Source and deposition of polycyclic aromatic hydrocarbons to Shanghai, China

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Abstract

Despite recent efforts to investigate the distribution and fate of polycyclic aromatic hydrocarbons (PAHs) in air, water, and soil, very little is known about their temporal change in wet deposition. As a result of increased attention to public health, a large-scale survey on the deposition flux and distribution of PAH contamination in rainwater was urgently conducted in Shanghai, China. In this study, 163 rainwater samples were collected from six sites, and 15 PAH compounds were detected by the use of a simple solid phase microextraction (SPME) technique coupled with gas chromatography-mass spectrometry. The dominant PAH species monitored were naphthalene, phenanthrene, anthracene, and fluoranthene. The concentration of total PAHs per event was between 74 and 980 ng/L, with an average value of 481 ng/L, which is at the high end of worldwide figures. The annual deposition flux of PAHs in rainwater was estimated to be 4148 kg/yr in the Shanghai area, suggesting rainfall as a major possible pathway for removing PAHs from the atmosphere. Diagnostic analysis by the ratios of An/178 and Fl/Fl+Py suggested that combustion of grass, wood, and coal was the major contributor to PAHs in the Shanghai region. Back trajectory analysis also indicated that the pollutant sources could be from the southern part of China.

Key words: polycyclic aromatic hydrocarbons; rainwater; deposition flux; source; Shanghai

DOI: 10.1016/S1001-0742(10)60638-9

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are semi-volatile organic compounds containing two or more fused benzene rings (Chen et al., 2007). Most of these compounds are suspected mutagens and carcinogens and are widely distributed in the air, water, and soil (Jiang et al., 2007; Ma et al., 2008). They are most formed during the incomplete combustion of organic materials (Sun et al., 2006; Wang et al., 2007). Once in the atmosphere, they may appear either in the gas or particle phase (Larsen and Baker, 2003). Studies have found that PAHs in the atmosphere are mostly (more than 90%) in the gas phase (Tsapakis and Stephanou, 2005). Rainwater may be a primary source of PAHs in the region because both gaseous and particulate PAHs can be easily scavenged by rainfall (Poster and Baker, 1996).

The distribution and concentration of PAHs in certain media, such as river water, lakes, sediments, and aerosol, have been studied (Hou et al., 2006; Jiang et al., 2007; Karlsson and Viklander, 2008; Simcik and Offenberg, 2006; Wang et al., 2007; Zhao et al., 2007). However, the research relating to PAH deposition in precipitation is scant, and only limited data have been reported (Gaga and Tuncel, 2003; Huang et al., 2009). The occurrence of PAHs in rural sites of the United States and Canada was found to

have mean total concentrations ranging from 26 to 90 ng/L (Sun et al., 2006). PAHs in precipitation in Guangzhou, China were reported to be in the range of 616.6 to 3486.7 ng/L (Huang et al., 2009). Such a high concentration of PAHs in precipitation will result in large amounts of PAHs settling on the land or sea every year, resulting in great environmental harm. Thus, monitoring PAHs in rainfall can provide valuable information about their environmental fate and their potential for ecological impact. The occurrence of PAHs in environmental matrices is usually in the parts per trillion (ng/L) level (Rianawati and Balasubramanian, 2009). Appropriate sample pretreatments are indispensable to extract and concentrate the analytes prior to their chromatographic determination. Conventional extraction methods mainly include supercritical fluid extraction, liquid-liquid extraction, and solid-phase extraction (Grynkiewicz et al., 2002; Melcher and Morabito, 1990; Shimmo et al., 2002). However, these methods have some intrinsic drawbacks; they are labor-intensive, consume a large volume of solvent, need special equipments and are time-consuming (King et al., 2003). Today there is an increasing demand for the development of a new extraction technique that is sensitive, fast, and economic. One such method is solid-phase micro-extraction (SPME) (Tang and Isacsson, 2008). It is a solvent-free technology, combining extraction, concentration, and sample introduction in one step, which has been successfully applied in different environmental matrices (Pino et al., 2004). To reduce the labor involved in the handling of numerous

large-volume rainwater samples, SPME was used in this investigation.

