Article

Industrial Source Contributions and Health Risk Assessment of Fine Particle-Bound Polycyclic Aromatic Hydrocarbons (PAHs) during Spring and Late Summer in the Baoshan Area, Shanghai

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Abstract: The main objective of this study was to examine the chemical characteristics, possible sources, and health risks of fine particle-bound Polycyclic Aromatic Hydrocarbons (PAHs) in the Baoshan area of Shanghai. Here, ambient particles with five-size ranges were collected during the spring and late summer of 2017. The PAHs were determined by the Gas Chromatography-Mass Spectrometry (GC-MS). Our results showed that the average mass concentration of 13 species of PAHs in spring and in late summer was 4.83 (1.88~12.1) ng/m³ and 4.27 (2.09~5.75) ng/m³ in Total Suspended Particles (TSPs), respectively. The higher PAH ratios (PM_{1.1}/TSPs) indicated that PAHs are mainly concentrated in PM_{1.1}, especially in late summer. The values of BaA/(BaA+CHR) were under 0.50 and IcdP/(IcdP+BghiP) were in range from 0.20 to 0.50 for TSP and PM_{1.1}, suggesting that petroleum combustion and diesel emissions could be considered as key sources of PAHs, which tend to be associated with PM_{1.1}. Moreover, the Principal Component Analysis (PCA) in PM_{1.1} identified the main PH sources, which include stationary and diesel emissions. The air mass backward trajectories and wind direction analysis showed that air masses were mainly derived from marine sources across the local industry area in late summer. Individual Carcinogenic Risk Inhalation (ILCR) was over 10^{−6} among the total six age groups in both of the sampling periods in TSPs, indicating the possible carcinogenic risk, especially for children and the young age group. Toxic PAHs belong to Heavy Molecular Weight (HMW) PAHs, especially Benzo[a]pyrene (BaP). Compared with PM_{1.1-2.0}, the Combustion-Derived PAHs group (COMPAHs) and Carcinogenic PAHs (CANPAHs) were highly concentrated in PM_{1.1}. Stationary sources, such as the developed steel industry, made a great contribution to the level of PAHs, especially in late summer.

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

1. Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are extensive organic contaminants comprising two or more benzene rings. They are widespread environmental contaminants generated as a result of the incomplete combustion of organic materials, such as fossil fuels [1–3]. Based on an ambient temperature, the nature of aerosol, and species of PAH, the PAHs in the atmosphere exist in the vapor phase or absorbed into ambient particles. It has already been 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 [4–7]. With their low vapor pressure, PAHs with heavier molecular

weights could be absorbed by the fine inhalable particles in the atmosphere. In addition, this has indicated that PAH compounds with 5–6 benzene rings are usually associated with $PM_{2.0}$ [6,8]. PAHs are one of the first atmospheric pollutants to be designated as suspected carcinogens. Moreover, PAHs are highly lipid-soluble and rapidly distributed in a wide variety of tissues, with a marked tendency for localization in body fat. As a result, the United States Environmental Protection Agency (USEPA) has listed 16 species of PAHs as priority pollutants, and the World Health Organization (WHO) has established that the BaP quality standard is 1 ng/m^3 [9,10]. The most significant health impact of inhaled exposure to PAHs is the lung cancer risk in all of the living organisms. It has been reported that about 1.6% of lung cancer morbidity might be due to inhalation exposure from atmospheric PAHs in the urban areas of China [3,4,11]. Although atmospheric PAHs exist at very low concentrations, epidemiologic studies have linked long-term, low-level PAH exposure with various health outcomes, especially cancer patients among adults. PAHs are more notably carcinogenic to humans than individual hydrocarbons [12–14].

Shanghai is a global commercial and financial center with a population of over 24 million in 2014 [15,16]. As one of the largest industrial and commercial cities in China, the Shanghai area suffers from heavy human-induced impacts and rapid urbanization. The Baoshan area located in the northeastern part of Shanghai is the main industrial district, with developed steel industries and several international ports [17–19]. Shanghai, located on the eastern coast of China, experiences four distinct seasons (spring, summer, autumn, and winter). The Shanghai Environmental Bulletin (2017), issued by the Shanghai Environmental Protection Bureau (SEPB), reported that atmospheric $PM_{2.5}$ values in the spring were normally heavier than in summer and early autumn [20]. Atmospheric PAHs from various sources are expected to continue to be displayed by spatiotemporal differences to raise the potential impacts on the environment and human health [6,17,21]. In this article, the main objective was to examine the chemical characteristics, possible sources, and health risks of fine particle-bound PAHs in two representative seasons, spring and late summer. The details of the study are as follows: First, we collected ambient particles with five-size ranges using a high flow rate sampler in the Baoshan area during the spring and late summer of 2017. Then, we measured the ambient PAHs composition by gas chromatography-mass spectrometry (GC-MS) and analyzed the PAH size distribution and chemical characteristics. Next, we evaluated the possible anthropogenic source by diagnostic ratios, PCA analysis, and air mass backward trajectories methods. Finally, we assessed the potential health effects using the inhalation exposure risk model, etc.

