

Seasonal variations of monocarbonyl and dicarbonyl in urban and sub-urban sites of Xi'an, China

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Abstract Seventeen airborne carbonyls including monocarbonyls and dicarbonyls were determined in urban and sub-urban sites of Xi'an, China in three seasons in 2010. In winter, acetone was the most abundant carbonyl in the urban site due to usage of organic solvents in constructions and laboratories and its slower atmospheric removal mechanisms by photolysis and reaction with hydroxyl radical than those of formaldehyde and acetaldehyde. In the sub-urban site, acetaldehyde was the most abundant carbonyl, followed by formaldehyde and

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acetone. During summer, however, formaldehyde was the most dominant carbonyl in both sites. The photooxidations of a wide range of volatile organic compounds (VOCs) yielded much more formaldehyde than other carbonyls under high solar radiation and temperature. In the urban site, the average concentrations of dicarbonyls (i.e., glyoxal and methylglyoxal) in spring and summer were higher than that in winter. Transformation of aromatic VOCs emitted from fuel evaporation leads to the formation of 1,2-dicarbonyls. A reverse trend was observed in sub-urban sites, as explained by the relatively low abundances and accumulations of VOC precursors in the rural atmosphere during warm seasons. Moreover, cumulative cancer risk based on measured outdoor carbonyls (formaldehyde and acetaldehyde) in Xi'an Jiaotong University and Heihe was estimated (8.82×10^{-5} and 4.96×10^{-5} , respectively). This study provides a clear map on the abundances of carbonyls and their source interpretation in the largest and the most economic city in Northwestern China.

Keywords Carbonyls · Glyoxal · Methylglyoxal ·
Northwestern China · Risk analysis

Introduction

Carbonyl compounds, including aldehydes and ketones, are ubiquitous components of the atmosphere, which play an important role in atmospheric chemistry and can act as precursors for the formation of free radicals, ozone, peroxyacyl nitrates, and secondary organic aerosol (SOA) (Carlier et al. 1986). Carbonyls have complex

primary and secondary sources. They can be emitted directly from incomplete combustion of biomass and fossil fuel or formed indirectly by photochemical oxidations of volatile organic compounds (VOCs) from any natural and anthropogenic sources (Possanzini et al. 2002). Industrial processes and vehicular exhaust are believed to be the primary sources of carbonyl compounds in urban sites. In addition to their photochemical impact to the atmosphere, many carbonyls are harmful to human health.

Dicarbonyls, especially glyoxal and methylglyoxal (Volkamer et al. 2007; Fu et al. 2008), are identified as precursors of SOA and are also formed from the atmospheric transformation of non-aromatic VOCs emitted from anthropogenic and biogenic sources (Atkinson and Arey 2003). However, direct emissions of glyoxal and methylglyoxal, including emissions from motor vehicle exhaust (Grosjean et al. 2001; Jakober et al. 2008), are viewed as being minor compared to in situ atmospheric formation from VOCs (Fu et al. 2008). Even though dicarbonyls influence greatly in the atmospheric chemistry, there are a limited number of reports on their concentration levels in China (Ho et al. 2002; Feng et al. 2005; Pang and Mu 2006; Wang et al. 2007; Weng et al. 2009; Lü et al. 2009, 2010). This is particularly true in Northwestern China where, to our best knowledge, only very limited studies have been conducted. With a permanent population density of 1,791 person/km² in urban districts (2007), Xi'an is considered the largest and the most economic city in Northwestern China. It is also one of the most polluted areas nationwide owing to its unique meteorological environment and energy structure (Cao et al. 2007). The climate of Xi'an is cold and dry in winter and hot and wet in summer. It is a typically monsoon-influenced region. Summer monsoon from the southeast carries abundance of rainfall to Xi'an; in contrast, winter monsoon from the northwest brings cold air at high wind speed which leads to low temperature and snow. The objectives of this study are to identify and quantify ambient mono- and dicarbonyls and to characterize their seasonal variations in urban and sub-urban sites of Xi'an.

Experiments

Sampling site

Xi'an (33.29°N–34.44°N and 107.40°E–109.49°E) is the capital city of Shaanxi province in Mainland China.

Air samples were collected from two sampling sites: Xi'an Jiaotong University (XJU) and Heihe (HH) (Fig. 1). Xi'an Jiaotong University is located in the southeastern part of the downtown area, about 100 m from a heavy traffic road (mean traffic flow is 661 vehicles per minute; Shen et al. 2010). The north and the east of the sampling site are residential areas and the campus of the university, while to the south and west are the South Second Ring Road and Xingqin Road. The sampling site is situated on the rooftop of a 15-m-high building in the campus of the university. Heihe is located near the Qinling Mountains, situating at the downwind location of urban areas. The sampling site is next to the Heihe National Forest Park and ~86 km away from the downtown of Xi'an. The monitoring station is located on the dam of the reservoir.

Sample collection

Daily 24-h integrated samples (from 10:00 a.m. to 10:00 a.m. the next day) were collected for three seasons in 2010: winter (XJU: from 27 January to 6 February; HH: from 12 to 26 January); spring (XJU: from 18 May to 2 June; HH: from 14 to 28 April); and summer (XJU: from 12 to 27 July; HH: from 12 to 27 July). The meteorological conditions on each sampling date are listed in Table 1. The air samples were collected in silica cartridges impregnated with acidified 2,4-dinitrophenylhydrazine (DNPH) (Sep-Pak DNPH-silica, 55–105 μm in particle size, 125 Å in pore size; Waters Corporation, Milford, MA) at a flow rate of 0.7 L min⁻¹. Collection efficiencies were measured under field conditions by sampling carbonyls into two identical cartridges connected in series. They are calculated as 100 % (1 - A_b / A_f), where A_f and A_b are the amounts of carbonyl collected on the front and back sampling tubes, respectively. No breakthrough was found at such sampling flow rate and sampling time. The flow rates were checked in the field at the beginning and end of each sampling using a calibrated flowmeter (Gilibrator Calibrator; Gilian Instruments, W. Caldwell, NJ, USA). A Teflon filter assembly (Whatman, Clifton, NJ, USA) and an ozone scrubber (Sep-Pak; Waters Corporation) were installed in front of the DNPH-silica cartridge, in order to remove any particulate matters and prevent possible influence of ozone, respectively (Spaulding et al. 1999). Six collocated samples were collected to examine the sample collection reproducibility, which was >95 % in the field. A cartridge was

