



Distribution and deposition of polycyclic aromatic hydrocarbons in precipitation in Guangzhou, South China

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) were measured in precipitation from March to August 2005 in Guangzhou, South China. Fourteen PAHs were studied, and their total concentrations varied from 616.6 to 3486.7 ng/L in dissolved phase and from 403.8 to 3125.5 ng/L in particulate phase. The estimated deposition loading of PAHs was 3568 $\mu\text{g}/\text{m}^2$ during the monitoring period. The deposition of PAHs was a potential source for Pearl River comparing with the contents of surface water. In addition, the high concentration in precipitation here implied that PAHs pollution was a potential environmental problem in Guangzhou. Most precipitation concentrations of PAHs in March (the last month in winter in Guangzhou) were higher than in the other months (in rainy season). PAHs inclined to be adsorbed to particulate phase with the increase of molecular weight in rainwater. Combustion of fossil fuel and biomass might be the major source of PAHs, while the direct leakage or volatilization from petroleum products might be insignificant.

Key words: polycyclic aromatic hydrocarbons; distribution coefficient; deposition flux; precipitation; Guangzhou

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Introduction

Polycyclic aromatic hydrocarbons (PAHs), containing two to eight rings, are identified as one of the persistent organic pollutants (POPs) in urban environments, and some of them are classified as priority pollutants by both the USEPA and the European Community. They are introduced into the environment mainly via incomplete combustion of organic matter in nature and anthropogenic processes. Due to their well-known carcinogenic and mutagenic properties, the distribution and sources of PAHs in different media were widely studied since 1980s. In general, vehicle exhaust, wood and coal combustion for space heating, and some stationary point source are regarded as the principal sources for PAHs in European cities (Wild and Jones, 1995). In North America, emission from oil and coal combustion in power plants is one of important sources for PAHs (Simcik *et al.*, 1999). But in China, especially in central cities and the eastern coast, vehicle exhaust, coal and wood combustion are identified to be the main sources for PAHs (Seung *et al.*, 2002).

In Pearl River Delta, South China, the fast economy

growth and urbanization in the past two decades resulted in the rapid deterioration of air and water quality due to the lack of rigorous and effective environmental regulations, which has raised great concerns from the public and the regulators. To date, the research regarding PAHs are mainly focused on the distribution and concentrations in certain media, such as river water (Deng *et al.*, 2006; Zhang *et al.*, 2004), sediments (Mai *et al.*, 2002), aerosol (Li *et al.*, 2006). However, the report on deposition of PAHs to land is very limited, which is important to understand the air-land/air-ocean exchange between Pear River Delta and South China Sea.

Guangzhou (113.3°E and 23.2°N) is the largest city in South China, with a population of approximately 10 million and an area of 7434 km², which is about 60 km from the downtown to the Pearl River Estuary. It is the geographical center of the fast developing metropolitan region, grouped with many cities in Pearl River Delta, including Hong Kong, Macao, Foshan, Dongguan, Shaoguan etc. The city is subject to typical subtropical Asian monsoon climates characterized by dry season from October to March (autumn and winter) and rainy season from April to September (spring and winter). In this study, we studied

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PAHs in the process of precipitation. Rainwater samples were collected and PAHs were measured. Our objectives were to: (1) obtain the concentrations of PAHs in precipitation and assess their tendency of partition between the dissolved and particulate phases; (2) examine monthly variation of PAH concentrations and evaluate possible sources; (3) estimate the deposition fluxes in different seasons. Furthermore, the information obtained from this study was used to evaluate whether precipitation is a potential source of PAHs for the surface water of Pearl River.

1 Materials and methods

1.1 Sample collection

In order to survey the mean levels of PAHs in rainwater, rain samples were collected at two monitoring sites in Guangzhou, China. One was on the rooftop of the Herbarium Building at South China Botanical Garden, which located in suburb. The other was on the rooftop of the Administration Building at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, which located in downtown. They were all about 20 m above the ground, and about 500 m away from the closest road. There were no buildings higher than 30 m around the two sampling sites. Six glass vats (40 cm length \times 40 cm width \times 20 cm height) with glass lids were placed on brackets (1 m in height) and were used to collect the rain sample. Before collection, the vats were cleaned with the distilled water until the conductivity of the water was about 2 μ S/cm. The rainwater was collected in pre-cleaned 5 L brown glass jars, which was rinsed three times with rainwater before sampling. Meanwhile the amount of rainfall was measured using tipping-bucket rain gauge.

