SOURCE APPORTIONMENT AND TOXIC EVALUATION OF PARTICLE-BOUND POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) IN $PM_{1.1}$ OF BAOSHAN INDUSTRIAL AREA, SHANGHAI

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ABSTRACT

Ambient particles with five size-stages ($PM_{1.1}$, $PM_{1.1–2.0}$, $PM_{2.0–3.3}$, $PM_{3.3–7.0}$, coarse particles (>7.0μm) in aerodynamic diameter) were collected in the Baoshan industrial area of Shanghai (China) during spring and early autumn, 2017. Thirteen species of polycyclic aromatic hydrocarbon (PAH) compounds were measured by gas chromatography mass spectrometry (GC-MS) to measure size distribution characteristics, possible source apportionment and health risk assessment. Average total PAHs (TPAHs) in total suspended particles (TSP) were 4.65 (1.71–12.1) ng/m^3 in spring and 3.85 (2.07–5.75) ng/m^3 in early autumn and they mainly massed in $PM_{1.1}$ at each sampling period, especially in early autumn periods (about 57.0%–79.0%). Combustion-derived PAHs (COMPAHs), carcinogenic PAHs (CANPAHs) were also main associated in fine particles, such as $PM_{1.1}$. Average lifetime lung cancer risk (LLCR) of PAH exposure by inhalation in $PM_{2.0}$ were under 1×10^{-6} to indicate no carcinogenic risk but LLCR from $PM_{1.1}$ in early autumn were higher than that in spring. Carcinogenic equivalent (BaP-TEQ), mutagenic equivalent (BaP-MEQ) and potency equivalent (BaP-PEQ) analysis showed that the toxic PAHs belonged to high molecular weight (HMW) PAHs, especially Benzo[a]pyrene(BaP). Diagnostic ratios of (BaA)/(BaA+Chy) under 0.50 and IndP/(IndP+BghiP) value (about 0.20–0.50) in $PM_{1.1}$ indicated that diesel missions and petroleum combustion might be key PAHs sources. Principal component analysis (PCA) pronounced that stationary sources and diesel emission are the main sources, and higher and BaP showed the great effects from developed steel industry group at local industrial area. Air masses backward trajectories also showed the main local industry efforts and some long-distance transport effects. In short, compared with $PM_{1.1–2.0}$, COMPAHs and CANPAHs could be considered that they were easier to gather in $PM_{1.1}$, especially in early summer periods.

Keywords: particle-bound PAHs, $PM_{1.1}$, health risk, possible sources, steel industry, Shanghai.

1 INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) as extensive organic contaminants which comprised of two or more benzene rings were primarily generated from the combustion of biomass and fossil fuels and the pyrosynthesis of species organic materials [1]–[3]. Due to ambient temperature, nature of aerosol, and species of PAHs, PAHs in ambient exist either or in the vapor phase or absorb into ambient particles and it is reported that the species of water-soluble inorganic ions in ambient particles could increase the solubility of toxic organic compounds, such as PAHs by acting as surface-active agents [4]–[6]. Most of the heavier PAHs presence in the particle-phase in the atmosphere because of their low vapor pressure and absorbed in on the fine inhalable particles and the 5–6 rings PAHs were usually associated with $PM_{2.0}$ [4], [5], [7], [8]. PAHs were reported as one of the first atmospheric pollutants which designated as suspected carcinogen and PAHs are highly lipid-soluble and rapidly distributed in a wide variety of tissues with a marked tendency for location in body fat, the most significant health effect to be expected from inhalation exposure to PAHs is an excess risk of lung cancer to all living organisms which has reported that about 1.6% of lung

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cancer morbidity might be got the effects by inhalation exposure to PAHs in atmosphere of the urban area in China [3], [9], [10].

Shanghai as a typical metropolis located on the eastern coast in China is the commercial and financial center with a population of more than 24 million in 2014 [11], [12]. Shanghai is also with developed industrial and transportation hub in China which always suffers with heavy human-induced impacts and drastic increases of built-up areas. Baoshan area is the main industrial one with the developed iron and steel industries [13]–[15]. PAHs in Shanghai are considered be from various sources and expected to continue display by spatiotemporal differences to raise the potential impacts on the environment and human health [8], [13]. In this article, the main objective is as follows: ambient particle-bound PAHs with five size-range in Baoshan zone of Shanghai was collected in spring and early autumn periods during 2017. Thirteen species of PAHs as the typical organic contents were measured by GC-MS to measure the chemical characteristics, toxic evaluation and possible sources. And diagnostic ratio methods and air masses trajectories also were selected to evaluate the possible sources.

