Spatial and Seasonal Variation of Polycyclic Aromatic Hydrocarbons (PAHs) Deposition Flux and Sources in Shanghai

Jian Wu
Shanghai Academy of Environmental Sciences

Chenyang Sha
Shanghai Academy of Environmental Sciences

Dayan Li
Shanghai Academy of Environmental Sciences

Cheng Shen
Shanghai Academy of Environmental Sciences

Hao Tang
Shanghai Academy of Environmental Sciences

Shenfa Huang (✉ saeshuangsf67@163.com)
Shanghai Academy of Environmental Sciences

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Abstract

Spatial and temporal variations of PAHs deposition flux and sources may significantly facilitate risk evaluations of super magacity in China. A study on polycyclic aromatic hydrocarbons of wet deposition and dry deposition in Shanghai was conducted from January to December, 2019. 17 sites were investigated located in four representative functional areas, covering iron and steel industry (BS), petrochemical industry (JS), central city (CC) and agricultural area (CM). The results showed that atmospheric PAHs level in shanghai was the lowest in autumn and the highest in winter. As industrial area, BS and JS demonstrated higher PAHs deposition fluxes than those in CC and CM sites. Triangle map indicated that the PAHs distribution in winter and spring samples were more homogeneous, suggesting possible common origins, whereas that of summer and autumn seemed to be more dispersed. Isomar ratio and positive matrix factorization model were employed to identify the potential sources of PAHs in specific functional areas. BS was dominated by a high percentage (46%) of coal combustion. In JS site, the petroleum volatilization source percentage was 47.6%. The highest biomass burning (55.3%) contributions were in CM. Vehicle emission (49.3%) was identified as the predominant source of PAHs in CC. This study highlighted that local emission sources have a greater influence on PAHs deposition to specific functional regions in Shanghai.

1. Introduction

The rapid growth of urbanization and industrialization has resulted in increasing changes to urban air quality (Boström et al. 2002). The health and quality of life of urban populations have seriously threatened by air pollution (Mastral et al. 2000; Chen and Liao 2006; Barth et al. 2007; Cachada et al. 2012; Bertrand et al. 2015). Some of the most prominent contaminants in the air are PAHs, which are a class of organic compounds with two or more than two benzene rings. As the ubiquitous environmental pollutants, PAHs have adverse effects on human health including immunotoxicity, genotoxicity, carcinogenicity, and reproductive effects (Chen et al. 2011; Kim et al. 2016). So 16 PAH compounds have been recommended as priority pollutants by the United States Environmental Protection Agency (USEPA 2003).

Sources of PAHs are complex and mostly come from human activities, such as petrochemical productions, vehicular exhaust, and incomplete combustion processes of petroleum and wood (Ravindra et al. 2008; Jia et al. 2017; Cetin et al. 2017). PAHs pollution emits to ambient air as particles and gases. Atmospheric PAHs are accumulated to land surfaces through dry and wet depositions, and influence water bodies via surface runoff (Shannigrahi and Fukushima 2005; Askin et al. 2011; Liu et al. 2013; Dong et al. 2006). There are few ways to measure the PAHs contaminations in the atmosphere, including the active and passive sampling techniques. The active collection detects the concentration of the pollution, and the passive measures the flux of the depositions (Esen et al. 2008; Garban et al. 2002; Gigliotti et al. 2005; Gocht et al. 2007; Schwarz et al. 2011). Passive collection means accumulation continuously in an open collector that would contain materials entering during wet and dry periods, consisting of wet and dry deposition, but excluding gas deposition. This method is important to assess
the impact of the long-term input of pollutants in to the region (Schifman and Boving 2015). Passive collectors in Germany quantified the bulk atmospheric PAHs deposition rates in rural and villages, ranging from 68.8 µg/m²/yr to 256.6 µg/m²/yr (Gocht et al. 2007). Wang (2011) used passive collectors to capture the atmospheric deposition of PAHs in Beijing-Tianjin region, total fluxes of PAHs were 11.81±4.61 µg/m²/yr.

