Seasonal and diurnal variations of mono- and di-carbonyls in Xi'an, China

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ABSTRACT

Seventeen carbonyls in urban ambient air were quantified in summer (June 2009) and winter (January 2010) in an urban site located in Xi'an, China. Formaldehyde, acetaldehyde and acetone were the three most abundant carbonyls in the atmosphere with the concentrations of 6.54 ± 2.38 ppbv, 2.08 ± 1.07 ppbv and 2.74 ± 1.14 ppbv in summer (from 14th to 24th June, 2009), respectively. In winter, the concentrations were 4.46 ± 1.74 ppbv, 6.52 ± 3.88 ppbv and 3.87 ± 2.33 ppbv respectively from 4th January, 2010 to 10th January, 2010. Most carbonyls had higher concentrations in winter than in summer. And majority of the species had higher concentrations in daytime than in nighttime, indicating photochemical oxidation/human activities played an important role in diurnal variation. Formaldehyde/acetaldehyde ratios (F/A) in summer (2.14) was much higher than that in winter (0.47), showing significant effect of photochemical oxidation in the urban air during summer. Acetaldehyde/propionaldehyde (A/P) average ratio was 12.2 in wintertime, implying anthropogenic emission was the major source of carbonyls in Xi'an. In addition, the ratio of acetone to methylglyoxal (A/M) is used to determine the impact of photochemistry in the atmosphere. The average acetone/methylglyoxal ratio (10.3 ± 2.3) in summer was lower than that in winter (21.3 ± 5.1) in Xi'an. Strong correlations among some carbonyls imply that they came from the same pollution sources. Formaldehyde and acetaldehyde play a very important role in photochemical smog formation. Methylglyoxal and glyoxal also have significant contribution to ozone formation potential.

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1. Introduction

Carbonyls, including aldehydes and ketones, are the important classes of oxygenated volatile organic compounds (OVOCs) in the global atmosphere. They are ubiquitous, which can be emitted directly from incomplete combustion of biomass and fossil fuel and formed indirectly in the photochemical oxidations of volatile organic compounds (VOCs) from any natural and anthropogenic sources (Possanzini et al., 2002; Grosjean et al., 1996). Being obligatory intermediates of the photo-oxidation of hydrocarbons, carbonyls play a bridging role in the atmospheric photochemistry. Carbonyls are the direct precursors of peroxyacyl nitrates and ozone through peroxy and $RC(O)O_2$ radicals generated by the carbonyls photolysis or reaction with hydroxyl radicals (•OH) (Finlayson-Pitts and Pitts, 1986; Lary and Shallcross, 2000). In addition, some carbonyls are irritants of the skin, eyes and nasopharyngeal membranes and are toxic to human health. And formaldehyde and acetaldehyde are suspected carcinogens and are mutagenic to humans (WHO, 1987).

Secondary organic aerosol (SOA) is produced in the atmosphere by oxidation of VOCs (Kanakidou et al., 2005). Dicarbonyls, including glyoxal (C_2) and methylglyoxal (C_3), are considered to be the precursors of SOA and are oxidized products of many VOCs in the atmosphere. They are highly

soluble in water. Several laboratory and photochemical model studies have recently suggested that the uptake of these dicarbonyls by aqueous aerosols and clouds, followed by oxidation and/or oligomerization, could be a significant source of SOA (Fu et al., 2008). Even though the dicarbonyls have a great influence in the atmospheric chemistry, there is no particular report on their airborne concentration levels in China.

Many carbonyl measurements have been done in urban and rural cities (Possanzini et al., 2002; Nguyen et al., 2001; Grosjean et al., 2002; Moussa et al., 2006; Feng et al., 2005; Báez et al., 2001; Ho et al., 2002; Guo et al., 2004; Pang and Mu, 2006; Santarsiero and Fuselli, 2008; Wang et al., 2007; Weng et al., 2009). However, to our best knowledge, limited studies have been conducted in Northwestern China. Xi'an is considered to be the largest and most economic city in Northwestern China, consisting of scientific research centers, high-educational institutes, and military and high-technological industries. It is also one of the most polluted areas nationwide owing to its special meteorological environment and energy structure (Cao et al., 2007). A number of 13 airborne mono-carbonyls were once measured by Wang et al. (2007) but no data for ambient levels of di-carbonyls has been reported. Due to the World Horticulture Exposition in 2011, air quality becomes a major concern in Xi'an and pollution issues must be urgently solved. The objectives of this study are to identify and quantify ambient mono- and di-carbonyls and characterize both seasonal and diurnal variations in Xi'an.

2. Experimental

2.1. 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 Mainland China. It is located at the Guanzhong Plain at the south edge of the Loess Plateau situated 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 is ~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).

