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Pollution Characteristic of Atmospheric Carbonyls during One Haze Event in Nanning, South China

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ABSTRACT

This study was the first to investigate pollution characteristics of atmospheric carbonyls in one haze event (July 17–22, 2012) in Nanning, south China. It was found that (1) acetaldehyde (29.74 ± 6.06 μg m^{-3}), formaldehyde (11.20 ± 1.72 μg m^{-3}), and acetone (9.18 ± 11.22 μg m^{-3}) were the most abundant in haze days, (2) concentrations and O_3 formation potentials of ambient carbonyls in haze days were significantly higher than those on normal days, and (3) visibility and wind speed in haze days were lower than those on normal days, indicating that haze days represented favorable pollution conditions for carbonyls. Diurnal variations of ambient carbonyls in haze days showed a pattern of two peaks occurring in two traffic rush-hour periods due to positive traffic emissions. Average concentration ratio of formaldehyde/acetaldehyde (C_1/C_2) in haze days (0.39 ± 0.10) was slightly lower than that (0.87 ± 0.23) on normal days, and the ratios in two traffic rush-hour periods were close to those in non rush-hour periods, likely implying that traffic emissions might not be a major source for ambient carbonyls. Correlation among formaldehyde, acetaldehyde, acetone, and total carbonyls was good (R^2 = 0.49–0.85) in haze days and excellent (R^2 = 0.80–0.98) on normal days, indicating that the sources of ambient carbonyls in haze days were more complex compared to normal days.

***Keywords*:** Pollution characteristic; Haze event; Carbonyls; Nanning.

INTRODUCTION

Haze, a weather event with the horizontal visibility of < 10 km, is formed from moisture, gaseous pollutants and fine particles in air. Haze occurs when sunlight is absorbed and scattered by high levels of atmospheric contaminants, which is closely related to contaminants that differ from those on normal days (Chen *et al*., 2003; Kang *et al*., 2004; Wang *et al*., 2006; Du *et al*., 2011; Cheng *et al*., 2013). Haze can change the climate on a regional or a global scale by altering the solar and infrared radiations in the atmosphere (Quinn and Bates, 2003; Li *et al*., 2008), and it can pollute air, increase traffic hazards, and affect human health (Tie *et al*., 2009; Chen *et al*., 2012).

Currently, haze has been the most disastrous event in economically developed regions in China due to its adverse impacts on human (Yadav *et al*., 2003; Wu *et al*., 2005; Sun *et al*., 2006; Che *et al*., 2009; Wang *et al*., 2012). Moreover, haze is now expanding to developing areas such as the Beibu Gulf region, south China. Nanning is the provincial capital in Guangxi, as well as a rapidly developing city in the Beibu Gulf region (Fig. 1). Recently, increasing urbanization has led to critical concerns about a rapid deterioration of local air quality, for example, both noticeable occurrences of haze events and high levels of air pollutants have been major contributors to the deteriorating air quality in Nanning (Che *et al*., 2009; Cheng and Zeng, 2013).

Carbonyls are ubiquitous organic pollutants in urban air (Cavalcante *et al*., 2006; Wang *et al*., 2010; Duan *et al*., 2012). They come from primary sources (Kim *et al*., 2008; Guo *et al*., 2009) or secondary oxidations of hydrocarbons (Duane *et al*., 2002; Tan *et al*., 2012; Guo and Chen, 2013; Guo *et al*., 2014a). They are also the sources of free radicals and organic aerosols and the precursors of organic acids and oxidants (Atkinson, 2000). Particularly, organic components (e.g., carbonyls) in haze episodes showed oxidation activities that differed significantly from those on normal days (Lü *et al*., 2009; Tan *et al*., 2009; Guo *et al*., 2012, 2014b). Although considerable attention has been paid on carbonyl occurrences in urban air (Duane *et al*., 2002; Cavalcante *et al*., 2006; Kim *et al*., 2008; Pang and Lee, 2010; Guo *et al*., 2014b), the insight into carbonyls from haze episodes to normal days still remains poor. Such poor insight was definitely unfavorable for comprehensively controlling haze events in China, and for effectively improving air quality in Nanning.

In this paper, carbonyls during one haze event (July,

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Fig. 1. The location of atmospheric sampling site in Nanning, south China.

2012) in urban air of Nanning were investigated for the first time. The objectives were (1) to study pollution characteristic of carbonyls from haze to normal days and (2) to provide useful information on carbonyl pollutants in haze event for guiding the maintenance of local air quality.