The rainwater was accumulated when the interval between the precipitation event and the next one was less than two days, and the volume of rainwater sample from each sampling event was not less than 3 L. Otherwise, the precipitation event would be given up to sample. We collected 20 rainwater samples ranged from 3 to 20 L in each site from March 2005 to January 2006. However, the sampling events concentrated from March to August 2005.

After sampling, the rainwater samples were transported to the laboratory immediately. Samples were filtered once through a glass fiber filter (GF/F, 47 mm diameter, 0.7 μ m pore size; Waterman International Ltd., Maidstone, England) and pre-combusted at 450°C for 5 h before use. The filtered matter and filtrate were characterized as particulate and dissolved phase, respectively.

For quality control and quality assurance (QC/QA), a bottle of deionized and contaminant-free water (10 L) was carried to each sampling site functioned as the filed blank, which was sampled and analyzed once a month following the same method for the rainwater samples.

1.2 Chemicals, materials and their preparation

This study analyzed 16 PAHs using the EPA Method 610. Five deuterated PAHs were used as surrogate

standards, including naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂ and perylene-d₁₂ purchased from Ultra Scientific Inc. (North Kingston, USA). Hexamethylbenzene at 99% purity was purchased from Aldrich Chemicals (Gillingham, Dorset, USA) and used as internal standard. The PAHs standard reference material (SRM 1941) was purchased from National Institute of Standards and Technology (NIST, Gaithersburg, USA). All reagents used in this experiment were redistilled in a full-glass distilling appliance, such as dichloromethane (DCM), hexane, methanol etc.

1.3 Analytical procedures

The similar procedure described elsewhere (Urbe and Ruana, 1997; Carrera *et al.*, 1998; Mai *et al.*, 2002) was used for extraction and concentration of PAHs from both the dissolved and particulate phases in rainwater samples. In brief, the deuterated PAHs standards were added to all samples as surrogates prior to extraction. To quantify organic pollutants in dissolved phase, 3–8 L filtrate of each sample were retained and extracted by C₁₈ extraction disks (47 mm diameter, 0.5 mm thickness; Supelco, Bellefonte, USA) with a glass fiber filter with a diameter of 47 mm (Envi-Disk, also from Supelco) and eluted by DCM. The extracts were concentrated by vacuum rotary evaporator (bath temperature < 30°C, Laborota 4000-efficient, Heidolph, Germany), and the solvent mixture was exchanged to hexane and further reduced to approximately 1 mL with a gentle N₂ flow. The filtered particulate on glass fiber papers were extracted for 72 h with DCM by the Soxhlet apparatus. The final extract for each sample was also concentrated to approximately 1 mL.

Interfering compounds were removed by liquid-solid chromatography using 2:1 silica-alumina column for all final concentrated extracts. The column was eluted with 15 mL hexane to remove the aliphatic chemical fraction, followed by 70 mL of DCM-hexane mixture (3:7, V/V) to obtain aromatic compounds fraction including PAHs, which were further concentrated to 0.2 mL under a gentle N₂ stream. Each sample was spiked with 5 μ L internal standard at 200 μ g/mL.

1.4 Sample analysis

The 16 PAHs in concentrated and purified extracts were quantified with a gas chromatograph (HP-5890, Agilent, USA) with a mass spectrometer (HP-5972, Agilent, USA) operated in electron impact and selective ion monitoring modes. A capillary GC column (60 m \times 0.32 mm \times 0.25 μ m, CP SIL CB8-MS, Varian, USA) was used. Details of the operating conditions of the GC-MS and quantification were described by Mai *et al.* (2002). The detection limits of the method ranged from 0.01 to 1.0 ng/L for PAHs. The average recoveries of surrogate standards are listed in Table 1. Because naphthalene-d₈ had low recovery efficiencies and DahA was not detected in all samples, Nap and DahA were thus not reported here. The final concentrations were corrected with the appropriate recovery efficiencies. PAHs were not detected in all the field and laboratory blanks in this study.

