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Characterization of Particulate-Phase High Molecular Weight Mono-Carbonyls (C# > 5) and Dicarbonyls in Urban Atmosphere of Xi'an, China

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ABSTRACT

An analytical method to quantify particulate-phase high molecular weight mono-carbonyls (C# > 5) and di-carbonyls has been developed by adopting 2,4-dinitrophenylhydrazine (DNPH) derivatization followed by high performance liquid chromatography/ultra-violet (HPLC/UV) detection. Satisfactory reproducibility and precision of the measurements were achieved. This method was applied to measure the carbonyls in $PM_{2.5}$ collected on quartz-fiber filters, sampled in Xi'an, China, from 2008 to 2009. Nonanaldehyde was the most abundant compound, followed by octanaldehyde, hexanaldehyde and heptaldehyde, accounting for 40%, 20%, 12% and 11% in the total quantified carbonyls. For dicarbonyls, the concentration of methylglyoxal was much higher than that of glyoxal. The seasonal variations of the particulate-phase mono-carbonyls and dicarbonyls were similar to those in the gas-phase, namely winter > autumn > spring > summer (except octanaldehyde). A strong correlation among those carbonyls was observed in winter, resulting from low temperature partitioning, weaker photochemical reaction, and more primary emission sources. In contrast, in summer, vehicle emissions, cooking emissions and photochemical reactions are the major pollution source in Xi'an.

Keywords: High molecular mono-carbonyls; Glyoxal; Methylglyoxal; $PM_{2.5}$; Xi'an.

INTRODUCTION

Carbonyls (aldehydes and ketones) are the major components of atmospheric photochemical reactions in the formation of oxidants and free radicals (Seinfeld, 1991). They are mainly produced by the photo-oxidation reactions of hydrocarbons, and also produced from biogenic and anthropogenic sources (e.g., vehicular exhaust, industrial emissions, household heating and cooking activities, etc.) (Atkinson, 1990). Biogenic isoprene leads to the largest global emissions of non-methane hydrocarbons (NMHCs), and the oxidation reaction with the hydroxyl can produce a series of carbonyls, including formaldehyde, methacrolein, glyoxal, methylglyoxal and other dicarbonyls (Seinfeld, 1991).

Semi-volatile organic compounds (SVOCs), especially the dicarbonyl compounds, are of major concern in environmental chemistry recently. Several laboratory and photochemical model studies have recently suggested that the uptake of glyoxal and methylglyoxal by aqueous aerosols and clouds, followed by oxidation and/or oligomerization, could be a significant source of secondary organic aerosol (SOA) (Fu *et al.*, 2008). High molecular weight carbonyls (with low vapor pressure) are more likely to deposit on the particulate matter (PM) (Grojean *et al.*, 1996b). Villanueva *et al.* (2004) reported that emission from plants is a major source of high molecular weight carbonyl compounds. Previous studies described that a variety of carbonyls (i.e., formaldehyde, acetaldehyde, acetone, valeraldehyde, hexanaldehyde, trans-2-hexene aldehydes and other carbonyls) were measured in a boreal coniferous forest or from higher plants (Fehsenfeld *et al.*, 1992; Fall, 1999). In addition, a growing number of studies have shown that emission from cooking fume (e.g., meat cooking or cooking oils) can release large amounts of high molecular weight carbonyls (Shimoda *et al.*, 1997; Schauer *et al.*, 2002). Semi-volatile dicarbonyl compounds exist in both gas and particle phases, which leads formation of organic aerosols with various pathways (Mu *et al.*, 2010). The heterogeneous reactions of aldehydes from biogenic volatile organic compounds (BVOCs) can generate hemiacetals/acetals, aldehyde hydrates and polymer in the presence of acid-catalyzed compounds, which have relatively lower vapor pressure (Jang *et al.*, 2001).

Several sampling and analytical methods have been employed for the determination of carbonyls in the gaseous

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and particulate phases (Báez *et al.*, 2001; Nguyen *et al.*, 2001; Grosjean *et al.*, 2002; Ho *et al.*, 2002; Possanzini *et al.*, 2002; Feng *et al.*, 2005; Moussa *et al.*, 2006; Pang *et al.*, 2006; Wang *et al.*, 2007; Santarsiero and Fuselli, 2008; Weng *et al.*, 2009; Wang *et al.*, 2010). Recent studies in the Mainland of China have mainly focused on low molecular weight airborne carbonyls such as formaldehyde, acetaldehyde, and acetone. (Xu *et al.*, 2006; Pal *et al.*, 2008; Weng *et al.*, 2009). However, only limited data can be found in the literatures with dicarbonyls and high molecular weight carbonyls (C# > 5) in atmospheric aerosols. Because of their relatively low abundances and high polarity, they are difficult to be measured and analyzed in any field study. Kiss *et al.* (1999) and Susana *et al.* (2006) explored and modified the preparation and detection method of carbonyls in atmospheric aerosols. Susana *et al.* (2006) reported that the concentrations of glyoxal and methylglyoxal in particulate matter with a diameter of 10 micrometers or less (PM_{10}) are 0.24 and 0.95 ng/m^3, respectively, in rural areas of Madrid, Spain. Wang *et al.* (2002) collected $PM_{2.5}$ and PM_{10} samples in Nanjing, China and detected a series of carboxylic acid and two aldehydes (methylglyoxal and 2-oxygenated malonaldehyde) with gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) methods. A combination of 2,4-dinitrophenylhydrazine-high performance liquid chromatography (DNPH-HPLC) method has been also employed to determine carbonyl concentrations in $PM_{2.5}$ samples collected in an urban area (Shanghai University, Baoshan District) and a background area (Shanghai Dongping National Forest Park) in Shanghai, China (Mu *et al.*, 2010). Even though glyoxal and methylglyoxal are ubiquitous in the atmosphere, the studies related to their roles in the fine particles are very scarce.

