



## Carbonyl compounds in the ambient air of hazy days and clear days in Guangzhou, China

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### ABSTRACT

Carbonyl compounds were measured in ambient air of Guangzhou in both hazy and clear days. Air samples were collected in two separate terms, 17–19th of November (the clear period) and 30th of November to 2nd of December 2005 (the hazy period). The total concentrations of carbonyls detected varied from 48.4 to 121.4  $\mu\text{g m}^{-3}$  (with a mean of 92.0  $\mu\text{g m}^{-3}$ ) in the hazy days and from 21.6 to 45.7  $\mu\text{g m}^{-3}$  (with a mean of 32.6  $\mu\text{g m}^{-3}$ ) in the clear days. Formaldehyde, acetaldehyde, and acetone were the most abundant carbonyl species in both haze and clear days, while the relative sum of these three compounds in the clear days contributed more than that in the hazy days to the total concentrations of carbonyls (66.0–72.8% vs 42.9–60.5%). The average concentration ratios of formaldehyde/acetaldehyde ( $C_1/C_2$ ) were fairly constant between the haze and clear days (0.87 vs 0.84, ( $\mu\text{g m}^{-3}$ )/( $\mu\text{g m}^{-3}$ ); 1.28 vs 1.23, ppbv/ppbv), whereas those of acetaldehyde/propionaldehyde ( $C_2/C_3$ ) showed large variations (ranging from 5.93 to 13.0, ( $\mu\text{g m}^{-3}$ )/( $\mu\text{g m}^{-3}$ ); from 7.82 to 18.3, ppbv/ppbv). The results of correlation analysis and principal component analysis indicated that vehicular exhaust might be the major source of carbonyls in the ambient air, with the biogenic emission as the potential source of some high molecular weight carbonyls. Moreover, biomass burning and accumulation of carbonyls might make significant contribution to the enhancement of carbonyls in the hazy days.

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## 1. Introduction

Carbonyl compounds are ubiquitous components in the atmosphere, which have received immense attention due to their potential adverse health effects on humans and to their important role in atmospheric chemistry. Ambient carbonyls can be produced directly from primary sources such as exhausts of motor vehicles, incomplete combustion of hydrocarbon fuels in industrial machinery and processes and biomass burning. They can also be formed from secondary source processes such as the atmospheric photooxidation of hydrocarbons (Grosjean and Moreira, 2002; Kim et al., 2008).

The distribution of carbonyl compounds in the ambient air at urban and rural areas has been widely investigated (Ho et al., 2002; Feng et al., 2004, 2005; Lü et al., 2006; Pang and Mu, 2006; Pal et al., 2008; Santarsiero and Fuselli, 2008; Weng et al., 2009). Studies on carbonyls in indoor/outdoor or some special sites (e.g., hospitals, ballrooms, etc.) have been also conducted (Báez et al., 2003; Feng et al., 2004; Lü et al., 2006). However, until recently, a very few studies have been performed to investigate carbonyls under particular weather conditions (e.g., a hazy day).

Haze pollution has caused an increased concern among the public, scientific, and governmental organizations due to its impact on visibility, public health, agriculture, and even the global climate (Yadav et al., 2003; Kang et al., 2004). Haze has been often observed in Beijing, Guangzhou, and in other big cities of China since 2001, and the occurrence of hazy days has

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increased during the years, especially during the winter and spring seasons (Sun et al., 2006). As shown in Fig. 1, the number of hazy days in Guangzhou was only 56 d in 2001 but increased sharply to 142 (2004) and 131 d (2007). In December of 2007 alone, 22 hazy days were observed (Wu et al., 2006; EPFGP, 2008). Meteorological conditions of the hazy days are different from those of the clear days, as the former is affected by the air contaminants with special characteristics.

Recent studies have focused on the distributions of pollutants in hazy days (Senaratne and Shooter, 2004; Sun et al., 2006; Mao et al., 2008). For instance, Mao et al. (2008) investigated the vertical distributions of volatile organic compounds (e.g., aromatic hydrocarbons) in the atmosphere of Beijing in the haze and clear days, and they reported that the average concentrations of total volatile organic compounds in the hazy days were greater by 7.6% to 89% than those in the clear days. Wang et al. (2006) investigated the characteristics and the different formation mechanisms of aerosols in dust, haze, and clear days in Beijing. Sun et al. (2006) and Wang et al. (2006) reported that the air quality in the hazy days was considerably worse than that in non-hazy days. Studies on carbonyl compounds in the ambient air of hazy days have seldomly been reported. Wang et al. (2006) pointed out that the chemical characteristics and mechanisms of haze formation are considerably different from those of normal urban aerosols. Many secondary aerosol particles (mainly sulfate, nitrate, and ammonium) which contribute to haze were formed during heavily polluted days (Fu et al., 2008). Due to the limited number of studies on the distribution of pollutants in hazy days and the rather limited current understanding of characteristics and mechanisms on the haze formation, precise assessment on severe pollution phenomena, e.g., haze, is of great importance for the maintenance of air quality. Thus, the objectives of this study were twofold, to investigate the carbonyl compounds in the ambient air of haze and clear days, and to attempt to identify the relevant sources of carbonyls.

## 2. Materials and methods

### 2.1. Chemicals and materials

All organic solvents applied were HPLC grade. Water was re-distilled and filtered by Milli-Q before use. The 2,4-dinitrophenylhydrazine (DNPH) was obtained from Fluka (USA) and further purified by recrystallizing twice in acetonitrile (Merck, Germany). A composite stock standard solution (ChemService,

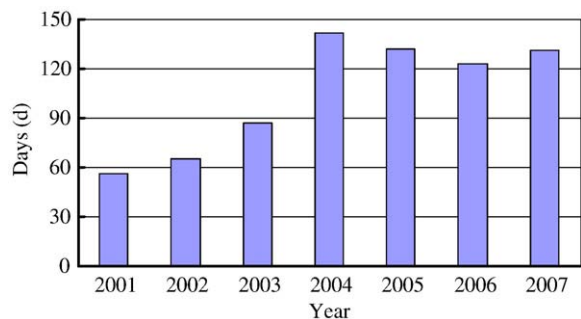


Fig. 1. Number of hazy days in Guangzhou between 2001 and 2007.

USA) contained 21 carbonyl-DNPH derivatives, including Mix 1 (DNPH derivatives of formaldehyde, acetaldehyde, acetone, acrolein, butyraldehyde, propionaldehyde, crotonaldehyde, benzaldehyde, 2,5-dimethylbenzaldehyde, hexaldehyde, isovaleraldehyde, valeraldehyde, *o*-tolualdehyde, *m*-tolualdehyde, and *p*-tolualdehyde), Mix 2 (DNPH derivatives of formaldehyde, acetaldehyde, crotonaldehyde, propionaldehyde, butyraldehyde, cyclohexanone, valeraldehyde, hexaldehyde, heptaldehyde, octylaldehyde, nonanaldehyde, and decylaldehyde) and 2-butanone-DNPH derivative.

