

Tracer-based source apportionment of polycyclic aromatic hydrocarbons in PM_{2.5} in Guangzhou, southern China, using positive matrix factorization (PMF)

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Abstract From 28 November to 23 December 2009, 24-h PM_{2.5} samples were collected simultaneously at six sites in Guangzhou. Concentrations of 18 polycyclic aromatic hydrocarbons (PAHs) together with certain molecular tracers for vehicular emissions (i.e., hopanes and elemental carbon), coal combustion (i.e., picene), and biomass burning (i.e., levoglucosan) were determined. Positive matrix factorization (PMF) receptor model combined with tracer data was applied to explore the source contributions to PAHs. Three sources were identified by both inspecting the dominant tracer(s) in each factor and comparing source profiles derived from PMF with determined profiles in Guangzhou or in the Pearl River Delta region. The three sources identified were vehicular emissions (VE), biomass burning (BB), and coal combustion (CC), accounting for 11±2 %, 31±4 %, and 58±4 % of the total PAHs, respectively. CC replaced VE to become the most important source of PAHs in Guangzhou, reflecting the effective control of VE in recent years. The three sources had different contributions to PAHs with different ring sizes, with higher BB contributions (75±3 %) to four-ring PAHs such as pyrene and higher CC contributions (57±4 %) to six-ring PAHs such as benzo[ghi]perylene. Temporal variations of VE and CC contributions were probably caused

by the change of weather conditions, while temporal variations of BB contributions were additionally influenced by the fluctuation of BB emissions. Source contributions also showed some spatial variations, probably due to the source emission variations near the sampling sites.

Keywords PAHs · Positive matrix factorization (PMF) · Source apportionment · Guangzhou · Vehicular emission · Coal combustion · Biomass burning

Introduction

Polycyclic aromatic hydrocarbons (PAHs), potential human carcinogens and mutagens, are primarily emitted from incomplete combustion of fossil fuels and other organic materials. They are ubiquitous in ambient atmosphere and can exert long-term toxic effect on public health. Hence, one of the most important tasks is to apportion their sources as knowing the relative contributions of different sources is essential for pollution control policy formulation and implementation.

Chemical mass balance (CMB) model has been widely used to estimate the source contributions to ambient pollutants (Larsen and Baker 2003; Lee et al. 2008). However, there are certain limitations in this model such as requiring the input of unique profile for each major source (Robinson et al. 2006; Shrivastava et al. 2007; van Drooge and Ballesta 2009). In contrast, positive matrix factorization (PMF) is a multivariate model that identifies factors without prior knowledge of source natures of a receptor site. A good result of PMF run is dependent on inputting proper species. If species having collinearity are selected for PMF input, there is a potential risk of misinterpreting or overlooking mixed factors and split factors (Belis et al. 2011). Therefore,

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selecting species characteristic of a source is very important. Molecular tracers are the species widely used in source apportionment studies (Birch and Cary 1996; Schauer et al. 1996; Fraser and Lakshmanan 2000; Simoneit 2002; van Drooge and Ballesta 2009).

Guangzhou, with an area of 7,434 km², is the economic and cultural center of the Pearl River Delta (PRD). During the past decade, the population in Guangzhou increased from 6.9 million in 2000 to 10.3 million in 2009. With the increase in population, more energy consumption is expected, which could lead to severe exposure to PAH-associated polluted air. Indeed, studies have been carried out to understand the sources of PAHs in urban Guangzhou (Bi et al. 2003; Li et al. 2006; Yang et al. 2010; Gao et al. 2011). However, these studies were either qualitative or based on principal component analysis using only PAH data. Limitations such as degradation of certain PAHs, overlapped ratios, and similar PAH profiles among different sources would hinder them from getting reliable results. In addition, as these studies were conducted at only one or two sites, they could not provide a full picture of PAHs in Guangzhou. Moreover, as it has been years since the last source apportionment study in Guangzhou, the dominant sources of PAHs may be significantly changed due to the fact that strict vehicular emission standards have been taken effect in the past decade and numerous high-emission vehicles have been phased out in Guangzhou. Therefore, it is necessary to reevaluate the sources of PAHs in Guangzhou in a quantitative way.

In this study, the PMF model was applied to the determined PAH data together with molecular tracers for potential sources, such as hopanes and elemental carbon (EC) for vehicle emissions (Birch and Cary 1996; van Drooge and Ballesta 2009), levoglucosan for biomass burning (Simoneit 2002; van Drooge and Ballesta 2009), and picene for coal combustion (Zhang et al. 2008; Oros and Simoneit 2000). Benefiting from the intensive sampling campaigns at six different sites in Guangzhou, from 28 November to 23 December 2009, 136 PM_{2.5} samples were collected in total. The large number of samples enabled stable and acceptable PMF results (Zhang et al. 2009a).

The aims of this study are (1) to identify the sources of PAHs in Guangzhou using the PMF model combined with tracer data, (2) to apportion the relative contributions of the major sources, and (3) to analyze the spatiotemporal variations of source contributions to PAHs.

Experimental

Sampling and analysis

The sample collection and chemical analyses used in this study were detailed by Gao et al. (2012). From 28 November

to 23 December 2009, 24-hPM_{2.5} samples were collected consecutively at six sites in Guangzhou, including two urban sites SZ and FC, two suburban sites PY and HD, and two rural sites KD and WQS (Fig. 1). Due to unstable weather conditions and logistical difficulty, samples were not taken occasionally. Eventually, 136 filter samples were collected in total.

A punch (1.5×1.0 cm) of each filter was taken for the measurements of organic carbon (OC) and EC using the thermo-optical transmittance method by an OC/EC Analyzer (Sunset Laboratory Inc.) Detailed information can be found in NIOSH (1999).

PAHs (including picene) and specific organic tracers levoglucosan and hopanes in PM_{2.5} were determined by following the procedures such as spiking labeled surrogates on the samples, ultrasonic extraction, concentration, derivatization (for levoglucosan), and gas chromatography–mass spectrometry analysis (Gao et al. 2012).

Field blanks and lab blanks were routinely analyzed to determine any background contamination. All results showed very low determinants and, in most cases, were not detectable in the blanks. Recovery efficiencies were determined by evaluating surrogate recovery standards spiked to the samples. The mean recoveries for surrogates in field samples were naphthalene-d8 30 %, acenaphthalene-d8 33 %, phenanthrene-d10 35 %, chrysene-d12 88 %, perylene-d12 70 %, tetracosane-d50 90 %, and levoglucosan-¹³C₆ 88 %.