MATERIALS AND METHODS

In this study, Chemicals and method used are described in the materials and methods of supplementary material. Carbonyls' statistical analyses was conducted by personal correlation matrix using the SPSS software (Lü *et al*., 2009), and sampling and analysis of carbonyl samples was based on our previous reports (Duan *et al*., 2012; Guo *et al*., 2014b). The sampling site was located on the roof of a building in the campus of Guangxi University in Nanning (Fig. 1). Fig. 1S plots annual trend of haze days during 2001–2014, and Fig. 2S shows plot of visibility variation during this sampling. Average daily visibility was approximately 11–16 km on July 16–18, and then decreased to 5–8 km on July 21–23 due to a raining event on July 19 and 20. Thus, July 21–23 were regarded as one haze event, and samples on July 17–19 were also collected for comparing the data of haze days with those of normal days. Carbonyls were collected at four intervals (including 0700–0900 (morning), 1130–1330 (noon), 1700–1900 (late afternoon), and 2200–2400 (midnight)) in each sampling day, each for 2 h at a flow rate of 2 L min^{-1}. Information on sampling, weather, and meteorological conditions is listed in Table 1S.

RESULTS AND DISCUSSION

Concentrations in Haze Days

This study investigated atmospheric carbonyls during one haze event in Nanning to evaluate their distribution characteristics from haze to normal days. Six carbonyls including formaldehyde, acetaldehyde, acetone, propionaldehyde, butyraldehyde and benzaldehyde were identified. Table 1 shows mean, maximum, and minimum values of both concentrations and fractions of measured carbonyls. Total carbonyls ranged from 33.38 to 100.03 μg m^{-3} (with a mean of 56.39 ± 20.78 μg m^{-3}) and 11.04 to 28.20 μg m^{-3} (19.53 ± 5.96 μg m^{-3}) in haze and normal days, respectively. In haze or normal days, formaldehyde, acetaldehyde, and acetone were the most abundant carbonyls, accounting for 88.9–95.5% of total carbonyls (Table 1). During the sampling of haze and normal days, acetaldehyde (19.89 ± 11.20 μg m^{-3}) was the most abundant, accounting for 54.4% of total carbonyls, followed by formaldehyde (9.70 ± 2.51 μg m^{-3}) and acetone (4.80 ± 8.97 μg m^{-3}) (Table 1). And the relative abundance followed the order of acetaldehyde > formaldehyde > acetone > benzaldehyde > propionaldehyde > butyraldehyde.

As presented in Table 1, concentrations of carbonyls in haze event were higher than those on normal days; for example, acetaldehyde concentration increased by approximately 196% from normal days to haze days. This trend has been observed for other pollutants such as hydrocarbons and particulates (Tan *et al*., 2009; Guo *et al*., 2012), indicating that haze days represent more severe pollution of carbonyls than normal days do. A previous study revealed that haze days possessed intensive oxidative activities, which could result in considerably more oxidative losses of hydrocarbons, particularly at noon with intensive sunlight and high temperature (Guo *et al*., 2012). Moreover, these oxidative losses of hydrocarbons contributed to ambient carbonyl levels (Guo and Chen, 2013). Fig. 2 shows a plot of average concentration ratios at noon (1130–1330) to that

Table 1. Average concentrations (μg m^{-3}) and mean fractions (%) of carbonyls during the sampling in Nanning.

	Normal days (July 17–19, 2013)				Haze days (July 21–23, 2013)			
	A.M. ± S.D. [b]	Min. [c]	Max. [c]	Fraction [d]	A.M. ± S.D. [b]	Min. [c]	Max. [c]	Fraction [d]
Formaldehyde	8.20 ± 2.30	4.33	11.66	42.0%	11.20 ± 1.72	9.00	14.56	19.9%
Acetaldehyde	10.03 ± 3.68	5.51	15.29	51.4%	29.74 ± 6.06	19.23	37.42	52.7%
Acetone	0.41 ± 0.40	0.08	1.22	2.1%	9.18 ± 11.22	1.54	42.10	16.3%
Propionaldehyde	0.23 ± 0.11	0.09	0.44	1.2%	1.41 ± 1.27	0.39	4.50	2.5%
Butyraldehyde	0.19 ± 0.07	0.09	0.29	1.0%	0.48 ± 0.17	0.18	0.79	0.8%
Benzaldehyde	0.47 ± 0.22	0.21	1.02	2.4%	4.37 ± 5.66	0.41	16.71	7.8%
Total carbonyls [e]	19.53 ± 5.96	11.04	28.20		56.39 ± 20.78	33.38	100.03	

[a] Total sampling days is the sum of normal and haze days during sampling.
[b] Arithmetic mean and standard deviation (A.M. ± S.D.) of carbonyls during sampling.
[c] Values of minimum (Min.) and maximum (Max.) for carbonyls during the sampling.
[d] Percentage contributions of individual carbonyl to the concentrations of total carbonyls.
[e] Total carbonyls refers to the sum of carbonyl concentrations in this table during sampling.