A cartridge was used as the sampling medium (a Sep-Pak Silica Gel Cartridge: Waters, Millipore Corp). Details on the preparation of the cartridge have been presented elsewhere (Feng et al., 2005 and Lü et al., 2006). Briefly, each cartridge was slowly rinsed with 10 mL of acetonitrile (ACN) and then coated by passing 7 mL of the freshly made coating solution, which contained 60-mL DNPH-ACN-saturated solution and 2 mL of concentrated *ortho*-phosphoric acid in 500-mL ACN, through the cartridge by gravity. When no further solution was flowing out of the cartridge, the cartridge was dried with a gentle flow of nitrogen for 15 min. The coated cartridges were wrapped in aluminum foil, sealed in hermetic Teflon bags, and stored in a refrigerator at 4 °C until use. Three blank cartridges from each cartridge batch were analyzed and the results were all below the EPA blank criteria.

### 2.2. Area description and air sampling

The sampling site selected for the purpose of this study was located at the roof of the library of Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, located in Tianhe District, North-East Guangzhou. There are two different residential areas and an expressway adjacent to the institute. Field sampling was conducted in the autumn, 2005. For the clear days, air samples were consecutively collected on three times per day basis (i.e., morning, noon, afternoon) and evenings during 17–19th of November 2005 ( $n = 12$ ). Prior to sampling, it rained and cleaned up afterwards (with visibility about 20–23 km). The temperature was between 16.5 °C and 29.5 °C, and the relative humidity varied from 40% to 80%. The ultraviolet light was lower than  $1856 \mu\text{W cm}^{-2}$ . For the hazy days, the same sampling procedure as that used in the clear days was conducted in days from 30th of November to 2nd of December, all of them presenting a low visibility (1.5–3 km). The temperature ranged from 20 °C to 31 °C, and the relative humidity varied from 31% to 64%. The ultraviolet light was lower than  $1334 \mu\text{W cm}^{-2}$ .

The sampling procedure has already been described (Feng et al., 2005; Lü et al., 2006). Briefly, samples were collected by drawing the air with a sampling pump (Thomas, USA) through the cartridge. Possanzini et al. (2000) and Pal and Kim (2008) reported that the application of the 2,4-DNPH-coated cartridge sampling method may involve analytical bias. In this study, before sampling, a breakthrough experiment was conducted by connecting two cartridges in series. The results showed that only acetone and 2-butanone were detected in the back cartridge when the sampling duration was 6 h at a flow rate of  $1.0 \text{ L min}^{-1}$ . Thus, during daytime (i.e., morning, noon and afternoon), the sampling duration was about 2–3 h at a flow rate at  $1.0 \text{ L min}^{-1}$ . The sampling duration in the evening (about 12 h) was much longer than that in daytime, thus to prevent a breakthrough, and

the flow rate in the evening was set at  $0.2 \text{ L min}^{-1}$ , lower than that used during daytime. Following sampling, each cartridge was first wrapped in aluminum foil and then stored in the refrigerator in a Teflon bag for analysis. The sampling program of each day included one laboratory blank and one field blank. At each sampling site, two field samples were collected with a back-up cartridge to evaluate breakthrough.

### 2.3. Analytical procedure, quality assurance and quality control

The cartridges above were eluted slowly with 2 mL of acetonitrile (ACN) into a 2-mL volumetric flask and stored in refrigerated conditions for subsequent analysis. The HPLC system (HP1100, Agilent, USA) was applied for the measurements of carbonyl compounds. A 10- $\mu\text{L}$  aliquot was injected into the HPLC system through an auto-sampler. The analytical conditions were as follows: Agilent SB-C18 reverse column

(250 mm  $\times$  4.6 mm  $\times$  5  $\mu\text{m}$ ); gradient mobile phase: 60–70% ACN of water solution for 20 min, 70–100% ACN for 3 min, 100% ACN for 4 min, 100–60% ACN for 1 min and then 60% ACN for 5 min; mobile-phase flow rate:  $1 \text{ mL min}^{-1}$ ; detector: UV at 360 nm.

Identification of carbonyl compounds was based on the comparison of retention time between samples and the standard solution containing 21 carbonyls. Quantification was performed by integration of peak areas. The instrument was calibrated using five standard concentrations (from 0.5 to  $10 \mu\text{g mL}^{-1}$ ) covering the concentration of interest. Strong linear relationships ( $R^2 > 0.999$ ) were recorded between the concentrations and responses for all carbonyls identified. A calibration standard was run on a daily basis to ensure the stabilization of the instruments. Cartridge collection efficiency was determined with two cartridges in series and over 99% of carbonyl compounds were recovered from the first cartridge,

**Table 1**

Concentrations ( $\mu\text{g m}^{-3}$ ) of carbonyls in the ambient air of the clear days (during 17–19th of November) and of the hazy days (during 30th of November–2nd of December).

