary organic aerosol potential coefficient (SOAP) developed by Derwent et al. (2010). As shown in Fig. 8, among the five carbonyls with available SOAP values, the contribution of carbonyls to SOA gradually increased as $PM_{2.5}$ pollution worsened, and since the SOAP of benzaldehyde is much higher than the other four carbonyl compounds, benzaldehyde contributed the most to SOA although it has relatively low concentration during the observation period.

3. Conclusions

In order to understand the pollution characteristics and environmental implications of atmospheric carbonyls in typical rural areas of the North China Plain, field measurement was carried out from November 13 to December 24, 2017. The total concentration of carbonyl compounds was 11.48 ± 6.23 ppbV, among which the principal species were formaldehyde, acetaldehyde and acetone, collectively accounting for up to 81% of the total carbonyl concentration. The carbonyl concentration in heavily polluted days was twice more than that in clean days. Comparing the proportion of various carbonyl at different air quality levels, we found that *m*-tolualdehyde had significantly different sources from other carbonyls. The relatively high concentration of *m*-tolualdehyde in clean days was mainly due to the exhaust emission of high-speed motor vehicles, while the residential household coal burning by farmers for winter heating may be the main source of other carbonyls under heavy pollution conditions of $PM_{2.5}$.

The ratios of three principal carbonyls to CO showed similar daily variation trends at different air quality levels, exhibiting distinct diurnal variations with minimal values at night, high values in daytime and maximal values around noontime. Multiple linear regression showed that, as air quality level worsened from clean to heavily polluted, the contributions from background sources to the three principal carbonyls increased significantly, while the contributions from primary sources to the three principal carbonyls decreased evidently, and the contributions of the secondary sources to the three principal carbonyls even increased sharply by a factor of 2–5, verifying that the photochemical reactivity at the heavily polluted level was still very strong.

The OH radical formation rate of formaldehyde increased significantly with the fast-growing photolysis rate of formaldehyde, and reached its peak value at noon, which is important to maintain relatively high OH levels to initiate the oxidation of various gas-phase pollutants for secondary pollutants formation at the rural site. By calculating the L_{OH} and OFP of carbonyls, formaldehyde and acetaldehyde were the dominant oxidative species throughout the observation period. In terms of OH radical consumption, the contribution of *n*-butyraldehyde and *m*-tolualdehyde cannot be ignored, while for OFP, *n*-butyraldehyde and propionaldehyde made significant contributions. In addition, the contribution of carbonyl

compounds to SOA was also significant and needs for further study.

Declaration of competing interest

The authors declare no conflict of interest.

Acknowledgments

This work was supported by National Key R&D Program of China (No. 2016YFF0201101), the National Natural Science Foundation of China (Nos. 91544211, 41727805, 41305124, and 21976106) and the Opening Project of Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention (Nos. FDLAP18005 and 19006). Jinhe Wang appreciates the supports from the Co-Innovation Center for Green Building of Shandong Province (No. X18027Z) and the Introduction and Cultivation Plan for Young Innovative Talents of Colleges and Universities by the Education Department of Shandong Province (No. 142, 2019).

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