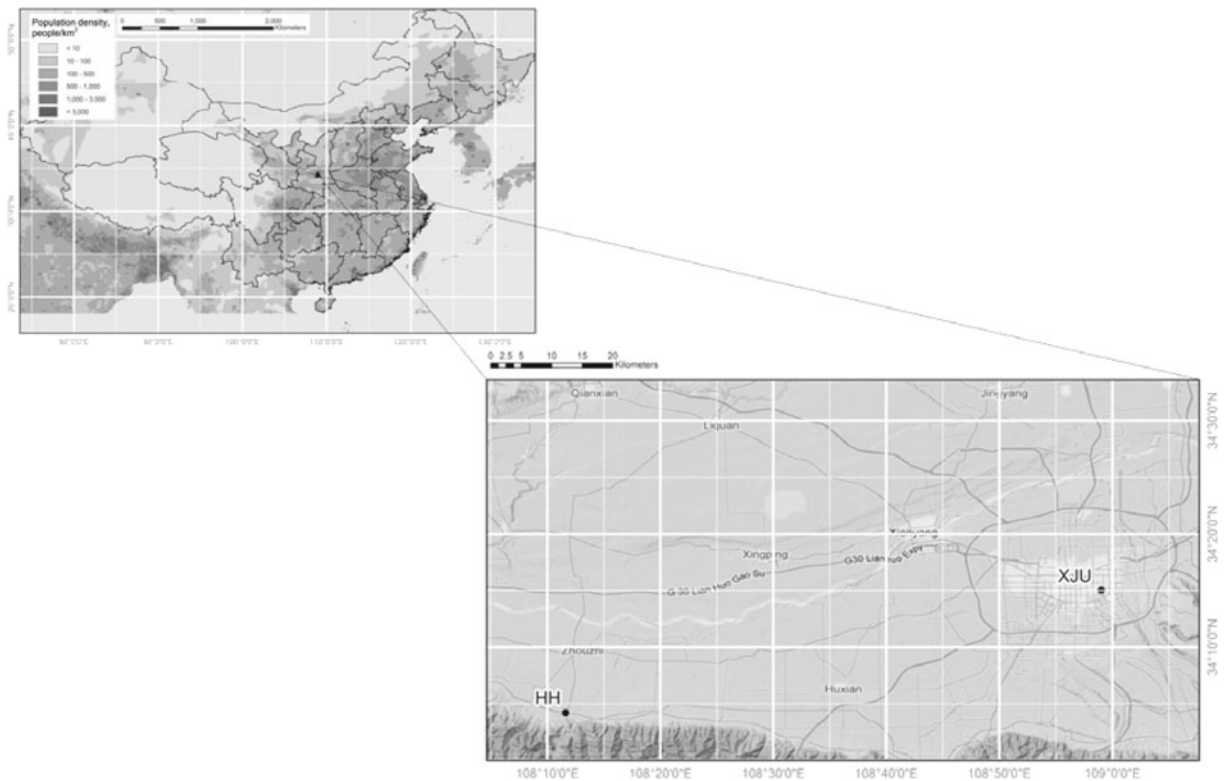


Fig. 1 The sampling locations in this study

reserved to serve as a field blank on each sampling trip and was handled in the same way as the sample cartridges. The amounts of carbonyls detected in the cartridges were corrected for the field blank when we computed the air concentrations of the carbonyls. After sampling, the DNPH-coated cartridges were stored at $<4^{\circ}\text{C}$ until analysis. Meteorological parameters, including temperature, air pressure, relative humidity (RH), rainfall, and wind speed and direction, were recorded during the sampling period.

Analytical methods

A total of 17 carbonyls were quantified, including formaldehyde, acetaldehyde, acetone, propionaldehyde, 2-butanone (MEK), *iso*+*n*-butyraldehyde, benzaldehyde, *iso*-valeraldehyde, *n*-valeraldehyde, *o*-tolualdehyde, *m*-tolualdehyde, *p*-tolualdehyde, hexanal, 2,5-dimethylbenzaldehyde, glyoxal, and methylglyoxal. Unsaturated carbonyls including acrolein and crotonaldehyde were detected, but their abundances were not reported in the study. The unsaturated carbonyl DNP-hydrazones can react with excess reagent to form

adducts, which could not be quantified accurately due to chromatographic and response factor issues (Ho et al. 2011; Schulte-Ladbeck et al. 2003).

Each DNPH-coated cartridge was eluted with 2.0 mL of acetone-free acetonitrile (HPLC/GCMS grade, J&K Scientific Ltd., Ontario, Canada) to a volumetric flask. Test has been done to demonstrate that there was not any DNPH and its derivatives remained in the cartridge after the 2.0 mL elution (Ho et al. 2007). Certified calibration standards of the monocarbonyl DNP-hydrazones were purchased from Supelco (Bellefonte, PA, USA) and diluted into concentration ranges of $0.015\text{--}3.0\ \mu\text{g mL}^{-1}$. Calibration standards of the dicarbonyls were prepared by mixing glyoxal and methylglyoxal from Sigma (St. Louis, MO, USA) in acetonitrile with 1 mL of $100\ \mu\text{g mL}^{-1}$ DNPH in an acidic aqueous solution. The mixtures were at standard room temperature for 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 to $2.0\ \mu\text{g mL}^{-1}$. Linearity was

Table 1 Sampling site description and meteorological parameters during the sampling periods

		Xi'an Jiaotong University	Heihe
Description		Urban	Rural
Latitude		34°15'2.10"	34°4'12.48"
Longitude		108°59'1.36"	108°11'36.88"
Winter	<i>T</i> (°C)	2.8	2.8
	RH (%)	50.0	50.0
	WS (m/s)	1.5	1.5
Spring	<i>T</i> (°C)	19.0	19.0
	RH (%)	68.2	68.2
	WS(m/s)	1.9	1.9
Summer	<i>T</i> (°C)	26.7	26.7
	RH (%)	81.2	81.2
	WS (m/s)	1.7	1.7

T temperature, *RH* relative humidity, *WS* wind speed

indicated by a correlation of determination (r^2) of at least 0.999. The cartridge extracts and calibration standards were analyzed by injecting 20 μL of the samples to a high-performance liquid chromatography (HPLC) system (Series 1200; Agilent Technology, Santa Clara, CA, USA) equipped with a photodiode array detector (DAD). The column for separation was a 4.6 \times 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/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 of 50 % A/50 % B for the next 8 min, to 100 % B for the next 10 min and to 100 % C for the next 6 min, and finally 100 % C for the next 5 min. The flow rate was 2.0 mL min^{-1} throughout the run. The absorbance at 360, 390, and 420 nm was used for the identification of the aliphatic carbonyls, aromatic carbonyls (benzaldehyde and tolualdehydes), and dicarbonyls, respectively. Identification and quantification of carbonyl compounds were based on retention times and peak areas of the corresponding calibration standards, respectively. The minimum detection limit (MDL) was done by analyzing a minimum of seven replicates of a standard solution containing the analytes at a concentration of 0.015 $\mu\text{g mL}^{-1}$. It is estimated using the following equation:

$$\text{MDL} = t_{(n-1, 1-\alpha=99\%)} \times S,$$

where $t_{(n-1, 1-\alpha=99\%)}$ is Student's *t* distribution value at $n-1$ degrees of freedom and *S* is the standard derivation of the

replicates. The MDLs of the target carbonyls ranged from 0.002 to 0.010 $\mu\text{g mL}^{-1}$, which can be translated to 0.016–0.12 parts per billion by volume (ppbv) with a sampling volume of 2.02 m^3 . The measurement precision for the analysis of ten replicates of a standard solution containing the analytes at a concentration of 1.0 $\mu\text{g mL}^{-1}$ ranges from 0.5 to 3.2 % and from 1.7 to 4.6 % for monocarbonyls and dicarbonyls, respectively.

Risk calculation model

The inhalation cancer risk for carbonyls was calculated using the following equation (Weng et al. 2009):

$$R_{ij} = E_{ij} \times \text{IUR}_j \tag{1}$$

where, R_{ij} is the estimated inhalation cancer risk from chemical *j* in each sampling site *i*, E_{ij} is the measured exposure concentration for chemical *j* in each sampling site *i*, and IUR_j is the inhalation unit risk ($\text{m}^3 \mu\text{g}^{-1}$) for chemical *j*. The IUR values are from U.S. Environmental Protection Agency's Integrated Risk Information System (IRIS). The IUR represents the excess cancer risk over background to a pollutant and is typically expressed as risk or probability of cancer for a 70-year exposure per 1 μg pollutant m^{-3} air (Zhou et al. 2011).

