Source seasonality of polycyclic aromatic hydrocarbons (PAHs) in a subtropical city, Guangzhou, South China

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Abstract

Mega-cities are large sources of air pollution on a regional base. Differences in energy structures, geographical settings and regional climate features lead to a large variety of air pollution sources from place to place. To understand the seasonality of air pollution sources is critical to precise emission inventories and a sound protection of human health. Based on a year-round dataset, the sources of PAHs in the air of Guangzhou were drawn by principal factor analysis (PCA) in combination with diagnostic ratios, and the seasonality of these sources were analyzed by PCA/MLR (multiple linear regressions) and discussed. The average total gaseous and particulate PAHs concentrations were 313 and 23.7 ng m^{-3}, respectively, with a higher concentration of vapor PAHs in summer and particulate PAHs in winter. In addition to vehicle exhaust, which contributed 69% of the particulate PAHs, coal combustion was still an important source and contributed 31% of the particulate PAHs. Relatively constant contribution from coal combustion was found through the year, implying that coal combustion in power plants was not a seasonally dependent source. Evaporation from contaminated ground may be an important source of light PAHs in summer, providing an average contribution of 68% to the total PAHs in this study. By comparing the PAH concentrations and meteorological parameters, we found that higher concentrations of particulate PAHs in winter resulted from enhanced vehicle exhaust under low temperature and accumulation of pollutants under decreased boundary layer, slower wind speed, and long-term dryness conditions. It is suggested that the typical subtropical monsoon climate in South China, cool and dry in winter, hot and humid in summer, may play a key role in controlling the source seasonality (by enhancing vehicle exhaust in winter, ground evaporation in summer), and hence the ambient concentrations of PAHs in the air.
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Keywords: Polycyclic aromatic hydrocarbons (PAHs); Source seasonality; Concentrations; Meteorological effect

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1. Introduction

Due to the intensified population, energy consumption, transportation and industries, mega-cities play an important role in the emission and air transport of anthropogenic air pollutants on a regional basis. People living in cities are exposed directly to more serious air pollution than those living in rural and remote places. Local energy structure, economic forms, climate and even living styles of people can affect the source characteristics of air pollutants in mega-cities; this will undoubtedly lead to a large variety of air pollution sources among different regions.

Polycyclic aromatic hydrocarbons (PAHs) were identified to be one of the major toxic air pollutants in urban environments. They are compounds containing two to eight rings that are mainly derived from the incomplete combustion of fossil fuels and wood and volatilization of uncombusted petroleum. Forest fires and volcanoes also contribute to the PAH burden, but by far, anthropogenic sources are responsible for the majority of the PAH input to the atmosphere (Bjorseth and Ramdahl, 1985). Due to their well-known carcinogenic and mutagenic properties, polycyclic aromatic hydrocarbons (PAHs) were widely studied regarding their environmental effects (Lee et al., 1981; Williams, 1990).

Concentrations and profiles of PAHs in ambient air are dependent on their sources and environmental variables (Wild and Jones, 1995; Lee and Jones, 1999; Lee et al., 1998; Dimashki et al., 2001 Vestreng and Klein, 2002;), which vary from region to region. In European cities, vehicle exhaust, wood/coal combustion for space heating, and some stationary point sources, such as metal smelting/process operation, were the principal sources for PAHs (Wild and Jones, 1995; Vestreng and Klein, 2002). In North America, emission from coal and oil combustion in power plants is one extra important source for PAHs (Simcik et al., 1999). Evaporations from contaminated ground have also identified/modeled to be an important source of PAHs in summer time (Lee and Jones, 1999; Lee et al., 1998; Dimashki et al., 2001). Among these, combustion for space heating and ground evaporation are obviously seasonally dependent, while vehicle exhaust and the emissions from power plants and other stationary sources may be assumed to be not or less. To understand the feature of seasonality of PAHs pollution sources is critical to precise PAHs emission inventories and hence a sound protection of human health.

The majority of population and cities in China reside along the eastern coast and in central plains. The outflow of air pollution from these highly populated regions has drawn attention in recent years (Wang et al., 2003a). Vehicle exhaust, coal combustion both for power generation and for space heating, as well as wood combustion were identified to be the major PAH sources in the cities (Wild and Jones, 1995; Simoneit et al., 1991; Simcik et al., 1999; Seung et al., 2002; Vestreng and Klein, 2002). As coal is widely used for cooking and space heating in North China, a previous study (Simoneit et al., 1991) suggested that more PAHs in aerosols in North China cities might come from coal combustion. Although residential heating normally is not necessary in South China cities, coal combustion is still the principal energy source in power plants in South China. Evaporation of PAHs from contaminated ground surface in warmer South China cities is possible, though this has not been assessed.

