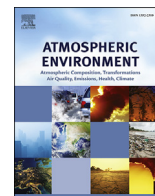




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Attributing risk burden of PM_{2.5}-bound polycyclic aromatic hydrocarbons to major emission sources: Case study in Guangzhou, south China



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H I G H L I G H T S

- Higher BaP_{eq} and PAH-related cancer risk in rural than in urban areas.
- Coal combustion and biomass burning contributed most to PAHs and BaP_{eq}.
- Vehicle emission only explained ~15% of ambient PM_{2.5}-bound BaP_{eq}.
- Biomass burning contributed most to BaP_{eq} in winter even at urban roadside.

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Polycyclic aromatic hydrocarbons (PAHs) have attracted an increasing concern in China's megacities. However, rare information is available on the spatial and seasonal variations of inhalation cancer risk (ICR) due to PAH exposure and their relations to specific sources. In this study, year-round PM_{2.5} samples were collected from 2013 to 2014 by high-volume samplers at four sites (one urban, two rural and one roadside station) in Guangzhou in the highly industrialized and densely populated Pearl River Delta (PRD) region and analyzed for 26 polycyclic aromatic hydrocarbons (PAHs) together with molecular tracers including levoglucosan, hopanes and elemental carbon. Higher molecular weight PAHs (5-ring or above) accounted for 64.3–87.5% of total PAHs. Estimated annual averages of benzo(*a*)pyrene-equivalent carcinogenic potency (BaP_{eq}) were 1.37, 2.31 and 1.56 ng/m³ at urban SZ, rural JL and rural WQS, respectively, much higher than that at the roadside station YJ in an urban street canyon. ICR of PAHs in wintertime reached 2.2×10^{-4} , nearly 3 times that in summer; and cancer risk of PAHs was surprisingly higher at the rural site than at other sites. Source contributions by positive matrix factorization (PMF) in the aid of molecular tracers revealed that overall coal combustion and biomass burning altogether contributed 73.8% of total PAHs and 85.2% of BaP_{eq}, and particularly in winter biomass burning became the most significant source of total PAHs and BaP_{eq} (51.8% and 52.5%), followed by coal combustion (32.0% and 39.1%) and vehicle emission (16.2% and 8.4%). The findings of this work suggest that even in China's megacities like Guangzhou, limiting biomass burning may benefit PAHs pollution control and cancer risk reduction.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic compounds with at least two aromatic rings. They are ubiquitous in

the atmosphere and emitted primarily from incomplete combustion of fossil fuels and biomass (Bi et al., 2003; Ravindra et al., 2008). Several PAHs have been proved to be human carcinogens and have a significant presence in particulate matter, these toxicants can deposit in the lungs and exert their carcinogenicity over long exposure periods (Collins et al., 1998; Armstrong et al., 2004). As semi-volatile persistent organic pollutants (POPs), airborne PAHs are capable of long range transport and impacting remote areas (Halsall et al., 2001; Ding et al., 2007; Liu et al., 2013).

With the rise in population, industrial activities and number of vehicles, PAH emissions have been increasing world widely. As the most energy-consuming country, China has become the largest PAH emitter in the world (Shen et al., 2013; Zhang and Tao, 2009). Up to 116,000 tons of 16 USEPA priority PAHs was estimated to be released by China in 2003 (Zhang et al., 2008) and the overall population attributable fraction (PAF) for lung cancer caused by inhalation exposure to PAHs was 1.6% in China (Zhang et al., 2009). Regulating PAH emissions in China is a challenging task in face of stricter National Ambient Air Quality Standards (NAAQS, GB 3095-2012) and the lack of emission control standard for coal combustion and biomass burning.

Guangzhou is the central city of the Pearl River delta (PRD) region, one of the most developed areas and hotspots of PAH emissions in Southern China. Long-term records in Guangzhou suggested good statistical evidence for a relationship between the degradation of air quality and lung cancer mortality (Tie et al., 2009), and in Guangzhou aromatic fractions were found to exhibit the greatest genotoxic potencies in extractable organic matter in fine particles (Xu et al., 2008). In the past few years, continued effort has been made to get better understanding of PAH distributions, risks and sources in Guangzhou (Bi et al., 2003; Li et al., 2006; Tan et al., 2006; Yang et al., 2010; Gao et al., 2011, 2012, 2013). However, these results were based on data either from few sites or specific seasons. A year-round multi-site study has not yet been implemented, which is important for knowing the seasonal behavior of PAHs in Guangzhou on the whole. In addition, risk assessments give still limited information about the carcinogenic potencies related to specific emission sources (Gao et al., 2015), especially from seasonal perspectives.

In this study, one year observation at four sites was carried out during 2013–2014 to: (1) investigate the spatial and seasonal

exposure to ambient PM_{2.5}-bound PAHs; (2) assess the carcinogenic risks of PAHs exposure; (3) quantify the source contributions to PAHs and their carcinogenic risks.

2. Sampling and chemical analysis

2.1. Description of the sampling sites

The PRD region in south China consists of nine cities within Guangdong province, namely Guangzhou, Shenzhen, Zhuhai, Dongguan, Foshan, Zhongshan, Jiangmen, Huizhou, and Zhaoqing, plus Hong Kong and Macau special administrative regions. It is made up of plains and alluvial delta. With a population of about 56 million (GPBS, 2012) and a land area of about 56,000 km², it is one of the most densely populated and highly industrialized regions in China. It features a typical Asian monsoon climate with South China Sea monsoon dominated during summer and the northeast monsoon dominated during fall to winter (Ding and Chan, 2005).

Four sites were selected for this campaign including Guangzhou Environmental Monitoring Center (SZ) and Yangji Roadside Station (YJ) in urban areas, Jiulong Town (JL) and Wanqingsha middle school (WQS) in rural areas. The SZ, JL and WQS sites are all air quality monitoring stations established by the local government environmental monitoring center, while YJ is a station to monitor ambient air quality of urban roadside microenvironments in street canyons. Their geographical locations are shown in Fig. 1. The meteorological data at WQS site were monitored throughout the year. The monthly average temperature (T), relative humidity (RH), wind speed (WS) and solar radiation (SR) were 13.7–28.9 °C, 66.0–92.6%, 5.0–7.7 km/h and 99.6–187.6 W/m², respectively (Table S1).

SZ (23.13°N, 113.27°E) and YJ (23.13°N, 113.32°E) are located in the city center, with heavy traffic and busy commercial activities. JL (23.30°N, 113.57°E) is in the northeast of Guangzhou, surrounded by forests with sparse population, about 46.8 km from urban center. WQS (22.71°N, 113.55°E) is located in a small town in the central PRD, surrounded by farmlands with very few textile and clothing workshops, about 55 km away from city center and adjacent to the Pearl River estuary. There are few local anthropogenic emissions in WQS and it is mainly affected by regionally transported pollutants.

