

# Characteristics of atmospheric carbonyls and VOCs in Forest Park in South China

Yingxin Yu · Sheng Wen · Huixiong Lü ·  
Yanli Feng · Xinming Wang · Guoying Sheng ·  
Jiamo Fu

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**Abstract** The diurnal variation of atmospheric carbonyls and VOCs in a forest in south China were studied in summer 2004. Twenty kinds of carbonyls and eight kinds of VOCs were identified and quantified. Formaldehyde and acetaldehyde were the two most abundant carbonyls, while the most abundant VOCs were isoprene, followed by o-xylene. Most C<sub>3</sub>-C<sub>10</sub> carbonyls had higher concentrations from 09:00 to 15:00, and their levels were lower during night-time and often reached the lowest in early morning. Formaldehyde and acetaldehyde, however, showed two high levels in their diurnal patterns partly due to their different sources and sinks. The VOCs had different diurnal patterns compared to most carbonyls. The highest concentrations were observed from 03:00 to 06:00 for 1-butene, from

06:00 to 12:00 for isoprene, and from 12:00 to 15:00 for  $\alpha$ -pinene. The highest levels for aromatic hydrocarbons occurred during midnight and the lowest in late afternoon. According to the study, emissions from vegetation and photo-oxidation of gas-phase hydrocarbons were the main sources for some carbonyls and VOCs in this region. Other compounds, such as formaldehyde, acetaldehyde and BTEX, showed anthropogenic sources.

**Keywords** Carbonyls · Volatile organic compounds · Forest · Diurnal variation

## Introduction

Carbonyls (low molecular weight ketones and aldehydes) and volatile organic compounds (VOCs) are ubiquitous in the atmosphere. They are of concern for their adverse effects to vegetation and human health, such as toxic, mutagenic and possible carcinogenic effect (Bakeas et al. 2003). They have both anthropogenic and biogenic origins (Biesenthal et al. 1998). In urban areas, they are directly emitted into the air by industrial processes, vehicular emissions and other stationary substance as primary sources; carbonyls are also produced by photochemical oxidation of VOCs and heterogeneous interactions of aldehydes as secondary pollutants (Altshuller 1993; Christensen et al. 2000; Jang and Kamens 2001; Grosjean et al. 2002; Mohamed et al. 2002; Possanzini et al. 2002). Photo-oxidation of VOCs and direct

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Y. Yu · Y. Feng · G. Sheng · J. Fu  
Institute of Environmental Pollution and Health,  
School of Environmental and Chemical Engineering,  
Shanghai University,  
Shanghai 200072, People's Republic of China

S. Wen · X. Wang · G. Sheng · J. Fu (✉)  
State Key Laboratory of Organic Geochemistry,  
Guangdong Key Laboratory of Environmental Resources  
Utilization and Protection, Guangzhou Institute of  
Geochemistry, Chinese Academy of Sciences,  
Guangzhou 510640, People's Republic of China  
e-mail: fujm@gig.ac.cn

H. Lü  
College of Natural Resources and Environment,  
South China Agricultural University,  
Guangzhou 510640, People's Republic of China

biogenic emission are important sources in rural areas (Singh et al. 1995; Borbon et al. 2004).

Compared with the urban atmospheric environment, there were only a few studies on atmospheric carbonyls in rural regions, especially in forests of China (Ho and Lee 2002; Ho et al. 2002; Feng et al. 2004; Lee and Wang 2004; Lü et al. 2006). To our knowledge, data on the diurnal variations of atmospheric concentrations of carbonyls and VOCs are also limited (Christensen et al. 2000; Sharma et al. 2000; Klemp et al. 2002; Borbon et al. 2004; McLaren et al. 2004). Future data is needed regarding the implications and roles of carbonyls and VOCs in the global atmospheric environment. With these in mind, the present study aims to investigate the diurnal variation of atmospheric carbonyls and VOCs, as well as their possible sources and sinks, in a semi-tropical forest in South China.

## Samples and methods

### Sampling location

Air samples were collected in Prince Hill Forest Park, north of the town of Timian located in the northern part of the Huadu District, between Qingyuan and Conghua (Fig. 1). Timian, about 90 km away at the north of Guangzhou, is surrounded by green forested hill and the National Highway No.106 passes through the town. The forest is mainly of broad-leaf evergreen trees. The sampling site is situated in a valley of Prince Hill at an elevation of 571.9 m, far away from villages. A small stream passes the sampling site. All samples were collected at a height of 1 m above ground under a canopy.

