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## Technical Information

# Characteristics and Health Risks of Particulate Polycyclic Aromatic Hydrocarbons and Nitro-polycyclic Aromatic Hydrocarbons at Urban and Suburban Elementary Schools in Shanghai, China

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**ABSTRACT** PM<sub>2.1</sub> was collected at urban and suburban elementary schools in Shanghai during two sampling periods in cold and warm seasons in 2007. Nine polycyclic aromatic hydrocarbons (PAHs) and ten nitro-polycyclic aromatic hydrocarbons (NPAHs) in PM<sub>2.1</sub> were determined. During both seasons, the concentrations of PAHs and NPAHs at urban and suburban schools were not significantly different ( $p > 0.05$ ) and were higher in the cold period than in the warm period. According to the diagnostic ratios, PAHs and NPAHs at both schools were subject to the mixed effects of vehicle emission and coal combustion during both periods. Moreover, the results of the backward trajectory showed that PAHs and NPAHs were more susceptible to external polluted air masses in the cold period. At both urban and suburban schools, the inhalation cancer risk of PAHs and NPAHs in PM<sub>2.1</sub> for children during elementary period was dozens of times of the acceptable risk level regulated by the U.S.EPA, highlighting the adverse impact of exposure to PAHs and NPAHs on the healthy development of children.

**KEY WORDS** Children, Fine particles, Vehicle emission, Coal combustion, Toxicity equivalent factor, Exposure parameter, Inhalation cancer risk

## 1. INTRODUCTION

Epidemiological findings have revealed the association of atmospheric particulate pollution with increased morbidity and mortality from cardiopulmonary diseases (Li *et al.*, 2018; Feng and Yang, 2012). Short-term particulate exposure has been found to cause a decrease in global DNA methylation levels in the lungs and heart, while long-term exposure could jeopardize more organs (Li *et al.*, 2019). The potential toxicity of atmospheric particles depends primarily on the size and chemical composition of the particles. Smaller particles, such as PM<sub>2.5</sub>, can deposit effectively in the alveoli and enter the bloodstream circulation, exhibiting a broader range of toxic effects (Möller *et al.*, 2008). The cytotoxicity and genotoxicity of particles are linked with its organic components, and polycyclic aromatic hydrocarbons (PAHs) have a stake in the carcinogenic activity of particles

(Liu *et al.*, 2016). PAHs are widely derived from incomplete combustion of organic materials (Zhang *et al.*, 2020). Some PAHs are carcinogenic and/or mutagenic. For example, benzo[*a*]pyrene (BaP) has been identified as a human carcinogen (Group 1) by the International Agency for Research on Cancer; benz[*a*]anthracene (BaA) and dibenz[*a,h*]anthracene have been classified as probable carcinogens (Group 2A) (IARC, 2019). The nitro derivatives of PAHs (NPAHs), such as 1-nitropyrene (1-NP) and 1,3-, 1,6-, 1,8-dinitropyrenes (DNPs), are considered to have more significant direct-acting mutagenicity (Hayakawa *et al.*, 2018; Ames *et al.*, 1975), increasing the health risk of exposed populations.

Children are a special subgroup of susceptible populations to air pollution, because their physiological functions are still developing (WHO, 2006). Moreover, children were found a higher particulate intake and higher levels of PAH biometabolites relative to adults (Zipf *et al.*, 2013). Acute exposure to PAHs was associated with increased respiratory symptoms, and the positive correlation between symptoms and PAHs exposure levels increased with the exposure duration (Liu *et al.*, 2016). In addition, early exposure to genotoxic carcinogens can lead to a higher lifetime risk of cancer later in life (Pohl and Abadin, 2008). Therefore, investigating PAH exposure levels in children is of great significance to assess health impacts.

Elementary school is a main exposure microenvironment for children, where they spend 6 to 10 h a day. Based on available data, Asian children are exposed to higher levels of particles and PAHs in elementary school than children in Europe, North America and Oceania, and children in polluted cities are at higher health risks (Oliveira *et al.*, 2019; Zhang *et al.*, 2019). Shanghai is one of the most developed cities in China and the economic center of Yangtze River Delta Agglomeration. The annual average concentration of PM<sub>10</sub> was ranged from 51 to 88 µg/m<sup>3</sup> (2007 to 2018) and that of PM<sub>2.5</sub> was ranged from 36 to 62 µg/m<sup>3</sup> (2013 to 2018) (Shanghai MBEE, 2019). These levels exceeded the guidelines of WHO (2006), posing a potential threat to human health. In addition, more than 80% of particulate PAHs and NAPHS were distributed in PM<sub>2.5</sub> in Shanghai (Tang *et al.*, 2013). They were mainly affected by local vehicle emissions (Tang *et al.*, 2013), and homologues such as benzo[*b*]fluoranthene (BbF) and 1-NP released by this high-temperature combustion have relatively high carci-