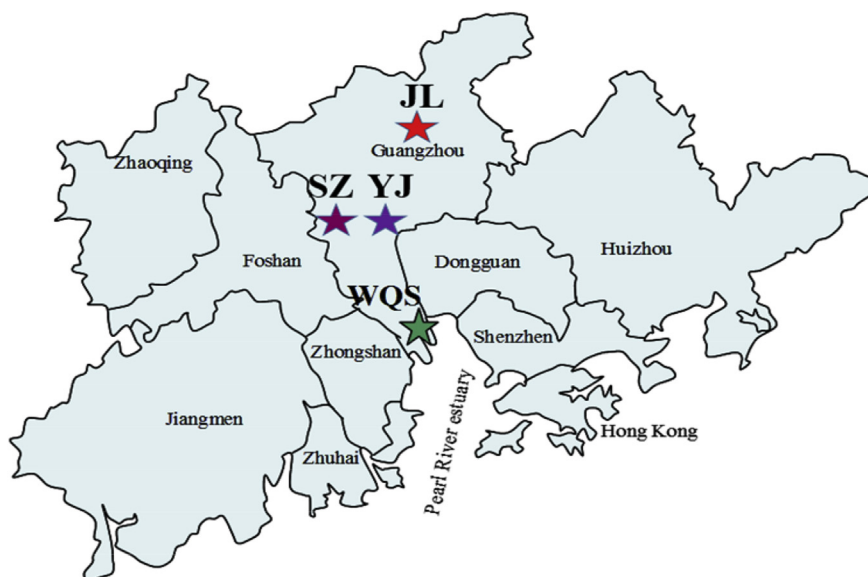


Fig. 1. Locations of the four sampling sites in Guangzhou.

2.2. Fine particle sampling

24-h PM_{2.5} sampling was performed every five days from August 26, 2013 to April 29, 2014 at SZ, August 20, 2013 to May 29, 2014 at YJ, July 23, 2013 to May 29, 2014 at JL, July 24 to August 29, 2013 and November 12, 2013 to February 7, 2014 at WQS. Meanwhile, samples were collected every day in August and in November at all the sites to capture typical atmospheric chemical and pollution processes. Samples were collected using a high volume sampler (Tisch Environmental, Inc.) with a constant flow rate of 1.1 m³ min⁻¹ at each site. Quartz fiber filters (Whatman, Mainstone, UK) used as collection substrates were prebaked for 6 h at 450 °C.

2.3. Chemical analysis

A punch (1.5 × 1.0 cm) of each filter was taken to measure organic carbon (OC) and elemental carbon (EC) using the thermo-optical transmittance (TOT) method (NIOSH, 1999) by an OC/EC analyzer (Sunset Laboratory Inc., USA).

Before solvent extraction, isotope-labeled PAH compounds (naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂, perylene-d₁₂), tetracosane-d₅₀ and levoglucosan-¹³C₆ were spiked into samples as surrogates. Filters were ultrasonically extracted twice with the mixed solvent of dichloride methane (DCM)/hexane (1:1, vol/vol), then twice with the mixed solvent DCM/methanol (1:1, vol/vol). The extracts of each sample were combined, filtered and concentrated to ~1 mL and split into two parts. One (~0.5 mL) was blown to dryness under a gentle stream of nitrogen, added by 200 μL of DCM, 10 μL of methanol and 300 μL of freshly prepared diazomethane and kept at room temperature for 1 h. The methylated extract was reduced to ~500 μL and analyzed for PAHs, hopanes and other nonpolar species. The other part (~0.5 mL) was blown to dryness for silylation with 100 μL of pyridine and 200 μL of N, O-bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) plus 1% trimethylchlorosilane (TMCS) in an oven at 70 °C for 1 h. The silylated extract was analyzed for levoglucosan and other polar compounds. The samples were analyzed by an Agilent 7890/5975C gas chromatography/mass spectrometer detector (GC/MSD) equipped with a HP-5MS capillary column (30 m, 0.25 mm, 0.25 μm). High purity helium was used as the carrier gas, with a constant flow rate of 1.2 mL min⁻¹. 1 μL samples was injected in splitless mode with a 6 min solvent delay time using the automated injection device. The GC temperature was initiated at 65 °C, held for 2 min, then increased to 290 °C at 5 °C min⁻¹ and held for 20 min. Thirty-two compounds were quantified including twenty-six PAHs: Naphthalene (Nap), Acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Fl), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Flu), Acephenanthrylene (Acep), Pyrene (Pyr), Retene (Ret), Benzo(ghi)fluoranthene (BghiF), Cyclopenta(cd)pyrene (CPcdP), Benz(a)anthracene (BaA), Chrysene (Chr), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(j)fluoranthene (BjF), Benzo(e)pyrene (BeP), Benzo(a)pyrene (BaP), Perylene (Per), Indeno(cd)fluoranthene (IcdF), Indeno(cd)pyrene (IcdP), Picene (Pic), Dibenzo[a,h]anthracene (DahA), Benzo(ghi)perylene (BghiP), Coronene (Cor); five hopanes: 17α(H),21β(H)-30-norhopane (Norhopane), 18α(H)-29-Norneohopane (Norneohopane), 17α(H),21β(H)-hopane (Hopane), 31(S)-hopane, 31(R)-hopane and levoglucosan. Compounds were quantified by their authentic standards or approximated with their isomers/homologues closest in retention times as the alternative standards.

2.4. Quality control and quality assurance

Field and laboratory blanks were extracted and analyzed in the

same manner as the field samples. All the target compounds were not detected or showed negligible concentrations in the blanks. To evaluate the recoveries of the compounds, we extracted and analyzed the NIST Standard Reference Material (SRM1649b) Urban Dust (the certified values for PAHs are based on the agreement of results obtained from two or more chemically independent analytical techniques) as well, the recovery was 77 ± 12%, 80 ± 19%, 76 ± 11%, 83 ± 21%, 95 ± 12%, 116 ± 19%, 134 ± 11%, 125 ± 19%, 110 ± 16%, 138 ± 12%, 119 ± 14% and 95 ± 9% for Phe, Flu, Pyr, BghiF, BaA, Chr, BbF, BeP, BaP, Per, IcdP and BghiP, respectively. The method detection limits (MDLs) of target compounds ranged from 0.02 to 0.08 ng/m³.

2.5. Source apportionment with positive matrix factorization

USEPA PMF 5.0 model was applied in the present study to identify the sources of observed ambient PAHs. The detailed introduction of the model can be found somewhere else (Paatero and Tapper, 1994; Paatero, 1997; Paterson et al., 1999). Data values below the MDL were substituted with MDL/2. Missing data values were substituted with median concentrations (Polissar et al., 1998; Baumann et al., 2008).

If the concentration is greater than the MDL, the uncertainty is calculated by $Unc = \sqrt{(20\% \times con)^2 + MDL^2}$. If the concentration is less than the MDL, the uncertainty is calculated by $Unc = 5/6 \times MDL$. The species and number of factors were chosen based on the previous studies in Guangzhou and the result from the PCA/APCS (Bi et al., 2003; Larsen and Baker, 2003; Li et al., 2006).

3. Results and discussion

3.1. Total PAHs

Table 1 presents the concentrations of individual PAHs at each sampling site. The average concentrations of total PAHs (Σ PAHs) and 15 USEPA priority PAHs (Σ_{15} PAHs, excluding NaP due to its high volatility) were 13.04 (0.5–62.08) ng/m³ and 9.72 (0.29–56.97) ng/m³, respectively. The PAH concentrations in this study were consistent with previously reported values by Li et al. (2006) (23.7 ± 18.4 ng/m³) and Gao et al. (2012) (17.1 ng/m³) in Guangzhou, lower than that measured in Beijing (116 ng/m³) (Zhou et al., 2005), but higher than those measured in many other cities, such as Houston, USA (0.78 ng/m³) (Fraser et al., 2002), Lumpur, Malaysia (2.79 ng/m³) (Khan et al., 2015), Mount Taishan, China (6.88 ng/m³) (Li et al., 2010), Rio de Janeiro, Brazil (3.80 ± 2.88 ng/m³) (Oliveira et al., 2014).