### Reagents and materials

All solvents employed were HPLC grade. Water was double distilled and filtered through a Milli-Q system. 2, 4-dinitrophenylhydrazine (DNPH) and acetonitrile (ACN) were purchased from Merck (Germany) and Fluka (USA), respectively. DNPH was recrystallized twice in HPLC grade ACN. The calibration standards containing 21 compounds as the 2, 4-dinitrophenylhydrazones (DNPH derivatives of formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, crotonaldehyde, 2-butanone, butyraldehyde, benzaldehyde, isovaleraldehyde, cyclohexanone, valeraldehyde, p-tolualdehyde, m/o-tolualdehyde, hexaldehyde, 2, 5-dimethylbenzaldehyde,

heptaldehyde, octylaldehyde, nonanaldehyde and decylaldehyde) were purchased from ChemService (West Chester, USA). The VOCs standard gas mixtures were generously provided by the Rowland/Blake Group (University of California at Irvine).

### Sampling

The sampling substrates for carbonyls were prepared using commercial Sep-Pak silica gel cartridges (Waters, Millipore Corp.) and coating them with freshly made acidified DNPH ACN solution (Yu et al. 2006). The cartridges were dried with a gentle flow of high-purity nitrogen. Each cartridge was wrapped in aluminum foil and then packaged with a DNPH-impregnated filter paper to prevent contamination before use. Finally, cartridges packs were sealed in Teflon bags. All operations were carried out in a glove box (ZKX2, 80×60×70 cm, Nanjing University Instrument Plant, China) filled with high-purity nitrogen (Yu et al. 2006). The coated cartridges were stored at 4°C until use.

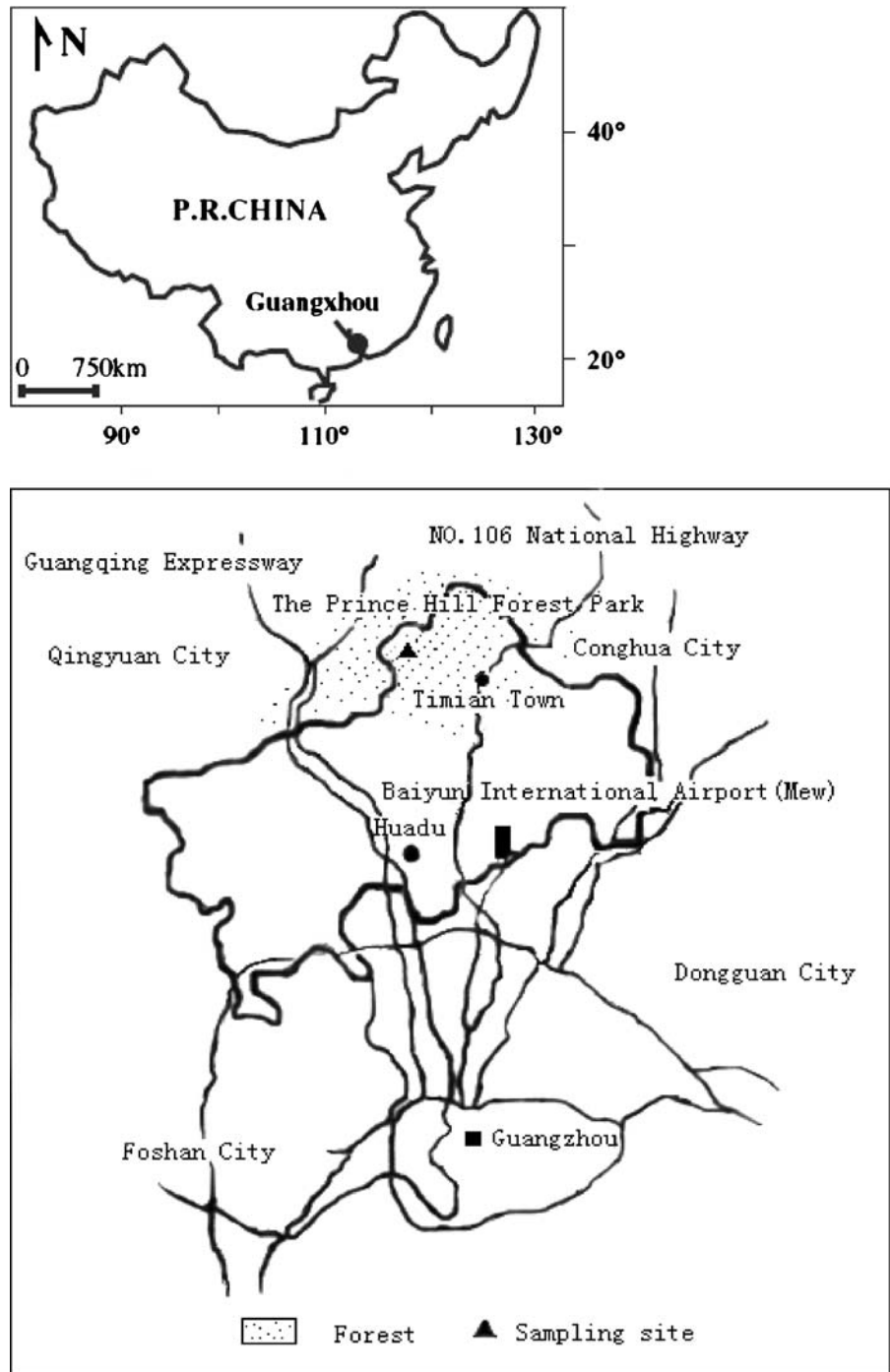
The carbonyl compound samples were collected by drawing air through the DNPH cartridges with a sampling pump (Thomas, USA) at a flow rate of 0.8–1.2 L min<sup>-1</sup>, which was measured by a digital flow meter (DryCal DC Lite, Bios Corp., USA) before and at the end of the sampling, every day eight 3-h samples were collected from 9 to 14 July, 2004. An ozone denuder (a copper tube coil of 1.2 m×0.5 mm i.d., inside coated with KI) was connected to the front of the cartridge to avoid degradation of the 2, 4-dinitrophenylhydrazones (Christensen et al. 2000; Müller et al. 2002). Each cartridge was sealed immediately after sampling, and then stored at 4°C. Upon arrived in the laboratory, they were back flushed with ACN into 2-mL volumetric flasks. The sample elutes were stored at 4°C in 2-mL vials until analyses by HPLC.

