Supplementary material

Pollution Characteristics of Atmospheric Carbonyls during One Haze Event in Nanning, south China

Song-jun Guo [1]*, Mei Chen [2]

[1] *School of the Environmental Studies, Guangxi University, Nanning, China*

[2] *School of the Mechanical and Security, Nanning College, Nanning, China*

Contents:

* Corresponding author.

Tel.: +86-0771-3270672; Fax: +86-0771-3270672.

E-mail address: guosj@gxu.edu.cn.

MATERIALS AND METHODS

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 until use. The standard solution (ChemService, USA) 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*-toualdehyde, *p*-tolualdehyde, cyclohexanone, heptaldehyde, octylaldehyde, nonanaldehyde, decylaldehyde, and *2*-butanone (Feng *et al*., 2004; Lü *et al*., 2009; Guo *et al*., 2014b).

Sampling

The sampling site is located on the roof of a building (round 20m above ground level) in the campus of Guangxi University, which is surrounded by urban roads, residential buildings and business offices in urban center of Nanning (see Fig. 1 in the main manuscript). In this study, haze episodes were characterized by visibility of ≤10km (CMA, 2003; Wang *et al*., 2006; Tan *et al*., 2009; Guo *et al*., 2012a). Figure 1S plots annual trend of haze days during 2001–2014 in Nanning, and Figure 2S shows the plot of visibility variation during this sampling in summer of Nanning (July 16–23, 2012). It can be seen that average daily visibility was round 11–16km on July 16–18, and then reached the lower values of 5–8km on July 21–23. In addition, there was a raining event in the two days on July 19–20. Therefore, the days of July 21–23 were regarded as one haze episode, and air samples from July 17–19 were also collected for data comparison of haze episode versus normal days. The detail

sampling procedure was similar to the descriptions in our previous studies (Duan *et al*., 2012; Guo *et al*., 2014a). In this study, meteorological data of visibility, wind speed, relativity humidity, temperature and pressure were collected from http://www.wunderground.com, and sunlight intensity was collected from the local meteorological department in Nanning named Nanning weather station, which were provided for us in time during the sampling periods. Meanwhile, data of sunlight intensity and weather conditions were also recorded by the staff who engaged in the air sampling on the field.

Briefly, samples were collected by drawing air with a sampling pump (Gast, USA) through DNPH-coated cartridges. A potassium iodide denuder was connected to the upstream of the cartridges to avoid the interference of ambient O_3. In addition, a breakthrough experiment was carried out by connecting two cartridges in series before sampling, indicating that no carbonyls were detected in the back cartridge when the sampling interval was 2h at a flow rate of 2L/min. Carbonyls were collected at four intervals (including 0700–0900 (in the morning), 1130–1330 (at noon), 1700–1900 (in the late afternoon) and 2200–2400 (in the midnight)) in haze episodes and normal days in summer (July 16–23, 2012), which were collected for 2h via a flow rate of 2L/min. The information of sampling, weather and meteorological conditions (including visibility, wind speed, relativity humidity, temperature, sunlight intensity and pressure) were listed in Table 1S. 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, and total 24 carbonyl samples and 12 blank samples were obtained.

Analysis

The analysis procedure of carbonyl samples was based on the EPA TO-11A method of United States (US EPA, 1996) and our previous studies (Lü *et al*., 2009; Guo *et al*., 2014b). Briefly, all cartridges were eluted with 2mL of ACN into a 2mL volumetric flask and then a

10μL was injected into the HPLC system (HP1100, Agilent, USA) through an auto-sampler. Analytical conditions: agilent RP-C_{18} reverse column (250mm×4.6mm×5μm); gradient mobile phase: 60% ACN of water solution (20min), 70–100% ACN (3min), 100% ACN (6min), 100–60% ACN (5min) and then 60% ACN (5min); mobile-phase flow rate: 1mL·min^{-1}; detector: UV at 360nm. 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 standard concentrations (0.2–10μg/mL), and strong linear relationship (R^2>0.99) was found between concentrations and responses. Cartridge collection efficiency was over 99% for carbonyls. Relative standard deviation for duplicate analysis was lower than 5%. Method detection limits were 0.05–0.15μg/m^3. One laboratory blank and one field blank were analyzed and the result in the blank cartridges did not show negative effects on field sampling according to the EPA blank criteria of United States (USEPA, 1996). In this study, carbonyls' statistical analyses was conducted by personal correlation matrix using the SPSS software and described in the reference Lü *et al*. 2009.