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Table 1 Average recoveries of surrogate standards in rainwater samples

Surrogate	Dissolved phase		Particulate phase	
	Average (%)	SD (%)	Average (%)	SD (%)
Naphthalene-d ₈	30	8.2	35	8.5
Acenaphthene-d ₁₀	56	14.7	70	15.6
Phenanthrene-d ₁₀	82	10.3	85	9.8
Chrysene-d ₁₂	85	11.2	87	9.6
Perylene-d ₁₂	91	12.3	88	10.4

The volume-weighted mean (VWM) concentrations of PAHs (\bar{C}) of the each sampling event from two sampling sites were calculated with Eq. (1):

$$\bar{C} = \frac{\sum_{i=1}^n C_i R_i}{\sum_{i=1}^n R_i} \quad (1)$$

where, R_i (mm) was the rainfall amount, C_i (ng/L) was the measured concentration. The monthly and entirely VWM concentrations of PAHs were calculated according to the data present in a month and over the entire monitoring period, respectively.

2 Results and discussion

2.1 Concentrations and temporal variation

As shown in Table 2, the average monthly total amount of PAHs in precipitation varied from 1264 to 6614 ng/L during monitoring period. In dissolved phase, the VWM concentrations of PAHs ranked in the following order: 3-ring > 4-ring > 5-ring > 6-ring. The predominant 3-ring compounds accounted for 77.3% of the total PAHs, ranging from 18.6 ± 18.1 to 372.0 ± 301.4 ng/L, including AcI, Ace, Fl, Phe, and Ant. The following was 4-ring PAHs (19.5%), ranging from 26.1 ± 28.3 to 125.8 ± 194.4 ng/L, including Flu, Pyr, BaA, and Chr. The 5-ring (BbF, BkF, and BaP) and the most hydrophobic 6-ring (IcdPy and BghiP) accounted for 2.8% and 0.4%, respectively.

In particulate phase, the VWM concentrations of PAHs over all the monitoring months were also presented in Table 2. The difference among individual PAHs was smaller compared with what in dissolved phase. The total VWM concentration of PAHs was 682 ng/L. The 3-ring PAHs accounted for 40.4%, 4-ring for 27.6%, 5-ring for 18.9%, and 6-ring for 13.1%. The predominant PAHs were also Phe and Ant, which accounted for 14.5% and 15.5% of the total PAHs, respectively, while the other individual PAHs were less than 10%. It was noted that the higher molecular PAH in particulate phase accounted for more proportion than in dissolved phase, such as 6-ring PAHs, i.e., IcdPy (7.0%) and BghiP (6.1%).

The temporal variation is apparent from monthly total concentrations in precipitation in Guangzhou. As can be seen in Table 2, the concentrations of most PAHs were high in March (the last month of winter in Guangzhou), and low in rainy season. But the pattern was reverse for 6-ring PAHs in dissolved phase, and the correlation between IcdPy and BghiP was strong ($R^2 = 0.99$), and the concentrations of Phe and Ant were higher than others in both winter (March) and rainy season (April to August).

2.2 Distribution coefficients between the dissolved and particulate phase

Distribution of PAHs between dissolved and particulate phases was likely involved highly dynamic sorption and desorption processes governed by temperature, pH, rainfall etc. Approximately 64% of PAHs in rainwater remained in the dissolved phase. Phe and Ant were the dominant compounds in both dissolved and particulate phases. In this study, the distribution coefficient (K_p) was defined as:

$$K_p = \frac{C_p}{C_d} \quad (2)$$

where, C_p (ng/L) and C_d (ng/L) were the concentrations of PAHs in the particulate and dissolved phase, respectively. As shown in Fig. 1 (Ace was not calculated in May and August, and IcdPy and BghiP were not calculated in March because they were not detected in most rainwater samples in those months), the features of variation of distribution coefficients can be summarized as: (1) in general, the K_p values increased with the increase of the molecular weight of PAHs in the same month; (2) the K_p values of a specific PAHs also varied in the different months.

