

Atmospheric deposition of polycyclic aromatic hydrocarbons (PAHs) in Shanghai: the spatio-temporal variation and source identification

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Abstract This study investigated the dry and wet deposition fluxes of atmospheric polycyclic aromatic hydrocarbons (PAHs) in Shanghai, China. The flux sources were traced based on composition and spatio-temporal variation. The results show that wet deposition concentrations of PAHs ranged from 0.07 to 0.67 $\mu\text{g}\cdot\text{L}^{-1}$ and were correlated with temperature ($P < 0.05$). Dry deposition of PAHs concentrations ranged from 3.60–92.15 $\mu\text{g}\cdot\text{L}^{-1}$ and were higher in winter and spring than in summer and autumn. The annual PAH average fluxes were 0.631 $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ and 4.06 $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ for wet and dry deposition, respectively. The highest wet deposition of PAH fluxes was observed in summer, while dry deposition fluxes were higher in winter and spring. Atmospheric PAHs were deposited as dry deposition in spring and winter, yet wet deposition was the dominant pathway during summer. Total atmospheric PAH fluxes were higher in the northern areas than in the southern areas of Shanghai, and were also observed to be higher in winter and spring. Annual deposition of atmospheric PAHs was about 10.8 t in across all of Shanghai. Wet deposition of PAHs was primarily composed of two, three, or four rings, while dry deposition of PAHs was composed of four, five, or six rings. The atmospheric PAHs, composed of four, five, or six rings, primarily existed in the form of particulates. Coal combustion and vehicle emissions were the dominant sources of PAH in the observed area of downtown Shanghai. In suburban areas, industrial pollution, from sources such as coke oven, incinerator, and oil fired power plant, was as significant as vehicle emissions in contributing to the deposition of PAHs.

Keywords PAHs, dry and wet deposition, temporal and spatial variation, Shanghai

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are non-volatile hydrocarbons produced by incomplete combustion of macromolecular compounds. The USA Environmental Protection Agency (USA EPA) found that half of the 16 priority controlled PAHs (Benzo[a]anthracene, Chrysene, Benzo [b] fluoranthene, Benzo [k] fluoranthene, Benzo [a] pyrene, Indeno [1,2,3-cd] pyrene, Dibenz [a,h] anthracene and Benzo [g,h,i] perylene) are possibly carcinogenic. Previous studies have shown that PAHs composed of four, five, or six rings have carcinogenic, teratogenic, and mutagenic effects on the carcinogenesis of the organism (Daane et al., 2001; Luo et al., 2008).

Shanghai is the most rapidly developing industrial city in China. As a result, atmospheric PAHs are imported to the land surface through both wet and dry deposition (McVeety and Hites, 1988; Dickhut and Gustafson, 1995; Park et al., 2002). This occurrence poses a potential health risk to people living in the area. Previous studies have shown that PAHs found in Shanghai soils were primarily derived from vehicle emissions, coal combustion, and biomass burning (Liu et al., 2010). To date, the concentration of PAH characteristics found in dust (Ren et al., 2007), atmospheric particulates (Jiang et al., 2009), fog drops (Li et al., 2011), and their sources (Liu et al., 2010; Wang et al., 2010; Liang et al., 2011) have been investigated. However, there is a paucity of studies on: 1) the dry and wet deposition of PAH fluxes imported into land surfaces, 2) characteristics of PAH temporal and spatial variation, and 3) the source analysis of PAHs over the entire urban

area.

Previous studies have shown that man-made PAHs are a direct result of incomplete combustion or pyrolysis under reduced conditions of mineral fuel, wood, paper, and other hydrocarbons (Wild and Jones, 1995). Numerous research studies have shown that vehicle emissions are one of the main sources of atmospheric PAHs in the urban area (Dunbar et al, 2001; Barakat, 2002; Ho and Lee, 2002; Liang et al., 2011). Dunbar et al (2001) pointed out that vehicle emissions contributed 46% of the atmospheric particulate PAHs in Boston, MD USA. The PAH emission inventories conducted by Xu et al. (2006) concluded that pyrolysis is found in biomass burning, domestic coal, and industrial firing coal was the predominant source of atmospheric PAHs in China.

In this study, the composition characteristics and fluxes from the atmosphere to land cover in the form of dry and wet deposition of the PAHs were investigated through seasonal and spatial sampling. By analyzing the data, this study traced the sources of the PAHs from the atmosphere to land cover and provided insights into the air and soil quality management and environmental risk assessment of Shanghai.

2 Materials and methods

2.1 Research area

Shanghai, one of the most developed cities in China, is located at the mouth of the Yangtze River. The city, covering a total area of 6340.5 km² (Bureau of Shanghai Municipal Statistics, 2015), is located in the subtropical monsoon climate zone and is characterized by four distinct seasons. The annual average wet deposition is 1147.3 mm.

Twenty sampling sites in 18 districts were set for this study, determined by the uniform distribution of space and the administrative division of Shanghai. The distribution of these sites is shown in Fig. 1, with detailed coordinates for each provided in Supplementary Materials Table S1.

