



Characteristics of fine particulate non-polar organic compounds in Guangzhou during the 16th Asian Games: Effectiveness of air pollution controls[☆]



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HIGHLIGHTS

- Vehicular emissions were the major contributors to atmosphere during the Games.
- *n*-Alkanes and PAHs were more abundant in the nighttime than those in the daytime.
- PAHs/biogenic OC were used to evaluate the effectiveness of air pollution controls.

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ABSTRACT

The concentrations of organic compounds, including *n*-alkanes and polycyclic aromatic hydrocarbons (PAHs), in fine particles (PM_{2.5}) were measured in an urban area of Guangzhou before, during, and after the 16th Asian Games (9–30 November 2010). Higher average concentrations of *n*-alkanes and PAHs occurred in the nighttime, presumably due to a restriction on motor vehicle operation during the day and the accumulation of pollutants due to temperature inversions at night. The carbon preference index, contributions of wax *n*-alkanes, and PAHs diagnostic ratios indicated that the main sources of *n*-alkanes and PAHs were anthropogenic, especially motor vehicle emissions. The CMAQ model was used to estimate the percentages of biogenic organic aerosol in the total organic aerosol, then the ratios of source marker PAHs to biogenic organic carbon were used to evaluate the air pollution control policies effectiveness during the Asian Games.

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1. Introduction

Organic compounds account for a large fraction of atmospheric particulate matter (PM), especially PM less than and equal to 2.5 μm (PM_{2.5}, He et al., 2006; Seinfeld and Pankow, 2003). Measurements

of the specific compounds can provide information on the sources for organic substances and their potential impacts on human health, air quality, and climate (Dockery et al., 1993; Mauderly and Chow, 2008; Jacobson et al., 2000; Turpin et al., 2000). *n*-Alkanes and polycyclic aromatic hydrocarbons (PAHs) are non-polar organic compounds of special interest because they are ubiquitous in the atmosphere and some of those compounds are emitted from known sources (Schauer et al., 1996; Tobiszewski and Namiesnik, 2012; Zheng et al., 2002).

The 16th Asian Games were held in Guangzhou, China, which is on the northern margin of the Pearl River Delta (PRD) area, in

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November 2010. The Municipal Government of Guangzhou implemented a series of measures to reduce air pollution during the games, promoting the goal of “Green Asian Games”. One of these measures was a restriction on motor vehicle operation (vehicles with license plates ending in odd numbers were banned from the roads on even-numbered calendar days and vice versa); this policy was implemented from 7:00 to 20:00 from 1 to 29 November 2010 throughout the city (Supplemental Table 1).

Our studies investigated whether the pollution control measures implemented for the Asian Games affected the loadings of *n*-alkanes and PAHs. The objectives of this study were to: (1) determine daytime and nighttime *n*-alkane and PAH loadings in PM_{2.5} before, during, and after the Asian Games; (2) identify potential pollution sources; and (3) evaluate the effectiveness of the air quality-management policies.

2. Materials and methods

2.1. Site description

PM_{2.5} filter samples were collected at the South China Institute of Environmental Sciences from 9 to 30 November 2010. The site is located in an urban area of Guangzhou (23°07' N, 113°21' E), ~5.0 km southwest of the Guangzhou National Olympic Sports Center. No obvious pollution sources are located near the site, which is surrounded by resident and commercial buildings. The sampling equipment was installed on the roof (50 m above ground level) of the office building (Tao et al., 2009, 2012).

2.2. Continuous observations of gases and meteorological parameters

Gaseous criteria pollutants (measured every 5 min) were monitored from 1 September to 31 December 2010. Carbon monoxide (CO), nitrogen oxides (NO_x), sulfur dioxide (SO₂), and ozone (O₃) were measured with species specific analyzers (Models 48i, 42i, 43i, and 49i, respectively, Thermo Fisher Scientific Inc., Franklin, MA, USA). All gas analyzers were calibrated weekly with the use of a Model 146i Multigas Calibrator (Thermo Fisher Scientific Inc.), and zero checks were performed daily with a Model 111 Zero Air Supply (Thermo Fisher Scientific Inc.). Minimum detection limits (MDLs), precisions of the analyses, and measurement ranges – in that order – were as follows: 0.05 mg m⁻³, ±0.12 mg m⁻³, and 0–5.76 mg m⁻³ for CO analyzer; 0.76 μg m⁻³, ±0.76 μg m⁻³, and 0–0.95 mg m⁻³ for NO_x analyzer; 2.64 μg m⁻³, ±2.64 μg m⁻³, and 0–1.32 mg m⁻³ for SO₂ analyzer; 0.49 μg m⁻³, ±1.98 μg m⁻³, and 0–0.99 mg m⁻³ for O₃ analyzer, respectively.

Meteorological parameters, including temperature, relative humidity (RH), and wind speed were measured every 30 min. Ambient temperature and RH were measured with the use of a temperature/RH probe (Model QMH102, Vaisala); wind speed was recorded by a wind monitor (Model QMW110A, Vaisala, Helsinki, Finland).