Σ PAHs and Σ_{15} PAHs at rural JL (17.61 ± 3.19 ng/m³ and 13.14 ± 2.35 ng/m³) showed significantly higher levels ($p < 0.05$) than those at urban SZ (11.56 ± 2.04 ng/m³ and 8.54 ± 1.46 ng/m³) and YJ (9.26 ± 1.21 ng/m³ and 7.04 ± 0.83 ng/m³) but had no significant difference when compared to another rural site WQS (13.69 ± 2.86 ng/m³ and 10.14 ± 2.13 ng/m³) (Table 1).

Σ PAHs were higher ($p < 0.05$) in winter than in summer at all sites. Similar trends have been reported in other studies (Terzi and Samara, 2004; Esen et al., 2008; Vardar et al., 2008; Morville et al., 2011). As we can see from Table S2, the correlation of PAHs with temperature, humidity and wind speed were all significantly negative ($p < 0.05$), while the solar radiation showed no significant correlation with PAHs. In summer, the south wind dominated and brought clean oceanic air from the South China Sea and southeast coast, whereas in winter air masses mainly from the west and the northwest brought pollutants from mainland (Fig. S1) (He et al., 2014). Relatively higher temperature, humidity and wind speed in summer also led to stronger photolysis and dispersion of PAHs (Yang et al., 2010). All these contributed to lower PAH

Table 1
Concentrations of PAHs (ng/m³), hopanes (ng/m³), levoglucosan (ng/m³) and EC (μg/m³) at the four sampling sites in Guangzhou.

	SZ (n = 92)		YJ (n = 101)		JL (n = 107)		WQS (n = 83)	
	Mean (95%CI) ^a	Range	Mean (95%CI) ^a	Range	Mean (95%CI) ^a	Range	Mean (95%CI) ^a	Range
Acey	0.03 (0.01)	nd-0.17	0.02 (0.01)	nd-0.20	0.05 (0.02)	nd-0.34	0.05 (0.02)	nd-0.35
Ace	0.02 (0.00)	nd-0.10	0.02 (0.00)	nd-0.07	0.02 (0.00)	nd-0.15	0.02 (0.00)	nd-0.11
Fl	0.14 (0.03)	nd-0.83	0.11 (0.03)	nd-0.72	0.12 (0.03)	nd-0.53	0.23 (0.09)	nd-2.59
Phe	0.39 (0.07)	0.06–1.85	0.33 (0.05)	nd-1.23	0.44 (0.08)	nd-1.55	0.35 (0.09)	nd-2.17
Ant	0.14 (0.02)	nd-0.53	0.13 (0.02)	nd-0.52	0.15 (0.03)	nd-0.65	0.16 (0.03)	nd-0.49
Flu	0.55 (0.13)	0.05–3.08	0.47 (0.09)	0.06–2.18	0.84 (0.19)	0.06–3.84	0.85 (0.20)	0.05–3.89
Acep	0.09 (0.02)	nd-0.58	0.06 (0.02)	nd-0.34	0.18 (0.05)	nd-1.32	0.17 (0.04)	nd-0.84
Pyr	0.51 (0.11)	0.11–2.77	0.44 (0.08)	nd-1.60	0.85 (0.19)	nd-4.42	0.82 (0.18)	nd-3.38
Ret	0.08 (0.04)	nd-0.67	0.06 (0.03)	nd-0.48	0.05 (0.01)	nd-0.28	0.07 (0.02)	nd-0.41
BghiF	0.24 (0.06)	nd-1.51	0.17 (0.04)	nd-0.88	0.41 (0.11)	nd-2.87	0.40 (0.10)	nd-2.18
CcdP	0.15 (0.04)	nd-1.05	0.10 (0.03)	nd-0.78	0.27 (0.11)	nd-3.43	0.24 (0.07)	nd-1.78
BaA	0.37 (0.11)	nd-2.93	0.25 (0.06)	nd-1.53	0.68 (0.23)	nd-6.19	0.53 (0.14)	nd-3.13
Chr	0.76 (0.17)	0.10–4.31	0.59 (0.11)	nd-2.80	1.19 (0.33)	nd-8.21	1.04 (0.26)	nd-5.26
BbF	1.17 (0.19)	0.23–5.80	1.03 (0.11)	0.31–2.94	1.79 (0.31)	nd-8.71	1.34 (0.29)	nd-6.89
BkF	1.14 (0.20)	0.29–6.45	1.01 (0.11)	0.37–3.35	1.87 (0.32)	nd-8.53	1.32 (0.27)	nd-5.82
BjF	0.17 (0.05)	nd-1.66	0.12 (0.03)	nd-0.72	0.33 (0.09)	nd-2.49	0.22 (0.06)	nd-1.32
BeP	1.00 (0.16)	0.19–5.04	0.89 (0.09)	0.26–2.62	1.52 (0.23)	nd-6.08	1.07 (0.21)	nd-4.71
BaP	0.66 (0.15)	nd-4.96	0.53 (0.08)	nd-2.51	1.14 (0.26)	nd-6.79	0.82 (0.21)	nd-4.85
Per	0.13 (0.03)	nd-1.02	0.10 (0.02)	nd-0.48	0.21 (0.05)	nd-1.20	0.37 (0.23)	nd-5.72
IcdF	0.46 (0.08)	nd-2.43	0.35 (0.05)	nd-1.45	0.70 (0.12)	nd-3.31	0.45 (0.10)	nd-2.08
IcdP	1.36 (0.24)	nd-7.80	1.07 (0.12)	nd-3.96	2.07 (0.31)	nd-8.32	1.34 (0.28)	nd-6.19
Pic	0.12 (0.03)	nd-0.83	0.07 (0.01)	nd-0.41	0.18 (0.04)	nd-1.17	0.12 (0.03)	nd-0.71
DahA	0.15 (0.00)	nd-1.09	0.09 (0.02)	nd-0.54	0.24 (0.05)	nd-1.53	0.15 (0.04)	nd-0.93
BghiP	1.16 (0.19)	0.10–6.29	0.96 (0.10)	0.14–3.12	1.68 (0.23)	nd-5.45	1.13 (0.22)	nd-5.08
Cor	0.57 (0.15)	nd-4.78	0.29 (0.06)	nd-1.95	0.62 (0.12)	nd-2.32	0.44 (0.12)	nd-2.58
∑PAHs	11.56 (2.04)	1.96–62.93	9.26 (1.21)	2.02–30.09	17.61 (3.19)	0.50–78.46	13.69 (2.86)	0.50–62.08
∑ ₁₅ PAHs ^b	8.54 (1.46)	1.52–44.31	7.04 (0.83)	1.56–22.51	13.14 (2.35)	0.29–56.97	10.14 (2.13)	0.29–45.23
∑Hopanes ^c	1.05 (0.24)	0.04–5.41	1.14 (0.16)	0.04–3.74	0.69 (0.12)	0.04–2.90	0.92 (0.22)	0.04–3.54
Levo ^d	141.99 (25.15)	20.66–602.92	163.76 (28.62)	27.98–901.57	236.09 (40.43)	10.63–922.83	151.76 (32.75)	6.5–617.04
EC	2.15 (0.20)	0.69–5.71	2.61 (0.19)	0.67–5.93	2.26 (0.27)	0.44–6.72	1.77 (0.24)	0.29–4.81

^a Number in parentheses are the 95% confidence intervals.