The collection apparatus for wet deposition samples consisted of a self-designed rainfall collector. The upper section of the funnel measured 100 cm in diameter, with the lower section measuring 2 cm in diameter (see Supplementary Materials Fig. S1). Each sampling site was monitored continually, 24 hours a day, from Nov. 2010 to Oct. 2011. As rainfall events were forecast, a 2 L brown glass bottle, acid-washed in advance, was placed under the

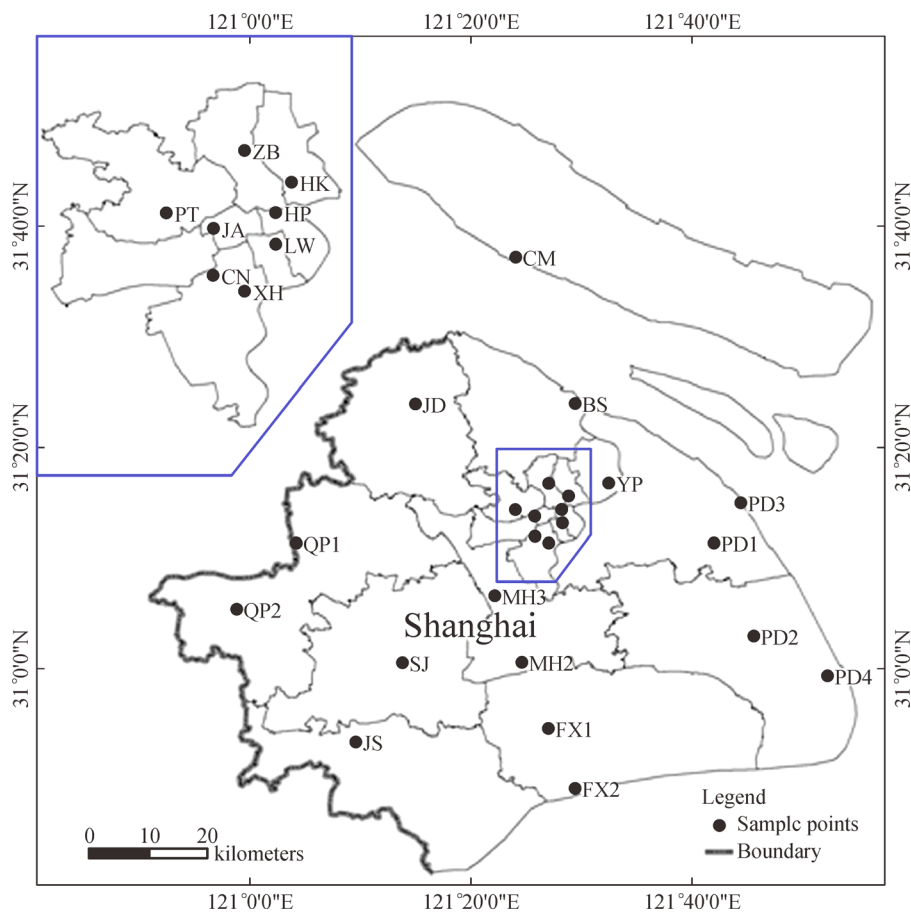


Fig. 1 Map of the research region and a collection of sampling sites 2.2.

collection mouth of the collector. Subsequently, the bottles were stored in an ice box to maintain a low temperature (0–4°C). Dry deposition samples were collected in a container similar to that used for the wet method. The containers, made of polyethylene (70 cm×50 cm×45 cm), were placed at each sampling site with 15 L deionized water which was added to prevent the loss of dry deposition samples. Appropriate amounts of CuSO₄ were added to inhibit the growth of algae in summer (GB/T15265-94). The sample quantity of each month is provided in Supplementary Materials Table S2.

2.2 Sample analysis

After the wet and dry deposition samples (collected by the wet method) were transported to the laboratory, they were filtered by a GF/F glass fiber filter (Waterman, UK) that had been burned in a muffle furnace under 400°C and weighed. The dry deposition of each sample was calculated as the sum of the PAHs in the filter and the filtrate. The filtrate was extracted through the solid phase extraction column (HLB, waters, USA) and concentrated by the automatic quantitative concentration meter DryVap, LabTech, USA). The filtrate was then purified using a chromatographic column, concentrated, and diluted with water to 1 mL for analysis (Nadal et al., 2004). The filters were freeze dried (CHRIST ALPHA 1-4/LD plus, Germany) and weighed. Dry deposition was taken as the weight difference between the samples before and after filtering. The frozen dried filters were extracted by an ASE300 accelerated solvent extraction (Dionex, USA), concentrated by an automatic quantitative concentration meter (DryVap, LabTech, USA), purified using the chromatographic column, concentrated again, and then diluted with water to 1 mL for analysis (Odabasi et al., 2006).

All samples were analyzed using a GC-MS (Agilent 7890 A GC/5975 GC-MS, USA) equipped with a CTC automatic sample injector. The chromatographic analyses were carried out using an HP-5MS fused silica capillary column (30 cm×0.25 mm×0.25 μm). A 1 μL sample was injected using a split less sampling method. The temperatures of the injection port, quadrupole, and transmission line were 300°C, 150°C, and 280°C, respectively. The ionization mode was EI with a voltage of 70 eV. The carrier gas was Helium. The standard sample was a mix of 18 PAH samples (Supel co, USA). Each sample was analyzed for Nap, Acy, Ace, Flo, Phe, Ant, Fla, Pyr, BaA, Chr, BbF, BkF, BaP, IcdP, DahA, BghiP.

2.3 Quality control

The deuterated PAH surrogate standards containing d8-Nap, d10-Ace, d10-Phe, d12-Chr, and d12-Per were added to all samples before extraction to monitor procedure performance and matrix effects. The wet deposition

recovery rate ranged from 68.6% to 104.2%, the dry deposition recovery rate was ranged from 60.8% to 95.2% (reference Supplementary Material, 2003 Cerilliant Corporation). Parallel and blank samples were added during the experiment to analyze every 20 samples, ensuring a deviation less than 15%.

2.4 Flux calculations

2.4.1 Deposition flux

$$F_{d/w} = M_{d/w} \times A^{-1} \times T^{-1}, \quad (1)$$

where $F_{d/w}$ is the flux of dry deposition (dry deposition, $\text{g} \cdot \text{m}^{-2} \cdot \text{month}^{-1}$) or wet deposition (wet deposition, $\text{L} \cdot \text{m}^{-2} \cdot \text{month}^{-1}$); $M_{d/w}$ is the weight of dry deposition (g) or volume (L) of wet deposition; A is the area of deposition receptor (m^2); and T is the duration of sample collection (month). In this study, $M_{d/w}$ is recorded for each collected sample, A is the area of deposition receptor (a circle with a diameter of 100 cm and a rectangle of 70 cm×50 cm×45 cm), and T is one month.