2.2. Sampling collection

Twelve-hour integrated samples (daytime: from 06:00 to 18:00; nighttime: from 18:00 to 06:00 the next day) were collected from 14th June 2009 to 24th June 2009 (summer) and from 4th January, 2010 to 10th January, 2010 (winter). The air samples were collected into silica cartridges impregnated with acidified 2,4-dinitrophenylhydrazine (DNPH) (Sep-Pak DNPH-silica, 55–105 μm particle size, 125 Å 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 were calculated as 100% $(1 - A_b/A_f)$, where A_f and A_b were the amounts of carbonyl collected on the front and the back sampling tubes, respectively. No breakthrough was found at such sampling flow rates and sampling times. The flow rates were checked in the field in the beginning and at the end of each sampling using a calibrated flow meter (Gilibrator Calibrator; Gilian Instruments, W. Caldwell, NJ). A Teflon filter assembly (Whatman, Clifton, NJ) 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). The recovery of carbonyl collection was not affected by the ozone trap (Ho and Yu, 2002). Collocated samples were collected to examine the sample collection reproducibility, which was >95% in the field. A cartridge was reserved to serve as a field blank on each
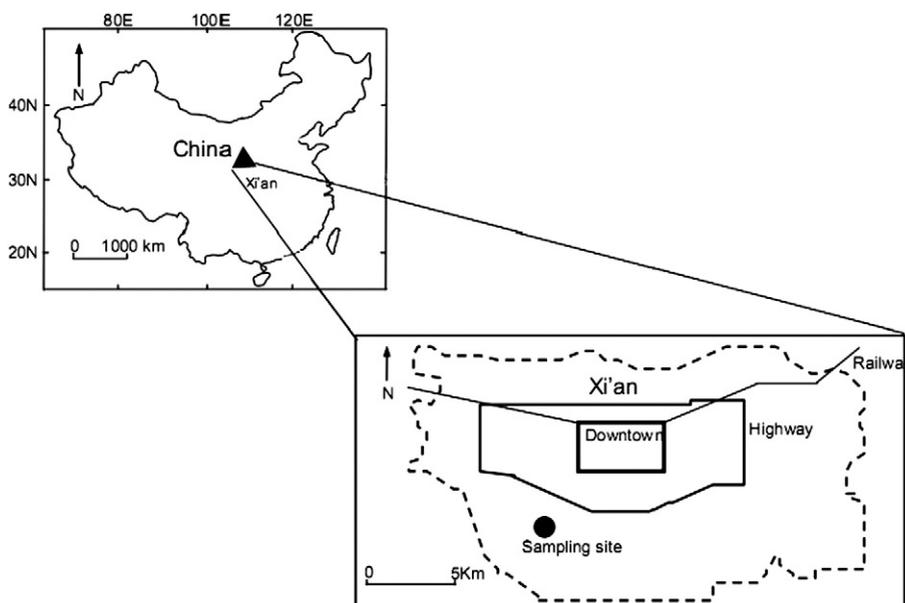
Fig. 1. A geographical map showing the location of Xi'an in China (upper plot) and sampling site IEECAS (black spot in bottom plot).

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. The DNPH-coated cartridges were stored in a refrigerator at <4 °C after sampling and before analysis. Meteorological parameters, including temperature, air pressure, RH, rainfall, and wind speed and direction, were recorded during the sampling period.

2.3. Analytical methods

A total of 17 carbonyls was 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 methyglyoxal. 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 acetonitrile (HPLC/GCMS grade, J&K Scientific Ltd., Ontario, Canada) to a volumetric flask. Test has been done to demonstrate that no any DNPH and its derivatives remained in the cartridge after the 2.0 mL elution. 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^{-1}. 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^{-1} DNPH in an acidic aqueous solution. The mixtures were allowed to stand at room temperature for at least 6 h for a complete derivatization. The recoveries for glyoxal and methylglyoxal are 95% and 97%, respectively. 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 μg mL^{-1}. Linearity was 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-pressure liquid chromatography (HPLC) system (Series 1200; Agilent Technology, Santa Clara, CA) 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) 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 of 50% A/50%B for the next 8 min, to 100% B for the next 10 min, to 100% C for the next 6 min, and finally to 100% C for the next 5 min. The flow rate was 2.0 mL min^{-1} throughout the run. The absorbance at 360 nm, 390 nm, and 420 nm was used for 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 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^{-1}. It is estimated using the equation:

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

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^{-1}, which can be translated to 0.016– 0.12 ppbv with a sampling volume of 2.02 m^3. 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 predefined 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% to 1.7–4.6% for monocarbonyls and dicarbonyls, respectively.

3. Results and discussion

3.1. Characterization of carbonyl compounds

The annual average concentrations of 17 carbonyls in Xi'an (in ppbv) are shown in Table 1. Formaldehyde was the most abundant carbonyl, accounting for 35% of the total quantified carbonyl concentrations. Motor vehicle exhaust is a significant source of carbonyls, which are also key compounds participating in photochemical air pollution (Carlier et al., 1986). Formaldehyde is the most abundant carbonyl produced from traffic sources (Ho and Yu, 2002; Ho et al., 2007, 2012). A huge daily emission from either diesel- or gasoline-fueled vehicles (the amount of vehicles in 2009 is ~981,711) is expected to be the major source in Xi'an. Acetaldehyde and acetone were the next two most abundant carbonyls, which had a molar contribution of 28% and 21%, respectively, to the total quantified carbonyls. Acetaldehyde is generated from anthropogenic combustions and is also produced by thermal degradation of polymers in plastic-processing industry (Vainio et al., 1980). In 2009, there are 837 light industrial enterprises above designated size in Shaanxi province, of which production of cigarettes is 80.5 billion sticks and plastic products is 182 thousand tons. Acetone is widely used as a solvent in various industries and chemical plants. The sampling location of IEECAS is within

Table 1
Ambient concentrations of carbonyls (ppbv) in summer and winter in Xi'an, China.