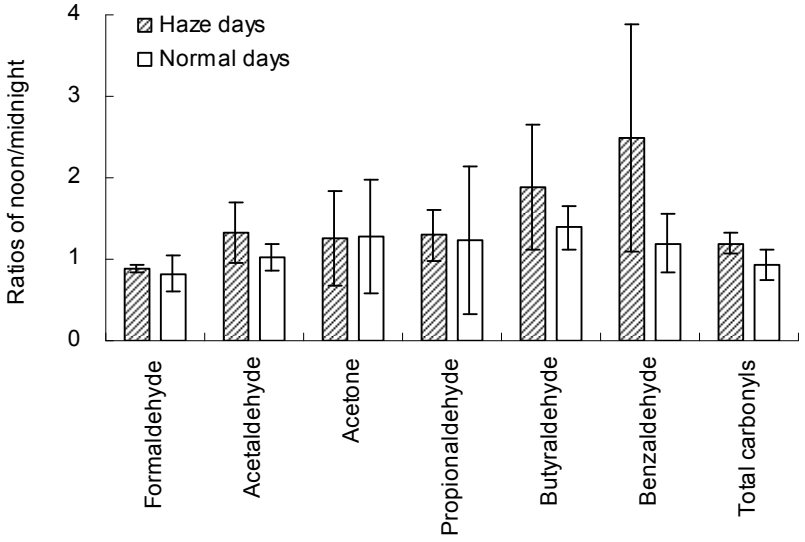

Fig. 2. Concentration ratios of noon to midnight for ambient carbonyls during the sampling.

at midnight (2200–2400) for ambient carbonyls. The ratios in haze days were slightly more than those on normal days for most carbonyls; for example, the ratios were 1.3 in haze days and 1.0 on normal days for acetaldehyde. The ratios likely indicated that haze days were more oxidative than normal days for loss of hydrocarbons, which was favorable for increasing ambient carbonyl levels. In addition, higher levels of carbonyls in haze days might be due to steady weather; for example, lower visibility (6–9 km) and wind speed (1.0–1.7 m s^{-1}) (Table 1S), because these steady weather conditions are not favorable for the diffusion of air pollutants, thus resulting in the accumulation of carbonyls in haze days.

To evaluate concentrations of ambient carbonyls in haze days, a comparison of Nanning and other urban areas is presented in Table 2S. It is a limited comparison because the presented data was provided from six sampling days. On normal days, both formaldehyde and acetaldehyde showed similar concentrations, and acetone concentration was lower than that in other urban cities. For example, acetone concentration was 0.41 μg m^{-3} in Nanning, which was significantly lower than those (5.0–52.5 μg m^{-3}) in other cities (Table 2S) such as Beijing (Duan *et al*., 2012), Guangzhou (Lü *et al*., 2009), and Guiyang (Pang and Lee, 2010). In haze days, formaldehyde and acetone showed similar levels, and acetaldehyde concentration was significantly higher (29.74 μg m^{-3}) than those (2.1–36.6 μg m^{-3}) in other cities in China; in particular, it was considerably higher than those in highly polluted Beijing (Duan *et al*., 2012) and Guangzhou (Lü *et al*., 2009) (Table 2S). Many new industrial estate projects have begun in Nanning in the past 10 years. Furthermore, explosive increases in industry and population have led to severe air pollution in the city (Che *et al*., 2009; Cheng and Zeng, 2013). Occurrences of the three abundant carbonyls likely implied that these increases have negative impacts on the local air quality.

Effect of Meteorological Conditions

Meteorology can affect air components and has been recognized as being associated with the worst air pollutant episodes (Kang *et al*., 2004; Sun *et al*., 2006; Pang *et al*., 2009; Guo *et al*., 2011). Fig. 3 shows the relationship of carbonyl concentrations with visibility, wind speed, relativity