The cumulative cancer risks are the summation of available individual compound risks (Eq. 2):

$$\text{CR}_i = \sum_j R_{ij} \tag{2}$$

where R_{ij} is the estimated inhalation cancer risk from chemical *j* in each sampling site *i*, and CR_i is the cumulative cancer risk estimate in each sampling site *i*.

Results and discussion

Characterization of carbonyl compounds

Seventeen carbonyl compounds were detected in the ambient samples, while *p*-tolualdehyde was detected in only one sample in XJU and two samples in HH. The average concentrations and statistical summary of the carbonyl compounds (in ppbv) are shown in Table 2. The total concentrations of quantified carbonyls ranged from 3.35 to 24.6 ppbv (average 12.1 ppbv) and from 1.51 to 17.9 ppbv (average 7.83 ppbv) at XJU and HH, respectively. Formaldehyde was the most abundant species detected during the sampling periods, with the concentrations ranging from 0.31 to 9.09 ppbv (average concentration: XJU=4.86 ppbv and HH=2.53 ppbv), followed by acetaldehyde and acetone, with the concentration ranging from 0.25 to 6.24 ppbv (average concentration: XJU=2.65 ppbv and HH=2.30 ppbv) and from 0.08 to 11.3 ppbv (average concentration: XJU=2.85 ppbv and HH=1.78 ppbv), respectively.

Figure 2 shows the relative molar contributions of carbonyl concentrations at XJU and HH. Formaldehyde, acetaldehyde, and acetone were the top three carbonyl compounds in the atmosphere of Xi'an, accounting for 86 and 84 % of the total quantified carbonyls at XJU and HH, respectively. Emissions from motor vehicles and industries are the major sources of carbonyls in the urban areas of Xi'an. Formaldehyde and acetaldehyde are the most abundant carbonyls produced from either diesel- or gasoline-fueled vehicles (the total number of registered vehicles is 981,711 in 2009) (Ho and Yu 2002; Ho et al. 2007). Other than the pollutants transported from upwind source areas and formed from atmospheric photooxidation reactions, biomass burning and vegetative emission are the potential sources of the carbonyls in the rural sites of Xi'an. Minor carbonyls (i.e., propionaldehyde, MEK, *iso*+*n*-butyraldehyde, benzaldehyde, *iso*-valeraldehyde, *n*-valeraldehyde, *o*-tolualdehyde, *m*-tolualdehyde, *p*-tolualdehyde, hexanal, and 2,5-dimethylbenzaldehyde) were also found in the atmosphere, each accounted for 0.1–2.7 % of the total quantified carbonyl concentrations only. For the dicarbonyls, however, the sum of glyoxal and methylglyoxal accounted significantly for 4.4 and 6.0 % of the total quantified carbonyl concentrations in XJU and HH, respectively.

Table 3 compares the carbonyl concentrations among the cities in Mainland China. The unit has been

converted from parts per billion by volume to microgram per cubic meter since mass concentration was given in most of the reference papers. Consistent with the other studies, formaldehyde, acetaldehyde, and acetone were the three most abundant carbonyls in the ambient air in the Chinese cities. In the urban site, the total measured carbonyl concentrations in Xi'an were lower than those in most of the cities in China, such as Hangzhou (Weng et al. 2009), Guangzhou (Tang 2002; Feng et al. 2004, 2005; Lü et al. 2006), Shanghai, and Zhejiang (Huang et al. 2009). However, the concentration of formaldehyde in Xi'an was much higher than that in Beijing and Qingdao in the winter (Tan et al. 2002; Wang et al. 2007) and also in Hong Kong annually (Ho et al. 2002), representing that carbonyl contributions varied with the locations and their regional and local pollution sources. The carbonyl levels in HH were similar to those of sub-urban and rural sites in China. The concentrations of airborne glyoxal and methylglyoxal were scarcely reported in China. Dai et al. (2012) reported the glyoxal and methylglyoxal concentration in the urban site in Xi'an, which were lower than the values measured in urban sites but higher than the values measured in sub-urban sites.

Seasonal variation

The distinct seasonal variations of carbonyl concentrations were observed at the two sampling sites (Table 2, Fig. 3). Carbonyl concentrations in ambient air are affected by many factors such as primary emissions and secondary formations (mainly from vehicular exhaust and photooxidation of hydrocarbons), meteorological conditions, and their sinks (e.g., photodecomposition, reaction with hydroxyl radical (OH), and dry deposition; Pang and Mu 2006). Previous studies (Possanzini et al. 1996; Ho et al. 2002) reported that the high photochemical activities resulted in increased levels of some carbonyl compounds in summer. However, the average total carbonyl concentration in XJU decreased in the order of winter > spring > summer, while in HH, it decreased in the order of winter > summer ≈ spring. In winter, acetone was the most abundant carbonyl in XJU, with an average concentration of 5.15 ppbv, followed by formaldehyde (3.64 ppbv) and acetaldehyde (3.45 ppbv). Therefore, the sources and sinks of carbonyl compounds were possibly non-identical in winter. Acetone is widely used as an organic solvent in various industries and chemical plants (WHO

Table 2 The average concentrations and statistical summary of 17 carbonyls (in ppbv)