2.3. Fine particulate matter (PM_{2.5}) collection

The filter sampling period was divided into intervals: (1) pre-Asian Games (pre-AG): nighttime 9 November to daytime 12 November; (2) during the games (dur-AG): nighttime 12 November to nighttime 27 November; and (3) post-AG: daytime 28 November to nighttime 30 November. The PM_{2.5} samples were collected with a Gravisol Sequential Ambient Particulate Monitor (Casella Monitor Inc., UK), which uses a cyclone to separate PM_{2.5} and was operated at a flow rate of 16.7 L min⁻¹. The Gravisol sampler has an automatic filter-changing system with a capacity of up to 18 filters, and it uses

an active volumetric flow-control system. The air stream was connected to a 47 mm Whatman quartz-fibre filter (QM/A®, Whatman Inc., UK). Before sampling, the quartz filters were baked at 800 °C for at least 4 h to remove adsorbed organic vapors. The flow rate of the PM_{2.5} sampler was calibrated every three days by using the Defender 510 Volumetric Primary Flow Standard (Bios International Corporation, Butler, NJ, USA). The relative error was approximately ±2%. In all, 21 daytime (from 8:00 a.m. to 7:00 p.m. local time) and 21 nighttime (from 8:00 p.m. to 7:00 a.m. the next day) samples were collected. Three field blanks were collected and used to account for any artifacts caused by gas absorption. The aerosol-loaded filter samples were stored in a freezer at 20 °C before analysis to prevent the volatilization of particles.

2.4. Mass and carbonaceous aerosol analyses

For the aerosol mass determinations, the PM_{2.5} quartz filters were weighed before and after sampling. The filters were weighed using a Sartorius ME 5-F electronic microbalance (±1 μg sensitivity, Sartorius, Gottingen, Germany) (Cao et al., 2005). Organic carbon (OC) and elemental carbon (EC) were determined for punches (0.53 cm²) of the PM_{2.5} filters. A Desert Research Institute (DRI) Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, CA, USA) was used for the analyses. Detailed information on the procedures used for mass and OC/EC determinations along with QA/QC has been presented in Cao et al. (2003, 2005).

2.5. Non-polar organic analysis

Solvent extraction (SE) followed by gas chromatography/mass spectrometry (GC/MS) (USEPA Method TO-13A, 1997) is a commonly used method for quantifying organic compounds in environmental samples. Thermal desorption (TD) coupled with GC/MS is an alternative method (Van Drooge et al., 2009; Chow et al., 2007; Ho and Yu, 2004), and an in-injection port TD-GC/MS procedure as used in our study involves a short sample preparation time (<1 min), avoids contamination from solvent impurities, and is highly sensitive (Ho and Yu, 2004; Ho et al., 2008, 2011).

Details of this method have been described in previously (Ho and Yu, 2004; Ho et al., 2008, 2011). Briefly, different sized aliquots of the filters (0.53–2.63 cm²) were used for analyses because the aerosol loadings were different. The aliquots were cut into small pieces and inserted into the TD tube, which was the same dimension as GC/MS injector liner. The temperature of the injector port was lowered to 50 °C before analysis; it was then raised to 275 °C for desorption in a splitless mode while the GC oven temperature was kept at 30 °C. After the injector temperature reached 275 °C, the GC analysis and MS detection began. QA/QC information of our TD-GC/MS method may be found in Supplemental Table 2 and Cao et al. (2012).

2.6. CMAQ model

We used the community multiscale air-quality model (the CMAQ, version 4.7.1, Binkowski and Roselle, 2003) to simulate the organic aerosol, including the secondary organic aerosol contributions from glyoxal and methylglyoxal (Li et al., 2013). The model was driven by meteorological fields simulated by the Weather Research and Forecasting model (WRF, version 3.2.1, Skamarock et al., 2008). We set three nested model domains, with horizontal resolutions of 27 km, 9 km, and 3 km, with the innermost domain covering Guangzhou. Twenty-six vertical layers extended from the surface to 50 hPa, with 17 layers in the bottom 1 km. Initial and boundary concentrations for the simulation were taken from

monthly mean concentrations simulated by a global chemical transport model (Fu et al., 2012).

Emissions for the CMAQ model were from biogenic and anthropogenic sources, including biomass burning. Anthropogenic emissions of primary organic carbon (POC) and non-methane volatile organic compounds (NMVOCs) were taken from Zhang et al. (2009): for the PRD, anthropogenic OC and NMVOC emissions were 39.8 GgC y^{-1} and 527.2 Gg y^{-1} , respectively. We applied seasonal and diurnal variations to these emissions based on provincial statistics. Biomass burning emissions of POC (9.8 GgC y^{-1}) and NMVOC (34.0 Gg y^{-1}) were taken from the inventories developed by He et al. (2011) and Streets et al. (2003). Biogenic emissions of NMVOC precursors were taken from the Model of Emissions of Gases and Aerosols from Nature (MEGAN, version 2.04, Guenther et al., 2006). Seasonal and diurnal variations of the MEGAN biogenic emissions were driven by meteorological fields simulated by the WRF. The emissions of isoprene and the monoterpenes, the main biogenic VOC precursors in the PRD, were 176 Gg y^{-1} and 149 Gg y^{-1} , respectively.