Positive matrix factorization

PMF is a least-squares-based factor analysis model that decomposes a matrix of speciated sample data into two matrices—factor contributions and factor profiles which can be interpreted as to what sources are represented based on observations at the receptor site (Paatero and Tapper 1994; Paatero 1997). Briefly, a mass balance equation can be written to illustrate *j* chemical species in the *i*th sample as concentrations from *p* independent sources.

$$x_{ij} = \sum_{k=1}^p g_{ik}f_{kj} + e_{ij}, \tag{1}$$

where *x_{ij}* is the *j*th species concentration determined in the *i*th sample, *g_{ik}* is the particulate mass concentration from the *k*th source contributing to the *i*th sample, *f_{kj}* is the *j*th species mass fraction from the *k*th source, *e_{ij}* is the residual associated with the *j*th species concentration determined in the *i*th sample, and *p* is the total number of independent sources (Paatero 1997). PMF provides source profiles and contribution matrices without any prior knowledge of source types. Results are constrained so that no samples can have a negative source contribution. The “object function,” *Q*, can be used to review

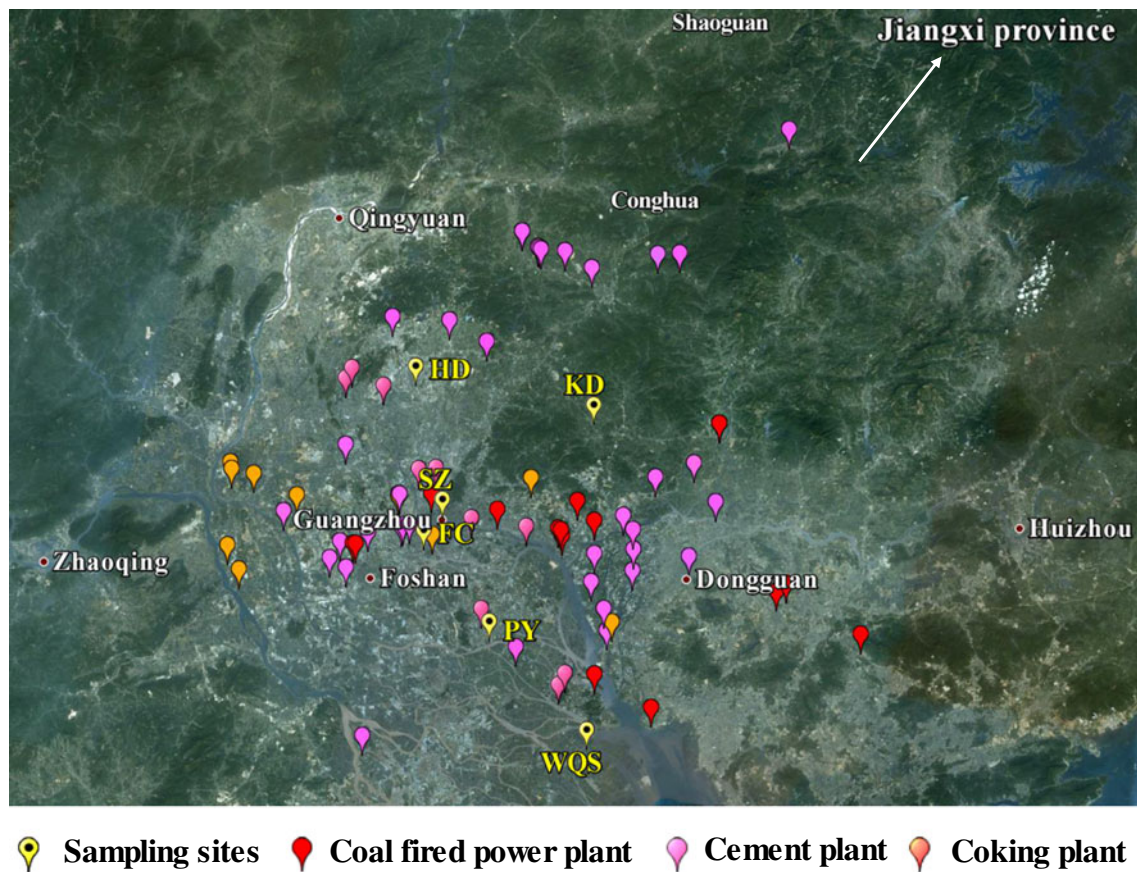


Fig. 1 Sampling sites and the surrounding environment

the distribution for each species to evaluate the stability of the solution.

$$Q = \sum_{i=1}^n \sum_{j=1}^m \left[\frac{x_{ij} - \sum_{k=1}^p g_{ik} f_{kj}}{u_{ij}} \right]^2, \quad (2)$$

where u_{ij} is an estimate of the “uncertainty” in the j th variable determined in the i th sample.

The uncertainties for all of the selected species were calculated by

$$\sqrt{(20\% \times \text{Conc.})^2 + \text{MDL}^2}, \quad (3)$$

where Conc. and MDL are the determined concentration and method detection limit of the species, respectively. MDL was expressed as 3 times the mean blank concentration.

PMF v3.0 was utilized in this study. Sample collected on 12 December at FC was excluded because of the extremely high species levels at this site than those at the other sites. Values below the detection limit were replaced by half of the detection limit values, and their overall uncertainties were set at 5/6 of the detection limit values. For all of the selected species, the signal-to-noise ratios were all larger than 3.

Initially, 30 base runs with all of the species categorized as “strong” and three factors were operated. Three factors were eventually selected because (1) previous studies reported that the main sources of PAHs in Guangzhou were vehicular emissions, biomass burning, and coal combustion (Bi et al. 2003; Li et al. 2006; Yang et al. 2010; Gao et al. 2011), (2) principal component analysis extracted three components with an eigenvalue larger than 1, and (3) three-factor solution produced a good fit to the data and was the most reasonably interpretable. Additional factors made negligible contributions to PAHs and caused factor splitting for tracers. Therefore, more than three factors did not produce meaningful results compared with that of three factors. After the initial run, the Q values were stable, and the Q values in the robust mode were approximately equal to the degrees of freedom. All of the scaled residuals were between -3 and 3 , except some for levoglucosan which were greater than 3 . By examining the observed versus predicted scatter plots, it was found that the correlation coefficients (R^2) for all species except levoglucosan were larger than 0.85 , indicating that most of the species were simulated well. Levoglucosan was moderately modeled ($R^2=0.66$), partly because the uncertainty for levoglucosan was too low. Levoglucosan was finally categorized as “weak” to increase its uncertainty by

a factor of 3. The three-factor solution was bootstrapped 100 times with block size of 8 and minimum correlation R value of 0.6 to estimate its stability. Of the 100 runs, all factors were mapped to a base factor in every run, and no factors were unmapped, indicating that the solution was stable. The factors did not show oblique edges, indicating that there was little rotation for the solution. These features demonstrated that the model simulation results were acceptable.