For the VOCs, the samples were collected using 2-L stainless steel canisters which were pre-cleaned five times using high-purity nitrogen and pre-evacuated by a canister cleaner (ENTECH Instruments Inc, Model 3100) before sampling. Air was sampled at 3-h intervals from 9 to 12 July, 2004. The sampling duration was 15 min for each sample.

### Analyses

Concentrations of carbonyls were determined using a high-performance liquid chromatograph (HPLC, HP

**Fig. 1** Location of the sampling site



1100) connected to a photo-diode-array detector (PDAD) at 360 nm and an Agilent SB-C<sub>18</sub> reverse column (250 mm×4.6 mm×5 μm). A 10 μl aliquot was injected into the HPLC through an auto-injection system and

analyzed under the following analytical sequence: mobile-phase gradient with a flow rate of 1 mL min<sup>-1</sup> from 60 to 70% ACN in water (v/v) for the first 20 min, 70 to 100% ACN for the next 3 min, 100% ACN

isocratic elution for another 4 min, and then 100 to 60% ACN for 1 min, finally, 60% ACN for 5 min isocratic. The lab blank cartridges were analyzed by HPLC and the results were below the EPA blank criteria (US EPA 1999b).

Measurements of VOCs were performed according to the US EPA Method TO-14A (US EPA 1997, 1999a) using gas chromatography/mass spectrometry (GC/MS, Agilent 6890N/5973N) equipped with a cryogenic concentrator (ENTECH Instruments Inc, Model 7100). During the enrichment by Entech 7100, 250 ml (1 atm, 0°C) air samples were drawn and underwent three-step (cryogenic trapping/water removing, CO<sub>2</sub> removing and cryo-focus) preconcentration. The concentrated target compounds were then thermally desorbed and carried by ultra-pure helium into the GC in splitless mode. The separation of the analytes was achieved with an HP-VOC capillary column (60 m×0.32 mm i.d., 1.8 μm film thickness). The helium carrier gas flow rate was 1.2 mL min<sup>-1</sup> and kept constant by varying the column head pressure as a function of column programmed temperature. The column temperature was initially hold at 40°C for 2 min, programmed at 6°C min<sup>-1</sup> to 230°C, and isothermal hold for 10 min. The mass-selective detector (MSD) was operated in the scan mode from 35–350 Da with ionization mode of EI.

The temperature and relative humidity were measured during sample acquisition using a TSI 8551 QTrak with CO Indoor Air Quality (IAQ) Analyzer. The data were collected consecutively every 3 h. In addition, the wind direction and velocity were also measured using a wind direction and velocity indicator (Nanjing Instrument Ltd., China). However, the wind velocities were generally below the limit of detection (LOD) the indicator, except during rain showers.

#### Quality control and quality assurance (QC/QA)

The sampling efficiency and breakthrough behavior of the prepared DNPH coated cartridges were investigated in earlier work (Feng et al. 2004). Identification and quantification of carbonyls were undertaken according to the retention times and peak areas of the corresponding calibration standards. Five standard stock solutions (from 0.5–10 ng μl<sup>-1</sup>) covering the expected concentrations for the samples were used. Calibration plots had excellent linear regression coefficients ( $r^2 > 0.999$ ) for all of the compounds.

Relative standard deviations (RSDs) for replicate analyses and method detection limits (MDLs) were also discussed previously (Feng et al. 2004).

Identification and quantification of VOCs were carried out according to their retention times and mass spectra. Standard VOC gas mixtures (Supelco TO-14 Calibration Mix) were dynamically diluted to different concentrations covering the concentration range of the samples. A seven-point calibration (0.0, 1.0, 5.0, 10.0, 20.0, 40.0, 50.0 ppbv) was carried out for quantification. The MDLs for all compounds were <0.2 ppbv (Zhao et al. 2004).