2. Materials and Methods

2.1. Ambient Particulate Collection in the Shanghai Suburban Sampling Site

Monthly $PM_{2.5}$ from 2014 to 2016, shown in Figure 1a, indicated that $PM_{2.5}$ in March and April was usually higher in September and October. The sampling campaign from 21 March to 7 April was called the spring sampling campaign (spring), and the so-called late summer sampling campaign (late summer) was conducted from 14 September to 4 October in 2017. Both the spring and late summer sampling sites were several hundred meters apart on the Baoshan campus of Shanghai University in Shanghai, as shown in Figure 1b. The sites were located on the ground, about 4 m in height above sea level, and we chose to ignore the impact of sampling location. There were several main traffic roads near these two sampling sites, and the steel group was located about 10 km northeast of the sampling sites [6]. An Andersen high-volume air sampler (AHV-600F, Shibata Co., Tokyo, Japan) was placed on the ground to collect the ambient particle samples with five-size segregations, such as particles with a diameter of $1.1\text{ }\mu\text{m}$ or less ($PM_{1.1}$), particles with a diameter between 1.1 and $2.0\text{ }\mu\text{m}$ ($PM_{1.1-2.0}$), particles with a diameter between 2.0 and $3.3\text{ }\mu\text{m}$ ($PM_{2.0-3.3}$), particles with a diameter between 3.3 and $7.0\text{ }\mu\text{m}$ ($PM_{3.3-7.0}$), and coarse particles ($>7.0\text{ }\mu\text{m}$) in an aerodynamic diameter. The air sampler flow rate was $0.566\text{ m}^3/\text{min}$, and each sampling event lasted up to 48 h. Ambient particles were collected on quartz fiber filters (Pallflex-2500QATUP, Tokyo Dylec Corp, Tokyo, Japan), with 6 h

of heat treatment to remove any possible organic compounds. The filtered samples after collection were wrapped in an aluminum foil sealed bag and remained at $-30\text{ }^{\circ}\text{C}$ until the compounds were analyzed. Simultaneously, the meteorological factors (Supplementary Table S1) were referred from Tianqihoubao website (<http://www.tianqihoubao.com/>, accessed on 20 May 2021), and the air quality factors (Supplementary Figure S1) were referred from the aqistudy website (<https://www.aqistudy.cn/historydata/>, accessed on 20 May 2021) during both sampling periods.

Figure 1. (a) Monthly PM_{2.5} values collected from SEPB from 2014 to 2017; (b) location of the spring and late summer sampling sites in Shanghai (the red mark of the steel company appeared on Google maps using the ‘Baosteel’ keyword in Chinese).

2.2. PAH Analysis by Gas Chromatography-Mass Spectrometry (GC-MS)

The PAH organic extraction method and GC-MS analysis system factor were mainly used from the (component analysis of fine particulate matter—manual for component measurement of fine particulate matter (PM_{2.5}) in the atmosphere), which was published by the Ministry of the Environment, Japan (<https://www.env.go.jp/air/osen/pm/ca/manual.html> accessed on 21 May 2021). The detailed protocol was mainly followed from laboratory-published research [6]. The Sigma-Aldrich EPA 16 PAHs mixture was used as the standard chemical (Sigma-Aldrich, 4S8743, St. Louis, Missouri, USA). The extract solution with an internal standard was used in a volume of up to 0.1 mL and measured by GC-MS (GC-MS, Model Agilent 5973N, Agilent Technologies, Inc., Santa Clara, CA, USA). The GC-MS analyses were performed on an InertCap 17 column (0.25 mm × 30 m and 0.25 µm film thickness) using an HP6890 GC interfaced into an HP5973 MS detector. The initial column temperature was 50 °C, and this temperature was held constant for 2 min. Thereafter, the temperature increased from 15 °C/min to 185 °C and then from 8 °C/min to 320 °C. This temperature was held constant for 22 min. MS detection was run in the selected ion monitoring mode (SIM). The sample volume injection was 1 µL. High-purity helium was used as the carrier gas at a constant flow rate of 1.3 mL min⁻¹. The identification of the individual PAH was based on the retention time of the target ion peak (within ±0.05 min of the retention of the calibration standard). Each sample was determined 3 times and the statistical analysis was processed by Microsoft Excel 2016. The analyzed PAHs were Acenaphthene (ACY), Anthracene (ACE), Benz[a]anthracene (BaA), Benzo[a]pyrene (BaP), Benzo[b]fluorathene (BbF), Benzo[ghi]perylene (BghiP), Benzo[k]-fluoranthene (BkF), Chrysene (CHR), Diben-z[a,h]anthracene (DahA), Fluoranthene (FLA),

Fluorene (FL), Indeno[1,2,3-cd]pyrene (IcdP), Naphthalene (NP), Phenanthrene (PHE), and Pyrene (PYR).

2.3. Source Apportionment Techniques of PAHs

Recently, the PAH diagnostic ratios have been commonly used as a method for identifying and assessing pollution emission sources. Typical diagnostic ratios and their typical values are listed in Table 1 [6,17,22–24]. Furthermore, the Principal Component Analysis (PCA) was selected for use in identifying the PAH sources in PM_{1.1}, which was performed using the SPSS statistical software package (SPSS 26, IBM, Endicott, NY, USA). The selected principal components have cumulative variances that exceed 85% of the total variance after the application of the varimax rotation. These factors could be considered in order to reflect the specific chemical sources of target pollutants [25,26].