3. Results and discussion

3.1. *n*-Alkane and PAH concentrations

Twenty-two *n*-alkanes and eighteen PAHs were detected in all samples; their average concentrations were $48.1 \pm 20.8 \text{ ng m}^{-3}$ and $19.0 \pm 17.5 \text{ ng m}^{-3}$, respectively. The *n*-alkanes ranged from 15.9 ng m^{-3} (17 November day) to 121.1 ng m^{-3} (10 November night), while the PAHs ranged from 3.3 to 102.1 ng m^{-3} (the lowest and highest values were in the same samples as the *n*-alkanes, Fig. 1).

During the night of 10 November, the criteria gaseous pollutants, *n*-alkanes and PAHs all peaked simultaneously (Fig. 1). This

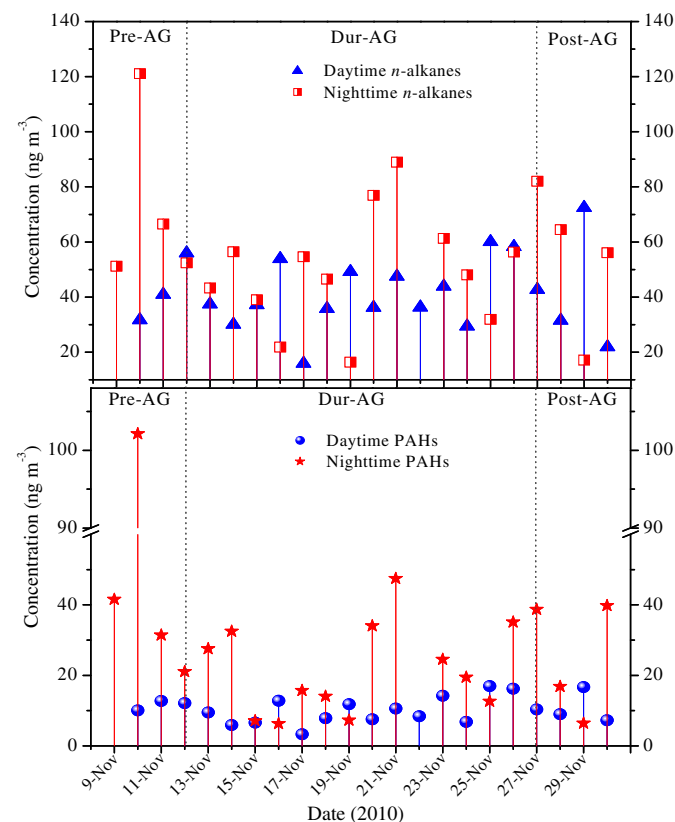


Fig. 1. Time series of *n*-alkane and PAH concentrations (units: ng m^{-3}).

pollution episode clearly is not representative of typical *n*-alkane and PAH concentrations in Guangzhou, and since we are mainly concerned in this paper with the effectiveness of the pollution control measures implemented for the Asian Games, not specific events, we did not include this sample in the following discussion. The average concentrations of the *n*-alkanes were 49.3 ± 13.5 , 46.3 ± 17.3 , and $43.9 \pm 23.4 \text{ ng m}^{-3}$ in pre-AG, dur-AG, and post-AG, respectively. For the PAHs, average concentrations were 21.6 ± 14.1 , 16.4 ± 11.4 , and $16.0 \pm 12.5 \text{ ng m}^{-3}$ in pre-, dur-, and post-AG, respectively (Table 1). All of these three periods were within the Asian Games pollution control period, but the concentrations of both *n*-alkanes and PAHs were slightly higher in the pre-AG samples.

The 11-h average *n*-alkane and PAH concentrations during the night (51.6 ± 19.9 and $24.0 \pm 13.1 \text{ ng m}^{-3}$, respectively) were much higher than those in the day (41.3 ± 13.6 and $10.3 \pm 3.7 \text{ ng m}^{-3}$, Table 1). The average night to day ratios (N/D) were 1.3 for *n*-alkanes and 2.3 for the PAHs. The high nighttime concentrations and high N/D ratios can be explained by the fact that the odd-even day traffic restriction scheme was only enforced from 7:00 a.m. to 8:00 p.m. Pollutants presumably also accumulated at night due to temperature inversions.

