



## Seasonal and Diurnal Characteristics of Carbonyls in Urban Air in Qinzhou, China

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### ABSTRACT

Ambient carbonyls in urban air in Qinzhou were studied from October 2011 to July 2012 to investigate their distribution characteristics and sources. Acetaldehyde ( $8.04 \pm 9.00 \mu\text{g}/\text{m}^3$ ), formaldehyde ( $6.70 \pm 6.36 \mu\text{g}/\text{m}^3$ ) and acetone ( $2.43 \pm 2.81 \mu\text{g}/\text{m}^3$ ) were three most abundant carbonyls, accounting for ~90% of the seven carbonyls identified. Concentrations of most carbonyls showed significantly higher levels in spring and summer than those in autumn and winter. Seasonal and diurnal variations indicated that formaldehyde and acetaldehyde were related to barbecue emissions and photochemical loss, while solvent usage was responsible for acetone. The average  $C_1/C_2$  ratio was higher (1.92) in summer than that during other seasons (0.52–1.78), implying the positive impact of photochemical loss or formation; and a significantly lower  $C_2/C_3$  ratio (2.57) was observed in winter than during other seasons (12.47–52.82), suggesting significant emissions from straw burning and barbecues. Formaldehyde and acetaldehyde were the two major contributors (63–97%) to  $\text{O}_3$  formation, particularly in spring and summer.

**Keywords:** Formaldehyde; Acetaldehyde; Barbecue emission; Straw burning emission; Qinzhou.

### INTRODUCTION

Ambient carbonyls are receiving increasing attention as ubiquitous pollutants (Andreini *et al.*, 2000; Bakeas *et al.*, 2003; Cavalcante *et al.*, 2006; Pal *et al.*, 2008; Uchiyama *et al.*, 2012; Ho *et al.*, 2013) and as important participants and products in photochemical reactions influencing smog processes in air (Carlier *et al.*, 1986; Vairavamurthy *et al.*, 1992; Atkinson, 2000; Duane *et al.*, 2002; Guo *et al.*, 2009). They are the sources of free radicals and organic aerosols, as well as the precursors of organic acids and oxidants, including ozone ( $\text{O}_3$ ) and peroxy-carboxylic nitric anhydrides (Carlier *et al.*, 1986; Roberts, 1990; Atkinson, 2000). Carbonyls are emitted into the atmosphere from primary anthropogenic (Kean *et al.*, 2001; Kim *et al.*, 2008) and biogenic sources (Seco *et al.*, 2007; Guo *et al.*, 2009), or formed as reaction intermediates from the oxidations of hydrocarbons (Wiedinmyer *et al.*, 2001; Duane *et al.*, 2002; Guo *et al.*, 2013).

Interests in carbonyls continue to attract atmospheric chemists due to the carbonyls' important roles in atmospheric

photochemistry (Carlier *et al.*, 1986; Vairavamurthy *et al.*, 1992; Atkinson, 2000) and negative impacts on human health (Timmons *et al.*, 2002; Noisel *et al.*, 2007). Studies have been performed to evaluate carbonyls' levels and sources (Kean *et al.*, 2001; Seco *et al.*, 2007; Pal *et al.*, 2008), distributions (Moussa *et al.*, 2006; Cerón *et al.*, 2007; Pang *et al.*, 2009), photochemical formations (Wiedinmyer *et al.*, 2001; Duane *et al.*, 2002; Guo *et al.*, 2013), health risks (Cavalcante *et al.*, 2006; Noisel *et al.*, 2007; Weng *et al.*, 2009), and analytical approaches (Guo *et al.*, 2007; Kim and Pal, 2010; Ho *et al.*, 2011; Pang *et al.*, 2011; Saha *et al.*, 2012; Xie *et al.*, 2013). However in China, investigation on carbonyls in developing regions (e.g., in Guangxi) is very limited due to the poor economic capabilities compared to economically developed regions (Feng *et al.*, 2005; Duan *et al.*, 2008; Lü *et al.*, 2010; Guo *et al.*, 2011; Zhang *et al.*, 2012), resulting in that our current knowledge of carbonyls remains weak in these developing regions.

Qinzhou (longitude  $108^\circ 39'E$ , latitude  $21^\circ 58'N$ ) is located in southern China, with a total population of ~3.1 million and covering an area of ~10,800  $\text{m}^2$  (Wang *et al.*, 2013). It is one important developing city in Guangxi, as well as the advance position of permanent venue for the China-Association of Southeast Asian Nations Expo. The climate is between subtropical and tropical monsoon. To the east there is Pearl River Delta, to the south there is Beibu Gulf and South China Sea, and to the west there is Vietnam

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(Fig. 1). Qinzhou is also a typical coastal city, as well as one of the most important economic cities in southern China. For instance, the coal-fired power plant will be built to be the largest thermal power base in Guangxi, and the petrochemical industrial plant has been the largest investment project, as well as the center base of industrial manufacturing in Guangxi.

In the developing process of industrialization in recent years, the increase in industry of the city has led to public concerns about local air pollution because large amounts of pollutants were discharged into the atmosphere, resulting in a rapid deterioration of local air quality, e.g., NO<sub>2</sub> exhibited an increasing trend due to the local industrial development (Shi, 2007). Considering that environmental pollution has become one of most important concerns to be solved, which is closely related to the mankind's sustainable development, both the observed trend of pollutant levels and the deteriorating air have attracted great concerns of the local government. To accurately evaluate the status of air pollution in Qinzhou, it is necessary for the local government to better understand the distribution characteristics of carbonyls.

Air monitoring is fundamental to the understanding of atmospheric chemical processes of organic compounds, which is the first step for the assessment on air pollutants, and the result of air monitoring can be an effective indicator to reflect the status of air pollution (Cerón *et al.*, 2007; Lü *et al.*, 2010; Zhang *et al.*, 2012). However, atmospheric carbonyls in the developing Qinzhou have not been studied up to the present day, resulting in negative effects that: (1) no information on them are provided for the public; and (2) our current knowledge of local carbonyl pollution still remains poor. To better understand the local carbonyls, and to effectively investigate their distribution characteristics and possible sources, a monitoring program was conducted in this study in Qinzhou from October 2011 to July 2012.