2 MATERIALS AND METHODS

2.1 Ambient particle sample collection in Shanghai sampling site

Baoshan sampling sites as shown in Fig. 1 were located in Shanghai University (Baoshan campus), Shanghai. They are near to the residential zone and with several main traffic roads. Steel Group is located about 15 km northeast of these sampling sites and there were also plenty of industrial plants near to campus. The spring sampling site (N 31.32°, E 121.40°) and the early autumn sampling site (N 31.32°, E 121.33°) were very near. The spring sampling phase was from 21 March to 11 April, 2017 and the early autumn sampling phase was from 14 September to 4 October, 2017. An Andersen high volume air sampler (AHV-1000R, Shibata Co., Tokyo, Japan) with 566 L/min flow rate was to collect the ambient particle samples with five size-segregated (PM$_{1.1}$, PM$_{1.1–2.0}$, PM$_{2.0–3.3}$, PM$_{3.3–7.0}$, coarse particles (>7.0 µm) in aerodynamic diameter). Each sampling case was last to 48 hours in principle. Meteorological factors were gathered from Tianqihoubao (http://www.tianqihoubao.com/) and air quality factors were gathered from Shanghai Environmental Monitoring Center.

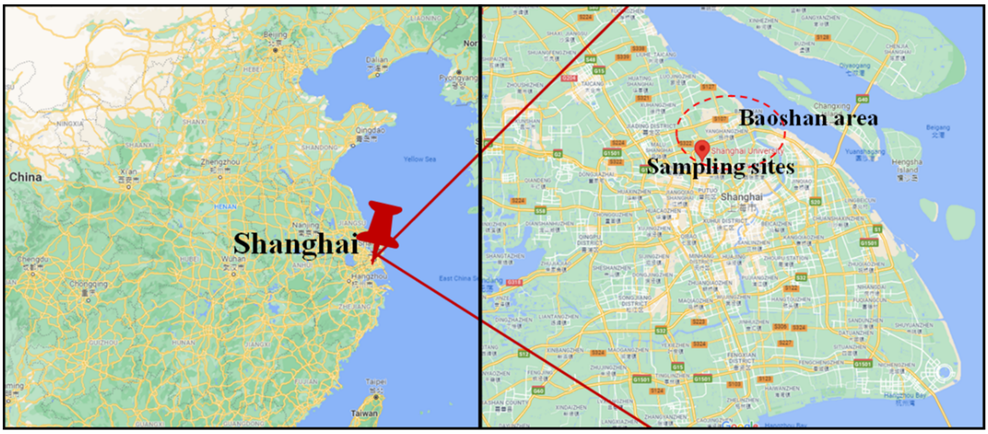

Figure 1: Distribution of sampling sites in Shanghai, China.

2.2 Analysis of particle-bound PAHs by the gas chromatography mass spectrometry (GC/MS) and statistical analysis

The PAHs organic extraction method and the GC/MS analysis system were mainly referred from the previous study [8]. The standard chemicals of 16 species PAHs classified by United States Environmental Protection Agency (USEPA) were obtained from Sigma-Aldrich. The extract sample solution was enriched to 0.1 ml and analysed by GC-MS (Model Agilent 5973N, Agilent Technologies. Inc., USA). All the samplers were determined by three times and then made the suitable statistical analysis for the data processing by Microsoft Excel 2016. These particle-bound PAHs are: Dibenz[a,h]anthracene (DB[a,h]A), Benzo[a]pyrene (BaP), Benzo[a]anthracene (BaA), Benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene (BkF), Indeno[1,2,3-c,d]pyrene (IcdP), Anthracene (ANT), Benzo[g,h,i]perylene (BghiP), Chrysene (CHR), Fluoranthene (FLA), Fluorene (FL), Pyrene (PYR), Phenanthrene (PHE), separately.

2.3 Carcinogenic risk and mutagenicity for particle-bound PAHs

Toxic equivalency factors (TEF) based on Benzo[a]pyrene (BaP) were chosen to obtain the assessment of the potential risk of exposure to a mixture PAHs and these methods also included the carcinogenic equivalency factors and the individual mutagenicity [8], [16], [17]. The carcinogenic equivalent (BaP-TEQ), potency equivalent (BaP-PEQ) and mutagenic equivalent (BaP-MEQ) for total PAHs were calculated to estimate human health risk with the respiratory system. BaPeq (TEQ), BaPeq (PEQ) and BaPeq (MEQ) from $PM_{1.1}$ and $PM_{1.1–2.0}$ samples were calculated by the published article [18].