Table 1. Diagnostic ratios used with their typically reported values for particle processes.

PAH Ratio	Value Range	Source	Reference
LMW/HMW	<1	Pyrogenic	Zhang, Wei et al., 2008
	>1	Petrogenic	
COMB/PAHs	~1	Combustion	Ravindra, Khaiwal 2008
	<0.5	Petrol emissions	
Fl/(Fl+Pyr)	>0.5	Diesel emissions	Ravindra, Khaiwal 2008
	<0.1	Petrogenic	
ANT/(ANT+PHE)	>0.1	Pyrogenic	Pies, Carmen et al., 2008
	<0.4	Petrogenic	
FLA/(FLA+PYR)	0.4–0.5	Fossil fuel combustion	Roberto, J. 2009
	>0.5	Grass, wood, coal combustion	
BaA/(BaA+CHR)	<0.2	Petrogenic	Akyüz et al., 2010, Yunker et al., 2002
	0.2–0.35	Coal combustion	
IcdP/(IcdP+BghiP)	>0.35	Vehicular emissions, combustion	Yunker, Mark B. et al., 2002
	<0.2	Petrogenic	
Bap/BghiP	0.2–0.5	Petroleum combustion	Katsoyiannis 2007
	>0.5	Grass, wood, coal combustion	
	<0.6	Non-traffic emissions	
	>0.6	Traffic emissions	

LMW: Low molecular weight PAHs; HMW: High molecular weight PAHs; COMB: Combustion-derived PAHs group.

The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model is one of the most extensively used atmospheric transport and dispersion models in the atmospheric sciences community [6,27,28]. Air mass backward trajectories are calculated by the HYSPLIT model with the Global Data Assimilation System (GDAS) from the National Oceanic and Atmospheric Administration (NOAA) Air Resource to assess the air mass transport effort [26].

2.4. Health Risk Assessment of PAHs

2.4.1. Average Dose Estimation

An estimation of the absorbed dose could be considered as the result of the procedure for the determination of the exposure at risk assessment. The Lifetime Average Daily Intake (LADD) of the pollutant (e.g., PAHs) by inhalation could be calculated by the following equation [26]:

$$\text{LADDi} = \frac{\text{CA} \times \text{IR} \times \text{ET} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \quad (1)$$

Here, the unit of LADDi (PAH) is mg/(kg·day), CA is the PAH (BaP) concentration (mg/m³) in the air, and CA (PAHs) is the converted BaP toxic equivalent (TEQ_{BaP}) by the

Toxic Equivalency Factors (TEF) [29]. The TEF values for individual PAHs are as follows: BaP, 1; BaA, 0.1; BbF, 0.1; BghiP, 0.01; BkF, 0.1; CHR, 0.01; DahA, 1; FLA, 0.001; FL, 0.001; IcdP, 0.1; PHE, 0.001; PYR, 0.001.

IR is the volume of air inhaled per day ($\text{m}^3 \cdot \text{h}^{-1}$), ET is the exposure time ($\text{h} \cdot \text{day}^{-1}$), EF is the exposure frequency ($350, \text{days} \cdot \text{year}^{-1}$), ED is the duration of exposure (year), BW is the individual body weight (kg), and AT is the average exposure time (days). The average exposure time is calculated as $\text{AT} = \text{ED} \cdot 365$ to account for the lifelong non-threshold carcinogenic effects of pollution. The LADD value, which is important for the determination of the exposure to carcinogenic contaminants, should be calculated. The calculated LADD value expresses the level of average lifetime exposure to estimate the probability of malignancy caused by the Individual Lifetime Cancer Risk (ILCR).

2.4.2. Carcinogenic Risk Assessment

A lifetime exposure scenario with different 6 age groups is as following, Group (Birth to 1), BW, 8.8 kg, ED, 0.5 year, EF, 350, $\text{days} \cdot \text{year}^{-1}$, ET, $1.5 \text{ h} \cdot \text{day}^{-1}$, IR, $5.4 \text{ m}^3/\text{Day}$; Group(1 to 6), BW, 14.5 kg, ED, 3.5 years, EF, 350 $\text{days} \cdot \text{year}^{-1}$, ET, $1.5 \text{ h} \cdot \text{day}^{-1}$, IR, $9 \text{ m}^3/\text{Day}$; Group(6 to 16), BW, 43 kg, ED, 11 years, EF, 350 $\text{days} \cdot \text{year}^{-1}$, ET, $3 \text{ h} \cdot \text{day}^{-1}$, IR, $13.6 \text{ m}^3/\text{Day}$; Group(16 to 31), BW, 65 kg, ED, 23.5 years, EF, 350 $\text{days} \cdot \text{year}^{-1}$, ET, $3 \text{ h} \cdot \text{day}^{-1}$, IR, $16 \text{ m}^3/\text{Day}$; Group(31 to 51), BW, 71.2 kg, ED, 41 years, EF, 350 $\text{days} \cdot \text{year}^{-1}$, ET, $3 \text{ h} \cdot \text{day}^{-1}$, IR, $16 \text{ m}^3/\text{Day}$; Group(51 to 81), BW, 70 kg, ED, 66 years, EF, 350 $\text{days} \cdot \text{year}^{-1}$, ET, $3 \text{ h} \cdot \text{day}^{-1}$, IR, $15 \text{ m}^3/\text{Day}$, separately. These exposure factors from the USEPA were used to assess the different age groups [26,30]. Additionally, the LADD is calculated for outdoor activities only. An estimate of the lifelong effects of a pollutant is used for health risk assessments of exposure to carcinogenic substances. The ILCR value could be calculated by the following equation:

$$\text{ILCR} = 1 - e^{(-\text{ICPF} \cdot \text{LADD})} \quad (2)$$

Here, the ICPF refers to the inhalation cancer potency factor, which is equal to $3.9 \text{ mg}/\text{kg} \cdot \text{day}$ for BaP [31]. The ILCR calculated by this formula is considered to be the theoretical increase in the probability of cancer occurrence above the general population average. When the ILCR value is lower than 1×10^{-6} , it could be considered an acceptable level of carcinogenic risk. This value can be interpreted as the probability of malignancy due to the harmful effects of a substance, which is higher than the normal occurrence in the case of one person in one million in an area with more than 100 exposed people.

3. Results and Discussion

3.1. Size Distribution and Characteristics of Representative PAH Patterns

Usually, Nap, Ace, and Ant are considered the main volatile PAHs reported, of which the total percentage found in the particulate phase is below 5% [32–35], while the other 13 species of PAH classified as priority contaminants by USEPA were defined as mainly particle-bound PAH species (see Figure 2 and Supplementary Table S2). The average PAH values in the TSP were $4826.3 \text{ pg}/\text{m}^3$ in spring and $4279.3 \text{ pg}/\text{m}^3$ in late summer. In spring, the PAHs in TSP were high, reaching $12,060.45 \text{ pg}/\text{m}^3$, in the March 25–26 event and low, reaching $1884.53 \text{ pg}/\text{m}^3$, in 29–30 March. Moreover, the higher $\text{PM}_{2.5}$, SO_2 , and NO_2 occurred during the 25–26 March event and it rained during 29–30 March, which could clean the air conditions (see Supplementary Figure S1). The Pearson Product-Moment Correlation Coefficient (PCC) analysis, given in Supplementary Table S3, indicated that the PAHs in TSP have a positive strong correlation coefficient with SO_2 ($r = 0.61$) and NO_2 ($r = 0.52$) in spring. During the late summer, the PAH levels saw a high of $5747.12 \text{ pg}/\text{m}^3$ on 14–16 September and low of $2070.95 \text{ pg}/\text{m}^3$ on 29–30 September (a rainy event). In addition, the PAH levels showed a strong correlation with the daily average temperature ($r = 0.60$) and a middle correlation with O_3 ($r = 0.49$). Furthermore, the PAHs in TSP showed a strong correlation with the particle size. In particular, over 51.6% (51.6–77.2%) of PAHs in spring were associated with $\text{PM}_{2.0}$ ($\text{PM}_{2.0} = \text{PM}_{1.1} + \text{PM}_{1.1-2.0}$) and over 57.0% (57.0–79.0%)

of PAHs in late summer were associated with $PM_{1.1}$, which showed that the PAHs mainly associate with fine particles and were highly concentrated in the fine particles of $PM_{1.1}$ in late summer.

Figure 2. PAHs size distribution at each sampling case during the spring and late summer sampling periods.

Synchronously, several studies have been undertaken to identify the PAHs in different seasons, as shown in Table 2. Dayana found that 16 PAH levels in $PM_{1.0}$ in the summer were about half of the levels in winter [5]. The authors studied about 16 PAHs in the $PM_{2.1}$ of Nanjing during spring and found that their levels were higher than in the summer [36]. Moreover, Wang studied 37 different species of PAHs in the summer of 2015 in Shanghai and found that about 50% were associated with $PM_{1.1}$ [6]. Furthermore, Ren measured the PAHs in $PM_{1.1}$ in two megacities and found that the PAHs of Xi'an in the summer were 1/10 of the levels in winter: About 33 ng/m^3 in winter and 3.4 ng/m^3 in the summer. In addition, the summer levels in the $PM_{1.1}$ of Guangzhou were half of the levels in winter [28]. Moreover, the PAHs in this article were dominant in $PM_{1.1}$, which seems very consistent with those reported from numerous articles. However, particular attention should be given to the levels of PAHs in late summer, as they are higher than in spring.

Table 2. PAHs concentrations in particulate samples in the previous studies.