Compound	Winter				Spring				Summer				S/W
	Mean±SD	Max	Min	%	Mean±SD	Max	Min	%	Mean±SD	Max	Min	%	Mean
XJU Formaldehyde	3.64±1.40	5.60	0.79	26	6.62±1.84	9.09	4.10	52	4.62±1.43	5.83	2.64	50	1.27 ^a
Acetaldehyde	3.45±1.50	6.24	1.04	24	2.25±1.02	3.61	0.82	18	2.07±0.72	3.18	1.07	23	0.60 ^a
Acetone	5.15±2.95	11.31	0.98	36	2.13±0.96	3.60	1.15	17	0.69±0.42	1.31	0.08	7	0.13 ^a
Propionaldehyde	0.35±0.16	0.63	0.11	2.4	0.20±0.11	0.35	0.10	1.6	0.24±0.18	0.47	0.02	2.6	0.69 ^a
Methyl ethyl ketone	0.44±0.19	0.71	0.12	3.1	0.23±0.10	0.33	0.07	1.8	0.17±0.08	0.29	0.02	1.9	0.39 ^a
<i>iso</i> + <i>n</i> -Butyraldehyde	0.09±0.04	0.14	0.03	0.6	0.04±0.03	0.09	0.01	0.3	0.20±0.12	0.33	0.01	2.2	2.24 ^a
Benzaldehyde	0.13±0.06	0.22	0.04	0.9	0.10±0.04	0.14	0.05	0.8	0.11±0.06	0.19	0.03	1.2	0.82 ^a
<i>iso</i> -Valeraldehyde	0.38±0.18	0.67	0.09	2.6	0.31±0.13	0.52	0.13	2.4	0.18±0.13	0.34	0.04	2	0.48 ^a
<i>n</i> -Valeraldehyde	0.03±0.01	0.05	0.01	0.2	0.03±0.02	0.06	0.01	0.2	0.05±0.03	0.11	0.02	0.6	1.65 ^a
<i>o</i> -Tolualdehyde	0.01±0.00	0.01	0.00	0	0.05±0.02	0.08	0.01	0.4	bd	bd	bd	bd	/
<i>m</i> -Tolualdehyde	0.09±0.12	0.41	0.01	0.7	bd	bd	bd	bd	0.03±0.03	0.09	0.01	0.3	0.29 ^a
<i>p</i> -Tolualdehyde	bd	bd	bd	bd	bd	bd	bd	bd	0.02±0.00	0.02	0.00	0.2	/
Hexaldehyde	0.07±0.03	0.14	0.03	0.5	0.08±0.06	0.16	0.01	0.6	0.16±0.14	0.36	0.01	1.7	2.22 ^a
2,5-Dimethylbenzaldehyde	bd	bd	bd	bd	bd	bd	bd	bd	0.12±0.00	0.12	0.00	1.4	/
Glyoxal	0.18±0.11	0.34	0.02	1.3	0.30±0.12	0.50	0.14	2.4	0.23±0.15	0.46	0.04	2.5	1.26 ^a
Methylglyoxal	0.24±0.09	0.37	0.05	1.7	0.39±0.18	0.67	0.16	3.1	0.30±0.20	0.62	0.07	3.3	1.25 ^a
Total	14.24±6.83	24.56	3.35	100	12.73±4.62	17.56	7.42	100	9.16±3.67	11.59	4.74	100	0.64 ^a
HH Formaldehyde	3.22±1.49	5.65	1.38	31	1.67±1.09	3.46	0.65	35	1.84±1.22	3.27	0.31	37	0.57 ^b
Acetaldehyde	3.54±1.79	6.14	1.10	33	0.89±0.39	1.44	0.43	18	0.81±0.53	1.38	0.25	16	0.23 ^b
Acetone	2.27±1.03	3.98	0.96	22	1.43±0.44	2.15	0.88	30	0.79±0.29	1.10	0.44	16	0.35 ^b
Propionaldehyde	0.12±0.10	0.35	0.02	1.1	0.02±0.00	0.02	0.00	0.4	0.51±0.52	0.87	0.14	10	4.22 ^b
Methyl ethyl ketone	0.32±0.16	0.57	0.11	3.1	0.06±0.04	0.12	0.02	1.3	0.14±0.07	0.19	0.04	2.8	0.42 ^b
<i>iso</i> + <i>n</i> -Butyraldehyde	0.05±0.05	0.18	0.01	0.4	0.01±0.00	0.02	0.00	0.2	0.34±0.38	0.90	0.02	6.9	7.26 ^b
Benzaldehyde	0.10±0.06	0.20	0.03	0.9	0.04±0.02	0.07	0.01	0.8	0.05±0.02	0.06	0.02	0.9	0.47 ^b
<i>iso</i> -Valeraldehyde	0.28±0.13	0.59	0.11	2.6	0.11±0.07	0.24	0.06	2.3	0.08±0.05	0.14	0.03	1.5	0.27 ^b
<i>n</i> -Valeraldehyde	0.02±0.01	0.03	0.01	0.1	0.01±0.00	0.01	0.00	0.2	0.04±0.01	0.05	0.03	0.8	2.52 ^b
<i>o</i> -Tolualdehyde	bd	bd	bd	bd	0.05±0.03	0.11	0.02	1	bd	bd	bd	bd	/
<i>m</i> -Tolualdehyde	0.02±0.01	0.03	0.00	0.2	bd	bd	bd	bd	0.02±0.02	0.04	0.01	0.5	1.23 ^b
<i>p</i> -Tolualdehyde	0.01±0.00	0.01	0.00	0.1	bd	bd	bd	bd	bd	bd	bd	bd	/
Hexaldehyde	0.05±0.04	0.14	0.01	0.5	0.01±0.01	0.02	0.01	0.3	0.15±0.04	0.19	0.12	3	3.10 ^b
2,5-Dimethylbenzaldehyde	0.02±0.01	0.03	0.01	0.2	0.06±0.02	0.09	0.02	1.2	bd	bd	bd	bd	/
Glyoxal	0.17±0.08	0.31	0.07	1.6	0.08±0.05	0.18	0.04	1.8	0.06±0.04	0.10	0.03	1.2	0.33 ^b
Methylglyoxal	0.37±0.20	0.73	0.15	3.6	0.36±0.72	2.13	0.05	7.6	0.13±0.08	0.22	0.07	2.6	0.35 ^b
Total	10.55±5.16	18.36	5.04	100	4.80±2.89	9.59	2.72	100	4.94±3.25	4.80	1.51	100	0.47 ^b

bd below limit of detection

^a S/W represents the mean carbonyl concentration ratio in summer to winter in XJU

^b S/W represents the mean carbonyl concentration ratio in summer to winter in HH

1998). The high acetone concentrations may be caused by the usage of solvents in construction sites or chemical industries near XJU. Another explanation for the high acetone concentrations is that the lifetimes for removal of acetone by photolysis (40 days) and reaction with OH (20 days) are longer than those of formaldehyde

and acetaldehyde (1.5 h and 1 day, respectively) in the atmosphere (Atkinson 2000). However, in HH, acetaldehyde was the most abundant carbonyl in winter. The average concentration of acetaldehyde was 3.54 ppbv. Formaldehyde and acetone were the second and third abundant species, respectively. When the ambient

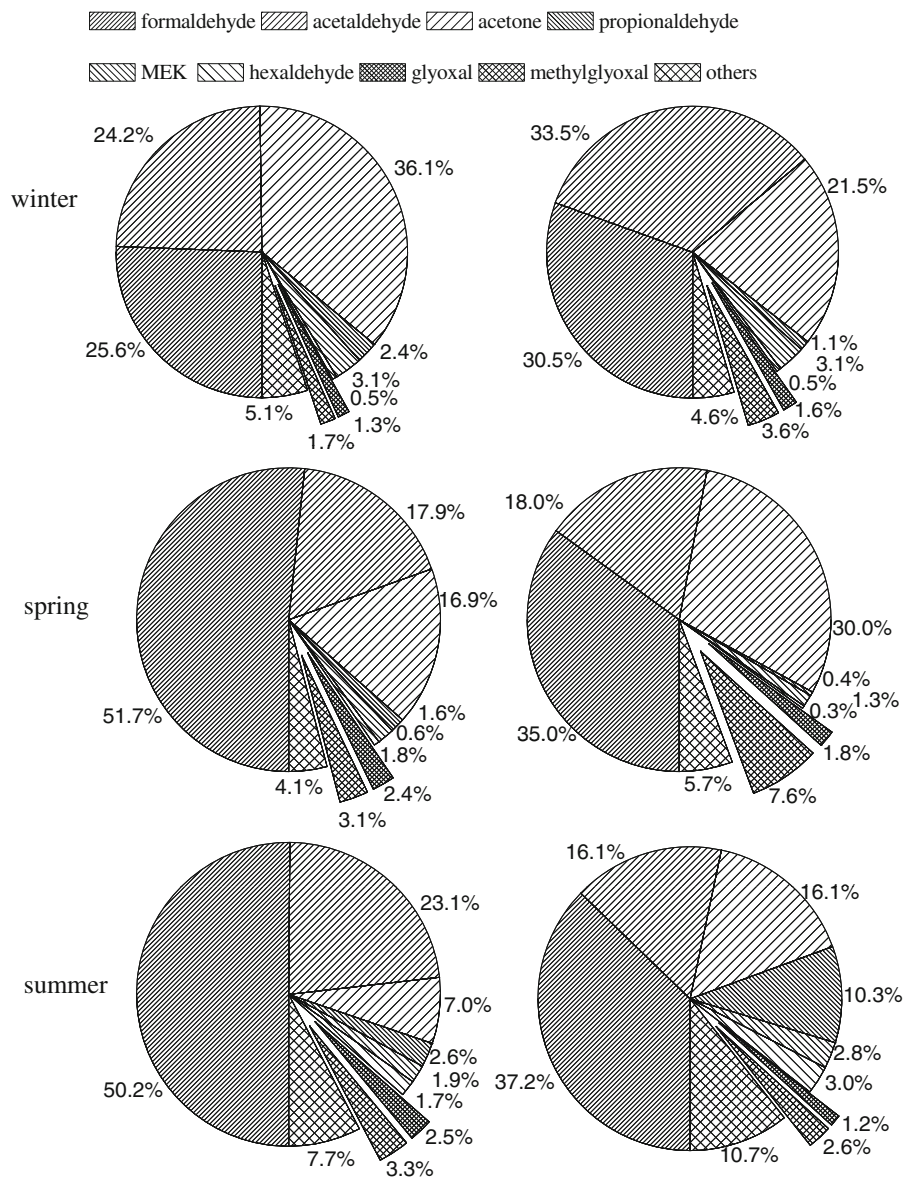


Fig. 2 The relative molar contributions of carbonyl concentrations at XJU and HH in three seasons