High levels of PAHs have been frequently found in environmental samples in China in recent years, suggesting that significant sources of PAHs remain active (Lang et al., 2007). Shanghai, the biggest city in China, contains rich waterways and numerous entrances to the coastal ocean. The rapid economic development and urbanization in this region during the last two decades have resulted in severe air and water pollution (Liu et al., 2007, 2008). Because it is in the northern subtropical zone, the mild temperature and frequent rainfall all year round facilitate the transport of contaminants to the aquatic environments. This project aimed to survey rainwater in the Shanghai region and to monitor the concentration levels and deposition flux of fifteen selected PAH compounds. A newly developed SPME-based sampling technique coupled with gas chromatography-mass spectrometry (GC-MS) analysis was applied to fulfill these objectives. Associated with each rainfall flux, the deposition amount of PAHs per event was calculated directly. The obtained data provided valuable information for further research in precipitation pollution. The potential source analysis of PAHs was also evaluated. This study was important to set environmental protection policy and to prevent PAH precipitation pollution.

1 Materials and methods

1.1 Study site

Shanghai (31°14′N/121°29′E) is located on the eastern coast of China, surrounded by the Yangtze River estuary, the East China Sea, and Hangzhou Bay. It is the largest city in China, with a population of approximately 18 million and an area of 7037.5 km^2. It is also a strong commercial and industrial base, with the largest petrochemical complex and the largest steel output in China. The average annual rainfall of Shanghai was 1042.6 mm in the last ten years.

The six sampling sites and their various surroundings (educational area (Yangpu, YP), industrial zone (Baoshan, BS), high-tech industrial development zone (Pudong, PD), chemical industry estates (Songjiang, SJ), agricultural district (Fengxian, FX), and business center (Xujiahui, XJH)), are shown in Fig. 1 and described in Table 1. The mean values of PAHs in the rainwater of Shanghai can be measured from samples from these six sites.

1.2 Sample collection

The rainwater samples at the YP site were sampled manually on the roof of the Building of the Department of Environmental Science and Engineering at Fudan University, 3 m above the ground. Samples at the other five sites were collected in the same manner. All the rainwater samples were collected in sampling buckets (24.5 cm in diameter), which were rinsed thoroughly by deionized water several times before sampling. Once in the laboratory, the samples were filtered through a 0.45-μm millipore membrane filter after the volume and the pH were measured, and then stored in a pre-cleaned brown

Fig. 1 Schematic diagram of the rainwater study sites. Numbers correspond with those in Table 1.

bottle at 4°C for further analysis.

1.3 Chemicals and instruments

The standard mixture solution of PAHs (15 compounds: Naphthalene (NaP), Acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Flo), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Fluo), Pyrene (Pyr), Chrysene (Chry), Benzo(a)anthracene (BaA), Cyclopenta[c,d]pyrene (Cyc), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Benzo(e)pyrene (BeP), and Benzo(b)fluoranthene (BbF)) was purchased from Caienfu (Shanghai, China). The concentration was 100 ng/μL in dichloromethane. This standard was stored at 4°C, protected from light. HPLC-grade dichloromethane, acetone, and other organic solvents were purchased from the Reagent Factory of Shanghai (China).

A typical SPME sampler used for the study was purchased from Supelco (Belefonte, USA). It consists of a manual SPME holder and a fiber coated with non-polar polydimethylsiloxane (PDMS, 100 μm film thickness).

GC-MS consisted of an Agilent 6890 Series GC system coupled with a HP 5973 Mass Selective Detector (Agilent Technologies, USA). Separation of analytes was achieved using a HP5MS capillary column (0.32 mm × 30 m × 0.25 μm)

1.4 SPME procedure

Rainwater samples were extracted by the SPME method. The fiber was conditioned before use according to the manufacturer's instructions (30 min at 250°C). A blank analysis was performed to verify that there were no extraneous compounds, possibly introduced during the fiber preparation or desorption process. All vials storing working solutions were pre-washed with acetone to prevent contaminant leaching from the glass during the microextraction procedure. For all the analyses, 30 mL of aqueous solution was placed into a 40 mL screw cap vial equipped with Teflon lined septa. The solution was continuously stirred with a magnetic stirrer at a constant speed of 1000 r/min. In the extraction process, the SPME fiber was directly immersed into the sample solution for appropriate

Table 1   Characteristics of sampling sites in Shanghai

Number in Fig. 1	Sampling site	Location	Environmental situation	Latitude/longitude
1	Yangpu (YP)	Fudan University	Educational area	31°20′N/121°29′E
2	Baoshan (BS)	Youyi Road	Industrial districts	31°24′N/121°27′E
3	Pudong (PD)	Jinxiu Road hightech	Industrial development zone	31°14′N/121°26′E
4	Songjiang (SJ)	Nanqing Road	Chemical industry estate	31°02′N/121°14′E
5	Fengxian (FX)	Hangnan Road	Agricultural eco-orchard	30°56′N/121°29′E
6	Xujiahui (XJH)	Puxi Road	Business center	31°12′N/121°26′E

time. The extraction temperature was controlled by an external water bath. Because SPME is an equilibrium extraction procedure, extraction time and temperature were optimized in this investigation. Following extraction, the fiber was placed in the GC injector for desorption for 2 min at 280°C. After each extraction, the fiber was cleaned at 280°C for 1 min in a Helium atmosphere to minimize possible carryover.