In this study, due to low recovery, naphthalene to anthracene were not included in the PMF model simulation. Considering the high pair wise correlations of hopanes, four dominant hopanes, i.e., $17\alpha(\text{H})\text{-}21\beta(\text{H})\text{-}29\text{-norhopane}$ (norhopane), $17\alpha(\text{H})\text{-}21\beta(\text{H})\text{-hopane}$ (hopane), 22S-homohopane (31S-hopane), and 22R-homohopane (31R-hopane), were selected for PMF.

Backward trajectory calculation

Air mass back trajectories on 10–12 and 18–20 December were calculated for the discussion in “Temporal variations of absolute source contributions (in ngm^{-3})” using NOAA-HYSPLIT (v4.9) model. Meteorological data that drove the model were from the Global Data Assimilation System (GDAS) data set (3 hourly, global, 1° in longitude and latitude, and 23 pressure levels). For each day, 10-h backward trajectories starting at 0000, 0600, 1200, and 1800 hours with the ending point of 200 m above sea level were configured. Finally, 12 back trajectories were obtained for each period.

Results and discussion

The statistical description of the data collected and a qualitative source identification using tracer/PAH ratio method were previously described in detail by Gao et al. (2012). In summary, the total PAH concentrations ranged from 2.67 to 68.9 ngm^{-3} , with an average value of 17.1 ngm^{-3} , comparable to those reported in previous studies in winter Guangzhou (Li et al. 2006; Yang et al. 2010). The dominant species were five- to seven-ring PAHs, accounting for ~80 % of the total PAHs. There was no obvious concentration gradient for total and five- to six-ring PAHs from urban to rural sites. However, four-ring PAHs exhibited significantly higher levels at rural site than that at urban/suburban sites ($p < 0.01$), implying the differences in source emission strengths, micro-environmental meteorological conditions, and atmospheric transportations among the sites. Individual PAHs and tracers used in this study exhibited similar temporal patterns, consistent with the variations of meteorological condition. PAHs showed moderate to good correlations with tracers, reflecting the main sources of PAHs. Tracer/PAH ratio results showed that vehicular emissions (VE)

were no longer the dominant sources of PAHs in Guangzhou. However, this conclusion and, to a further extent, the relative contributions of different sources should be examined by a receptor model, i.e., the PMF model.

Factor identification

The factor species distributions in percentage of total species are shown in Fig. 2. It can be clearly seen that there were distinct distributions for all of the species among factors, especially for the tracers, which would give us useful information to interpret each factor.

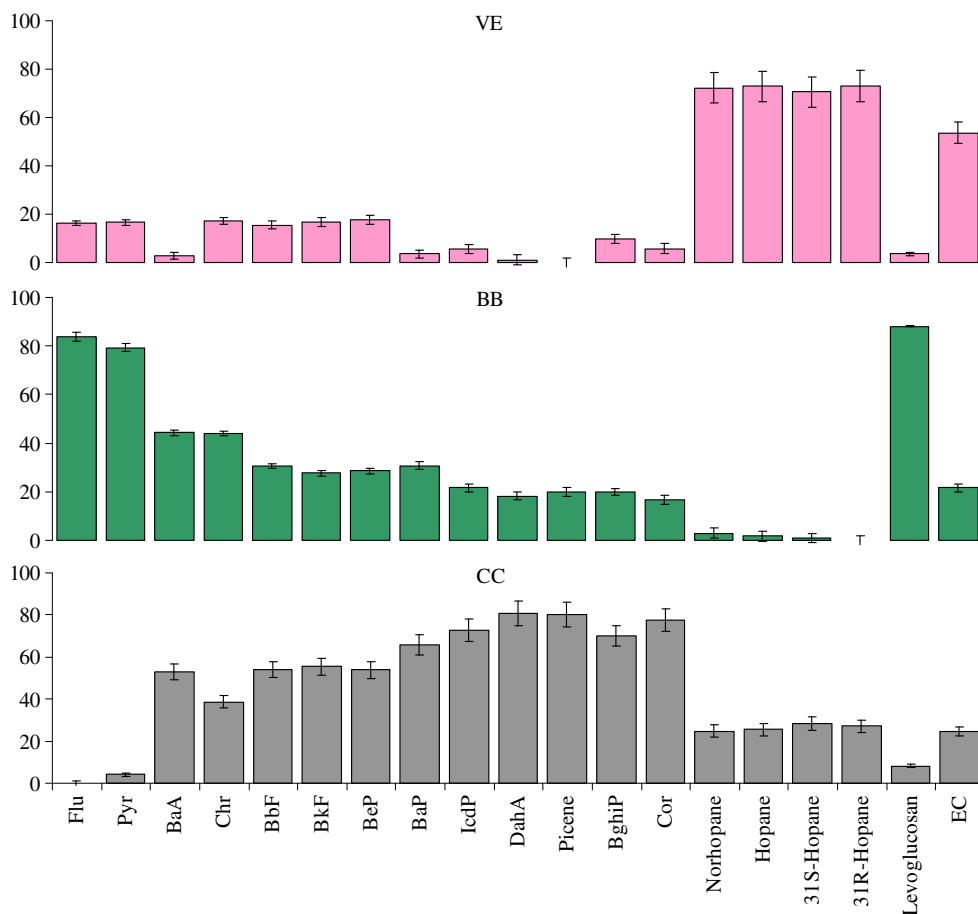
The first source was characterized by high percentage of hopanes and EC, accounting for 70 and 55 % of the total respective species. Hopanes and EC are tracers of both diesel and gasoline VE (Birch and Cary 1996; van Drooge and Ballesta 2009). Although hopanes may undergo degradation, EC is chemically stable during atmospheric transportation. Therefore, jointly using both of them helped us basically identify the first source as VE. To get a further proof of the interpretation, we compared the VE concentration profile resolved by PMF with the real VE profile determined in Zhujiang Tunnel in the western urban area of Guangzhou (He et al. 2008). For comparison purposes, the profiles were normalized by setting the value of the dominant species in each profile equal to 100. Figure 3 shows the comparison of the normalized profiles between determined and model-derived values. It can be seen that the two VE profiles were rather similar, especially for the dominant species, i.e., EC, hopanes, and benzo[g,h,i]perylene (BghiP). In this regard, we confirmed that the first source was VE.