^b ∑₁₅PAHs include: Ace, Acey, Fl, Phe, Ant, Flu, Pyr, BaA, Chr, BbF, BkF, BaP, DahA, IcdP and BghiP.

^c The five hopanes are 17α(H),21β(H)-30-norhopane (Norhopane), 18α(H)-29-Norneohopane (Norneohopane), 17α(H), 21β(H)-hopane (Hopane), 31 (S)-hopane and 31 (R)-hopane.

^d Levoglucosan.

concentrations in summer than in winter. However, the seasonal trends had slight differences at each site (Fig. 2). Highest levels were observed in spring at SZ, in winter at YJ and JL and in autumn-winter at WQS, respectively, suggesting different source contributions at each site.

3.2. PAH compositions

It was not hard to find that the concentrations of BbF, BkF, BeP, IcdP and BghiP were higher than other compounds at the four sampling sites (Table 1), similar to that in previous studies (Gao et al., 2011, 2012). We divided PAHs into lower molecular weight (LMW, three-ringed PAHs), middle molecular weight (MMW, four-ringed PAHs), and higher molecular weight (HMW, five-, six-, and seven-ringed PAHs). HMW PAHs were predominant in all seasons, accounting for 64.3–84.0%, 65.6–83.2%, 67.5–87.5% and 65.2–83.1% of ∑PAHs at SZ, YJ, JL and WQS respectively, while MMW and LMW PAHs only accounted for 10.1–27.7% and 2.4–8.5% of ∑PAHs (Fig. 2). Comparable results were reported in Guangzhou from 2012 to 2013 (Liu et al., 2015). The percentages of LMW and MMW PAHs showed increasing trends from summer to winter, indicating that more volatile species were transferred from gas phase to particle phase in cold period.

3.3. Potency of carcinogenic PAHs

BaP has been widely used as an indicator of total PAHs in the inhalation risk assessment due to its high carcinogenicity and atmospheric presence. Indeed, BaP levels showed similar spatial and

seasonal variations as ∑PAHs (Figs. 2 and 3a). The average BaP concentrations at SZ, YJ, JL and WQS were 0.66 ± 0.15 ng/m³, 0.53 ± 0.08 ng/m³, 1.14 ± 0.26 ng/m³ and 0.82 ± 0.21 ng/m³, with 18.5%, 8.9%, 39.3% and 28.9% of the samples, respectively exceeding 1.0 ng/m³, the limit of the annual average BaP in the NAAQS (GB 3095-2012). The days exceeding the standard (1.0 ng/m³) mainly concentrated in autumn, winter and spring at the four sampling sites. It is worth noting that in winter at JL, the standard-exceeding rate reached as high as 71.4% (15 out of 21 days).

Besides BaP, other PAHs like BaA, BbF, DahA and IcdP are also believed to have carcinogenic potency (IARC, 2001). To more reasonably assess the carcinogenicity of PAHs, BaP carcinogenic equivalent concentration (BaP_{eq}) was calculated as: $BaP_{eq} = \sum_{i=1}^n PAH_i \times TEF_i$. TEF_i is the toxic equivalency factor (TEF) for each PAH_i taken from Masiol et al. (2012): 0.001 for Flu and Pyr, 0.01 for Chr and BghiP, 0.1 for BaA, BbF, BkF, BeP, and IcdP, and 1 for BaP and DahA. The average levels of BaP_{eq} at SZ, YJ, JL and WQS were 1.37 ± 0.27 ng/m³ (0.15–8.97 ng/m³), 1.11 ± 0.14 ng/m³ (0.20–4.44 ng/m³), 2.31 ± 0.43 ng/m³ (0.07–10.84 ng/m³) and 1.56 ± 0.35 ng/m³ (0.07–8.35 ng/m³), with 55.4%, 48.5%, 70.1% and 55.4% of the samples, respectively exceeding the NAAQS (GB 3095-2012), 1 ng/m³, indicating higher cancer risk for people at JL than at other sites. BaP_{eq} levels in winter (2.49 ng/m³) was 2.8 times those in summer (0.88 ng/m³), indicating higher cancer risk in cold period (Fig. 3b). The values of BaP_{eq} in previous studies in Guangzhou calculated by using same TEFs were listed in Table 2 for comparison. BaP_{eq} in this study was lower than those in previous studies (Li et al., 2006; Tan et al., 2006; Yang et al., 2010). The most carcinogenic PAHs, like BaP and DahA with TEFs of 1.0, comes

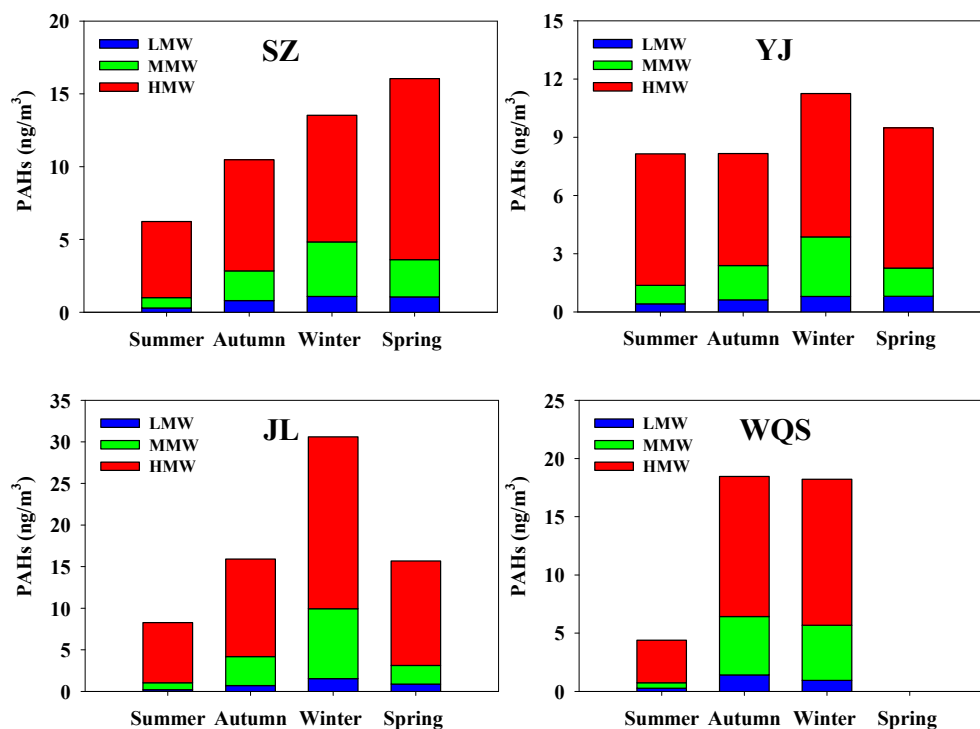


Fig. 2. Seasonal variations of different rings PAHs at the four sampling sites in Guangzhou. LMW, MMW and HMW represent lower molecular weight (three-ringed PAHs), middle molecular weight (four-ringed PAHs), and higher molecular weight (five-, six-, and seven-ringed) PAHs, respectively. Samples were not collected regularly in spring at WQS.

mainly from coal burning (Liu et al., 2009) and are major contributors to BaP_{eq} . As mentioned hereafter the enhancement of biomass burning and the decrease in coal consumption in Guangzhou could largely explain the much lower BaP_{eq} but comparable total PAHs, although differences in monitoring sites, meteorological conditions and atmospheric transport might also influence the comparison.

