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Seasonal and diurnal characteristics of atmospheric carbonyls in Nanning, China

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ABSTRACT

For the first time, atmospheric carbonyls were measured to identify seasonal and diurnal variations in Nanning from October 2011 to July 2012. Formaldehyde (6.79 ± 3.39 μg/m^3), acetaldehyde (15.81 ± 10.48 μg/m^3) and acetone (5.43 ± 6.91 μg/m^3) were the three most abundant carbonyls, accounting for ~85% of the total carbonyls. The average total concentrations of carbonyls and three abundant carbonyls showed significant high levels in summer compared to those in winter. Diurnal variations suggested that photochemical conditions, combustion of charcoal and straw, and solvent usage are important for the distributions of atmospheric carbonyls. The highest average C_1/C_2 ratio was observed in summer (0.75) compared to those (0.31–0.70) in other seasons, implying the positive effect of photochemical activities on raising C_1/C_2 ratio, and the significant low C_2/C_3 ratio (12.01–18.23) in winter and autumn than those (95.83–24.49) in both spring and summer suggested the important anthropogenic emissions such as charcoal and biomass combustion. O_3 formation potentials in summer and spring were significantly higher by ~2 times than those in autumn and winter. Formaldehyde and acetaldehyde are the top two carbonyls which contribute 82–97% to total O_3 formation potentials.

1. Introduction

Carbonyls are ubiquitous organic compounds in the atmosphere, which have been receiving increasing attention for its adverse effects on human health (Andreini et al., 2000; Bakeas et al., 2003; Cavalcante et al., 2006; Pal et al., 2008; Uchiyama et al., 2012) and are also precursors of atmospheric oxidants and secondary organic aerosols (Carlier et al., 1986; Roberts, 1990; Atkinson, 2000; Tan et al., 2009). Carbonyls are emitted directly from primary anthropogenic sources, such as emissions from various incomplete combustion (Kean et al., 2001; Kim et al., 2008) or biogenic sources, such as plants (Seco et al., 2007; Guo et al., 2009). Atmospheric photo-oxidation is an important secondary source of carbonyls, and involves a series of chemical reactions of atmospheric oxidants with volatile organic compounds (Wiedinmyer et al., 2001; Duane et al., 2002; Guo et al., 2014).

Many studies have been conducted to investigate the level (Kean et al., 2001; Seco et al., 2007; Pal et al., 2008; Yuan et al., 2012), temporal and spatial variation (Moussa et al., 2006; Cerón et al., 2007), transformation and sources (Wiedinmyer et al., 2001; Duane et al., 2002; Guo and Chen, 2013; Guo et al., 2014; Ullah et al., 2015) of atmospheric carbonyls in recent years. However in China, the relevant studies were generally conducted in the developed regions, especially in three typical megacity regions including Pearl River Delta, Yangtz River delta and Capital Region (Feng et al., 2004; Duan et al., 2008, 2012; Pang et al., 2009; Lü et al., 2010; Zhang et al., 2012), and few studies on atmospheric carbonyls were investigated in the developing regions, such as Guangxi province of Southern China.

Nanning is the capital city of Guangxi province with a total population of 7.86 million (Liu et al., 2012) and located in the fringe zone (Fig. 1) of Southern China, Southwestern China and Southeastern Asian Economic Circles; and it is a confluence of several economic centers, including ASEAN (Association of Southeast Asian Nations Expo), Great Mekong River Sub-region, Pan-Pearl River Delta Economic Zone, Nanning-Guiyang-Kunming Economic Belt and Beibu Gulf Economic Zone. Besides, it is also an important economic center along Beibu Gulf and a key gateway and passage leading to ASEAN countries. With the substantial urbanization development, large amounts of air pollutants were emitted into air and there has been a growing concern on the adverse health effects from hazardous air pollutants on people in this city (Zhu et al., 2004). Haze episode showed an increasing trend in Nanning (Che et al., 2009) and toluene was observed as much as 159.2 μg/m^3 in urban air of Nanning (He et al., 2005). Thus, the favorable climatic conditions (e.g., high ambient temperature and high solar radiation) and the increase of precursors for carbonyls were expected to increase the formation of atmospheric carbonyls in Nanning.