2.4.2 Deposition flux of PAHs

$$F_{pd/pw} = C_{pd/pw} \times F_{d/w}, \quad (2)$$

where $F_{pd/pw}$ is the flux of PAHs ($\mu\text{g} \cdot \text{m}^{-2} \cdot \text{month}^{-1}$) of dry deposition (dry deposition) or wet deposition (wet deposition); $C_{pd/pw}$ is the concentration of PAHs in dry deposition ($\mu\text{g} \cdot \text{g}^{-1}$) or concentration in wet deposition ($\mu\text{g} \cdot \text{L}^{-1}$), and $F_{d/w}$ is the flux of dry deposition ($\text{g} \cdot \text{m}^{-2} \cdot \text{month}^{-1}$) or wet deposition ($\text{L} \cdot \text{m}^{-2} \cdot \text{month}^{-1}$).

2.5 Graphs and maps

The figures were created by using ESRI ArcGIS software. We used a local projected coordinate system based on the Gauss-Kruger coordinate system.

3 Results and discussion

3.1 Temporal and spatial variation of wet and dry deposition flux

Pronounced seasonal variations of wet and dry deposition were observed all in Shanghai during this study period (Table 1). Wet deposition was primarily observed in summer. Dry deposition fluxes varied from 0.69–32.3 $\text{g} \cdot \text{m}^{-2} \cdot \text{month}^{-1}$, but were generally higher in winter and spring than in summer and autumn. These fluxes were also influenced by extreme weather over a short period. Air quality observations were ongoing from April 28 to May 18, 2011. The mass concentrations of PM₁₀ and PM_{2.5} during the dust episodes were much higher than those in non-dust episodes, with the maximum daily mass

concentrations of PM_{10} and $PM_{2.5}$ reaching $787.2 \mu\text{g}\cdot\text{m}^{-3}$ and $139.5 \mu\text{g}\cdot\text{m}^{-3}$. The average $PM_{2.5}/PM_{10}$ ratio was $(32.9\pm 14.6)\%$ (15.6%–85.1%) (Li et al., 2014). The maximum of dry deposition fluxes were recorded in April and May, 2011 due to sandstorms, a result from an increase in the fluxes.

In general, fluxes decreased from north to south along with the cumulative wet deposition throughout the year. There was less wet deposition in the east and west (see Supplementary Materials Fig. S2 and Table S3). The dry deposition fluxes were distinctly higher in northern Shanghai than in the southern areas (see Supplementary Materials Fig. S3). The Baoshan District (BS) located in the northwest section of Shanghai, is an important industrial zone. The downtown area is also situated in the north sector of the city. The dust from traffic and construction is likely the cause of high dust fluxes in this northern region.

3.2 Temporal and spatial variation of PAH concentrations in wet and dry deposition

The average PAH concentrations of wet deposition was lowest in November 2010 ($0.07 \mu\text{g}\cdot\text{L}^{-1}$) and highest in June 2011 ($0.67 \mu\text{g}\cdot\text{L}^{-1}$) during the study period. PAH concentrations of wet deposition in Shanghai were lower than those in atmospheric concentrations of wet deposition in the urban area of Paris (51–995 $\text{ng}\cdot\text{L}^{-1}$, Ollivon et al., 2002). The monthly average was distinctly higher in spring than in summer (Fig. 2, Supplementary Materials Table S4).

The PAH concentrations in dry deposition varied from $3.60 \mu\text{g}\cdot\text{g}^{-1}$ to $92.2 \mu\text{g}\cdot\text{g}^{-1}$, with the maximum occurring in March and the minimum in August 2011, respectively. However, the data showed no obvious difference among the monthly averages. A temporal analysis revealed that

summer had relatively lower PAH concentrations in dry deposition (Fig. 3).

The spatial variation showed no difference between urban and suburban areas of Shanghai in terms of the PAH concentrations in wet deposition. The average PAH concentrations in wet deposition of each sampling site ranged from $0.13 \mu\text{g}\cdot\text{L}^{-1}$ (in CN and ZB) to $0.30 \mu\text{g}\cdot\text{L}^{-1}$ (in QP) (Fig. 4). The highest average concentration of PAHs in dry deposition was in CM ($35.92 \mu\text{g}\cdot\text{g}^{-1}$), which is more than 3 times higher than FX ($10.56 \mu\text{g}\cdot\text{g}^{-1}$). There was also no difference between average PAH concentrations in dry deposition of at each site. The high PAHs in the samples indicated local contamination (Fig. 5).

3.3 Temporal and spatial variation of PAH fluxes in wet and dry deposition in Shanghai

The atmospheric PAH deposition load of Shanghai was about 10.8 t throughout the year. The uneven wet deposition varied from $0.36 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{month}^{-1}$ to $290.1 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{month}^{-1}$ and was highest in June and August, resulting in the higher PAH flux. During this study period, PAH fluxes in dry deposition ranged from 18.3 – $1288.1 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{month}^{-1}$ (Table 2) and were higher in winter and spring than in summer and autumn. This scenario was mainly dependent on the dry deposition flux and the PAH concentration. It may be concluded that the sand-dust storms in east China in April and May led to the higher flux. Compared to other seasons, PAH fluxes from dry deposition were higher in winter and spring which could be due to an increase in coal combustion. A previous study based in central South Korea found that the PAH dry deposition fluxes were higher in winter (10 – $24 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$) than in spring (4.1 – $8.2 \mu\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$) (Bae et al., 2002), but in our research there was no significant difference of dry deposition between in winter and spring.