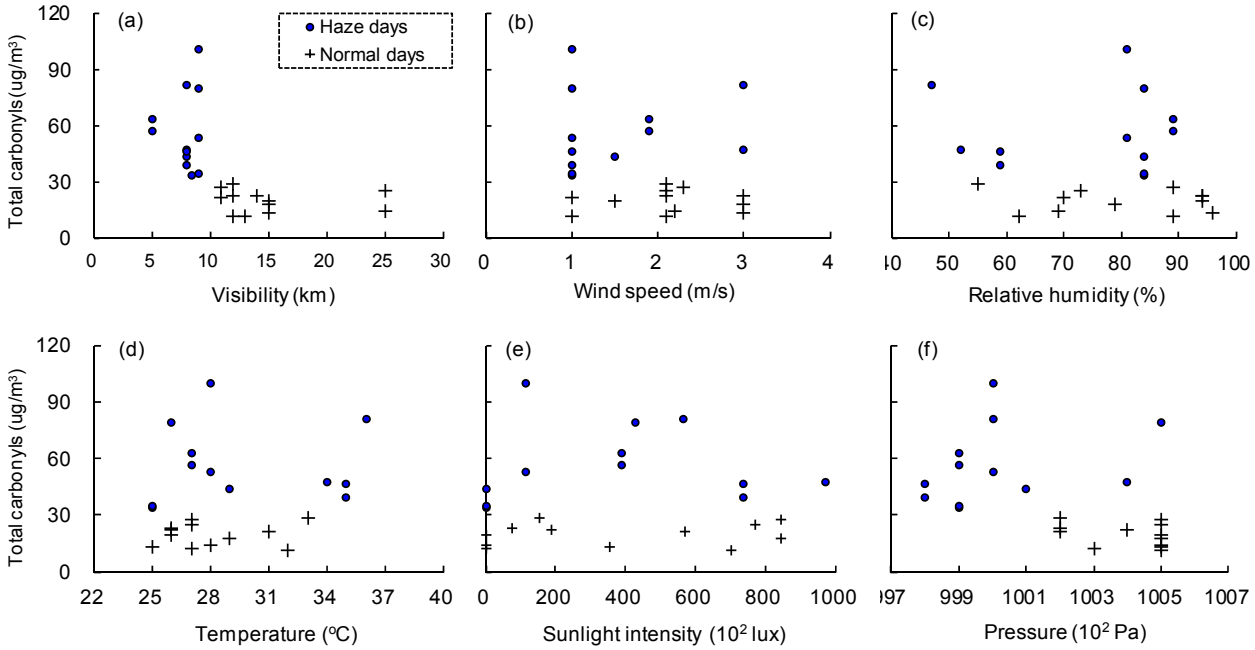

Fig. 3. Relations of carbonyl levels with meteorological conditions during the sampling.

humidity, temperature, sunlight intensity and pressure. In haze days, total carbonyls showed no clear variation trend under low visibility conditions (0–10 km), whereas it decreased with an increase in visibility when visibility was ≥ 10 km on normal days (Fig. 3(a)). Moreover, total carbonyls in haze days showed no variation trend when wind speed was ≤ 2 m s^{-1} for most samples (Fig. 3(b)), indicating that the dilution effect from wind speed was negligible in haze days. And no distinct boundaries or variation trends were observed for relative humidity, temperature, pressure, or sunlight intensity between haze days and normal days (Figs. 3(c)–(e)). In addition, pressure in haze and normal days (Fig. 3(f)) showed no significant fluctuation during the sampling periods. Overall, haze days represent low visibility (< 10 km), low wind speed (≤ 2 m s^{-1}), and high carbonyl levels compared with normal days.

Effect on O_3 Formation

Carbonyls are the major precursors of O_3 formation, and an individual carbonyl has a different photochemical reactivity. The contribution of carbonyls to the production of photochemical O_3 is related to their reactions with hydroxyl radical (OH·) in the complex photo-oxidation mechanism, and the mechanism of O_3 formation for each carbonyl varies greatly. In this study, maximum incremental reactivity (MIR) (Duan *et al*., 2008) was calculated to estimate the contribution of an individual carbonyl to photochemical O_3 formation. Ozone formation potential (OFP) can be evaluated as the product from carbonyl concentration based on MIR coefficient (it is the dimensionless constant referring to gram of O_3 produced by per gram of carbonyl). The photochemical formation of O_3 is influenced by many factors in addition to the reactivity of carbonyls such as NO_x concentration, solar radiation intensity, and meteorology. MIR is an accurate indicator for comparing OFP of an individual carbonyl. The following equation was used to calculate the contribution of an individual carbonyl to O_3 formation under optimal conditions: OFP (*i*) = Concentration (*i*) × MIR coefficient (*i*), and MIR coefficients were taken from Carter (2009). In this study, the reaction rates and MIR coefficients were calculated as average values obtained from the individual reaction rates of carbonyls.