Shanghai is one of the global financial centers as well as a large industrial city, and its air quality has been concerned for several years. In order to provide better environment for its citizens and to restore the existing environmental damage, a large number of heavily polluted enterprises had been relocated from central city to the remote areas. The functional regions division of Shanghai is becoming more and more obvious. Jinshan petrochemical industrial zone and Baoshan iron and steel industrial zone are considered as the two major core industrial clusters in the north and the south edges of Shanghai. The central city is suffered by typical heavy traffic, and the number of vehicles peak a historical high in Shanghai recently (Wang et al. 2015a; Wang et al. 2016). As an ecological friendly island, Chongming is mainly covered with wetland and farmland. Furthermore, deposition of PAHs in Shanghai does not only vary spatially, but also temporally. It is important to analysis the seasonal variation of PAHs in Shanghai, as the PAHs emission will change with the variation of residents’ activities and ambient weather. 2~3 times higher deposition rates and concentrations of particle associated PAH were observed in China, Europe and the eastern United States during the cold season, which was attributed to increased residential heating(Wang et al. 2015a). Therefore, this promoted us to deploy atmospheric bulk deposition samplers at specific functional areas across Shanghai at monthly basis. It is not only helping us to understand precisely the role of deposition in the transport of PAHs in urban system, but also identifying the pollutant sources in order to reduce them. Furthermore, deposition of PAHs in Shanghai does not only vary temporally, but also spatially.

Recently, several studies had been conducted on spatial variation of PAHs’ atmospheric deposition in Shanghai. For example, Wang (2016) examined atmospheric deposition of PAHs at urban and suburban sites in Shanghai, but only based on 2 sites, covering a small area of Shanghai. Feng (2017) investigated seven sampling sites along transect from the suburban to the city center of Shanghai and observed a spatial variation of atmospheric deposition with little discussion on tracing the specific PAHs emission sources. Liu (2017) investigated the spatial distribution of the atmospheric particulate PAHs in urban and rural areas in Shanghai, without the specific functional regions. Therefore, limited information is available about the impact of atmospheric deposition on PAHs contamination contributed by the influence of the most representative functional regions in Shanghai. Special goals in this study were: 1) to study the spatial and seasonal variation of dry and wet deposition of PAHs in Shanghai; 2) to identify the potential PAHs sources of atmospheric deposition of PAHs in four specific functional regions (central city, iron and steel industrial area, petrochemical industry area, and agriculture land) in Shanghai.

2. Materials And Methods
2.1 Study area and sampling

Shanghai is located on the east boundary of the Asian continent, its west is Jiangsu and Zhejiang Province, Hangzhou Bay is connecting to the south side, and its east is linking to the East China Sea. Shanghai has northern subtropical monsoon climate with four distinctive seasons, which is warm and humid. Atmospheric bulk deposition samplers were deployed from January to December 2019. As shown in Fig. 1, Baoshan Industrial area (BS), Jinshan Industrial area (JS), Central urban area (CC) and Chongming Island (CM) were selected as four sampling areas according to their different functions. Baoshan industrial area is located on the north edge of Shanghai, mainly conducting iron and steel smelting and metal processing. Jinshan industrial zone is located in the south of Shanghai City, mainly with petrochemical industry, and is one of the largest petrochemical industrial zones in China. The central city is located in the center of Shanghai. It is mainly the commercial area, densely populated and well developed in traffic. Chongming Island is next to the mouth of the Yangtze River to the sea, mainly used for agriculture (Fig. 1).

Atmospheric bulk deposition was determined with a time-integrating passive sampler which was 30 cm high; 15 cm inner-diameter cylindrical dust collectors collected the non-separated dry and wet deposition samples on the 10 meters high roof. The cylindrical dust collector fixed and supported by a 1.5 meters high three-foot stainless steel.