In this study, an advanced DNPH-HPLC/ultra-violet (UV) method was established and examined to determine high molecular weight mono-carbonyls (C# 6–9) and dicarbonyls in $PM_{2.5}$. Seasonal variations of the six carbonyls were shown between 2008 and 2009 collected in Xi'an, China.

EXPERIMENTAL SECTION

Sampling Site

Xi'an (33.29°N–34.44°N and 107.40°E–109.49°E) is the capital city of the Shaanxi province in the Mainland of China. It is located at the Guanzhong Plain at the south edge of the Loess Plateau where 400 m above the sea level (Fig. 1). Monitoring station was set up on rooftop of a two-story building at the Institute of Earth Environment, Chinese Academy of Sciences (IEECAS) (Cao *et al.*, 2005). The location is within an urban-scale zone surrounded by a residential area and ~15 km south of the downtown of Xi'an. The weather is wet and hot in summer with an average ambient temperature of 26°C and relative humidity (RH) of 70%. In winter, the weather is cold and dry with an average ambient temperature of –1.3°C and RH of 50% (http://www.weather.com.cn).

Sampling Collection

Twenty-four hour $PM_{2.5}$ samples were collected every 12 days (from 10:00 to the next day 10:00) on pre-baked (780°C, 3 h) quartz-fiber filters (203 mm × 254 mm, Whatman QM-A, USA) using TE-6070MFC Hi-Vol $PM_{2.5}$ air samplers (Tisch, OH, USA) at a flow rate of 1.0 m^3/min from 5 July, 2008 to 8 August, 2009. Filters were stored at < –10°C after sampling. Meteorological parameters, including temperature, air pressure, RH, rainfall, and wind speed and direction, were recorded during the sampling period. Field blank was collected at each site to subtract positive artifacts that resulted from passive adsorption of gas-phase organic compounds onto the filter during and/or after sampling.

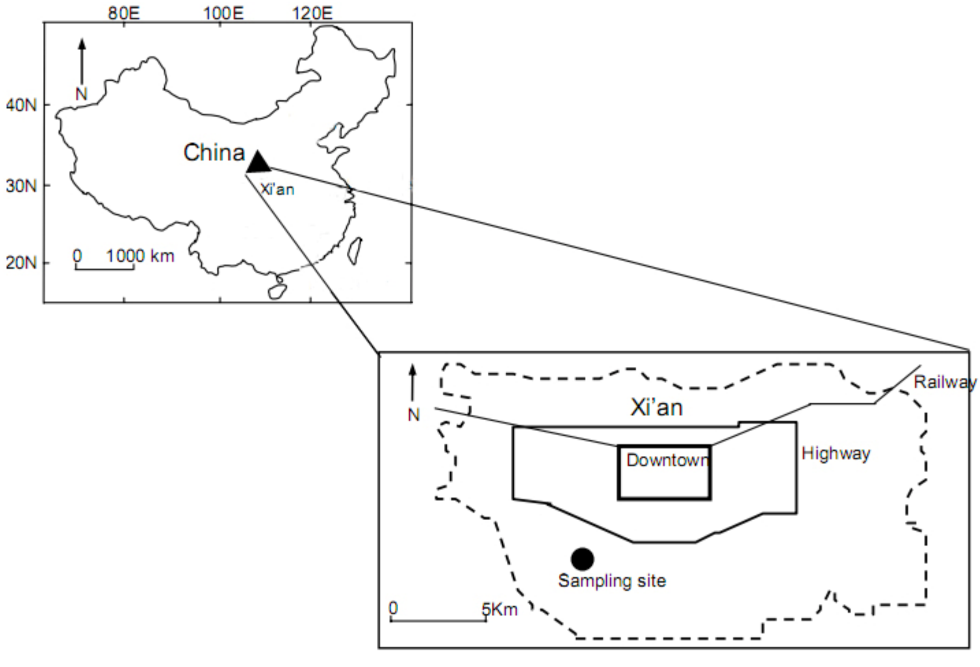

Fig. 1. A geographical map showing the location of Xi'an in China (upper plot) and sampling site.