## EXPERIMENTAL

### Chemicals

Water was re-distilled and filtered by Milli-Q prior to use. Acetonitrile (ACN) was purchased from Merck (Darmstadt,

Germany). 2,4-dinitrophenylhydrazine (DNPH)-coated cartridges (Sep-Pak Silica Gel Cartridge, Waters, Millipore Co.) were sealed in hermetic Teflon bags and stored in a 4°C refrigerator before use. The standard solution (ChemService, USA) of containing 21 carbonyl-DNPH derivatives were commercially supplied by Shanghai Anpel Scientific Instrument Co., Ltd including DNPH derivatives of formaldehyde, acetaldehyde, acetone, acrolein, butyraldehyde, propionaldehyde, crotonaldehyde, benzaldehyde, 2,5-dimethylbenzaldehyde, hexaldehyde, isovaleraldehyde, valeraldehyde, *o*-tolualdehyde, *m*-tolualdehyde, *p*-tolualdehyde, cyclohexanone, heptaldehyde, octylaldehyde, nonanaldehyde, decylaldehyde, 2-butanone (Feng *et al.*, 2005; Lü *et al.*, 2010).

### Sampling

Sampling was based on the TO-11A (USEPA, 1996, 1999) due to its simplicity and good reproducibility. Potential drawbacks existed in the method for sampling air carbonyls using DNPH-coated silica cartridges, mainly including: (1) ambient O<sub>3</sub> was the critical interference using DNPH-coated solid sorbent cartridges; (2) environmental relative humidity could inhibit derivatization kinetics and contributed to degradation of carbonyl-DNPH derivatives during sampling (Saha *et al.*, 2012; Ho *et al.*, 2013); (3) sampling volume and concentration also influenced the analysis of carbonyls using DNPH cartridges (Pal and Kim, 2008a); (4) unsaturated carbonyls such as acrolein were not accurately quantified using the DNPH method (Ho *et al.*, 2011); and (5) the HPLC method was reliable for low-weight carbonyls, while gas chromatography was more suitable for high-weight carbonyls (Pal and Kim, 2008b; Kim and Pal, 2010; Pang *et al.*, 2011; Xie *et al.*, 2013). However, these potential drawbacks could be minimized though the experiments of quality assurance in the method (Feng *et al.*, 2005; Lü *et al.*, 2010).

In this study, to ensure the reliability of air sampling and minimize the biases caused by the drawbacks above, the breakthrough experiment by connecting two cartridges in series was conducted before sampling, and no carbonyls



**Fig. 1.** The location of atmospheric sampling site in Qinzhou in southern China.

were detected in the back cartridge when sampling time was 2 h at a flow rate of 2 L/min; cartridge collection efficiency (CE) experiment showed that over 99% of carbonyls were recovered by the first cartridge, indicating the complete recovery of all carbonyls (Table 1); a potassium iodide (KI) denuder was connected to the upstream of the cartridges to avoid the interference of ambient O<sub>3</sub> (Lü *et al.*, 2010; Ho *et al.*, 2011; Duan *et al.*, 2012; Ho *et al.*, 2013); other experiments of quality assurance and detail sampling procedure were described by our previous reports (Feng *et al.*, 2005; Lü *et al.*, 2010; Duan *et al.*, 2012). Based on these experiments, air samples were collected from October 2011 to July 2012 in one site in urban center in Qinzhou, which was located on the roof of a building (~35 m above ground level), and surrounded by roads, buildings and offices (Fig. 1). The information of sampling date and meteorological conditions were listed in Table 2.

Briefly, air samples were collected by drawing the air with a sampling pump (Gast, USA) through DNPH-coated cartridges, the KI denuder was connected to the upstream of the cartridges. And the sampling time was 2 h at a flow rate of 2 L/min (a sample volume of 240 L), which was conducted at four intervals in a day, including morning (07:00–09:00), noon (12:00–14:00), late afternoon (17:00–19:00) and midnight (22:00–24:00). After sampling, each cartridge was firstly wrapped in a Teflon bag with aluminum foil and then stored in a 4°C refrigerator until analysis. The sampling program of each day included one laboratory blank and one field blank, total eighty air samples and forty blank samples were obtained.

### Analysis and Quality Assurance

Analysis procedure of carbonyls was based on the EPA TO-11A method (USEPA, 1996; Lü *et al.*, 2010; Duan *et al.*, 2012). All cartridges were eluted with 2 mL of ACN into a 2 mL volumetric flask to get sample solutions, and then a 10 µL of the concentrated sample solutions was injected into the HPLC system (HP1100, Agilent, USA) through an auto-sampler. Analytical conditions were: agilent RP-C<sub>18</sub> reverse column (250 mm × 4.6 mm × 5 µm); gradient mobile phase: 60% ACN of water solution (20 min), 70–100% ACN (3min), 100% ACN (6min), 100–60% ACN (5 min) and then 60% ACN (5 min); mobile-phase flow rate: 1 mL/min; detector: UV at 360 nm. Identification of carbonyls was based on the comparison of retention time between samples and the standard solution, and quantification was conducted by integration of peak areas.

The instrument was calibrated using six standards (0.2–10 µg/mL). Strong linear relationship ( $R^2 > 0.995$ ) was found between concentrations and responses for all carbonyls identified. Method detection limits (MDL) were 0.05–0.15 µg/m<sup>3</sup> for various carbonyls, which were determined by using seven replicate analyses ( $n = 7$ ) of the working standards at the lowest concentration (Table 1). Relative standard deviation (RSD) for duplicate analysis was lower than 5%, and method precision (RSD,  $n = 7$ ) was 3.01–9.65% for seven replicate analyses. Analysis of two blank cartridges (including one laboratory and one field blank) did not show negative effects on the air sampling according to EPA blank criteria (USEPA, 1996). For a sample volume of 240 L air in this study, the MDL were 0.07, 0.09, 0.11, 0.10,

**Table 1.** Method detection limits (MDL, µg/m<sup>3</sup>), method precision (RSD), cartridge collection efficiency (CE) and mass values of carbonyls (ng) in this study.

	CE <sup>a</sup>	MDL <sup>b</sup>	RSD <sup>c</sup>	Mass <sup>d</sup>
Formaldehyde	100.2%	0.07	3.01%	1.68
Acetaldehyde	99.8%	0.09	3.89%	2.16
Acetone	99.5%	0.11	9.65%	2.64
Propionaldehyde	99.4%	0.10	3.78%	2.40
Crotonaldehyde	99.2%	0.13	4.01%	3.12
2-butanone	99.9%	0.12	5.16%	2.88
Butyraldehyde	99.0%	0.14	7.48%	3.36

<sup>a</sup> Collection efficiency was determined by connecting two DNPH-cartridges in series to collect 240L gas of containing gaseous carbonyls (8 µg/m<sup>3</sup>), and detail sampling procedure was similar to previous studies (Francois *et al.*, 2005; Guo *et al.*, 2009; Pang *et al.*, 2011).