It is generally known that the K_p values as obtained in the field samples are influenced by many geochemical factors (Zhou *et al.*, 1999), which may include the particulate size, the contents and types of organic matter in particulate, and the temperature of rainwater. The mean monthly temperature varied from 17.2 to 29.9°C during the sampling period, which might result in the variation of K_p value for individual PAH. But different compounds showed different potential. For example, K_p values of the two 6-ring PAHs were the highest in August and were the lowest in May, but not for other PAHs. We have not more appropriate reason to explain it in this study. Furthermore, it was interesting to note that the K_p values also varied in the same month, which should be a consequence of the different hydrophobicity of different PAHs. The hydrophobicity of higher molecular weight PAHs is stronger than that of lower molecular weight PAHs, which could be more easily adsorbed to particulate. Although it is a well-understood principle that the high molecular weight PAHs would incline to distribute in particulate phase, the pattern was reverse for the relatively low molecular weight

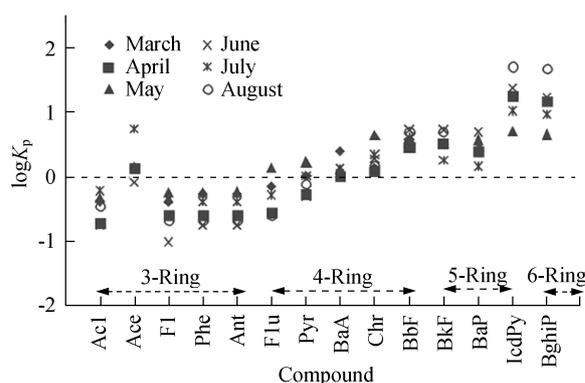


Fig. 1 The monthly variation in distribution coefficients of PAHs between dissolved and particulate phases.

Table 2 Mean concentrations of PAHs (mean \pm SD, ng/L) in precipitation and the rainfall (mm)