City	Site Description	Year	Sample Matrix	16 PAHs ng/m^3		Ref.
				Summer	Other	
Shanghai	Urban/industrial	2017	$PM_{1.1}$	2.86 (13 PAHs)	2.41 spring	This study
			TSP	4.28	4.83	This study
Canoas	Roadside/traffic	2011~2013	$PM_{1.0}$	1.32	2.02 winter	D.M. (2014) [36]
Sapucaia do Sul	Urban road/traffic	2011~2013	$PM_{1.0}$	1.57	3.05 winter	D.M. (2014)
Shanghai	Suburban	2015	$PM_{1.1}$	4.97 (37 PAHs)		Wang (2016) [6]
Nanjing	Suburban	2009~2010	$PM_{2.1}$	30.76	43.5 spring	HE 2014 [37]
	Urban		$PM_{2.1}$	25.92	56.92 spring	HE 2014
Xi'an	Urban	2013	$PM_{1.1}$	3.4	33 winter	Ren 2017 [28]
			TSP	6	57 winter	Ren 2017
Guangzhou	Urban	2013	$PM_{1.1}$	2.2	4.4 winter	Ren 2017
			TSP	2.8	18 winter	Ren 2017

Based on the PAH molecular weight, these PAHs could be divided into three groups [6,38,39]: FL, PHE, and ANT. In this case, 2- and 3-ring PAHs could be classified as Low Molecular Weight (LMW) PAHs; FLA, PYR, CHR, and BaA with 4-ring PAHs could be defined as Middle Molecular Weight (MMW); while BbF, BkF, BaP, IcdP, DahA, and BghiP with 5-and 6-ring PAHs are always defined as High Molecular Weight (HMW) PAHs. Generally, LMW PAHs are usually considered to have formed during low temperature processes (such as biomass burning), while HMW PAHs are emitted from relatively megathermal reactions, such as fuel combustion, which react to form stable PAHs during pyrosynthesis. These PAHs are less alkylated and they easily contain more aromatic rings [38,39]. Based on Table 3, LMW PAH distributions in spring were 25.9% in PM_{1.1}, 19.0% in PM_{1.1-2.0}, 18.3% in PM_{2.0-3.3}, 19.8% in PM_{3.3-7.0}, and 17.1% in coarse particles >7 µm. LMW PAHs in late summer were 46.9% in PM_{1.1}, 11.9% in PM_{1.1-2.0}, 13.8% in PM_{2.0-3.3}, 11.5% in PM_{3.3-7.0}, and 15.9% in coarse particles (>7 µm). With the similarity with LMW PAHs in TSP, it could be seen that LMW PAHs in late summer were mainly found in the fine particles of PM_{1.1}.

Table 3. Average concentration and percentage of LMW, MMW, HMW, COMPAHs, and CANPAHs in five-range ambient particles during the sampling and late summer sampling periods.

		Concentrations (pg/m ³)					PM/TSP (%)					
		PM1.1	PM1.1–2.0	PM2.0–3.3	PM3.3–7.0	>7.0 µm	TSP	PM1.1	PM1.1–2.0	PM2.0–3.3	PM3.3–7.0	>7.0 µm
Spring AVG.	LMW	95.0	69.5	66.9	72.4	62.7	366.3	25.9	19.0	18.3	19.8	17.1
	MMW	810.9	392.0	224.9	187.0	225.9	1840.6	44.1	21.3	12.2	10.2	12.3
	HMW	1502.1	542.5	235.7	153.9	185.7	2619.9	57.3	20.7	9.00	5.87	7.09
	TPAHs	2407.9	1004.0	527.4	413.3	474.2	4826.8	49.9	20.8	10.9	8.56	9.82
	COMPAHs	2198.0	889.3	438.9	348.9	385.1	4260.3	51.6	20.9	10.3	8.19	9.04
	CANPAHs	1608.2	604.9	285.8	199.8	240.1	2938.8	54.7	20.6	9.73	6.80	8.17
Late summer AVG.	LMW	144.7	36.6	42.6	35.3	49.1	308.2	46.9	11.9	13.8	11.4	15.9
	MMW	1072.3	118.8	124.8	114.9	159.8	1590.6	67.4	7.469	7.846	7.225	10.0
	HMW	1638.7	219.5	203.1	131.1	188.2	2380.5	68.8	9.22	8.53	5.51	7.91
	TPAHs	2855.6	374.8	370.5	281.3	397.1	4279.3	66.7	8.76	8.66	6.57	9.28
	COMPAHs	2442.0	328.2	306.5	235.5	329.7	3642.1	67.0	9.01	8.42	6.47	9.05
	CANPAHs	2118.7	242.8	242.3	180.2	232.3	3016.3	70.2	8.05	8.03	5.97	7.70

The MMW PAH levels in TSP were about 5 times higher than the LMW PAHs in the two sampling periods. The MMW PAH levels in spring were 44.1% in PM_{1.1}, 21.3% in PM_{1.1-2.0}, 12.2% in PM_{2.0-3.3}, 10.2% in PM_{3.3-7.0}, and 12.3% in coarse particles (>7 µm). The MMW PAH levels in late summer were about 67.4% in PM_{1.1} and 10.1% in coarse particles (>7 µm). These results showed that the MMW PAHs are more concentrated in the fine particles (PM_{1.1}, PM_{1.1-2.0}) than the LMW PAHs. The HMW PAHs were about 8 times higher than the LMW PAHs and about 1.5 times higher in both spring and late summer. The size distributions of MMW PAHs were 57.3% in PM_{1.1} and 20.7% in PM_{1.1-2.0} in spring, as well as 68.8% in PM_{1.1} and 9.22% in PM_{1.1-2.0} in late summer. The HMW PAHs almost always remain in fine particles, which could be explained by their non-volatile characteristics [5,6,8]. Although the TPAHs in the TSP of spring were higher than in late summer, the TPAH levels in the PM_{1.1} of late summer were also higher for the HMW, LMW, and MMW groups. Compared with the levels in spring, PAHs were more likely to concentrate in PM_{1.1} during late summer.