<sup>b</sup> Method detection limits (MDL) was determined by using seven replicate analyses of the working standards at the lowest concentration (0.2 µg/mL).

<sup>c</sup> Method precision (RSD) was determined by HPLC for seven replicate analyses.

<sup>d</sup> Absolute mass values of carbonyls needed in the air samples for the HPLC analysis.

**Table 2.** The information of sampling and meteorological conditions during sampling in Qinzhou.<sup>a</sup>

	Sampling date	Temp (°C)	RH (%)	II (×10 <sup>2</sup> lux)	Weather
Spring	April 6–10, 2012	26–36	78–100	0–1150	Clear/cloudy
Summer	July 3–7, 2012	34–46	70–94	0–1350	Sunny/clear
Autumn	October 16–20, 2011	20–29	33–94	0–1050	Clear/cloudy
Winter	January 12–16, 2012	3–15	57–100	0–300	Cloudy/fog

<sup>a</sup> Temperature (Temp), relative humidity (RH), illumination intensity (II) of sunlight, and weather conditions were recorded by the staff who engaged in the air sampling on the field.

0.13, 0.12 and 0.14  $\mu\text{g}/\text{m}^3$  for formaldehyde, acetaldehyde, acetone, propionaldehyde, cyclohexanone, 2-butanone and butyraldehyde, respectively (Table 1).

## RESULTS AND DISCUSSION

### Concentration Levels

Total seven carbonyls including formaldehyde, acetaldehyde, acetone, propionaldehyde, cyclohexanone, 2-butanone and butyraldehyde were identified in urban air in Qinzhou (Table 3). The sum of total carbonyls was  $19.13 \pm 14.12 \mu\text{g}/\text{m}^3$ , ranging of 3.03 to  $44.89 \mu\text{g}/\text{m}^3$ . Acetaldehyde was the most abundant carbonyl, which made up 42.05% of the total carbonyls. Concentration of acetaldehyde ranged from 0.21 to  $29.17 \mu\text{g}/\text{m}^3$  (average of  $8.04 \pm 9.00 \mu\text{g}/\text{m}^3$ ). Formaldehyde (average of  $6.70 \pm 6.36 \mu\text{g}/\text{m}^3$ ) was the second abundant, ranging from 0.36 to  $24.50 \mu\text{g}/\text{m}^3$ , followed by acetone ( $2.43 \pm 2.81 \mu\text{g}/\text{m}^3$ ). The relative abundance followed the order: acetaldehyde > formaldehyde > acetone > 2-butanone > butyraldehyde > propionaldehyde  $\approx$  cyclohexanone. Considering that (1) formaldehyde, acetaldehyde and acetone accounted for  $\sim 90\%$  of the total carbonyls (Table 3) and (2) they were by far the principal carbonyls at urban areas (Cavalcante *et al.*, 2006; Kim *et*

*al.*, 2008; Lü *et al.*, 2010; Zhang *et al.*, 2012), these three carbonyls were mainly discussed in the next sections.

Table 4 presents a comparison between Qinzhou and other cities for concentrations of formaldehyde, acetaldehyde and acetone. The concentration order of ambient formaldehyde and acetaldehyde in Qinzhou were in agreement with that in Guiyang (Pang and Lee, 2010), which followed the order: acetaldehyde > formaldehyde. Beside the well-known existence of gas phase, carbonyls also existed in liquid phase (e.g., water droplets) in the troposphere (Matsumoto *et al.*, 2005; Poulain *et al.*, 2012). The partitioning between gas and liquid phases was provided by Henry's law constant  $H$  (Allou *et al.*, 2011). And the  $H$  values of formaldehyde and acetaldehyde were  $\sim 2.97 \times 10^3$  and  $1.14 \times 10^1$  M/atm, respectively (Matsumoto *et al.*, 2005; Poulain *et al.*, 2010). The much higher  $H$  value was more conducive to formaldehyde's translation from gas to liquid (Matsumoto *et al.*, 2005), resulting in the more solubility into liquid droplets compared to acetaldehyde.

Other than primary emissions (Kim *et al.*, 2008; Tsai *et al.*, 2012), secondary formation is another important source (Wiedinmyer *et al.*, 2001; Duane *et al.*, 2002; Guo *et al.*, 2009; Kourtchev *et al.*, 2012; Guo *et al.*, 2013). Qinzhou is a developing coastal city with respect to Guiyang (a provincial

**Table 3.** Average concentrations of atmospheric carbonyls and their mean fractions in the total carbonyls in Qinzhou, China.

	Concentrations ( $\mu\text{g}/\text{m}^3$ )		Fractions <sup>c</sup>
	A.M. $\pm$ S.D. <sup>a</sup>	Min.–Max. <sup>b</sup>	
Formaldehyde	$6.70 \pm 6.36$	0.36–24.50	35.05%
Acetaldehyde	$8.04 \pm 9.00$	0.21–29.17	42.05%
Acetone	$2.43 \pm 2.81$	0.16–18.39	12.69%
Propionaldehyde	$0.35 \pm 0.25$	0.12–1.20	1.82%
Crotonaldehyde	$0.35 \pm 0.12$	0.20–0.72	1.81%
2-butanone	$0.76 \pm 0.22$	0.54–1.72	3.97%
Butyraldehyde	$0.50 \pm 0.14$	0.32–0.87	2.61%
Total carbonyls <sup>d</sup>	$19.13 \pm 14.12$	3.03–44.89	

<sup>a</sup> Arithmetic mean and standard deviation (A.M.  $\pm$  S.D.) of carbonyls.

<sup>b</sup> Value ranges of minimum (Min.) to maximum (Max.) for carbonyls.

<sup>c</sup> Percentage contributions of individual carbonyl to the total carbonyls.

<sup>d</sup> Total carbonyls refers to the sum of all measured carbonyls in this table.

**Table 4.** A comparison of concentrations ( $\mu\text{g}/\text{m}^3$ ) for atmospheric formaldehyde, acetaldehyde and acetone in different cities.