2.2 Sampling Analysis

In the laboratory, the samples were filtered with filter membrane GF/F (Whatman, USA), and the filter membrane was pre-baked in the muffle furnace for 4 hours (<450°C). After filtration, the dried filter membrane by Freezer Dryer (CHRIST ALPHA 1-4/LD plus Germany) was weighed, the membrane, anhydrous sodium sulfate (Na$_2$SO$_4$) and a small amount of copper powder in the cellulose thimble were placed, and Soxhlet extraction was conducted (Extractant: 120mL dichloromethane and acetone mixture, the volume ratio of 1:1,18h). Reflux times controlled in 4~5 /h. The extraction was rotated, concentrated and purified through silica gel (activated for 12h at 130°C)/ aluminum oxide/ Na$_2$SO$_4$ (burned by muffle furnace burning at 450°C for 4h) Composite Chromatography Column. Dichloromethane and hexane (volume ratio 3:7) were used for eluting and collecting the aromatic hydrocarbons. The eluent was rotated and concentrated to 1mL, transferred to the GC sample bottle, stored at -4°C to be measured.

The filtered filtrate was rapidly solid phase extracted (SPE) by C-18 extraction column (Supelco, USA). The SPE column (HC-18SPE) was pre-activated and balanced by 5mL dichloromethane, methanol and DI water. The filtrates’ PAHs contents were adsorbed by SPE column; the sample injection rate was controlled at 5 mL/min. 15mL dichloromethane and hexane mixed solvent (volume ratio of 1:3) eluting though SPE column, the collected eluent was dried by aNa$_2$SO$_4$, rotary evaporated to 2mL, using 15mL n-hexane to substitute and concentrate the eluent to 1mL, transferred to the GC sample bottle and stored at -4°C to be measured.
A total of 15 kinds of PAHs were assessed by gas chromatography-mass spectrometry (GC-MS, Agilent 7890A/5975C). The standard of chromatographic column was DB5-MS (30m*0.25mm*0.25µm). The column temperature program was as follows: column initial temperature was 80°C, kept for 1 min, the temperature was increased to 235°C with the speed of 10°C/min, then increased by 4°C/min until the temperature reached the 300°C for 4 minutes; The carrier gas was high purified He (flow rate 1mL/min), mass spectrometry ionization mode was conducted: EI source, ion source temperature was 270°C, the voltage was 70eV and the current was 350µA, the scanning range was 50~500m/z, the scanning frequency was 1.5scan/s.

2.3 Quality assurance and quality control

In this study, the qualities were controlled by procedure blanks and solvent blanks. 2 blank samples were set with each 10 normal samples. The average values of the blanks were used to adjust the PAHs concentrations. The triple replication was applied in this study and the relative standard deviation for triplicated samples was less than 20%. Furthermore, 5 deuterated PAHs (crysene-d12, perylene-d12, phenanthrene-d10, acenaphthene-d10 and naphthalene-d8) surrogates were used as the internal standard; the content was calculated by internal standard method. Among 16 atmospheric deposited PAHs, the recovery of the dissolved phase and particle phase contents was 78.3%~102.4% and 83.4%~108.6%. The target pollutants were not detected in all blank samples.

2.4 Data analysis by the positive matrix factorization (PMF) method

The EPA PMF ver.5.0 was applied in our study. The input data were based on 15 species of PAHs and 12 months’ results. The random seed mode with 100 of the numbers of random starting point was selected. The number of factors from 4 to 7 was examined. The sum of estimated PAHs concentrations from the PMF estimation was compared with that of observed PAHs concentrations from our field measurement. 4 factors that gave the best correlation were selected for further discussion in this study. No result obtained from rotation was adopted since the strength of rotation was unknown to be pulled to estimate the uncertainty due to a rotational ambiguity.