Compounds	Morning	Noon	Afternoon	Evening	Min	Max	Mean
<i>In the clear days</i>							
Formaldehyde	5.30 $\pm$ 1.15	7.15 $\pm$ 0.21	5.98 $\pm$ 0.07	5.62 $\pm$ 1.14	4.61	7.37	6.02
Acetaldehyde	7.36 $\pm$ 1.48	9.67 $\pm$ 1.04	6.79 $\pm$ 0.58	5.47 $\pm$ 0.93	4.81	10.50	7.37
Acrolein	ND <sup>a</sup>	ND	0.41 <sup>b</sup>	ND	–	0.41	0.04
Acetone	11.6 $\pm$ 3.4	7.06 $\pm$ 0.73	8.95 $\pm$ 2.66	5.89 $\pm$ 1.45	4.22	15.54	8.33
Propionaldehyde	1.53 $\pm$ 0.98	1.15 $\pm$ 0.50	0.37 $\pm$ 0.35	0.42 $\pm$ 0.13 <sup>c</sup>	0.12	2.61	0.87
Crotonaldehyde	ND	ND	ND	0.11 <sup>b</sup>	–	–	0.01
2-Butanone	1.25 $\pm$ 0.24	1.39 $\pm$ 0.12	1.05 $\pm$ 0.06	0.80 $\pm$ 0.12	0.67	1.53	1.13
Butyraldehyde	3.01 $\pm$ 0.54	3.82 $\pm$ 0.13	1.83 $\pm$ 0.26	0.71 $\pm$ 0.05	0.66	3.94	2.39
Benzaldehyde	0.45 $\pm$ 0.32	0.39 $\pm$ 0.10	0.33 $\pm$ 0.11	2.35 $\pm$ 3.76	0.17	6.69	0.93
Isovaleraldehyde	0.40 $\pm$ 0.41	0.45 $\pm$ 0.53	0.48 $\pm$ 0.47	0.46 $\pm$ 0.18	0.09	1.06	0.44
Cyclohexanone	1.12 $\pm$ 0.38 <sup>c</sup>	1.09 $\pm$ 0.13 <sup>c</sup>	0.98 <sup>b</sup>	0.58 <sup>b</sup>	0.58	1.39	0.86
Valeraldehyde	0.60 $\pm$ 0.17	0.86 $\pm$ 0.07	0.50 $\pm$ 0.09	0.36 $\pm$ 0.13	0.25	0.91	0.59
<i>p</i> -Tolualdehyde	ND	ND	ND	ND	–	–	0.00
<i>m/o</i> -Tolualdehyde	0.52 $\pm$ 0.08 <sup>c</sup>	0.28 $\pm$ 0.01 <sup>c</sup>	0.48 $\pm$ 0.36	0.47 $\pm$ 0.08 <sup>c</sup>	0.23	0.73	0.32
Hexaldehyde	0.66 $\pm$ 0.30	0.41 $\pm$ 0.08	0.22 $\pm$ 0.08	0.24 $\pm$ 0.03 <sup>c</sup>	0.16	0.93	0.38
2,5-Dimethyl-benzaldehyde	2.31 $\pm$ 2.49 <sup>c</sup>	ND	ND	ND	–	4.07	0.42
Heptaldehyde	0.21 $\pm$ 0.06	0.34 $\pm$ 0.01	2.39 $\pm$ 3.04	0.14 $\pm$ 0.04 <sup>c</sup>	0.11	4.54	0.61
Octylaldehyde	0.44 $\pm$ 0.10	0.66 $\pm$ 0.11	0.44 $\pm$ 0.13	0.23 $\pm$ 0.07 <sup>c</sup>	0.18	0.78	0.42
Nonanaldehyde	0.86 $\pm$ 0.70	1.19 $\pm$ 0.34	0.78 $\pm$ 0.11	0.51 $\pm$ 0.08	0.16	1.55	0.84
Decylaldehyde	0.40 $\pm$ 0.21	0.65 $\pm$ 0.22	0.42 $\pm$ 0.04	0.28 $\pm$ 0.09 <sup>c</sup>	0.22	0.89	0.41
Total	36.8 $\pm$ 8.05	36.1 $\pm$ 0.51	31.7 $\pm$ 5.76	23.6 $\pm$ 3.24	21.6	45.7	32.1
<i>In the hazy days</i>							
Formaldehyde	14.3 $\pm$ 9.49	13.6 $\pm$ 8.77	14.2 $\pm$ 6.25	16.3 $\pm$ 3.18	6.24	24.7	14.6
Acetaldehyde	13.6 $\pm$ 5.48	13.6 $\pm$ 5.40	17.0 $\pm$ 6.73	22.3 $\pm$ 1.65	9.26	23.6	16.6
Acrolein	ND <sup>a</sup>	ND	ND	ND	–	–	–
Acetone	12.1 $\pm$ 9.62	13.3 $\pm$ 4.55	16.9 $\pm$ 13.3	19.4 $\pm$ 7.38	1.00	32.2	15.4
Propionaldehyde	2.76 $\pm$ 1.31	2.94 $\pm$ 1.69	2.69 $\pm$ 1.18	3.05 $\pm$ 0.42	1.37	4.89	2.86
Crotonaldehyde	0.53 $\pm$ 0.13	0.58 $\pm$ 0.19	0.38 $\pm$ 0.10	1.26 $\pm$ 0.11	0.26	1.35	0.69
2-Butanone	7.71 $\pm$ 5.23	5.34 $\pm$ 3.79	4.82 $\pm$ 3.85	6.28 $\pm$ 1.99	2.19	13.4	6.04
Butyraldehyde	2.29 $\pm$ 0.60	2.33 $\pm$ 0.98	2.10 $\pm$ 0.67	3.18 $\pm$ 1.03	1.34	3.94	2.48
Benzaldehyde	2.26 $\pm$ 0.94	1.72 $\pm$ 1.09	1.39 $\pm$ 0.62	1.47 $\pm$ 0.09	0.89	3.24	1.71
Isovaleraldehyde	0.93 $\pm$ 0.65	0.70 $\pm$ 0.39 <sup>b</sup>	0.57 $\pm$ 0.19	0.72 $\pm$ 0.24	0.40	1.64	0.67
Cyclohexanone	4.09 $\pm$ 2.39	3.19 $\pm$ 2.04	2.48 $\pm$ 1.00	4.83 $\pm$ 1.02	0.93	6.84	3.65
Valeraldehyde	9.12 $\pm$ 2.05	12.7 $\pm$ 3.71	6.09 $\pm$ 2.08	12.2 $\pm$ 0.65	3.77	16.0	10.0
<i>p</i> -Tolualdehyde	ND	ND	ND	ND	–	–	–
<i>m/o</i> -Tolualdehyde	12.5 $\pm$ 2.04	6.70 $\pm$ 5.00	3.79 $\pm$ 0.86	17.5 $\pm$ 1.75	1.31	19.5	10.1
Hexaldehyde	3.17 $\pm$ 0.26	3.01 $\pm$ 0.25	1.57 $\pm$ 0.34	3.51 $\pm$ 0.06	1.27	3.58	2.81
2,5-Dimethyl-benzaldehyde	ND	0.37 <sup>b</sup>	0.23 <sup>b</sup>	ND	0.23	0.37	0.05
Heptaldehyde	1.18 $\pm$ 0.49 <sup>c</sup>	1.41 $\pm$ 0.53	0.69 $\pm$ 0.15	0.62 $\pm$ 0.07	0.57	1.96	0.88
Octylaldehyde	0.41 $\pm$ 0.05	0.61 $\pm$ 0.22	0.40 $\pm$ 0.14	0.41 $\pm$ 0.10	0.30	0.87	0.46
Nonanaldehyde	2.47 $\pm$ 0.31	2.89 $\pm$ 0.19	2.15 $\pm$ 0.32	2.07 $\pm$ 0.41	1.69	3.10	2.40
Decylaldehyde	0.54 $\pm$ 0.07	0.65 $\pm$ 0.05	0.48 $\pm$ 0.01	0.39 $\pm$ 0.12	0.26	0.68	0.52
Total	89.5 $\pm$ 28.1	85.1 $\pm$ 32.3	77.7 $\pm$ 32.2	116 $\pm$ 6.51	48.4	121	92.0

<sup>a</sup>Not detectable; <sup>b</sup>detected only in one sample; <sup>c</sup>detected only in two samples.

indicating the complete recovery of all carbonyls. Relative percent differences for duplicate analysis were less than 5%. Method detection limits (MDLs) were determined by using seven replicate analyses of the working standards at the lowest concentration. The MDLs of this study fell in the range of 6 to 18 ng in absolute mass unit and ranged from 0.05 to 0.15  $\mu\text{g m}^{-3}$  (from 0.041 to 0.122 ppbv) for various carbonyls of 120-L sampling volume. The sum concentrations of *m*-tolualdehyde and *o*-tolualdehyde were reported because they were not separated by the analytical method.