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Table 1S. The information of sampling time and meteorological conditions during sampling in Nanning, south China.

Date	Meteorology	Morning	Noon	Late afternoon	Midnight
Normal days (July 17–19, 2013)	Visibility (km) [a]	16.7 ± 7.4	14.3 ± 1.2	11.7 ± 0.6	17.3 ± 6.8
	Wind speed (m/s) [a]	2.4 ± 0.5	2.7 ± 0.6	1.7 ± 0.6	1.5 ± 0.5
	Relativity humidity (%) [a]	85.3 ± 11.0	79.0 ± 17.0	73.0 ± 19.7	84.0 ± 13.2
	Temperature (^oC) [a]	26.7 ± 0.6	28.7 ± 3.5	30.0 ± 3.6	27.0 ± 1.0
	Pressure (10^2 Pa) [a]	1004.7 ± 0.6	1005.0 ± 0.0	1002.0 ± 0.0	1004.3 ± 1.2
	Sunlight intensity (10^2 lx) [b]	602.3 ± 635.3	268.0 ± 0.0	517.0 ± 775.0	116.0 ± 0.0
	Weather conditions [b]	clear	clear/sunny	clear	clear/cloudy
Haze episodes (July 21–23, 2013)	Visibility (km) [a]	9.0 ± 0.0	8.0 ± 0.0	6.0 ± 1.7	8.5 ± 0.5
	Wind speed (m/s) [a]	1.0 ± 0.0	1.7 ± 1.2	1.3 ± 0.6	1.2 ± 0.3
	Relativity humidity (%) [a]	82.0 ± 1.7	56.7 ± 4.0	75.0 ± 24.2	84.0 ± 0.0
	Temperature (^oC) [a]	27.3 ± 1.2	34.7 ± 0.6	30.0 ± 5.2	26.3 ± 2.3
	Pressure (10^2 Pa) [a]	1001.7 ± 2.9	1000.0 ± 3.5	999.3 ± 0.6	999.7 ± 1.2
	Sunlight intensity (10^2 lx) [b]	220.0 ± 817.3	446.7 ± 0.0	115.0 ± 751.0	377.3 ± 190.7
	Weather conditions [b]	sunny	sunny/cloudy	sunny/cloudy	cloudy

[a] Visibility, wind speed, relativity humidity, temperature and pressure were collected from http: //www.wunderground.com.
[b] Data of sunlight intensity and weather conditions were recorded by the staff who engaged in the air sampling on the field.

Table 2S. Atmospheric concentrations (μg/m^3) of formaldehyde, acetaldehyde and acetone in different urban cities.

	Date	Formaldehyde	Acetaldehyde	Acetone	References
Fortaleza, Brazil	November–December 2004	12.4	2.90	52.5	Cavalcante *et al*. (2006)
Shimizu, Japan	Summer–August 2000	2.77	2.29		Ohura *et al*. (2006)
Beirut, Lebanon	August–September 2004	4.60	2.10	5.00	Moussa *et al*. (2006)
Xi'an, China	July–August 2004	9.90	12.6		Wang *et al*. (2007)
Ansan, South Korea	August 2004–September 2005	24.1	36.6	38.4	Kim *et al*. (2008)
Guangzhou, China	November–December 2005	14.6	16.6	15.4	Lü *et al*. (2009)
Guiyang, China	December 2008–August 2009	4.80	5.70	5.10	Pang and Lee (2010)
Niterói, Brazil	January 2010	3.22	6.53	7.27	Ochs *et al*. (2011)
Beijing, China	August 2006	35.65	15.65	8.83	Duan *et al*. (2012)
Qinzhou, China	October 2011–July 2012	6.70	8.04	2.43	Guo *et al*. (2014b)
Nanning, China	Normal days, July 2013	8.20	10.03	0.41	This study
Nanning, China	Haze days, July 2013	11.20	29.74	9.18	This study

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

Note: the references in the Table 2S were presented in this Supplementary material and the main manuscript.