**Fig. 1.** Location of Changyi (CY) and Baolin (BL) elementary schools in Shanghai.

nogenicity (IARC, 2019) and increase the health risk. However, there is a lack of research on particulate PAHs and NPAHs at elementary schools in Shanghai. Therefore, the purpose of this study was to clarify the concentration and distribution characteristics of particulate PAHs and NPAHs at urban and suburban elementary schools in Shanghai, to identify their main sources, and to estimate the health risks during elementary school years.

## 2. MATERIALS AND METHODS

### 2.1 Particulate Sampling

Particulate sampling was operated simultaneously at two elementary schools (Fig. 1): Changyi elementary school (CY; 31.2°N, 121.5°E) is located in the Pudong New District (urban site); Baolin 3rd elementary school (BL; 31.4°N, 121.4°E) is located in the Baoshan District (suburban site). These two elementary schools are both in residential areas and near the roads. The distance between two schools is about 25 km. PM<sub>2.1</sub> (particulate matters having an aerodynamic diameter of 2.1 µm or smaller) was collected by using Andersen low-volume air samplers (AN-200, Sibata Sci. Tech.,

Tokyo, Japan) at a flow rate of 28.3 L/min, loading on quartz fiber filters (2500QAT-UP, Pallflex Products, Putnam, CT, U. S. A.) with the diameter of 80 mm. Samplers were settled in the flag-raising platform of each school and were 1 m above the floor. In order to bypass the winter and summer vacations and avoid interfering with routine schoolwork, the sampling was operated for one week in the first and second semesters (two semesters per academic year), respectively. Twenty-four-hour sampling started at 14:00. The sampling in the cold period was performed from Mar. 18 to 25, 2007. The sampling in the warm period was performed from Sep. 12 to 17, 2007 at CY and from Sep. 10 to 17, 2007 at BL.

## 2.2 Chemicals

U.S. EPA 610 PAHs mix, including fluoranthene (Flu), pyrene (Pyr), BaA, chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), BaP, benzo[*ghi*]perylene (BgPe), indeno[1,2,3-*cd*]pyrene (IDP), was purchased from Supelco Park (Bellefonte, PA, USA). Two internal standards for PAHs (Pyr-*d*<sub>10</sub> and BaP-*d*<sub>12</sub>) were purchased from Wako Pure Chemicals (Osaka, Japan). Eleven NPAHs including 2-nitrofluorene (2-NF), 9-nitroanthracenes (9-NA), 1-, 4-NPs, 6-nitrochrysene (6-NC), 7-nitrobenz[*a*]anthracene (7-NBaA), 6-NBaP, 1-nitroperylene (1-NPer) and DNPs, the internal standard for NPAHs, 2-fluoro-7-nitrofluorene (FNF), were purchased from Chiron AS (Trondheim, Norway). All additional reagents were analytical reagent grade.

## 2.3 PAHs and NPAHs Analysis

The methods employed for detecting PAHs and NPAHs in PM<sub>2.5</sub> samples were detailed in our previous studies (Tang *et al.*, 2013, 2005, 2003). In brief, each filter (with an area of 50.3 cm<sup>2</sup>) was cut into small pieces and placed in a flask with benzene/ethanol (3:1, v/v) solution. 100 µL of each internal standard (Pyr-*d*<sub>10</sub>, 0.14 mM and BaP-*d*<sub>12</sub>, 0.11 mM for PAHs, FNF, 0.01 mM for NPAHs) was then introduced into the flask. After two 15 min-ultrasound extractions, the extract was filtered onto filter paper (Advantec, Toyo No. 6, Toyo Roshi Kaisha, Ltd., Tokyo, Japan). The filtrate was then washed sequentially with 5% (v/v) sodium hydroxide solution, 20% (v/v) sulfuric acid solution, and twice with ultrapure water. After filtering the organic solution with a hydrophobic membrane (pore size

0.45 µm, Kanto Chemical Co., Tokyo, Japan), the filtrate was concentrated to 100 µL with 100 µL of dimethyl sulfoxide using a rotation evaporator and then diluted to 1 mL with ethanol. An aliquot (20 µL for PAHs, 100 µL for NPAHs) of the solution was injected into a high-performance liquid chromatographic (HPLC) system for quantitative determination.