The levels of *n*-alkanes and PAHs we observed are lower than those reported for previous studies in Guangzhou (Feng et al., 2006a; Gao et al., 2011; Tan et al., 2011; Wang et al., 2006; Yang et al., 2010a; Zheng et al., 2011a,b). For example, Feng et al. (2006a) reported average concentrations of *n*-alkanes (98 ng m^{-3}) and PAHs (38 ng m^{-3}) that were more than twice those found in this study, with higher concentrations in the winter. Similarly, Zheng et al. (2011a) reported average concentrations of *n*-alkanes and PAHs in Guangzhou during 2002–2003 of 105.6 and 38.1 ng m^{-3} .

The levels of *n*-alkanes and PAHs in our study were lower than those reported for several Chinese cities, including Nanjing (Wang and Kawamura, 2005; Wang et al., 2007), Beijing (Duan et al., 2010; Feng et al., 2006a; Ma et al., 2011), and Tianjin (Li et al., 2010). However, the concentrations were comparable to those in Shanghai (Feng et al., 2006a,b; Gu et al., 2010) and much higher (only for the PAHs) than in Xiamen (Zhao et al., 2010), Changsha (Yang et al., 2010b), or Dalian (Tian et al., 2009). *n*-Alkane and PAH concentrations in the USA (Rinehart et al., 2006; Yan et al., 2009) are typically one to three orders-of-magnitude lower than those in Guangzhou.

Table 1

Basic information and results from this study for the different sampling periods.

Study period	Number of samples		Temperature ($^{\circ}\text{C}$)		Relative humidity (%)		Wind speed (m s^{-1})	
	Day	Night	Day	Night	Day	Night	Day	Night
Pre-AG	3	3	25.2	20.8	26	40	0.3	0.0
Dur-AG	15	15	23.0	20.1	45	60	0.4	0.3
Post-AG	3	3	23.2	19.7	49	61	0.3	0.3
Average	/	/	23.3	20.1	43	58	0.4	0.3
	CO (mg m^{-3})		NO _x (mg m^{-3})		SO ₂ ($\mu\text{g m}^{-3}$)		O ₃ (mg m^{-3})	
	Day	Night	Day	Night	Day	Night	Day	Night
Pre-AG	0.88	1.21	0.16	0.32	13.99	17.86	0.10	0.01
Dur-AG	1.20	1.32	0.10	0.19	7.01	7.82	0.09	0.02
Post-AG	2.00	2.10	0.11	0.14	6.89	7.00	0.08	0.02
Average	1.26	1.43	0.11	0.19	7.99	8.70	0.09	0.02
	Total <i>n</i> -alkanes (ng m^{-3})		Total PAHs (ng m^{-3})					
	Day	Night	Day	Night				
Pre-AG	42.9 ± 12.3	58.9 ± 10.3	11.6 ± 1.4	36.5 ± 7.2				
Dur-AG	40.9 ± 11.7	51.8 ± 20.5	9.9 ± 3.9	22.9 ± 12.7				
Post-AG	42.0 ± 26.8	45.9 ± 25.3	11.0 ± 5.0	21.0 ± 17.1				
Average	41.3 ± 13.6	51.6 ± 19.9	10.3 ± 3.7	24.0 ± 13.1				

Even though *n*-alkane and PAH concentrations may have declined somewhat in Guangzhou, the high loadings are still a cause for concern.

3.2. *n*-Alkanes

C_{max} , that is, the *n*-alkane exhibiting the highest concentration, has been used to distinguish biogenic from anthropogenic sources (Simoneit, 1984, 1985). Lower molecular weight (LMW $\leq C_{26}$) *n*-alkanes are mainly derived from fossil fuel combustion while higher MW (HMW $> C_{26}$) *n*-alkanes are typically biogenic (Simoneit, 1984, 1985). The carbon preference index (CPI, the relative quantities of odd/even carbon number *n*-alkanes) and the contribution of wax *n*-alkanes (% wax C_n) also have been used to evaluate the contributions of biogenic versus anthropogenic sources (Peltzer and Gagosian, 1989; Simoneit, 1985). Here the % wax C_n (Simoneit et al., 1991) was calculated as:

$$\% \text{ wax } C_n = \frac{\sum (C_n - 0.5(C_{n-1} + C_{n+1}))}{\sum C_n} \times 100 \quad (1)$$

where negative values are taken as zero, wax C_n is the concentration of a plant wax *n*-alkane. Higher % wax C_n values indicate greater contributions from biogenic sources (Bi et al., 2003; Wang et al., 2006).

Our analyses showed that the middle chain length (C_{24} – C_{31}) *n*-alkanes were the most abundant; they accounted for $\sim 70\%$ of the total *n*-alkanes (Fig. 2). No odd/even C preference was observed for either the C_{19} to C_{26} or the C_{35} to C_{40} *n*-alkanes, but a strong odd carbon number predominance was seen for C_{27} to C_{34} , with $C_{max} = C_{29}$ (average concentration = 5.7 ng m^{-3}) accounting for 11.8% of *n*-alkanes. The results for C_{27} to C_{34} indicate that primary biogenic sources do contribute to organic aerosol loadings in Guangzhou. Feng et al. (2006a,b) reported similar findings for Guangzhou, Beijing and Shanghai. Nevertheless, the CPI values (range 1.2–1.7, average = 1.4) were higher than unity, and this suggests moderate to strong contributions from petroleum, diesel residues and gasoline emissions.