Statistical analyses (including principal components analysis, PCA) were performed using SPSS 10.0 for Windows. Arithmetic means were provided to express the average concentrations of carbonyls.

### 3. Results and discussion

#### 3.1. Concentrations of carbonyls in ambient air

In the clear days, twenty out of 21 carbonyl compounds were detected in the ambient air, while *p*-tolualdehyde was not detected in any ambient air samples. Acrolein and crotonaldehyde were detected in only one sample, while 2,5-dimethylbenzaldehyde was detected in two samples. A statistical summary of carbonyls is provided in Table 1. The total concentrations of 20 carbonyls varied from 21.6 to 45.7  $\mu\text{g m}^{-3}$  (with a mean of 32.1  $\mu\text{g m}^{-3}$ ) (from 10.9 to 21.0 ppbv, with a mean of 15.4 ppbv; Table 1S of Supplementary data). The total concentrations of carbonyls in daytime were greater than those in the evening by 34.3–55.9%.

In the hazy days, nineteen carbonyl compounds were detected in the ambient air, and concentrations of acrolein and *p*-tolualdehyde were all times below the MDLs. The total concentrations of 19 carbonyls ranged from 48.4 to 121  $\mu\text{g m}^{-3}$  (with a mean of 92.0  $\mu\text{g m}^{-3}$ ) (Table 1) (from 21.4 to 55.4 ppbv, with a mean of 39.8 ppbv; Table 1S of Supplementary data). Obviously, in hazy days, the average total concentration of carbonyls in the evening (116  $\mu\text{g m}^{-3}$ ) was higher than that in the daytime, being different from those in the clear days. Pal et al. (2008) reported that, if the concentrations are compared in terms of diurnal variations, higher concentrations were generally observed in the daytime samples. Cerón et al. (2007) found that concentrations of carbonyls (especially for formaldehyde, acetaldehyde) were higher between 13:00 and 16:00, when solar radiation is intense and traffic density is heavier during the summer and autumn. However, they observed higher concentrations of carbonyls between 19:00 and 22:00 during the winter. These results indicate that seasonal variations and climate conditions can play important roles in the daily variations of carbonyls.

Moreover, our study indicated that the average total concentrations of carbonyls in hazy days were higher than those in clear days by one to four-time (e.g., 89.5 vs 36.8  $\mu\text{g m}^{-3}$  for the morning, 85.1 vs 36.1  $\mu\text{g m}^{-3}$  at noon, 77.7 vs 31.7  $\mu\text{g m}^{-3}$  for the afternoon, and 116 vs 23.6  $\mu\text{g m}^{-3}$  for the evening). These results suggest that the ambient air in the hazy days was more severely contaminated by carbonyls than in the clear days. This might be due to accumulation of carbonyls under steady weather conditions.

Air carbonyls have been measured in many cities (Ho et al., 2002; Feng et al., 2005; Pang and Mu, 2006; Cerón et al., 2007;

Wang et al., 2007; Pal et al., 2008; Weng et al., 2009). The carbonyl concentrations measured in this study were lower than those measured in five districts in Guangzhou (e.g., a residential area, an industrial area, a botanical garden, a downtown area, and a semi-rural area) from 15 July to 20 September 2003 (Feng et al., 2005). This might be related to the seasonal variation. For example, Cerón et al. (2007) reported that carbonyl levels in Mexico showed a strong seasonal trend in decreasing order of summer, autumn and winter. Pang and Mu (2006) observed that the average concentrations of formaldehyde, acetaldehyde, and acetone in summer were greater than those in winter by one to three times. This study was conducted in winter, when carbonyls were produced photochemically at a lower level than in summer (Cerón et al., 2007). These results suggest the dependence of carbonyl sources on seasonal factors.

The diurnal patterns were examined between the different carbonyl compounds. In the clear days, formaldehyde (4.61–7.37  $\mu\text{g m}^{-3}$ ), acetaldehyde (4.81–10.5  $\mu\text{g m}^{-3}$ ) and acetone (4.22–15.5  $\mu\text{g m}^{-3}$ ) were the three most abundant species, while the concentrations of the other carbonyls (e.g., benzaldehyde, valeraldehyde, *m/o*-tolualdehyde, hexaldehyde, octylaldehyde and decylaldehyde) were generally below 5.0  $\mu\text{g m}^{-3}$ , even lower than 1.0  $\mu\text{g m}^{-3}$  (Table 1). In the hazy days formaldehyde, acetaldehyde, and acetone were also the three most abundant compounds and they showed wider range of concentrations than in the clear days (Table 1). In the clear days, formaldehyde, acetaldehyde or acetone contributed generally more than 20% to the total concentrations of carbonyls (Fig. 2a). However, in the hazy days, these three compounds accounted for <20% of the total concentrations of carbonyls (Fig. 2b). The contribution of the sum of

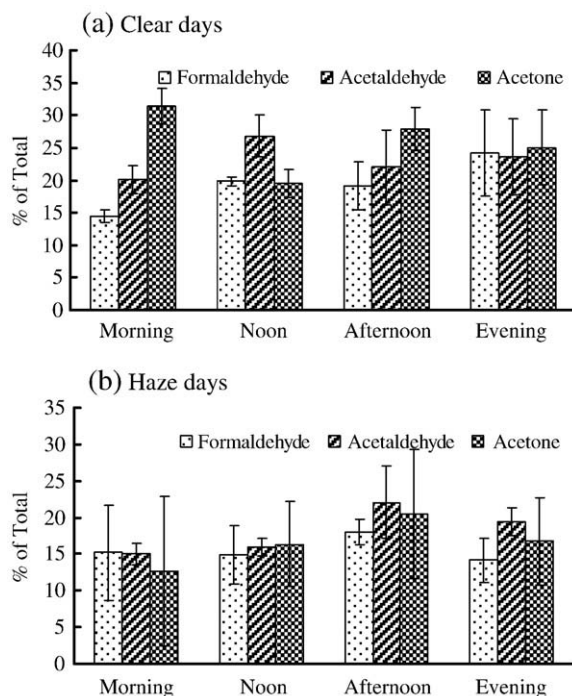


Fig. 2. Percentage contributions of formaldehyde, acetaldehyde and acetone to the total concentrations of carbonyls in the clear days (a) and hazy days (b).

these three compounds to the total concentration of carbonyls in the clear days was higher than in the hazy days (66.0–72.8% vs 42.9–60.5%). This could be explained by the fact that the concentrations of the other compounds in the hazy days were higher than those in the clear days. For example, in the hazy days, the maximum concentrations of 2-butanone, cyclohexanone, valeraldehyde, and *m/o*-tolualdehyde were more than  $5.0 \mu\text{g m}^{-3}$  (Table 1). Only the concentrations of 2,5-dimethylbenzaldehyde, octylaldehyde, and decylaldehyde were below  $1.0 \mu\text{g m}^{-3}$ .