	Sampling periods	Formaldehyde	Acetaldehyde	Acetone	References
Shimizu, Japan	Summer–August 2000	2.77	2.29		Ohura <i>et al.</i> (2006)
Beirut, Lebanon	August–September 2004	4.60	2.10	5.00	Moussa <i>et al.</i> (2006)
Xi'an, China	July–August 2004	9.90	12.6		Wang <i>et al.</i> (2007)
Ansan, South Korea	August 2004–September 2005	24.1	36.6	38.4	Kim <i>et al.</i> (2008)
Shanghai, China	January–October 2007	19.4	15.9	11.9	Huang <i>et al.</i> (2008)
Hangzhou, China	March–April 2006	22.2	6.40	18.4	Weng <i>et al.</i> (2009)
Guangzhou, China	November–December 2005	14.6	16.6	15.4	Lü <i>et al.</i> (2009)
Guiyang, China	December 2008–August 2009	4.80	5.70	5.10	Pang and Lee (2010)
Nan-Chie and Kaohsiung, Taiwan	May–December 2006	18.3	14.9	1.23	Wang <i>et al.</i> (2010)
Niterói, Brazil	January 2010	3.22	6.53	7.27	Ochs <i>et al.</i> (2011)
Beijing, China	August 2006	35.65	15.65	8.83	Duan <i>et al.</i> (2012)
Qinzhou, China	October 2011–July 2012	6.70	8.04	2.43	This study

Blank refers to the data were not available in the relative references.

city in Guizhou) and has much lower latitude than other southern cities like Guiyang (106°37'E, 26°39'N). The recorded sunlight and temperature were relatively higher (Table 2), which was more beneficial to photochemical oxidations of hydrocarbons. Both formaldehyde and acetaldehyde showed higher levels than that (4.80 and 5.70  $\mu\text{g}/\text{m}^3$ , respectively) in Guiyang (Table 4), which was likely related to the photochemical formation. Formaldehyde, acetaldehyde and acetone in Qinzhou were significantly lower than those in other megacities in China, e.g., Beijing, Shanghai and Guangzhou (Table 4). These cities were highly polluted by pollutants such as airborne particles compared to Qinzhou. Due to the much lower latitude and less airborne particles in Qinzhou, the local actinic flux was expected to be relatively higher (Stockwell and Gol, 2004), likely resulted in the faster photochemical loss of carbonyls (Finlayson-Pitts and Pitts, 1986; Possanzini *et al.*, 2002; Pang and Lee, 2010; Liu *et al.*, 2013) and decreased their gaseous concentrations.

### Seasonal and Diurnal Variations

Ambient carbonyl levels are influenced by multiple factors such as direct emissions, photochemical process (Moussa *et al.*, 2006; Pang and Mu, 2006; Cerón *et al.*, 2007; Pang *et al.*, 2009; Pang and Lee, 2010; Duan *et al.*, 2012), and metrological conditions (Ho *et al.*, 2002; Pang and Mu, 2006; Pang *et al.*, 2009). To estimate the possible impacts from these factors, seasonal and diurnal variations of carbonyls in Qinzhou are presented in Table 5. Approximately, the total carbonyls decreased in order of summer (30.54  $\mu\text{g}/\text{m}^3$ )  $\approx$  spring (32.18  $\mu\text{g}/\text{m}^3$ ) > autumn (9.55  $\mu\text{g}/\text{m}^3$ ) > winter (4.24  $\mu\text{g}/\text{m}^3$ ), and the similar seasonal trend applied to most carbonyls. Especially, ambient acetaldehyde exhibited significantly lower concentration in summer than that in spring, and this trend was contrary to formaldehyde (Table 5).

High temperature and intense sunlight favored the photochemical oxidations of organic pollutants (e.g., carbonyls) (Atkinson, 2000; Duane *et al.*, 2002; Possanzini *et al.*, 2002; Leungsook *et al.*, 2005; Pang and Lee, 2010). Long-chain low-weight carbonyls were more reactive than those short-chain carbonyls (Atkinson, 2000; Ji *et al.*, 2012), which could result in the faster photochemical loss of the former under high temperature condition. As presented in Table 2, the recorded temperature and sunlight intensity were higher in summer than that in spring. The significantly lower concentration of acetaldehyde in summer was likely related to the faster photochemical loss. In addition, the  $H$  values of carbonyls would decrease with the increase of temperature (Allou *et al.*, 2011), and raised the translation from liquid to gas. Especially, the  $H$  value of formaldehyde is  $\sim 3$  orders of magnitude higher than that of acetaldehyde (Matsumoto *et al.*, 2005). The higher concentration of formaldehyde in summer likely implied the positive effect of  $H$  decrease compared to acetaldehyde.

Diurnal variations of carbonyls did not appear a similar variation pattern during four sampling seasons (Table 5). Approximately, average concentration of the total carbonyls in the nighttime (refers to midnight in this study) was the highest in spring, summer and autumn; and in winter, it

maintained stable in the daytime (including morning, noon and late afternoon) and nighttime. Particularly, average concentrations of formaldehyde and acetaldehyde exhibited higher values in the nighttime, while acetone exhibited higher value in the daytime except for in winter (Fig. 2), implying that the source of acetone differed from that of formaldehyde and acetaldehyde. Qinzhou is a developing city, and there are a certain number of paint factories. Considering that (1) people in the city often go to work in the daytime and ceased their production activities in the nighttime in the city and (2) acetone might be used as industrial solvent in paint manufacturing (Feng *et al.*, 2005; Pang and Lee, 2010), the possible reason for the higher level of acetone in the daytime might be related to solvent usage of containing acetone in the production activities.

It is very interesting that both formaldehyde and acetaldehyde showed higher concentrations in the nighttime (refers to midnight) compared to the daytime except for in winter (Table 5). On one hand, formaldehyde and acetaldehyde are usually important products in photochemical oxidations of hydrocarbons (Sumner *et al.*, 2001; Wiedinmyer *et al.*, 2001; Duane *et al.*, 2002; Guo *et al.*, 2009, 2013); on the other hand, they are the important participants in atmospheric photochemical reactions, e.g., photolysis and reactions with  $\text{OH}\cdot$  (Atkinson, 2000). Intensive sunlight and high temperature were recorded in spring, summer and autumn, particularly in summer (Table 2). It was expected that the photochemical process concerning carbonyls were likely rather reactive. In summer for example, formaldehyde, acetaldehyde and the total carbonyls exhibited the lowest levels in late afternoon (Table 5). One possible reason for the higher concentrations of formaldehyde and acetaldehyde in the nighttime was the significant photochemical loss in the daytime (Atkinson, 2000).

Especially, residential wood combustions also could emit gaseous formaldehyde and acetaldehyde pollutants (Cerqueira *et al.*, 2013). In the nighttime, the residents in Qinzhou usually have barbecue which uses charcoal and wood as fuels, particularly in the nighttime around 22:00. The barbecue service is usually supplied for the local residents in spring, summer and autumn in the city. And people occasionally have barbecue in winter because of the colder weather in contrast to other seasons (including spring, summer and autumn) (Table 2). Another reason for the higher concentrations of formaldehyde and acetaldehyde in the nighttime was likely attributed to the barbecue emission such as the use of charcoal and wood, because the burning of these fuels could emit a large number of gaseous pollutants such as formaldehyde and acetaldehyde (Kim *et al.*, 2008; Ohura *et al.*, 2011; Cerqueira *et al.*, 2013).