Table 1 Wet deposition and dry deposition fluxes in Shanghai from Nov. 2010 to Oct. 2011

Month	Wet deposition/mm				Dry deposition/($\text{g}\cdot\text{m}^{-2}\cdot\text{month}^{-1}$)			
	Range	Median	Mean	SD	Range	Median	Mean	SD
2010-11	0.70–23.7	10.4	10.7	5.11	2.23–10.8	3.16	3.84	1.90
2010-12	30.1–94.8	44.1	46.3	12.7	4.54–18.1	6.03	7.00	3.15
2011-01	5.10–21.2	18.3	15.9	5.33	2.25–16.6	5.61	6.28	3.08
2011-02	6.00–24.7	18.3	16.9	4.48	1.85–9.31	3.89	3.98	1.68
2011-03	21.2–53.2	32.2	33.8	8.54	2.36–14.0	5.30	5.55	2.37
2011-04	16.8–47.3	31.1	32.0	8.45	4.18–32.3	8.74	10.3	6.45
2011-05	5.90–50.0	28.9	28.1	9.94	4.09–15.8	7.68	8.56	3.52
2011-06	240.5–612.4	312.4	340.3	84.8	1.32–5.88	3.00	3.20	1.28
2011-07	9.80–124.0	58.8	58.6	28.4	1.22–7.69	3.75	4.42	1.98
2011-08	98.5–732.0	282.1	275.0	98.7	0.96–17.7	1.02	1.30	0.94
2011-09	8.16–59.7	33.0	32.4	13.8	1.85–13.2	4.69	5.14	2.80
2011-10	6.00–55.3	17.5	22.3	13.7	0.69–7.29	1.81	2.14	1.68

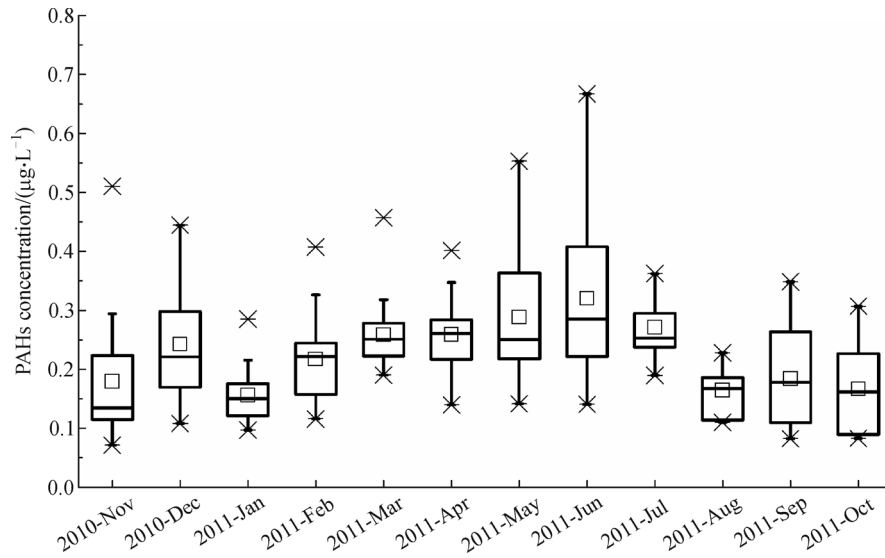


Fig. 2 Monthly variation of PAH concentrations in wet deposition.

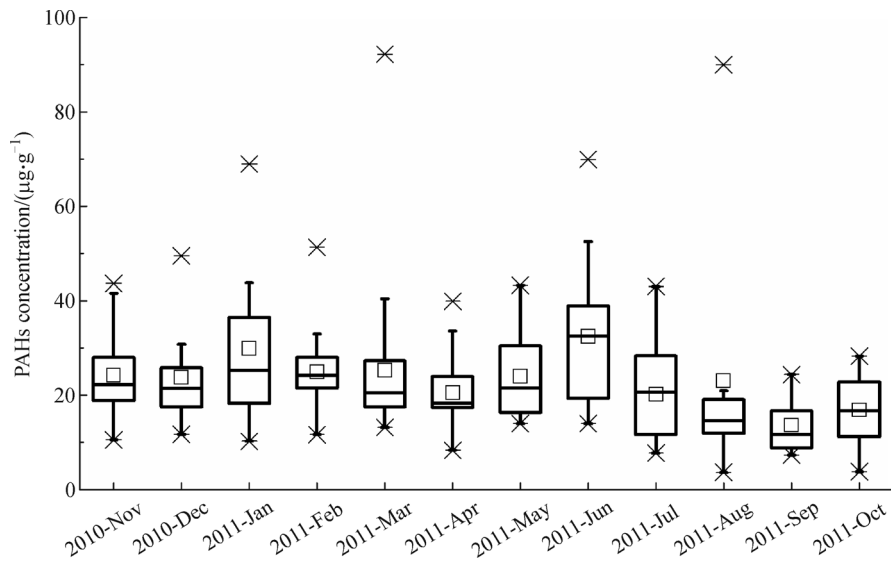


Fig. 3 Monthly variation of PAH concentrations in dry deposition.

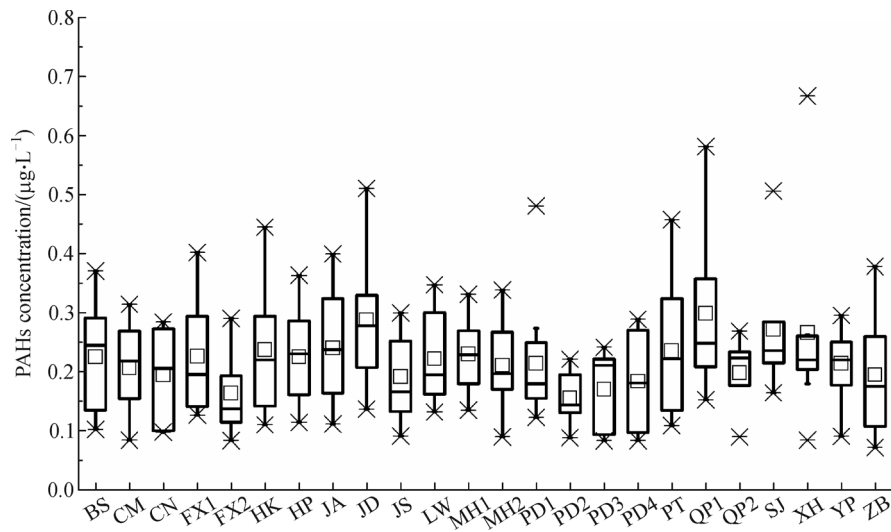


Fig. 4 Spatial variation of PAH concentrations in wet deposition at all sampling sites.