### 3.2. Concentration ratios of carbonyl compounds

The concentration ratios of formaldehyde/acetaldehyde ( $C_1/C_2$ ) and acetaldehyde/propionaldehyde ( $C_2/C_3$ ) were calculated using  $(\mu\text{g m}^{-3})/(\mu\text{g m}^{-3})$  and ppbv/ppbv (Table 2). In this study,  $C_1/C_2$  ratios varied from 0.69 to 1.06 with a mean of 0.84  $(\mu\text{g m}^{-3})/(\mu\text{g m}^{-3})$  (from 1.01 to 1.55 with a mean of 1.23; ppbv/ppbv) in the clear days and from 0.59 to 1.24 with a mean of 0.87  $(\mu\text{g m}^{-3})/(\mu\text{g m}^{-3})$  (from 0.86 to 1.82 with a mean of 1.28; ppbv/ppbv) in the hazy days. These ratios were quite similar to those reported in the hospitals of Guangzhou, China (mean for all data, 0.99) (Lü et al., 2006) and in three urban areas of the United States (mean for all data, 1.10) (Liu et al., 2006). The results of our study thus were in good agreement with the common finding in which  $C_1/C_2$  ratios normally vary from 1 to 2 in urban area (Sin et al., 2001; Ho et al., 2002; Feng et al., 2004; Liu et al., 2006; Pang and Mu, 2006; Santarsiero and Fuselli, 2008). The diurnal patterns of  $C_1/C_2$  ratios were different during the clear days and the hazy days. The lower  $C_1/C_2$  ratio at night (0.72) compared to the ratio at daytime (0.83–0.99) was observed in the hazy days, while the reverse trend applies to the clear days. This might be due to the higher dry deposition velocity of formaldehyde as compared to that of acetaldehyde at night during the haze day (Pang and Mu, 2006).

$C_2/C_3$  ratios showed large variations, especially in the clear days (Table 2). For example, the maximum of  $C_2/C_3$  ratio in the clear days was up to 54.3  $(\mu\text{g m}^{-3})/(\mu\text{g m}^{-3})$  (up to 71.5; ppbv/ppbv), and the average ratio was 13.0  $(\mu\text{g m}^{-3})/(\mu\text{g m}^{-3})$  (was 18.3; ppbv/ppbv).  $C_2/C_3$  ratio has often been widely used as an effective indicator of anthropogenic source for carbonyls in the ambient air (Possanzini et al., 1996; Ho et al., 2002; Feng et al., 2004), because propionaldehyde was supposed to be associated only with anthropogenic emissions, in contrast to other carbonyls associated with both

natural and anthropogenic sources. Thus,  $C_2/C_3$  ratios would be high in rural atmospheres and low in the contaminated urban air. In the present study, the average  $C_2/C_3$  ratio in the hazy days was 5.93, being close to values reported in hotel ballrooms (ratio, 6.2) (Feng et al., 2004) and hospitals (ratio, 5.0) (Lü et al., 2006) in Guangzhou, China, and lower than the value reported in the urban area of Hong Kong (ratio, 8.4) (Ho et al., 2002). The results indicated the influence of anthropogenic sources in the hazy days. Nevertheless, the use of the  $C_2/C_3$  ratios should be made cautiously in diagnosing the effects of anthropogenic source for the carbonyl pollution in air, since some studies have reported that the  $C_2/C_3$  ratios often show large variations (Grosjean, 1992; Ho et al., 2002). In addition, it has been reported that photolysis and reactions with hydroxyl radicals would change the distribution of acetaldehyde and propionaldehyde in the atmosphere (Christensen et al., 2000).

### 3.3. Source interpretation through correlations and principal component analysis

To clarify the distribution patterns and emission sources of carbonyls, correlation analysis was performed using concentrations of ambient carbonyls. The Pearson's correlation matrix of carbonyls for both clear and hazy days is presented in Tables 3 and 4, respectively. Significant correlations were found between some of the carbonyls, such as between formaldehyde and acetaldehyde, indicating that these compounds came from almost the same sources (i.e., vehicles exhaust). Low correlations were observed among many carbonyls, e.g., formaldehyde and acetone, acetaldehyde and acetone, suggesting different sources of these compounds. Generally, acetone comes from both anthropogenic and biogenic emissions. Low correlations between acetone and other carbonyls might potentially be due to those brought in by the prevailing northeast wind in winter (Ho et al., 2002) or to other sources of acetone.

Principal component analysis (PCA) is a multivariate statistical method that has been applied extensively to interpret relationships between a set of correlated variables, e.g., airborne pollutants. Moreover, the factor loading plot extracting from PCA can minimize the scatter within groups and help to determine the clusters of variables. In this study, PCA was applied to investigate the distribution of different carbonyls and potential emission sources and possible influences of carbonyls on the ambient air of a local area.

**Table 2**

Concentration ratios of formaldehyde/acetaldehyde ( $C_1/C_2$ ) and acetaldehyde/propionaldehyde ( $C_2/C_3$ ).

		Morning	Noon	Afternoon	Evening	Min	Max	Mean
<i>Clear days</i>								
$C_1/C_2$	$(\mu\text{g m}^{-3})/(\mu\text{g m}^{-3})$	$0.72 \pm 0.03$	$0.74 \pm 0.06$	$0.88 \pm 0.07$	$1.02 \pm 0.04$	0.69	1.06	0.84
	ppbv/ppbv	$1.05 \pm 0.04$	$1.09 \pm 0.09$	$1.30 \pm 0.10$	$1.50 \pm 0.05$	1.01	1.55	1.23
$C_2/C_3$	$(\mu\text{g m}^{-3})/(\mu\text{g m}^{-3})$	$8.12 \pm 5.20$	$9.59 \pm 4.04$	$23.4 \pm 27.0$	$8.26 \pm 7.73$	–	54.3	13.0
	ppbv/ppbv	$8.38 \pm 4.74$	$12.6 \pm 5.32$	$43.5 \pm 39.6$	$16.3 \pm 5.48$	–	71.5	18.3
<i>Hazy days</i>								
$C_1/C_2$	$(\mu\text{g m}^{-3})/(\mu\text{g m}^{-3})$	$0.99 \pm 0.35$	$0.94 \pm 0.24$	$0.83 \pm 0.12$	$0.72 \pm 0.09$	0.59	1.24	0.87
	ppbv/ppbv	$1.45 \pm 0.52$	$1.38 \pm 0.36$	$1.22 \pm 0.17$	$1.06 \pm 0.14$	0.86	1.82	1.28
$C_2/C_3$	$(\mu\text{g m}^{-3})/(\mu\text{g m}^{-3})$	$5.07 \pm 0.62$	$4.90 \pm 0.74$	$6.41 \pm 0.42$	$7.36 \pm 0.58$	4.05	7.86	5.93
	ppbv/ppbv	$6.69 \pm 0.82$	$6.46 \pm 0.98$	$8.45 \pm 0.55$	$9.70 \pm 0.77$	5.34	10.4	7.82

**Table 3**

Concentration correlations of carbonyl compounds in ambient air of clear days.