In addition, a Combustion-Derived PAHs group (COMPAHs) has been classified to include FL, PYR, BaA, CHR, BbF, BkF, BaP, IcdP, and BghiP [1,40]. COMPAHs/TPAHs are characteristic PAH diagnostic parameters for producing the stationary sources. When this value is near 1.00, this points to the dominant combustion source [37,41]. As shown in Table 3, the COMPAH levels in TSP in spring were high at 4260.4 pg/m³ and the COMPAH/TPAH was 0.88. The COMPAH levels in the TSP of late summer were 3642.1 pg/m³, which accounts for 85.1% of TPAHs and 67.1% are in PM_{1.1}. The COMPAHs/TPAHs values in spring (0.88) and late summer (0.85) showed that the combustion source was indeed a major PAH source. Carcinogenic PAHs (CANPAHs) are defined to assess the carcinogenic potential of PAHs in exposed people and usually include BaA, CHR, BkF, BaP, IcdP, and

DahA [32,41]. The results presented in Table 3 show that the CANPAHs in spring were mainly located in $PM_{1.1}$ and $PM_{1.1-2.0}$. CANPAHs in late summer were 70.2% located in $PM_{1.1}$, showing that the CANPAHs were generally mainly located in $PM_{1.1}$. In general, CANPAHs and COMPAHs were mainly distributed in $PM_{1.1}$ and $PM_{1.1-2.0}$, respectively. Furthermore, CANPAHs belong to the COMPAHs group, which indicates the possibility that combustion emissions might show the health risks.

3.2. Possible Anthropogenic Source Apportionment of PAHs in $PM_{1.1}$

The LMW/HMW PAH ratio could be used to distinguish pyrogenic from petrogenic sources. When the ratio is over 1.00, this could indicate that the main source might be petrogenic, and if the ratio is below 1.00, the main source might be pyrogenic [6,12,38]. Here, a lower LMW/HMW ratio and higher COMPAHs/TPAHs ratios in TSP (Table 3) during the two sampling periods indicated that the combustion sources might play an important role in PAH generation. This is supported by the negative correlation between LMW/HMW and COMPAHs (spring, $r = -0.54$; late summer, $r = -0.36$) and the positive correlation between COMPAHs and TPAHs (spring, $r = 1.00$; late summer, $r = 0.996$). Therefore, combustion sources could be thought of as the dominant PAH source in the Baoshan sampling area.

On the contrary, the PAH diagnosis ratio method is used to identify the source of PAHs by the frequently found PAH ratio. The typical PAH isomer pair ratios are shown in Table 1 [38,42,43]. Considering the size distribution of the PAHs, the PAH ratios in $PM_{1.1}$ and TSP were observed and shown in Figure 3. In the spring, the values of $BaA/(BaA+CHR)$ in $PM_{1.1}$ and TSP varied from 0.107 to 0.241, revealing that the main source was petrogenic. The values of $IcdP/(IcdP+BghiP)$ in $PM_{1.1}$ and TSP were between 0.4 and 0.5, indicating that the dominant petroleum combustion source, $Bap/BghiP$, was close to 0.60, which shows the traffic emissions effects, especially for diesel vehicles. The values of $FLA/(FLA+PYR)$ were about 0.30 to 0.60, showing the main fossil fuel combustion sources with some effects from biomass coal combustion and petrogenic sources. In summary, it could be considered that the source of PAHs in $PM_{1.1}$ and TSP was mainly traffic emissions. This observation is consistent with the ionic and elemental source analysis [24]. In late summer, the values of $BaA/(BaA+CHR)$ in $PM_{1.1}$ and TSP were between 0.20 to 0.35, which showed that the key coal combustion levels of $IcdP/(IcdP+BghiP)$ were mostly close to 0.4~0.5, indicating the effect of petroleum combustion. The $Bap/BghiP$ ratio showed both the traffic and non-traffic emissions. Compared with spring, the PAH source varied to several sources in late summer.

Figure 3. Diagnostics ratio cross plotting in $PM_{1.1}$ and TSP, (a) $IcdP/(IcdP+BghiP)$ and $BaA/(BaA+CHR)$, (b) $FLA/(FLA+PYR)$ and $BaP/BghiP$.