	Mar. 2005 (n ^a = 4)	Apr. 2005 (n = 12)	May 2005 (n = 4)	Jun. 2005 (n = 4)	Jul. 2005 (n = 8)	Aug. 2005 (n = 8)	VWM ^b (n = 40)
Dissolved phase							
Acl	158.1 \pm 8.5	76.8 \pm 38.0	59.9 \pm 25.0	70.1 \pm 9.6	40.2 \pm 2.2	40.5 \pm 13.4	85.1 \pm 41.7
Ace	53.9 \pm 12.5	28.8 \pm 17.3	15.6 \pm 5.6	12.7 \pm 20.6	14.3 \pm 8.6	17.1 \pm 4.9	18.6 \pm 18.1
Fl	262.6 \pm 41.5	150.1 \pm 86.1	73.3 \pm 13.3	164.5 \pm 47.7	114.1 \pm 42.1	114.8 \pm 50.2	131.0 \pm 71.4
Phe	859.0 \pm 262.5	512.3 \pm 373.0	157.0 \pm 40.2	341.6 \pm 123.8	336.5 \pm 137.6	277.1 \pm 123.0	346.2 \pm 283.0
Ant	915.0 \pm 282.9	546.0 \pm 398.3	164.2 \pm 44.2	369.6 \pm 134.0	364.0 \pm 149.0	299.7 \pm 133.2	372.0 \pm 301.4
Flu	495.6 \pm 407.6	222.1 \pm 212.0	31.8 \pm 18.6	89.2 \pm 82.3	148.6 \pm 132.1	84.8 \pm 80.2	125.8 \pm 194.4
Pyr	268.2 \pm 179.1	83.7 \pm 91.5	18.8 \pm 16.8	36.6 \pm 17.5	69.1 \pm 56.4	22.8 \pm 20.9	48.4 \pm 93.5
BaA	78.7 \pm 10.7	45.5 \pm 30.3	25.3 \pm 2.4	16.7 \pm 27.2	29.5 \pm 25.9	18.9 \pm 14.7	26.1 \pm 28.3
Chr	241.4 \pm 165.2	68.1 \pm 59.3	14.4 \pm 17.7	19.6 \pm 32.0	58.5 \pm 55.6	26.5 \pm 17.4	40.4 \pm 79.4
BbF	63.6 \pm 48.0	20.3 \pm 25.7	15.2 \pm 11.2	5.8 \pm 9.5	29.9 \pm 34.3	7.7 \pm 11.8	13.1 \pm 27.1
BkF	56.6 \pm 64.0	19.5 \pm 26.5	16.0 \pm 11.5	5.8 \pm 9.5	29.9 \pm 34.4	7.8 \pm 11.9	12.8 \pm 28.0
BaP	34.0 \pm 25.2	12.1 \pm 11.1	6.4 \pm 6.9	2.7 \pm 4.4	19.1 \pm 17.8	6.8 \pm 2.6	8.2 \pm 13.5
IcdPy	nd ^c	3.0 \pm 8.4	9.9 \pm 1.9	1.6 \pm 2.5	10.7 \pm 12.6	0.6 \pm 1.9	2.5 \pm 7.8
BghiP	nd	3.5 \pm 9.6	8.8 \pm 3.5	1.6 \pm 2.6	11.0 \pm 12.9	0.5 \pm 1.6	2.5 \pm 8.4
Σ PAHs	3488 \pm 1508	1792 \pm 1387	617 \pm 219	1138 \pm 523	1275 \pm 722	926 \pm 488	1233 \pm 1196
Particulate phase							
Acl	66.3 \pm 6.0	14.7 \pm 43.9	28.3 \pm 16.4	12.5 \pm 1.2	24.5 \pm 10.5	14.3 \pm 3.2	17.8 \pm 28.7
Ace	75.7 \pm 13.4	38.7 \pm 40.5	nd	10.3 \pm 12.8	78.1 \pm 40.8	nd	20.4 \pm 44.3
Fl	109.8 \pm 14.6	38.3 \pm 71.4	41.0 \pm 25.5	16.1 \pm 3.3	51.8 \pm 26.4	24.5 \pm 3.2	32.1 \pm 48.7
Phe	475.4 \pm 10.6	131.0 \pm 67.1	89.1 \pm 16.6	61.5 \pm 7.6	138.1 \pm 50.3	58.6 \pm 1.7	99.2 \pm 129.0
Ant	491.5 \pm 23.6	140.7 \pm 72.3	95.0 \pm 15.7	66.5 \pm 8.2	149.5 \pm 54.4	62.5 \pm 1.6	106.0 \pm 133.9
Flu	357.0 \pm 22.5	61.0 \pm 33.1	43.7 \pm 17.2	23.3 \pm 5.1	78.1 \pm 52.7	21.8 \pm 0.2	48.6 \pm 104.6
Pyr	276.8 \pm 23.3	44.6 \pm 21.9	31.9 \pm 11.0	18.3 \pm 1.7	70.7 \pm 47.1	17.3 \pm 2.2	37.7 \pm 82.0
BaA	199.4 \pm 20.1	45.8 \pm 28.5	33.3 \pm 26.5	22.9 \pm 15.9	33.8 \pm 24.2	19.3 \pm 8.7	34.9 \pm 58.3
Chr	327.1 \pm 25.6	81.4 \pm 47.9	63.0 \pm 32.9	37.6 \pm 30.0	130.9 \pm 126.9	38.8 \pm 17.2	67.3 \pm 105.2
BbF	239.5 \pm 36.0	58.4 \pm 23.8	54.0 \pm 38.1	31.5 \pm 28.5	121.0 \pm 123.1	39.4 \pm 16.6	55.7 \pm 85.2
BkF	176.0 \pm 90.5	63.3 \pm 33.5	54.2 \pm 37.5	31.3 \pm 28.2	54.8 \pm 83.8	39.5 \pm 17.0	50.1 \pm 58.7
BaP	81.9 \pm 20.4	29.7 \pm 16.4	23.9 \pm 16.6	13.2 \pm 11.6	28.0 \pm 24.2	18.0 \pm 6.8	23.0 \pm 25.3
IcdPy	117.5 \pm 49.6	54.4 \pm 20.0	49.8 \pm 27.1	36.0 \pm 28.5	111.4 \pm 115.2	27.9 \pm 16.4	47.9 \pm 63.0
BghiP	131.7 \pm 44.2	49.5 \pm 18.1	39.5 \pm 22.7	27.2 \pm 21.8	103.3 \pm 110.9	21.8 \pm 12.2	41.4 \pm 63.5
Σ PAHs	3126 \pm 400	851 \pm 538	647 \pm 304	408 \pm 204	1174 \pm 890	404 \pm 107	682 \pm 1030
Total PAHs ^d	6614 \pm 1908	2643 \pm 1925	1264 \pm 523	1546 \pm 727	2449 \pm 1612	1330 \pm 595	1915 \pm 2226
Bulk rainfall ^e	121.2	209.1	395.2	581.5	131.5	371.2	

^a Number of samples; ^b the volume-weighted mean concentration according to the rainfall from March to August 2005; ^c not detected; ^d Σ PAHs in dissolved phase + Σ PAHs in particulate phase; ^e accumulative rainfall of every precipitation event.