To certify the possible impact from the barbecue emission, additional samples (2m above the ground) were collected at the center of one biggest barbecue in Qinzhou during the sampling. Four carbonyl samples were obtained at the barbecue during the daytime (07:00–09:00, 12:00–14:00 and 17:00–19:00) and nighttime (22:00–24:00) on July 5, 2012 (Table 6). All measured carbonyls at the barbecue showed significantly higher levels in the nighttime than those in the daytime (Table 6). For example, acetaldehyde

**Table 5.** Seasonal and diurnal concentrations ( $\mu\text{g}/\text{m}^3$ ) of atmospheric carbonyls in spring, summer, autumn and winter in Qinzhou, China.<sup>a</sup>

	Spring (April 6–10, 2012)							Summer (July 3–7, 2012)							
	Morning	Noon	Late afternoon	Midnight	Mean <sup>b</sup>	Morning	Noon	Late afternoon	Midnight	Mean <sup>b</sup>	Morning	Noon	Late afternoon	Midnight	Mean <sup>b</sup>
Formaldehyde	9.00 ± 0.70	5.23 ± 5.21	10.37 ± 0.96	11.29 ± 0.62	8.47 ± 3.06	17.16 ± 5.62	14.10 ± 1.54	10.18 ± 8.80	17.09 ± 3.54	14.63 ± 5.65	11.60 ± 4.39	6.50 ± 0.97	4.26 ± 3.33	12.28 ± 6.65	8.66 ± 5.12
Acetaldehyde	9.44 ± 0.95	25.05 ± 4.06	20.09 ± 2.81	25.91 ± 3.35	20.12 ± 7.32	11.60 ± 4.39	6.50 ± 0.97	4.26 ± 3.33	12.28 ± 6.65	8.66 ± 5.12	2.53 ± 2.75	9.58 ± 7.63	3.47 ± 1.15	3.20 ± 4.49	4.70 ± 4.97
Acetone	1.96 ± 0.25	1.66 ± 0.04	2.28 ± 1.39	0.26 ± 0.09	1.54 ± 1.01	2.53 ± 2.75	9.58 ± 7.63	3.47 ± 1.15	3.20 ± 4.49	4.70 ± 4.97	0.55 ± 0.32	0.82 ± 0.34	0.41 ± 0.17	0.48 ± 0.38	0.56 ± 0.31
Propionaldehyde	0.39 ± 0.01	0.68 ± 0.35	0.48 ± 0.12	0.26 ± 0.02	0.45 ± 0.23	0.55 ± 0.32	0.82 ± 0.34	0.41 ± 0.17	0.48 ± 0.38	0.56 ± 0.31	0.50 ± 0.12	0.47 ± 0.18	0.29 ± 0.07	0.54 ± 0.17	0.45 ± 0.16
Crotonaldehyde	0.44 ± 0.01	0.39 ± 0.20	0.26 ± 0.07	0.34 ± 0.03	0.36 ± 0.12	0.50 ± 0.12	0.47 ± 0.18	0.29 ± 0.07	0.54 ± 0.17	0.45 ± 0.16	0.77 ± 0.17	1.03 ± 0.27	0.96 ± 0.16	0.82 ± 0.32	0.90 ± 0.23
2-Butanone	0.64 ± 0.03	0.97 ± 0.65	0.68 ± 0.03	0.63 ± 0.05	0.73 ± 0.31	0.77 ± 0.17	1.03 ± 0.27	0.96 ± 0.16	0.82 ± 0.32	0.90 ± 0.23	0.62 ± 0.06	0.85 ± 0.02	0.56 ± 0.21	0.56 ± 0.20	0.65 ± 0.18
Butyraldehyde	0.49 ± 0.02	0.61 ± 0.01	0.54 ± 0.06	0.37 ± 0.06	0.50 ± 0.10	0.62 ± 0.06	0.85 ± 0.02	0.56 ± 0.21	0.56 ± 0.20	0.65 ± 0.18	33.73	33.36	20.12	34.96	30.54
Total carbonyls <sup>c</sup>	22.36	34.60	34.69	39.07	32.18	33.73	33.36	20.12	34.96	30.54	Winter (January 12–16, 2012)				
											Morning	Noon	Late afternoon	Midnight	Mean <sup>b</sup>
Formaldehyde	2.46 ± 1.48	1.85 ± 1.28	2.52 ± 0.08	5.16 ± 3.92	3.00 ± 2.29	0.78 ± 0.42	0.93 ± 0.54	0.60 ± 0.07	0.55 ± 0.20	0.72 ± 0.35	0.78 ± 0.42	0.93 ± 0.54	0.60 ± 0.07	0.55 ± 0.20	0.72 ± 0.35
Acetaldehyde	0.82 ± 0.22	1.29 ± 0.59	2.20 ± 1.23	7.54 ± 6.27	2.96 ± 3.92	0.32 ± 0.09	0.62 ± 0.28	0.49 ± 0.18	0.28 ± 0.08	0.43 ± 0.21	0.32 ± 0.09	0.62 ± 0.28	0.49 ± 0.18	0.28 ± 0.08	0.43 ± 0.21
Acetone	1.64 ± 0.10	2.12 ± 0.93	2.48 ± 0.20	1.53 ± 0.13	1.94 ± 0.57	1.41 ± 0.18	1.81 ± 0.36	1.72 ± 0.50	1.18 ± 0.18	1.53 ± 0.39	1.41 ± 0.18	1.81 ± 0.36	1.72 ± 0.50	1.18 ± 0.18	1.53 ± 0.39
Propionaldehyde	0.17 ± 0.04	0.25 ± 0.03	0.23 ± 0.03	0.23 ± 0.04	0.22 ± 0.05	0.15 ± 0.01	0.17 ± 0.00	0.17 ± 0.02	0.16 ± 0.02	0.16 ± 0.02	0.15 ± 0.01	0.17 ± 0.00	0.17 ± 0.02	0.16 ± 0.02	0.16 ± 0.02
Crotonaldehyde	0.33 ± 0.03	0.33 ± 0.03	0.28 ± 0.05	0.24 ± 0.02	0.29 ± 0.05	0.32 ± 0.10	0.28 ± 0.04	0.25 ± 0.01	0.27 ± 0.01	0.28 ± 0.05	0.32 ± 0.10	0.28 ± 0.04	0.25 ± 0.01	0.27 ± 0.01	0.28 ± 0.05
2-Butanone	0.67 ± 0.07	0.71 ± 0.02	0.80 ± 0.30	0.66 ± 0.11	0.71 ± 0.15	0.72 ± 0.04	0.70 ± 0.05	0.71 ± 0.03	0.69 ± 0.08	0.70 ± 0.05	0.72 ± 0.04	0.70 ± 0.05	0.71 ± 0.03	0.69 ± 0.08	0.70 ± 0.05
Butyraldehyde	0.43 ± 0.01	0.44 ± 0.08	0.41 ± 0.05	0.41 ± 0.00	0.42 ± 0.04	0.45 ± 0.03	0.42 ± 0.04	0.39 ± 0.05	0.43 ± 0.08	0.42 ± 0.05	0.45 ± 0.03	0.42 ± 0.04	0.39 ± 0.05	0.43 ± 0.08	0.42 ± 0.05
Total carbonyls <sup>c</sup>	6.52	7.00	8.90	15.76	9.55	4.14	4.92	4.33	3.58	4.24	4.14	4.92	4.33	3.58	4.24