## Results and discussion

### Levels

Forty carbonyl samples, each for 3-h duration, were collected during the campaign and 20 kinds of carbonyl compounds were identified and quantified. Their concentrations were corrected by subtracting the average concentrations of four field blanks. Acetone was not quantified due to the high acetone background in the laboratory. The average concentrations of the carbonyls during the sampling intervals are summarized in Table 1. Total carbonyl concentrations ranged from 13.45 to 74.84 μg m<sup>-3</sup>. Formaldehyde (3.70±4.38 μg m<sup>-3</sup>) was the most abundant carbonyl compound in Prince Hill Forest Park, followed by acetaldehyde (3.33±3.65 μg m<sup>-3</sup>). The diurnal concentrations of formaldehyde and acetaldehyde varied from 1.44 to 6.05 μg m<sup>-3</sup> and 0.96 to 5.60 μg m<sup>-3</sup>, respectively. Their levels were similar to other reports in forests or rural sites, and lower than those in the urban sites (Table 2). Crotonaldehyde, which occurs naturally in foods or forms during combustion of fossil fuels and biomass (<http://monographs.iarc.fr/htdocs/monographs/vol63/crotonaldehyde.htm>), was detected only in six samples during the campaign. Acrolein, a common component in environmental tobacco smoke and vehicle emissions, was not detected. The concentrations of other carbonyls varied from 0.74 to 1.78 μg m<sup>-3</sup>.

In this study, many species of VOCs were detected, however only eight compounds were selected to be quantified according to the following criteria: (1) highly reactive compounds, which are important in ozone formation, photochemical oxidants and

**Table 1** Statistical summary concentrations ( $\mu\text{g m}^{-3}$ ) of carbonyls at Prince Hill Forest Park

Compounds	AM <sup>a</sup>											AM $\pm$ SD <sup>b</sup>	N	Max.	Min.
	0:00–3:00	3:00–6:00	6:00–9:00	9:00–12:00	12:00–15:00	15:00–18:00	18:00–21:00	21:00–0:00							
Formaldehyde	2.97	4.53	1.44	4.79	4.79	3.37	6.05	1.65	3.70 $\pm$ 4.38	40	17.93	0.24			
Acetaldehyde	2.82	3.01	0.96	5.60	4.83	2.65	4.15	2.30	3.33 $\pm$ 3.65	38	12.91	0.02			
Acrolein	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd		Nd	Nd			
Propionaldehyde	0.82	0.74	0.80	1.15	1.16	0.86	0.88	0.76	0.90 $\pm$ 0.24	40	1.62	0.63			
Crotonaldehyde	1.15	1.02	Nd	1.13	1.00	Nd	1.04	Nd	1.06 $\pm$ 0.07	6	1.15	0.99			
2-Butanone	0.87	0.93	0.85	1.90	1.96	1.15	1.09	0.87	1.20 $\pm$ 0.60	40	2.75	0.57			
Butyraldehyde	1.00	0.96	0.94	1.10	1.06	1.01	0.99	0.96	1.00 $\pm$ 0.10	40	1.31	0.81			
Benzaldehyde	0.85	0.79	0.87	1.03	1.04	0.84	0.81	0.81	0.88 $\pm$ 0.15	40	1.40	0.70			
Isovaleraldehyde	0.78	0.77	0.72	0.87	0.91	0.81	0.77	0.77	0.80 $\pm$ 0.11	40	1.06	0.63			
Cyclohexanone	0.64	0.66	0.67	1.02	0.92	0.68	0.74	0.60	0.74 $\pm$ 0.20	39	1.24	0.48			
Valeraldehyde	1.37	1.40	1.35	1.66	1.61	1.48	1.40	1.25	1.44 $\pm$ 0.19	40	2.10	1.17			
p-Tolualdehyde	1.00	1.00	0.91	1.07	0.93	0.92	1.00	1.02	0.98 $\pm$ 0.11	40	1.24	0.75			
m/o-Tolualdehyde <sup>c</sup>	2.64	3.01	3.15	3.53	4.18	3.32	2.96	2.81	3.20 $\pm$ 1.05	40	7.13	1.86			
Hexaldehyde	1.47	1.40	1.44	2.05	2.58	1.92	1.98	1.44	1.78 $\pm$ 0.54	40	3.44	1.21			
2, 5-DMBal	1.03	1.05	0.99	1.23	1.17	1.02	0.97	1.03	1.06 $\pm$ 0.12	23	1.44	0.91			
Heptaldehyde	0.75	0.76	0.70	1.35	0.72	0.63	0.59	0.6	0.81 $\pm$ 0.47	26	2.87	0.55			
Octylaldehyde	1.47	1.07	1.03	1.47	0.99	1.10	0.74	3.76	1.33 $\pm$ 1.56	33	9.23	0.61			
Nonanalaldehyde	0.78	0.75	0.83	1.77	3.13	1.63	1.59	1.23	1.46 $\pm$ 0.93	40	4.11	0.66			
Decylaldehyde	0.89	0.74	0.87	1.15	1.23	0.94	0.83	0.79	0.93 $\pm$ 0.26	40	1.91	0.66			

2, 5-DMBal: 2, 5-Dimethylbenzaldehyde; N: number of samples calculated using only those with detectable carbonyls; Nd: not detected; <sup>a</sup>the arithmetic mean during the same sampling interval; <sup>b</sup>the arithmetic mean and standard deviation for all samples; <sup>c</sup>these two compounds could not be separated entirely in HPLC and were quantified as the sum.