Due to the main $PM_{1.1}$ distribution, the Principal Component Analysis (PCA), shown in Table 4, is presented with three and four factors in $PM_{1.1}$, explaining 96.9% and 88.3% of

the data variance during the spring and late summer sampling periods. In spring, Factor 1 explained 62.8% of the total variance and was highly loaded with BaA, BaP, CHR, BghiP, BkF, PHE, FLA, and ANT, which almost belonged to HMW PAHs. BaA and BaP could be used as stationary source indicators, such as the steel industry, and CHR, FLA, and PHE are the indicators of diesel vehicle emissions [44]. Therefore, this factor could indicate industry sources and diesel vehicle emissions [44,45]. Factor 2 explained 18.6% of the total variance and was highly loaded with DahA (factor loading > 0.928), serving as a tracer for gasoline exhaust [44,46,47]. Therefore, Factor 2 was associated with gasoline vehicle emissions. Factor 3 explained 15.6% of the total variance and was highly loaded with PYR and FLA (factor loading > 0.60), and PYR has been used as a tracer for roadside soil particle and combustion sources. In late summer, the stationary sources and diesel vehicle emission (35.6%), biomass and coal combustion (25.2%), gasoline vehicle emissions (18.0%), and roadside soil particles are mainly responsible for the PAHs in PM_{1.1}. Both in spring and late summer, the main sources were stationary (e.g., the steel industry) and diesel vehicle emissions, and the Baowu steel group was within close proximity. Generally, local activities showed more variable effects on PAHs in late summer than in spring.

Table 4. PCA loading factors for PAH compounds in fine particles of PM_{1.1} during the spring and late summer sampling periods.

PAHs	Spring			Late Summer			
	F 1	F2	F3	F1	F2	F3	F4
BaA	0.950	0.204	0.223	0.879	0.113	0.333	0.239
BaP	0.938	0.264	0.213	0.037	0.870	0.446	0.169
CHR	0.925	0.270	0.255	0.771	0.176	0.254	0.312
BghiP	0.918	0.366	0.144	0.944	−0.013	−0.212	0.095
BkF	0.877	0.408	0.248	−0.200	0.835	−0.310	0.291
IcdP	0.868	0.426	0.249	0.731	0.506	−0.008	−0.108
BbF	0.864	0.409	0.279	0.378	0.857	0.002	0.256
PHE	0.849	0.361	0.376	0.825	0.357	0.212	0.320
FLA	0.787	0.001	0.605	0.196	0.312	−0.049	0.865
ANT	0.758	0.161	0.481	0.865	−0.118	−0.002	−0.134
DahA	0.232	0.928	0.222	0.144	0.169	0.932	0.030
FL	0.626	0.661	0.227	0.317	0.328	0.783	0.002
PYR	0.233	0.359	0.895	0.261	0.641	0.551	−0.030
Variance (%)	62.8	18.6	15.6	35.6	25.2	18.0	9.41
Sources	industrial emissions, diesel vehicle emissions	gasoline vehicle emissions	coal combustion, roadside soil particle	stationary sources, diesel vehicle emissions	biomass and coal combustion	gasoline vehicle emissions	roadside soil particle

To discover the air mass transport patterns and impacts, the Wind Direction (WD) frequency during the sampling periods is shown in Figure 4a. The wind in the spring came mainly from the North (N), East (E), and West (W), while it came mainly from the East (E) and Northeast (NE) during the late summer period. The air mass backward trajectories in the sampling sites are shown in Figure 4b, which are the four representative sampling cases selected, such as 25–26 March (largest TPAH levels in spring), 29–30 March (the lightest one), 14–16 September (the heaviest one in late summer), and 3–4 October (the lightest one). The air masses on 25–26 March were across the northwest part of China to Shanghai, which is mainly a coal combustion area, and the pollutants could affect Shanghai through the air mass long distance transport to cause a sudden pollutant increase [6,27]. The 29–30 March case showed that the air masses came from the marine area in the northeast, which could play a cleaning role in atmospheric contamination. Air masses in the 14–16 September case showed that they came from the Korean area across the water to Shanghai. The 3–4 October case showed that the air masses came from the northern part of China across the marine

area to Shanghai. Additionally, the air mass frequencies showed that the northern part of the sampling site made a non-negligible contribution. There are plenty of steel-related industries as well as several ports and mounts of transport vehicles and steamships, which indicate that the stationary sources are the main sources of pollution. Moreover, the air condition in spring could lead to more long-range transport of air masses with species pollutants, which could be an important factor in explaining the occurrence of the relatively severe air pollution events. Considering the main anthropogenic sources and assembled CANPAHs in fine particles is an important factor to evaluate the health risks of PAHs.

Figure 4. (a) Wind direction frequency (WD%) in the spring and late summer sampling periods (N: North; S: South; E: East; W: West); (b) air mass backward trajectories at the four sampling cases, 25–26 March; 29–30 March; 14–16 September; 3–4 October.

3.3. Carcinogenic Risk and Mutagenicity of PAHs in $PM_{1.1}$ and $PM_{2.0}$

About 40% of the $PM_{2.5}$ content is organic matter, which might be carcinogenic and mutagenic [48–51]. These PAHs are considered to pose a high risk to human health among the atmospheric trace chemical substances [38]. PAHs could cause adverse respiratory

effects in humans [52] with mutagenic and carcinogenic consequences [2]. Here, the PAH health risk analysis was based on the model assessment of carcinogenic risk associated with exposure to PAHs by the inhalation pathway. Additionally, there are six age-group analysis results shown in Figure 5. The Level of Carcinogenic Risk (ILCR) of TSP among all of the six age groups were over 1×10^{-6} in both the spring and late summer periods. However, the levels in spring were higher than in the late summer. For the size distribution, PAHs in $PM_{1.1}$ were shown as the principal contributors to this carcinogenic risk, especially for the birth to age 1, 1 to 6, and 6–16 age groups, which are considered the children and young age group. The ILCR values in $PM_{1.1}$ were higher than 1×10^{-6} , indicating high risks. On the contrary, the ILCR showed the risk from PAHs in both $PM_{1.1}$ and $PM_{1.1-2.0}$ in spring, and only $PM_{1.1}$ in late summer. This could be explained by the PAHs that were mainly found in $PM_{1.1}$ during the late summer.