To estimate the cancer risk from PAH exposure, inhalation cancer risk (ICR) was calculated by multiplying BaP_{eq} by the inhalation unit risk (IUR_{BaP} , m^3/ng , defined as the risk of cancer from lifetime (70-year) inhalation of unit mass of BaP). WHO suggested a IUR_{BaP} of $8.7 \times 10^{-5} m^3/ng$ (WHO, 1987). The ICRs at SZ, YJ, JL and WQS averaged 1.2×10^{-4} , 9.7×10^{-5} , 2.0×10^{-4} and 1.4×10^{-4} , respectively. What is more, the ICR reached 3.9×10^{-4} in winter at JL. All these values far exceeded the health-based guideline level of 10^{-5} (Bostrom et al., 2002) and indicated the health risk of exposure to the carcinogenic PAHs in Guangzhou.

3.4. Source apportionment

Previously studies revealed that the main sources of PAHs were vehicle emission, coal combustion and biomass burning (Bi et al., 2003; Li et al., 2006; Yang et al., 2010; Gao et al., 2013). Biomass burning (BB) in the PRD region includes four types: direct burning of crop straw in the field, direct burning of crop straw in households, burning firewood and forest wildfires, which accounted for 24.2%, 18.1%, 57.6%, 0.1%, respectively of total BB emissions in 2008 (Zhang et al., 2013). Since Guangzhou is a subtropical city, which is absent of domestic heating, power plant is the main source of coal combustion (Gao et al., 2011).

3.4.1. PAH ratios

Ratios of PAHs are a widely used tool to distinguish PAH sources (Harrison et al., 1996; Guo et al., 2003; Ding et al., 2007; Liu et al.,

2007, 2014). As Flu/Pyr and IcdP/BghiP isomer pairs photolytically degrade at comparable rates and hence their ratios preserve the original compositional information during atmospheric transport, the ratios $IcdP/BghiP + IcdP$ and $Flu/Pyr + Flu$ were selected in this paper. Fig. 4a presents scatter plots of $IcdP/BghiP + IcdP$ vs. $Flu/Pyr + Flu$ with boundary values proposed by Yunker et al. (2002) as (<0.2 , <0.4) for petroleum, (0.2–0.5, 0.4–0.5) for petroleum combustion and (>0.5 , >0.5) for grass/wood/coal combustion. Petroleum combustion and grass/wood/coal combustion are shown to be major source types at the four sampling sites, but the site-site source variations is vague because the ratios are partially overlapped for these sites (Table 3). $Flu/Pyr + Flu$ were 0.42–0.57, 0.41–0.58, 0.34–0.57 and 0.41–0.58, while $IcdP/BghiP + IcdP$ were 0.40–0.62, 0.41–0.57, 0.35–0.60 and 0.41–0.57 at SZ, YJ, JL and WQS, respectively. However, $Flu/Pyr + Flu$ ratios seemed to be more sensitive to the seasonal change than $IcdP/BghiP + IcdP$ ratios (Fig. 4b). $Flu/Pyr + Flu$ ratios exhibited significant differences ($p < 0.05$) between summer and winter at SZ (0.48 ± 0.02 and 0.52 ± 0.01), YJ (0.48 ± 0.02 and 0.53 ± 0.01) and JL (0.43 ± 0.01 and 0.51 ± 0.01) (Table 3).

3.4.2. Positive matrix factorization (PMF)

PMF model was used to quantitatively evaluate the source variations among different sites and in different seasons. Three sources were resolved and their profiles are shown in Fig. 5. The first source biomass burning was identified by significant amounts of its markers levoglucosan and retene and confirmed by negligible proportions of hopanes (Ramdahl, 1983; van Drooge and Ballesta, 2009). The second source was considered as vehicle emission with high percentages of hopanes and EC (Cass, 1998; Schauer et al., 2002; van Drooge and Ballesta, 2009). The third source was identified as coal combustion by a significant presence of its marker picene (Oros and Simoneit, 2000). The predicted and measured PAHs showed significant correlation ($R^2 = 0.99$) (Fig. S2). Coal

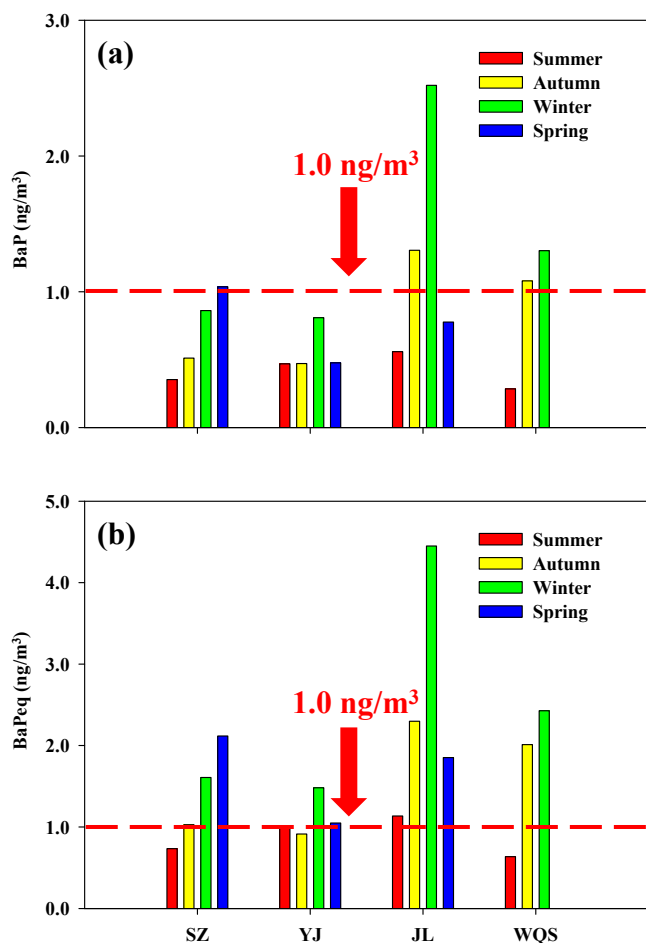


Fig. 3. Seasonal variations of BaP (a) and BaP_{eq} (b) at the four sampling sites. 1.0 ng/m³ represents the limit of the annual average BaP in the NAAQS (GB 3095-2012).