OFPs are tabulated in Table 2. In haze days, OFPs ranged from 205.47 to 303.75 μg m^{-3}, with an average of 258.59 μg m^{-3}. Both formaldehyde and acetaldehyde were top contributors to O_3 formation, accounting for approximately 95% of total O_3 formation. The OFP from an individual carbonyl followed the order of acetaldehyde (163.58 μg m^{-3}) > formaldehyde (80.65 μg m^{-3}) > propionaldehyde (9.19 μg m^{-3}) > acetone (5.14 μg m^{-3}) > butyraldehyde (2.51 μg m^{-3}) > benzaldehyde (−2.49 μg m^{-3}). On normal days, OFPs ranged from 84.06 to 145.87 μg m^{-3}, with an average of 116.68 μg m^{-3}. Formaldehyde and acetaldehyde were top contributors to O_3 formation, accounting for approximately 98% of total O_3 formation. OFP from an individual carbonyl followed the order of formaldehyde (59.07 μg m^{-3}) > acetaldehyde (55.16 μg m^{-3}) > propionaldehyde (1.50 μg m^{-3}) > butyraldehyde (0.99 μg m^{-3}) > acetone (0.23 μg m^{-3}) > benzaldehyde (−0.27 μg m^{-3}). As Table 2 shows, OFPs in haze days were significantly higher by approximately 2.5 times those on normal days; both formaldehyde and acetaldehyde were the top two carbonyl contributors (95%–98%). This result implies a possible contribution of carbonyls to photochemical O_3 pollution in haze days, particularly from formaldehyde and acetaldehyde.

Diurnal Patterns in Haze Days

Ambient carbonyl level is influenced by many factors, including vehicular exhaust, photochemical oxidation of hydrocarbons, combustion of fuels, and their sinks such as

Table 2. O_3 production (μg m^{-3}) of atmospheric carbonyls in normal and haze days during the sampling. [a]

	Carbonyls	MIR [b]	Morning	Noon	Late afternoon	Mean [c]
Normal days	Formaldehyde	7.2	67.29	43.27	72.51	59.07
	Acetaldehyde	5.5	75.32	39.06	67.33	55.16
	Acetone	0.56	0.38	0.09	0.38	0.23
	Propionaldehyde	6.5	1.98	0.96	1.98	1.50
	Butyraldehyde	5.28	1.28	0.89	1.18	0.99
	Benzaldehyde	–0.57	–0.37	–0.20	–0.31	–0.27
	Total carbonyls		145.87	84.06	143.07	116.68
Haze days	Formaldehyde	7.2	90.81	67.66	87.90	80.65
	Acetaldehyde	5.5	186.20	155.63	189.94	163.58
	Acetone	0.56	11.29	2.21	5.47	5.14
	Propionaldehyde	6.5	16.89	5.16	10.73	9.19
	Butyraldehyde	5.28	2.90	2.38	3.37	2.51
	Benzaldehyde	–0.57	–4.34	–0.69	–4.63	–2.49
	Total carbonyls		303.75	232.33	292.79	258.59

[a] Average values for calculated data at different sampling intervals.
[b] MIR denotes the maximum incremental reactivity (g O_3/g carbonyl) (Carter, 2009).
[c] Average values for all calculated data during sampling in normal days or haze days.

photodecomposition and reaction with OH· (Atkinson, 2000; Duane *et al*., 2002; Kim *et al*., 2008; Guo and Chen, 2013). In particular, meteorological conditions significantly influence the distributions of atmospheric carbonyls, such as temperature, wind speed, and solar irradiation (Pang *et al*., 2009).

As listed in Table 3, diurnal variations in carbonyls showed a clear variation trend in haze or normal days; that is, ambient carbonyls showed a pattern of two peaks occurring in the morning and late afternoon. The lowest concentrations were observed at midnight for most carbonyls. For example, formaldehyde in haze days decreased by approximately 25% from morning to noon, increased by approximately 30% from noon to late afternoon, and then decreased by approximately 14% from late afternoon to midnight. On normal days, formaldehyde decreased by approximately 36% from morning to noon, increased by approximately 67% from noon to late afternoon, and then decreased by approximately 27% from late afternoon to midnight. This pattern was observed for all carbonyls during the sampling (Table 3). The pattern of higher concentrations occurred reasonably at two traffic rush-hour periods of 0700–0900 and 1700–1900. This diurnal pattern was observed in other urban areas such as carbonyls and hydrocarbons in Beijing and Foshan (Duan *et al*., 2008; Guo *et al*., 2011), implying the positive contributions of traffic emissions to ambient carbonyls, because traffic is at their highest level at the two periods.

In addition, the influence of meteorological conditions on carbonyl distributions was considered. As presented in Table 1S, average wind speed at noon was higher than other times in the morning, late afternoon, and midnight; for example, average wind speed in haze episodes was 1.7 m s^{-1} at noon and 1.0–1.3 m s^{-1} at other three sampling intervals (2.7 m s^{-1} versus 1.5–2.4 m s^{-1} on normal days). Higher wind speed at noon can result in unpredictable ventilation that dilutes air pollutants to a certain extent. The higher wind speed at noon appeared to play a positive role in the dispersion of air pollutants, which was favorable for the dispersion of ambient carbonyls. And the noon speed on hazy days (1.0–1.7 m s^{-1}) is slightly lower than that (1.5–2.7 m s^{-1}) on normal days. It is possible that lower carbonyl levels at noon were likely related to the favorable dispersion conditions, e.g., higher wind speed during the sampling.