To better understand pollution characteristics of carbonyls in the local urban air, atmospheric carbonyls were measured and analyzed for the first time from October 2011 to July 2012 in Nanning to: investigate the levels of carbonyls, identify diurnal and seasonal variations, and assess

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their possible sources. To our knowledge, this is the first time to investigate carbonyls in ambient air of Nanning.

2. Experimental

2.1. Sampling

Field sampling was conducted in the campus of Guangxi University, downtown center of Nanning city from October 2011 to July 2012. The sampling site is located on the roof of an 11 storey building (about 35 m above ground) of School of the Environment, which is surrounded by traffic roads, residential buildings and business offices (Fig. 1). There are no obvious emission sources of atmospheric carbonyl in the vicinity of the sampling site. The sampling information and meteorological conditions were listed in Table 1. The detail sampling procedures could be found elsewhere (Lü et al., 2010; Duan et al., 2012).

Briefly, carbonyls were collected by drawing the air with a pump (Gast, USA) through DNPH-coated cartridges (Sep-Pak Silica Gel Cartridge, Waters, Millipore Co.). A potassium iodide (KI) denuder was connected to the upstream of the cartridges to avoid the interference of atmospheric oxidants. In addition, a breakthrough experiment was carried out by connecting two cartridges in series and no carbonyls were detected in the back cartridge. Each sample was collected for 2 h at a flow rate of 2 L/min. Four samples were collected each day at morning (07:00–09:00), noon (12:00–14:00), late afternoon (17:00–19:00) and midnight (22:00–24:00), respectively. After sampling, each cartridge was wrapped in a Teflon bag with aluminum foil and then stored in a 4 °C refrigerator until analysis. One laboratory blank and one field blank were collected each day and a total of 112 samples were obtained.

2.2. Analysis

The analysis of atmospheric carbonyls was based on the EPA Method TO-11A (EPA, 1996), and the details could be found elsewhere (Lü et al., 2010; Duan et al., 2012; Guo et al., 2014). Briefly, all cartridges were eluted with 2 mL of ACN (Merck, Darmstadt, Germany) into a 2 mL flask and then the elution was injected into the HPLC system (HP1100, Agilent, USA). The analytical apparatus consisted of an HPLC pumping system (Hewlett Packard 1100) connected to a UV detector (Hewlett Packard, UV at 360 nm) with an Agilent RP-C_{18} reverse column (250 mm × 4.6 mm × 5 μm).

Individual carbonyl was identified based on the comparison of retention time with derivative standard solutions, and quantified by the integration of peak area. A total of 9 carbonyls including formaldehyde, acetaldehyde, acetone, propionaldehyde, cyclohexanone, butyraldehyde, benzaldehyde, valeraldehyde and hexaldehyde were identified in this study. To ensure the reliability of air sampling, a breakthrough experiment by connecting two cartridges in series was conducted before sampling; the sampling time was 2 h at a flow rate of 2 L/min and then carbonyls were detected in the cartridges. The breakthrough experiment showed that over 99% of carbonyls were recovered by the first cartridge, indicating the complete recovery of all carbonyls. Six standard concentrations (0.2–10 μg/mL) were used to calibrate the HPLC analytical apparatus covering the concentration of interest. Strong linear relationship ($R^2 > 0.995$) was found between concentrations and responses for all carbonyls identified. Method detection limits were 0.05–0.15 μg/m^3 for various carbonyls. The relative percent deviations of replicates were within 5%. Relative standard deviation (RSD) for duplicate analysis was lower than 5%, and method precision 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 USEPA blank criteria (EPA, 1996).