Lying below the Tropic of Cancer and on the coast, Guangzhou features a typical monsoon-controlled climate, wet and hot in summer, and dry and cool in winter. It is the largest city in South China, with a population reaching 10 million (Fig. 1). Grouped with Hong Kong and many other cities in the Pearl River Delta, e.g. Shenzhen, Foshan, Zhongshan and Dongguan etc., it is becoming the geographical center of a fast developing metropolitan region, which has a population of over 38 million, contributing to 1/10 of China's gross domestic product (excluding Hong Kong). With the fast urbanization and industrialization in the last two decades, the environmental quality in the region has been severely deteriorated (Xie et al., 2002). Huge and vast haze has been observed hanging over the Pearl River Delta especially in winter time, accompanied by high concentrations of total suspended particulate (TSP); PM10, PM2.5, and particulate PAHs (Panther et al., 1999; Lee et al., 2001; Bi et al., 2003; Guo et al., 2003). A boundary layer outflow of air pollution from the region to the West Pacific was assumed (Wang et al., 2003b; Chan et

Fig. 1. Location of Guangzhou and the Pearl River Delta.

al., 2002). For PAHs, Panther et al. (1999) suggested that the higher PAH concentration in the dry season might be caused by increased biomass burning. Guo et al. (2003) and Lee et al. (2001) considered that higher winter PAH concentration was from local emission sources superimposed by highly polluted air masses from mainland China. Based on molecular markers, Bi et al. (2003) suggested that the major PAH sources in Guangzhou were vehicle exhaust and wood combustion. However, no quantitative source apportionment has been made for atmospheric PAHs in the region, and the seasonality of the potential sources remains unknown.

Based on year-round monitoring of particulate and gaseous PAHs in the air of Guangzhou, the present paper suggested that enhanced vehicle exhaust, lower boundary layer accompanied by long-term dry weather may be responsible for the high PAH concentration in winter, and that evaporation from contaminated ground may be an important source of light PAHs in summer. Relative constant contribution from coal combustion was found through the year, implying that coal combustion in power plants was not a seasonally dependent source.

2. Experimental section

2.1. Field site and sampling

The sampling site is at a meteorological station located in Luhu Park in the north of Guangzhou city, at the south range of Baiyun Mountain. Sampling was conducted for a consecutive 24 h period during whole day and night on a weekly base from April 2001 to March 2002. Samplers were collected with a high-volume air sampler, at a flow rate of 335 m^3 day^{-1}. Suspended particulate was retained on a Whatman glass microfiber filter (GFF) (grade GF/A, 20.3×25.4 cm), and vapor phase absorbed on a polyurethane foam plug (PUF) (length 8.0 cm, diameter 6.25 cm, density 0.035 g cm^{-3}). During the sampling time, the meteorological parameters, including ambient temperature, relative humidity, wind speed/direction, and precipitation, were recorded.

Prior to sampling, the filter papers were baked at 450 °C for 4 h. The PUFs were pre-extracted in dichloromethane (DCM) for 48 h, dried under vacuum, and sealed in pre-cleaned glass jars prior to use. After sampling, the filters were folded and sealed in aluminum foil envelopes until weighing for determi-

nation of total suspended particulate (TSP) mass. The PUFs were sealed in the jar and stored in a freezer at $-20\ °C$ until further analysis.

2.2. Analytical procedure

Sixteen PAHs (naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flua), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (Ind), dibenz[a,h]anthracene (DbahA), and benzo[g,h,I]perylene (BghiP)) in a mixture and deuterated PAHs standards, consisting of naphthalene-D_8; acenaphthene-D_{10}; phenanthrene-D_{10}; chrysene-D_{12} and perylene-D_{12}, were obtained from Ultra Scientific Inc. (North Kingston, RI, USA). Internal standard (hexamethylbenzene) were acquired initially as a solid of 99% purity (Aldrich Chemical, Gillingham, Dorset, USA). All reagents utilized were redistilled in a full-glass distilling appliance.

Deuterated PAHs standards were added as surrogates prior to extraction. All PUF and filters were extracted for 40 h with dichloromethane (DCM) in a soxhlet apparatus. The organic extract was combined, filtered and concentrated on a Büchi Rotary evaporator (bath temperature $\leq 30\ °C$). Interfering compounds were removed by liquid–solid chromatography using 2 : 1 silica–alumina column. The fraction of PAHs was collected by eluting the column with 70 mL of DCM–hexane at a ratio of 3 : 7. Then the samples were reduced to 0.2 mL under a gentle stream of nitrogen. Internal standard hexamethylbenzene was added prior to the GC-MS analysis.