The second source was interpreted as biomass burning (BB) by the significantly high percentage (88 %) of levoglucosan, which has been regarded as a tracer of biomass burning in general (Simoneit 2002; van Drooge and Ballesta 2009). In addition, hopanes for VE had negligible proportion in this source.

The third source was dominated by high-molecular-weight PAHs, including picene, a tracer for coal combustion (CC) (Oros and Simoneit 2000; Zhang et al. 2008). Hopanes and EC for VE and levoglucosan for BB had low percentages in this source. Therefore, this source was assigned to CC.

Many studies also found that ambient PAH data can be explained by the combustion sources identified in this study (Zhang et al. 2009b; van Drooge and Ballesta 2009; Sheesley et al. 2011; Vestenius et al. 2011). For example, Sheesley et al. (2011) identified that petroleum combustion, CC, and BB were the main PAH sources in winter aerosol samples, while van Drooge and Ballesta (2009) found that wood combustion and traffic emissions were dominant PAH sources. Zhang et al. (2009b) identified six PAH sources by applying PMF model to aerosol data collected in five cities in the Midwestern United States. Of the six sources, urban

Fig. 2 Source profiles (percentage of species total) resolved from PMF. *VE* represents vehicular emission, *BB* represents biomass burning, and *CC* represents coal combustion. PAH compounds are given as abbreviations as follows: fluoranthene (*Flu*), pyrene (*Pyr*), benz[a]anthracene (*BaA*), chrysene (*Chr*), benzo[b]fluoranthene (*BbF*), benzo[k]fluoranthene (*BkF*), benzo[e]pyrene (*BeP*), benzo[a]pyrene (*BaP*), indeno[1,2,3-cd]pyrene (*IcdP*), benzo[g,h,i]perylene (*BghiP*), dibenz[a,h]anthracene (*DahA*), and coronene (*Cor*)



primary sources, mobile sources, and other combustion sources were dominant. In addition, Vestenius et al. (2011) found that PAHs in southeastern Finland were mainly from combustion sources.

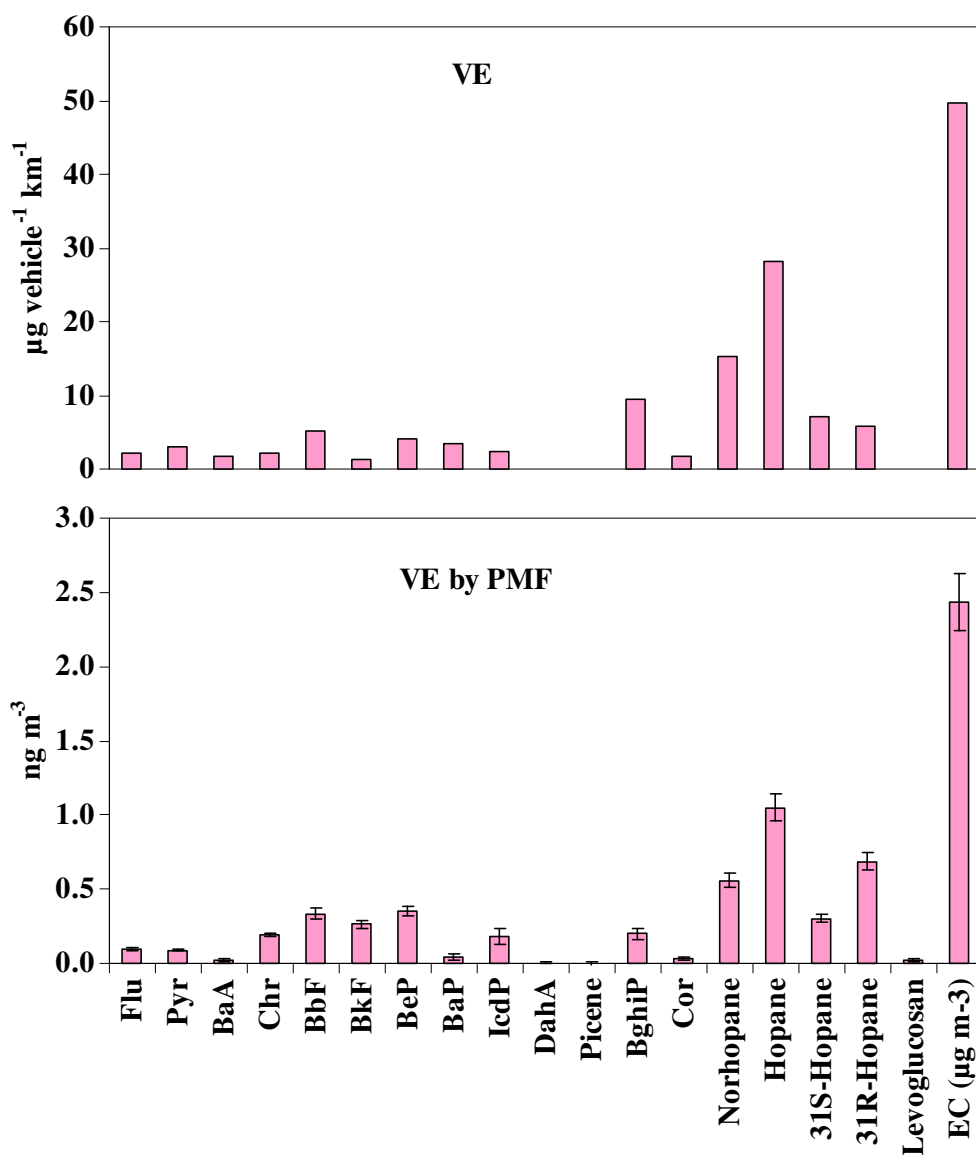
Source contributions to total PAHs

The average contributions of each source to the total PAHs in Guangzhou are illustrated in Fig. 4a. It was found that CC made the most significant contribution (58 ± 4 % of the total PAHs), followed by BB (31 ± 4 %) and VE (11 ± 2 %). A previous study claimed VE as the dominant source of PAHs in winter Guangzhou (Li et al. 2006). The authors used principal component analysis in combination with multiple linear regressions (PCA-MLR) to estimate the relative source contributions to particulate PAHs. They found that on average, VE and CC contributed 69 and 31 %, respectively, to the total particulate PAHs from 2001 to 2002, and VE contribution was even higher in winter. Guo et al. (2003) reported that VE was the predominant source of PAHs in Hong Kong from 2000 to 2001 by PCA results. However, Gao et al. (2011) found that BB and CC could be the dominant sources of PAHs in winter Guangzhou in 2006 after ratio-to-ratio plotting. This study further quantified that VE was no longer the dominant source of PAHs in winter