Compounds	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Formaldehyde 1	1																		
Acetaldehyde 2	0.80**	1																	
Acrolein 3	-0.02	-0.17	1																
Acetone 4	-0.13	0.16	0.27	1															
Propionaldehyde 5	-0.13	0.24	-0.33	0.33*	1														
Crotonaldehyde 6	-0.40**	-0.45	-0.10	-0.18	-0.16	1													
2-Butanone 7	0.54**	0.87**	-0.05	0.46**	0.53**	-0.28	1												
Butyraldehyde 8	0.50**	0.88**	-0.19	0.37*	0.56*	-0.43	0.92**	1											
Benzaldehyde 9	-0.22	-0.36	-0.09	-0.10	-0.22	-0.13	-0.50	-0.39	1										
Isovaleraldehyde 10	-0.16	-0.01	-0.28	-0.15	-0.32	0.10	-0.25	-0.05	0.10	1									
Cyclohexanone 11	0.43**	0.42**	0.26	0.47**	0.42**	-0.32	0.64**	0.48**	-0.26	-0.85	1								
Valeraldehyde 12	0.75**	0.91**	-0.04	0.23	0.29	-0.39	0.87**	0.90**	-0.44	-0.21	0.61**	1							
<i>m/o</i> -Tolualdehyde 13	-0.35	-0.31	0.54**	0.41*	-0.37	0.28	-0.16	-0.18	0.16	-0.03	0.04	-0.13	1						
Hexaldehyde 14	-0.03	0.36*	-0.28	0.75**	0.79**	-0.14	0.67**	0.62**	-0.14	-0.23	0.52**	0.38*	-0.07	1					
2,5-Dimethyl-benzaldehyde 15	-0.42	-0.15	-0.11	0.27	0.79**	-0.11	0.18	0.09	-0.13	-0.37	0.25	-0.18	-0.40	0.54**	1				
Heptaldehyde 16	0.03	-0.10	1.00**	0.29	-0.30	-0.13	0.02	-0.12	-0.14	-0.29	0.30*	0.03	0.52**	-0.24	-0.12	1			
Octylaldehyde 17	0.49**	0.73**	0.16	0.27	0.34*	-0.21	0.79**	0.85**	-0.59	-0.13	0.49**	0.88**	0.09	0.34*	-0.14	0.24	1		
Nonanaldehyde 18	0.60**	0.66**	0.02	0.41*	0.10	-0.18	0.65**	0.69**	-0.22	-0.13	0.55**	0.82**	0.27	0.41*	-0.44	0.07	0.76**	1	
Decylaldehyde 19	0.59**	0.69**	0.05	0.27	0.33*	-0.09	0.77**	0.76**	-0.52	-0.30	0.64**	0.86**	0.08	0.42**	-0.20	0.12	0.90**	0.88**	1

\*, \*\*: Statistically significant at the probability levels 0.05 and 0.01, respectively.

**Table 4**

Concentration correlations of carbonyl compounds in ambient air of hazy days.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Formaldehyde 1	1																	
Acetaldehyde 2	0.79**	1																
Acetone 3	0.38*	0.54**	1															
Propionaldehyde 4	0.93**	0.78**	0.46**	1														
Crotonaldehyde 5	0.00	0.46**	0.28	0.01	1													
2-Butanone 6	0.76**	0.55**	0.65**	0.78**	0.04	1												
Butyraldehyde 7	0.78**	0.83**	0.27	0.80**	0.42**	0.54**	1											
Benzaldehyde 8	0.78**	0.35*	0.24	0.74**	-0.27	0.81**	0.46***	1										
Isovaleraldehyde 9	0.79**	0.57**	0.31*	0.77**	-0.02	0.84**	0.67**	0.72**	1									
Cyclohexanone 10	0.76**	0.67**	0.39*	0.68**	0.36*	0.78**	0.64**	0.61**	0.78	1								
Valeraldehyde 11	0.28	0.26	-0.10	0.27	0.45**	0.10	0.41*	0.13	0.10	0.54**	1							
<i>m/o</i> -Tolualdehyde 12	0.22	0.38*	0.09	0.18	0.69**	0.26	0.53**	0.17	0.34	0.60**	0.51**	1						
Hexaldehyde 13	0.08	0.17	-0.06	0.17	0.65**	0.18	0.41*	0.16	0.19	0.46**	0.72**	0.79**	1					
2,5-Dimethyl-benzaldehyde 14	-0.38	-0.50	-0.33	-0.47	-0.25	-0.44	-0.44	-0.48	-0.28	-0.20	0.17	-0.28	-0.24	1				
Heptaldehyde 15	-0.52	-0.48	-0.18	-0.25	-0.09	-0.37	-0.26	-0.26	-0.56	-0.63	-0.02	-0.28	0.15	-0.08	1			
Octylaldehyde 16	-0.27	-0.28	-0.41	-0.17	-0.08	-0.43	-0.22	-0.37	-0.28	-0.14	0.54	-0.19	0.21	0.61**	0.27	1		
Nonanaldehyde 17	-0.30	-0.47	-0.11	-0.16	-0.23	-0.16	-0.43	0.05	-0.46	-0.29	0.29	-0.31	0.20	0.05	0.66**	0.51**	1	
Decylaldehyde 18	-0.19	-0.55	-0.37	-0.07	-0.59	-0.24	-0.39	0.10	-0.26	-0.32	0.21	-0.38	0.03	0.34	0.50**	0.65**	0.78**	1

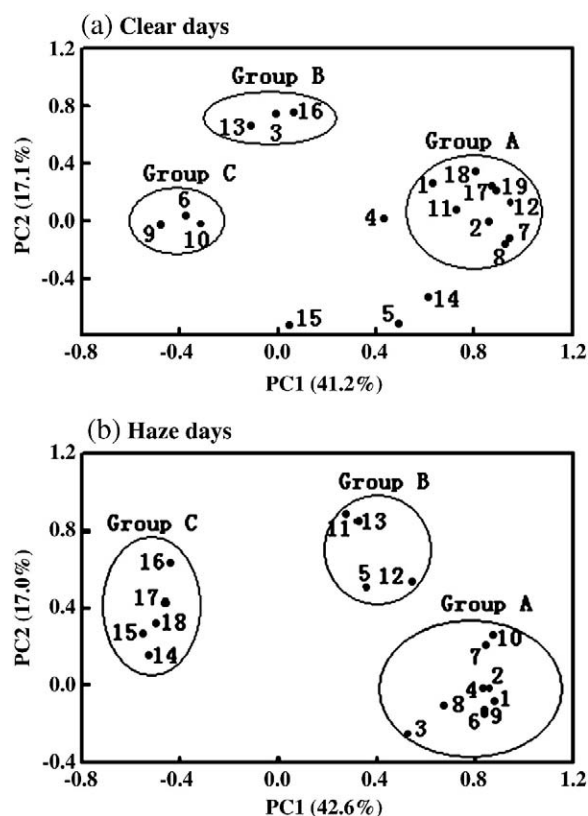
\*, \*\*: Statistically significant at the probability levels 0.05 and 0.01, respectively.