temperature increased, formaldehyde replaced acetaldehyde and acetone as the predominant carbonyl in both sites. In Xi'an, the temperatures were between 26 and 37 °C in summer and -2 and 8 °C in winter (Table 1). High ambient temperature in summer could enhance the photochemical reactions. The photooxidations of a wide range of VOCs can yield much more formaldehyde than acetaldehyde, which is an explanation for the elevation of formaldehyde abundance in summer (Shepson et al. 1991; Duane et al. 2002). This indicates that both

photochemical activity and temperature play important roles in the formation of formaldehyde during summer.

In the urban site (XJU), the average concentrations of glyoxal and methylglyoxal in spring (0.30 and 0.39 ppbv, respectively) or summer (0.23 and 0.30 ppbv, respectively) were higher ($p < 0.05$) than those in winter (0.18 and 0.24 ppbv, respectively). Under atmospheric conditions, transformation of aromatic VOCs such as toluene and xylenes emitted from fuel evaporation during warm seasons (spring and summer) leads to the

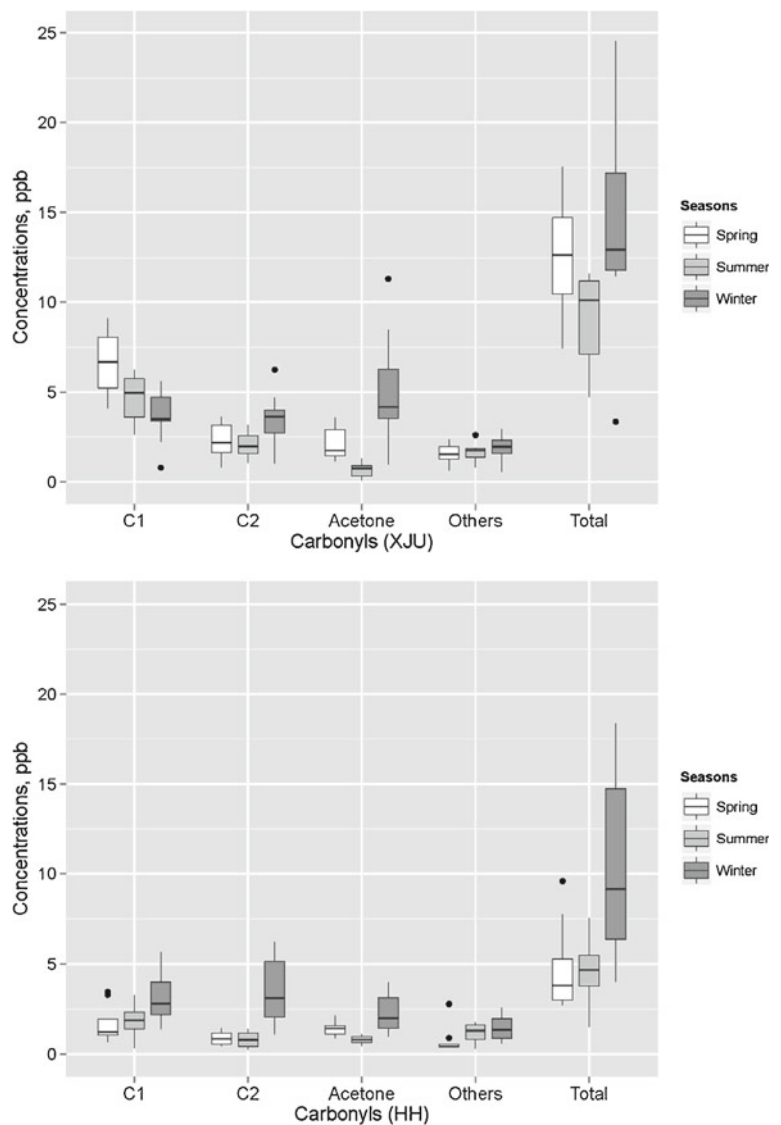
Table 3 Comparison of the carbonyl concentrations in the cities of mainland China

Locations City, Country	Concentrations				Seasons	Reference
	Formaldehyde	Acetaldehyde	Glyoxal	Methylglyoxal		
Urban sites						
Xi'an, China (XJU)	4.8	6.7	0.5	0.8	Winter (2010)	This work
Xi'an, China (XJU)	8.9	4.6	0.8	1.4	Spring (2010)	This work
Xi'an, China (XJU)	5.5	3.6	0.5	0.9	Summer (2010)	This work
Xi'an, China (IEECAS)	7.92	3.7	0.16	0.67	Summer (2009)	Dai et al. (2012)
Xi'an, China (IEECAS)	5.57	12	0.46	0.55	Winter (2010)	Dai et al. (2012)
Xi'an, China	6.5	12.1	–	–	Winter (2004–2005)	Wang et al. (2007)
Xi'an, China	9.9	12.6	–	–	Summer (2004)	Wang et al. (2007)
Beijing, China	7.1	7.5	–	–	Summer (2008)	Xu et al. (2010)
Beijing, China	4.8	10.2	–	–	Fall (2004–2005)	Pang and Mu (2006)
Beijing, China	4.7	6.7	–	–	Winter (2004–2005)	Wang et al. (2007)
Beijing, China	25.4	15.1	–	–	Summer (2004)	Wang et al. (2007)
Shanghai, China	19.4	15.9	–	–	Spring/summer/fall (2007)	Huang et al. (2009)
Guangzhou, China	14.5	8.9	–	–	Summer (2002)	Tang (2002)
Guangzhou, China	10.5	8.5	–	–	Winter (2004–2005)	Wang et al. (2007)
Guangzhou, China	15	10.7	–	–	Summer (2004)	Wang et al. (2007)
Guangzhou, China	13.88	7.92	–	–	Fall (2002)	Feng et al. (2004)
Guangzhou, China	12.09	9.51	–	–	Summer (2003)	Feng et al. (2005)
Guangzhou, China	10.53	11.7	–	–	Winter/spring (2004)	Lü et al. (2006)
Foshan, China	6.03	–	–	–	Summer (2006)	Yuan et al. (2012)
Hangzhou, China	22.2	6.37	–	–	Spring (2006)	Weng et al. (2009)
Qingdao, China	3.64	4.18	–	–	Winter (1997)	Tan et al. (2002)
Qingdao, China	9.95	7	–	–	Summer (1998)	Tan et al. (2002)
Jiaxing, Zhejiang, China	13.99	8.76	–	–	Summer (2006)	Huang et al. (2009)
Guiyang, China	4.8	5.7	–	–	Winter/spring/summer (2008–2009)	Pang and Lee (2010)
Hong Kong, China	4.13	2.01	–	–	Whole year (1999–2000)	Ho et al. (2002)
Kaohsiung, Taiwan	18.74	15.72	–	–	Whole year (2006)	Wang et al. (2010)
Rural (or sub-urban) sites						
Xi'an, China (HH)	4.3	6.9	0.4	1.2	Winter (2010)	This work
Xi'an, China (HH)	2.1	1.6	0.2	1.1	Spring (2010)	This work
Xi'an, China (HH)	2.2	1.4	0.1	0.4	Summer (2010)	This work
Prince Hill Forest Park, Guangzhou, China	3.7	3.33	–	–	summer (2004)	Yu et al. (2008)
Liwan, Guangzhou, China	5.87	7.26	–	–	Whole year (2005)	Lü et al. (2010)
Waliguan, Qinghai, China (ppbv)	4.16	4.25	–	–	Fall (2005)	Mu et al. (2007)
Waliguan, Qinghai, China (ppbv)	1.48	3.91	–	–	Winter (2005)	Mu et al. (2007)