3 RESULTS AND DISCUSSIONS

3.1 Size distribution characteristics of total and separate particle-bound PAHs patterns

Due to Nap, Ace and Ant as the main volatile PAHs [22], the other 13 species PAHs were considered as particle-bound PAHs research objective to analyse the size distribution and characterizations. Fig. 2 showed that total PAHs in ambient particles at each sampling event. The average TPAHs in TSP was 4.65 ng/m^3 (1.71–12.1 ng/m^3) in spring and 3.85 ng/m^3 (2.07–5.75 ng/m^3) in early autumn, respectively. The largest TPAHs occurred on 25–26 March (12.1 ng/m^3) and 14–16 September (5.75 ng/m^3), the lowest one occurred on 8–9 April and 3–4 October, about 47.9% (35.4%–56.2%) TPAHs in spring were mainly measured in $PM_{1.1}$, about 23.3% (20.0%–28.8%) were in $PM_{1.1–2.0}$. In early autumn, about 66.3% (57.0%–5.8%) TPAHs were in $PM_{1.1}$, 8.94% (6.75%–12.5%) were in $PM_{1.1–2.0}$. Also, TPAHs in TSP have a very strong correlation with these in $PM_{1.1}$ ($r = 0.99$), $PM_{1.1–2.0}$ ($r = 0.97$) of spring and $PM_{1.1}$ ($r = 0.95$), $PM_{1.1–2.0}$ ($r = 0.87$) of early autumn. It could be indicated that TPAHs in $PM_{1.1}$ played an important role to PAHs in ambient particles. Agudelo-Castañeda et al. studied 16 PAHs in $PM_{1.0}$ of Canoas in Brazil were 1.32 ng/m^3 in summer and 2.02 ng/m^3 in winter [18]. He et al. studied about 16 PAHs in $PM_{2.1}$ of Nanjing were about 58.2 ng/m^3 in 2010 with those PAHs in spring higher than those in summer [23]. Wang et al. also survived about 37 species PAHs of Shanghai in summer of 2015 were on average of 9.41 ng/m^3 in TSP and 4.97 ng/m^3 in $PM_{1.1}$ [8]. Ren et al. also measured 16 species of PAHs in Xi'an and Guangzhou of China in winter and summer of 2013, it was said that they were main in $PM_{1.1}$ and that in winter was higher than that in summer [24]. Compared with those PAHs from the reported articles, PAHs in this article were also dominant in $PM_{1.1}$ which seems very consistent with those reported. And all of these were showed the analogous distribution trend which PAHs were mainly in $PM_{1.1}$ and PAHs in summer were shown the relatively light concentrations than these in other seasons.

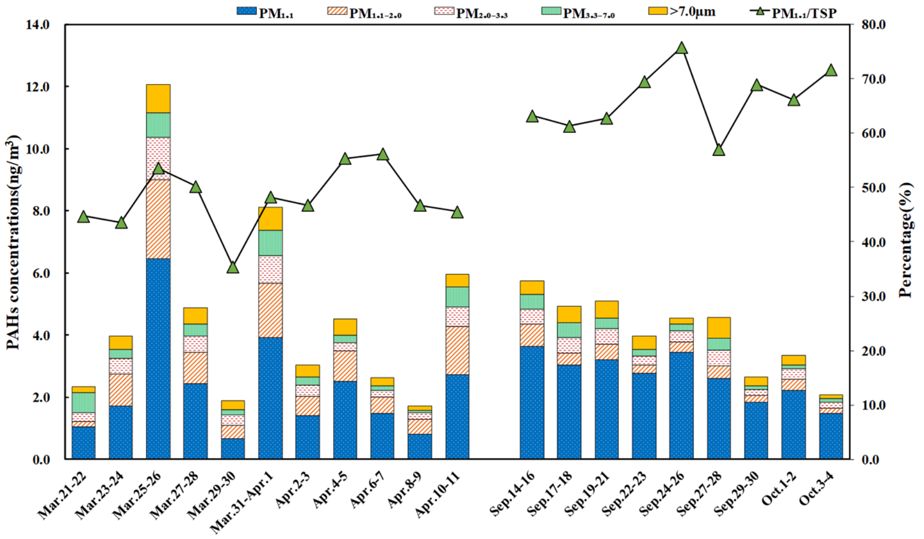

Figure 2: Size distribution of 13 PAHs in each sampling case during both spring and early autumn sampling periods.

3.2 Characteristics of total and separate PAHs patterns in $PM_{1.1}$

According to the molecular weight, PAHs could be divided into three groups, Flu, Phe and Ant with 2- and 3-ring PAHs as low molecular weight (LMW) PAHs, FLN, Pyr, Chy, BaA with 4-ring PAHs as middle molecular weight (MMW) PAHs, BbF, BkF, BaP, IndP, DB[a,h]A and BghiP which with 5- and 6-ring PAHs as high molecular weight (HMW) PAHs, separately [8], [19], [25]. As shown in Fig. 3, LMW PAHs groups, there were about 25.1% in $PM_{1.1}$, 18.9% in $PM_{1.1-2.0}$ in spring, and about 46.9% in $PM_{1.1}$, 11.9% in $PM_{1.1-2.0}$ in early autumn period. There are about 44.0% MMW PAHs in $PM_{1.1}$ and 22.2% in $PM_{1.1-2.0}$ in spring, about 67.5% in $PM_{1.1,}$ 7.48% in $PM_{1.1-2.0}$ in early autumn. There are about 56.5% HMW PAHs in $PM_{1.1}$, 21.8% in $PM_{1.1-2.0}$ in spring, about 66.7% in $PM_{1.1}$, 9.92% in $PM_{1.1-2.0}$ in early autumn. It is easy to find that the over 50% HMW were located in $PM_{1.1}$. For LMW PAHs, this is the first time to find that LMW PAHs in early autumn were mostly distributed in $PM_{1.1}$. Fig. 3 also showed that all of the largest LMW, MMW and HMW in spring were on 25–26 March, largest LMW and HMW PAHs in early autumn were on 14–16 September while the largest MMW were on 19–21 September. In spring, average values of LMW:MMW:HMW in $PM_{1.1}$ were 1:8.39:15.50 and 1:5.64:7.94 in $PM_{1.1-2.0}$. In early autumn, the ratios of LMW:MMW:HMW in $PM_{1.1}$ were 1:7.44:10.2 and 1:3.34:6.22 in $PM_{1.1-2.0}$, Though TPAHs in spring were higher those in early autumn, the LMW, MMW, HMW PAHs in $PM_{1.1}$ were higher than those in spring which indicated that the PAHs might be distributed in finer particles of the early autumn which could be explained by temperature effects ($r = 0.60$). and HMW PAHs are expected to require a much longer time to partition to coarse particles than LMW PAHs and HMW PAHs only stay in fine particle with their non-volatile characteristic [8], [18], [26].