In addition, air temperature and wet deposition were important factors for dry and wet deposition fluxes and the photo degradation of PAHs (Ho and Lee, 2002).

Tasdemir and Holsen (2005) observed dry PAH fluxes of $34.96 \pm 16.54 \mu\text{g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ in an urban area of Turkey, higher than wet deposition fluxes of $28.4 \mu\text{g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ reported by Birgül et al. (2011). Guor et al. (2008) found the mean dry deposition velocities for LMW PAHs (Nap, AcPy and AcP) of (0.054, 0.040 and 0.15) $\text{cm} \cdot \text{sec}^{-1}$ in ambient air of central Taiwan at Wu - Chi, Sha - Lu, Ta - Duh, and the Expressway Interchange in the city of Taichung. Ozaki et al. (2006) found that the total PAH concentration of fine particles ranged from 0.14–16.3 $\text{ng} \cdot \text{m}^{-3}$, and range for coarse particles was 0.01–0.77 $\text{ng} \cdot \text{m}^{-3}$ from August to December in Higashi-Hiroshima City, Japan. For total (dry + wet) depositions, the PM flux was 1.9–11.2 $\text{mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, and the total PAH

flux was 1.9–97.2 $\text{ng} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$.

In Shanghai, the atmospheric deposition for PAHs was typically in the form of dry deposition, except for summer (from June to August). The average dry deposition flux of PAHs was $4.06 \mu\text{g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, higher than in wet deposition ($0.63 \mu\text{g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$) by an order of magnitude. The increase in wet deposition flux in summer became the major path of PAHs from the atmosphere to land surface. In summary, the dry deposition was the main atmospheric deposition pathway in all seasons except summer, when both wet and dry deposition were high. The wet deposition may be a determining factor for the ratio of dry to wet deposition of atmospheric PAHs. For example, the dry deposition of PAH fluxes was $5.14 \mu\text{g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ (Zhang et al., 2008) in the southern suburban area of Beijing, located in northern China. However, the dry deposition of PAHs in the Pearl River Delta (Li et al., 2010), a southern region of China

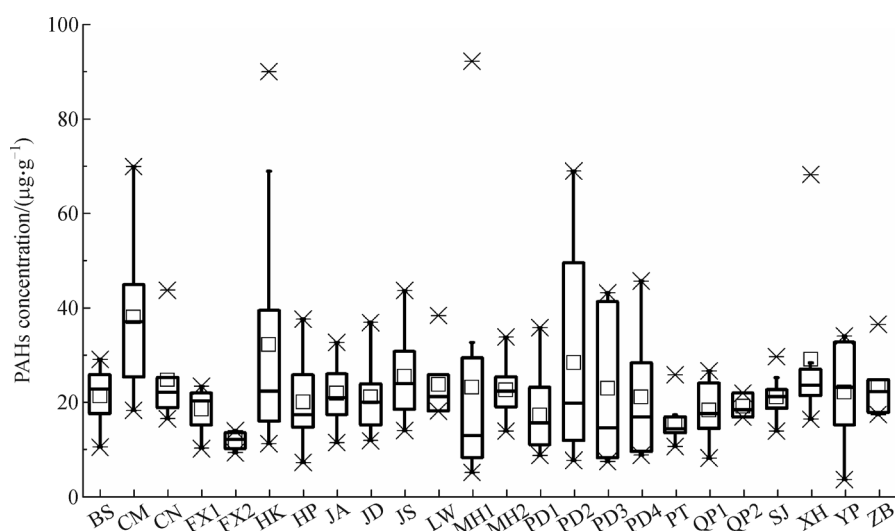


Fig. 5 Spatial variation of PAH concentrations in dry deposition of all sampling sites.

Table 2 Fluxes of the Σ PAHs in wet deposition and dry deposition in Shanghai from Nov. 2010 to Oct. 2011

Month	Σ PAHs ($\mu\text{g} \cdot \text{m}^{-2} \cdot \text{month}^{-1}$) in wet deposition				Σ PAHs ($\mu\text{g} \cdot \text{m}^{-2} \cdot \text{month}^{-1}$) in dry deposition			
	Range	Median	Mean	SD	Range	Median	Mean	SD
2010-11	0.36–4.94	1.41	1.76	1.18	42.56–129.15	77.11	83.26	24.53
2010-12	4.75–42.13	8.81	11.88	8.43	75.07–466.39	119.95	167.1	103.87
2011-01	0.91–4.46	2.44	2.41	0.95	31.28–1145.98	142.12	204.02	248.86
2011-02	0.78–4.90	3.56	3.58	1	34.41–255.83	84.97	97.95	49.51
2011-03	4.88–13.98	8.49	8.71	2.74	68.69–217.61	113.32	123.36	47.4
2011-04	3.38–19.00	7.87	8.43	3.53	55.62–1288.08	154.49	223.31	257.43
2011-05	0.83–17.79	7.73	7.79	4.22	87.45–678.35	159.51	210.12	139
2011-06	36.93–290.06	82.84	110.78	67.07	18.32–209.99	98.52	103.73	55.43
2011-07	5.86–29.65	16.55	16.98	7.57	25.54–217.63	72.92	83.57	54.69
2011-08	14.36–84.79	47.81	45.16	22.91	12.26–336.23	39.00	66.83	78.17
2011-09	0.68–17.97	5.16	6.24	4.35	16.54–158.42	59.17	66.59	37.50
2011-10	0.53–13.55	2.55	3.48	2.94	9.41–76.37	28.12	31.38	18.56

with high rainfall, was significantly less than in northern China, ranging from 0.06 to 0.57 $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$.