The average plant wax contribution to the total *n*-alkanes was 19.5% (range: 9.9–28.0%), with a daytime average of 21.2% and a nighttime average of 17.8%. In other words, $\sim 80\%$ of the *n*-alkanes apparently were from anthropogenic sources. Typically, the individual *n*-alkane concentrations were higher at night than

in the day, and as discussed above, this was likely due to anthropogenic activities, especially the operation of motor vehicles (Schauer et al., 1996) and meteorology.

3.3. PAHs

The average concentrations of individual PAH in the different sampling periods are shown in Fig. 3. BeP was the most abundant PAH, followed by BbF and BaP, and this is consistent with some previous studies in Guangzhou (Duan et al., 2007). The average BeP concentration was 3.0 ng m^{-3} , and it accounted for up to 15.6% of the total measured PAHs. BaP is important in the sense that it has been considered a general indicator of carcinogenicity (Bi et al., 2003; Wang et al., 2006): its average concentration was 2.0 ng m^{-3} , which is double the concentration in the air quality guidelines of the World Health Organization (WHO). The average BaP concentrations were lower (0.9 ng m^{-3}) in the daytime than at night (3.1 ng m^{-3}), and therefore the health risks evidently were greater at night.

Generally, 3- and 4-ring PAHs (MW < 252) can exist in both vapor and particulate phases while 5- and 6-ring PAHs (MW ≥ 252) are mainly particulate (Bi et al., 2003; Ho et al., 2009; Tan et al., 2011). Here the PAHs were separated into three groups based on their volatilities, that is, 3 + 4-ring, 5-ring, and 6-ring PAHs (Supplemental Fig. 1). The average percent contribution of 3 + 4-ring PAHs was 21% at night, which was less than that in the day (39%); this is likely due to the fact that 5- and 6-ring PAHs are more readily destroyed by photochemical degradation than the 3 + 4-ring compounds (Tan et al., 2011). Even so, the 5-ring PAHs were the most abundant, accounting for 51% of the measured total. The loadings of the 5- and 6-ring PAHs at night were higher than in the day, and this we attribute to the photo-degradation of HMW light-sensitive compounds combined with the temperature inversions and the lack of motor vehicle restrictions at night.

Diagnostic ratios of atmospheric PAHs with similar MWs have been used in source identification studies (Yunker et al., 2002; Tobiszewski and Namiesnik, 2012). Most of the samples from our study had average values of ~ 0.4 for ANT/(ANT + PHE) and ~ 0.5 for FLU/(FLU + PYR); that is, the bulk of the data fell in the center area of Fig. 4. This is consistent with a strong influence from pyrogenic sources, especially petroleum combustion. Moreover, several data points plotted to the right side in Fig. 4; these all were collected at night and this is another indication of a strong influence from petroleum sources at night.

3.4. Evaluation of the pollution control measures

3.4.1. $PM_{2.5}$, OC and EC concentrations

The concentrations of $PM_{2.5}$, OC, EC, and the ratios of OC/ $PM_{2.5}$, EC/ $PM_{2.5}$ in the pre-, dur-, and post-AG periods, as well as their N/D ratios are presented in Table 2. In general, all variables displayed their highest values in the pre-AG samples, and this matched the pattern of the non-polar organic compounds mentioned above. There was one particularly notable difference in the day versus night samples: the N/D ratios of EC and EC/ $PM_{2.5}$ were much higher than those of $PM_{2.5}$, OC or OC/ $PM_{2.5}$. This is most readily explained by diurnal differences in EC emissions, most likely the restrictions on motor vehicle operation. Although less dramatic, the average OC concentrations also were higher at night ($14.45 \mu\text{g m}^{-3}$) than in the day ($11.67 \mu\text{g m}^{-3}$); these data will be used in the CMAQ model in Section 3.4.3 below.

3.4.2. Diurnal variations of gaseous pollutants

By comparing the SO_2 and NO_x concentrations and the variations between the “non-control period” and “control period”

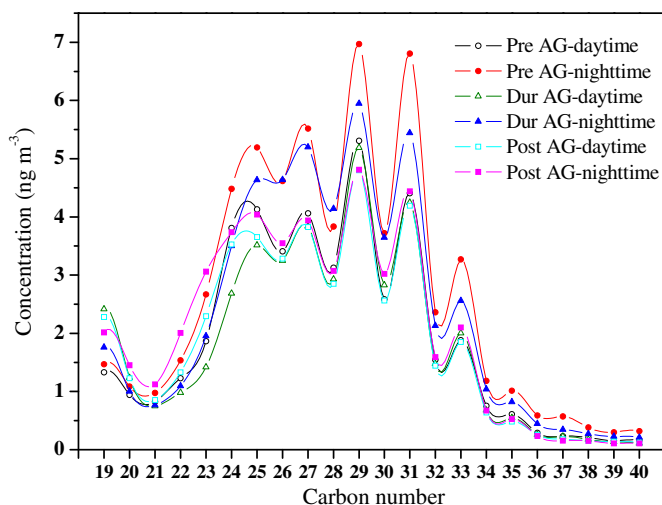


Fig. 2. Distribution of *n*-alkane homologs (C_{19} to C_{40}) during different sampling periods.