1.5 GC-MS conditions

The detailed experimental parameters for GC-MS are presented below. The Helium carrier gas (99.999%) was maintained at a constant pressure of 4.92 psi, with a flow rate of 2.0 mL/min. The injector and interface temperatures were both maintained at 280°C. The GC temperature was programmed as follows: initial 60°C, hold 2 min, to 150°C at 30°C/min, then to 300°C at 6.0°C/min, hold 10 min. The total run time was 40 min per sample. The MS was operated in electron impact (EI) mode with an ion source temperature of 230°C. The target compounds were quantified in the selected ion monitoring (SIM) mode, using the molecular ion and one qualifier ion for each compound. The GC-MS was tuned once a week.

1.6 Quantitative analysis

A series of concentration gradients of standard solutions ranging from 1 to 1000 ng/L were prepared to generate calibration curves, and external standard method was used. The extraction and analysis were performed at least three times for each concentration, using the same SPME GC-MS method. The concentrations of PAHs in rainwater samples were calculated using these calibration curves. The precision of the SPME-GC method, expressed as percentage of relative standard deviation (RSD), was determined from a set of seven replicates. Blank values were subtracted for each analysis.

The rainfall R_i (mm) of each event can be calculated by Eq. (1):

$$R_i = \frac{V_i}{S_b} \tag{1}$$

where, V_i (mL) is the sampling amount of a rain event at each site and S_b is the area of the sampling bucket (about 471.4 cm²).

The volume-weighted mean (VWM) concentrations of PAHs ($\bar{C}$) per year can be calculated by Eq. (2):

$$\bar{C} = \sum_{i-1}^{n} C_i R_i \Big/ \sum_{i-1}^{n} R_i \tag{2}$$

where, R_i (mm) is the total rainfall of each event in

Shanghai and C_i (ng/L) is the VWM concentration of PAHs of each event.

Associated with each rainfall flux, the deposition rate of PAHs per event (F_i) can be calculated directly from Eq. (3):

$$F_i = C_i R_i \tag{3}$$

Similarly, the annual flux of PAHs in Shanghai ($\bar{F}$) can be calculated by Eq. (4):

$$\bar{F} = \bar{C} \bar{R} S_t \tag{4}$$

where, $\bar{R}$ is the annual rainfall of Shanghai in the last ten years (its value is about 1042.6 mm) and S_t is the area of Shanghai (about 7035.7 km²).

1.7 Back trajectory analysis

To identify the influence of air masses from different directions on PAH deposition in each rainfall event in Shanghai, the air mass trajectories were calculated using the National Oceanic and Atmospheric Administration (NOAA) Air Resource Laboratory's Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (http://www.arl.noaa.gov/ready/hysplit4.html) (Hafner and Hites, 2005). For each sampling day, a 48 hr two-day backward air trajectory was computed at the occurrence UTC (Universal Time Coordinated) time of the rainfall, at 1000 m above the ground.

2 Results and discussion

2.1 Characteristics of rainfall in Shanghai

Fifty seven rain events were recorded and 163 samples were collected from six sites in Shanghai from April to September in 2009. Because of intensive iron and steel industry activity and heavy dust pollution in the air, Baoshan District (BS site) was chosen to study the relation of precipitation and pH. Table 2 shows the characteristics of five sampled discrete rain events at the BS site, selected at random during the period from June to August. The rain intensity ranged from 0.46 to 13.75 mm/hr, the precipitation varied between 3.8 and 95.6 mm, and the duration was from 2 to 10 hr. There was no strict positive correlation between rain intensity and precipitation, due to the different duration for each rain event we have measured.