3. Result And Discussion

3.1 Seasonal variation of PAHs

The climate of Shanghai is broadly classified into four seasons, spring (March-May), summer (June-August), autumn (September-November) and winter (December-February). \( \sum 15 \) PAHs exerted similar seasonal distributions among the four sites (BS, JS, CC, and CM). On seasonal average, \( \sum 15 \) PAHs concentrations were the highest in winter (3116.91 ng/ (m\(^2\)-d)), followed by spring (2712.52 ng/ (m\(^2\)-d)); then in summer (1957.12 ng/ (m\(^2\)-d)), and the lowest in autumn (1633.92 ng/ (m\(^2\)-d)) (Fig. 2). This was consistent with those reported in previous studies, which might be affected by both source emissions and meteorological conditions (Wang et al. 2014; Wang et al. 2015b).
In winter, both meteorological conditions and increased energy demand affect PAHs concentrations in Shanghai. PAHs from inner-city vehicle exhaust and industrial activities enter the atmospheric environment. The combustion in the car engine is incomplete in the cold days, and the PAHs concentrations in the exhaust particular matter increases accordingly. Moreover, the north China is centralized heated in winter, causing a large number of organic pollutants emitted to the atmospheric environment. Under the effect of cold air from the north to the south, these pollutants are carried by winter monsoon wind from the northern to the eastern coastal areas, increasing air pollution in east China. In our study, the concentrations of PM2.5 in winter were about 1.9, 1.9, 1.8, and 1.9 times higher than that in summer at BS, JS, CC, and CM sites respectively. Wang et al. (Wang et al. 2016) also speculated that long-range transport from western regions contributed to PM2.5, particularly to PAHs in Shanghai. Cold northwest winds from Siberia in winter can cause nighttime temperatures to drop below freezing, which certainly facilitates condensation and deposition of atmospheric PAHs. In our study, PAHs concentration in the industrial areas were the highest in January, such as Baoshan industry area (11792.59 ng/(m²·d)) and petrochemical Jinshan industry area (20167.56 ng/(m²·d)). The PAHs concentration in central city had some fluctuations through the year, which had peaked (4871.17 ng/(m²·d)) in April. The PAHs concentration in Chongming was mainly concentrated between December to April, the highest value was found in April (2546.42 ng/(m²·d)) (Fig. 2). This might be mainly related to the different source emission contributes at different sites (Liu et al. 2017), which would be further discussed below.

Distinct from winter/spring, summer/autumn period was clearly characterized by higher temperature, relative humidity, low atmospheric pressure and air pollution control as well (Fig. 2). The influence of south easterly wind affected by the Western North Pacific Subtropical High brings clean marine air to Shanghai. Moreover, this study had the lowest PAHs concentration in autumn, potentially reflecting recent controls on air pollution in Shanghai (data from China Environmental Informationization). The PM$_{2.5}$ was 27, 29, 28 and 24 respectively for BS, JS, CC, and CM, which were the lowest among all the seasons (Fig. 2). Atmospheric PAHs concentrations were highly related to the seasonal variations of particulate matter concentrations. Significant positive correlations (p<0.05) were observed between PAHs and PM$_{2.5}$ concentration at Baoshan Site and Chongming Site.