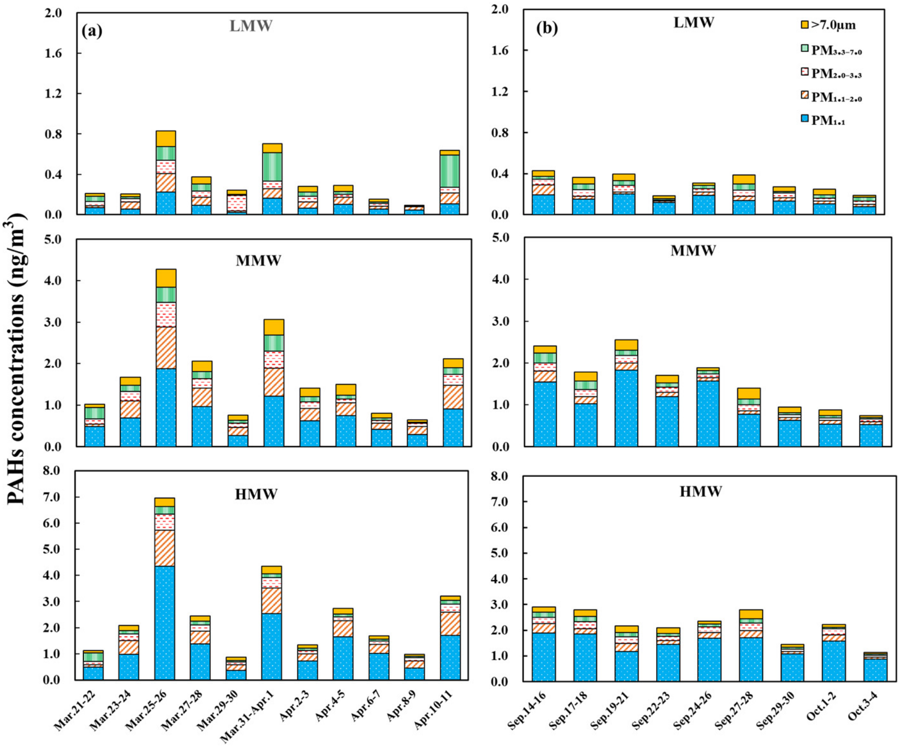

Figure 3: Variation of particle bounds LMW,MMW and HMW PAHs in each sampling case. (a), spring sampling period; and (b), early autumn period.

In addition, COMPAHs has been classified including Flu, Pyr, BaA, Chy, BbF, BkF, BaP, IndP and BghiP and COMPAHs/TPAHs is a characteristic diagnostic parameter for PAHs produced by stationary sources [23], [27]. The ratios of COMPAHs/TPAHs in $PM_{1.1}$ were 72.3%–92.7% in spring and 85.8%–92.7% in early autumn. The lower ratios of LMW/HMW and the higher ratios of COMPAHs/ TPAHs in $PM_{1.1}$ and $PM_{1.1–2.0}$ could be indicated that combustion sources might play an important role in fine particles. CANPAHs are to assess the carcinogenic potential of PAHs to the exposed people and usually including BaA, Chy, BkF, BaP, IndP and DB[a,h]A [22], [28]. Species CANPAHS are from COMPAHs group. The ratios of CANPAHs to TPAHs in TSP were 45.04% (39.9–48.6%) in spring and 49.26% (43.0%–59.5%) in early autumn. Moreover, over 70% of CANPAHS were a trend to distributed in $PM_{2.0}$ ($PM_{1.1}$+$PM_{1.1–2.0}$) in both spring and early autumn. Compared with those in spring, CANPAHS in early autumn were more trend to locate in $PM_{1.1.}$ These PAHs are of interest due to their potential toxicity, carcinogenic, and mutagenicity.

3.3 Health risk evaluation of PAHs patterns in $PM_{1.1}$ and $PM_{2.0}$

Although atmospheric PAHs exist at relatively low concentrations, epidemiologic studies have linked long-term low-level PAH exposure with various health outcomes, including cancers among adult populations [16]. Carcinogenic risk and mutagenicity were calculated in combination with measured PAHs in fine particles. The BaP-equivalent comparison of

BaP-TEQ$_{(13PAHs)}$, BaP-TEQ$_{(6PAHs)}$, BaP-PEQ and BaP-MEQ of PM$_{1.1}$ and PM$_{2.0}$ in spring and early autumn were shown in Table 1.