Analytical Methods

Acetonitrile (ACN) and tetrahydrofuran (THF) (HPLC/GCMS grade) were purchased from J&K Scientific Ltd., Ontario, Canada. DNPH and pyridine were from Sigma Corporation, USA. The ultra pure water was obtained from Milli-Q system from Millipore (Milford, MA, USA). The DNPH derivatizing agent solution was prepared by adding 250 mg DNPH and 10 µL concentrated hydrochloride acid (HCl) into a 25 mL volumetric flask. The mixture was then mixed up with a mixture of ACN and pyridine (4:1). An aliquot of the sample (20 × Φ14 mm punches) was cut and put it into a 4 mL reaction vial with addition of 4 mL derivatizing agent solution. The samples were allowed to react at 70°C for 30 min, followed by ultrasonication for 15 min (Wang *et al.*, 2002). This procedure was repeated twice. The extract was filtered through a 0.22 µm membrane filter in order to remove any particles and filter debris. The filtrate after rinsing with pyridine was finally transferred into a 5 mL volumetric flask.

Certified calibration standards of the monocarbonyl DNP-hydrazones were purchased from Supelco (Bellefonte, PA) and diluted into concentration ranges of 0.015–3.0 mg/mL. Calibration standards of the dicarbonyls were prepared by mixing glyoxal and methylglyoxal from Sigma (St. Louis, MO) in acetonitrile with 1 mL of 100 µg/mL DNPH in an acidic aqueous solution. The mixtures were allowed to stand at room temperature at least 6 h for a complete derivatization. The final volume of each calibration mixture was made to be 2.0 mL with 8:2 (v/v) of acetonitrile/pyridine (HPLC/GCMS grade; Sigma). Concentrations of the dicarbonyl DNP-hydrazones in the calibration standards ranged from 0.01–2.0 µg/mL. Linearity was indicated by a correlation of determination (r^2) of at least 0.999.

The extracts and calibration standards were analyzed by injecting 20 µL of the samples to an Agilent 1200 HPLC system (Santa Clara, CA, USA) equipped with a photodiode array detector (DAD). The column for separation was a 4.6 × 250 mm Spheri-5 ODS 5 µm C-18 reversed-phase column (PerkinElmer, Norwalk, CT, USA) operated at room temperature. The mobile phase consisted of three solvent mixtures: mixture A, 6:3:1 (v/v) of water/acetonitrile/tetrahydrofuran; mixture B, 4:6 (v/v) of water/acetonitrile; and mixture C, acetonitrile. The gradient program was 80% A/20% B for 1 min, followed by linear gradients to 50% A/50% B for next 8 min, to 100% B for next 10 min and to 100% C for next 6 min, and finally 100% C for next 5 min. The flow rate was 2.0 mL/min throughout the run. The absorbance at 360 nm and 420 nm were used for identification of the aliphatic mono-carbonyls and dicarbonyls, respectively. Identification and quantification of carbonyl compounds were based on retention times and peak areas of the corresponding calibration standards, respectively. The limit of detection (LOD) was done by analyzing a minimum of seven replicates of a standard solution containing the analytes at a concentration of 0.015 µg/mL. It is estimated using the equation

$$\mathrm{LOD} = t_{(n-1,\ 1-\alpha = 99\%)} \times S \quad (1)$$

where $t_{(n-1,\ 1-\alpha = 99\%)}$ is the student's t-distribution value at n-1 degrees of freedom, and S is the standard derivation of the replicates. The LODs of the target carbonyls ranged from 0.002 to 0.010 µg/mL, which can be translated to 0.016–0.12 ng/m^3 with a sampling volume of 2.02 m^3 (Table 1). Every measurement consists of four attributes: a value, a precision, an accuracy, and a validity (e.g., Hidy, 1985). Quality assurance is the complementary part of the measurement process which provides the precision, accuracy, and validity estimates and guarantees that these attributes are within acceptable limits. The quality assurance program includes two types of activities: quality control (QC), and quality assurance (QA). The QC activities are on-going activities of measurement and data processing personnel. QC activities consist of written standard operating procedures to be followed during sample collection, sample analysis, and data processing. These procedures define schedules for periodic calibrations and performance tests (including blank and replicate analyses). They specify pre-defined tolerances which are not to be exceeded by performance tests and the actions to be taken when they are exceeded. The QC activities also include equipment maintenance and acceptance testing, and operator training, supervision, and support. The measurement precision ranges from 0.5–3.2% and 1.7–4.6% for monocarbonyls and dicarbonyls, respectively.

A total of six carbonyls were quantified, including hexanaldehyde, heptaldehyde, octanaldehyde, nonanaldehyde, glyoxal and methyglyoxal. Their recoveries are 91 ± 4%, 95 ± 8%, 92 ± 7%, 99 ± 5%, 96 ± 5% and 93 ± 6%. Low molecular weight carbonyls were detected but their abundances were not reported in this study, because of their instability in ambient fine particles.

Carbonaceous species [organic carbon (OC), elemental carbon (EC) and eight carbon fractions] were analyzed by a DRI (Model 2001A) Thermal/Optical Carbon Analyzer

Table 1. Statistical summary of particulate-phase carbonyl compounds and OC in Xi'an.