### 3.2 Spatial variation of PAHs

Due to the likely distinct characteristics of PAHs observed at different sites, the spatial distribution of PAHs in Shanghai need to be discussed. Average PAHs deposition flux and standard deviation of four sampling sites were calculated from the data. The average PAHs in all sampling sites was 2562.92 ± 3287.93 ng/ (m²·d). The total PAHs deposition flux in BS, JS, CC, and CM sampling sites were 3749.78 ± 4084.19 ng/(m²·d), 3180.15 ± 3624.87 ng/(m²·d), 1909.16 ± 1059.22 ng/(m²·d) and 1412.60 ± 605.40 ng/(m²·d), respectively (Fig. 3). Contrasted with the foreign cities, PAHs atmospheric deposition fluxes were significantly higher in the central and rural areas of Shanghai than those in other cities. The PAHs atmospheric deposition fluxes in city and suburb of Paris were 151-1294 ng/(m²·d) and 50 ng/(m²·d), respectively; and PAHs fluxes in city and rural areas of Korea were 810 and 560 ng/(m²·d), respectively.
respectively (Garban et al. 2002; Moon et al. 2004). Atmospheric PAHs concentration in industrial zone was approaching to that in Turkey (5792 ng/(m$^2$·d) for winter, and 2650 ng/(m$^2$·d) for summer), and slightly higher than that in Italy (1262 ng/(m$^2$·d)) (Bozlaker et al. 2008; Amodio et al. 2014). Comparing Shanghai with Chinese southern cities, urban PAHs deposition fluxes in Shanghai were higher than that in Hong Kong (260 ng/(m$^2$·d)) and Guangzhou (1200 ng/(m$^2$·d)) (Liu et al. 2013). Furthermore, the PAHs deposition fluxes in urban and suburb of Shanghai were lower than those in Northern cities, such as Beijing (8280 ng/(m$^2$·d) and 3910 ng/(m$^2$·d)), Tianjin (5235 ng/(m$^2$·d) and 218 ng/(m$^2$·d)) (Wang et al. 2011; Wu et al. 2005). Comparing with previous studies, Shanghai PAHs atmospheric deposition fluxes were decreasing these years. In 2012, PAHs atmospheric deposition fluxes in industrial zone, urban and suburb of Shanghai were 7380 ng/(m$^2$·d), 4570 ng/(m$^2$·d) and 1510 ng/(m$^2$·d), which had been considerably contributed to Shanghai air pollution control since 2016 (Feng et al. 2017).

Contrasting four sampling sites, high PAHs fluxes in BS site were mainly produced by industry activities, such as iron casting, steel smelting and metal processing. In our study, three PAHs (BaA, Chr and Bap) in BS were respectively 3.3, 1.8 and 1.3 times as those in CM (Fig. 4). Amodio et al (Amodio et al. 2014) monitored the deposition of PAHs in Tarano (Italy) and found that BaP, BaA, and BkF near the iron and steel works were much greater than that of the other zone in the city. Total PAHs concentration in JS was lower than that in BS. The petrochemical and natural gas industry are the key development industry. Based on those industries, new chemical materials and fine chemical products are synthetized and produced. Phe was the most dominate PAH in JS site (Fig. 4). Esen et al found that fluoranthene was the most dominated PAH compound followed by phenanthrene, which accounted more than 50% of the whole value in a petrochemical industry site. The PAHs of CC was mainly influenced by intense automobile traffic. On the other hand, observed value of PAH was the lowest in CM site (agricultural site). Azimi et al (Azimi et al. 2005) found that the highest values of PAHs were observed in Paris center area, reflecting the urban center as a source of pollutants, with a decline in many atmospheric deposits when moving away from urban areas. These results above indicated that PAHs concentration was strongly linked to the land use of the site.

### 3.3 Proportion composition of PAHs

Triangular maps were made to describe the proportion of three types of PAHs (3 rings, 4-5 rings and 6 rings PAHs) detected of different functional areas in four seasons. In winter, the dominant PAHs were 4-5 rings PAHs. The PAHs’ proportion contribution in spring was very similar to that in winter. The 4-5 rings PAHs were still the dominant component (0.5 ~ 0.9), but the 3-rings PAHs proportion was slightly increased. In summer, the distribution of PAHs proportion was dispersed. The proportion contribution of 4-5 rings PAHs was widened (0.25 ~ 0.75). Then, in autumn, the 4-5 rings PAHs proportions decreased sharply, except part of Baoshan sampling sites, 4-5 rings PAHs proportions detected in most sampling sites were smaller than 0.5. 3 rings PAHs took the dominant position (Fig. 5). The PAHs distribution in winter and spring samples were more homogeneous, suggesting possible common origins, whereas that of summer and autumn seemed to be more variable, disperse and heterogeneous. Based on the observed
pattern, different seasons did not make detectable influence on 6 ring PAHs as the proportion of 6 ring PAHs was very steady in each season, accounting for less than 18% in all samples. On the contrary, different seasons had more influence on the proportion of 3 and 4-5 rings PAHs. This might be attributed to an increasing contribution in consumption of coal in winter dominating the PAHs source in dust fall during heating season; the samples collected during no heating season from city center, industrial area, and rural area had different sources.