Table 1: BaP-equivalent and individual cancer risk for inhalation for PAHs in PM$_{2.0}$ and PM$_{1.1}$ in Shanghai, during spring and early autumn sampling periods.

	BaP-equivalent(ng/m^3)			**Individual cancer risk for inhalation**			**Potential cases per million people exposed**		
	PM$_{2.0}$			PM$_{2.0}$			PM$_{2.0}$		
Spring	Ave.	Max.	Min.	Ave.	Max.	Min.	Ave.	Max.	Min.
(BAP-TEQ)13PAHs	0.424	1.261	0.118	4.67E-07	1.39E-06	1.30E-07	0.467	1.387	0.130
(BAP-TEQ)7PAHs	0.394	1.174	0.109	4.34E-07	1.29E-06	1.20E-07	0.434	1.292	0.120
(BAP-PEQ)6PAHs	0.385	1.194	0.108	4.23E-07	1.31E-06	1.19E-07	0.423	1.314	0.119
(BAP-MEQ)8PAHs	0.665	1.982	0.192						
Early autumn									
(BAP-TEQ)13PAHs	0.358	0.519	0.179	3.94E-07	5.71E-07	1.96E-07	0.394	0.571	0.196
(BAP-TEQ)7PAHs	0.328	0.480	0.158	3.61E-07	5.28E-07	1.74E-07	0.361	0.528	0.174
(BAP-PEQ)6PAHs	0.326	0.499	0.155	3.59E-07	5.48E-07	1.71E-07	0.359	0.548	0.171
(BAP-MEQ)8PAHs	0.554	0.790	0.329						
	BaP-equivalent(ng/m^3)			**Individual cancer risk for inhalation**			**Potential cases per million people exposed**		
	PM$_{1.1}$			PM$_{1.1}$			PM$_{1.1}$		
Spring	Ave.	Max.	Min.	Ave.	Max.	Min.	Ave.	Max.	Min.
(BAP-TEQ)13PAHs	0.299	0.953	0.070	3.28E-07	1.05E-06	7.66E-08	0.328	1.048	0.077
(BAP-TEQ)7PAHs	0.277	0.888	0.064	3.05E-07	9.77E-07	6.99E-08	0.305	0.977	0.070
(BAP-PEQ)6PAHs	0.274	0.914	0.064	3.01E-07	1.01E-06	7.01E-08	0.301	1.005	0.070
(BAP-MEQ)8PAHs	0.477	1.515	0.118						
Early autumn									
(BAP-TEQ)13PAHs	0.320	0.462	0.163	3.52E-07	5.08E-07	1.80E-07	0.352	0.508	0.180
(BAP-TEQ)7PAHs	0.294	0.430	0.144	3.23E-07	4.73E-07	1.59E-07	0.323	0.473	0.159
(BAP-PEQ)6PAHs	0.294	0.445	0.142	3.23E-07	4.90E-07	1.56E-07	0.323	0.490	0.156
(BAP-MEQ)8PAHs	0.490	0.687	0.300						

13 PAHs, Pyr, Phe,FLU, FLN, Chy, B[ghi]P, ANT, IndP, BkF, BbF, BaA, BaP, DB[a,h]A;
7 PAHs, IndP, BkF, BbF, BaA, BaP, DB[a,h]A, Chy;
6 PAHs, BkF, BbF, BaA, BaP, IndP, Chy;
8 PAHs, BkF, BbF, BaA, BaP, DB[a,h]A, Chy, IndP.