**Table 2** Average (or range) of formaldehyde and acetaldehyde concentrations in ambient compared with other studies ( $\mu\text{g m}^{-3}$ )

Location	Date	Formaldehyde	Acetaldehyde
Forest			
Guangzhou <sup>a</sup>	Aug 2004	3.70±4.38	3.33±3.65
New Mexico <sup>b</sup>	Jun–Aug 1997	1.7±1.7	0.5±0.04
Bavaria <sup>c</sup>	Jun 2001,2002	4.9	2.8
Rural			
Socorro, NM <sup>b</sup>	Jun–Aug 1997	2.5±1.0	0.7±0.5
Paris <sup>b</sup>	Jul 1986	5.2–7.5	1.5
Leipzig <sup>d</sup>	May 1998	5.5±3.0	0.8±0.3
Urban			
Los Angeles <sup>b</sup>	Oct 1993	4.0±1.8	2.0±1.2
Guangzhou <sup>e</sup>	Jul–Sep 2003	13.68	8.33
Rio de Janeiro <sup>f</sup>	May–Nov 2000	10.8±4.1	10.4±4.6

<sup>a</sup>This study.<sup>b</sup>Fierro et al. (2004).<sup>c</sup>Müller et al. (2006).<sup>d</sup>Müller et al. (2002).<sup>e</sup>Feng et al. (2004).<sup>f</sup>Grosjean et al. (2002).

precursors of carbonyls (e.g. isoprene); and (2) have adverse effects to human health (e.g. BTEX). The average concentrations of the selected VOCs during the same sampling interval are shown in Fig. 2. The most abundant VOC was isoprene ( $14.90 \mu\text{g m}^{-3}$ ), followed by o-xylene ( $2.21 \mu\text{g m}^{-3}$ ) and m/p-xylene ( $2.15 \mu\text{g m}^{-3}$ , these two compounds could not be separated entirely in GC and were quantified as the sum). Ethylbenzene was not detected in this study. The total average concentration of BTEX was  $6.29 \mu\text{g m}^{-3}$ , which were lower than those in urban regions (Wang et al. 2002; Takigawa et al. 2004; Lü et al. 2006).

#### Meteorological conditions, sources and photochemical activity in relation to diurnal trends

Meteorological conditions at the sampling site have to be taken into account when attempting to understand not only the sources of the targeted compounds, but also their diurnal variations. During the campaign, it was hot summer in south China, with occasional rain showers. The highest air temperatures were found at noon while the relative humidity was the lowest, when the sunlight was strong and surface temperature was

high. Far away from the urban areas, the site had less anthropogenic interference.

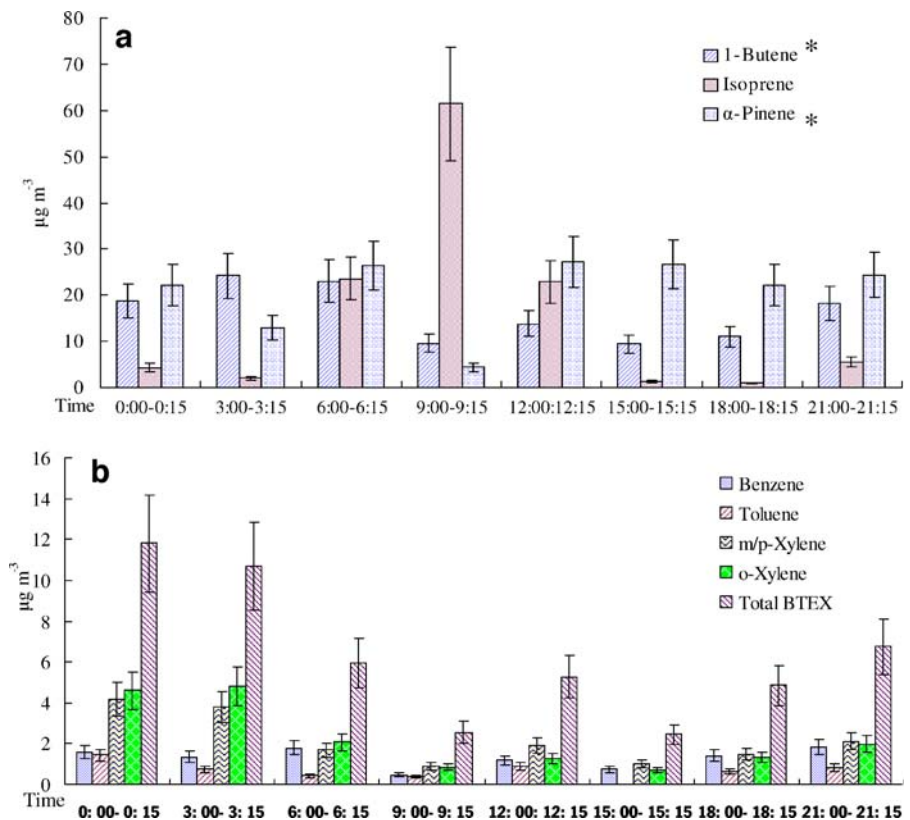
The concentrations of the targeted carbonyls and VOCs showed different diurnal profiles. This might be explained by vegetation emissions, long-range transportation, or photochemical production and removal. In the forested sampling site, the vegetation emission and chemical removal should play important roles. The hydroxyl radical (OH), ozone and NO<sub>x</sub> are the major tropospheric oxidants responsible for the removal of many anthropogenic pollutants and biogenic VOCs. In forested regions, the dominant biogenic VOC species from vegetation, like isoprene and  $\alpha$ -pinene, would undergo rapid reaction with the OH radical during the daytime and NO<sub>x</sub>-initiated reactions at night. The OH-initiated oxidation is believed to follow the general pattern of hydrocarbon oxidation in the presence of NO<sub>x</sub> and lead to the formation of carbonyl compounds.