<sup>a</sup> Arithmetic mean and standard deviation of measured carbonyls.<sup>b</sup> Average concentration and standard deviation for all measured concentrations.<sup>c</sup> Total carbonyls is equal to the sum of measured carbonyls presented in this table.

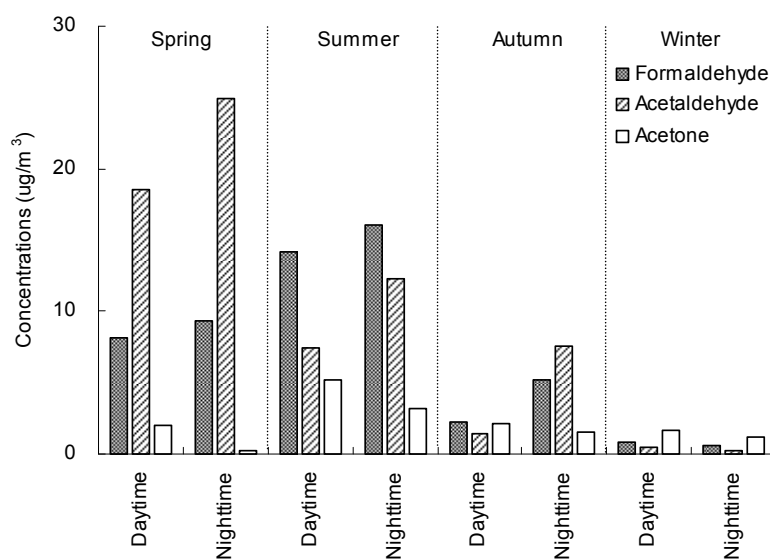


Fig. 2. A comparison of daytime to nighttime for average concentrations of carbonyls in Qinzhou.

Table 6. Ambient carbonyls ( $\mu\text{g}/\text{m}^3$ ) at the center of the biggest barbecue in Qinzhou.<sup>a</sup>

	Morning	Noon	Late afternoon	Midnight
Formaldehyde	12.50	11.45	13.94	20.36
Acetaldehyde	12.92	12.11	11.18	24.10
Acetone	3.28	3.45	2.34	12.87
Propionaldehyde	1.81	1.13	1.79	13.65
Crotonaldehyde	1.40	1.27	1.44	5.14
2-Butanone	1.81	1.54	1.95	3.43
Butyraldehyde	1.92	1.43	1.87	2.54
Total carbonyls <sup>b</sup>	36.64	32.38	34.51	82.09

<sup>a</sup> One sample was obtained during morning, noon, late afternoon and midnight on July 5, 2012, respectively.

<sup>b</sup> Total carbonyls is equal to the sum of measured carbonyls presented in this table.

was  $24.10 \mu\text{g}/\text{m}^3$  in the nighttime compared to  $11.45$ – $13.94 \mu\text{g}/\text{m}^3$  in the daytime. And concentrations of measured carbonyls at the barbecue also showed significantly higher levels in the nighttime (Table 6) than those at the air sampling site (Table 5). In summer for example, formaldehyde concentration in the nighttime was  $20.36 \mu\text{g}/\text{m}^3$  at the barbecue and  $17.07 \mu\text{g}/\text{m}^3$  at the air sampling site (Tables 5–6). The accordance in observed peak pattern suggested that ambient carbonyls were related to the barbecue emission, particularly in the nighttime.

### Concentration Ratios

Concentration ratio of formaldehyde/acetaldehyde ( $C_1/C_2$ ) was used to compare the sources of carbonyls at different locations (Shepson *et al.*, 1991; Lü *et al.*, 2010; Duan *et al.*, 2012). And it was likely an effective indicator for identifying ambient carbonyls between urban and rural areas. The calculated  $C_1/C_2$  ratio was  $1.48 \pm 0.90$  (Table 7), which was close to that ( $1.07$ – $1.4$ ) in urban air in Carmen (Cérón *et al.*, 2007) and an industrial area ( $1.98$ ) in Guangzhou (Feng *et al.*, 2005), complying with the common finding in that  $C_1/C_2$  normally varied from 1 to 2 in urban areas (Feng *et al.*, 2005; Huang *et al.*, 2008; Ochs *et al.*, 2011). However, recent studies reported that the  $C_1/C_2$  ratio

was  $\sim 0.87$  in Guangzhou (Lü *et al.*, 2009, 2010), and caution should be exercised when using it.

When compared with different seasons (Table 7), the highest  $C_1/C_2$  ratio was observed in summer ( $1.92$ ), followed by winter ( $1.78$ ), autumn ( $1.68$ ) and spring ( $0.52$ ). Photolysis and reactions with  $\text{OH}\cdot$  could change the distributions of carbonyls (Atkinson, 2000; Pang and Lee, 2010), and the reaction with  $\text{OH}\cdot$  was often the dominant loss (Atkinson, 2000), depending on reaction rate constants, e.g., the reaction rate constants are  $0.98$  and  $1.58 (\times 10^{11} \text{ cm}^3/\text{molecule/s})$  for formaldehyde and acetaldehyde, respectively. The relative long-chain low-weight carbonyls were more reactive than those short-chain carbonyls in the atmosphere (Ji *et al.*, 2012). So, the expected  $C_1/C_2$  ratio would increase under active photochemical conditions. And hot weather (e.g., high temperature) in summer (Table 2) also significantly favored the photochemical loss. The observed highest  $C_1/C_2$  ratio in summer ( $1.92$ ) likely implied the more intensive photochemical loss of acetaldehyde compared to formaldehyde.