Table 3S. A comparison of C_1/C_2 concentration ratios during sampling in Nanning with other urban areas.

	Date	C_1/C_2	Range	References
Rio de Janeiro, Brazil	May–November 2000	1.04	0.84–3.54	Grosjean *et al*. (2002)
Athens, Greece	June–December 2000	1.27		Bakeans *et al*. (2003)
Guangzhou, China	August–September 2002	1.81	1.30–2.42	Feng *et al*. (2004)
Carmen City, Mexico	October–November2004		1.07–1. 4	Cerón *et al*. (2007)
Shanghai, China	July 2007	1.36		Huang *et al*. (2008)
Guangzhou, China	November–December 2005	0.87	0.59–1.24	Lü *et al*. (2009)
Niterói, Brazil	January 2010	2.00		Ochs *et al*. (2011)
Beijing, China	August 2006	2.69	1.39–3.78	Duan *et al*. (2012)
Qinzhou, China	October 2011–July 2012	1.48	0.33–13.49	Guo *et al*. (2014)
Nanning, China	July 2012	0.63	0.29–1.27	This study

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

Note: the references in the Table 3S were presented in this Supplementary material and the main manuscript.

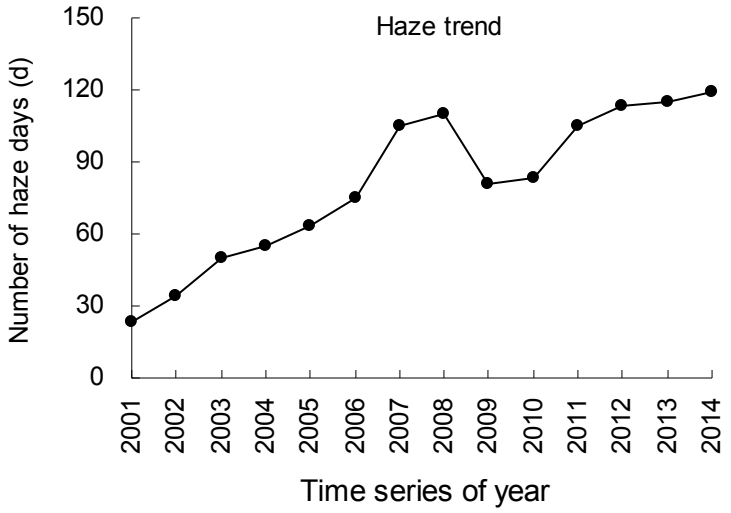

Fig. 1S. Annual trend for number of haze days during 2001–2014 for ambient air in Nanning, south China.

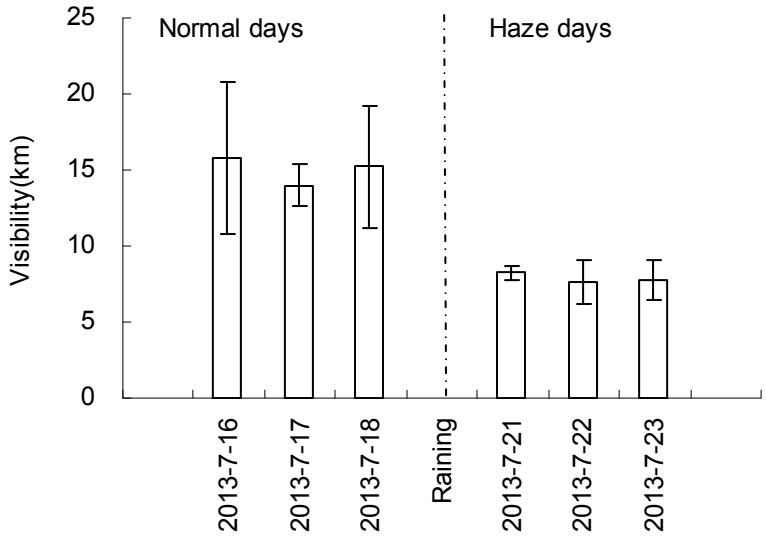

Fig. 2S. The variation trend of visibility during the sampling periods (July 16–23, 2012) in Nanning.