The pH of the rainwater ranged from 4.06 to 7.44 (Table 2). Based on the study of each precipitation at

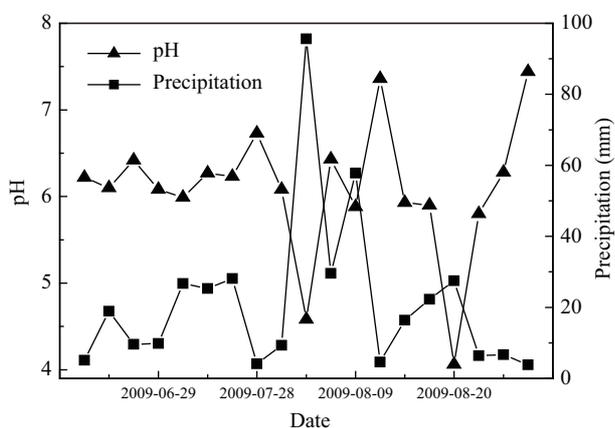**Table 2** Characteristics of the sampled rain events at the BS site

Date	Rain intensity (mm/hr)	Precipitation (mm)	Duration (hr)	pH
2009-06-21	1.02	5.1	5	6.22
2009-06-30	3.81	26.7	7	5.99
2009-07-12	4.22	25.3	6	6.27
2009-08-01	9.56	95.6	10	4.58
2009-08-11	0.46	4.6	10	7.36
2009-08-20	13.75	27.5	2	4.06
2009-08-30	0.95	3.8	4	7.44

the BS site, an obvious negative correlation was found, as shown in Fig. 2. As the precipitation increased, the value of pH decreased. Floating dust, which is mostly alkaline, exists in the air and increases the pH of rainwater during precipitation. When the precipitation increases, the floating dust is removed and its ability to basify rainwater is decreased, resulting in a more acidic precipitation. Because Shanghai is in the northern subtropical zone, mild temperatures and frequent rainfall occur all year around, resulting in the potential for acid rain pollution in this area.

2.2 Optimization and validation of the SPME method

The extraction efficiency of SPME can be affected by experimental conditions such as extraction time and temperature, so it was optimized. Because SPME is an equilibrium extraction method, the maximum amount of analyte that can be extracted by the fiber is achieved at equilibrium time (Rianawati and Balasubramanian, 2009). The external water bath was maintained at 30°C while the sample was magnetically stirred at 1000 r/min. Extraction time was varied between 5–60 min to study the adsorption profile. The standard concentration of PAHs was 200 ng/L. The signal intensities (peak area) after the GC-MS analysis were compared. As shown by the experimental results, most of the PAH compounds reached equilibrium at 40 min. At longer time the extraction capability remained constant. Therefore, 40 min was chosen as the optimum extraction time.

Extraction temperature was also investigated because it plays a significant role in SPME method sensitivity. It can affect the distribution coefficient and diffusion rate for PAHs migrating from the aqueous sample to the fiber coating (Rianawati and Balasubramanian, 2009). The ex-

traction was performed at an increasing temperature range, from 10 to 80°C. The majority of PAHs showed a signal enhancement at temperatures up to 30°C, indicating that increasing the temperature favored the mass transfer of the analytes from the solution to the fiber. It was also observed that low molecular weight (LMW) PAHs easily reach equilibrium at a lower temperature compared to the high molecular weight (HMW) PAHs. Although higher temperatures can favor the volatilization of PAH compounds, the distribution coefficients of PAHs decreased at higher temperatures. Therefore, the appropriate sample temperature was set to 30°C, close to the environmental temperature at which PAHs occur.

The optimized SPME technique was validated by determining the calibration curves, limits of detection (LODs), RSDs, and relative coefficients (R). This validation test was carried out using a standard solution of 200 ng/L. The results are presented in Table 3. Calibration using the SPME technique gave a satisfactory result, with R ranging between 0.989 and 0.999 for all PAHs. The results were mostly linear in the 1 to 1000 ng/L range. The limits of detection obtained were 0.1–5.0 ng/L based on a signal-noise (S/N) ratio of 3. The RSD of the whole method was in the range of 4.1% to 10.9%. This range indicates that SPME can be applied to the analysis of all the target PAH compounds at a trace level.

Based on these optimized conditions, a representative chromatogram of PAHs from a rainwater sample is presented in Fig. 3. Almost all PAHs were sufficiently separated, indicating that this newly-developed SPME method coupled with GC-MS analysis could be used to determine PAH levels in natural rainwater samples.