Weather conditions are crucial for the distribution of carbonyls (Pang *et al*., 2009). Nanning is surrounded by mountains on the east and west. The climate in summer around Nanning is mainly controlled by a subtropical monsoon, and both temperature and sunlight intensity were high in haze or normal days (Table 1S). For example, average sunlight intensity was 115.0–602.3 × 10^2 lux during the sampling. Sunlight is intensive and temperature is high in Nanning, particularly at noon (Table 1S). For instance, temperature at noon was approximately 5–9°C higher than those in other three sampling internals in haze days. Carbonyls are usually the oxidation products of photochemical reactions of hydrocarbons (Duane *et al*., 2002; Guo and Chen, 2013). Furthermore, high temperature and intense sunlight can increase positive photochemical oxidations of hydrocarbons and generate more carbonyls (Moussa *et al*., 2006; Cerón *et al*., 2007; Pang and Lee, 2010). This positive generation is apparent from both higher concentrations at noon compared with those at midnight (Table 3) and noon/midnight ratios of > 1 (Fig. 2) for most carbonyls, particularly in haze days. In addition, carbonyls are the major participants in photochemical processes; for example, photolysis and reactions with OH· and O_3 in the atmosphere (Atkinson, 2000) can consume carbonyls, and then reducing their levels in ambient air. The possible reason for the lowest carbonyl concentrations at midnight was that positive photochemical oxidations increased carbonyl concentrations at noon.

Variations in C_1/C_2 Concentration Ratios

The distribution of ambient carbonyls during haze days in Nanning were influenced by anthropogenic emissions, such

Table 3. Diurnal variations of atmospheric concentrations (μg m^{-3}) of carbonyls in normal and haze days during the sampling. [a]

	Normal days				Haze days			
	Morning	Noon	Late afternoon	Midnight	Morning	Noon	Late afternoon	Midnight
Formaldehyde	9.35 ± 2.01	6.01 ± 1.94	10.07 ± 1.62	7.39 ± 1.82	12.61 ± 1.83	9.40 ± 0.39	12.21 ± 1.40	10.59 ± 0.92
Acetaldehyde	13.69 ± 1.40	7.10 ± 1.71	12.24 ± 3.40	7.08 ± 2.19	33.85 ± 2.00	28.30 ± 3.91	34.54 ± 3.10	22.28 ± 5.14
Acetone	0.68 ± 0.52	0.15 ± 0.07	0.67 ± 0.39	0.13 ± 0.03	20.17± 19.20	3.94 ± 3.34	9.76 ± 5.39	2.87 ± 1.27
Propionaldehyde	0.30 ± 0.10	0.15 ± 0.06	0.30 ± 0.12	0.16 ± 0.09	2.60 ± 1.96	0.79 ± 0.38	1.65 ± 1.02	0.61 ± 0.22
Butyraldehyde	0.24 ± 0.07	0.17 ± 0.08	0.22 ± 0.02	0.12 ± 0.03	0.55 ± 0.02	0.45 ± 0.04	0.64 ± 0.15	0.26 ± 0.10
Benzaldehyde	0.65 ± 0.33	0.36 ± 0.12	0.54 ± 0.05	0.32 ± 0.15	7.62 ± 6.61	1.21 ± 0.39	8.12 ± 7.64	0.53 ± 0.10
Total carbonyls [b]	24.92 ± 2.40	13.94 ± 3.42	24.06 ± 3.65	15.20 ± 3.90	77.40 ± 23.55	44.09 ± 4.38	66.92 ± 12.61	37.15 ± 5.62

[a] Arithmetic mean and standard deviation of carbonyls at different sampling intervals.
[b] Total carbonyls refers to average concentration and standard deviation for all measured carbonyls.

as vehicular emissions, atmospheric photochemical processes of concerning carbonyls, and meteorological conditions such as wind speed. Concentration ratio of formaldehyde/acetaldehyde (C_1/C_2) was used to compare carbonyl sources at different locations (Duan *et al*., 2012) because the C_1/C_2 ratio is usually 1–2 in urban areas and approximately 10 in rural areas (Guo *et al*., 2014b). As presented in Table 4, C_1/C_2 ratios in haze days varied from 0.29 to 0.59 with a mean of 0.39 ± 0.10. In addition, on normal days, average C_1/C_2 ratio was 0.87 ± 0.23 (ranging from 0.29 to 1.27), which was close to that in urban areas such as Guangzhou (0.87) (Lü *et al*., 2009) (Table 3S). Moreover, C_1/C_2 ratios in haze days were slightly lower than those on normal days for a certain sampling interval (Table 4); for example, C_1/C_2 ratios at noon were 0.34 ± 0.04 and 0.84 ± 0.07 in haze days and on normal days, respectively. Nevertheless, the data might not represent the statistical result due to limited sampling days form one haze event, and hence further research on haze events is need in our future work in Nanning.