combustion and biomass burning were two major sources that altogether accounted for 73.8% of total PAHs. The annual contribution of each source to the total PAHs based on PMF model at the four sites is presented in Fig. 6a. Vehicle emission played a less

important role (22.2%, 20.0% and 18.9%) than coal combustion and biomass burning, which accounted for 39.7% and 38.1%, 49.6% and 30.3% and 28.9% and 52.2% of PAHs at SZ, JL and WQS, respectively. At the roadside site YJ, vehicle emission contributed to a larger proportion of the PAHs (41.0%), followed by coal combustion (33.1%) and biomass burning (26.0%). In winter, vehicle emission became an even minor source, accounting for 16.7%, 27.0%, 11.0% and 7.1% of PAHs at SZ, YJ, JL and WQS, respectively (Fig. 6b). This is consistent with the finding by Gao et al. (2012, 2013) that vehicle emission is no longer the dominant source in winter of Guangzhou, reflecting the effectiveness of the level IV vehicle emission standard implemented since 2010. However, biomass burning was estimated to be the biggest source accounting for 51.8%, followed by coal combustion (32.0%) and vehicle emission (16.2%), different from the result conducted in Guangzhou of 2009, in which coal combustion was the dominant source (58 ± 4%) (Gao et al., 2013). Nevertheless, the conclusion that biomass burning ranked first in winter is supported by the increased number of fire spots by the Moderate Resolution Imaging Spectroradiometer (MODIS), aboard the Terra and Aqua satellites (<https://firms.modaps.eosdis.nasa.gov>) (Fig. S3). One reason for the enhancement of biomass burning from 2009 to 2013 is the unsuccessful control of agricultural waste burning. Beginning in 1997, the government has enacted a series of regulations to prohibit field burning of crop straws. However, these regulations have not been thoroughly implemented and large amount of crop straws is still being burned in the harvest seasons in the PRD region (Yan et al., 2006; Zhang et al., 2013). Levoglucosan levels and the levoglucosan/EC ratio in winter 2013 (205.4–438.2 ng/m³ and 72.1 × 10⁻³–135.4 × 10⁻³) were significantly elevated as compared to those in winter 2009 (110.0–179.0 ng/m³ and 21.2 × 10⁻³–62.5 × 10⁻³) (Fig. S4), consistent with the fire counts in winters of 2009–2013 (Fig. S5) in the PRD region. Another reason for the enhancement of biomass burning from 2009 to 2013 might be the increased use of alternative biofuel. During “the 11th Five-year Plan Period (2006–2010)”, China had already made great progress in diversified utilization of biofuels and large-scale utilization of a variety of biofuels emerged (Zhou et al., 2016). In its “12th Five-year Plan”, China set a target of utilizing 10 million tons of biomass molded fuels (BMF) each year; and in the “Medium and Long-Term Development Plan for Renewable Energy in China”, a target was set that by 2020, the annual use of BMF will reach 50 million tons. The consumption of

Table 2
Calculated BaP_{eq} (ng/m³) concentrations in selected studies using the same TEFs.

Sampling site/Type	Sampling period	Size	BaP _{eq}	Reference
Guangzhou-SZ/urban	Aug 2013–Apr 2014	PM _{2.5}	1.37	This study ^a
Guangzhou-YJ/urban	Aug 2013–May 2014	PM _{2.5}	1.11	This study ^a
Guangzhou-JL/rural	July 2013–May 2014	PM _{2.5}	2.31	This study ^a
Guangzhou-WQS/background	July–Aug 2013 and Nov 2013–Feb 2014	PM _{2.5}	1.56	This study ^a
Guangzhou-Luhu Park/background	Apr 2001–Mar 2002	TSP	3.60	Li et al. 2006 ^b
Guangzhou-LiWan/urban	Mar–May 2002	PM ₁₀	4.86	Tan et al. 2006 ^a
Guangzhou-LiWan/urban	June–Aug 2002	PM ₁₀	3.16	Tan et al. 2006 ^a
Guangzhou-LiWan/urban	Sep–Nov 2002	PM ₁₀	6.63	Tan et al. 2006 ^a
Guangzhou-LiWan/urban	Dec 2002–Feb 2003 ^c	PM ₁₀	15.88	Tan et al. 2006 ^a
Guangzhou-LiWan/urban	Dec 2002–Feb 2003 ^d	PM ₁₀	5.25	Tan et al. 2006 ^a
Guangzhou-Wushan/urban	Mar–May 2002	PM ₁₀	6.24	Tan et al. 2006 ^a
Guangzhou-Wushan/urban	June–Aug 2002	PM ₁₀	4.23	Tan et al. 2006 ^a
Guangzhou-Wushan/urban	Sep–Nov 2002	PM ₁₀	6.95	Tan et al. 2006 ^a
Guangzhou-Wushan/urban	Dec 2002–Feb 2003 ^c	PM ₁₀	16.66	Tan et al. 2006 ^a
Guangzhou-Wushan/urban	Dec 2002–Feb 2003 ^d	PM ₁₀	5.32	Tan et al. 2006 ^a
Guangzhou-GCAS/urban	Apr 2005–Mar 2006	TSP	2.80	Yang et al. 2010 ^b
Guangzhou-SCBG/suburban	Apr 2005–Mar 2006	TSP	2.55	Yang et al. 2010 ^b

^a Input species include Flu, Pyr, BaA, Chr, BbF, BkF, BaP, BeP, IcdP, DahA and BghiP.

^b Input species include Flu, Pyr, BaA, Chr, BbF, BkF, BaP, IcdP, DahA and BghiP.

^c Characterized by relative high temperature (19.5 °C), high humidity (78%), and low wind speed (1.2 m/s).

^d Characterized by low temperature (13 °C), low humidity (63%), and high wind speed (4.6 m/s).