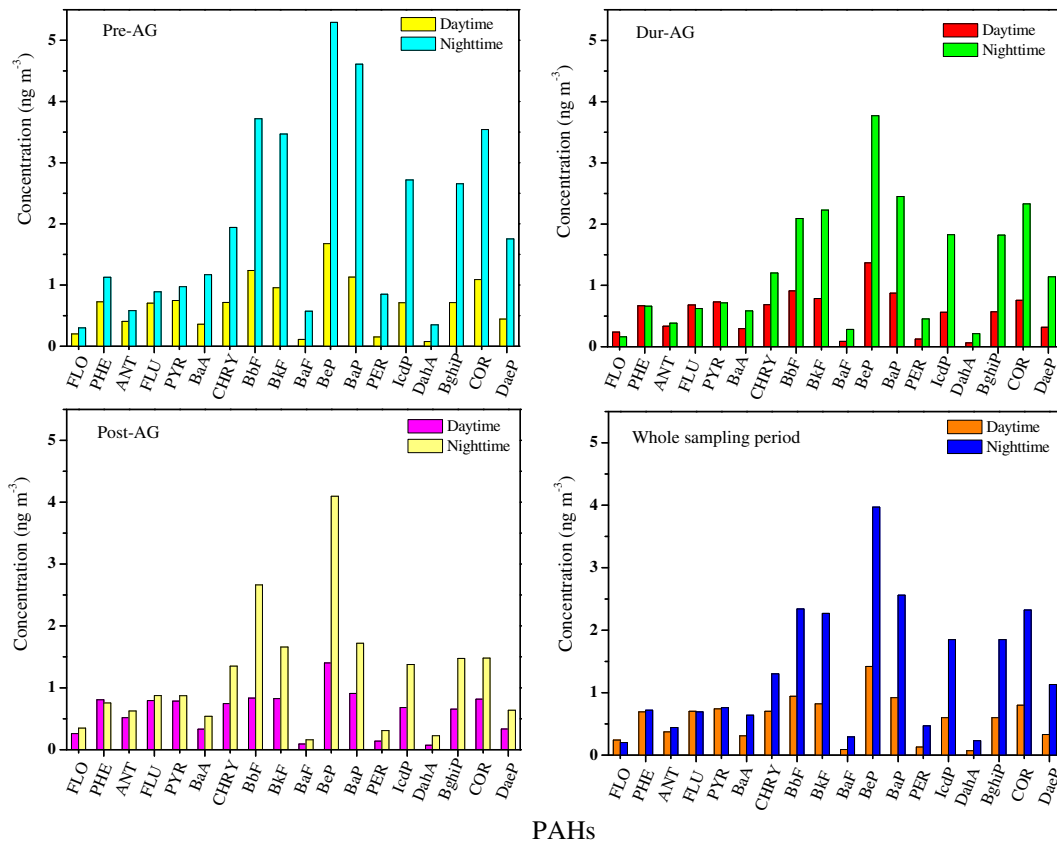


Fig. 3. Comparisons of PAH (units: ng m^{-3}) distributions in pre-, dur-, post-Asian Games periods and the whole sampling period.

samples (See Supplemental Table 1), we can evaluate the effectiveness of the pollution control policies. Pronounced diurnal variations in SO_2 and NO_x were observed in both non-control and control periods, but with significant differences in their daily patterns (Fig. 5). That is, the lowest SO_2 concentrations generally were observed from 1:00 p.m. to 7:00 p.m.; they increased during the night and peaked at 7:00 a.m. to 9:00 a.m.

More notably, the SO_2 average concentration during the control period ($9.1 \mu\text{g m}^{-3}$) was more than a factor of 3 lower than in non-control period ($33.7 \mu\text{g m}^{-3}$). Emissions from coal-fired power plants and industry are major sources for SO_2 , and the control policies targeting SO_2 during the Asian Games included the shut-

down, discontinuance, or limited operation for small and sub-standard heat-engine plants and factories. These controls were in place 24 h per day from 1 November to 20 December, 2010. The observed 3-fold difference in SO_2 is convincing evidence that the control measures were effective.

NO_x was much less variable than SO_2 for the two periods. Time-series plots of NO_x exhibited two peaks, one at 7:00 a.m. (morning rush hour) and another at 9:00 p.m. (Fig. 5). Although the concentrations and diurnal variations were similar for the control and non-control periods, the NO_x N/D ratios did differ for the two periods. NO_x levels during the days of the control period were lower than those of non-control period, but they were higher during the nights of control period than the non-control period. As a result, the average N/D ratios of NO_x were 1.7 and 1.1 in the control and non-control periods.