#### Carbonyls

During the field campaign, the study showed that most carbonyls (C<sub>3</sub>–C<sub>10</sub>) exhibited a significant diurnal cycle, with the exception of formaldehyde, acetaldehyde and octylaldehyde. Their typically high values were found from 09:00 to 15:00, when the sunlight and radiation were strong. Their concentrations decreased during nighttime till early in the morning (Table 1). Recent studies found that some plants could emit various carbonyls, most of which had higher molecular weights (Lü et al. 2006). The directly emission from vegetation might be the main primary sources, while the photochemical oxidation of gas-phase hydrocarbons and heterogeneous interactions of carbonyls might be the secondary sources.

It was reported that the diurnal profiles of OH radical were maximal at noon and minimal at 18:00 in forests (Kavouras et al. 1999). The concentration of ozone also has a clear diurnal variation with higher level at noon to 18:00, and lower level was measured between midnight and 06:00 (Kavouras et al. 1999). The diurnal variations of most carbonyls are associated with the inferred concentrations of OH radical and ozone according to this study. Here the high concentrations of carbonyls were observed before OH radical and ozone reached their maxima. These characteristics were similar to the report of Müller et al. (2002). During this campaign, samples were collected in hot summer in south China with occasional rain showers. However,

**Fig. 2** Diurnal concentrations of 1-butene, isoprene,  $\alpha$ -pinene and BTEX measured during August, 2004, in Forest Park in South China. Asterisk: the concentrations of the compounds were magnified 20 times on the graph



the carbonyl concentrations, except formaldehyde and acetaldehyde, seemed to be not affected by rain, probably due to their lower water solubility. So the carbonyl concentrations might be controlled by the photochemical production from reactions of precursor VOCs with OH radical, ozone and NO<sub>x</sub>, heterogeneous interactions of aldehydes, direct emissions from vegetation, and by removal from their reactions with OH radical and NO<sub>x</sub>.

However, the two most abundant carbonyls, formaldehyde and acetaldehyde, showed different diurnal profiles with the other carbonyls, which suggested different formation mechanisms and sinks compared to the others. Their similar diurnal variations suggested their similar formation and decomposition pathways. Formaldehyde and acetaldehyde originate from directly biogenic emissions and secondary formation in a forest region. The reactions of alkenes, terpenes and other organic compounds emitted by vegetation with ozone or OH radical are very important for their secondary formation (Feltham et al. 2000). For example, (Z)-3-hexene-1-ol and (Z)-3-hexenylacetate, emitted by many plants, can be transformed to formaldehyde and

acetaldehyde in the atmosphere (Atkinson 1990). Methanol from vegetation also contributes to the production of formaldehyde (MacDonald and Fall 1993; Nemecek-Marshall et al. 1995).

The formaldehyde/acetaldehyde ( $C_1/C_2$ ) concentration ratio, which has been proposed as an indicator of formaldehyde sources, was 0.87 using the slope derived from linear regression analysis (Shepson et al. 1991). It was lower than that reported in a semi-rural site by Christensen et al. (2000). The diurnal  $C_1/C_2$  ranged between 0.72 and 1.50 (Fig. 3). This may be due to the different production and removal rates of formaldehyde and acetaldehyde over a diurnal cycle. The main sources of formaldehyde and acetaldehyde during the day are biogenic and secondary formation by photo-oxidation of VOCs, while the main removal processes during nighttime might be the reaction with nitrate radicals, wet and dry deposition (Christensen et al. 2000). The rate constants for the reactions of nitrate radicals (half-lives 3–10 s) with formaldehyde are  $3.23 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $1.2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  with acetaldehyde. Dry deposition is an