PAHs. This is an evidence to support the proposal that the volatilization was an important process in determining the fate of the low molecular weight PAHs including Phe and Ant, while PAHs with molecular weight > 200 mostly occurred in the particulate phase (Readman *et al.*, 1982).

2.3 Relationship between the concentration and the rainfall

There was no significant correlation between the concentration of PAHs in dissolved phase and the rainfall during the monitoring period, which implied that the dissolved PAHs in precipitation were not markedly diluted by the increasing rainfall. Many previous researches have demonstrated that PAHs were mainly from the human being activities, especially the contribution of the combustion of fuel (Fernandes *et al.*, 1997; Budzinski *et al.*, 1997; Simcik *et al.*, 1999; Soclo *et al.*, 2000; Yunker *et al.*, 2002), producing much vapor PAHs into the atmospheric environment. The vapor PAHs could diffuse faster than in particulate phase, leading to quick replenishment. Furthermore, vapor PAHs are also not easily scavenged from air by rainwater due to their hydrophobic property. Therefore, the concentration of the dissolved PAH in precipitation would not decrease rapidly with the rainfall.

However, it was found that the power law approximation

could approximate the relationship between the concentration in particulate phase and the rainfall (Fig. 2). The larger the amount of precipitation was, the lower the PAHs concentrations were. The result suggests that the concentration of PAHs could be diluted by a large amount of rainfall since they were not easily desorbed from particulate due to their hydrophobicity. This explained the high concentrations of PAHs in dry season (March 2005) and relatively low concentration in rainy season (April to August 2006) (Table 2). It was consistent with the previous researches (Liu *et al.*, 2006; Shimamura *et al.*,

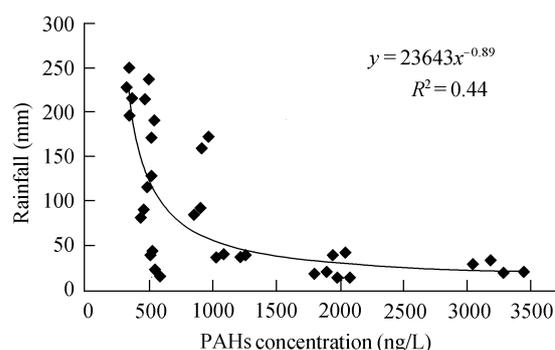


Fig. 2 Relationship between the PAHs concentrations in particulate phase and the rainfall.

2006), who demonstrated that the relationship between the rainfall and the ion concentrations in precipitation well fit the exponential or power model.

2.4 Sources of PAHs

To date, there are many methods to identify the sources of the PAHs, such as the receptor modeling using both chemical mass balance (CMB) model and principal component analysis (PCA) in environment (Harrison *et al.*, 1996; Simcik *et al.*, 1999; Larsen and Baker, 2003). In this study, the distribution patterns of the isomeric PAHs were applied to identify the source of PAHs in precipitation, because it was simple and applied widely in various environments (Gogou *et al.*, 1996; Budzinski *et al.*, 1997; Yunker *et al.*, 2002).

It was reported that the concentration ratios of Ant to the combined Ant + Phe (Ant/178), Flu to the combined Flu + Pyr (Flu/202), and BaA to the combined BaA + Chr (BaA/228) were distinctly different for PAHs with petrogenic vs. pyrolytic and combustion vs. petroleum origins (Budzinski *et al.*, 1997; Yunker *et al.*, 2002). For example, an Ant/178 ratio < 0.1 is often considered as an indicator of petroleum source, whereas an Ant/178 ratio > 0.1 indicates combustion is a dominant source of PAHs (Budzinski *et al.*, 1997). The petroleum boundary ratio is closer to 0.4 for Flu/202, and ratios varied between 0.4 and 0.5 are more characteristic of liquid fossil fuel (vehicle and crude oil) combustion, whereas ratios > 0.5 are characteristic of grass, wood or coal combustion (Yunker *et al.*, 2002). For BaA/228 ratio, < 0.2 usually implies the petroleum source, from 0.2 to 0.35 indicates either petroleum or combustion, and combustion source is most likely if the ratio > 0.35 (Yunker *et al.*, 2002). Alternatively, other PAH isomer ratios have also been used to assign PAHs sources (Simcik *et al.*, 1999; Soclo *et al.*, 2000), such as Phe/Ant and Flu/Pyr. They are approximately equivalent to those of Ant/178 and Flu/202, respectively, i.e., a Phe/Ant ratio of > 10 is usually considered as an indicator of petroleum while a ratio of < 10 indicates a dominant pyrolytic source (Budzinski *et al.*, 1997), and the Flu/Pyr ratio of > 1 is usually regarded as an indication of pyrolytic source while a ratio of < 1 implies a dominant petroleum source (Sicre *et al.*, 1987).