2.3 Distribution of PAHs

The average monthly concentrations of all fifteen PAH compounds in Shanghai from April to September, 2009 are shown in Table 4. One hundred and sixty three rainwater samples were collected from the six sites during the monitoring period. The calculated VWM concentration of PAHs per event ranged from 74 to 980 ng/L, with an

Fig. 2 Precipitation and pH at the BS site.
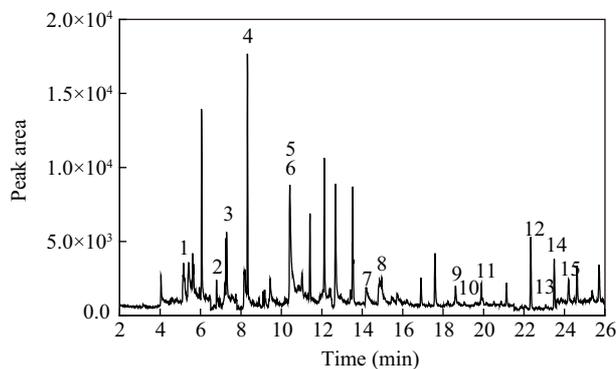
Fig. 3 Representative chromatograph of PAHs in rainwater: (1) Naphthalene (NaP), (2) Acenaphthylene (Acy), (3) Acenaphthene (Ace), (4) Fluorene (Flo), (5) Phenanthrene (Phe), (6) Anthracene (Ant), (7) Fluoranthene (Fluo), (8) Pyrene (Pyr), (9) Cyclopenta[c,d]pyrene (Cyc), (10) Benzo(a)anthracene (BaA), (11) Chrysene (Chry), (12) Benzo(e)pyrene (BeP), (13) Benzo(b)fluoranthene (BbF), (14) Benzo(k)fluoranthene (BkF), (15) Benzo(a)pyrene (BaP).

Table 3   Target compounds, calibration curve equation, relative coefficient (R), limits of detection (LODs), linearity range, and RSD ($n = 7$)

PAHs	Calibration curve equation	R	LODs (ng/L)	Linearity range (ng/L)	RSD
Nap	$Y = -9242.5 + 348.5X$	0.989	0.1	1–1000	7.0%
Acy	$Y = -73895.5 + 944.7X$	0.990	5.0	50–1000	8.5%
Ace	$Y = -28426.3 + 930.2X$	0.994	0.1	1–1000	6.2%
Flo	$Y = 11577.4 + 1200.0X$	0.999	0.1	1–1000	8.3%
Phe	$Y = 8562.9 + 2632.8X$	0.997	4.0	50–1000	6.9%
Ant	$Y = 3936.6 + 2369.6X$	0.997	5.0	50–1000	7.9%
Flu	$Y = -50857.1 + 3723.0X$	0.997	0.1	1–1000	4.4%
Pyr	$Y = -31006.6 + 3392.2X$	0.996	0.1	1–1000	6.1%
Cyc	$Y = -112557.3 + 1805.1X$	0.994	2.0	20–1000	6.7%
BaA	$Y = -31784.2 + 2087.9X$	0.996	0.9	1–1000	4.1%
Chry	$Y = -69404.6 + 2886.5X$	0.998	0.1	1–1000	5.3%
BeP	$Y = -39676.0 + 1908.0X$	0.999	1.5	20–1000	8.7%
BbF	$Y = -15201.7 + 2377.5X$	0.998	0.1	1–1000	4.9%
BkF	$Y = -68483.8 + 1634.7X$	0.991	0.1	1–1000	4.9%
BaP	$Y = -7492.4 + 1032.9X$	0.996	1.6	20–1000	10.9%

Table 4   Average monthly concentrations of PAHs in rainwater and the rainfall

	May 2009 ($n = 7$)	Jun 2009 ($n = 45$)	Jul 2009 ($n = 47$)	Aug 2009 ($n = 59$)	Sep 2009 ($n = 5$)	VWM ($n = 163$)
NaP (ng/L)	223.0	105.9	99.3	107.8	36.8	108.7
Acy (ng/L)	18.8	40.5	60.9	53.6	ND	51.1
Ace (ng/L)	7.7	28.2	18.7	21.1	8.0	21.7
Flo (ng/L)	36.7	97.3	55.8	64.3	7.9	69.1
Phe (ng/L)	65.4	72.1	71.9	88.1	104.6	78.6
Ant (ng/L)	75.5	83.6	83.7	101.8	118.5	91.1
Flu (ng/L)	19.7	27.2	24.4	30.9	49.9	27.7
Pyr (ng/L)	13.7	17.7	17.1	19.1	24.8	18.0
Cyc (ng/L)	ND	13.8	2.3	33.8	ND	18.4
BaA (ng/L)	ND	7.4	0.6	7.3	5.9	5.1
Chry (ng/L)	ND	7.1	ND	10.7	7.3	6.3
BeP (ng/L)	23.4	15.6	13.4	21.6	17.2	17.8
BbF (ng/L)	10.4	8.4	6.3	11.2	10.2	9.0
BkF (ng/L)	3.3	21.8	44.5	42.4	7.4	36.5
BaP (ng/L)	0.9	4.7	9.4	6.0	ND	6.5
∑PAHs (ng/L)	498.4	551.3	508.0	619.7	398.6	565.6
Rainfall (mm)	100.9	738.6	854.5	1243.8	4.4	