formation of 1,2-dicarbonyls (Arey et al. 2009 and references therein). However, a reverse trend was observed in HH, the average concentration of glyoxal in winter (0.17 ppbv) was higher ($p < 0.05$) than that in

spring (0.08 ppbv) and in summer (0.06 ppbv). This could be supported by the low abundances and accumulations of VOC precursors (e.g., toluene and xylenes) from fuel evaporation in sub-urban atmosphere in warm

Fig. 3 Seasonal variations of major and total measured carbonyl compounds at XJU and HH



seasons, and therefore less 1,2-dicarbonyls were photochemically formed. The concentrations of other minor carbonyls ($\geq C_3$) were well below 1.0 ppbv in both the winter and summer samples.

Summer to winter (S/W) ratios of the carbonyls in this study were calculated and shown in Table 2. It was found that the mean ratios of S/W were greater than 1.0 for formaldehyde, *iso*+*n*-butyraldehyde, benzaldehyde, *n*-valeraldehyde, hexanal, glyoxal, and methylglyoxal in XJU, and propionaldehyde, *iso*+*n*-butyraldehyde, *n*-valeraldehyde, and hexanal in HH. These are in good agreement with most of the previous studies found in urban sites (Pang and Mu 2006; Lü et al. 2010). Photochemical reaction is one of the predominant sources of

these carbonyls in summer. The relatively high RH and concentrations of precursors are in favor of urban photochemistry, potentially explaining the elevation of carbonyl concentrations (Pang and Mu 2006). In addition, the photochemical activity gradually decreases in winter, and hence, the contribution from the photooxidation of VOCs to atmospheric carbonyls reduced accordingly. For other carbonyls, the S/W ratios were <1.0 , implying that the carbonyl concentrations were lower in summer than in winter. Acetone and acetaldehyde had the lowest S/W ratio in XJU and HH, respectively. Acetone and acetaldehyde are the most abundant carbonyls emitted from automobiles and industries (Grosjean et al. 2001; Kean et al. 2001). Therefore, more acetaldehyde and acetone

Table 4 The molar ratios of formaldehyde/acetaldehyde (C_1/C_2) in both sampling sites

Season	Location	Formaldehyde/acetaldehyde (C_1/C_2)		
		Mean	Min	Max
Winter	XJU	1.10	0.57	1.43
	HH	0.95	0.73	1.26
Spring	XJU	3.36	2.21	6.54
	HH	1.82	1.50	2.08
Summer	XJU	2.32	1.64	3.10
	HH	3.14	0.64	7.96

accumulated in the atmosphere with limit sinks (i.e., photooxidation by OH radicals and photolysis) in winter. In addition, there are some unfavorable meteorological conditions in winter: stable atmospheric layer and low mixing depth prevented the dispersion of pollutants and increased the density of pollutants in the atmosphere; moreover, low and small variability of wind speed and temperature in winter favored the accumulation of pollutants.

Moreover, lower S/W ratios of formaldehyde, glyoxal, and methyglyoxal were observed in HH than in XJU. These three carbonyls in the sub-urban sites are greatly influenced by many factors such as primary precursor VOC emissions, meteorological conditions, and their sinks. To some extent, the seasonal variations can reflect the influences from the multiple and combined factors. Important sinks for carbonyls include (a) photolysis, (b) reaction with OH radicals, and (c) wet and dry deposition. The main removal processes for carbonyls during the daytime are photolysis and oxidation by OH radicals. It is obvious that distinct seasonal variations of these carbonyls were seen in summer, suggesting sinks for these carbonyls were more dominant in HH.

Carbonyl ratios

The molar ratios of formaldehyde/acetaldehyde (C_1/C_2) were determined in both sampling sites (Table 4). The C_1/C_2 ratio has been widely used as an indicator of possible sources for formaldehyde (Shepson et al. 1991) which usually varies from ~1 to 2 for urban sites and up to ~10 for rural sites (Shepson et al. 1991; Possanzini et al. 1996). A high value of the C_1/C_2 ratio implied that the photooxidation of natural hydrocarbons such as isoprene yields more formaldehyde than acetaldehyde (Shepson et al. 1991; Duane et al. 2002), even though few argued that the ratios

often have large variations subject to the dominance of the pollution sources and meteorological conditions (Grosjean 1992). In this study, the C_1/C_2 ratio varied from 0.57 to 6.54 (with a mean of 2.17) in XJU and from 0.73 to 7.96 (with a mean of 1.56) in HH. These ratios were close to that measured in urban areas in Beijing, Guangzhou, and Hong Kong (Ho et al. 2002; Feng et al. 2005). Compared with seasonal values, the highest C_1/C_2 ratio for XJU was observed in spring (May), followed by summer, while the highest ratio for HH was recorded in summer, followed by spring. This indicates the sufficiency of temperature for the production of formaldehyde from the photooxidations in summer or spring. The results suggest that the anthropogenic activities were still the dominant sources in both urban and sub-urban locations in winter.

Correlations analysis

To identify potential emission sources of carbonyl compounds, correlation analysis was applied using concentrations of ambient carbonyls in XJU and HH. Pearson's correlation matrix of 16 carbonyls for both sampling sites is presented in additional data in Online Resource 1, respectively. Significant correlations ($R=0.85-0.96$) were found between most of the carbonyls in HH during the three seasons, such as among formaldehyde, acetaldehyde, acetone, MEK, and benzaldehyde, indicating that these carbonyls come from the same sources (e.g., biomass burning and photochemically aged pollutants transported from other regions). However, poor or fair correlations (i.e., formaldehyde and acetaldehyde, acetaldehyde and acetone) were observed among carbonyls in XJU, suggesting that there is seasonal variation of pollution sources for these compounds determined. Significantly higher correlations ($p<0.001$) among the carbonyls in winter/spring than in summer were observed in XJU. Moreover, only fair correlations were found in summertime because the photochemical degradation under high solar radiation and the vertical mixing of the pollutants varied between summer and winter.