Even though no remarkable differences were in the daily average concentrations of NO_x between non-control and control periods, that does not necessarily mean that the traffic control policies were not effective. This is because high average wind speed during

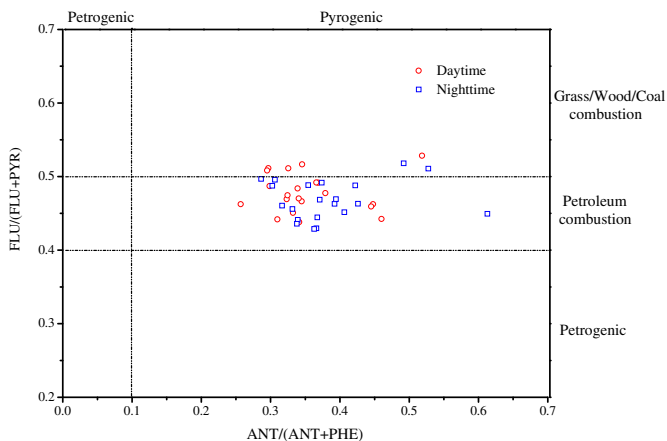


Fig. 4. Correlations between PAHs diagnostic ratios.

Table 2
The concentrations of $\text{PM}_{2.5}$, OC, EC ($\mu\text{g m}^{-3}$), and some ratios in different sampling periods.

	$\text{PM}_{2.5}$	OC	EC	$\text{OC}/\text{PM}_{2.5}$	$\text{EC}/\text{PM}_{2.5}$
Pre-AG	86.67	17.34	10.02	20.5%	11.1%
Dur-AG	77.82	11.97	6.17	15.5%	7.6%
Post-AG	82.09	14.23	5.66	17.4%	6.8%
Average	79.70	13.06	6.65	16.5%	8.0%
Night	88.10	14.45	8.55	16.6%	9.4%
Day	71.29	11.67	4.75	16.4%	6.5%
N/D	1.2	1.2	1.8	1.0	1.5

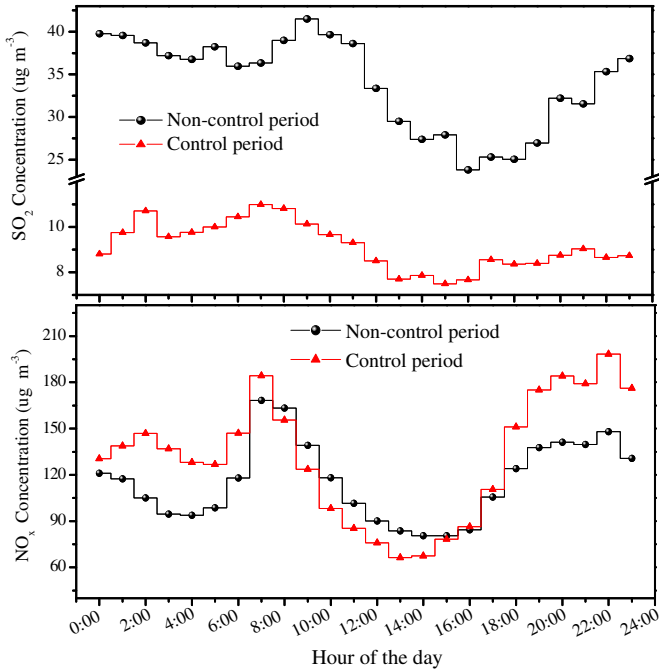


Fig. 5. Diurnal variations of SO_2 and NO_x concentrations (units: $\mu\text{g m}^{-3}$) in non-control and control periods.

non-control period (1.2 versus 0.4 m s^{-1} in control period) favored the dispersal and dilution of pollutants. Therefore, it is possible if not likely that the traffic control policies some effect on NO_x emissions; indeed the NO_x N/D ratios in the control period were higher than in non-control period.

3.4.3. The ratios of PAH species and biogenic organic carbon

A new approach for evaluating the diurnal variability of pollutants was developed: it was based on the ratios of specific PAH species to biogenic organic carbon, and it minimized the effects of influences other than changes in organic pollutants emissions. Comparisons of the N/D ratios between PAH source markers and biogenic OA (OA_{bio}) were used to evaluate the effectiveness of the odd-even day vehicle operation scheme. Sensitivity simulations using the CMAQ model also were carried out to evaluate the contribution of OA_{bio} to the total OA (OA_{tot}). The emissions of biogenic organic aerosol (OA_{bio}) were assumed to remain constant in the day or at night throughout the observation period.