PAHs compounds were separated on a $30\ m \times 0.25$ mm i.d. HP-5 capillary column (film thickness 0.25 μm) and analyzed using a Hewlett-Packard 5890 gas chromatography and 5972 mass selective detector operated in the electron impact mode (70 eV). The chromatographic conditions were as follows: injector temperature, $280\ °C$; ion source temperature, $180\ °C$; temperature program: $60\ °C$ (2 min), $60–290\ °C$ at 3 $°C\ min^{-1}$, $290\ °C$ (30 min). The carrier gas was helium at a constant flow of $1.5\ mL\ min^{-1}$. A 1 μL sample was injected in splitless/split model with a solvent delay of 3 min. Mass range m/z 50 and 500 were used for quantitative determinations. Data acqui-

sition and processing were by a HP Chemstation data system. Chromatographic peaks of samples were identified by mass spectra and by comparison with the standards.

2.3. Quality control

Field blanks, which accompanied samples to the sampling sites, were used to determine any background contamination. Lab blanks and field blanks showed no detectable PAHs. In addition, surrogate standards were added to all the samples (including QA samples) to monitor procedural performance and matrix effects. The mean recoveries for surrogates in field samples were naphthalene-D_8 30%; acenaphthene-D_{10} 79%; phenanthrene-D_{10} 101%; chrysene-D_{12} 95% and perylene-D_{12} 88%. PAH concentrations were corrected for recovery efficiency. A backup PUF was attached to the sampler to check the possible breakthrough of gaseous PAHs. Typically, the backup PUF contained <5% of the total vapor phase component, with greater penetration to the second plug observed for the lighter PAH compounds (henanthrene 3.3%, fluorene 1.6%, anthracene 0.9% and fluoranthene 0.5%).

3. Results

3.1. General characteristics of PAHs

A summary of individual and total atmospheric PAH concentrations are provided in Table 1. Average total (vapor+particulate) PAH concentration was $337 \pm 137\ ng\ m^{-3}$, ranged from 60.9 to $602\ ng\ m^{-3}$. The total PAH concentration in the vapor phase ranged from 49.6 to $585\ ng\ m^{-3}$ (mean of $313 \pm 138\ ng\ m^{-3}$). The total particulate PAHs in the air ranged from 4.7 to $98.7\ ng\ m^{-3}$ (mean of $23.7 \pm 18.4\ ng\ m^{-3}$). Particulate PAHs accounted for 1.8% during the summertime and 46.2% in winter of the total PAHs present in the samples. The predominant PAHs in the vapor phase were two- to four-ring compounds, including phenanthrene (61.4%), fluoranthene (10.7%), anthracene (9.1%), fluorene (8.6%), and pyrene (6.5%), and in the particulate PAHs were predominantly five- to six-ring PAH compounds (MW 250–300) with low vapor pressure, including benzo[b]fluoranthene, benzo[g,h,i]perylene,

Table 1
The average concentrations of PAHs in gas and particle phase in Guangzhou ($n=51$)

	Vapor (ng m^{-3})	Particle (ng m^{-3})	Total (ng m^{-3})
Naphthelene	2.1 ± 1.9	0.6 ± 0.3	2.7 ± 2.0
Acenaphthylene	3.9 ± 3.5	0.1 ± 0.1	4.0 ± 3.5
Acenaphthene	0.8 ± 0.5	0.0 ± 0.0	0.8 ± 0.5
Fluorene	22.0 ± 8.8	0.2 ± 0.1	22.2 ± 8.8
Phenanthrene	196 ± 92	1.6 ± 0.9	198 ± 92
Anthracene	29.8 ± 15.4	0.2 ± 0.1	30.0 ± 15.4
Fluoranthene	35.4 ± 19.7	1.5 ± 1.4	36.9 ± 19.3
Pyrene	21.2 ± 11.3	1.6 ± 1.6	22.8 ± 10.9
Benzo(a)anthracene	0.6 ± 0.4	1.4 ± 1.3	2.0 ± 1.3
Chrysene	0.8 ± 0.5	2.7 ± 2.3	3.6 ± 2.3
Benzo(b)fluoranthene	NA[a]	2.6 ± 2.1	2.6 ± 2.1
Benzo(k)fluoranthene	NA	2.7 ± 2.3	2.7 ± 2.3
Benzo(a)pyrene	NA	2.3 ± 2.1	2.3 ± 2.1
Indeno(1,2,3-cd)pyrene	NA	2.7 ± 1.9	2.7 ± 1.9
Dibenz(a,h)anthracene	NA	0.3 ± 0.4	0.3 ± 0.4
Benzo(g,h,i)perylene	NA	3.1 ± 2.2	3.1 ± 2.2
Total	313 ± 138	23.7 ± 18.4	337 ± 137