Guangzhou in 2009 (11 ± 2 %). Instead, CC became the most important source of PAHs (58 ± 4 %), and the VE contribution was even lower than the BB contribution (31 ± 4 %). The result was consistent with our previous study which used tracer-to-PAH ratio approach to identify sources at the six sites in Guangzhou (Gao et al. 2012). The shift of dominant PAH source from VE to CC may be owing to the fact that from 2000 to 2009, stricter vehicle emission standards took effect in PRD. For both light- and heavy-duty vehicles, China standards (level I) were adopted from 2000 to 2004, China standards (level II) were implemented in 2005, and China standards (level III) took effect from 2006 to 2009 in this region (Fung et al. 2010). The pollutant levels were cut down by 50–75 % due to the shift of China standards (level I) to China standard (level III). On the other hand, as there were no emission standards for CC and BB, their emissions were not well controlled, and their contributions to PAHs became outstanding. Considering the high emission factors of CC, it was not surprising that CC contributed relatively more to PAHs than ever.

Lee and Kim (2007) applied CMB model to quantify seven sources of PAHs in Seoul, South Korea from 2002 to 2003 and found that in winter, the major sources were BB, CC for residential heating, and coke oven, accounting for 40, 28, and 14 %, respectively, of the total particulate

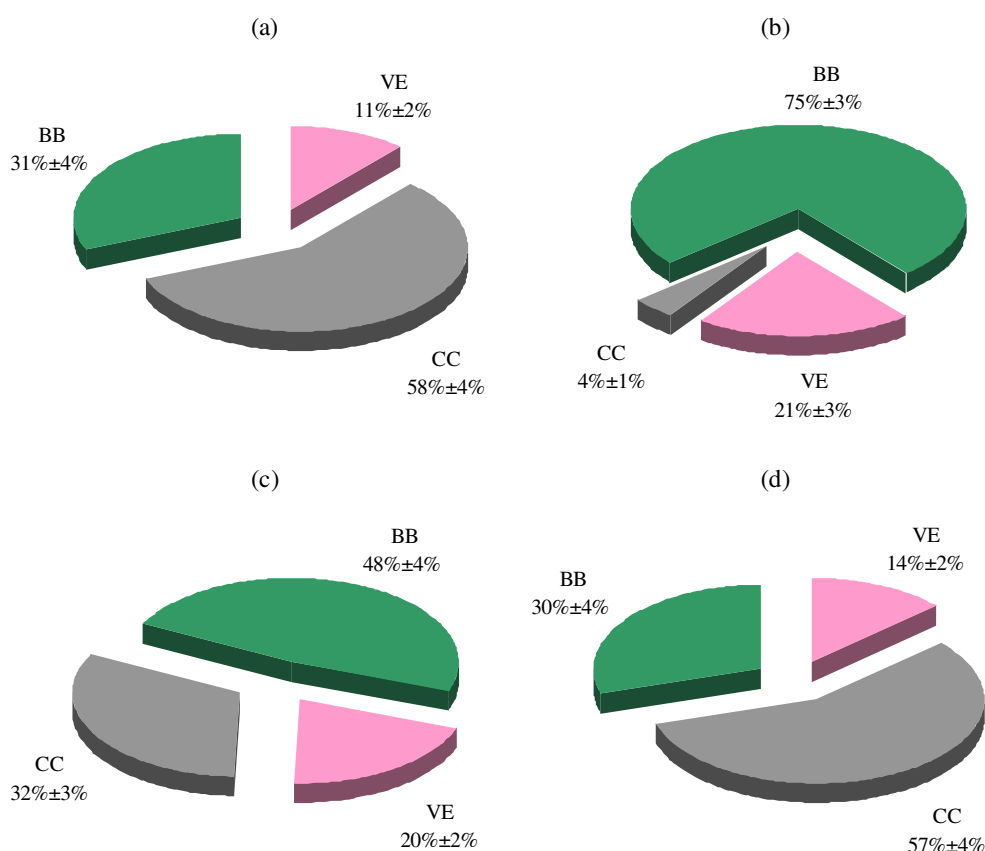
Fig. 3 Comparison of VE source profile resolved by PMF with that from data collected in Zhujiang Tunnel in the western urban area of Guangzhou (He et al. 2008). The missing bars are species not reported in the literature



PAHs. They attributed the high BB and CC contributions in winter to the transported PAHs from China. Inomata et al. (2012) used a newly developed PAH emission inventory for northeast Asia to investigate the spatiotemporal distributions of particulate PAH concentrations in 2005. They found that in winter, domestic coal, domestic biofuel, and other coal transformations contributed 20–59 %, 11–18 %, and 4–18 %, respectively, to benzo[a]pyrene at the Noto station, Japan. They argued that under the westerly winds, the source region was in China. However, it was reported that in winter, PAH outflows reaching North Asian counties were mainly from North China Plain and northeast China, whereas Southeast China including Guangdong province was the major contributor to the PAH outflow reaching the South China Sea and Southeast Asia (Lang et al. 2007, 2008). Indeed, many studies using PAH ratios and/or factor analysis identified that CC for residential heating was the

major source of PAHs in cities in northern China (Okuda et al. 2006, 2010; Tian et al. 2009; Li et al. 2011; Ma et al. 2011). With the help of the PCA-MLR technique, Ma et al. (2011) found that pyrogenic sources (including CC for residential heating), coke oven, and unidentified sources contributed 44, 39, and 17 %, respectively, to the total PAHs in winter Beijing. By using factor analysis with non-negative constraints, Tian et al. (2009) identified that coal-fired boiler emission (56 %), CC for residential heating (33 %), and VE (11 %) were the main sources of PAHs in winter Dalian. Okuda et al. (2010) concluded that CC for residential heating, oil combustion, gasoline VE, BB, waste incineration, and others contributed 26, 22, 19, 13, 13, and 6 %, respectively, to the total PAHs in winter Xi’an. However, it is noteworthy that the emission sources of PAHs varied from place to place, given the difference in energy use, source strength, and landform (Xu et al. 2006). In

Fig. 4 Average source contributions to **a** the total PAHs, **b** Pyr, **c** Chr, and **d** BghiP in Guangzhou (mean \pm standard error)



particular, unlike the cities in northern China where CC for residential heating is a common practice, Guangzhou is a subtropical city in southern China absent of CC for residential heating (Li et al. 2006). Therefore, it was reasonable to infer that CC for power plant and industry became the dominant source of PAHs in Guangzhou. Indeed, there are many power plants, cement plants, and coking plants using coal as fuel in Guangzhou (Fig. 1).