Average individual cancer risk for inhalation by BaP-TEQ$_{(13\ PAHs)}$, BaP-TEQ$_{(6\ PAHs)}$, BaP-PEQ both from PM$_{2.0}$ and PM$_{1.1}$ were under 10^{-6} which indicated that there are no cancer risk under these conditions. In spring, BaP-TEQ$_{(13\ PAHs)}$ in PM$_{2.0}$ were about 0.424 ng/m^3 BaP-equivalent indicated that potential cancer cases for per million people exposed with this condition was 0.467, and average BaP-TEQ$_{(13\ PAHs)}$ in PM$_{1.1}$ were 0.299 ng/m^3 with 70.5% contribution to that in PM$_{2.0}$. In early autumn, BaP-TEQ$_{(13\ PAHs)}$ in PM$_{2.0}$ was 0.358 ng/m^3 BaP-equivalent with the 0.394 potential cancer cases for per million people exposed under this condition and they are almost from PM$_{1.1}$. In PM$_{2.0}$, BaP-TEQ$_{(6\ PAHs)}$ in spring were 0.394 ng/m^3 and 0.328 ng/m^3 early autumn. According to these two different calculation methods of BaP-TEQ, max and average BaP-TEQ in spring were higher than in early autumn while the min BaP-TEQ were higher in early autumn. It was also amazing that the average BaP-TEQ $_{(13\ \mathrm{PAHs})}$ and BaP-TEQ $_{(6\ \mathrm{PAHs})}$ in $PM_{1.1}$ were higher in early autumn period while these in spring were higher in $PM_{2.0}$. Also the min BaP-TEQ in $PM_{1.1}$ of the early autumn period were higher than in spring. For the BaP-PEQ, the average in spring were 0.385 ng/m^3 in $PM_{2.0}$ with 0.423 potential cases for per million people and 0.274 ng/m^3 in $PM_{1.1}$ with 0.328 potential cases for per million people. In early autumn, the average of BaP-PEQ were 0.326 ng/m^3 in $PM_{2.0}$ and 0.294 ng/m^3 in $PM_{1.1}$. For the BaP-MEQ, the average values in spring were 0.665 ng/m^3 in $PM_{2.0}$ and 0.477 ng/m^3 in $PM_{1.1}$. In early autumn, the average of BaP-MEQ were 0.554 ng/m^3 in $PM_{2.0}$ and 0.490 ng/m^3 in $PM_{1.1}$. Both BaP-PEQ and BaP-MEQ could be considered that these values were directly affected from these relative PAHs from $PM_{1.1}$. In $PM_{1.1}$, average BaP-TEQ $_{(13\ \mathrm{PAHs})}$, BaP-TEQ $_{(6\ \mathrm{PAHs})}$, BaP-PEQ and BaP-MEQ in early autumn were higher than in spring. Over 50% BaP-equivalent of BaP-TEQ, BaP-PEQ and BaP-MEQ in $PM_{2.0}$ were from $PM_{1.1}$ and PAHs distributed in $PM_{1.1}$ could be considered to pose a stronger toxicity and do great harm to the health.

According to BaP-equivalent values, species dominant PAHs contribution rate to BaP-TEQ, BaP-PEQ and BaP-MEQ were calculated. In both $PM_{1.1}$ and $PM_{2.0}$ of spring, BaP, BbF and IndP could be considered as the main contributor to kinds of BaP-equivalent values, especially for BaP. In early autumn, BaP and BbF were shown to make the mostly contribution to BaP-TEQ, BaP-PEQ and BaP-MEQ in both $PM_{1.1}$ and $PM_{2.0.}$ It should be noticed that not only BaP but BbF and IndP also could be considered make the great contribution to kinds of health risks. It was obvious to find that BaP-TEQ$_{(13\ \mathrm{PAHs})}$, BaP-TEQ$_{(6\ \mathrm{PAHs})}$, BaP-PEQ and BaP-MEQ in $PM_{2.0}$ were main from these in $PM_{1.1}$. The average of them in $PM_{1.1}$ was larger in early autumn rather than spring. The main contributor PAHs to BaP-TEQ$_{(13\ \mathrm{PAHs})}$, BaP-TEQ$_{(6\ \mathrm{PAHs})}$, BaP-PEQ and BaP-MEQ in spring was obviously BaP. In $PM_{1.1}$ of early autumn, BaP and BbF played more important role to BaP-TEQ$_{(13\ \mathrm{PAHs})}$, BaP-TEQ$_{(6\ \mathrm{PAHs})}$ and BaP-PEQ while the BaP-MEQ. This result seems to consistent with the previous articles such as Agudelo-Castaneda et al. showed the BaP-TEQ (0.324 ng/m^3), BaP-PEQ (0.194 ng/m^3) and BaP-MEQ (0.489 ng/m^3) in $PM_{1.0}$ of metropolitan area of Porto Alegera area [16]. Wang et al. also studied to find that the toxicity of PAHs in $PM_{1.1}$ posed the significant health risks in Shanghai [8]. Ren et al. surveyed the BaP-TEQ and BaP-MEQ in atmosphere of two megacity named Xi'an and Guangzhou in China which showed PAHs in $PM_{1.1}$ were also showed more toxic in both Xi'an and Guangzhou [24].These PAHs with great health risks were belonging to HMW-PAHs and a group named COMPAHs. HMW PAHs and COMPAHs associated with $PM_{1.1}$ indicated the contribution of dense traffic, especially of heavy vehicles, as reported in previous studies. To know more about the sources of them is also one important study point.

3.4 Possible anthropogenic sources of atmospheric particles

PAHs are as one group of persistent pollutants which originate primarily from the incomplete combustion of fuel, especially from vehicular emissions and heating and so on [19]. In spring, LMW/HMW were 0.065 in $PM_{1.1}$ and 0.126 in $PM_{1.1–2.0}$, all COMB/TPAHs values in $PM_{1.1}$ and $PM_{1.1–2.0}$ were over 0.90 which indicated the main combustion sources in these research areas which Wang et al.'s study showed the similar sources for Shanghai [8]. Nowadays, diagnostic ratios have been widely calculated for characterizing the sources for atmospheric PAHs and several marker compounds are often used to indicate the prevalence of gasoline or diesel engines as well as the relative contribution of traffic, domestic heating, wood combustion and other sources [29], [30]. Fig. 4 showed typical PAHs diagnostic ratios in $PM_{1.1}$and $PM_{1.1–2.0}$ in both sampling periods.