	Mean±SD (ng/m^3) (n = 33)	LOD	Max.	Min.	%
hexanaldehyde	2.09 ± 2.30	0.091	8.07	0.17	12.3
heptaldehyde	1.86 ± 1.36	0.120	5.02	0.59	10.9
octanaldehyde	3.46 ± 2.59	0.056	12.55	0.77	20.3
nonanaldehyde	6.77 ± 5.96	0.023	20.47	0.81	39.7
glyoxal	0.60 ± 0.39	0.016	1.43	0.19	3.5
methylglyoxal	2.25 ± 0.48	0.045	3.34	1.43	13.2
Total measured carbonyls	17.04 ± 13.07		50.88	3.96	100.0
OC(µg/m^3)	23.77 ± 14.21		58.67	9.24	

Note: n represents sample number.

(Atmoslytic Inc., Calabasas, CA, USA). The IMPROVE_A protocol (Zhu *et al.*, 2010; Chow *et al.*, 2011) produces four OC fractions (OC1, OC2, OC3, and OC4 in a helium (He) atmosphere at 140°C, 280°C, 480°C, and 580°C, respectively), a pyrolyzed carbon fraction (OP, determined when reflected laser light attained its original intensity after oxygen (O_2) was added to the combustion atmosphere); and three EC fractions (EC1, EC2, and EC3 in a 2% oxygen/98% helium atmosphere at 580°C, 740°C, and 840°C, respectively). OC is defined as OC1 + OC2 + OC3 + OC4 + OP and EC as EC1 + EC2 + EC3 – OP. The analyzer was calibrated with known quantities of CH_4 daily (Chow *et al.*, 2011). Replicate analyses were performed at the rate of one per group of ten samples. Field blank samples were also analyzed and the sample results were corrected by the blank sample concentration. More detailed descriptions of QA/QC procedures can be found in Cao *et al.* (2003) and Chow *et al.* (2011).

RESULTS AND DISCUSSION

Concentrations of Particulate-phase Carbonyl Compounds

The average concentrations of particulate-phase carbonyls are shown in Table 1. Nonanaldehyde (6.77 ng/m^3 ± 5.96 ng/m^3) was the most abundant high molecular weight carbonyls, followed by octanaldehyde (3.46 ng/m^3 ± 2.59 ng/m^3), hexanaldehyde (2.09 ng/m^3 ± 2.30 ng/m^3) and heptaldehyde (1.86 ng/m^3 ± 1.36 ng/m^3), accounting for 40%, 20%, 12% and 11% in the total quantified carbonyls, respectively. For dicarbonyls, the concentrations of methylglyoxal (2.25 ng/m^3 ± 0.48 ng/m^3) were much higher than that of glyoxal (0.60 ng/m^3 ± 0.39 ng/m^3), contributing 13% of the total quantified carbonyls. The predominance of nonanaldehyde recognized in the atmosphere was probably related to the biogenic emissions (Grosjean *et al.*, 2002; Feng *et al.*, 2005). In previous study, the highest concentration of nonanaldehyde was observed during the growth period of Mediterranean plants in Italy (Ciccioli *et al.*, 1993). Yokouchi *et al.* (1990) found that nonanaldehyde was always the most abundant specie in two remote islands and in an inland local city in Japan.

Motor vehicle exhaust, biogenic emissions, and cooking fume are the essential inputs of high molecular weight carbonyls (Ho *et al.*, 2006). Our sampling location is close to the South Fenghui Road, Tangyan Road and the First Keji Road, where are the busiest roads in the High-tech Zone area. In addition, the site is 20 m away from the Tang Dynasty City Wall Park, which is in 3.7 km length and 120 km width with a total area of 444,000 m^2 total area. Therefore, vehicular exhaust and biogenic emissions are likely to the major sources of high molecular weight carbonyls in this residential area of Xi'an. Rather than these major pollution sources, cooking fume from nearby commercial restaurants is another possible source for the targeted carbonyls. High contributions of long chain saturated carbonyls were found in determination of organic compounds emission rates from frying vegetables in different seed oils (Schauer *et al.*, 2002). Nonanaldehyde was thus found to be most abundant aliphatic long chain aldehydes. Rogge *et al.* (1991) observed that large amounts of semi-volatile aldehydes, especially nonanaldehyde, could be released during charbroiling and meat-cooking operations. For dicarbonyls, the concentrations of methylglyoxal are higher than that of glyoxal, possibly because of its longer lifetime (2.9 h, determined by photolysis) compared with glyoxal (1.6 h) (Fu *et al.*, 2008). This results an enrichment of methylglyoxal in the surface of aerosol. On average, the six quantified carbonyls have a contribution to total organic carbon (OC) (Table1) of 0.072%.

Seasonal Variation of Particulate Phase Carbonyls

The time series plot of the carbonyls and corresponding meteorological conditions are shown in Fig. 2. According to local climatic conditions in Xi'an, the sampling period was divided into four seasons in order to explore the seasonal variation of carbonyls. Therefore, we defined spring season as March, April and May, summer season as June, July and August, fall season as September, October and November and winter season as December, January and February. The abundances of carbonyl compounds are dependent on the meteorological conditions (i.e., temperature, wind speed and solar irradiation, etc.) and variations of emission sources. In summer, the high level of photochemical activities results in increased levels of some carbonyl compounds (Liu *et al.*, 2006).