Distribution of the normalized data of air carbonyls among the primary and secondary principal component (PC1 and PC2) axes is shown in Fig. 3. In the clear days, the first two PCs contributed only 58.3% to the total variance (41.2% for PC1 and 17.1% for PC2) (Fig. 3a), suggesting a different distribution of various carbonyl compounds and their different sources. Briefly, three groups were discriminated on the factor loading plot. Group A clusters compounds of formaldehyde, acetaldehyde, 2-butanone, butyraldehyde, cyclohexanone, valeraldehyde, octylaldehyde, nonanaldehyde, and decylaldehyde. Along the axis of PC1, these compounds were found on the positive-coordinate side. Moreover, strong significant correlations ( $p < 0.05$ ) were observed between formaldehyde and these compounds (Table 3), which corroborates the results reported by other studies (Ho et al., 2002; Feng et al., 2004; Pal et al., 2008). These results indicate that these compounds might derive from identical sources (i.e., vehicular emission). Group B clusters compounds of acrolein, *m/o*-tolualdehyde and heptaldehyde (Fig. 3a), and significant correlations ( $p < 0.05$ )

were observed between them (Table 3). Group C clusters compounds of crotonaldehyde, benzaldehyde and isovaleraldehyde, showing poor correlation ( $p > 0.05$ ). The remaining four compounds (i.e., acetone, propionaldehyde, hexaldehyde and 2,5-dimethylbenzaldehyde) exhibited quite scatter with low correlations among them.

In the hazy days, the majority of the variance (83.9%) of the scaled data is explained by four eigenvectors-principal components (42.6% for PC1, 17.0% for PC2, 14.9% for PC3 and 9.3% for PC4, respectively). The plot of PC1 and PC2 is shown in Fig. 3b, and the 18 carbonyl compounds can also be clustered in three groups. Group A clusters nine compounds, i.e., formaldehyde, acetaldehyde, acetone, propionaldehyde, 2-butanone, butyraldehyde, benzaldehyde, isovaleraldehyde, and cyclohexanone. Significant positive correlations ( $p < 0.05$ ) were found in Group A between formaldehyde and the other compounds and between acetaldehyde and the other compounds (Table 4). This suggests that these compounds might have similar sources to those of formaldehyde and acetaldehyde. Four compounds (i.e., crotonaldehyde, valeraldehyde, *m/o*-tolualdehyde, and hexaldehyde) fell in Group B and displayed significant correlations ( $p < 0.05$ ) (Table 4). Group C clusters compounds of 2,5-dimethylbenzaldehyde, heptaldehyde, octylaldehyde, nonanaldehyde, and decylaldehyde.

The sources of carbonyls included motor vehicles, gasoline evaporation, use of solvents, leakages of liquefied petroleum gas (LPG), photochemical processes, various industrial emission, and biogenic emission. Generally, direct emissions from vehicles and other combustion sources are supposed to be the most important sources of carbonyls in the ambient air. However, other sources, such as photooxidation of VOCs, might partially contribute to carbonyls, especially in hot daytime. Previous studies reported that vehicular exhaust was the primary source of carbonyls in winter (Possanzini et al., 1996; Ho et al., 2002). It has also been reported that accumulation of vehicular emissions (especially diesel) contributed most to the appearance of brown haze in Auckland, New Zealand (Senaratne and Shooter, 2004). Liu et al. (2008) reported that vehicle exhaust was the largest source of VOCs, contributing to >50% of ambient VOCs at the three urban sites (Guangzhou, Foshan, and Zhongshan). On-road measurements by Kean et al. (2001) showed that carbonyl compounds accounted for 30–60% of the gas-phase organic compounds emitted from diesel-fueled vehicles and 3–5% for gasoline-fueled vehicles. In this study, there is an expressway close to the sampling site (about 500 m). In Guangzhou city as well as Guangdong Province, the number of registered motor vehicles has increased by about 125% between 1998 and 2004 (Tang et al., 2008). In Guangzhou alone, over 1.84 million motor vehicles were running in 2008. It is estimated that 6466 diesel-fueled buses and 16,025 gasoline-fueled taxis used LPG as a substitute for diesel and gasoline at the end of 2005, consuming 0.28 million tonnes of LPG in 2007 (<http://www.gz.gov.cn>). Feng et al. (2006) reported that 21 carbonyls were detected in the bus station in Guangzhou, being formaldehyde, acetaldehyde and acetone the most abundant carbonyls, while contributing 76.2% to the total concentrations of carbonyls. Kean et al. (2001) investigated carbonyl emission factors for California light-duty motor vehicles and reported that formaldehyde and acetaldehyde accounted for 45% and 12% of the measured carbonyls, respectively. These findings were in good accordance with the finding of this study in which



**Fig. 3.** PCA loading of PC1 and PC2 for the clear days (a) and hazy days (b). The corresponding compounds in (a): 1 = Formaldehyde; 2 = Acetaldehyde; 3 = Acrolein; 4 = Acetone; 5 = Propionaldehyde; 6 = Crotonaldehyde; 7 = 2-Butanone; 8 = Butyraldehyde; 9 = Benzaldehyde; 10 = Isovaleraldehyde; 11 = Cyclohexanone; 12 = Valeraldehyde; 13 = *m/o*-Tolualdehyde; 14 = Hexaldehyde; 15 = 2,5-Dimethylbenzaldehyde; 16 = Heptaldehyde; 17 = Octylaldehyde; 18 = Nonanaldehyde; 19 = Decylaldehyde. The corresponding compounds in (b): 1 = Formaldehyde; 2 = Acetaldehyde; 3 = Acetone; 4 = Propionaldehyde; 5 = Crotonaldehyde; 6 = 2-Butanone; 7 = Butyraldehyde; 8 = Benzaldehyde; 9 = Isovaleraldehyde; 10 = Cyclohexanone; 11 = Valeraldehyde; 12 = *m/o*-Tolualdehyde; 13 = Hexaldehyde; 14 = 2,5-Dimethylbenzaldehyde; 15 = Heptaldehyde; 16 = Octylaldehyde; 17 = Nonanaldehyde; 18 = Decylaldehyde.

formaldehyde and acetaldehyde were the two abundant carbonyls (Table 1). Moreover, formaldehyde showed significant strong correlations with some of carbonyls in both clear days (Table 3) and hazy days (Table 4), which were closely associated with PC1 (Fig. 3), confirming that motor vehicle exhaust was the major source of carbonyls in the ambient air of this study.