[a] NA: not analyzed.

indeno[1,2,3-c,d]pyrene, benzo[a]pyrene, and benzo[k]fluoranthene. Four-ring compounds (MW=228) like benz[a]anthracene and chrysene had similar concentrations in the vapor and particulate phases. PAHs with different molecular weights have different particle–gas distribution coefficients, the gas phase contribution generally decreased with increasing molecular weight from 99.2% to <0.01%. Two- and three-ring PAHs were associated primarily with the gas phase, 5- and 6-rings were associated mainly with particulate phase (Table 1). These results were consistent with other studies (Ligocki et al., 1985; Baek et al., 1991; Odabasi et al., 1999, Bi et al., 2003). The average total PAH concentration in Guangzhou was comparable to that found in Chicago, USA (Odabasi et al., 1999; Bi et al., 2003), higher than that of many other urban areas reported in the world (Baek et al., 1991; Halsall et al., 1994; Smith and Harrison, 1996; Seung et al., 2002).

Fig. 2 showed the variations of total vapor and particulate PAH concentrations during our sampling time. Seasonal trends were apparent in the vapor phase PAH concentrations, with higher levels in summer and gradually decreased to the lowest levels in winter. An exponential increase in gaseous PAH (phenanthrene, anthracene, fluoranthene, and pyrene) concentrations with temperature was observed, suggesting an evaporation of these light PAHs from

contaminated ground surface under higher ambient temperature (Gustafson and Dickhut, 1997; Odabasi et al., 1999; Dimashki et al., 2001). No significant relationship was found between the vapor phase PAH concentrations and wind speed/direction.

For particulate $\sum$PAHs, seasonal trends were observed in the opposite direction, with lower concentrations in summer and higher in winter, and the coefficient of variations of particulate PAH concentrations in winter (CV=67) was higher than that in summer (CV=48), suggesting that there might be more factors affecting the particulate PAHs in winter.

3.2. Source estimates from PCA/MLR

While the molecular markers approach has been widely applied to source reconciliation of PAHs in various environments (Simoneit et al., 1991; Li and Kamens, 1993; Gogou et al., 1996), its use has been limited due to the lack of suitable "source signature" (Sporstol et al., 1983). Receptor modeling using both the chemical mass balance (CMB) model and principal component analysis (PCA) has also been used to identify the sources of organic compounds (Duval and Friedlander, 1981; Pistikopoulos et al., 1990; Li and Kamens, 1993; Harrison et al., 1996; Simcik et al., 1999; Larsen and Baker, 2003). There are certain limitations in requiring the input of source emission profiles to calculate source contributions when CMB model have been used to identify and quantify the sources of organic material in atmosphere (Duval and Friedlander, 1981). Principal component analysis (PCA), which can provide information on source contributions bases on the time-variation of the organic composition, in conjunction with multiple linear regression (MLR) were performed to identity and apportion the total PAHs (gas+particulate phase) in urban air in many cities (Simcik et al., 1999; Larsen and Baker, 2003; Harrison et al., 1996).

However, there is still little report on the source apportionment using gas phase and particulate compounds respectively. This is largely due to the consideration that various PAHs may partition between gas and particulate phase. This effect may not be important in subtropical areas as there is less variation in temperature over the years. From the data of Hinckley et al. (1990) and the review of Wania et al. (1998), PAHs significantly affected by temperature on their
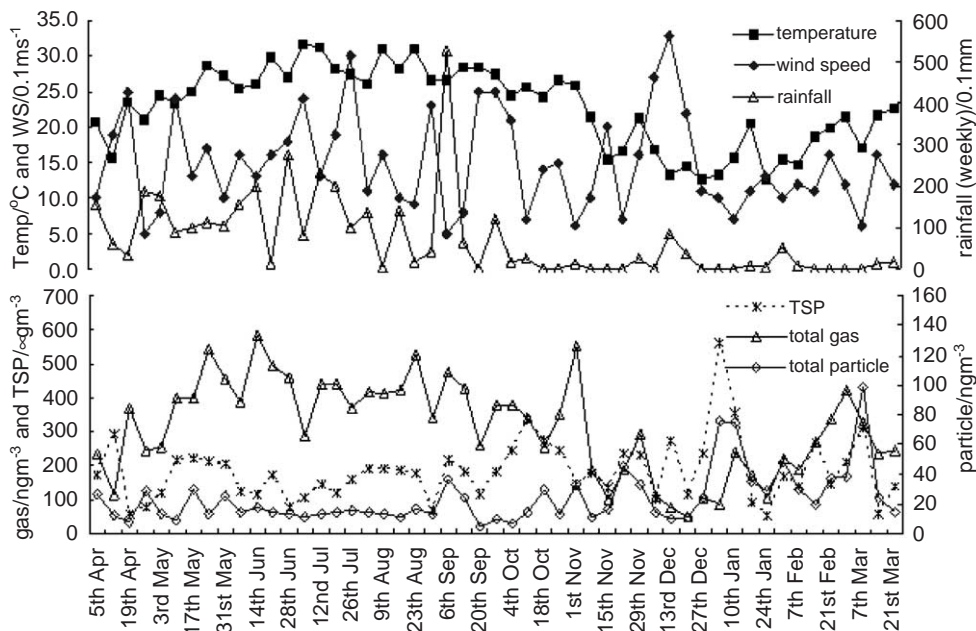
Fig. 2. Seasonal variations of total particulate and gas PAHs and meteorological parameters.