The PAH deposition fluxes were spatially variable at city scale. Fang et al. (2004) found that the PAHs deposition fluxes were (58.5, 48.8, 38.6) $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ in an industrial park, urban area, and countryside of Taichung, Taiwan, respectively. In Shanghai, the total deposition flux (dry and wet) was higher in the north areas than in the south. The total flux (dry and wet) was calculated by the dry deposition (F_{pd}) plus the wet deposition (F_{pw}). Baoshan District and downtown Shanghai experienced the highest PAH fluxes during winter. Baoshan is a significant industrial hub of Shanghai, which is likely the cause for the high concentration of PAHs in the area. The high total PAHs deposition flux in spring (from April to June) was controlled by the high dry and wet deposition. The highest atmospheric deposition of PAHs (62.2%) occurred in winter (December and January) and spring (from April to June) (Fig. 6, Supplementary Materials Table S5).

3.4 Analysis of the source of PAHs in wet and dry deposition in Shanghai

Major anthropogenic sources of PAHs are from combustion, collection and application of petrochemical products, incineration and coking of various solid wastes, incomplete combustion and pyrolysis for reducing conditions of wood, paper, and other hydrocarbons, etc. (Dallarosa et al., 2005). The combustion or usage of organic compounds of different properties result in different properties and types

of PAHs. Khalili et al. (1995) indicated that Flu was one of the main characteristic compounds produced by coking coal combustion. Lim et al. (2005) suggested that the ratio of Phe and Ant concentration can be used for identifying the source of PAHs from oil and from fuel burned at very high temperatures. Therefore, understanding the composition of PAHs can be used effectively to estimate their origin. In this study, significant correlations were observed ($P < 0.05$) between temperature and the ΣPAHs in wet deposition by using the Pearson product-moment correlation coefficient (Table 3).

Table 3 The Pearson correlation coefficient between the temperature and the ΣPAHs in wet deposition

	ΣPAHs	T
ΣPAHs	1	0.131*
T	0.131*	1

*Correlation is significant at the 0.05 level (2-tailed).

The characteristic ratio of the PAH composition in wet and dry deposition can be regarded as an important index for identifying their atmospheric and land cover source. Yunker et al.'s (2002) analysis from previous research found that when $\text{Phe}/\text{Ant} > 10$ or $0 < \text{Fla}/(\text{Fla} + \text{Pyr}) < 0.4$, the main source of PAHs was oil, when $0 < \text{Phe}/\text{Ant} < 10$, the main source was incomplete combustion; and when $0.4 < \text{Fla}/(\text{Fla} + \text{Pyr}) < 0.5$, the main source was incomplete combustion of oil, yet while $\text{Fla}/(\text{Fla} + \text{Pyr}) > 0.5$, PAHs were shown to be primarily

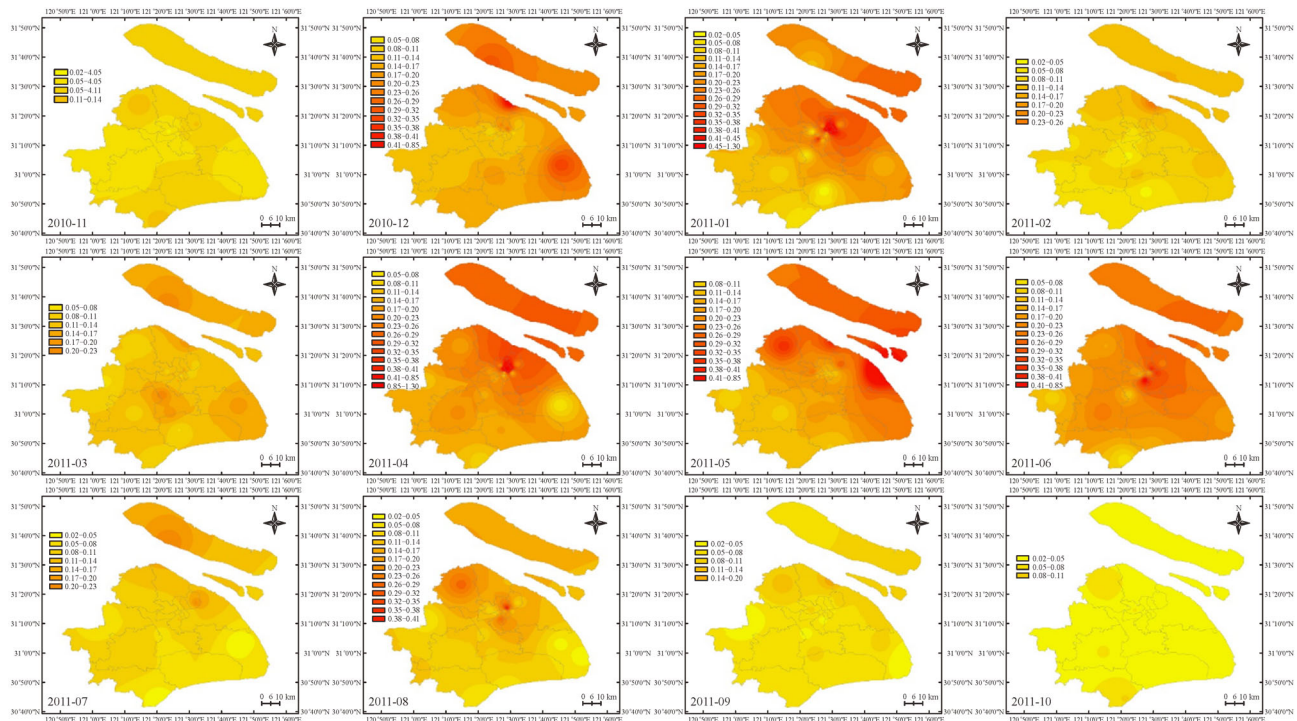


Fig. 6 The temporal and spatial variation of total deposition fluxes of PAHs (dry and wet).

caused by the incomplete combustion of wood, coal, and grass. Nielsen (1996) took BaP as the indicator of PAH source analysis to estimate the ratio of BghiP and BaP. The results showed that the ratio of BghiP/BaP was 2.02 times that caused by transportation and 0.8 from other sources. Previous research results of related domestic and foreign literature, and the data summary of monitoring characteristic ratio from industrial emission sources in Shanghai, can be found in Tables S4 and S5.