To clarify the effect of meteorological conditions, the correlations among the carbonyls and meteorological factors during the whole investigated period were analyzed. It was found that the levels of formaldehyde ($R=-0.45$; or total quantified carbonyls, $R=-0.55$) decreased as the ambient temperature increased in XJU, which indicated that photolysis rates and OH radical reactions greatly exceeded the formation rates of carbonyls through photooxidation of hydrocarbons under

Table 5 ozone production and photochemical reaction with OH of carbonyls in XJU and HH

	Winter			Spring			Summer		
	$10^{11} \times K_{OH}^a$	$\mu\text{g m}^{-3}$	Percentage	Prop-Equiv	$\mu\text{g m}^{-3}$	Percentage	Prop-Equiv	$\mu\text{g m}^{-3}$	Percentage
XJU									
Formaldehyde	0.94	3.64	30.16	3.42	6.62	53.79	6.20	4.62	44.48
Acetaldehyde	1.50	3.45	45.67	5.17	2.25	29.29	3.38	2.07	31.84
Acetone	0.02	5.15	0.77	0.09	2.13	0.31	0.04	0.69	0.1
Propionaldehyde	2.00	0.35	6.10	0.69	0.20	3.52	0.41	0.24	4.91
MEK	0.12	0.44	0.47	0.05	0.23	0.24	0.03	0.17	0.22
<i>iso</i> + <i>n</i> -Butyraldehyde	2.40	0.09	1.86	0.21	0.04	0.73	0.08	0.20	4.86
Benzaldehyde	1.20	0.13	1.36	0.15	0.10	1.01	0.12	0.11	1.31
<i>iso</i> -Valeraldehyde	2.80	0.38	9.31	1.05	0.31	7.63	0.88	0.18	5.16
<i>n</i> -Valeraldehyde	2.80	0.03	0.81	0.09	0.03	0.68	0.08	0.05	1.55
<i>m</i> -Tolualdehyde	1.75	0.09	1.44	0.16	bd			0.03	0.49
<i>o</i> -Tolualdehyde	1.75	0.01	0.15	0.02	0.05	0.76	0.09	bd	
<i>p</i> -Tolualdehyde	1.30	bd			bd			0.02	0.21
Hexaldehyde	3.00	0.07	1.88	0.21	0.08	2.03	0.23	0.16	4.86
Total			100.00	11.32		100.00	11.53		100.00
	MIR ^b	$(\mu\text{g m}^{-3})^c$	$\% \Delta\text{O}_3^d$	$\mu\text{g O}_3 \text{ m}^{-3}$	$(\mu\text{g m}^{-3})^e$	$\% \Delta\text{O}_3^d$	$\mu\text{g O}_3 \text{ m}^{-3}$	$(\mu\text{g m}^{-3})^e$	$\% \Delta\text{O}_3^d$
Formaldehyde	9.46	3.64	48.64	34.48	6.62	67.84	62.63	4.62	62.33
Acetaldehyde	6.54	3.45	31.81	22.55	2.25	15.95	14.73	2.07	19.27
Acetone	0.36	5.15	2.61	1.85	2.13	0.83	0.77	0.69	0.35
Propionaldehyde	7.08	0.35	3.45	2.44	0.20	1.56	1.44	0.24	2.41
MEK	1.48	0.44	0.92	0.65	0.23	0.36	0.34	0.17	0.36
<i>iso</i> + <i>n</i> -Butyraldehyde	5.97	0.09	0.74	0.53	0.04	0.23	0.21	0.20	1.68
Benzaldehyde	-0.67	0.13	-0.12	-0.09	0.10	-0.07	-0.07	0.11	-0.10
<i>iso</i> -Valeraldehyde	4.97	0.38	2.64	1.87	0.31	1.69	1.56	0.18	1.27
<i>n</i> -Valeraldehyde	5.08	0.03	0.24	0.17	0.03	0.15	0.14	0.05	0.39
<i>m</i> -Tolualdehyde	-0.59	0.09	-0.07	-0.05	bd	0.00	0.14	0.03	-0.03
<i>o</i> -Tolualdehyde	-0.59	0.01	-0.01	-0.01	0.05	-0.03	-0.03	bd	0.00
Hexaldehyde	4.35	0.07	0.43	0.30	0.08	0.38	0.35	0.16	0.99
Glyoxal	12.50	0.18	3.16	2.24	0.30	4.05	3.74	0.23	4.03
Methylglyoxal	16.56	0.24	5.57	3.95	0.39	7.06	6.52	0.30	7.04
Total			100.00	70.90		100.00	92.32		100.00
HH	$10^{11} \times K_{OH}^a$	$\mu\text{g m}^{-3}$	Percentage	Prop-Equiv	$\mu\text{g m}^{-3}$	Percentage	Prop-Equiv	$\mu\text{g m}^{-3}$	Percentage
Formaldehyde	0.94	4.26	20.00	3.99	2.11	29.35	1.97	2.19	16.83
Acetaldehyde	1.50	6.86	51.59	10.29	1.64	36.67	2.47	1.42	17.41

Table 5 (continued)

	Winter			Spring			Summer			
	MIR ^b	($\mu\text{g m}^{-3}$) ^c	($\mu\text{g O}_3 \text{ m}^{-3}$) ^c	($\mu\text{g m}^{-3}$) ^c	($\mu\text{g m}^{-3}$) ^c	($\mu\text{g O}_3 \text{ m}^{-3}$) ^c	($\mu\text{g m}^{-3}$) ^c	($\mu\text{g m}^{-3}$) ^c	($\mu\text{g O}_3 \text{ m}^{-3}$) ^c	% $\Delta\text{O}_3^{\text{d}}$
Acetone	0.02	5.80	0.10	0.49	3.49	0.06	0.88	1.83	0.03	0.25
Propionaldehyde	2.00	0.31	0.61	3.06	0.04	0.09	1.34	1.16	2.33	19.06
MEK	0.12	1.03	0.13	0.63	0.18	0.02	0.33	0.39	0.05	0.39
<i>iso</i> + <i>n</i> -Butyraldehyde	2.40	0.15	0.36	1.78	0.03	0.06	0.91	0.97	2.32	19.04
Benzaldehyde	1.20	0.45	0.54	2.72	0.18	0.21	3.18	0.19	0.23	1.87
<i>iso</i> -Valeraldehyde	2.80	1.06	2.96	14.82	0.39	1.09	16.26	0.26	0.72	5.91
<i>n</i> -Valeraldehyde	2.80	0.06	0.16	0.81	0.03	0.09	1.41	0.13	0.37	3.05
<i>m</i> -Tolualdehyde	1.75	0.10	0.18	0.90	0.00	0.35	0.00	0.10	0.18	1.43
<i>o</i> -Tolualdehyde	1.75	bd			0.20		5.21	bd		
<i>p</i> -Tolualdehyde	1.30	bd			bd			bd		
Hexaldehyde	3.00	0.21	0.64	3.18	0.10	0.30	4.46	0.60	1.80	14.75
Total			19.95	100.00	6.72	100.00	12.20	100.00		
	MIR ^b	($\mu\text{g m}^{-3}$) ^c	($\mu\text{g O}_3 \text{ m}^{-3}$) ^c	% $\Delta\text{O}_3^{\text{d}}$	($\mu\text{g m}^{-3}$) ^c	($\mu\text{g O}_3 \text{ m}^{-3}$) ^c	% $\Delta\text{O}_3^{\text{d}}$	($\mu\text{g m}^{-3}$) ^c	($\mu\text{g O}_3 \text{ m}^{-3}$) ^c	% $\Delta\text{O}_3^{\text{d}}$
Formaldehyde	9.46	4.26	40.29	32.70	2.11	19.92	35.77	2.19	20.73	36.05
Acetaldehyde	6.54	6.86	44.88	36.43	1.64	10.75	19.30	1.42	9.27	16.11
Acetone	0.36	5.80	2.09	1.70	3.49	1.26	2.25	1.83	0.66	1.15
Propionaldehyde	7.08	0.31	2.16	1.76	0.04	0.32	0.57	1.16	8.23	14.32
MEK	1.48	1.03	1.52	1.23	0.18	0.27	0.49	0.39	0.58	1.01
<i>iso</i> + <i>n</i> -Butyraldehyde	5.97	0.15	0.89	0.72	0.03	0.15	0.27	0.97	5.78	10.05
Benzaldehyde	-0.67	0.45	-0.30	-0.25	0.18	-0.12	-0.21	0.19	-0.13	-0.22
<i>iso</i> -Valeraldehyde	4.97	1.06	5.25	4.26	0.39	1.94	3.48	0.26	1.28	2.23
<i>n</i> -Valeraldehyde	5.08	0.06	0.29	0.24	0.03	0.17	0.31	0.13	0.67	1.17
<i>m</i> -Tolualdehyde	-0.59	0.10	-0.06	-0.05	0.00		0.00	0.10	-0.06	-0.10
<i>o</i> -Tolualdehyde	-0.59		0.00	0.00	0.20	-0.12	-0.21	0.00	0.00	0.00
Hexaldehyde	4.35	0.21	0.92	0.75	0.10	0.44	0.78	0.60	2.61	4.54
Glyoxal	12.50	0.44	5.56	4.51	0.20	2.50	4.49	0.10	1.25	2.17
Methylglyoxal	16.56	1.19	19.70	15.99	1.10	18.22	32.71	0.40	6.62	11.52
Total			123.18	100.00		55.69	100.00		57.51	100.00