3.4 PAHs source analysis and source contribution assessment

3.4.1 PAHs source identification by isomer ratios

This study utilized the isomer ratios to analysis the source of the PAHs pollutions, which distinguished the source of PAHs by plotting ratios of Flu/(Flu+Pyr) and InP/(InP+BghiP). 0.2<InP/(InP+BghiP)<0.5 represents the petroleum combustion, and InP/(InP+BghiP)>0.5 indicates coal, wood and other biomass combustion sourced PAHs(Yunker et al. 1999). Flu/(Flu+Pyr) ratio can distinguish among biomass combustion, petroleum combustion and petroleum volatilization (Yunker et al. 1999). Depending on the distribution of the data, the source of the PAHs in the specific season and site could have a single or a mixed source.

For winter/spring, the distribution pattern of Flu/(Flu+Pyr) indicated that the coal & biomass combustion dominated the winter/spring PAHs pollution. Combining the InP/(InP+BghiP) ratio, majority PAHs sampling sites’ pollution was sourced from both petroleum combustion and coal & biomass combustion, while the minority was mostly sourced from coal & biomass combustion (Fig. 6). In winter and spring, there was no clear spatial variance observed in PAHs sources. Every sites shared the similar source, which was conform to the pattern observed in triangular composition analysis, without clear difference among the 3, 4-5 and 6 ring PAHs compositions in each sampling site. Homologous and non-regional difference PAHs sources were detected in winter. Accordingly, only in winter it was conjectured that there were few sources of strong air pollutions that accumulates in Shanghai, covering the spatial difference between sampling sites. This external air pollution source might be transported from the northern, central China and Yellow Sea, as the air pollution concentrations were rapidly increased when Shanghai had west or north wind (Wang et al. 2016). In addition, as Shanghai had poor atmospheric diffusion ability in winter, the external air pollution had such considerable impact on domestic PAHs compositions.

In summer and autumn, only CM had single pollution source, which was biomass & coal combustion. PAHs sources in CM displayed a clear seasonal variation. During the harvest seasons, burning organic matter would increase the atmospheric concentration of PAHs. Then, in BS, majority sampling points’ pollutions were dominantly sourced from petroleum combustion and the rest points had relatively pure biomass & coal combustion source. It was found in BS that the biomass & coal combustion source predominated in winter/spring and transferred to petroleum combustion dominant in summer/autumn. The dominant source in JS and CC shared similar pattern as BS.
3.4.2 Positive matrix factorization

To further elucidate contributions of specific combustion sources to a site, a PMF analysis was carried out. PMF was strongly recommended for use, due to it is a powerful multivariate technique that constraints the solution to be non-negative and considers the uncertainty of the observed data (Paatero et al. 1994; Pant et al. 2012). The factor profiles of PAHs from the PMF model are shown in Fig. (7). Each profile obtained by PMF in this study was compared with several profiles reported by the previous works. According to previous studies, vehicular emission (e.g., gasoline and diesel vehicle), coal combustion, biomass burning (e.g., crop straw), industrial process (e.g., iron-steel plant, coke oven emission, and petrochemical productions) are the major sources of PAHs in urban atmosphere (Wang et al. 2015a; Harrison et al. 1996; Larsen et al. 2003). In our study, PMF analyses were conducted to evaluate the major sources of atmospheric PAHs in Shanghai. Four distinct sources of PAHs were identified as 1) coal combustion, 2) petroleum volatilization, 3) biomass burning, and 4) petroleum volatilization.