ND: not detected.
VWM: the volume-weighted mean concentration according to the rainfall from May to September 2009.

average value of 481 ng/L. This is similar to the PAH concentrations measured in rainwater collected in Alsace, France (1.6 to 968.1 ng/L) (Delhomme et al., 2007). However, it has been reported that the concentration of PAHs in precipitation in rural sites of the United States and Canada was only from 26 to 90 ng/L (Sun et al., 2006). Our results clearly showed that the PAH concentration in the rainwater of Shanghai was at the high end of worldwide figures. This is probably due to the great number of industries and the dense population in the Shanghai region.

This investigation showed that the predominant PAHs were NaP, Flo, Phe, and Ant; other compounds were at a lower concentration and frequency of occurrence. The detailed PAH concentrations can be clearly seen in Table 4. The total mean concentrations of NaP, Flo, Phe, and Ant from April to September, 2009 were 108.7, 69.1, 78.6, and 91.1 ng/L, respectively. Based on these values, the corresponding percent of each compound in the total PAH concentration (565.6 ng/L) was 19.2%, 12.2%, 13.9%, and 16.1%, respectively. Similar conclusions can be derived from PAH deposition in Guangzhou, where NaP, Acy, Phe, and Ant were in the majority (Huang et al., 2009). As seen in Fig. 4, the 15 PAH compounds can be divided into three

groups of 2–3 rings, 4 rings, and 5 rings, according to the number of benzene rings present in the molecule. For both high and low precipitation, 2–3-ring PAHs were the major components. This suggests that the LMW PAHs are mostly in the vapor phase due to their lower hydrophobicity, whereas HMW PAHs prefer to attach to the particulate phase. The LMW PAHs have a significant acute toxicity, whereas the HMW show high carcinogenic and mutagenic potential (Perugini et al., 2007). This result shows that rainwater in Shanghai has been polluted by toxic PAHs at a high concentration level.

2.4 Analysis of the deposition flux of PAHs

PAH deposition fluxes in rainwater during the monitoring period can be estimated by the combination of PAH concentrations in Eq. (3). The mean deposition flux of PAHs per event was 24 μg/m² and ranged from 0.02 to 333 μg/m² during the monitoring period. The deposition rate of PAHs in Shanghai was 590 μg/(m²·yr), which was far below the values in Guangzhou (Huang et al., 2009) and Izmit Bay, Turkey (Pekey et al., 2007), which were 3568 μg/m² and 1716 μg/m² respectively, and larger than the 130 μg/(m²·yr) value in Galveston Bay (Park et al.,

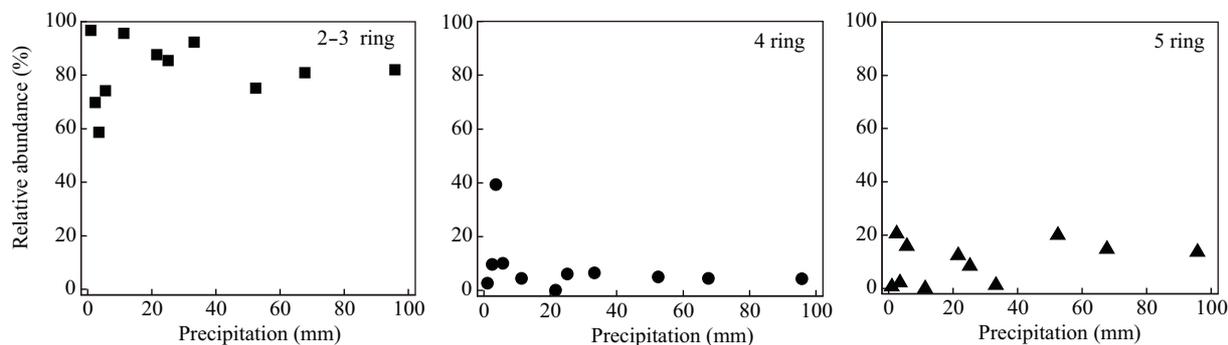**Fig. 4** Relationship between precipitation and the relative abundance.