PAHs were determined by an HPLC equipped with a fluorescence detector and a reversed-phase column (Inertsil ODS-P, 4.6 i.d. × 250 mm, GL Sciences Inc., Tokyo, Japan). The mobile phase was a mixture of acetonitrile and water with a gradient concentration of acetonitrile. The flow rate was 1 mL/min. The running program of the fluorescence detector was set manually based on the optimum excitation and emission wavelengths for each PAH. NPAHs were determined by an HPLC equipped with a chemiluminescence detector and two reversed-phase columns (Cosmosil 5C18-MS, 4.6 i.d. × (250 + 150) mm, Nacalai Tesque, Tokyo, Japan). The eluent was an imidazole buffer (0.68 g/L, pH = 7.6)/acetonitrile (1:1, v/v) mixture with a flow rate of 1 mL/min. The chemiluminescence reagent solution was prepared by dissolving bis (2,4,6-trichlorophenyl) oxalate and hydrogen peroxide into acetonitrile. The flow rate was 1 mL/min. Other conditions were consistent with our previous studies (Tang *et al.*, 2013, 2005, 2003).

## 2.4 Quality Assurance and Quality Control

Before particulate sampling, quartz fiber filters were heated at 600°C for 6 h and then balanced in a desiccator with constant temperature (21.5 ± 1.5°C) and humidity (50 ± 5%) and protected from light for 48 h. After sampling, the filters were balanced under the same conditions and then were stored at -20°C until analysis. During sample collection, blank and sample filters were pretreated using the identical methods and taken to the sampling site to check the background variance. No contamination occurred during the filters' storage and transportation. The relative standard deviation (RSD) (*n* = 7 in the cold period, *n* = 5 for CY and *n* = 7 for BL in the warm period) for the blanks was less than 5%. The concentration of each compound was calculated by deducting the corresponding field blank from the measurement.

Before detecting PAHs and NPAHs, standard solutions were injected into the systems for method validation. The correlation coefficients for the calibration

curves of all PAHs and NPAHs were greater than 0.995 and the RSD ( $n=3$ ) was less than 5%. Internal standards were used to calibrate the recovery and quantification of each PAH and NPAH. The recoveries ranged from 80 to 120%. The limit of determination and limit of quantification of each PAH and NPAH were presented in our previous studies (Tang *et al.*, 2013, 2005, 2003).

## 2.5 Inhalation Cancer Risk Calculation

The BaP equivalent toxicity ( $BaP_{eq}$ ) concentration of the mixture of PAHs and NPAHs in  $PM_{2.1}$  was calculated using the toxicity equivalent factor (TEF) method (U.S. EPA, 2010; OEHHA, 2005):

$$BaP_{eq} = \sum(C_i \times TEF_i) \quad \text{Eq. (1)}$$

where  $C_i$  is the concentration of each individual PAH and NPAH in  $PM_{2.5}$  ( $\text{ng}/\text{m}^3$ );  $TEF_i$  is the toxic equivalent potency of each individual PAH and NPAH relative to BaP. In this study, the  $BaP_{eq}$  is the sum of 9 PAHs and 7 NPAHs. TEFs of PAHs and NPAHs were collected from documents and literature (U.S. EPA, 2010; OEHHA, 2005; Durant *et al.*, 1996).

The inhalation CR of exposure to PAHs and NPAHs in  $PM_{2.1}$  for children during elementary education was calculated according to the guidelines of the U.S. EPA (2005) and OEHHA (2005):

$$CR = \frac{CPF_{BaP} \times IR}{BW \times 10^6} \times \frac{\sum_{cold+warm} [\sum(BaP_{eq} \times ET) \times EF] \times ED}{AT} \quad \text{Eq. (2)}$$

where  $CPF_{BaP}$  is the inhalation cancer potency factor of BaP,  $3.9 (\text{mg}/\text{kg}/\text{d})^{-1}$  (OEHHA, 2005); IR is the daily inspiration rate,  $12.2 \text{ m}^3/\text{d}$  (MEE, 2016); BW is the average body weight of the children aged 6 to 12 years,  $33.8 \text{ kg}$  (MEE, 2016);  $10^6$  is the conversion factor between mg and ng; ET is the daily exposure time,  $6 \text{ h}/\text{d}$ ; EF is the one year exposure frequency,  $90 \text{ d}/\text{a}$  in the cold season,  $180 \text{ d}/\text{a}$  in the warm season; ED is the exposure duration,  $6 \text{ a}$ ; AT is the lifetime (70 years) average exposure time,  $613,200 \text{ h}$  (U.S. EPA, 2005). ET, EF and ED are provided by the schools.