Table 1
The information of sampling and meteorological conditions in Nanning, China.

	Sampling duration	Temp (°C)[a]	RH (%)[a]	WS (m/s)[a]	SI (×10^2 lx)[b]	Weather[b]
Spring (6–12 on April 2012)	Morning	19–22	79–96	2–3	3–250	Overcast
	Noon	19–24	84–100	2–3	300–530	Fog/fogdrop
	Late afternoon	21–23	877–95	3–5	1–120	Cloudy
	Midnight	19–20	86–96	3–4	0	Cloudy
Summer (3–9 on July 2012)	Morning	28–30	89–95	2–3	160–900	Clear
	Noon	32–36	79–81	1–2	990–1300	Sunny
	Late afternoon	28–40	73–96	1–2	120–500	Sunny
	Midnight	28–31	88–95	2–3	0	Cloudy
Autumn (16–22 on October 2011)	Morning	20–26	63–95	2–4	15–500	Clear/cloudy
	Noon	28–31	35–56	3–5	610–868	Clear
	Late afternoon	26–29	50–71	2–3	60–400	Clear/cloudy
	Midnight	20–24	80–96	1–2	0	Cloudy
Winter (12–18 on January 2012)	Morning	5–17	79–100	1–3	5–260	Clear
	Noon	15–18	91–100	4–5	300–700	Clear/cloudy
	Late afternoon	14–16	59–95	3–6	1–115	Cloudy
	Midnight	13–15	85–100	2–3	0	Cloudy

[a] Data of temperature (Temp), relative humidity (RH) and wind speed (WS) were collected from website http://www.wunderground.com/.
[b] Data of sunlight intensity (SI) of and weather conditions were recorded by the staff who engaged in the sampling on the field.

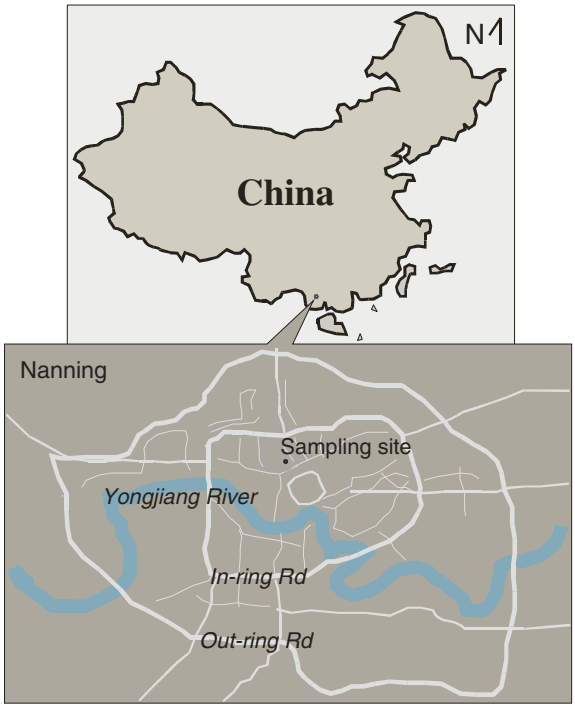

Fig. 1. The location of atmospheric sampling site in the urban area of Nanning, China.

3. Results and discussion

3.1. The level of atmospheric carbonyl

Table 2 shows the average, maximum and minimum concentrations and fractions of carbonyls during the sampling period in Nanning city. The total concentration of carbonyls was 33.21 ± 15.12 μg/m^3 with a range from 12.50 μg/m^3 to 88.45 μg/m^3. Acetaldehyde ranged from 3.55 to 37.24 μg/m^3, with an average of 15.81 ± 10.48 μg/m^3 and was the most abundant carbonyl, which contributed 47.60% of total carbonyls. Formaldehyde was the second highest carbonyl and its average concentration was 6.79 ± 3.39 μg/m^3. The abundance was in the order as below: acetaldehyde > formaldehyde > acetone > benzaldehyde >