The average relative errors ($RE = |\text{observed concentration} - \text{modeled concentration}| / \text{observed concentration}$, where modeled concentration was the sum of concentrations contributed by each sources) for individual PAH compounds ranged from $5.5 \pm 0.8\%$ to $10.9 \pm 1.3\%$, indicating the validity of source contribution results. Correlation analysis on the concentrations of individual PAHs for all of the sampling sites revealed that three groups of PAHs had strong correlations, with correlation coefficients $R^2 > 0.85$: (1) fluoranthene (Flu) versus pyrene (Pyr), (2) benz[a]anthracene (BaA) versus chrysene (Chr), and (3) five- to seven-ring PAHs. This indicates that PAHs with comparative ring sizes had similar physiochemical properties and/or emission sources, while PAHs with distinct ring sizes may have different behaviors. Hence, three typical PAHs, i.e., Pyr, Chr, and BghiP, were selected to represent each corresponding group above. The average contributions of each source to the three PAHs are also shown in Fig. 4. It

can be seen that the source contributions to the three PAHs were different. BB was the largest contributor to Pyr ($75 \pm 3\%$). With the increase of molecular weight, BB played less important role, whereas CC became more important. The source contributions to BghiP were similar to those of total PAHs due to the fact that high-molecular-weight PAHs were the dominant species in the total PAHs ($78 \pm 2\%$).

Temporal variations of absolute source contributions (in ng m^{-3})

Figure 5 shows the temporal variations of absolute source contributions (ASC) to the three typical PAHs. Large variations of ASC were found, perhaps due to the combined effect of the change of weather conditions and source emissions. The ASC of VE and CC had similar temporal variations, both of which exhibited three high-value episodes, i.e., 4–6, 10–12, and 21–23 December, and two low-value episodes, i.e., 29 November–3 December and 15–20 December. CC is mainly used for power generation in Guangzhou. Therefore, PAH emissions from CC might not have large daily variations (Li et al. 2006; Gao et al. 2011), neither did daily PAH emissions from VE because the number and density of vehicles were relatively constant each day in Guangzhou. Therefore, the temporal variations of ASC for VE and CC may be largely due to the change of

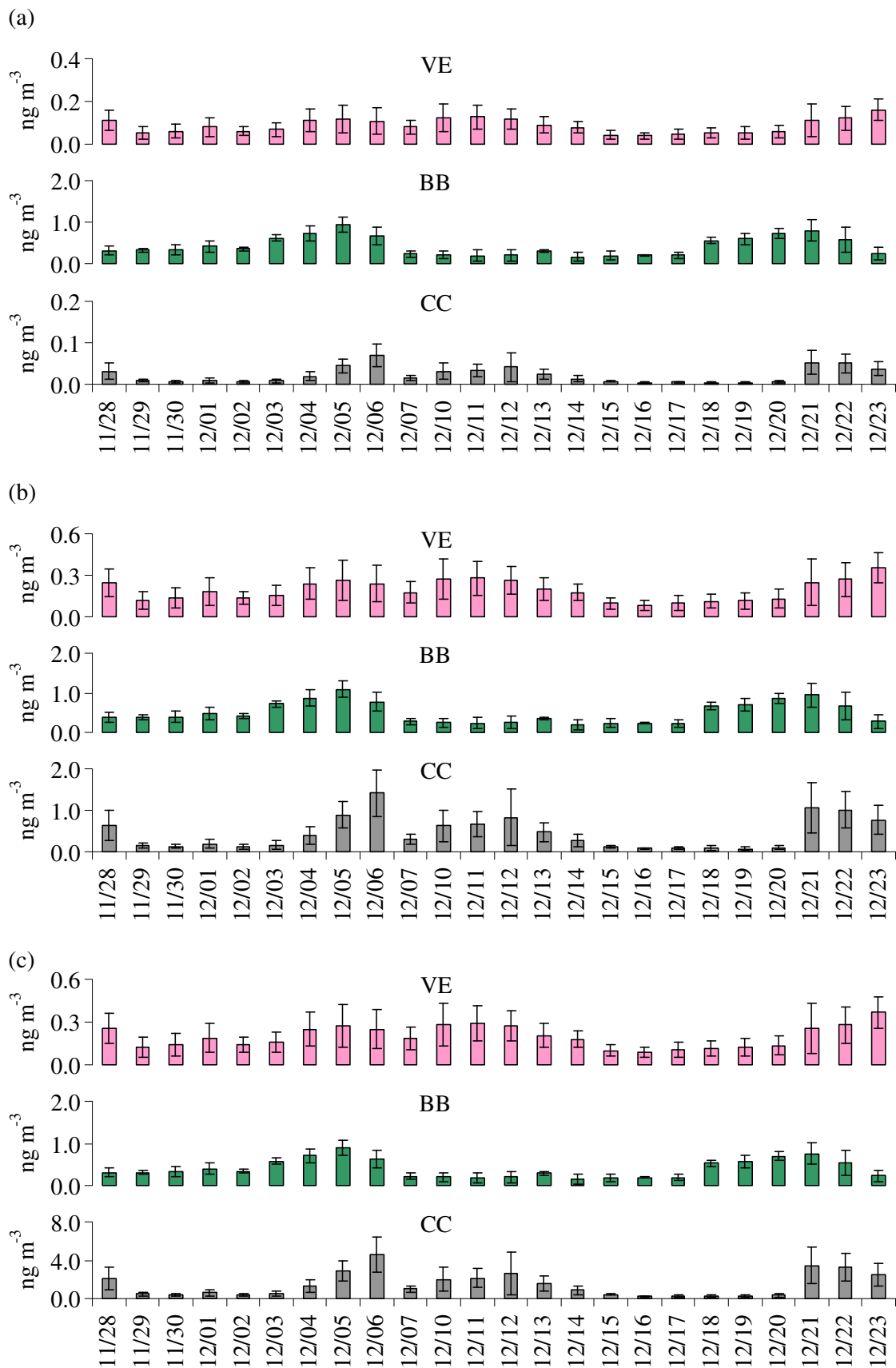


Fig. 5 Temporal variations of absolute source contributions (in ng m^{-3}) to **a** Pyr, **b** Chr, and **c** BghiP

weather conditions. As discussed in our previous paper (Gao et al. 2012), during the three high-value episodes, the weather conditions were stable, namely, high temperature and solar radiation, and low wind speed, which were favorable for the accumulation of PAHs. On the other hand, during the two low-value episodes, there were two cooling processes caused by cold front and/or rain belts, which lowered the PAH concentrations.