In general, most of the carbonyls show a very consistent seasonal variation with lower concentrations in summer but high concentrations in the winter, except octanaldehyde. More specifically, heptaldehyde is in trace level in the summertime, indicating that it can be produced by a particular pollution source in winter. The seasonal variations of carbonyls in $PM_{2.5}$ are similar with the gas-phase carbonyls, namely winter > autumn > spring > summer (except octanaldehyde). The average concentrations of the targeted carbonyls in the four seasons were plotted as Fig. 3. The higher concentrations in wintertime can be due to more stable atmospheric stratification, higher vehicular emissions from a cold start at low temperature, and larger consumption of heating fuel combustion. The highest concentrations of other air pollutants were also found in winter. For instance, the OC levels in winter (46.7 µg/m^3) is much higher than other seasons (23.1 µg/m^3 in autumn > 18.9 µg/m^3 in spring > 14.3 µg/m^3 in summer). Nonanaldehyde has been demonstrated the greatest seasonal variability, and its average concentration in winter (15.0 ng/m^3) is nearly six times of that in summertime (2.56 ng/m^3). That means there are some additional sources supplied in winter. However, octanaldehyde has a reverse seasonal variation from other carbonyls and its average winter to summer ratio is 0.26. The highest concentration of octanaldehyde was determined in autumn, followed by summer, spring, and winter. Atmospheric photooxidation may be an important secondary source of this carbonyl in summer and autumn, since its abundance have a good correlation with the ambient temperature. For dicarbonyls, compared with the variations in summer, the primary emission was more dominant in winter. A low temperature environment inhibits the formation of ozone (O_3) and other oxidants, resulting in less consumption of primary dicarbonyls and higher abundance in winter.

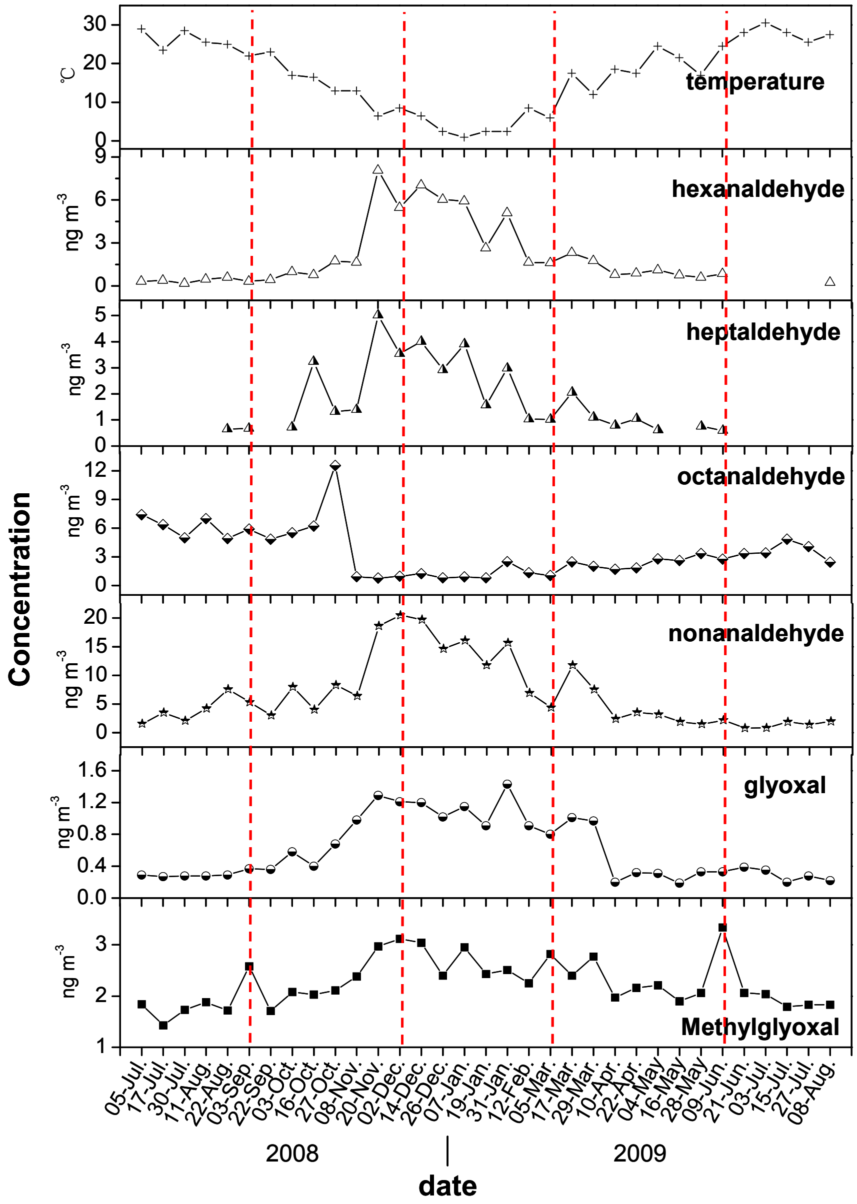

Fig. 2. The time series plot of the carbonyls concentration and corresponding meteorological conditions during the sampling period.