Carbonyls	LOD (ppm)	Annual	Summer			Winter			S/W[a]	S/W[b]	S/W[c]
		Mean ± S.D. (ppbv)	Mean ± S.D. (ppbv)	Max. (ppbv)	Min. (ppbv)	Mean ± S.D. (ppbv)	Max. (ppbv)	Min. (ppbv)	Mean		
Formaldehyde	0.003	5.46 ± 2.29	6.54 ± 2.38	11.44	2.78	4.46 ± 1.74	6.88	1.4	1.47	0.68	6.43
Acetaldehyde	0.005	4.38 ± 3.63	2.08 ± 1.07	4.6	0.87	6.52 ± 3.88	12.30	1.04	0.32	1.90	3.64
Acetone	0.005	3.32 ± 1.91	2.74 ± 1.14	4.76	1.67	3.87 ± 2.33	7.79	0.59	0.71	0.57	2.74
Propionaldehyde	0.004	0.36 ± 0.35	0.09 ± 0.10	0.22	0.02	0.54 ± 0.33	1.17	0.09	0.17	1.70	6.35
Methyl ethyl ketone	0.005	0.95 ± 0.98	0.37 ± 0.28	0.84	0.08	1.48 ± 1.11	3.43	0.17	0.25	/	8.51
iso + *n*-butyraldehyde	0.002	0.14 ± 0.12	0.07 ± 0.08	0.18	0.01	0.19 ± 0.12	0.39	0.04	0.39	/	14.40
Benzaldehyde	0.002	0.15 ± 0.12	0.09 ± 0.03	0.15	0.04	0.20 ± 0.14	0.52	0.01	0.44	2.71	8.62
iso-Valeraldehyde	0.005	0.40 ± 0.28	0.33 ± 0.14	0.54	0.10	0.46 ± 0.36	1.28	0.04	0.72	/	10.79
n-Valeraldehyde	0.004	0.06 ± 0.05	0.03 ± 0.02	0.06	0.01	0.07 ± 0.05	0.17	0.02	0.40	/	/
m-Tolualdehyde	0.005	0.04 ± 0.03	0.03 ± 0.02	0.08	0.01	0.06 ± 0.04	0.14	0.01	0.59	/	/
p-Tolualdehyde	0.006	0.05 ± 0.02	0.03 ± 0.01	0.03	0.02	0.07 ± 0.02	0.09	0.04	0.44	/	/
Hexaldehyde	0.010	0.15 ± 0.08	0.10 ± 0.04	0.16	0.06	0.17 ± 0.08	0.38	0.07	0.57	2.51	10.63
2,5-Dimethylbenzaldehyde	0.010	0.12 ± 0.15	0.02 ± 0.00	0.02	0.00	0.13 ± 0.15	0.51	0.01	0.17	/	/
Glyoxal	0.006	0.13 ± 0.09	0.07 ± 0.04	0.14	0.02	0.19 ± 0.09	0.35	0.05	0.36	1.58	5.08
Methylglyoxal	0.008	0.21 ± 0.13	0.23 ± 0.17	0.74	0.08	0.18 ± 0.07	0.28	0.07	1.25	1.36	5.22
Total		15.68 ± 7.95	12.67 ± 4.66	23.96	5.77	18.47 ± 9.43	35.68	3.65	0.69	/	/

[a] S/W represents the mean carbonyl concentration ratio in summer to winter in Xi'an, China.
[b] S/W represents the mean carbonyl concentration ratio in summer to winter in Elizabeth, New Jersey, US.
[c] S/W represents the mean carbonyl concentration ratio in summer to winter at Montelibretti, Rome, Italy.

the industrial zone in Xi'an, where it has been listed as a national torch program for biomedical manufacturing base (Shaanxi yearbook, 2010). The ambient level of acetone may be also affected by a medicine packing plant near the IEECAS. A large number of industrial processing units can believably elevate background acetone concentration to the area. In addition, acetone has a longer lifetime [53 days uptake by •OH consumption and ~60 days uptake by photolysis] than those of formaldehyde and acetaldehyde (formaldehyde has a lifetime of 1.2 days due to reaction with •OH radicals and 4 hours uptake by photolysis; acetaldehyde has a lifetime of 8.8 h due to reaction with •OH radicals and 6 days uptake by photolysis) in the atmosphere (Atkinson, 2000). For dicarbonyls, the sum of glyoxal and methylglyoxal accounted for 2.3% in summer and 2.0% in winter to the total quantified carbonyl concentrations.

A comparison of the carbonyl concentrations between this study and other reports is illustrated in Table 2. The unit has been converted from ppbv to $\mu g\ m^{-3}$ since no molar concentration was expressed in the reference papers. Consistent with other studies, formaldehyde, acetaldehyde and acetone were the most three abundant carbonyls in the ambient air in the Mainland China and other countries. Wang et al. (2007) reported that the concentrations of formaldehyde in the urban area in Xi'an were 9.90 and 6.50 $\mu g\ m^{-3}$ in summer and winter, respectively. The values are very close to our average value of 7.92 and 5.57 $\mu g\ m^{-3}$ in summer and winter respectively in the same sampling place. However, the concentration of formaldehyde in Xi'an was much higher than that in Beijing in winter (4.7 $\mu g\ m^{-3}$) (Wang et al., 2007). For acetaldehyde, the concentration in Xi'an was also higher than that in other cities in China such as Beijing (6.7 $\mu g\ m^{-3}$) and Guangzhou (10.5 $\mu g\ m^{-3}$) in winter (Wang et al., 2007). However, the total measured carbonyl concentrations in this study were lower than that of the other cities including Beijing, Shanghai and Guangzhou (Wang et al., 2007; Pang and Mu, 2006; Huang et al., 2009; Feng et al., 2005), representing that the carbonyl contributions varied

along the locations and on their regional and local sources. On a worldwide basis, the carbonyl concentrations in Xi'an were slightly lower than the cities, such as Rome, Italy (Possanzini et al., 1996), Rio de Janeiro, Brazil (Grosjean et al., 2002) and Mexico City, Mexico (Báez et al., 2003). Among these cities, the emission from motor vehicles was identified as the most important sources of carbonyls. For instance, in the metropolitan area of Mexico City, there were approximately 3.5 million gasoline- and diesel-fueled vehicles that emitted substantial amounts of formaldehyde and acetaldehyde (Báez et al., 2003). Other emissions from chemical industries (i.e., paints and solvent production, polyurethane, synthetic fabrics, and petrochemical plants) also contributed to the carbonyl production in the atmosphere (Báez et al., 2003). These explain that the highest carbonyl concentrations were observed in Mexico City. The concentrations of airborne glyoxal and methylglyoxal were scarcely reported. Ortiz et al. (2006, 2009) reported the glyoxal and methylglyoxal concentrations in the urban areas at Tokyo and Meguro, Japan which were much lower than our values measured in Xi'an. However, the concentrations of glyoxal and methylglyoxal in the Euramerican developed country (Elizabeth, New Jersey, US; Montelibretti, Rome, Italy) in summertime were significantly higher by nearly one magnitude than that in Xi'an city.