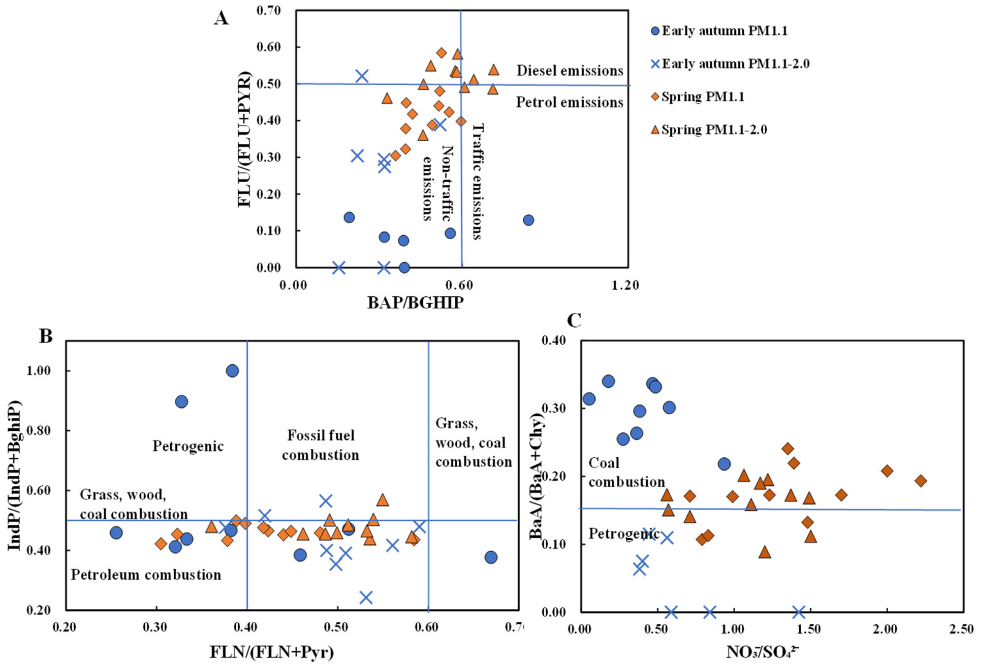

Figure 4: Correlation between PAHs diagnostic ratios and NO_3^-/SO_4^{2-} for source identification in $PM_{1.1}$ and $PM_{1.1-2.0}$ of spring and early autumn. (a) BaP/BghiP, Flu/(Flu+Pyr); (b) Fln/(Fln+Pyr), IndP/(IndP+BghiP); and (c) BaA/(BaA+Chy), NO_3^-/SO_4^{2-}.

In spring, the Flu/(Flu+Pyr) in $PM_{1.1}$ were almost under 0.50 to show the important sources of petrol emissions. Flu/(Flu+Pyr) in $PM_{1.1-2.0}$ indicated the sources of diesel emissions and petrol emissions [7]. Bap/Bghip in $PM_{1.1}$ were main got the efforts from non-traffic emissions, and $PM_{1.1-2.0}$ were sometimes got efforts from traffic emissions [7]. Fig. 4 showed values of IndP/(IndP+BghiP) in $PM_{1.1}$ and $PM_{1.1-2.0}$ were got the main efforts from petroleum combustions. The values of FLN/(FLN+Pyr) in $PM_{1.1}$ indicated two main sources such as petrogenic and fossil fuel combustion (e.g., coal combustion) while the $PM_{1.1-2.0}$ showed the main sources from combustion such as fossil fuel and grass, wood and coal combustion. The ratios of BaA/(BaA+Chy) in $PM_{1.1}$ showed that they might be got the efforts from petrogenic and coal combustion sources and mostly got the efforts from petrogenic sources in $PM_{1.1-2.0}$. Generally, it could be considered the traffic emissions and coal combustion are the important PAHs sources. PCA analysis also showed the main sources in $PM_{1.1}$ were from traffic emissions and coal and diesel combustion. In early autumn, Flu/(Flu+Pyr) in $PM_{1.1}$ and $PM_{1.1-2.0}$ showed the main sources of petrol emissions, BaP/BghiP in $PM_{1.1}$ occasionally were over 0.60 which indicated the traffic emissions to $PM_{1.1}$. FLN/(FLN+Pyr) in $PM_{1.1}$ were almost under 0.40 showed the important from petrogenic sources and these values in $PM_{1.1-2.0}$ were almost over 0.40 showed the main efforted from grass, wood, coal and fossil fuel combustion. IndP/(IndP+BghiP) in $PM_{1.1}$ and $PM_{1.1-2.0}$ were almost under 0.50 which showed the important sources of petroleum combustion. BaA/(BaA+Chy) in $PM_{1.1}$ were in the range 0.20–0.35 which showed the main sources from coal combustion. And the values in PM$_{1.1\text{–}2.0}$ were below 0.20 which showed the main effects from petrogenic sources. The mass ratios of NO$_3^-$/SO$_4^{2-}$ in PM$_{1.1}$ and PM$_{1.1\text{–}2.0}$ were almost below 1.0 which showed the important sources of stationary sources. It was obviously shown that the important sources in PM$_{1.1}$ were petroleum combustion and coal combustion, and the sources in PM$_{1.1\text{–}2.0}$ might be fossil fuel combustion and petrogenic sources. PCA analysis also showed the main sources in PM$_{1.1}$ were from coal and diesel combustion. And it was interesting that the source in PM$_{1.1}$ and PM$_{1.1\text{–}2.0}$ not only in spring but in early autumn showed some obvious different source efforts.