partition between gas and particulate phase were BaA and Chr when the ambient temperature is in the range of 13–31 °C. Since the sum of BaA and Chr only weighted less than 1% of the total gas phase PAHs in this study, the contribution from particulate PAHs to gaseous PAHs by partition in this case may be negligible. Heavy PAHs with more than four aromatic rings, such as BghiP, occurred predominantly in particulate phase in this temperature range. Temperature-controlled gas-particulate partition hence has little effect on their phase distribution. The 4-ring PAHs were well correlated with BghiP in particulate phase ($r > 0.933$), although the air temperatures varied from sample to sample, indicating that the influence of temperature-controlled partition of BaA and Chr was not significant. Consequently, the source apportionment of gas and particulate PAHs were separately performed by PCA/MLR.

Principal component analysis (PCA) followed by multiple linear regression (MLR) was performed using SPSS software.

3.2.1. Particulate PAHs

Factor analysis was conducted for 15 PAHs, except for Ace with concentrations below MDL in particulate phase. The first two factors accounted for 91.2% of the total variance in the data set. Factor 1 explained 64% of the total variance. As shown in Fig. 3, Flua, Pyr, BaA, Chr, BbF, BkF, BaP, Ind, DBahA, and BghiP formed a closely associated group. Among these compounds, BkF, Ind and BghiP were considered to be the tracers of vehicle emission (Miguel and Pereira, 1989; Li and Kamens, 1993; Harrison et al., 1996), and Flua, Pyr, BghiP, BbF, BkF were identified as tracers of vehicle exhaust (Duval and Friedlander, 1981). Nap, Acy, Ant, and Phe form another group (Fig. 3). Harrison et al. (1996) reported that Phe was also related to vehicle emissions. Simcik et al. (1999) suggested Acy is indicative of vehicle emissions. Previous studies also suggested that vehicles were a dominant source of particulate phase PAHs in the cities of Pearl River Delta (Bi et al., 2003). Therefore, we suggest that factor 1 was mostly related to vehicle emissions. The second factor, which accounted for 27.2% of total variance, is highly loaded on lightweight PAHs (Flu, Phe, Ant, Nap, and Acy). Flu was reported to be the dominant PAHs in coke oven emission (Khalili et al., 1995), and was also used as the tracer of coal combustion factor in PCA (Simcik et al., 1999). A study of
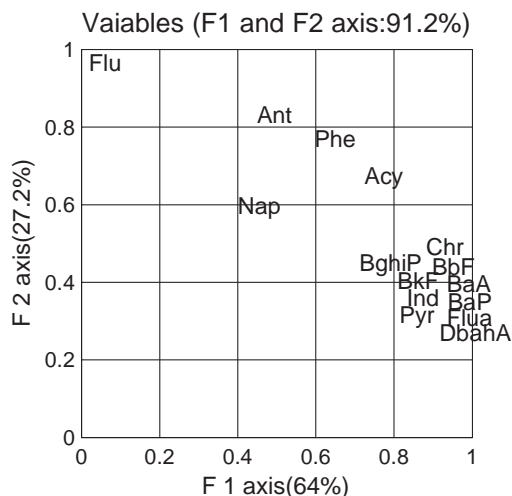
Fig. 3. Rotated factor pattern for PAHs in particulate phase from the Guangzhou atmosphere.