2001) and the 182 μg/(m²·yr) value in Corpus Christi Bay (Park et al., 2002), Texas, USA. These results suggested that the annual amount of PAHs deposited in Shanghai is at an intermediate level. It also indicated that the pollution may be aggravated by rapid development and motorization.

The monthly variation in deposition flux of PAHs in Shanghai from June to August can be observed from Fig. 5. Monthly trends were not clear because this period was in the summer, and no obvious weather changes in these months occurred. In individual PAH compound deposition flux research, NaP, Flo, Phe, and Ant were still the dominant species. This result was consistent with the mean concentration values described in Section 2.3. The average deposition fluxes of these four main compounds from April to September were estimated at 5391, 2941, 3334, and 3863 ng/m², and accounted for 22.3%, 12.1%, 13.8%, and 15.9% of the total deposition loadings (24,228 ng/m²), respectively.

Because Shanghai covers an area of 7037.5 km², the calculated flux of PAHs in an event in the city is approximately 170 kg. Therefore the annual flux of PAHs in rainwater in Shanghai is 4148 kg, as calculated by Eq. (4). This means that every year there will be 4148 kg PAH compounds deposited on the Shanghai region. The high deposition flux of PAHs in rainwater also indicates that rain is a good way to remove PAH compounds from the atmosphere. Because LMW PAHs appear in the dissolved phase and HMW PAHs in the particulate phase, the modes

Fig. 5 Monthly variations of individual PAH deposition from June to August.

of removal are different. For the former, the main method of removal is below-cloud washout, whereas the HMW PAH compounds are removed by in-cloud scavenging (Poster and Baker, 1996)

To sum up, the atmospheric environment has been significantly affected by anthropogenic activities, and PAH pollution is a potential challenge to environmental protection in Shanghai.

2.5 PAH sources by diagnostic analysis

Many methods have been used to identify sources of PAHs, such as receptor modeling using both a chemical mass balance model and a principal component analysis in the environment (Larsen and Baker, 2003). The ratios of certain PAH components of the same molecular weight is well-established as an index to identify the source of PAHs in rainwater because it is simple and applied widely in various environments (Yunkera et al., 2002). PAHs of molecular weight 178 and 202 are commonly used to distinguish between combustion and petroleum. For compounds of molecular weight 178, an anthracene to anthracene plus phenanthrene (An/178) ratio below 0.1 is usually taken as an indication of petroleum, whereas a ratio greater than 0.1 indicates the dominance of combustion. For molecular weight 202, a fluoranthene to fluoranthene plus pyrene (Fl/Fl+Py) ratio of 0.4 is usually defined as the petroleum limit; ratios between 0.40 and 0.50 are more characteristic of liquid fossil fuel (vehicle and crude oil) combustion, and ratios greater than 0.50 are suggestive of grass, wood or coal combustion.

Figure 6 shows molecular ratios of PAHs in rainwater during the monitoring period. Ratios of Ant/178 in all the rainwater samples varied between 0.4 and 0.8 and were generally approximately 0.5. The data indicate that combustion is the dominant source of PAHs in Shanghai. The ratios of Flu/202 were generally greater than 0.5, implying that the combustion of grass, wood, and coal could be the possible source of PAHs in rainwater.