The climate characteristic around Nanning is intensive sunlight and high temperature throughout the year, particularly at noon in summer (Table 1S). And local photochemical conditions are expected to be favorable for atmospheric carbonyls. Photolysis and reactions with OH· and O_3 could change carbonyl distributions in the atmosphere (Atkinson, 2000; Huang *et al*., 2008; Pang and Lee, 2010; Duan *et al*., 2012). Among them, reaction with OH· is often the dominant loss process for carbonyls in photochemically polluted air (Atkinson, 2000), which depends on reaction rate constants of carbonyls; for example, the reaction rate constants are 0.98 and 1.58 × 10^{11}·cm^3·$molecule^{-1}$·s^{-1} for formaldehyde and acetaldehyde, respectively. If the loss process was significant for carbonyls, C_1/C_2 ratio would become greater at noon under intensive photochemical conditions. But formaldehyde was often the dominant initial oxidation product in the photochemical oxidation of many hydrocarbons, which we have confirmed in our recent studies (Guo *et al*., 2009; Guo and Chen, 2013). And if the photochemical oxidations were strong for atmospheric active hydrocarbons, they would contribute to evaluating C_1/C_2 ratio at noon.

We have indicated that oxidative activities of volatile organic compounds in haze days were more intensive than those on normal days (Lü *et al*., 2009; Guo *et al*., 2012), and this was favorable for the production of ambient carbonyls. If the two aforementioned conditions played positive roles in carbonyl distributions, C_1/C_2 ratio at noon in haze days should be higher than those on normal days. As presented in Table 4, although average C_1/C_2 ratio at noon (0.34 ± 0.04) in haze days was slightly lower than that (0.84 ± 0.07) on normal days, that is, the ratios were still close to each other, likely implying photochemical production or loss was not so significant for ambient carbonyls between haze and normal days. Concentration variation showed that haze days represented more severe pollution of carbonyls than normal days did (Table 1), and diurnal variations indicated that ambient carbonyls were likely dominated by traffic emissions in the morning and late afternoon (Table 3).

Table 4. Concentration ratios of formaldehyde/acetaldehyde (C_1/C_2) during the sampling. [a]

	Morning	Noon	Late afternoon	Midnight	Average [b]	Min. [c]	Max. [c]
Normal days	0.69 ± 0.20	0.84 ± 0.07	0.88 ± 0.35	1.06 ± 0.14	0.87 ± 0.23	0.54	1.27
Haze days	0.37 ± 0.06	0.34 ± 0.04	0.36 ± 0.07	0.50 ± 0.14	0.39 ± 0.10	0.29	0.59
Total sampling days [d]	0.53 ± 0.22	0.59 ± 0.28	0.62 ± 0.36	0.78 ± 0.33	0.63 ± 0.30	0.29	1.27

[a] Arithmetic mean and standard deviation of concentration ratios.
[b] Average values and standard deviations for all calculated concentration ratios.
[c] Values of minimum (Min.) or maximum (Max.) in all calculated concentration ratios.
[d] Total sampling days is the sum of normal days and haze days during the sampling.

Assuming that ambient carbonyls in the morning and late afternoon originated from traffic emissions and other direct sources (e.g., plant emission) were neglected during the sampling, C_1/C_2 ratios in two traffic rush-hour periods (morning and late afternoon) likely represented the ratio characteristics from traffic emissions. C_1/C_2 ratios in two rush-hour periods were extremely close to those in non rush-hour periods (noon and midnight) in haze or normal days (Table 4). In haze days, for example, the average C_1/C_2 ratio was 0.36–0.37 in the morning and late afternoon, which was extremely close to 0.34–0.50 at non traffic hours. These diurnal variations in C_1/C_2 ratio likely implied that traffic emissions might not to be a major source for ambient carbonyls in urban air of Nanning.