In addition, photochemical formation played positive roles in the distributions of formaldehyde and acetaldehyde (Guo *et al.*, 2009, 2013), and formaldehyde was the dominant initial carbonyl product in the photochemical oxidations of



**Table 7.** Concentration ratios of formaldehyde/acetaldehyde ( $C_1/C_2$ ) and acetaldehyde/propionaldehyde ( $C_2/C_3$ ) in urban air in Qinzhou, China.<sup>a</sup>

	Ratios	Morning	Noon	Late afternoon	Midnight	Range <sup>b</sup>	Mean <sup>c</sup>
Spring	$C_1/C_2$	$0.95 \pm 0.02$	$0.23 \pm 0.26$	$0.52 \pm 0.03$	$0.38 \pm 0.04$	0.07–0.98	$0.52 \pm 0.31$
	$C_2/C_3$	$24.43 \pm 1.70$	$45.84 \pm 22.66$	$45.51 \pm 19.94$	$95.50 \pm .63$	19.68–104.28	$52.82 \pm 30.35$
Summer	$C_1/C_2$	$1.81 \pm 1.11$	$2.18 \pm 0.17$	$1.94 \pm 0.86$	$1.76 \pm 1.38$	0.74–3.34	$1.92 \pm 0.86$
	$C_2/C_3$	$27.89 \pm 19.69$	$8.61 \pm 2.71$	$9.01 \pm 6.25$	$41.66 \pm 32.66$	2.18–71.26	$21.80 \pm 21.97$
Autumn	$C_1/C_2$	$2.86 \pm 0.94$	$1.35 \pm 0.52$	$1.35 \pm 0.55$	$1.16 \pm 0.86$	0.66–3.92	$1.68 \pm 0.96$
	$C_2/C_3$	$5.42 \pm 3.18$	$4.95 \pm 1.88$	$9.30 \pm 3.83$	$30.21 \pm 24.74$	1.64–44.49	$12.47 \pm 15.30$
Winter	$C_1/C_2$	$2.31 \pm 0.60$	$1.47 \pm 0.23$	$1.33 \pm 0.50$	$2.01 \pm 0.67$	0.95–2.98	$1.78 \pm 0.61$
	$C_2/C_3$	$2.13 \pm 0.40$	$3.70 \pm 1.67$	$2.75 \pm 0.78$	$1.69 \pm 0.28$	1.39–5.62	$2.57 \pm 1.13$
Average <sup>d</sup>	$C_1/C_2$	$1.99 \pm 0.99$	$1.31 \pm 0.78$	$1.29 \pm 0.72$	$1.33 \pm 1.00$	0.07–3.92	$1.48 \pm 0.90$
	$C_2/C_3$	$14.97 \pm 14.58$	$15.77 \pm 20.69$	$16.64 \pm 19.82$	$42.26 \pm 39.72$	1.39–104.28	$22.41 \pm 27.31$

<sup>a</sup> Arithmetic mean and standard deviation of concentration ratios.

<sup>b</sup> Value range of calculated concentration ratios in a certain season during sampling.

<sup>c</sup> Average value and standard deviation for calculated concentration ratios in a certain season.

<sup>d</sup> Average arithmetic mean and standard deviation for all calculated ratios at different sampling intervals.

hydrocarbons with a high yield of 63–84% (Sumner *et al.*, 2001; Wiedinmyer *et al.*, 2001; Duane *et al.*, 2002). Qinzhou has the lower latitude (108°39'E, 21°58'N) with the intensive sunlight and high temperature in summer (Table 2), which favors photochemical oxidations of atmospheric hydrocarbons. Life times of active hydrocarbons like isoprene and  $\beta$ -pinene are significantly low (1.4–2.6h) (Atkinson, 2000), which is beneficial to carbonyl formation in their photochemical oxidations (Sumner *et al.*, 2001; Wiedinmyer *et al.*, 2001; Duane *et al.*, 2002; Guo *et al.*, 2013). And this positive photochemical formation could raise the  $C_1/C_2$  ratio in summer, as observed in this study.

Concentration ratio of acetaldehyde/propionaldehyde ( $C_2/C_3$ ) was often used as an effective indicator for anthropogenic source (Ho *et al.*, 2002). The  $C_2/C_3$  ratio was  $52.82 \pm 30.35$ ,  $21.80 \pm 21.97$ ,  $12.47 \pm 15.30$  and  $2.57 \pm 1.13$  in spring, summer, autumn and winter (Table 7). Average  $C_2/C_3$  ratio ( $22.41 \pm 27.31$ ) was much higher than those in Guangzhou (5.02–13.90), Shanghai (5.31–24.51) and Beijing (6.29) (Huang *et al.*, 2008; Lü *et al.*, 2010; Duan *et al.*, 2012). The residents in Qinzhou are mainly made up of local farmers around the city. In winter, they prefer to burning fuels such as straw to keep them warm due to the relative lower temperature (3–15°C) (Table 2), and they occasionally have barbecue in winter, particular in the nighttime. Such straw burning and barbecue could emit gaseous carbonyls (Kim *et al.*, 2008; Ohura *et al.*, 2011; Cerqueira *et al.*, 2013). In winter, the average  $C_2/C_3$  ratio was  $1.69 \pm 0.28$  in the midnight,  $2.13 \pm 0.40$  in the morning,  $3.70 \pm 1.67$  at noon and  $2.75 \pm 0.78$  in the late afternoon (Table 7), which was close to the roughly estimated  $C_2/C_3$  ratio (~1.76) at the barbecue (Table 6). As propionaldehyde was related to anthropogenic source (Ho *et al.*, 2002) with the low  $C_2/C_3$  ratio, both the lower ratio in winter (2.57) and the lowest ratio in the midnight (1.69) suggested the anthropogenic emissions of straw burning and barbecue.

To further elevate the sources of ambient carbonyls at the sampling site (e.g., the emissions of barbecue and/or straw burning), correlation coefficients ( $R^2$ ,  $p < 0.05$ ) of formaldehyde, acetaldehyde, acetone, and the total carbonyls

were calculated in Table 8. Formaldehyde showed correlation with acetaldehyde ( $R^2 = 0.41$ ), and the two carbonyls corrected well with the total carbonyls ( $R^2 = 0.70$ – $0.74$ ), indicating similar sources, e.g., the emission of barbecue and/or straw burning. Rather weak correlations ( $R^2 = 0.01$ – $0.13$ ) of acetone with formaldehyde, acetaldehyde and the total carbonyls were observed, indicating that acetone might have the source (e.g., solvent usage) differing from that of formaldehyde and acetaldehyde.