The simulated OA_{tot} concentrations were $11.61 \mu\text{g m}^{-3}$ both in the daytime and at night. When the biogenic emissions in the model were turned off, the OA values from anthropogenic sources and biomass burning were $6.50 \mu\text{g m}^{-3}$ in the daytime and $6.87 \mu\text{g m}^{-3}$ at night. Therefore, on average OA_{bio} accounted for 44.3% of the OA_{tot} in the day and slightly less, 40.9%, at night. These relationships can be represented as follows:

$$OA_{bio-D} = 44.3\% \times OA_{tot-D} \quad (2)$$

$$OA_{bio-N} = 40.9\% \times OA_{tot-N} \quad (3)$$

where the subscripts D and N denote day and night, respectively. We assumed that

$$OA_{tot} = x \times OC_{tot} \quad (4)$$

$$OA_{bio} = y \times OC_{bio} \quad (5)$$

where x denotes the ratio of OA_{tot} to OC_{tot} and y denotes the ratio of OA_{bio} to OC_{bio} . Finally, OC_{bio} was calculated by re-arranging Equation (5) and substituting values for $OC_{tot-D} = 11.67 \mu\text{g m}^{-3}$ and $OC_{tot-N} = 14.45 \mu\text{g m}^{-3}$.

$$OC_{bio-D} = OA_{bio-D}/y \quad (6)$$

$$OC_{bio-D} = \frac{44.3\% \times OA_{tot-D}}{y} \quad (7)$$

Converting OA to OC,

$$OC_{bio-D} = x/y \times 44.3\% \times OC_{tot-D} \quad (8)$$

$$OC_{bio-D} = 5.17x/y (\mu\text{g m}^{-3}) \quad (9)$$

Similarly, it can be shown that

$$OC_{bio-N} = 5.91x/y (\mu\text{g m}^{-3}) \quad (10)$$

We used the relationships together with data for organic tracers to evaluate the effectiveness of the odd-even day motor vehicle restrictions. Although *CHRY* and *BghiP* can be generated by both coal and gasoline combustions, *CHRY* is predominately from coal combustion while *BghiP* is mainly from gasoline emissions (Baek et al., 1991; Mazquiarán and Pinedo, 2007; Wang et al., 2006, 2007). The N/D ratio for $CHRY/OC_{bio}$ was calculated from the observed values for $CHRY_{-D}$ (0.7 ng m^{-3}) and $CHRY_{-N}$ (1.5 ng m^{-3}).

$$(CHRY/OC_{bio})_{N/D} = \frac{CHRY_{-N}}{OC_{bio-N}} = \frac{OC_{bio-N}}{CHRY_{-D}} \quad (11)$$

$$(CHRY/OC_{bio})_{N/D} = \frac{CHRY_{-N}}{5.91 \times x/y} = \frac{OC_{bio-N}}{5.17 \times x/y} \quad (12)$$

$$(CHRY/OC_{bio})_{N/D} = 1.9 \quad (13)$$

In the same way, we used *BghiP* as the indicator of gasoline emissions. The N/D ratio (for $BghiP_{-D} = 0.6 \text{ ng m}^{-3}$ and $BghiP_{-N} = 2.1 \text{ ng m}^{-3}$) was calculated as follows:

$$(BghiP/OC_{bio})_{N/D} = \frac{BghiP_{-N}}{OC_{bio-N}} = \frac{OC_{bio-N}}{BghiP_{-D}} \quad (14)$$

$$(BghiP/OC_{bio})_{N/D} = 3.1 \quad (15)$$

The N/D ratio of $CHRY/OC_{bio}$ (1.9) implies that the nighttime concentration for any pollutant should be approximately 1.9 times that during the day, assuming that the independent variations for that pollutant can be neglected. The night/day difference for the generic pollutant could be due to the meteorology (mixing height, wind speed, and so on) or any of a number of other reasons. The N/D ratio for $BghiP/OC_{bio}$ (3.1) was much higher than 1.9; and this implies that the motor vehicle emissions showed greater diurnal variability than those from coal combustion. This can be explained by the odd-even day vehicle policy, which must have led to reduced motor vehicle emissions during the day. This is an indication of the effectiveness of the traffic control policy during the Asian Games.

4. Conclusions

The concentrations of 22 *n*-alkanes and 18 PAHs were determined in PM_{2.5} collected in Guangzhou during the 16th Asian Games. The average concentrations of *n*-alkanes and PAHs were much higher in the nighttime (51.6 and 24.0 ng m⁻³) than during the day (41.3 and 10.3 ng m⁻³). The average CPI during the sampling period was 1.4, and the average contribution of wax *n*-alkanes was 19.5%; therefore, PM_{2.5} was mainly from anthropogenic sources but minor contributions from biogenic sources could be detected. Diagnostic ratios used for source identification confirmed that petroleum combustion was the dominant source of PAHs. Finally, variations in PM_{2.5}, OC, EC and gaseous pollutants, their N/D ratios, and the ratios of special PAH species and biogenic organic carbon simulated by the CMAQ model clearly demonstrated that the control measures implemented for the Asian Games led to a reduction in air pollution.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2012.12.037>.

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