Carbonyl Ratios

Although atmospheric degradation of carbonyls has been extensively discussed, formation mechanisms of carbonyls, including dicarbonyls, are poorly understood. Field studies have suggested that glyoxal has multiple common emission sources, including wood combustion (Macdonald *et al.*, 2001) vehicular emission (Grosjean *et al.*, 2001), and cooking activities (Ho *et al.*, 2006). Smog chamber studies have also shown that glyoxal can be formed from the atmospheric oxidation of isoprene, toluene, acetylene, ethylene, and other aromatic hydrocarbons (Yu *et al.*, 1995; Yu *et al.*, 1997; Yu *et al.*, 1998, Yu *et al.*, 1999a, b). Even if there is only a small fraction of methylglyoxal and glyoxal partitioning onto particles, it could still affect the global SOA budget significantly.

In this study, ratios of six target carbonyls to atmospheric EC were determined to indicate the anthropogenic origin of ambient carbonyls (Table 2), since EC was believed to be associated only with primary anthropogenic sources. However, carbonyl compounds may be emitted directly from sources as primary emissions, and can also be formed in the atmosphere from the low vapor pressure products by atmospheric chemical reactions. The ratios of carbonyls to EC can be used to indicate the presence of secondary formed carbonyls. Except octanaldehyde and methylglyoxal, all (hexanaldehyde, heptaldehyde, nonanaldehyde, glyoxal) have the highest ratios in winter. Lower mixing heights, surface inversion layers, and infrequent precipitation in winter may also contribute to higher carbonyl concentrations. Higher ratios of methylglyoxal/EC and octanaldehyde/EC were found in summer than in spring, autumn or winter (Table 2), atmospheric photooxidation was an important secondary

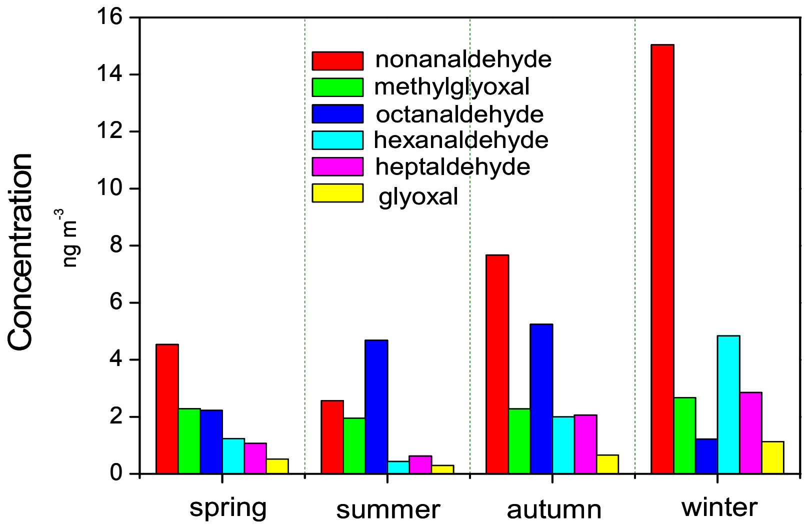

Fig. 3. The average carbonyls concentration in four seasons.

Table 2. The ratios of carbonyl compounds to EC on seasonal basis in $PM_{2.5}$.

Seasons	Hexanaldehyde/EC $(\times 10^{-3})$	Heptaldehyde/EC $(\times 10^{-3})$	Octanaldehyde/EC $(\times 10^{-3})$	Nonanaldehyde/EC $(\times 10^{-3})$	Glyoxal/EC $(\times 10^{-3})$	Methylglyoxal/EC $(\times 10^{-3})$
Spring	0.16	0.14	0.33	0.55	0.07	0.32
Summer	0.12	0.09	1.18	0.61	0.07	0.46
Autumn	0.17	0.18	0.76	0.76	0.07	0.29
Winter	0.44	0.26	0.09	1.28	0.09	0.24

source of these carbonyls, which further supporting the importance of secondary formation of these carbonyls in summer. The results matched to our previous study in Xi'an that the concentrations of the gas-phase formaldehyde and methylglyoxal increased with increasing temperature.

Correlation of Carbonyl Compounds and Sources

The correlations among six carbonyls and OC/EC in $PM_{2.5}$ during one-year monitoring program and four seasons were evaluated by correlation analysis. Their correlation coefficients (*r*) are shown in Table 3(a) and (b). As the concentrations of heptaldehyde were low in summer, it has not been used for this statistical analysis. Negative correlations were found between octanaldehyde and other carbonyls. It indicated that octanaldehyde has a very different source from the other carbonyls, which may be inferred from photooxidation rather than direct local source emissions. In Table 3(b), the correlations of the carbonyls in winter are much stronger than other seasons, because the vehicular exhaust, cooking fume and combustion source emission were the major common sources in winter. However, only fair correlations were found in summer because of the photochemical degradation during high solar radiation and the vertical mixing of the pollutants were different in summer and wintertime. In autumn, strong correlation between the six carbonyls and EC concentration, maybe implies that biomass burning have a significant contribution to the carbonyls. In addition, studies have shown that plants can generate more carbonyls in stress conditions, such as mechanical damage, exposure to ozone (O_3) or carbon dioxide (CO_2) in the ambient atmosphere.