important sink for formaldehyde with a rate once estimated to be  $0.45 \text{ cm s}^{-1}$  (Thompson 1980), but the dry deposition velocity for acetaldehyde is very low (Wesely 1989; Kanakidou et al. 1991). In the present study due to high relative humidity during the nighttime, dry deposition might not play an important role, but the long-distance transport far away from the polluted urban should be considered. This could be confirmed by the higher nighttime concentration of octylaldehyde, which are produced by the oxidation of octane contained in gasoline. The concentration of BTEX as discussed below also confirmed this contribution from transport. These processes all tended to increase  $C_1/C_2$  during the night and decrease the ratio during the day. Due to the high aqueous solubility of formaldehyde and acetaldehyde, their concentrations were strongly affected by rain showers, i.e., low concentrations after rain.

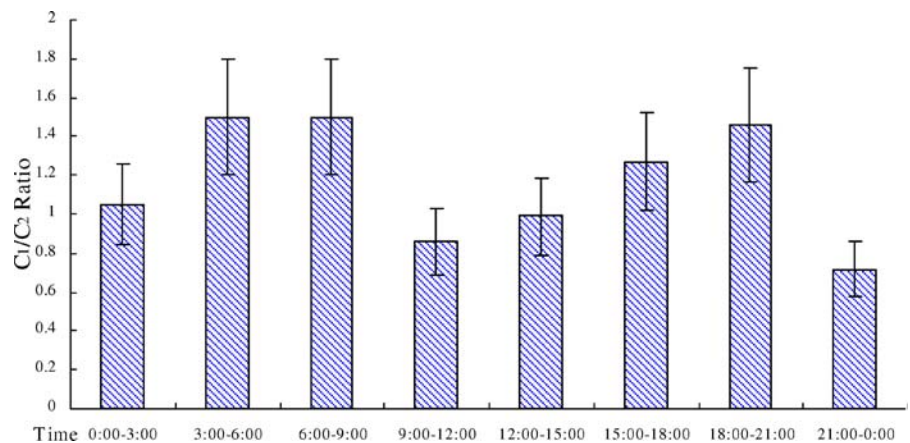
#### Alkene, isoprene and monoterpenes

Alkenes and terpenes, such as isoprene, 1-butene and  $\alpha$ -pinene, which are all reactive species in the atmospheric environment, are considered to be the most prominent compounds produced by vegetations, especially in forests (Kesselmeier et al. 1997; Kesselmeier and Staudt 1999). The diurnal variations of these active compounds reflect the diverse environment factors, such as light, temperature and emission rates from different trees, shrubs or other vegetation (Yokouchi and Ambe 1984). For instance, the *Sphagnum* fen was found to emit significant amounts of isoprene with the emission rate averaging  $912 \pm 750 \text{ nmol m}^{-2} \text{ h}^{-1}$  ( $55 \pm 45 \text{ } \mu\text{gC m}^{-2}$

$\text{h}^{-1}$ ) in June and  $6,800 \pm 4,000 \text{ nmol m}^{-2} \text{ h}^{-1}$  ( $408 \pm 240 \text{ } \mu\text{gC m}^{-2} \text{ h}^{-1}$ ) in August (Janson et al. 1999).

As the lifetimes of these active compounds are affected by the atmospheric oxidants (Fierro et al. 2004), including OH, ozone and NO<sub>x</sub>, their diurnal cycle are also of concern. In this study, higher concentrations for 1-butene were observed from 03:00 to 06:00 with the minimal concentrations of OH radical and ozone (Kavouras et al. 1999) and low temperature. With the increasing concentrations of OH radical and ozone, the lower levels were measured. The photochemical oxidation process was the main removal way for 1-butene. Isoprene and  $\alpha$ -pinene were known as light and temperature dependent for their vegetation emissions; their removal also depends on reactions with OH radical, ozone and NO<sub>x</sub>. Higher levels of isoprene were measured from 06:00 to noon, different from another report with maximum in late afternoon (Wiedinmyer et al. 2001).  $\alpha$ -pinene had higher levels from 12:00 to 15:00 and lower ones during the late afternoon and nighttime (Fig. 2). The higher concentration of  $\alpha$ -pinene appeared immediately before the maximum inferred concentration of OH radical and ozone (Kavouras et al. 1999), and then decreased through the noon. Its diurnal pattern was similar to previous studies (Goldan et al. 1995; Beienthal et al. 1998). These reflected their differences in emissions and photochemical processes. The major species reacting with OH during the day was isoprene, with the  $\alpha$ -pinene becoming more important at nighttime. The isoprene emission rate is both temperature and light intensity dependent and hence low during the night, whereas emissions of  $\alpha$ -pinene from vegetation depend exponentially upon temperature, peaking

**Fig. 3** Diurnal concentration ratio variations of formaldehyde/acetaldehyde ( $C_1/C_2$ ) measured during August 2004, in Forest Park in South China





during daylight hours, but continuing through the night (Harrison et al. 2001). However, the rapid reaction of  $\alpha$ -pinene with OH ensured that its concentration peak at night. The daytime isoprene emission rate is much greater than that of  $\alpha$ -pinene (Harrison et al. 2001), which explains its elevated concentration despite its rapid rate of reaction with OH.