3.2. Seasonal variation

The average total carbonyl concentration was higher in winter than in summer (Table 1). In summer, formaldehyde was the most abundant carbonyl which had an average concentration of 6.54 ppbv. Lower concentration of formaldehyde, on an average of 4.46 ppbv, was found in winter. However, acetaldehyde was the most abundant carbonyl in winter. The average concentration of acetaldehyde was 6.52 ppbv, compared to only 2.08 ppbv in summer. Acetone was the third most abundant carbonyl. The average concentrations of acetone were 2.74 and 3.87 ppbv in summer and

Table 2
Comparisons of carbonyl concentrations ($\mu g\ m^{-3}$) to other cities worldwide.

Locations (city, country)	Concentration ($\mu g\ m^{-3}$)					Season	Reference
	Formaldehyde	Acetaldehyde	Acetone	Glyoxal	Methylglyoxal		
Xi'an, China	5.57	12.0	9.33	0.46	0.55	Winter	This work
Xi'an, China	6.5	12.1	–	–	–	Winter	Wang et al. (2007)
Xi'an, China	7.92	3.7	6.41	0.16	0.67	Summer	This work
Xi'an, China	9.9	12.6	–	–	–	Summer	Wang et al. (2007)
Beijing, China	7.1	7.5	15.1	–	–	Summer	Xu et al. (2010)
Beijing, China	14.8	10.2	16.6	–	–	Fall	Pang and Mu (2006)
Beijing, China	4.7	6.7	–	–	–	Winter	Wang et al. (2007)
Beijing, China	25.4	15.1	–	–	–	Summer	Wang et al. (2007)
Shanghai, China	19.4	15.9	11.9	–	–	Spring/summer/fall	Huang et al. (2009)
Shanghai, China	9.2	12.4	–	–	–	Winter	Wang et al. (2007)
Shanghai, China	16.3	11.1	–	–	–	Summer	Wang et al. (2007)
Guangzhou, China	10.5	8.5	–	–	–	Winter	Wang et al. (2007)
Guangzhou, China	15	10.7	–	–	–	Summer	Wang et al. (2007)
Guangzhou, China	13.8	8.3	17.8	–	–	Summer	Feng et al. (2005)
Hong Kong, China	6	1.8	0.7	–	–	Summer	Guo et al. (2004)
Hong Kong, China	4.13	2.01	1.43	–	–	Annal	Ho et al. (2002)
Osaka, Japan	10.1	7.5	1.3	–	–	Winter/summer	Nguyen et al. (2001)
Tokyo, Japan	–	–	–	0.06	0.11	Summer	Ortiz et al. (2006)
Meguro, Japan	–	–	–	0.16	0.43	Summer	Ortiz et al. (2009)
Elizabeth, NJ	7.59	4.77	4.01	1.16	1.60	Winter	Liu et al. (2006)
Elizabeth, NJ	5.17	9.07	2.29	1.83	2.18	Summer	Liu et al. (2006)
Montelibretti RM, Italy	1.36	0.92	4.57	0.37	0.95	Winter	Possanzini et al. (2007)
Montelibretti RM, Italy	8.75	3.35	12.50	1.88	4.96	Summer	Possanzini et al. (2007)
Ansan, South Korea	24.1	36.6	38.4	–	–	Summer	Pal et al. (2008)
Beirut, Lebanon	5.7	4.1	12.9	–	–	Summer	Moussa et al. (2006)
Rio de Janeiro, Brazil	10.8	10.4	4.1	–	–	Summer	Grosjean et al. (2002)
Xalapa, Mexico	3.7	21	8.4	–	–	Summer/winter	Báez et al. (2001)
Rome, Italy	22.8	18.3	17.6	–	–	Winter	Possanzini et al. (1996)
New Mexico, USA	18.6	13	11.1	–	–	Summer	Gaffney et al. (1997)
Mexico City, Mexico	43.5	28.6	–	–	–	Spring	Báez et al. (1995)

winter, respectively. For dicarbonyls, the average concentration of glyoxal was 0.07 ppbv in summer which was much lower than that in winter (0.19 ppbv). A reverse trend was observed for methylglyoxal. The average concentration of methylglyoxal was 0.23 ppbv which was slightly higher than that in winter (0.18 ppbv). 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 and other two studies (in Elizabeth, New Jersey, US; and in Montelibretti, Rome, Italy) (Liu et al., 2006; Possanzini et al., 2007) were calculated and shown in Table 1. In this study, the S/W ratios of formaldehyde and methylglyoxal were 1.47 and 1.25, respectively. Photochemical reaction is one of the predominant sources of these two carbonyls in summer. The photo-oxidation of VOCs with •OH radicals can produce significant amount of formaldehyde in the air. It is well known that formaldehyde is one important oxidation product of methanol, which can be synthesized in a vascular plant (Fall, 1999). Methanol has a relatively long lifetime (for 3–6 days in the surface boundary layer and for 9 days in the clouds) and is the second most abundant VOCs in the ambient atmosphere (Joseph and Kelsey, 2000). Such oxidation is typically enhanced in summer, resulting in more production of formaldehyde. In addition, the photochemical activity gradually decreases in winter and hence the contribution from the photo-oxidation of biogenic VOCs (e.g., isoprene) to atmospheric formaldehyde reduced accordingly. Pang and Mu (2006) proved a decrease of the

contribution for formaldehyde from summer to autumn in their study done in Beijing in the years 2004–2005. The production of formaldehyde from the photochemical reactions is reduced in winter.

For other carbonyls, the S/W ratios were <1.0, implying that the carbonyl concentrations were lower in summer than that in winter. Rather than 2,5-dimethylbenzaldehyde, propionaldehyde and MEK, acetaldehyde had the lowest S/W ratio. Acetaldehyde, acetone, and propionaldehyde are the most abundant carbonyls emitted from automobiles (Grosjean et al., 2001; Kean et al., 2001). Therefore, more acetaldehyde are thus accumulated in the atmosphere with limit sinks (i.e., photo-oxidation by •OH radical and photolysis) in winter.