Table 2
Factor pattern for PAHs in gas phase from Guangzhou atmosphere

Factors	1	2	3
Nap	−0.232	0.815	−0.325
Acy	−0.400	0.806	−0.211
Ace	−0.382	0.853	−0.032
Flu	0.138	0.635	0.728
Phe	0.931	0.234	0.191
Ant	0.909	0.180	0.265
Flua	0.972	0.119	−0.097
Pyr	0.961	0.158	−0.153
BaA	0.959	−0.044	−0.125
Chr	0.869	0.162	−0.379
Expl. var	5.616	2.598	0.981
Prp. total	0.562	0.260	0.098

coal combustion under different conditions by Masclet et al. (1987) showed that Flu was the major PAHs product. Duval and Friedlander (1981) identified that Ant, Phe, Flua, Pyr, BaA, Chr, BaP, and BghiP were the source fingerprints of coal combustion and coke production. Therefore, we suggested that factor 2 might be related to coal consumption, including coal combustion, coal gas production and coke oven etc in the city.

Seasonality of sources could be quantitatively analyzed by the multiple linear regressions. Detail procedure of multiple linear regressions was described elsewhere by Larsen and Baker (2003). The estimated daily contributions for each of the proposed source are shown in Fig. 4. The figure clearly shows an enhanced

vehicle exhaust in winter, and a relatively constant coal combustion contribution throughout the year.

3.2.2. Gas phase PAHs

Three principal factors were identified by PCA, explaining 91.9% of the total variance in the data (Table 2). Factor 1, accounted for the majority of total variance (56%), is highly loaded with Phe, Ant, Flua, Pyr, BaA and Chr. Those compounds had significantly positive correlation($r > 0.75$, $p < 0.01$) with the ambient temperature. Wania et al. (1998) introduced two simple models to explain the dependence of semivolatile organic compounds (SVOCs) air concentration on temperature. On the basis of those models, the concentration of SVOCs positively correlated with the ambient temperature in an urban area may be volatilized from contaminated ground surface (soils, road, vegetation and water etc). Gustafson and Dickhut (1997) observed exponential increases in gaseous
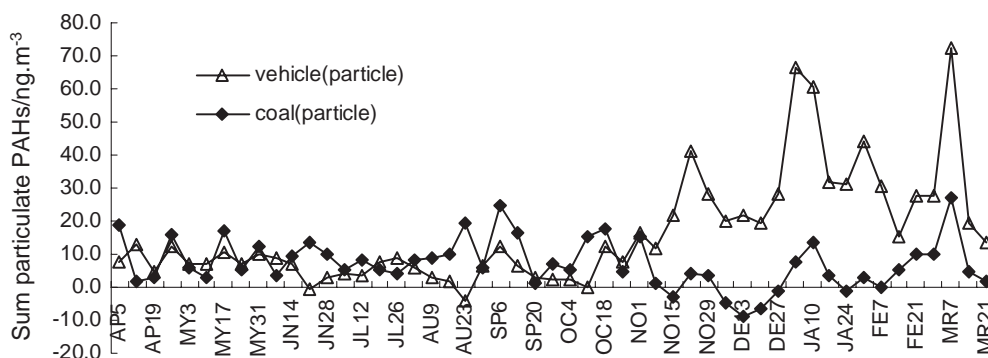

Fig. 4. Time series of daily source contributions of particle phase PAHs based on principal component analysis/multiple linear regression model.
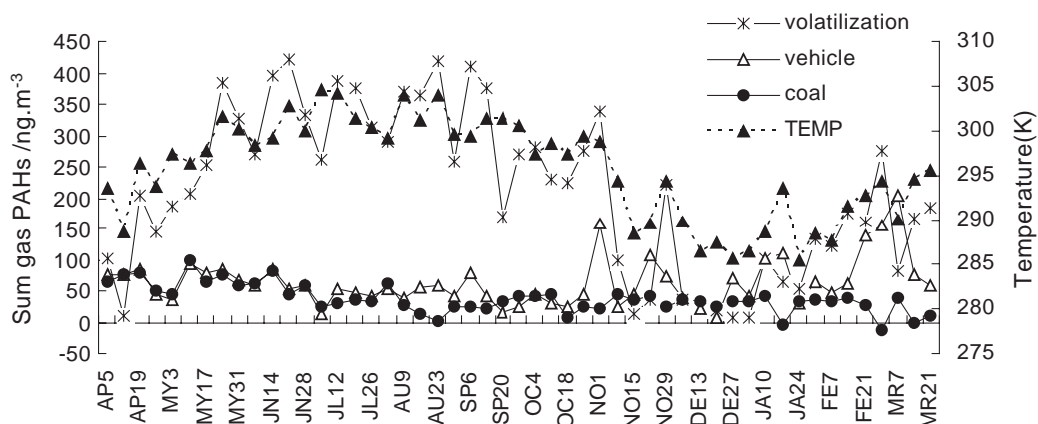
Fig. 5. Time series of daily source contributions of gas phase PAHs based on principal compound analysis/multiple linear regression model.