Comparison with Other Studies

Like many other semivolatile hydrocarbons, some carbonyl compounds have the capacity to co-exist in gaseous and particulate phases in the atmosphere. The concentration of glyoxal and methylglyoxal in gas phase in the atmosphere depends on the concentrations of oxidants and their VOCs precursors. Their levels could vary from several tens of ng/m^3 in rural area to several µg/m^3 in urban ambient environment. However, in the particulate-phase, the ambient concentrations of glyoxal and methylglyoxal ranged from tens to hundreds of ng/m^3. Consistent distributions of dicarbonyls have been observed in many cities (Kawamura *et al.*, 1996; Wang *et al.*, 2002; Kawamura and Yasui, 2005; Li and Yu, 2005; García-alonso *et al.*, 2006; Ho *et al.*, 2006; Ho *et al.*, 2007; Ortiz *et al.*, 2009; Mu *et al.*, 2010). The concentrations of targeted carbonyls in $PM_{2.5}$ are compared in Table 4, but high molecular weight carbonyls (C# > 5) are rarely studied and reported, so more attention has been paid to the dicarbonyls. Overall, the concentrations of glyoxal and methylglyoxal in coastal and rural areas were the lowest, well below the concentration measured in other cities. Average $PM_{2.5}$ glyoxal concentrations in Xi'an in summer is 0.29 ng/m^3, slightly higher than those reported for roadside location in Hong Kong (0.19 ng/m^3 in summer), but lower than those in other cities. Similar to glyoxal, the average concentrations of $PM_{2.5}$ methylglyoxal was lower than those quantified in Tokyo, Japan and a few Chinese cities (e.g., Nanjing and Shanghai). Different extraction and

Table 3(a). Correlations among six carbonyls and OC/EC in $PM_{2.5}$ during whole year (n = 33).

	1	2	3	4	5	6	7	8
1. hexaldehyde	1.00							
2. heptaldehyde	0.90	1.00						
3. octanaldehyde	–0.49	–0.29	1.00					
4. nonanaldehyde	0.93	0.84	–0.38	1.00				
5. glyoxal	0.86	0.73	–0.47	0.90	1.00			
6. methylglyoxal	0.66	0.47	–0.52	0.65	0.71	1.00		
7. OC	0.89	0.84	–0.46	0.93	0.88	0.63	1.00	
8. EC	0.76	0.76	–0.45	0.82	0.78	0.61	0.76	1.00

Table 3(b). Correlations among six carbonyls and OC/EC in $PM_{2.5}$ during four seasons.

Compounds	Spring (n = 8)								Summer (n = 11)							
	1	2	3	4	5	6	7	8	1	2	3	4	5	6	7	8
1. hexaldehyde	1.00								1.00							
2. heptaldehyde	0.83	1.00							—	—						
3. octanaldehyde	–0.29	–0.07	1.00						–0.27	—	1.00					
4. nonanaldehyde	0.95	0.93	–0.13	1.00					0.34	—	0.33	1.00				
5. glyoxal	0.94	0.74	–0.29	0.88	1.00				0.74	—	–0.22	–0.20	1.00			
6. methylglyoxal	0.74	0.31	–0.53	0.56	0.86	1.00			0.77	—	–0.50	–0.22	0.42	1.00		
7. OC	0.89	0.79	0.11	0.95	0.77	0.40	1.00		0.22	—	–0.04	0.36	–0.21	0.05	1.00	
8. EC	0.79	0.60	–0.21	0.82	0.69	0.46	0.87	1.00	0.48	—	–0.34	0.36	–0.39	0.07	0.81	1.00
Compounds	Autumn (n = 7)								Winter (n = 7)							
	1	2	3	4	5	6	7	8	1	2	3	4	5	6	7	8
1. hexaldehyde	1.00								1.00							
2. heptaldehyde	0.83	1.00							0.96	1.00						
3. octanaldehyde	–0.45	–0.42	1.00						–0.01	–0.01	1.00					
4. nonanaldehyde	0.96	0.69	–0.34	1.00					0.87	0.92	–0.01	1.00				
5. glyoxal	0.87	0.60	–0.53	0.86	1.00				0.62	0.68	0.70	0.68	1.00			
6. methylglyoxal	0.75	0.52	–0.47	0.78	0.72	1.00			0.70	0.85	–0.18	0.88	0.49	1.00		
7. OC	0.86	0.88	–0.41	0.85	0.88	0.72	1.00		0.82	0.93	–0.13	0.84	0.92	0.90	1.00	
8. EC	0.91	0.93	–0.49	0.89	0.85	0.78	0.98	1.00	0.34	0.43	–0.05	0.74	0.69	0.69	0.38	1.00

analytical methods may greatly vary the value of glyoxal and methylglyoxal in the aerosol samples. Further improvement and standardization of the analytical method applied to determine particulate-phase dicarbonyls are thus important task.