#### Photochemical O<sub>3</sub> Formation Potentials

Carbonyls are important precursors of O<sub>3</sub> formation and individual carbonyl has different photochemical reactivity. To estimate the reactivity and contribution to photochemical O<sub>3</sub> formation from individual carbonyl, both propylene-equivalent concentration (Prop-Equiv) and maximum incremental reactivity (MIR) are calculated (Chameides *et al.*, 1992; Carter, 1994; Duan *et al.*, 2008; Tan *et al.*, 2012). Prop-Equiv ( $j$ ) of carbonyl  $j$  is defined as: Prop-Equiv ( $j$ ) = Conc. ( $j$ )  $\times k_{OH}$  ( $j$ ) /  $k_{OH}$  (propene), where Conc. ( $j$ ) is the concentration of carbonyl  $j$  expressed in  $\mu\text{g}/\text{m}^3$ ;  $k_{OH}$  ( $j$ ) or  $k_{OH}$  (propene) are rate constants for the reaction between carbonyl  $j$  or propene and OH. Prop-Equiv ( $j$ ) is a measure of the concentration of carbonyl  $j$  on an OH-reactivity based scale normalized to the reactivity of propene. O<sub>3</sub> formation potential (OFP) can be evaluated as the product of the concentration of carbonyl and the MIR coefficient (dimensionless, gram of O<sub>3</sub> produced per gram of carbonyl  $j$ ). The following equation was used to calculate the contribution of O<sub>3</sub> formation by individual carbonyl under optimal conditions: O<sub>3</sub> formation potential ( $i$ ) = Concentration ( $i$ )  $\times$  MIR coefficient ( $i$ ), and MIR coefficients were taken from Carter (1994). In this study, reaction rates and MIR coefficients were calculated as an average from the reaction rates of individual carbonyls.

Prop-Equiv concentrations were 15.43, 11.35, 3.43 and 1.12  $\text{g}/\text{m}^3$  in spring, summer, autumn and winter, respectively (Table 9). Acetaldehyde and formaldehyde were the top two carbonyls, accounting for 43–94% of the Prop-Equiv concentrations, particularly in spring and summer (89–94%).



**Table 8.** Correlations ( $R^2$ ,  $p < 0.05$ ) of atmospheric formaldehyde, acetaldehyde and acetone in Qinzhou, China.

	Formaldehyde	Acetaldehyde	Acetone	Total carbonyls <sup>a</sup>
Formaldehyde	1			
Acetaldehyde	0.41*	1		
Acetone	0.13	0.01	1	
Total carbonyls <sup>a</sup>	0.65*	0.74*	0.10	1

\* Correlation coefficients of the data are significant at the 95% levels.

<sup>a</sup> Total carbonyls refer to the sum of measured seven carbonyls during the sampling.

**Table 9.** O<sub>3</sub> production ( $\mu\text{g}/\text{m}^3$ ) and photochemical property of atmospheric carbonyls in Qinzhou, China.

	$k_{\text{OH}} (\times 10^{12})^{\text{a}}$	Prop-Equiv			
		Spring	Summer	Autumn	Winter
Formaldehyde	9.37	3.02	5.21	1.07	0.25
Acetaldehyde	15	11.5	4.94	1.69	0.24
Acetone	0.17	0.01	0.03	0.01	0.01
Propionaldehyde	20	0.34	0.43	0.17	0.12
Crotonaldehyde	6.4	0.08	0.11	0.07	0.07
2-Butanone	1.22	0.03	0.04	0.03	0.03
Butyraldehyde	24	0.46	0.59	0.39	0.38
Total carbonyls <sup>c</sup>		15.43	11.35	3.43	1.12
		O <sub>3</sub> formation			
	MIR <sup>b</sup>	Spring	Summer	Autumn	Winter
Formaldehyde	7.2	61.01	105.35	21.59	5.15
Acetaldehyde	5.5	110.68	47.62	16.28	2.35
Acetone	0.56	0.86	2.63	1.09	0.86
Propionaldehyde	6.5	2.94	3.65	1.42	1.06
Crotonaldehyde	0.85	0.30	0.38	0.25	0.24
2-Butanone					
Butyraldehyde	5.28	2.65	3.42	2.23	2.23
Total carbonyls <sup>c</sup>		178.44	163.05	42.86	11.88

<sup>a</sup> Rate constant of carbonyls react with OH at 298K ( $\text{cm}^3/\text{molecule}/\text{s}$ ) (Atkinson and Arey, 2003).

<sup>b</sup> MIR denotes maximum incremental reactivity ( $\text{g O}_3/\text{g carbonyls}$ ) (Carter, 1994).

<sup>c</sup> Total carbonyls is equal to the sum of calculated values listed in this table.

Blank refers to the data were not available in the relative reference.

O<sub>3</sub> formation potentials ranged from 11.88 to 178.44  $\mu\text{g}/\text{m}^3$ . O<sub>3</sub> formation potentials were 163.05 to 178.44  $\mu\text{g}/\text{m}^3$  in summer and spring, which were significantly higher by ~5 times than those (ranging from 11.88 to 42.86  $\mu\text{g}/\text{m}^3$ ) in autumn and winter (Table 9). Acetaldehyde and formaldehyde were also the top two carbonyls which contribute 63–97% to total O<sub>3</sub> formation potentials, especially in summer and spring. Based on O<sub>3</sub> formation potentials and Prop-Equiv concentrations, both formaldehyde and acetaldehyde were the two major contributors in the total carbonyls.

## CONCLUSIONS

Ambient carbonyls were measured from October 2011 to July 2012 in urban air in Qinzhou, China. Formaldehyde, acetaldehyde and acetone were three most abundant carbonyls, accounting for ~90% of total seven carbonyls identified. Seasonal and diurnal variations indicated that barbecue emission, photochemical loss and solvent usage were important for the carbonyl distributions. Analysis of C<sub>1</sub>/C<sub>2</sub> and C<sub>2</sub>/C<sub>3</sub> ratios also implied the positive impact of daytime photochemical formation and loss, as well as the

significant emissions of barbecue and straw burning, particularly in the nighttime. In addition, formaldehyde and acetaldehyde were two major carbonyls, which contributed 63–97% to O<sub>3</sub> formation potentials.

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