The temporal variations of ASC for BB showed some differences from those for VE and CC. For example, the ASC of BB was low on 10–12 December and was high on 18–20 December. The difference may be caused by the variations of BB emissions. Indeed, back trajectory analysis and the Moderate Resolution Imaging Spectroradiometer (MODIS) fire maps (<http://firefly.geog.umd.edu/firemap/>) showed that on 10–12 December, the air masses originated from eastern inland PRD, i.e., Huizhou and Shenzhen, where no BB activities (fire spots) were observed during that period (Fig. 6a), resulting in low BB emissions. In contrast, on 18–20 December, the air masses originating from northern outland PRD passed over many fire spots

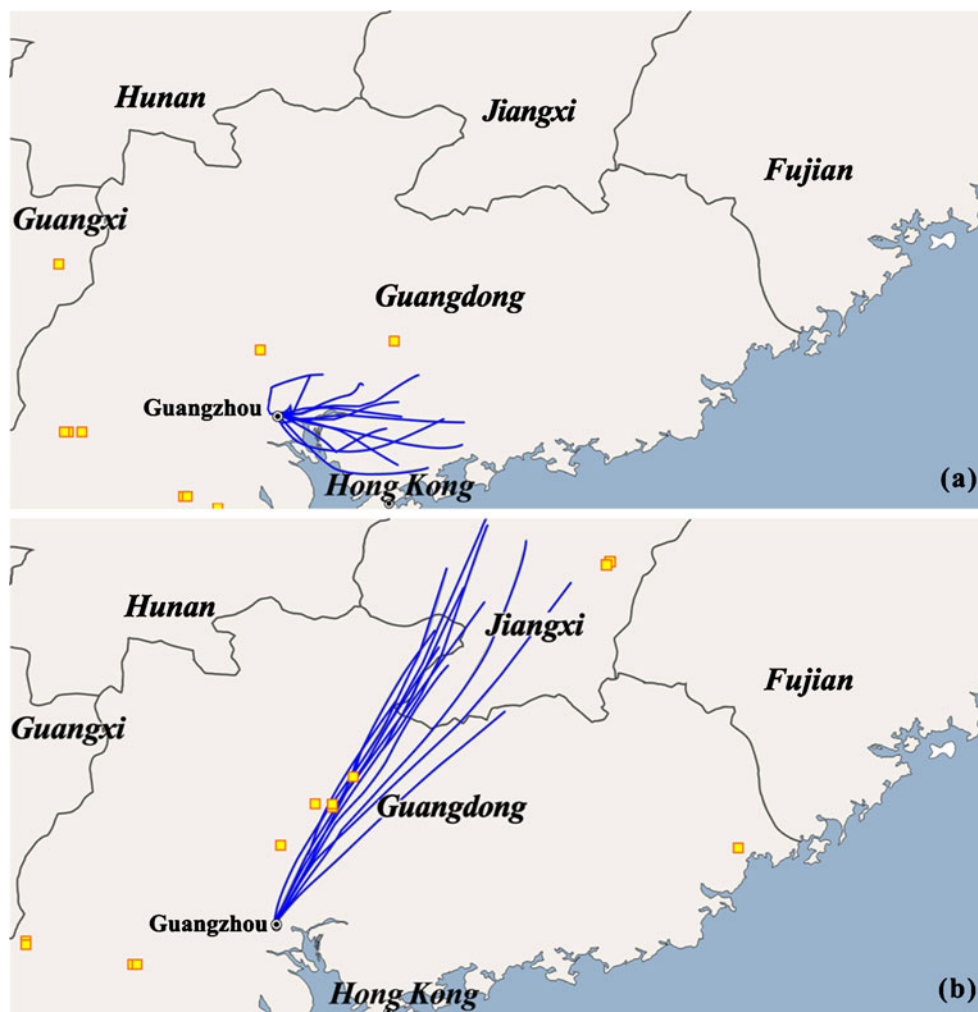
in Jiangxi province and in Shaoguan and Conghua in Guangdong province, leading to high BB emissions (Fig. 6b). The dominance of weak easterly winds on 10–12 December and strong northeasterly winds on 18–20 December in Guangzhou (Gao et al. 2012), to a certain extent, was consistent with the back trajectory results.

It is noteworthy that high-resolution meteorological data are crucial for reliable back trajectory results. Uncertainty is inevitable when using a lower resolution meteorological data such as GDAS (1°). However, higher resolution global meteorological data were not available for 2009, and simulating a high-resolution meteorological field by meteorological models such as Weather Research and Forecasting model was extremely time consuming. Nevertheless, further study is warranted to reduce the uncertainties in backward trajectories caused by the resolution of meteorological data.

Spatial variations of ASC

Box plots were used to display the spatial variations of ASC to the three typical PAHs in Guangzhou (Fig. 7). It was

Fig. 6 Back trajectories and the MODIS fire maps during the two periods in Guangzhou **a** 10–12 December and **b** 18–20 December 2009. The *yellow spots* in the maps represent the fire events