Generally, vehicular exhaust was supposed to be the primary source in winter, while both vehicular exhaust and photochemical reactions were the major sources in summer (Possanzini et al., 1996; Ho et al., 2002). Feng et al. (2004) reported that the main source of carbonyls in Guangzhou might be vehicular exhaust, and the photochemical reactions might contribute only a small part of carbonyl compounds from August to September. The sampling time of this study was in the early winter of Guangzhou, a subtropical city with subtropical monsoon climate, with temperature during sampling within the range 16.5 °C–31 °C. Thus, photochemical reactions may make fewer contributions of carbonyls in winter than those reported by Feng et al. (2004). Guo et al. (2004) reported that in Hong Kong, higher levels of carbonyls in winter may be either due to poor dilution or to the contributions of emissions from the Pearl River Delta under the influence of Asian monsoon system, the weaker vertical mixing and the slower photochemical reaction. Moreover, the levels of carbonyls in the evening period exhibited the result of photochemical reactions of the day (Ho et al., 2006), which might explain partially that the concentrations of carbonyls in the evening of hazy days were higher than that of the daytime.

As described above, PC2, PC3 and PC4 also contributed partly to the total variance of carbonyls, implying different sources of carbonyls in the ambient air apart from motor vehicle exhaust. Kim et al. (2008) reported that high concentrations of carbonyls were also observed in air from various industrial emission sources. Guangzhou is heavily industrialized, with chemical, food and beverage, leather and shoes production, and pulp and paper industries, which might have contributed to the high concentrations of carbonyls detected in air. Other direct emissions from construction materials and furnishings or even from human's activity and presence (e.g., tobacco smoke), might be important sources of carbonyls in the ambient air (Shaughnessy et al., 2001). Close to the sampling sites of this study (about 300 m), two different residential areas were being built and decorated, which might have partially contributed to the concentrations of carbonyls. Therefore, according to the PCA results, direct vehicular emission probably was the primary source of carbonyls in both clear and hazy days of Guangzhou, and other emission made partial contribution.

In the clear days, no significant correlation was found between acetone and other carbonyl compounds (except *m/o*-tolualdehyde) (Table 3) and acetone was not clustered in Groups A, B and C (Fig. 3a). Similarly, Moussa et al. (2006) and Feng et al. (2005) observed the relatively high concentration of acetone and the poor correlations with formaldehyde and acetaldehyde in the urban environment. These results suggest that acetone had other different sources from other carbonyls (e.g., formaldehyde and acetaldehyde). Acetone is widely used as an industrial solvent in many paint manufacturing and other industries, and then acetone could be released into the ambient air. Báez et al. (2003) reported that, in Mexico City, high concentrations of acetone were mainly derived from the

emission of LPG, which is widely used in hotels, houses, motor and many small industries. In addition to vehicle and industrial emissions, the high concentration of acetone might be partially attributed to the evaporation of acetone from solvent containers heavily used in Guangzhou Institute of Geochemistry, close to the sampling location of this study. Furthermore, acetone has a long lifetime in the atmosphere, therefore a high level of acetone has frequently been recorded in the ambient air of Guangzhou (Feng et al., 2004, 2005; Lü et al., 2006) and other areas (Moussa et al., 2006; Pal et al., 2008; Pang and Mu, 2006; Santarsiero and Fuselli, 2008).

It is evident that, in the clear and hazy days, the distributions of various carbonyls were different (Fig. 3) and their concentrations in the hazy days were greater than in the clear days (Table 1), implying that in the hazy days there were other sources of carbonyls except the ones detected in the clear days. According to a comprehensive review by Lemieux et al. (2004), biomass burning sources typically produce higher levels of carbonyls than anthropogenic sources on a mass emitted per mass burned basis. In Guangzhou, biomass burning contributed significantly to the regional haze (Andreae et al., 2008). Thus, biomass burning might be an important source of carbonyls in the hazy days of Guangzhou. Further research is necessary to investigate the contribution of biomass burning to carbonyl levels in the hazy days.

Furthermore, in the hazy days, the high molecular weight carbonyls (i.e., heptaldehyde, octylaldehyde, nonanaldehyde, decylaldehyde) had lower correlations with formaldehyde and acetaldehyde, being similar to those observed in the hotel ballrooms in Guangzhou (Feng et al., 2004). These results suggested different sources derived, most probably, from biogenetic emissions apart from vehicular exhaust and photochemical reaction. Some kind of plants could emit high molecular weight carbonyls (Ciccioli et al., 1993). Moreover, carbonyls, NH<sub>3</sub>, H<sub>2</sub>S, and other trace pollutants could be produced during aerobic process of biowaste (Smet et al., 1999), or during burning of yard waste (especially open burning) (Lemieux et al., 2004). The presence of many trees and grass surrounding the building where the sampling site was located, suggested that the emission of vegetation might also have been a potential source of high molecular weight carbonyls identified in this study.

Higher accumulation of vehicle emissions (particularly diesel emissions) occurred in the hazy days due to steady atmospheric conditions (Senaratne and Shooter, 2004). This was reflected by the fact that, in the hazy days, the concentrations of carbonyls (e.g., formaldehyde, acetaldehyde, acetone, and the total concentrations) in the evening were remarkably higher than those in the daytime (Table 1), being different from the distribution pattern in the clear days. Therefore, accumulation of carbonyls in the hazy days under steady conditions played an important role for the higher concentrations of carbonyls in the ambient air, particularly in the evening.

#### 4. Conclusion

This study investigated 21 carbonyl compounds of ambient air in the haze and clear days of winter in Guangzhou. In general, concentrations of carbonyls in the hazy days were greater than those in the clear days. Formaldehyde, acetaldehyde and



acetone were the most abundant carbonyl species, and these three compounds contributed 66.0–72.8% and 42.9–60.5% to the total concentrations of carbonyls in the clear and hazy days, respectively. The mean  $C_1/C_2$  ratios were 0.84 in clear days and 0.87 in hazy days, while the mean  $C_2/C_3$  ratios were 13.0 in clear days and 5.93 in hazy days. These two ratios suggested potential anthropogenic sources of carbonyls in Guangzhou. The results of correlation analysis and principal component analysis indicated that vehicular exhaust was a possible major source of carbonyls while other emission (e.g., various industries, biogenic, biomass burning) might have partially contributed to the ambient concentrations of carbonyls during clear and hazy days. Accumulation might have also resulted in elevated concentrations of carbonyls in the hazy days. It is suggested that further studies using compound-specific carbon isotopic compositions are necessary to identify the contribution of different sources to the carbonyl level in both hazy and clear days. This will allow the development of improved pollution control measurements in Guangzhou, which are required to contribute to a sustainable development.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.atmosres.2009.06.014](https://doi.org/10.1016/j.atmosres.2009.06.014).

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