We assumed that all PAHs in air were scavenged or adsorbed into rainwater as the same proportion. The data of the distribution patterns of the isomeric PAHs were compiled in Table 3. The Ant/178 > 0.1 , Flu/202 > 0.5 , Phe/Ant < 10 , and Flu/Pyr > 1 were obvious in precipitation in all monitoring months. But it should be noticed that BaA/228 ratios were above 0.35 in April, May, June, and August, and varied between 0.2 and 0.35 in March and July. These indicated that the major source of PAHs in precipitation was combustion of fossil fuels and biomass, and the direct petroleum contamination could be a minor source. This result were consistent with previous research that the PAHs in air at Guangzhou were mainly from vehicle exhaust and coal combustion (Li *et al.*, 2006)

Table 3 Monthly ratios of isomeric PAH pairs

Ratio	Mar. 2005	Apr. 2005	May 2005	Jun. 2005	Jul. 2005	Aug. 2005
Ant/178	0.51	0.52	0.51	0.52	0.52	0.52
Flu/202	0.61	0.69	0.60	0.67	0.62	0.73
BaA/228	0.33	0.38	0.43	0.41	0.25	0.37
Phe/Ant	0.95	0.94	0.95	0.92	0.92	0.93
Flu/Pyr	1.56	2.21	1.49	2.05	1.62	2.66

Ant/178: Ant/(Ant + Phe); Flu/202: Flu/(Flu + Pyr); BaA/228: BaA/(BaA + Chr).

2.5 Factors influencing the temporal variation of PAHs

Most concentrations of PAHs in precipitation in March (in winter) were higher than other months (in rainy season), similar to general observation in other countries and regions (Wild and Jones, 1995; Panther *et al.*, 1999; Dimashki *et al.*, 2001; Guo *et al.*, 2003). The variation of concentrations in precipitation must be affected by the seasonal variation, the meteorological and geographical conditions in Guangzhou.

In Europe and North America, wood/coal combustion for space heating in winter was one of the major seasonally dependent sources for PAHs (Wild and Jones, 1995; Simcik *et al.*, 1999). However, in the case of Guangzhou, combustion for space heating is not necessary because it locates in subtropical zone. Fossil fuel combustion in power plants is the important source for PAHs. Statistic data from government showed that about 70% of energy was generated from coal power plants in Guangzhou in 2000. Therefore, the fuel combustion, especially the coal combustion has been acting as a relatively stable contribution for PAHs in Guangzhou, rather than a seasonally dependent source. Vehicle exhaust is another major source for PAHs, especially in winter, more PAHs were produced by enhancing vehicle exhaust under cold weather. It was obvious that the temperature in March (17.2°C) was lower than that in rainy season (22.6–29.9°C) in Guangzhou despite of it is subjected to the subtropical climate.

Wind speed might also play a pivotal role in the fluctuation of the PAHs in precipitation. The wind is usually light and stable in winter, but very variable in rainy season due to the affection of warm current and typhoon from western ocean. This will cause that the contents in atmosphere diffuse more difficult in winter than in summer. Furthermore, the majority of rainfall took place in rainy season and accounted for more than 90% of annual precipitation in this study. Semi-continuous washing by rainfall also efficiently lowered the contents in air. In contrast, high concentrations of PAHs were expected in the rainwater in winter because of high abundance of aerosol and gas accumulation in atmosphere under long-term dryness.