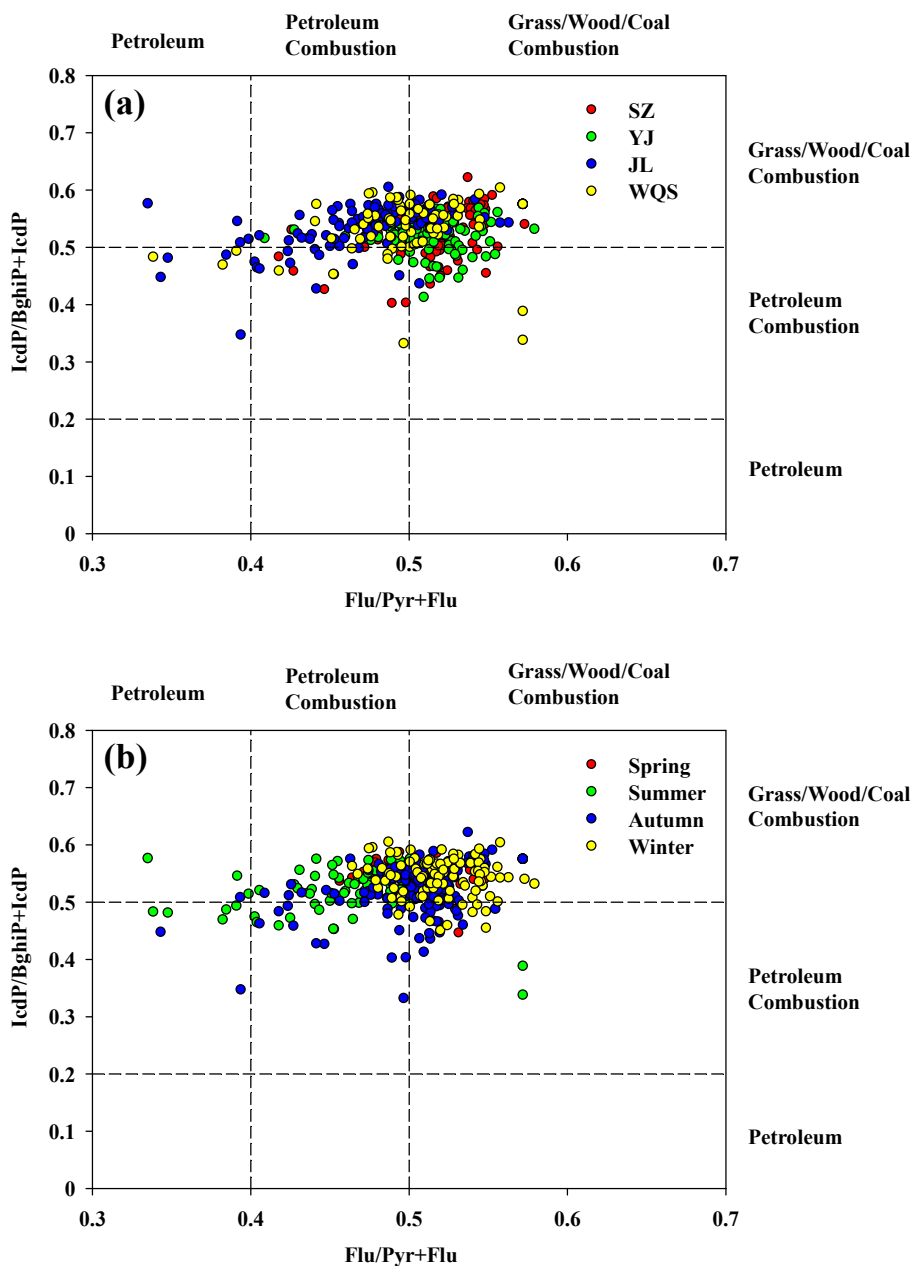


Fig. 4. Spatial (a) and seasonal (b) variations of ratios of IcdP/BghiP + IcdP versus Flu/Pyr + Flu in Guangzhou.

BMF in South China in 2014 reached 2,205,000 tons/a (Xu et al., 2015). Particularly in recent years, many industrial boilers in Guangzhou replaced coal with BMF, but the emission control for the BMF boilers are not as strict as those previously coal-fired ones. The increase BMF use and loosened emission control for BMF boilers would therefore enhance the input of PAHs from biomass burning. Lee and Kim (2007) also found that biomass burning accounted for 40% of total PAHs in Seoul, South Korea in winter 2002–2003. In addition, the coal consumption decreased from 20,293,000 tons in 2009 to 19,889,000 tons in 2013 in Guangdong province (GPBS, 2010, 2014). Some urban areas in the PRD region, like Tianhe district in Guangzhou, have become coal-free areas where coal-burning is totally banned.

Source contributions of BaP_{eq} were calculated by the sum of product of the contribution to each carcinogenic PAH and its TEF. The annual average results revealed that coal combustion and

biomass burning were the main sources, which accounted for 53.2% and 32.0% of BaP_{eq}, while vehicle emission represented a smaller contribution (14.8%). However, biomass burning became the biggest source in winter (52.5%), followed by coal combustion (39.1%) and vehicle emission (8.4%), which is different from the results obtained in Guangzhou of 2009, in which coal combustion was the dominant source (66.0%) (Gao et al., 2015). The source contributions showed strong but different monthly variation at each site (Fig. 7). At SZ, coal combustion was the dominant sources in all months (53.6%–82.1%) except that biomass burning became dominant in November–December (40.6%–53.2%). At YJ, vehicle emission contributed most in all months (65.4%–84.5%) except biomass burning contributed most in November–February (28.5%–56.4%). At JL, coal combustion ranked first in July–September (56.6%–73.3%) and March–May (55.7%–57.9%) and biomass burning ranked first in November–February (50.0%–67.5%). At

Table 3
Diagnostic ratios of PAHs in different seasons at the four sampling sites in Guangzhou.

Sampling site	Season	Flu/Flu + Pyr Mean (95% CI)	IcdP/IcdP + BghiP Mean (95% CI)
SZ	summer	0.48 (0.02)	0.52 (0.01)
	autumn	0.51 (0.01)	0.51 (0.03)
	winter	0.52 (0.01)	0.53 (0.01)
	spring	0.52 (0.01)	0.55 (0.01)
YJ	summer	0.48 (0.02)	0.53 (0.01)
	autumn	0.51 (0.01)	0.51 (0.01)
	winter	0.53 (0.01)	0.53 (0.01)
	spring	0.50 (0.01)	0.52 (0.02)
JL	summer	0.43 (0.01)	0.52 (0.01)
	autumn	0.47 (0.02)	0.52 (0.02)
	winter	0.51 (0.01)	0.56 (0.01)
	spring	0.49 (0.01)	0.56 (0.01)
WQS	summer	0.49 (0.02)	0.52 (0.02)
	autumn	0.51 (0.01)	0.53 (0.03)
	winter	0.51 (0.01)	0.56 (0.01)

WQS, the dominant source changed from coal combustion in July–August (40.2%–68.8%) to biomass burning in November–February (66.8%–80.0%). We did cluster analysis using HYSPLIT model to identify the origins and pathways of air masses reaching WQS in August (Fig. S6). We can see that the air masses mainly came from South China Sea (SCS) and the southeast coast with many coal-fired power plants but relatively fewer fire spots. This might explain coal combustion being the main PAH source in

August.

4. Conclusion

PM_{2.5} Samples were collected at four sites (one urban, two rural and one urban roadside station) from 2013 to 2014 in Guangzhou. We found that measured total PAHs were dominated by high molecular weight (HMW) compounds, and that PAH levels and their ICR were significantly elevated from summer to winter. Although from this study levels of PAHs and BaP_{eq} were dropped drastically when compared to that measured in the same city years ago, PMF source apportioning of total PAHs and BaP_{eq} from this study revealed three alarming facts: 1) calculated average BaP_{eq} were higher at rural sites than at urban sites, indicating that the health risk of exposure to the carcinogenic PAHs in rural areas were higher than urban areas; 2) at the roadside station YJ that is heavily impacted by traffic emissions, average BaP_{eq} there was the lowest among the four sites. This suggests that even in megacities like the Pearl River Delta region, carcinogenic risk of PAHs in ambient air could be no longer dominated by vehicle emissions; 3) at the three governmental ambient air quality monitoring stations (SZ, JL and WQS) vehicle emission only contributed about 20% or less of total PAHs and BaP_{eq}, and coal combustion and biomass burning instead became the dominant sources. In winter, even at the roadside site biomass burning could ranked first among sources of PAHs and BaP_{eq}. Therefore, while motor vehicle emission control standards have been intensively upgraded in Guangzhou in recent years, control of