Wet deposition of PAHs were primarily composed of 2, 3, or 4 rings. The composition of PAHs showed regular seasonal variation (Supplementary Materials Fig. S4). The proportion of PAHs composed of 4, 5, or 6 rings in wet deposition was lower in winter than in summer. It decreased gradually from autumn to winter, while the proportion of PAHs composed of 2 or 3 rings increased over the same period. A gradual increase in the proportion of PAHs composed of 4, 5, or 6 rings was found in the spring and could be attributed to the high content of particulate matter in the spring rain. The atmospheric PAHs composed of two or three rings were mainly gaseous, but the weight from five or six rings was mainly from particles (Ciganek et al., 2004). The dry deposition of PAH was mainly composed of four, five, or six rings (Supplementary Materials Fig. S5). Shanghai experienced prevailing northerly winds in winter. The interaction between PAHs from internal provinces through long distance transportation and those produced locally in Shanghai resulted in a dispersed composition in dry deposition during winter. The proportion of PAHs composed of four, five, or six rings increased gradually in the spring and decreased after August.

Six characteristic ratios were chosen for identifying the source of PAHs: BaA/(Chr + BaA), BghiP/ BaP, Fla/(Fla + Pyr), Phe/Ant, Pyr/BghiP, from eight components which were Anthracene (Ant), Benzo (a) anthracene (BaA), Benzo (g,h,i) perylene (BghiP), Benzo (a) pyrene (BaP), Chr (Chrysene), Fluoranthene (Fla), Pyr (Pyrene) and Phenanthrene (Phe). These six ratios in the wet and dry deposition of PAHs in winter (from November to April) and summer (from May to October) were calculated (see Supplementary Materials Table S6 and Table S7).

Based on the compiled data of the characteristic ratio of PAHs from various sources in domestic and foreign related studies (Supplementary Materials Table S8) and industrial sources in Shanghai (Supplementary materials Table S9), the source of PAHs in the wet and dry deposition in Shanghai was partitioned. The results showed that in winter, the PAHs in wet deposition and dry deposition of downtown Shanghai were primarily from the combustion of gasoline, diesel, and coal, and vehicles. The source of PAHs in the suburban area was relatively complicated, including the combustion of fossil fuel, coke oven, incinerators, and oil fired power stations. The QP sampling sites (Supplementary Materials Table S1) were affected by road dust and vehicles, while JD sampling sites (Supple-

mentary Materials Table S1) were greatly influenced by industrial pollution. From May to October, the combustion of fossil fuel was considered as the main source of PAHs in wet and dry deposition in downtown Shanghai. It was suggested that the combustion of gasoline and diesel were PAH sources in all the districts of Shanghai whereas vehicle pollution accounted for the PAHs in wet deposition in some of the sampling sites. While PAHs in dry deposition originated mainly from the combustion of fossil fuel, road dust and oil fired power station should also be considered as possible causes. In the past decades, the economic development and rapid rise in the population and expansion of the urban area of Shanghai led to the development of high speed transportation. The consumption of fossil fuel and vehicle exhaust emissions has become the major factor affecting the quality of the atmospheric environment in Shanghai. Furthermore, the industrial increase and population distribution have resulted in slow diffusion of atmospheric pollutants, rendering downtown Shanghai the most severely polluted area from PAHs.

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References

- Bae S Y, Yi S M, Kim Y P (2002). Temporal and spatial variations of the particle size distribution of PAHs and their dry deposition fluxes in Korea. *Atmos Environ*, 36(35): 5491–5500
- Barakat A O (2002). PAHs and petroleum markers in the atmospheric environment of Alexandria City, Egypt. *Water Air Soil Pollut*, 139(1–4): 289–310
- Birgül A, Tasdemir Y, Cindoruk S S (2011). Atmospheric wet and dry deposition of polycyclic aromatic hydrocarbons (PAHs) determined using a modified sampler. *Atmos Res*, 101(1–2): 341–353
- Bureau of Shanghai Municipal Statistics (2015). *Statistical Yearbook of Shanghai 2014*. Concise statistical yearbook of Shanghai, 2015
- Ciganek M, Adamec V, Janosek J, Machala M (2004). A combined chemical and bioassay analysis of traffic emitted polycyclic aromatic hydrocarbons. *Sci Total Environ*, 334–335: 141–148
- Daane L L, Harjono I, Zvlstra G J, Häggblom M M (2001). Isolation and characterization of polycyclic aromatic hydrocarbon-degrading bacteria associated with the rhizosphere of salt marsh plants. *Appl Environ Microbiol*, 67(6): 2683–2691
- Dallarosa J B, Teixeira E C, Pires M, Fachel J (2005). Study of the profile of polycyclic aromatic hydrocarbons in atmospheric particles (PM10) using multivariate methods. *Atmos Environ*, 39(35): 6587–6596
- Dickhut R M, Gustafson K E (1995). Atmospheric inputs of selected polycyclic aromatic hydrocarbons and polychlorinated biphenyls to southern Chesapeake Bay. *Mar Pollut Bull*, 30(6): 385–396
- Dunbar J C, Lin C I, Vergucht I, Wong J, Durant J L (2001). Estimating