The PAHs profiles among the four factors for each site were similar and could be grouped into individual emission signature. Factor 1 was highly loaded with Ant, Phe, BkF, Flu, this source profile of PAHs has been reported in the literature to be mainly from biomass burning (Moon et al. 2002; Tian et al. 2011). Factor 2 was heavily weighted by BkF, DBA, BaA, and the high loading of 5-6 ring PAHs were used to indicate vehicle emission (Pant et al. 2012; Guarieiro et al. 2014). Factor 3 was predominated weighted by Chr, InP, BghiP, BbF, Pyr, BaP, interpreting as the tracers of coal burning (Khalili et al. 1995; Mu et al. 2013; Yang et al. 1998). Factor 4 was almost exclusively loaded with Acy, Ace, Fl, and the LMW PAHs as typical markers for volatilization of crude oil and petroleum products (Wang et al. 2016; Liu et al. 2015).

According to the PMF analysis, Baoshan site (BS) was dominated by a high percentage of coal combustion (46.6%), followed by petroleum volatilization (34.9%) (Fig. 8). This finding correlated with the site’s PAH isomer ratios (Fig. 6). According to Shanghai Urban Energy Internet White Paper, in the primary energy consumption structure of Shanghai in 2019, fossil energy accounted for about 82%, of which coal and oil accounted for about 74%. Baoshan Iron and Steel Industrial Zone is one of the largest iron and steel smelting industrial zones in the whole country. In the production process, fossil fuels occupy a dominant position in energy consumption. Baoshan sites (BS) are adjacent to Baoshan Iron and Steel Industrial Zone (<1 km), which is located in the downwind direction of the southeast wind. Moreover, large-scale coal combustion for household heating is technically not allowed in Shanghai. And relatively low contributions of coal combustion were found at central city (CC) and rural area (CM) sites in our study. Liu et al (Wang et al. 2015b) confirmed that over 97% of the total coal was consumed by industrial activities as well. It was also showed that the iron and steel industry was likely responsible for the high level of PAHs with five and six rings in BS site in our study. In our study, BS contributed more BaP in the ambient air to that of the other areas in Shanghai (Fig. 4). Wang et al. (Wang et al. 2010) the concentration of BaP in the air is very likely related to the iron and steel industry emissions. Thus, PAHs of BS might mostly transport from Baoshan Iron and Steel Industrial Zone.
In Jinshan petrochemical industry site (JS), the PMF petroleum volatilization source percentage was 47.6% (Fig. 8). This strong contribution of petroleum volatilization might be linked to the cracking and refining process of petrochemical industry that were being operated throughout the study less than 1 km from the sampling location. PAH isomer source ratios also indicated that the main PAH source was petroleum combustion in our study (Fig. 6). In our study, the petroleum volatilization had high loadings of low molecular weight compounds, which was also consistent with previous research that deposition values of PAH compounds in a petrochemical industry site of Turkey (Esen et al. 2008). PAHs emissions by petrochemical plants were mainly composed of two rings and three rings, whereas its volatility was generally strong (Park et al. 2001; Gariazzo et al. 2005; Nadal et al. 2011). Bozlaker et al (Bozlaker et al. 2008) studied 50 points of individual PAHs from an industrial region in Turkey, and distinguished steel plant, petroleum refinery and the petrochemical plant as the major Σ15PAHs sources in the area. Our results were consistent with the above views.

According to PMF model, vehicle emission (the sum of gasoline and diesel engine emission) was identified as the predominant source of PAHs in central city in our study (49.3%). As a world megacity, Shanghai has been experiencing a rapid increase in vehicles, especially those for private use. According to Shanghai Municipal Transportation Commission (http://www.jt.sh.cn/), Shanghai had 2.89×10^6 private vehicles in 2015, surely a significant use of gasoline by any measure. Moreover, diesel is commonly used instead of gasoline to power the ferry, cargo ships and trucks as well (Wang et al. 2015b). Wang et al. (Wang et al. 2014) also confirmed that vehicle emission sources accounted for 46.5% of PAHs source of PAHs in urban area. Chen et al. (Chen et al. 2011) considered that vehicles and coal consumption were the two important PAH emissions sources contributed about one third (suburban area) to one half (urban area) of PAH mass to Shanghai atmosphere. Thus, vehicles emitted in Shanghai central city area should be controlled concerning atmospheric PAHs.