Diagnostics ratios analysis showed petroleum and coal combustion which main from the industries and vehicle emissions. Air mass backward trajectories at four sampling events such as, S-MAX (25–26 March) with the max TPAHs in spring, S-MIN (8–9 April) with the light PAHs in spring and EA-MAX (14–16 September) which with the max PAHs in TSP in early autumn, EA-MIN (3–4 October) (light TPAHs in early autumn) were calculated on Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT) from NOAA Air Resources and shown in Fig. 5. Air masses at S-MAX sampling period across the northwest part of China to Shanghai, which is the main coal combustion area in China [8], [31]. At S-MIN, EA-MAX and EA-MIN sampling cases, the air masses were main from marine area with northeast direction and played cleaning role to the atmosphere. It could be considered that the atmospheric environment in spring was easy to get long-range transport air masses efforts with pollutants which could be as an important factor to explain the occurred of the relative severe air pollution events. Air masses at all sampling events were from the northeast direction where the steel group and port location indicated the important local source effect.

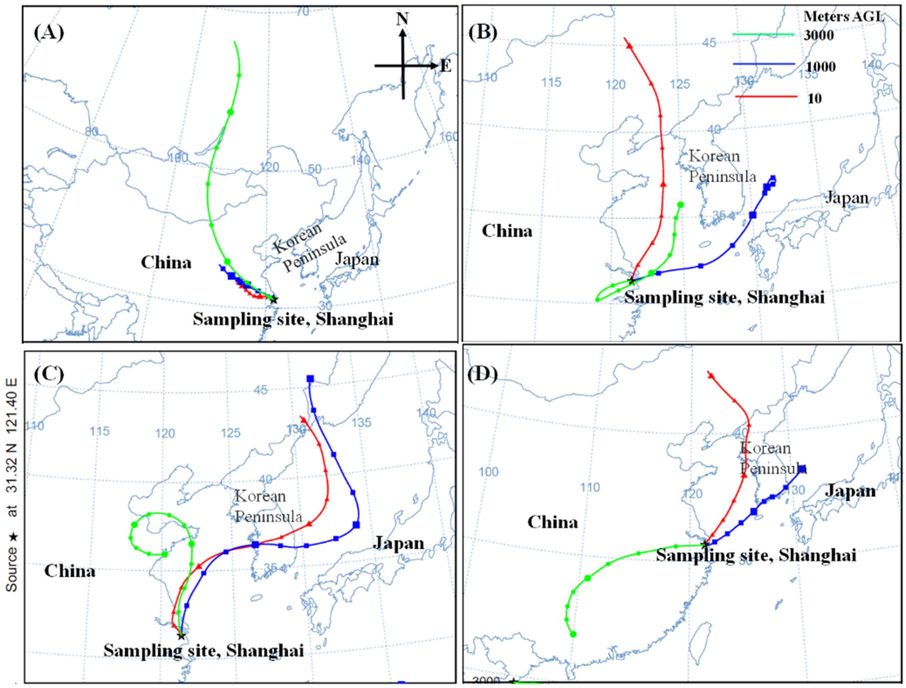

Figure 5: Air masses backward trajectories calculated by HYSPLIT model (GDAS meteorological data) with four sampling events. (a) S-MAX; (b) S-MIN; (c) EA-MAX; and (d) EA-MIN.

4 CONCLUSIONS

Particle-bound PAHs in ambient five size-ranges particle of Baoshan area of Shanghai were firstly collected to measure their chemical characterization, possible source and toxic evaluation during spring and early autumn. Chemical analysis indicated that PAHs were with higher accumulation efficiency in $PM_{1.1}$, especially in early autumn periods. We should do more study to evidence the conditions of PAHs accumulation efficiency, the influence of meteorological factors, high sunlight, along with the photochemical degradation of PAHs. Diagnostic ratios, PCA analysis and air mass backward trajectories showed that local stationary sources (e.g., diesel emission and industries source) are main PAHs sources which might be from steel industry and the possible relative transportation. Higher PAHs in $PM_{1.1}$ during early autumn could be explained by the effect from the steamship emissions on marine by air masses transport. BaP-equivalents of BaP-TEQ, BaP-PEQ and BaP-MEQ got great contribution from HMW groups, the most toxic one is BaP, which this result should be with more evidence by cytotoxicity experiments and simulation experiments and investigations. It was surprised that PAHs could be keep a relative high concentration with more finer particles though with good air quality. In addition to these PAHs, there are also several tens of components PAHs should be paid attention to, such as the nitro-PAHs and oxygen-PAHs, these ingredients also have serous effects on health and so on. Compared with particles' mass concentration, these PAH compounds and trace elements should also attract more attention to improve the environmental conditions.

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