- the contributions of mobile sources of PAH to urban air using real-time PAH monitoring. *Sci Total Environ*, 279(1–3): 1–19
- Fang G C, Chang K F, Lu C, Bai H (2004). Estimation of PAHs dry deposition and BaP toxic equivalency factors (TEFs) study at Urban, Industry Park and rural sampling sites in central Taiwan, Taichung. *Chemosphere*, 55(6): 787–796
- Guor C F, Cheng N C, Kuan F C (2008). Ambient air aerosols, total polycyclic aromatic hydrocarbons (PAHs) for day and night time in the traffic areas of Central Taiwan. *Toxicological & Environmental Chemistry*, 2008, 70(70): 15–27
- Ho K F, Lee S C (2002). Identification of atmospheric volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs) and carbonyl compounds in HongKong. *Sci Total Environ*, 289(1–3): 145–158
- Jiang Y, Hou X, Zhuang G, Li J, Wang Q, Zhang R, Lin Y (2009). The sources and seasonal variations of organic compounds in PM_{2.5} in Beijing and Shanghai. *J Atmos Chem*, 62(3): 175–192
- Khalili N R, Scheff P A, Holsen T M (1995). PAH source fingerprints for coke ovens, diesel and, gasoline engines, highway tunnels, and wood combustion emissions. *Atmos Environ*, 29(4): 533–542
- Li G, Zhou M, Chen C, Wang H, Wang Q, Lou S, Qiao L P, Tang X B, Li L, Huang H Y, Chen M H, Huang C, Zhang G F (2014). Characteristics of particulate matters and its chemical compositions during the dust episodes in Shanghai in spring, 2011. *Environ Sci*, 35(5): 1644–1653 (J)
- Li J, Liu X, Zhang G, Li X D (2010). Particle deposition fluxes of BDE-209, PAHs, DDTs, and chlordane in the Pearl River Delta, South China. *Sci Total Environ*, 408(17): 3664–3670
- Li X, Li P, Yan L, Chen J, Cheng T, Xu S (2011). Characterization of polycyclic aromatic hydrocarbons in fog–rain events. *J Environ Monit*, 13(11): 2988–2993
- Liang J, Ma G, Fang H, Chen L, Christie P (2011). Polycyclic aromatic hydrocarbon concentrations in urban soils representing different land use categories in Shanghai. *Environmental Earth Sciences*, 62(1): 33–42
- Lim M K C H, Ayoko G A, Morawska L (2005). Characterization of elemental and polycyclic aromatic hydrocarbon compositions of the urban air in Brisbane. *Atmos Environ*, 39(3): 463–476
- Liu Y, Chen L, Zhao J, Wei Y, Pan Z, Meng X Z, Huang Q, Li W (2010). Polycyclic aromatic hydrocarbons in the surface soil of Shanghai, China: concentrations, distribution and sources. *Org Geochem*, 41(4): 355–362
- Luo X J, She J C, Mai B X, Sheng G Y, Fu J M, Zeng E Y (2008). Distribution, source apportionment and transport of PAHs in sediments from the Pearl River Delta and the Northern South China Sea. *Arch Environ Contam Toxicol*, 55(1): 11–20
- McVeety B D, Hites R A (1988). Atmospheric deposition of polycyclic aromatic hydrocarbons to water surfaces: a mass balance approach. *Atmos Environ*, 22(3): 511–536
- Nadal M, Schuhmacher M, Domingo J L (2004). Levels of PAHs in soil and vegetation samples from Tarragona County, Spain. *Environ Pollut*, 132(1): 1–11
- Nielsen T (1996). Traffic contribution of polycyclic aromatic hydrocarbons in the center of a large city. *Atmos Environ*, 30(20): 3481–3490
- Odabasi M, Cetin E, Sofuoglu A (2006). Determination of octanol–air partition coefficients and supercooled liquid vapor pressures of PAHs as a function of temperature: application to gas–particle partitioning in an urban atmosphere. *Atmos Environ*, 40(34): 6615–6625
- Ollivon D, Blanchoud H, Motelay-Massei A, Garban B (2002). Atmospheric deposition of PAHs to an urban site, Pairs, France. *Atmos Environ*, 36(17): 2891–2900
- Ozaki N, Nitta K, Fukushima T (2006). Dispersion and dry and wet deposition of PAHs in an atmospheric environment. *Water Science & Technology A Journal of the International Association on Water Pollution Research*, 53(2): 215–24
- Park J S, Wade T L, Sweet S T (2002). Atmospheric deposition of PAHs, PCBs, and organochlorine pesticides to Corpus Christi Bay, Texas. *Atmos Environ*, 36(10): 1707–1720
- Ren N Q, Que M X, Li Y F, Liu Y, Wan X, Xu D, Sverko E, Ma J (2007). Polychlorinated biphenyls in Chinese surface soils. *Environ Sci Technol*, 41(11): 3871–3876
- Tasdemir Y, Holsen T M (2005). Measurement of particle phase dry deposition fluxes of polychlorinated biphenyls (PCBs) with a water surface sampler. *Atmos Environ*, 39(10): 1845–1854
- Wang X Y, Li Q B, Luo Y M, Ding Q, Xi L M, Ma J M, Li Y, Liu Y P, Cheng C L (2010). Characteristics and sources of atmospheric polycyclic aromatic hydrocarbons (PAHs) in Shanghai, China. *Environ Monit Assess*, 165(1–4): 295–305
- Wild S R, Jones K C (1995). Polynuclear aromatic hydrocarbons in United Kingdom Environment: a preliminary source inventory and budget. *Environ Pollut*, 88(1): 91–108
- Xu S, Liu W, Tao S (2006). Emission of polycyclic aromatic hydrocarbons in China. *Environ Sci Technol*, 40(3): 702–708
- Yunker M B, Macdonald R W, Vingarzan R, Mitchell R H, Goyette D, Sylvestre S (2002). PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Org Geochem*, 33(4): 489–515
- Zhang W S, Zhang C, Wan D, Yue D, Ye Y, Wang X (2008). Source diagnostics of polycyclic aromatic hydrocarbons in urban road runoff, dust, rain and canopy through fall. *Environ Pollut*, 153(3): 594–601