The highest biomass burning contributions were in Chongming Island rural area (CM), which was 55.2% (Fig. 8). In Chongming ecological island, less industrial activity and traffic pressure, probably resulting in low deposition rates of PAHs (Fig. 3). However, still some agricultural refuse, such as straws, stalks, and dead wood, are mostly used for cooking for the farmer in rural area. They are usually burned in primitive stoves without forced blasting, emitting ample organic pollutants, including PAHs. Moreover, the higher biomass burning contributions of Shanghai might also be due to wintertime residential biomass burning for heating as well (Wang et al. 2014). This finding was consistent with the study by Liu et al. (Wang et al. 2015b) that biomass burning was a predominant source in Chongming area of Shanghai. Furthermore, compared with northern China which mainly depends on residential coal combustion in rural areas (Wang et al. 2016), the different in household energy consumption could be a potential reason between Northern and Southern China for this observation as well.

4. Conclusions

Particulate PAHs were simultaneously collected and measured at 17 sites in four different functional areas in Shanghai. Spatial and temporal variation of composition profiles and sources of PAHs were
investigated. According to seasonal meteorological variations, pollutant emission sources, physical and chemical properties of PAHs, the sequence of Shanghai atmospheric $\sum_{n=1}^{15}$PAHs concentration value were in winter > spring > summer > autumn. And from spatial distribution, we found an increasing contribution in consumption of coal in winter. City center, industrial area, and rural area had different sources during no heating season. Two source identification and attribution methods were used as tools in assessing PAH sources. Four major sources of particulate PAHs (biomass combustion, petroleum volatilization, coal combustion and vehicle emission) had been determined. The PMF result indicated that local emission sources had a greater influence on PAH deposition to specific functional regions in Shanghai. Since urban functional regions changed with the rapid urbanization and industrialization of the city, long-term monitoring of atmospheric PAHs should be considered and investigated.

Declarations

Ethics approval and consent to participate: not applicable

Consent for publication: not applicable

Availability of data and materials: All data generated or analysed during this study are included in this published article

Competing interests: not applicable

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Figures
Figure 1

Map of the 17 sampling sites in 4 representative functional areas in Shanghai
Figure 2
Temporal variation of the PAHs deposition flux of four functional areas in Shanghai
Figure 3

The contents of PAHs in 4 functional areas

The box plots show the distribution of PAH deposition flux in ng/m²-d for JS, BS, CC, and CM. The whiskers indicate the range of values, the box shows the interquartile range, and the median is represented by the line within the box. The individual data points are also shown, with outliers indicated by dots outside the whiskers.

The bar graph provides a detailed breakdown of PAH deposition flux for each compound (Acy, Ace, Fl, Phe, Ant, Flu, Pyr, BaA, Chr, BbF, BkF, BaP, DBA, InP, BghiP) across the same functional areas. Each bar represents the average deposition flux for that compound and area.
Figure 4

Individual PAH deposition flux of 4 functional areas in Shanghai

Figure 5

Proportion composition of 3,4-5 and 6-ring PAHs of 4 functional areas under four seasons
Figure 6

PAHs isomer ratio Flu/(Flu+Pyr) vs. InP/(InP+BghiP) cross plot. White symbols represent the observation (n=4 sites*3 replications=12) in winter/spring, and the black symbols indicate the samples (n=12) in summer/autumn.
Figure 7

4-fator loadings of PAHs by PMF analysis in Shanghai
Figure 8

Average source contributions to PAHs at 4 functional areas