Acetone is a potential precursor for methylglyoxal (Alvarado et al., 1999; Chatfield et al., 1987; Orlando et al., 2000; Reissell et al., 1999; Singh and Hanst, 1981; Singh et al., 1994). More acetone was expected to be formed in the oxidation of iso-hydrocarbons and monoterpenes in summer (Alvarado et al., 1999; Chatfield et al., 1987; Orlando et al., 2000; Reissell et al., 1999; Singh and Hanst, 1981; Singh et al., 1994). However, our finding opposes this elucidation by showing the lower concentrations of acetone in summer. It is thus believable that the photochemical reactions can uptake airborne acetone, which is oxidized to methylglyoxal in the atmosphere. This further explains that higher concentrations of methylglyoxal were seen in summer and the S/W ratio for methylglyoxal was >1.0.

The low S/W ratios for other carbonyls also suggest that primary sources in Xi'an in winter were much important. 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. Compared with Elizabeth (US) and Rome (Italy) which are all developed countries, Xi'an has relatively lower S/W ratios. For instance, the S/W ratio of glyoxal and methylglyoxal are Rome (5.08) > Elizabeth (1.58) > Xi'an (0.36) and Rome (5.22) > Elizabeth (1.36) > Xi'an (1.25), respectively. This may indicate that there is stronger photochemical formation of carbonyl compounds in atmosphere in developed countries. Biomass burning, forest wild fires, agricultural practices and bio-fuel combustion, are co-dominated sources for the carbonyls. It has been reported that MEK, furfural, crotonaldehyde, hexaldehyde and heptanal are highly associated with biomass burning (Koppmann et al., 1997). Higher concentrations of MEK and hexaldehyde in winter than in summer indicated that biomass burning is the dominated source in winter in Xi'an.

Acetylene is a precursor of glyoxal. Coal and calcium carbide are the basic raw materials for the production of acetylene. In fact, coal is a common fuel used for house cooking and commercial and residential buildings warming in the Mainland China, but its combustion efficiency could be very low. However, coal burning is a dominant energy source in winter (from November to March every year), leading to heavy productions of glyoxal and aromatic carbonyls (i.e., benzaldehyde and tolualdehyde isomers). In 2009, 2.96 million tons of coal has been produced in Shaanxi Province, of which 23.3 million tons was from provincial coal mine production.

The seasonal molar carbonyl compositions are shown in Fig. 2. The highest contribution of formaldehyde to the total quantified carbonyls (51.6%) was seen in summer, which was twice higher than its contribution in winter (26.7%). A reverse trend was seen for acetaldehyde, which accounted for 15.9% and 33.3% of the total quantified carbonyls in summer and winter, respectively. The seasonal molar compositions were almost unchanged for acetone, which were 21.9% and 21.5%, respectively, in summer and winter. Seasonal variations on the molar composition for other carbonyls were not obvious except for MEK. MEK contributed 7.0% to the total quantified carbonyls in winter, which was much higher than in summer (3.2%). As mentioned previously, MEK can be emitted from biomass burning and is a precursor of atmospheric ozone (O_3). A low temperature environment inhibits the formation of O_3, resulting in less consumption of primary MEK and higher abundance in winter.

3.3. Diurnal variation

The daytime to nighttime (D/N) ratios of the carbonyls are shown in Table 3. The concentrations of most carbonyls were higher in daytime than in nighttime. Ambient carbonyl concentrations in urban areas are greatly influenced by many factors such as primary and secondary emission sources, meteorological conditions, and their sinks. To some extent, the diurnal variations can reflect the influences from these multiple factors. It is obvious that distinct diurnal variations in carbonyl concentrations were seen in summer (Table 3), suggesting that local photo-oxidation of hydrocarbons and
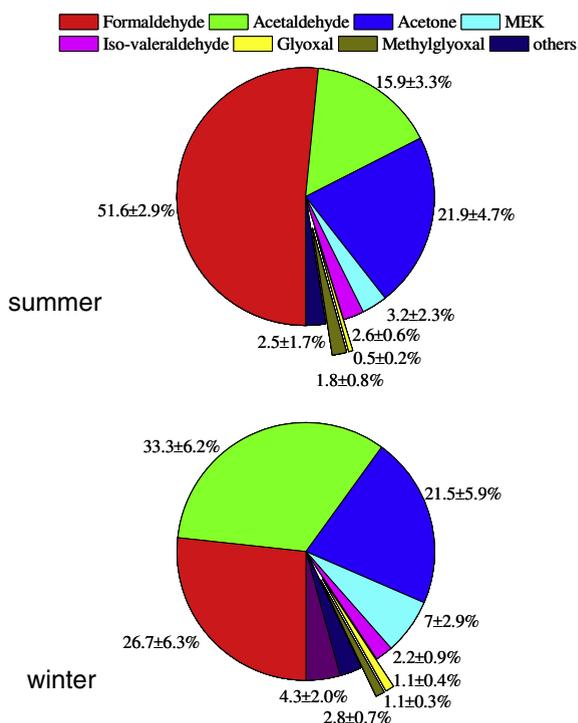
Fig. 2. Molar compositions of carbonyls in summer and winter in Xi'an.

daytime human activities are the dominant sources of carbonyls in Xi'an. Compared with the variations in winter, the primary emission was more dominant. For dicarbonyls, the photochemical production of O_3 is generally higher in daytime, corresponding to a higher formation of glyoxal from reaction with acetylene. Methylglyoxal is mainly produced from the reactions between acetone and hydrogen peroxide (H_2O_2) or other oxidants existing in the atmosphere. The concentration of methylglyoxal thus had a positive relationship to atmospheric acetone production.