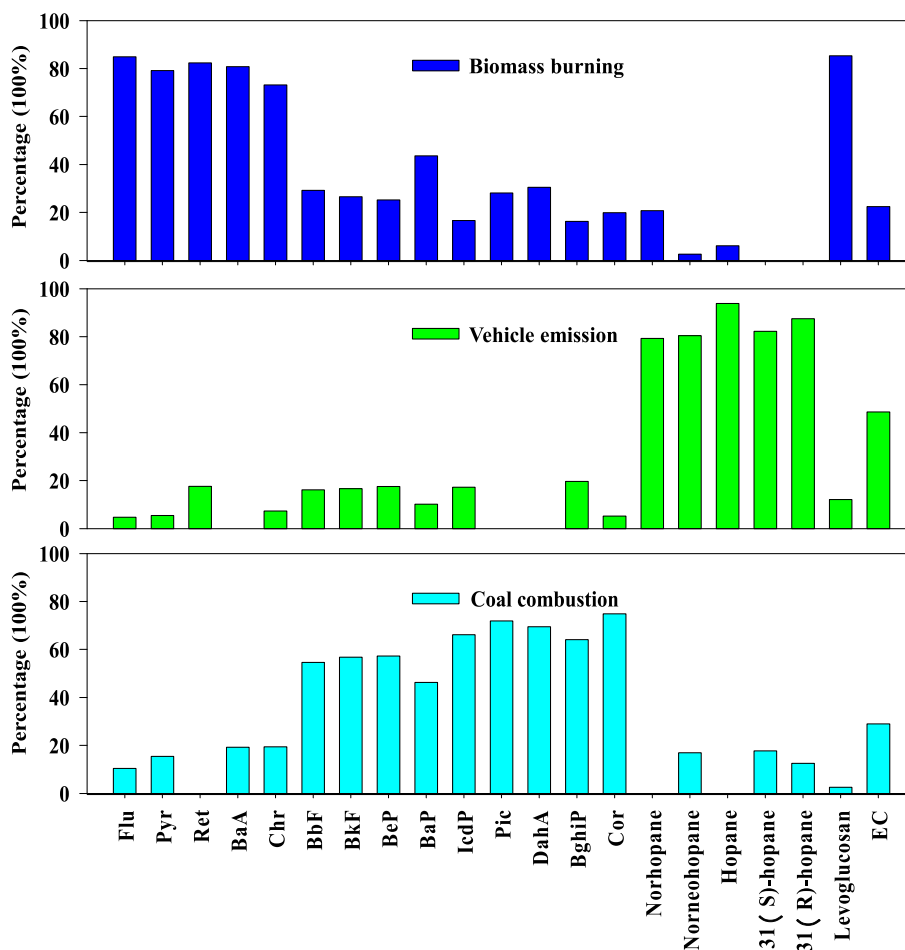


Fig. 5. Factor profiles (% of the species) for PAHs resolved by PMF.

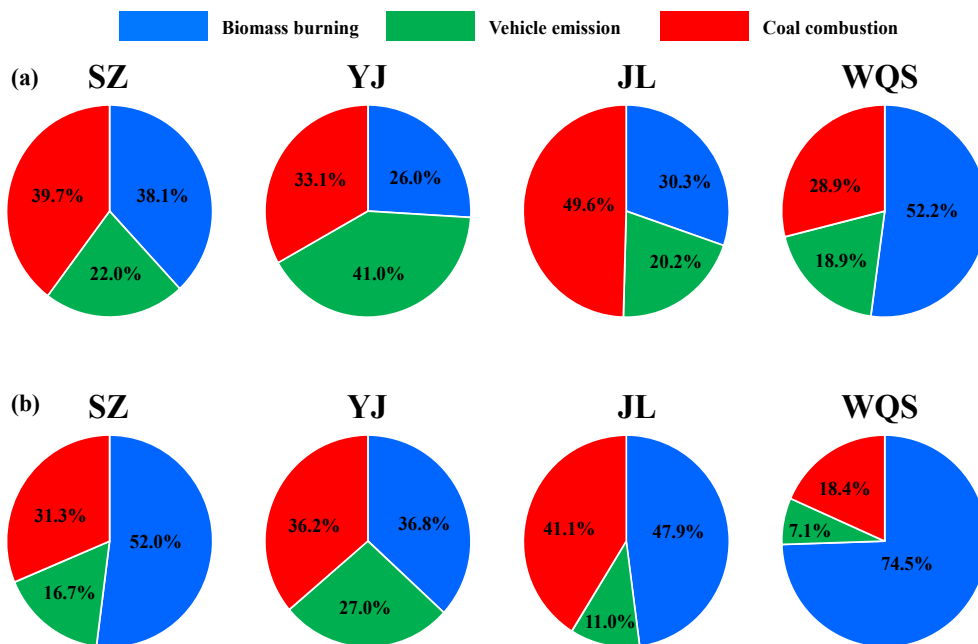


Fig. 6. Average source contributions to PAHs at the four sampling sites in the whole year (a) and in winter (b) of 2013–2014.

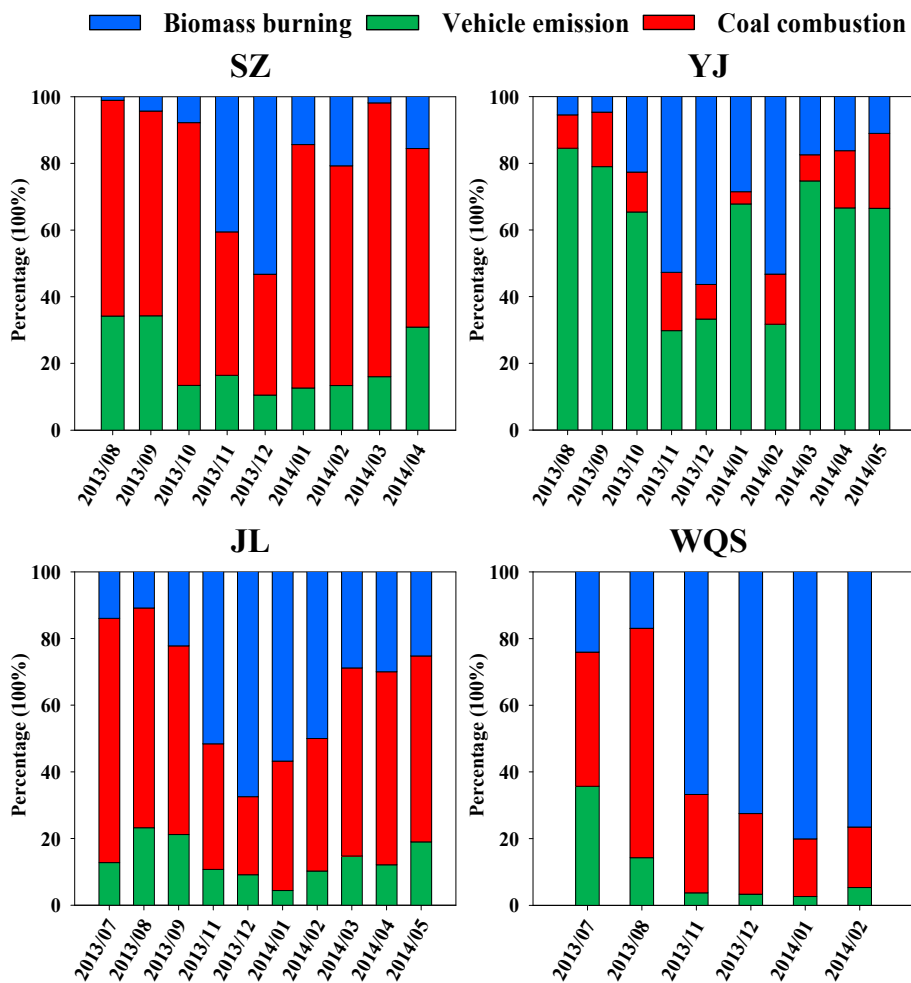


Fig. 7. Monthly variations of BaP_{eq} source contributions at the four sampling sites.

coal burning and biomass burning should also be strengthened for the reduction of carcinogenic PAHs, and particularly in rural areas control of biomass burning would be very effective in the reduction of the cancer risk of PAHs.

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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.2016.08.009>.

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