PAH concentrations with temperature, suggesting an evaporation from contaminated ground during warmer weather. Dimashki et al. (2001) also recognized this process and suggested that a process of volatilization of those compounds from surfaces might be appreciable to Phe, Flua and Flu in Birmingham atmosphere. Therefore, factor 1 may be linked to ground volatilization, of which direct evaporation of petrol from gasoline stations and vehicles may also be inclusive.

Factor 2 accounted for 26.2% of total variance, is highly loaded with Nap, Acy and Ace. Simcik et al. (1999) suggested Acy is a tracer of vehicle emissions. To further identify the relationship of this factor with vehicle emissions, the concentration of BghiP, which

was considered as a typical molecular marker of vehicle emission (Li and Kamens, 1993; Miguel and Pereira, 1989; Harrison et al., 1996) was added to data pool as supplementary variables. The result showed that BghiP, along with Nap, Acy, and Ace, is strongly and positively correlated to factor 2. Therefore, factor 2 should be related to vehicle emissions.

Factor 3, accounting for 9.8% of the total variance, is highly loaded with Flu and moderately loaded with Phe and Ant. This factor might be also related to coal combustion as Flu was considered to be an indicator of coal combustion.

Daily contributions of sources to the gaseous phase PAHs were obtained by the multiple linear regres-
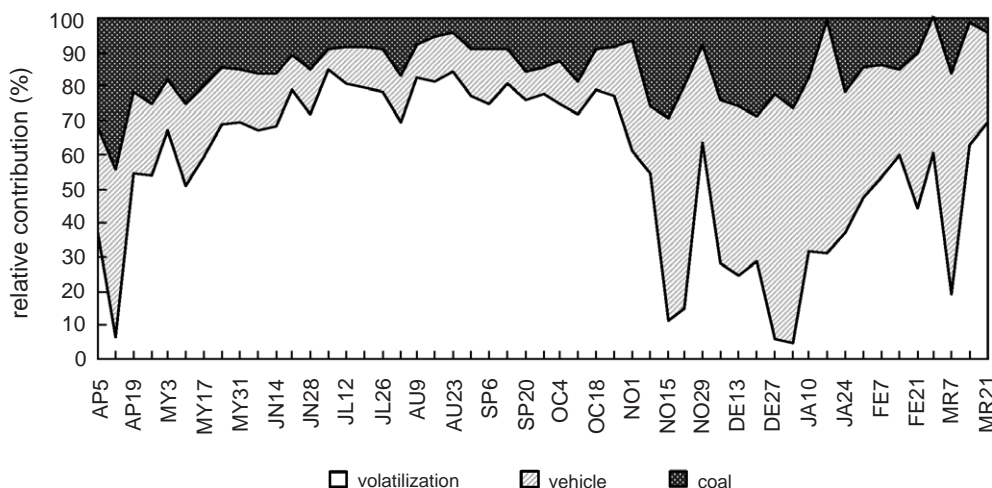

Fig. 6. The daily relative contribution of three major source of PAHs (gas+particle) in the Guangzhou atmosphere year-round.

sions. As shown in Fig. 5, daily contribution of volatilization varied with the ambient temperature year-round. The variations of vehicle emission and coal combustion contribution are generally consistent with the particle PAHs described above.

3.2.3. Total gas and particle

To verify the above results, we processed the total (gas + particle) PAHs dataset in the same way. Three major sources representing vehicle exhaust, coal combustion and ground evaporation were consistently extracted by PCA/MLR. Fig. 6 clearly shows that ground evaporation dominates the total PAH sources in summer, vehicle exhaust dominates in winter, and coal combustion as the third source contributes to the air PAHs with only limited seasonal variations.

4. Discussion

4.1. Source seasonality of PAHs

4.1.1. Vehicle exhaust

Vehicle exhaust has been widely documented to be a major source for PAHs. With the sharp increase of vehicle numbers in recent years, it was suggested that the air pollution is shifting from coal- to vehicle-type in Chinese large cities (1999 China Environmental Bulletin). Both vapor and particle phase PAHs from vehicle exhaust (Figs. 4 and 5) were higher in winter than in summer, despite the higher vapor phase PAH concentrations in summer. An enhanced vehicle exhaust under cold weather may be suggested to be responsible (Bjorseth and Ramdahl, 1985). The curves show larger variations in winter than in summer (Figs. 4 and 5). As in winter PAHs in the air is dominated by heavy PAHs mainly associated with particles (Fig. 2), wind speed may play an important role in the fluctuations of PAH concentrations. For instance, on December 13–21, when strong north wind from the north forest area prevailed, the curves reached their valley. Vehicle numbers on the road may be another variable affecting the vehicle exhaust contribution. As shown in Figs. 4 and 5, on around Feb 14 when the Chinese traditional Spring Festival took place with few vehicles on the move (people taking holiday out of the city), the vehicle exhaust was considerably low.