It is noted that C_1/C_2 ration should be treated with caution as it varies among seasons and areas, and even at the same interval on different days (Duan *et al*., 2012; Guo *et al*., 2014a) (Table 3S). As presented in Table 4, average C_1/C_2 ratios were 0.39 (range: 0.29–0.59) in three haze days and 0.87 (range: 0.54–1.27) on three normal days. Our recent study indicated that lower wind speed, weaker air convection, and weaker atmospheric diffusion in haze episodes are more prone to the accumulation of organic pollutants with high concentrations (Guo *et al*., 2012), which could result in a decrease in C_1/C_2 ratio compared with that on normal days. During haze days, acetaldehyde concentration was the highest, and its concentration was 29.74 ± 6.06 μg m^{-3} which accounted for 52.7% of total carbonyls (Table 1). Considering that that these data were obtained from investigation on several days, and it might not represent the statistical result. It is possible that the slightly lower C_1/C_2 ratios in haze days still implied that meteorological conditions such as lower wind speed influence carbonyl distributions.

Correlations of Ambient Carbonyls in Haze Days

The sampling site is mainly surrounded by urban roads and several residential buildings (Fig. 1), and there are no special industrial sources of carbonyls close to the sampling site. As discussed above, both diurnal patterns and C_1/C_2 ratios indicated that ambient carbonyls were likely associated with traffic emissions, and the influence of meteorological conditions on ambient carbonyls was not so significant in haze days. To determine the sources of carbonyls, correlation coefficient (R^2) was calculated among individual carbonyls during the sampling; the R^2 ($p < 0.05$) of formaldehyde, acetaldehyde, acetone, and total carbonyls was 0.49–0.85 in haze days and 0.80–0.98 on normal days (Table 5). These correlations clearly indicated that ambient formaldehyde, acetaldehyde, acetone, and total carbonyls originated from similar sources such as traffic emissions. However, the correlation was good in haze days (R^2 = 0.49–0.85) and excellent (R^2 = 0.80–0.98) on normal days. For example, the R^2 of formaldehyde with acetaldehyde was 0.49 in haze days and 0.80 on normal days (Table 5). The foregoing "*Diurnal patterns in haze days"* and *"Variations in C_1/C_2 concentration ratios"* sections concluded that photochemical and meteorological conditions have slight and not so significant impacts on distribution of ambient carbonyls in haze days. Furthermore, the lower R^2 of ambient carbonyls in haze days implied the slight impacts from photochemical and meteorological conditions, and the sources of ambient carbonyls were more complex compared to normal days. Overall, the correlation (R^2 = 0.49–0.98, $p < 0.05$) clearly indicated that ambient carbonyls were mainly controlled by similar sources during the sampling, maybe traffic emissions.

Traffic emissions are major sources of atmospheric organic pollutants in many urban areas; in addition, they were responsible for ambient carbonyls in haze days, particularly in traffic rush-hour periods (Table 3). Except for ubiquitous primary sources (e.g., direct plant emission), ambient carbonyls in haze days were likely associated with the significant traffic emissions. Assuming that ambient carbonyls during the sampling originated from traffic emissions and primary sources, that the strength of these primary sources was the same, and that the influence of other meteorological factors (e.g., wind speed) was neglected, the contribution of traffic emissions to formaldehyde, acetaldehyde, acetone, and total carbonyls could be estimated to be approximately 34%, 55%, 85%, and 60% in haze days, respectively; and they were approximately 55%, 73%, 80%, and 40% on normal days, respectively, by using the data in Table 3. In this study, ambient formaldehyde, acetaldehyde, and acetone accounted for 88.9–95.5% of total carbonyls (Table 1). Based on the correlation (R^2 = 0.49–0.85, $p < 0.05$), this rough estimation provides possible evidence that high concentrations of ambient carbonyls in haze days might be related to the local traffic emissions.

CONCLUSIONS

Atmospheric carbonyl pollutants in one haze event of Nanning were firstly studied on July 17–22, 2012. The main results are summarized as follows: (1) formaldehyde, acetaldehyde, and acetone accounted for approximately 88.9% of total carbonyls in haze days, (2) haze represented severe pollution of carbonyls, high levels of possible

Table 5. Correlations (R^2, $p < 0.05$) of formaldehyde, acetaldehyde and acetone in urban air of Nanning. [a]

	Carbonyls	Formaldehyde	Acetaldehyde	Acetone	Total carbonyls [b]
Normal days	Formaldehyde	1			
	Acetaldehyde	0.80	1		
	Acetone	0.86	0.97	1	
	Total carbonyls [b]	0.90	0.98	0.98	1
Haze episodes	Formaldehyde	1			
	Acetaldehyde	0.49	1		
	Acetone	0.69	0.56	1	
	Total carbonyls [b]	0.77	0.85	0.67	1

[a] Correlation coefficients of the data are significant at the 95% levels.
[b] Total carbonyls refer to the sum of measured six carbonyls during the sampling.

photochemical O_3 pollution, and favorable conditions for the accumulation of carbonyls, and (3) traffic emissions might be responsible for ambient carbonyls in haze days based on diurnal variations, C_1/C_2 ratios and correlations of carbonyl concentrations.

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SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

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