Figure 5. The ILCR values in five particles during the spring (a) and late summer (b) sampling periods.

According to TEQ (BaP), the total BaP measured in TSP during the spring and late summer was still below the WHO standard (1 ng/m^3). However, the total BaP measured in TSP on the 25–26 March sampling event was higher than this standard. BaP, BbF, and IcdP were the main contributors, especially BaP. Additionally, the results showed that not only BaP, but also BbF and IcdPm which belong to the HMW PAHs, and BaA made high contributions to ILCR in late summer. Moreover, this result is consistent with several published articles [5,9,28]. These PAHs with higher health risks belong to HMW PAHs and the COMPAHs group. It might be the case that CANPAHs are associated with airborne

particles rather than the gas phase, especially fine particles [9,24]. The relative contribution levels of BaP, BbF, IndP, and BaA to BaPeq showed the low concentrations of the pollutants in air, but they can still pose serious health risks. On the contrary, due to the limited chemical interactions and other parameters, more work is required regarding the health risk analysis in this area.

4. Conclusions

Particle-bound PAHs in the ambient Baoshan area of Shanghai were first measured for their chemical characterization, possible sources, and toxic evaluation during the spring and late summer. The chemical analysis indicated that PAHs had higher accumulation efficiency in fine particles of $PM_{1.1}$, especially in the late summer. More research is required to fully understand the conditions of PAH accumulation efficiency, the influence of meteorological factors and sunlight, as well as the photochemical degradation of PAHs. Diagnostic ratios, PCA analysis, and air mass backward trajectories showed that local stationary sources (e.g., the steel industry and the relative transportations) are key PAH sources. PAHs in the late summer tended to associate with $PM_{1.1}$, which could be explained by the effect of temperature and sunlight and some possible chemical responses. The ILCR values from the model assessment of carcinogenic risk by the inhalation pathway indicated that the young and children would have a higher health risk than the other age groups. The higher ILCR values in $PM_{1.1}$ indicated that toxic PAHs were found in fine particles. However, according to the finer size and large area characteristics of the fine particles, they may pose more serious health effects. Although the PAHs could be cleaned up by the rainy weather, they could maintain relatively high concentrations in finer particles with good air quality. In addition, there are still several tons of PAHs components in the atmosphere, such as Nitro-PAHs and Oxygen-PAHs. Therefore, significant attention should be paid to their serious effects on health. Furthermore, compared with the particles' mass concentration, particular attention should be paid to these PAHs, trace elements, and other compounds to improve the environmental conditions.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/pr9112016/s1>. Table S1: Meteorological factors in the Baoshan area of Shanghai during the spring and early autumn sampling periods. Table S2: PAHs concentrations in five-size range particles during the spring and late summer sampling periods. Table S3: Pearson's correlation matrix between the PAHs, PM, meteorological factors, and other contaminations. Figure S1: Air quality factors on each day during the sampling periods: A, spring; B, late summer.

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Abbreviations

PAHs	polycyclic aromatic hydrocarbons
NOAA	National Oceanic and Atmospheric Administration
NSAAQS	National Secondary Ambient Air Quality Standards
PM _{1.1}	fine particles with a diameter of 1.1 µm or less
PM _{1.1–2.0}	fine particles with sizes from 1.1 to 2.0 µm
PM _{2.0–3.3}	fine particles with sizes from 2.0 to 3.3 µm
PM _{2.0}	fine particles with sizes equal and below 2.0 µm
PM _{2.5}	fine particles with sizes equal and below 2.5 µm
PM _{3.3–7.0}	fine particles with sizes from 3.3 to 7.0 µm
HYSPLIT	Hybrid Single Particle Lagrangian Integrated Trajectory
GC-MS	Gas Chromatography-Mass spectrometry
GDAS	Global Data Assimilation System
USEPA	United States Environmental Protection Agency
LMW PAHs	low molecular weight PAHs
MMW PAHs	middle molecular weight PAHs
HMW PAHs	high molecular weight PAHs
TEF	toxic equivalency factors
CANPAHs	carcinogenic PAHs
COMPAHs	combustion-derived PAHs group
BaP-TEQ	carcinogenic equivalent
DB[a,h]A	Dibenz[a,h]anthracene
BaP	Benzo[a]pyrene
BaA	Benzo[a]anthracene
BbF	Benzo[b]fluoranthene
BkF	Benzo[k]fluoranthene
IcdP	Indeno[1,2,3-c,d]pyrene
ANT	Anthracene
BghiP	Benzo[g,h,i]perylene
CHR	Chrysene
FLA	Fluoranthene
FL	Fluorene
PYR	Pyrene
PHE	Phenanthrene
LADD	lifetime average daily intake
ILCR	individual lifetime cancer risk
N	north
S	south
E	east
W	west
WD	wind direction

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