CONCLUSIONS

High molecular weight carbonyl compounds (C# > 5) and dicarbonyls were studied in $PM_{2.5}$ samples collected at Xi'an from 5 July, 2008 to 8 August, 2009 to determine their seasonal variations. Through the DNPH derivatization followed by HPLC/UV detection, satisfy reproducibility and precision of the measurements were achieved for six carbonyl compounds in aerosol.

Nonanaldehyde (C9) was found as the most abundant high molecular weight carbonyl compounds, followed by octanaldehyde, hexanaldehyde and heptaldehyde, accounting for 40%, 20%, 12% and 11% in total measured carbonyls. For dicarbonyls, the concentrations of methylglyoxal were much higher than the concentrations of glyoxal, and 10% higher in total carbonyls. Seasonal variations of high molecular weight carbonyls were significant. Most carbonyls have higher concentrations in winter than in summer (except methylglyoxal). And the ratios of carbonyls to EC were explored to indicate the presence of secondary formed carbonyls. Except octanaldehyde and methylglyoxal, all carbonyls have the highest ratios in winter. Lower mixing heights, surface inversion layers, and infrequent precipitation in winter may also contribute to higher carbonyl concentrations in winter. High ratios of methylglyoxal/EC and octanaldehyde/EC were found in summer because photooxidation was an important source of these carbonyls in summer other than primary emissions.

Good correlation was obtained among carbonyls in wintertime, due to weak photochemical reaction under low temperature and significant primary emission sources. On the contrary, only fair correlation was obtained in summer, this may be due to more complex sources in summer, e.g. vehicle emission, cooking emission and photochemical reaction were the most important source in summer. This again suggests that secondary production of some specific carbonyls are more characteristic to summer season.

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Table 4. Comparisons of carbonyl concentrations (ng/m^3) in $PM_{2.5}$ to other cities.

Location	Hexanaldehyde	Heptaldehyde	Octanaldehyde	Nonanaldehyde	Glyoxal	Methylglyoxal	Sampling character	Particle size	Sampling period	Reference
Xi'an, China	1.23	1.06	2.22	4.53	0.51	2.28	Urban	$PM_{2.5}$	spring, 2009	This work
Xi'an, China	0.43	0.62	4.67	2.56	0.29	1.95	Urban	$PM_{2.5}$	summer, 2008	This work
Xi'an, China	2.00	2.06	5.24	7.67	0.66	2.27	Urban	$PM_{2.5}$	fall, 2008	This work
Xi'an, China	4.84	2.85	1.21	15.04	1.12	2.67	Urban	$PM_{2.5}$	winter, ,2008	This work
14 developing cities in China	—	—	—	—	2.72	2.47	Urban	$PM_{2.5}$	summer,2003	Ho *et al*., 2007
14 developing cities in China	—	—	—	—	3.02	14.5	Urban	$PM_{2.5}$	winter,2003	Ho *et al*., 2007
Roadside, Hong Kong	—	—	—	—	5.26	6.4	Urban	$PM_{2.5}$	winter,2003	Ho *et al*., 2006
Roadside, Hong Kong	—	—	—	—	0.19	10	Urban	$PM_{2.5}$	summer,2003	Ho *et al*., 2006
Nanjing,China	—	—	—	—	—	60.46	Urban	$PM_{2.5}$	winter,2001	Wang *et al*., 2002
Shanghai,China	—	—	—	—	792	143	Forest Park	$PM_{2.5}$	winter,2009	Mu *et al*., 2010
Shanghai,China	—	—	—	—	475	121	Urban	$PM_{2.5}$	winter,2009	Mu *et al*., 2010
Meguro,Japan	—	—	—	—	226	178	Urban	$PM_{2.5}$	summer,2004	Ortiz *et al*., 2009
Saitama, Japan	—	—	—	—	52	95	Suburban	$PM_{2.5}$	summer,2003	Ortiz *et al*., 2006
Nanjing,China	—	—	—	—	—	13.6	Urban	PM_{10}	winter,2001	Wang *et al*., 2002
Madrid, Spain	—	—	—	—	0.24	0.95	Rural site	PM_{10}	May, 2004–Feb., 2005	García-alonso *et al*., 2006
Hong Kong, China	—	—	—	2.80	23.7	63.6	Urban	TSP	Oct.–Dec.,2003	Li and Yu, 2005
Tokyo, Japan	—	—	—	—	19.9	26.2	Urban	TSP	Jun., 1989	Kawamura and Yasui, 2005
Artic	—	—	—	—	0.54	0.16	Marine	TSP	July 1987–Jun 1988	Kawamura *et al*., 1996
Tokyo, Japan	—	—	—	—	7.8	14	Urban	TSP	Jul., 1989	Kawamura and Yasui, 2005
Tokyo, Japan	—	—	—	—	21.5	24.1	Urban	TSP	Nov., 1989	Kawamura and Yasui, 2005

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