3.4. Carbonyl ratios

Fig. 3 compares the ratio of formaldehyde to acetaldehyde (F/A) on diurnal and seasonal bases. The F/A ratio has been widely used as an indicator for possible sources of formaldehyde (Shepson et al., 1991) which usually varies from ~1 to 2 for urban areas and up to ~10 for rural sites (Shepson et al., 1991; Possanzini et al., 1996). The average F/A ratio was 2.09 which is consistent with the values determined in Hong Kong, China (2.05) (Ho et al., 2002) and is also very close to that measured in urban area in Guangzhou, China (1.81) (Feng et al., 2005). The results prove the strong anthropogenic emissions in the urban area of Xi'an. In addition, a high F/A ratio can be usually explained by the photo-oxidation of natural hydrocarbons such as isoprene which yielded 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). From observations of the diurnal variations, most of the F/A ratios were higher in daytime than in nighttime. This

Table 3
Statistical summary of carbonyl compounds diurnal variation at IEECAS station.

Compounds	Summer			Winter		
	Day	Night	D/N[b]	Day	Night	D/N[b]
	Mean ± S.D. (ppbv)	Mean ± S.D. (ppbv)		Mean ± S.D. (ppbv)	Mean ± S.D. (ppbv)	
Formaldehyde	7.54 ± 2.94	5.68 ± 1.49	1.33	4.98 ± 1.89	3.94 ± 1.55	1.26
Acetaldehyde	2.52 ± 1.36	1.70 ± 0.63	1.48	6.26 ± 3.94	6.79 ± 4.11	0.92
Acetone	3.36 ± 1.41	2.21 ± 0.50	1.53	4.24 ± 2.28	3.49 ± 2.50	1.21
Propionaldehyde	0.02 ± 0.00	0.12 ± 0.11	0.19	0.54 ± 0.30	0.54 ± 0.39	1.01
Methyl ethyl ketone	0.19 ± 0.14	0.53 ± 0.27	0.35	1.67 ± 1.31	1.28 ± 0.94	1.30
iso + n-butyraldehyde	0.05 ± 0.07	0.09 ± 0.08	0.62	0.20 ± 0.10	0.17 ± 0.14	1.16
Benzaldehyde	0.09 ± 0.04	0.09 ± 0.02	1.05	0.21 ± 0.16	0.19 ± 0.13	1.06
iso-Valeraldehyde	0.38 ± 0.15	0.29 ± 0.12	1.34	0.47 ± 0.45	0.44 ± 0.27	1.07
n-Valeraldehyde	0.01 ± 0.00	0.04 ± 0.02	0.35	0.09 ± 0.07	0.06 ± 0.03	1.62
m-Tolualdehyde	0.04 ± 0.02	0.03 ± 0.02	1.18	0.06 ± 0.06	0.05 ± 0.01	1.19
p-Tolualdehyde	0.03 ± 0.00	0.02 ± 0.00	1.42	0.07 ± 0.02	0.06 ± 0.02	1.27
Hexaldehyde	bd[a]	0.10 ± 0.04	–	0.17 ± 0.10	0.17 ± 0.06	1.05
2,5-Dimethylbenzaldehyde	bd	0.02 ± 0.00	–	0.14 ± 0.19	0.11 ± 0.13	1.25
Glyoxal	0.10 ± 0.03	0.04 ± 0.01	2.62	0.24 ± 0.09	0.14 ± 0.06	1.69
Methylglyoxal	0.30 ± 0.24	0.17 ± 0.08	1.76	0.19 ± 0.08	0.18 ± 0.07	1.09
Total	14.9 ± 5.94	11.0 ± 2.69	1.32	19.4 ± 10.46	17.5 ± 9.00	1.11

[a] bd represents below limit of detection.
[b] D/N represents ratio of day to night for the carbonyl concentrations.

suggests the sufficiency of sunlight for the production of formaldehyde from photo-oxidations. On average, the F/A ratios in summer (ranged from 1.71 to 3.27) were much higher than that in winter (ranged from 0.26 to 1.11) suggesting a faster photochemical decomposition and oxidation of acetaldehyde leading to formaldehyde.

We here present a molar ratio of glyoxal to methylglyoxal (G/M) acting as an indicator for the degree of photolysis and sources of anthropogenic pollutions. Interpretation of airborne dicarbonyls has not been thoroughly discussed in the past. We calculated the diurnal variations of the G/M ratios determined in Xi'an. The G/M ratios were mostly higher in daytime (0.70) than in nighttime (0.44). Distinctively, a lower G/M ratio in daytime was measured on an episode date at 24 Jun, 2009, when the highest carbonyl concentrations were observed. Glyoxal and methylglyoxal are well-known precursors of SOA (Fu et al., 2008). The formation of SOA from gas-phase reactions potentially leads to a growth of atmospheric fine particulate matters (PM), which have climate and adverse health impacts (Griffin et al., 1999; Hoffmann et al., 1997; Kavouras et al., 1999). Fu et al. (2008) reported that atmospheric lifetimes of glyoxal and methylglyoxal are 2.9 h and 1.6 h, respectively, mostly determined by photolysis. Glyoxal is thus believable to have a stronger persistence than methylglyoxal in the presence of sunlight, as a result of higher concentrations in the ambient. The photochemical
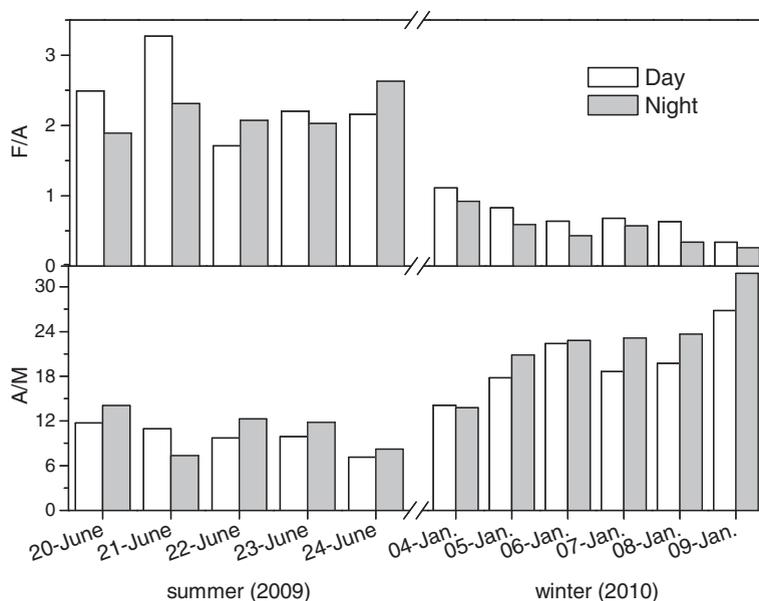
Fig. 3. Seasonal and diurnal variations for ratios of formaldehyde to acetaldehyde (F/A) and acetone to methylglyoxal (A/M).