^a Rate constant of carbonyls react with OH at 298 K ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)

^b Maximum incremental reactivity coefficient (unit: gram of ozone formed per gram of carbonyl); MIR coefficients are from Carter (2010)

^c Average carbonyl concentration (calculated over sampling period, $\mu\text{g m}^{-3}$)

^d Percentage of total O_3 formed by carbonyls

high temperature. However, a fairly positive correlation between formaldehyde levels and ambient temperature was observed in HH. This reflects that the formation rate of formaldehyde through photooxidation of hydrocarbons (especially biogenic hydrocarbon in HH) greatly exceeded its photolysis rates. The negative correlations ($R=-0.64$ at XJU; $R=-0.58$ at HH) between total measured carbonyls and wind speed suggested that wind is in favor of diffusion of pollutants. The influence of wind speed on atmospheric carbonyls was clearly exhibited in both sites. Although not measured in this study, the boundary layer height and state of atmospheric mixing should be taken into consideration. Large mixing flux in summer facilitates an effective dispersion of pollutants and favors the removal and dilution of ambient aldehydes.

Role of carbonyls in photochemical smog formation

Carbonyl compounds are precursors of ozone formation. Individual species have different photochemical reactivity. In previous studies, propene equivalent (Prop-Equiv) and the maximum incremental reactivity (MIR) have been used to estimate the photochemical reactivity of carbonyls with OH radicals and to evaluate the contributions of individual carbonyls to the ozone production (Carter 1994; Guo et al. 2004; Duan et al. 2008; Lü et al. 2010).

Prop-Equiv (j) is a measure of the concentration of compound j on an OH-reactivity-based scale normalized to the reactivity of propene. The ozone formation potential of the quantified carbonyl emissions was calculated using the MIR scale developed by Carter (2010). The averaged Prop-Equivalents and ozone formation potentials of each species are shown in Table 5 (except 2,5-dimethylbenzaldehyde, glyoxal, and methylglyoxal for Prop-Equiv (j); and 2,5-dimethylbenzaldehyde for ozone formation potential). In the three sampling periods, the largest contributors to Prop-Equiv concentrations were formaldehyde, acetaldehyde, propionaldehyde, and *iso*-valeraldehyde which accounted for 84–94 % of the total Prop-Equiv concentrations (except for summertime in HH, where *iso*-*n*-butyraldehydes are one of the major contributors of Prop-Equiv concentrations (19 %)). Ozone formation from ambient carbonyls in both sampling locations was dominated by formaldehyde, acetaldehyde, and methylglyoxal. These top three species contributed over 85 % of the total ozone formation potentials, except for summertime in HH. The contribution to ozone formation in HH during summer was dominated by

formaldehyde (36 %), acetaldehyde (16 %), propionaldehyde (14 %), and methylglyoxal (12 %). In XJU, formaldehyde, glyoxal, and methylglyoxal had higher ($p<0.01$) percentages in spring and summer than in winter. This observation emphasizes the importance of these carbonyls in urban air photochemistry under high temperature (18–30 °C). Methylglyoxal and glyoxal were emitted at low levels, but due to their high MIR value, they have substantial contribution to the total carbonyl reactivity.

Risk assessment

Despite numerous investigations implying that indoor concentrations of carbonyls are generally higher than outdoor concentrations, the adequate positive correlations between indoor and outdoor concentrations have been detected (Feng et al. 2004; Wang et al. 2007), indicating that indoor concentrations are to some extent dependent on ambient concentrations. To the best of our knowledge, there is no available study related to the assessment of health risk associated with the exposure of carbonyls in Xi'an. Compared with ingestion and dermal absorption, inhalation is a major pathway for intake of carbonyls by human. Potential health risks for two carbonyl compounds in Xi'an, including formaldehyde and acetaldehyde, were examined owing to their high abundances in the atmosphere and carcinogenicity classified by the U.S. Environmental Protection Agency (U.S. EPA 1998). Inhalation exposure is always related to exposure frequency, duration, and activity pattern. They are all essential factors in calculations of the lifetime cancer hazard risk. Few assumptions suggested by U.S. EPA have been taken in the relative carcinogenic assessment. The volume of air inspired per day is $20 \text{ m}^3 \text{ day}^{-1}$, and an average body weight of 70 kg is assumed. The risk below one in a million ($<1 \times 10^{-6}$) is usually considered under a concern level while the risk above 100 in a million ($>1 \times 10^{-4}$) represents that instant actions or interventions are necessary to protect human health (Lee et al. 2006).

Our results demonstrate that formaldehyde has a higher ($p<0.001$) cancer risk than acetaldehyde. The lifetime cancer hazard risks associated with formaldehyde and acetaldehyde in XJU and HH are 7.77×10^{-5} and 1.05×10^{-5} (XJU) and 4.04×10^{-5} and 9.11×10^{-6} (HH), respectively. The cumulative cancer risks based on ambient concentrations were higher ($p<0.001$) in XJU (8.82×10^{-5}) than in HH (4.96×10^{-5}). XJU presented the highest cumulative risk in spring, followed by

summer, but in HH, the highest risk was observed in winter followed by summer.

Conclusion

Formaldehyde, acetaldehyde, and acetone were the three most abundant carbonyls in the atmosphere of Xi'an, accounting for >84 % of the total quantified concentrations. Correlation analysis on most compounds suggests that pollution sources varied among the three seasons in the urban site. Seasonal variations were less significant in the sub-urban site, representing that biomass burning and photochemically aged pollutants transported from other regions are the major and stable sources. Both of the propene equivalent and the MIR proved that formaldehyde and the two dicarbonyls (glyoxal and methylglyoxal) have substantial contribution to the total carbonyl reactivity and contributions in ozone formations. Cumulative cancer risk based on measured outdoor carbonyls (formaldehyde and acetaldehyde) in the urban site during spring is 1.14×10^{-4} , indicating that instant actions or interventions are necessary to protect the human health. The results are informative for evaluation of the air quality in North-western China.

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