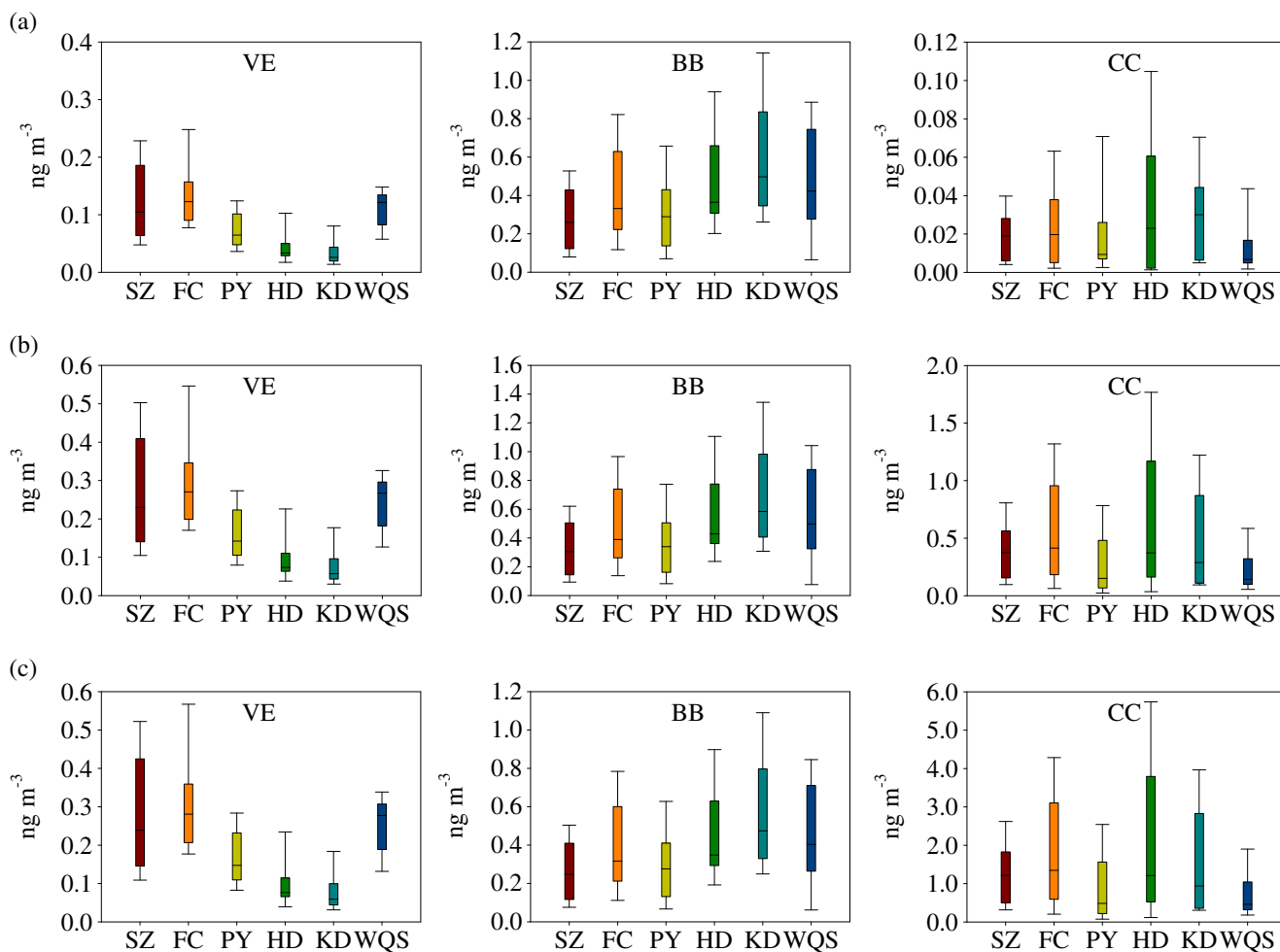


Fig. 7 Spatial variations of absolute source contributions (in ng m^{-3}) to **a** Pyr, **b** Chr, and **c** BghiP. Boxes indicate 25th to 75th percentiles, lower and upper bars indicate 10th to 90th percentiles, and lines inside the boxes show the median values

Fig. 8 MODIS fire maps during the whole sampling period in Guangzhou. Yellow squares represent fire spots



found that for all of the three PAHs, the ASCs of VE at the suburban site HD and the rural site KD were significantly lower than those at the other sites ($p < 0.05$, Fig. 7a). This is not surprising as both sites were adjacent to the northern border of the PRD region, upwind of the Guangzhou city, and there were no big cities in their upwind directions. Specifically, KD was located in a mountainous and hilly area where only one main road with rare traffic was approximately 200 m away from this site. And HD was surrounded by parks and schools with light traffic. In contrast, the two urban sites, i.e., SZ and FC, were in the city center, surrounded by main traffic roads. Hence, the ASCs of VE at these two sites were expected to be high. Indeed, the ASCs to BghiP for VE at SZ and FC (i.e., 0.28 ± 0.07 and $0.31 \pm 0.06 \text{ ngm}^{-3}$ (mean \pm 95 % confidence interval), respectively) were significantly higher than those at HD and KD (i.e., 0.11 ± 0.04 and $0.08 \pm 0.02 \text{ ngm}^{-3}$, respectively) ($p < 0.01$). The PY site was in a newly developed residential town with scattered houses, schools, and light traffic, while the WQS site was located in a small town surrounded by farmlands with few traffic and textile and clothing workshops. However, there were busy highways adjacent to the two sites. Under the influence of nearby vehicular emissions superimposed by the emissions from upwind Guangzhou urban center, the ASCs to BghiP for VE at PY and WQS (i.e., 0.17 ± 0.03 and $0.25 \pm 0.04 \text{ ngm}^{-3}$, respectively) were significantly higher than those at HD and KD ($p < 0.05$). Moreover, the ASC of VE at the rural site WQS was even similar to that at the urban sites SZ and FC ($p > 0.05$), reflecting the remarkable influence of highway traffics to the rural site.

On the other hand, due to large daily variations, all of the sites exhibited similar ASC values in terms of BB (Fig. 7b). Bearing the large variations in mind, the ASCs of BB at HD, KD, and WQS were slightly higher than those at the other three sites. Indeed, MODIS fire maps showed many open fires in the northern direction of HD during the sampling period (Fig. 8). And KD and WQS were in rural areas where the residents traditionally burned straws, stalks, and deadwood for cooking and heating. These indoor activities could be the reason for the high ASCs of BB at the two sites.

Although there were two big power plants situated upwind of the WQS site, it was interesting to find that the ASC value for CC was significantly lower at WQS than that at SZ, FC, HD, and KD ($p < 0.05$) (Fig. 4). Despite limited information available on the two power plants, it could be due to the fact that these two power plants adopted much stricter emission control measures. Furthermore, the lower ASC for CC at WQS could also be related to fewer small and low-efficient coal-fired boilers at WQS than at SZ and FC and to less domestic coal combustion at WQS than at HD and KD. Nevertheless, a firm conclusion needs further investigation.

Summary

The PMF model was applied to the measurement data of particle-phase PAHs and tracers for VE, BB, and CC for the estimation of the source contributions to airborne PAHs in Guangzhou. Results revealed that the contributions of VE, BB, and CC to the total PAHs were 11 ± 2 %, 31 ± 4 %, and 58 ± 4 %, respectively. PAHs with different ring sizes had different source contributions, with higher BB contributions to four-ring PAHs such as Pyr and higher CC contributions to six-ring PAHs such as BghiP. Large temporal variations of ASC for VE and CC to PAHs were found to be related to the change of weather conditions, whereas the temporal ASC for BB was caused by both the change of weather conditions and the fluctuation of BB emissions. Finally, the spatial variations of ASCs for the three main sources were likely associated with the variations of source emissions near the sampling sites.

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