Table 4
Correlations of the carbonyls in Xi'an in summer.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1 Formaldehyde	1													
2 Acetaldehyde	0.91	1												
3 Acetone	0.88	0.78	1											
4 Propionaldehyde	0.12	0.10	−0.27	1										
5 Methyl ethyl ketone	−0.11	−0.18	−0.35	0.47	1									
6 iso + n-butyraldehyde	0.60	0.64	0.23	0.69	0.26	1								
7 Benzaldehyde	0.61	0.62	0.43	0.06	0.29	0.36	1							
8 iso-Valeraldehyde	0.90	0.87	0.70	0.24	0.13	0.63	0.63	1						
9 n-Valeraldehyde	0.28	0.55	−0.39	0.97	0.47	0.91	0.03	0.32	1					
10 m-Tolualdehyde	−0.11	−0.10	−0.18	−0.04	0.17	−0.18	0.34	−0.16	−0.11	1				
11 p-Tolualdehyde	0.37	0.59	−0.02	bd	−0.02	0.49	0.32	0.78	bd	0.52	1			
12 Hexaldehyde	0.54	0.40	0.22	0.86	0.54	0.99	0.09	0.97	0.88	−0.35	bd	1		
13 Glyoxal	0.62	0.52	0.69	−0.38	−0.29	−0.14	0.36	0.67	−0.65	−0.09	0.56	0.86	1	
14 Methylglyoxal	0.58	0.36	0.56	−0.03	−0.01	−0.24	0.23	0.56	−0.58	−0.11	0.57	0.08	0.67	1

dissociation of methylglyoxal is more active in the day than in the night.

Acetone is a potential precursor of methyglyoxal (Alvarado et al., 1999; Chatfield et al., 1987; Orlando et al., 2000; Reissell et al., 1999; Singh and Hanst, 1981; Singh et al., 1994). Therefore, the ratio of acetone to methylglyoxal (A/M) can be used to determine the impact of photochemistry in the atmosphere. The average A/M ratio (10.3 ± 2.3) in summer was lower than that in winter (21.3 ± 5.1) in Xi'an. During the photochemical reactions, acetone can be oxidized to form methylglyoxal in the atmosphere. The photochemical reaction is more favorable in summer, resulting in decreased concentrations of acetone but increased concentrations of methylglyoxal. By using the data reported by Liu et al. (2006), the average A/M ratio (1.05) in summer was the lowest among the four seasons, compared to the values in spring (1.88), winter (2.51) and fall (4.02). The same trend was observed in Montelibretti in Rome, Italy (Possanzini et al., 2007). The lowest A/M (2.52) was found in summer at the average temperature of 32.4 °C whereas the A/M in autumn (22.6 °C on average) and in winter (8.5 °C on average) was > 4.0.

3.5. Correlation of carbonyl compounds

The correlations among 16 carbonyls during summer and winter were evaluated by regression analysis and their correlation coefficients (r) are shown in Tables 4 and 5. It indicates that there are overall good correlations among the carbonyls in winter, except for n-valeraldehyde. These agree with the study of Ho et al. (2002) which reported that vehicular exhaust was the primary source in winter while both vehicular exhaust and photochemical reactions were the major sources in summer. Moreover, it may be due to the lesser biogenic VOC emission in winter than in summer. Only fair correlations were found in summertime because of the photochemical degradation during high solar radiation and the vertical mixing of the pollutants was different in summer and wintertime. Strong correlation between formaldehyde and acetaldehyde, especially during summer sampling periods (R = 0.91) in 14th–24th June 2009, implies that these two aldehydes had common sources and sinks during summertime. The source of formaldehyde and acetaldehyde might either come from direct emission sources or formed by photochemical reaction under high solar radiation, which was one of the most important secondary sources of acetaldehyde and formaldehyde in summer. Significant positive correlations were also observed between carbonyl concentrations and ambient temperature, suggesting the existence of ambient conditions favorable to oxidation of hydrocarbons. The reaction rate (photochemical generation and photolysis) of each carbonyl was different; therefore, the variations of the concentrations of carbonyls in summertime varied dramatically.