Another point of interest is the chemical lifetime of the isoprene and  $\alpha$ -pinene. They have lifetimes of 3 h and 2–3 h in daytime, 1.5 h and 5–30 min during nighttime, respectively. Lifetimes are estimated in relation to the concentration of  $10^6$  molecules/cm<sup>3</sup> for OH radical and 20 ppb for ozone during daylight, and to 10 ppt for NO<sub>3</sub> radical and 20 ppb for ozone during the nighttime (Kesselmeier et al. 1997). They are also easily destroyed in the troposphere by reactions with OH radical and ozone. The reaction rate constants for isoprene and  $\alpha$ -pinene are  $1.01 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and  $5.37 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> with OH radical, and  $1.28 \times 10^{-17}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and  $8.66 \times 10^{-17}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> with ozone, respectively (Biesenthal et al. 1998). The chemical lifetime of the OH radical, defined as the reciprocal of the total pseudo first-order rate constant for reaction of OH, is typically around 0.1 s during the night, and increases to 0.15 s during the day (Carslaw et al. 2001). The shorter lifetime at night reflects the much higher concentrations of the  $\alpha$ -pinene. Isoprene is the most important species controlling the OH lifetime during the day, consequently, atmospheric concentrations of isoprene exhibit a strong diurnal cycle with a maximum in the daytime.

### BTEX

BTEX are less active VOCs in the atmosphere. In urban regions, automobiles are the dominant source of BTEX. These compounds are added to fuels to increasing the octane number and are emitted to the urban atmosphere as a component of automobile exhaust and by gasoline evaporation and spillage (Yassaa et al. 2006). In forested regions, some of BTEX, like toluene, was found emitted by many plants (Heiden et al. 1999).

In the present study, different diurnal profiles for BTEX compared to the alkenes and terpenes were found possibly due to their less reactivity. The higher values for BTEX were around midnight and lower in late afternoon. The night to daytime concentration ratios (night is defined as from 18:00 to 06:00 next day, and the day is 06:00 to 18:00) were 1.63, 1.26, 2.32,

3.35 for benzene, toluene, m/p-xylene and o-xylene, respectively. The diurnal ratio variations of these compounds are similar to the seasonal ratio variations of VOCs, higher in winter than in summer (Lee et al. 2002; Lü et al. 2006). This could be explained by meteorological factors, which affected the concentrations of BTEX in the day and nighttimes. First, their backgrounds are different during the day and the nighttime. Urban plume might be transported far away to the sampling locations during the night, thus BTEX concentrations reached their highest levels in the midnight. But there might be other reasons. Because benzene to toluene ratios can be used as indicators of air mass processing and the degrees to which OH and dilution affect the air mass. The dominant emissions of benzene and toluene are from petrochemical sources at a ratio of approximately 0.25 (Lee et al. 2006). But in this study, the average ratios were 0.96 and 1.48 during the daytime and nighttime, respectively. Chemical reaction processes, especially with OH radicals, are more important during the day. The rate constants ( $K_{OH}$ ) for the gas-phase reaction of OH radical with benzene, toluene, m-xylene, o-xylene and p-Xylene are  $1.23 \times 10^{-12}$ ,  $5.96 \times 10^{-12}$ ,  $7.1 \times 10^{-12}$ ,  $13.0 \times 10^{-12}$  and  $14.3 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively (Yassaa et al. 2006). Due to the higher OH radical concentration, sunlight and higher temperature in the daytime, their removal rates are faster in the day compared to nighttime.

### Summary and conclusion

Diurnal patterns of carbonyls and VOCs were measured in 2004 in Prince Hill Forest Park, Huadu District, 90 km north of Guangzhou, China. Twenty carbonyls were identified and quantified, and among them formaldehyde and acetaldehyde were the two most abundant carbonyls. Eight VOC species were also identified and quantified, and isoprene was the most abundant. The results showed C<sub>3</sub>-C<sub>10</sub> carbonyls exhibited similar diurnal cycle with high values typically from 09:00 to 15:00, while formaldehyde, acetaldehyde and octylaldehyde had two peak levels during a day. Compared to carbonyls, most VOCs showed different diurnal cycles. Higher concentrations for 1-butene were observed from 03:00 to 06:00 and from 06:00 to 12:00 for isoprene, different from other reports with maximums in late afternoon. Higher concentrations for  $\alpha$ -pinene

were found from 12:00 to 15:00. High levels of BTEX occurred around midnight and lower levels were found in late afternoon. The main sources and sinks of carbonyls and VOCs in this region were photo-oxidation and biogenic emissions. Some compounds, such as formaldehyde, acetaldehyde and BTEX, also showed anthropogenic sources.

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