2.6 Deposition of PAHs in precipitation

The wet deposition flux of individual PAHs in precipitation to the surface land or water during sampling period

Table 4 Literature data of PAH concentrations in precipitation and river water

Medium	Location	Range (ng/L)			N ^b Reference	
		Dissolved phase	Particulate phase	Bulk sample ^a		
Rainwater	Guangzhou, China	616.6–3486.7	403.8–3125.5	14	This study ^c	
	Lake Maggiore, Italy	66.4–84.4	25.5–29.5	14	Àngels Olivella, 2006	
	Galveston Bay, USA	44.1–247.0	5.5–162.3	20	Park <i>et al.</i> , 2001	
	Seine Basin, France			6.6–647	14	Blanchard <i>et al.</i> , 2007
	Lake Balaton, Hungary			164–1330	12	Kiss <i>et al.</i> , 2001
River water	Xijiang River, China	21.7–138	0.17–58.2	15	Deng <i>et al.</i> , 2006	
	Baiertang, China	701.4–2579.5	163.6–431.4	16	Luo <i>et al.</i> , 2004	

^a Dissolved + particulate; ^b number of PAHs compounds analyzed in each study; ^c Nap and DahA were not included in the calculations.

can be estimated with Eq. (3):

$$F_i = \sum_{j=3}^8 (C_{j,d} + C_{j,p})R_i \quad (3)$$

where, F_i ($\mu\text{g}/\text{m}^2$) was the deposition flux of individual PAHs, $C_{j,d}$ ($\mu\text{g}/\text{L}$) and $C_{j,p}$ ($\mu\text{g}/\text{L}$) are the VWM concentration of individual PAHs in dissolved and particulate phases, respectively, from March to August 2005, R_i (mm) is the rainfall in each month (Table 2).

The calculated deposition fluxes of 3-, 4-, 5- and 6-ring PAHs from March to August 2005 were 2221, 840, 322, and 185 $\mu\text{g}/\text{m}^2$, and accounted for 62.3%, 23.5%, 9.0%, and 5.2% of the total deposition loadings (3568 $\mu\text{g}/\text{m}^2$), respectively. The predominant PAHs were Phe (815 $\mu\text{g}/\text{m}^2$, 22.8%) and Ant (872 $\mu\text{g}/\text{m}^2$, 24.4%). The total loading of PAHs in precipitation during the monitoring period was comparable with in Izmit Bay (1716 $\mu\text{g}/\text{m}^2$), Turkey (Pekey *et al.*, 2007), and larger than in Galveston Bay (130 $\mu\text{g}/(\text{m}^2\cdot\text{year})$) (Park *et al.*, 2001) and Corpus Christi Bay (182 $\mu\text{g}/(\text{m}^2\cdot\text{year})$) (Park *et al.*, 2002) in Texas, USA. The VWM concentrations of total PAHs in this study ranged from 616.6 to 3486.7 ng/L in dissolved phase and from 403.8 to 3125.5 ng/L in particulate phase, which were comparable with the level in Lake Balaton, Hungary, and were larger than in Lake Maggiore, Italy, Galveston Bay, USA and Seine Basin, France (Table 4).

Deng *et al.* (2006) reported the concentrations of PAHs in Xijiang River which is less polluted aquatic systems and the major tributary of the Pearl River. The concentrations of PAHs were also presented in the Baiertang water column located in Guangzhou Channel of the Pearl River, lying in the center of Guangzhou City (Luo *et al.*, 2004). It was interesting to note that PAHs in river water were less than in precipitation (Table 3), suggesting that the wet deposition was likely to act as a potential source of PAHs for surface water in Guangzhou. Furthermore, according to the environmental quality standard for surface water in China, the standard value of carcinogenic and mutagenic BaP is 2.8 ng/L, which is several orders of magnitude lower than in precipitation in Guangzhou from this study. To sum up, the atmospheric environment has being highly affected by anthropogenic activities, and PAHs pollution is a potential challenge in environmental protection in Guangzhou.

3 Conclusions

(1) The 3- and 4-ring PAHs were the most abundant in precipitation. The level of PAHs in rainwater was higher than less polluted aquatic water and the urban river water in Guangzhou, China during the monitoring period. The estimated total loading of PAHs in precipitation was 3568 $\mu\text{g}/\text{m}^2$. PAHs pollution poses a potential challenge in environmental protection in Guangzhou.

(2) There was seasonal variation for PAHs concentrations, and the possible source of the PAHs contamination was mainly pyrolytic input derived from the combustion of fossil fuels and biomass.

(3) There were different distribution coefficients between the dissolved phase and the particulate phase for different PAHs in the same month, and the monthly distribution coefficients for individual PAHs in different seasons were also different.

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