4.1.2. Coal combustion

Coal combustion can be an important source for PAHs in coal-fueled power plants, coke manufacture, and domestic space heating. It was reported in North Europe and North America that space heating in winter was one of the major seasonally dependent sources for PAHs. In South China, combustion for space heating, especially in government buildings, is not necessary or prohibited. Bi et al. (2003) suggested that vehicle emission and wood combustion were major sources for PAHs in Guangzhou, excluded coal combustion. In fact, a large majority of power plants in China are coal-fueled. In Guangzhou, statistic data showed that 21.3 million ton standard coal were consumed during the year of 2000, which accounted for more than 50% of the total energy sources of the city, and about 70% power is generated from coal powered stations (Guangzhou Yearbook, 2000). There are over 20 power plants providing approximately 1 billion kW monthly located around Guangzhou, with a few even remain sited in the city center. Our result showed that coal combustion has been acting as a relatively stable PAH source contributing around 20–30% (Fig. 6) of PAHs in the air of Guangzhou, and suggested that coal combustion in power plants may not be a seasonally dependent source for PAHs.

4.1.3. Ground evaporation

Although evaporation from ground and/or directly from vehicles and gasoline stations has been suggested in many studies, our quantitative result shows that this source may contribute up to 85% of the total PAHs (Fig. 6) in summer in the subtropical city. The road surface temperatures in Guangzhou may reach 60–80 °C in summer, largely due to the subtropical hot weather. And most of the land cover in the modern city is concrete roads and buildings, which is considered to be less capable of retaining light PAHs, especially with high air relative humidity capable of decreasing their adsorption capability. This also implies that seasonal observation may be needed in assessing the quality of urban soils.

4.1.4. Higher PAH concentration in winter

Higher PAH concentration in winter was reported in many urban atmospheres (Wild and Jones, 1995; Panther et al., 1999; Dimashki et al., 2001; Vestreng

and Klein, 2002; Guo et al., 2003). Enhanced vehicle exhaust coupled with coal combustion for space heating was mostly proposed to be responsible for the increase of PAH emission. Guo et al. (2003) suggested that the higher PAH concentration in Hong Kong was resulted from the long-range transport of air pollutants from mainland China. The major source from air transport or local could be indicated by the BeP/ BaP ratio, which may be modified by the strong reactivity in the atmosphere in the process of air transport, since BaP is easily decomposed by light and oxidants (Grimmer et al., 1983). We observed that the ratios of BeP/BaP were negatively correlated ($r=-0.52$, $p<0.01$) to particulate PAH concentrations. This indicates that the major sources of particulate PAHs in heavily polluted winter days were not from air transport but tended to be local.

Dimashki et al. (2001) considered that the higher PAHs in winter in Birmingham were due to the decreased boundary layer depth in cold weather. Relationship between NO_x and temperature were used to evaluate the seasonal variations in boundary layer depth in the study. In this study, a negative relationship between NO_2 and temperature, statistically significant at the 99% level ($r=-0.31$) was also found. Therefore, decreased boundary layer depth in winter may be one of the reasons for higher particulate PAHs in Guangzhou. Besides, winter is concurrent with dry in South China. Long-term dryness may favor the retaining of particles in the air, and quiescence of air under decreased boundary layer makes the pollutants stay in where they were emitted. All above conditions hindered an effective disperse of air pollutants (Baek et al., 1991). For example, the most polluted days in winter (22 Nov, 3–10 Jan, 31 Jan, and 7 Mar) were found to be simultaneously cold, dry, and with slowest wind speeds (Fig. 2).

With the absence of coal combustion for space heating, we summarize that the higher concentrations of particulate PAHs in winter observed may be resulted from enhanced vehicle exhaust, and accumulation of the air pollutants under decreased boundary layer, slow wind speed, and long-term dryness. It is hence suggested that the typically subtropical monsoon climate in South China, cool and dry in winter, hot and humid in summer, may play a key role in controlling the source seasonality (by enhancing ve-

hicle exhaust in winter, ground evaporation in summer), and the ambient concentrations of PAHs in the air.

Acknowledgements

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