Table 5
Correlations of the carbonyls in Xi'an in winter.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1 Formaldehyde	1														
2 Acetaldehyde	0.79	1													
3 Acetone	0.56	0.70	1												
4 Propionaldehyde	0.83	0.96	0.52	1											
5 Methyl ethyl ketone	0.75	0.90	0.72	0.88	1										
6 iso + n-butyraldehyde	0.63	0.87	0.62	0.86	0.81	1									
7 Benzaldehyde	0.75	0.96	0.70	0.91	0.86	0.90	1								
8 iso-Valeraldehyde	0.75	0.93	0.66	0.89	0.86	0.82	0.97	1							
9 n-Valeraldehyde	−0.24	0.16	0.06	0.18	0.28	0.52	0.40	0.38	1						
10 m-Tolualdehyde	0.54	0.71	0.53	0.62	0.71	0.64	0.90	0.91	0.45	1					
11 p-Tolualdehyde	0.96	−0.86	−0.33	0.01	0.41	−0.88	−0.49	−0.09	−0.40	−0.15	1				
12 Hexaldehyde	0.66	0.73	0.50	0.70	0.66	0.57	0.83	0.83	0.27	0.92	−0.03	1			
13 2,5-dimethylbenzaldehyde	0.62	0.82	0.46	0.85	0.80	0.84	0.92	0.93	0.61	0.90	−0.18	0.82	1		
14 Glyoxal	0.93	0.59	0.52	0.63	0.60	0.50	0.61	0.60	−0.18	0.48	0.76	0.62	0.50	1	
15 Methylglyoxal	0.88	0.90	0.70	0.88	0.81	0.75	0.86	0.81	−0.10	0.64	−0.33	0.72	0.69	0.79	1

Table 6

Relative contributions of ambient air carbonyls to ozone production in Xi'an, China in summer and winter.

Carbonyl	MIR[b]	Summer			Winter		
		$\mu g\ m^{-3a}$	$\mu g\ O_3\ m^{-3}$	$\%\triangle O_3$[c]	$\mu g\ m^{-3}$	$\mu g\ O_3\ m^{-3}$	$\%\triangle O_3$[c]
Formaldehyde	9.46	7.92	74.92	59.27	5.57	52.69	29.30
Acetaldehyde	6.54	3.70	24.20	19.14	11.95	78.15	43.46
Acetone	0.36	6.41	2.31	1.83	9.33	3.36	1.87
Propionaldehyde	7.08	0.21	1.49	1.18	1.30	9.20	5.12
MEK	1.48	1.09	1.61	1.28	4.42	6.54	3.64
iso + n-butyraldehyde	5.97	0.21	1.25	0.99	0.57	3.40	1.89
Benzaldehyde	−0.67	0.37	−0.25	−0.20	0.88	−0.59	−0.33
iso-Valeraldehyde	4.97	1.15	5.72	4.52	1.64	8.15	4.53
n-Valeraldehyde	5.08	0.10	0.51	0.40	0.26	1.32	0.73
m-Tolualdehyde	−0.59	0.16	−0.09	−0.07	0.28	−0.17	−0.09
p-Tolualdehyde	−0.59	0.14	−0.08	−0.07	0.33	−0.19	−0.11
Hexaldehyde	4.35	0.40	1.74	1.38	0.71	3.09	1.72
Glyoxal	12.50	0.16	2.00	1.58	0.46	5.75	3.20
Methylglyoxal	16.56	0.67	11.10	8.78	0.55	9.11	5.07

[a] Average carbonyl concentration (calculated over June and January sampling period).
[b] Maximum Incremental Reactivity coefficient (units: gram of ozone formed per gram of carbonyl); MIR coefficients are from Carter (2010).
[c] Percent of total O_3 formed by carbonyls.

Acetone comes from both anthropogenic and biogenic emissions. A recent study (Singh et al., 2000) reported that the global acetone mixing ratio was predominantly biogenic. However in this study, acetone has a very strong relationship with both formaldehyde and acetaldehyde, showing acetone comes from both anthropogenic and biogenic emissions.

3.6. Role of carbonyls in photochemical smog formation

The ozone-forming potential of the quantified carbonyl emissions was calculated using the MIR scale developed by Carter (2010) (except for 2,5-dimethylbenzaldehyde where MIR value is not available). The reactivity with respect to ozone formation of ambient air carbonyls in summer and in winter is presented in Table 6. Ozone formation from ambient carbonyls in our sampling location in summer was dominated by formaldehyde (59% of the total) and acetaldehyde (19%), followed by methylglyoxal (9%), iso-valeraldehyde (5%), acetone (2%), glyoxal (2%) and hexaldehyde (1%). And the contribution to ozone formation of all the carbonyls in winter was accounted by acetaldehyde (43%), formaldehyde (29%), propionaldehyde (5%), methylglyoxal (5%), iso-valeraldehyde (5%), MEK (4%), glyoxal (3%), acetone (2%), iso + n-butyraldehyde (2%) and hexaldehyde (2%). All of them have higher percentage in wintertime than in summertime, except for formaldehyde and methylglyoxal. This observation emphasizes the importance of carbonyls in urban air photochemistry. Methylglyoxal and glyoxal were emitted at low levels, but due to their high MIR value, they have substantial contribution to total carbonyl reactivity.

4. Conclusion

The diurnal concentrations of seventeen carbonyl compounds were determined in Xi'an city during the two seasonal monitoring in June 2009 and in January 2010. Formaldehyde, acetaldehyde and acetone are the most abundant three carbonyls in the atmosphere of Xi'an. Seasonal and diurnal variations of carbonyl compounds were significant, with maxima in winter time (except formaldehyde and methylglyoxal),

indicating a much higher primary emission and unfavorable meteorological conditions that favored the accumulation of pollutants. However, majority of the species had higher concentrations in daytime than in nighttime, indicating photochemical oxidation also played an important role in diurnal variations of carbonyls. The F/A ratios revealed that the principal source of carbonyls in Xi'an is anthropogenic. Moreover, diurnal variations of G/M ratios and seasonal variations of A/M ratios were used as an indicator for the degree of photolysis and the impact of photochemistry, respectively. A lower G/M ratio determined in the daytime implied that the photochemical dissociation of methylglyoxal is more active in the day than in the night while a lower A/M ratio determined in summer implied that the photochemical reaction is more favorable in summer to oxidize acetone to form methylglyoxal. Strong correlations (especially in winter) among carbonyls (especially formaldehyde and acetaldehyde) indicate that these carbonyl compounds had common sources and sinks. Formaldehyde and acetaldehyde play a very important role in ozone formation. However, methylglyoxal and glyoxal also have significant contribution to ozone formation potential even though their concentrations were low in the atmosphere.

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