2.6 Source identification by back trajectory model

Although PAH compounds are produced by local emission, air masses containing pollutants can be transported from one place to another. Therefore, PAHs transported from other remote areas by wind could also be an important source. The YP site was chosen as an example to do the back trajectory analysis because the six sites are so close
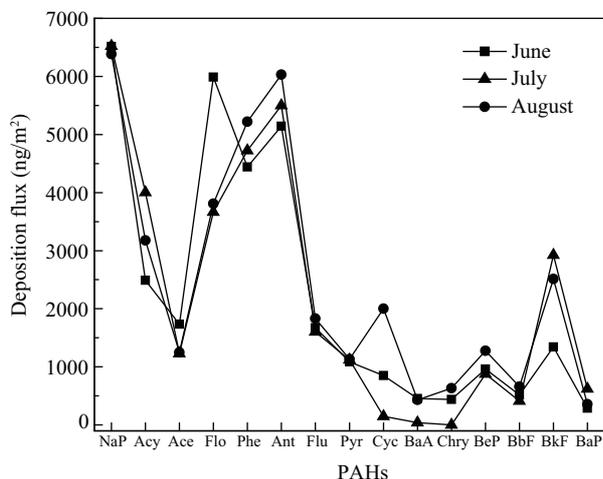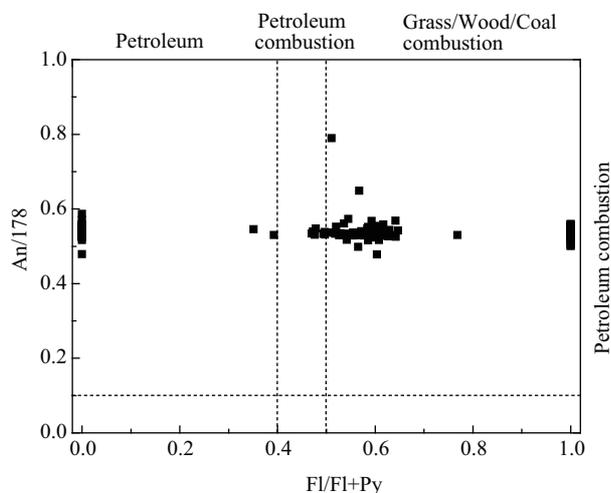
Fig. 6 PAH cross plot for the ratios of An/178 vs. Fl/Fl+Py.

that their trajectories are almost the same. The 48-hr back trajectory presented in Fig. 7 provides information on the advective transport on a representative day (Jun 29). The back trajectories of all rain events at 1000 m show that more than 90% of the air mass was transported from the southern part of China to Shanghai before each rain event.

Whether PAHs observed in the rainwater samples are derived from local emission or from long-range transport has still to be determined. The question of which source plays a more important role will be considered in future work.
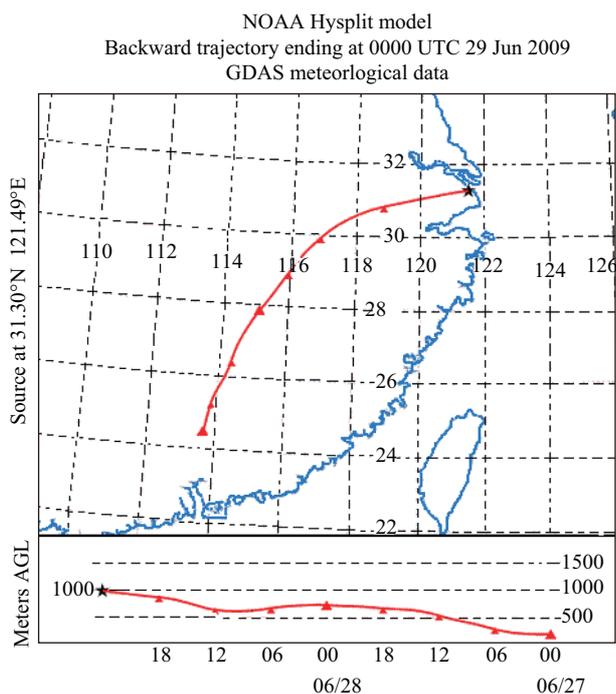

Fig. 7 Forty-eight hour back-trajectory arriving in Shanghai at 8:00 a.m., 29 June 2009.

3 Conclusions

One hundred and sixty three rainwater samples were collected from six sites in the urban area of Shanghai from

April to September, 2009 and were analyzed by SPME coupled to a GC-MS method. It was discovered that the LMW PAHs were the most abundant of the fifteen PAH compounds identified. The mean total concentration and deposition flux of PAHs in rainwater samples per event were 481 ng/L and 24,228 ng/m^2, respectively. The annual deposition flux of PAHs in Shanghai was 590 μg/m^2. The annual deposition of PAHs associated with rainwater was calculated to be 4148 kg, posing a potential challenge to environmental protection in Shanghai.

Source identification by diagnostic analysis of the ratios of An/178 and Fl/Fl+Py indicated that the combustion of grass, wood, and coal could be the possible sources of PAHs in rainwater. Back trajectory analysis also indicates that pollutant sources could be from the southern part of China, although whether the local source or the long-range transport is the dominant modality needs further study.

Shanghai is the industrial and commercial center of China, and may represent the typical environmental status of most Chinese cities. Similarly, this situation may also exist in other developing countries with similar climatic, geographical and socioeconomic conditions. More studies need to be undertaken to understand the impact of PAHs on the environment in developing countries and regions. A higher level of environmental vigilance will be required for the Shanghai region.

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