## 2.6 Data Analysis

Statistics were performed using SPSS version 24.0 (IBM Corp., Armonk, NY, U.S.). Differences in concentration between urban and suburban elementary schools and between cold and warm periods were eval-

uated using a Mann-Whitney U test. A  $p$ -value of less than 0.05 indicates that the results are statistically significant. The backward trajectory model (HYSPPLIT-WEB, Internet-based, the NOAA Air Resources Laboratory) was used to trace the transport routes of air masses to Shanghai during the sampling periods. The backtracking time was set to 24 h in the cold and warm periods. An altitude of 500 m above ground level in Shanghai was chose for calculations.

## 3. RESULTS AND DISCUSSION

### 3.1 Concentration of $PM_{2.1}$ , PAHs and NPAHs

The mean concentration  $\pm$  standard deviation (SD) of  $PM_{2.1}$ , PAHs and NPAHs at CY and BL during the sampling periods are given in Table 1. The mean  $PM_{2.1}$  concentration at CY was  $71.6 \pm 56.4 \mu\text{g}/\text{m}^3$  and  $59.2 \pm 15.5 \mu\text{g}/\text{m}^3$  in the cold and warm periods, respectively.  $PM_{2.1}$  was in lower levels at BL than those at CY during both periods, but there were no significant special differences ( $p > 0.05$ ). The mean  $PM_{2.1}$  level at both CY and BL during sampling in different seasons were 2 to 3 times the guideline value of  $PM_{2.5}$  ( $25 \mu\text{g}/\text{m}^3$ ) regulated by WHO (2006), suggesting that  $PM_{2.1}$  at these two schools increased health risks for children.

The mean concentration of PAHs (Table 1) was  $7.91 \pm 4.78 \text{ ng}/\text{m}^3$  and  $1.98 \pm 0.45 \text{ ng}/\text{m}^3$  at CY in the cold and warm periods, respectively, which was  $8.43 \pm 7.68 \text{ ng}/\text{m}^3$  and  $2.10 \pm 0.20 \text{ ng}/\text{m}^3$  at BL in the cold and warm periods, respectively. The mean concentration of NPAHs were  $344 \pm 178 \text{ pg}/\text{m}^3$  (cold period) and  $162 \pm 42.7 \text{ pg}/\text{m}^3$  (warm period) at CY, and were  $405 \pm 293 \text{ pg}/\text{m}^3$  (cold period) and  $133 \pm 33.6 \text{ pg}/\text{m}^3$  (warm period) at BL. There were no significant differences ( $p > 0.05$ ) in the concentrations of PAHs and NPAHs between the urban school (CY) and suburban school (BL).

### 3.2 Variation between Sampling Periods

The concentrations of  $PM_{2.1}$  at CY and BL were higher in the cold period than in the warm period with no significant differences ( $p > 0.05$ ). Dissimilarly, the concentrations of PAHs and NPAHs in  $PM_{2.1}$  at both schools were significantly higher in the cold period than in the warm period ( $p < 0.01$ ). And the contents of PAHs and NPAHs in  $PM_{2.1}$  were 2 to 4 times higher in the cold period than in the warm period. These find-

**Table 1.** Mean concentration and standard deviation (SD) of PM<sub>2.1</sub>, PAHs and NPAHs at CY and BL during the sampling periods.

Compound	CY		BL	
	Cold ( <i>n</i> <sup>a</sup> =7)	Warm ( <i>n</i> =5)	Cold ( <i>n</i> =7)	Warm ( <i>n</i> =7)
PM <sub>2.1</sub> (μg/m <sup>3</sup> )	71.6±56.4	59.2±15.5	62.9±56.2	49.9±13.5
PAHs (ng/m <sup>3</sup> )	Flu	0.48±0.34	0.18±0.07	0.62±0.51
	Pyr	0.40±0.31	0.17±0.05	0.57±0.49
	BaA	0.31±0.20	0.05±0.02	0.38±0.34
	Chr	0.56±0.34	0.13±0.04	0.66±0.48
	BbF	1.74±0.90	0.35±0.09	1.70±1.65
	BkF	0.56±0.36	0.12±0.03	0.60±0.57
	BaP	0.57±0.49	0.12±0.03	0.77±0.84
	BgPe	2.06±1.25	0.54±0.11	1.95±1.86
	IDP	1.24±0.84	0.32±0.07	1.18±1.15
	Total PAHs	7.91±4.78	1.98±0.45	8.43±7.68
NPAHs (pg/m <sup>3</sup> )	2-NF	147±68.2	83.8±24.1	207±147
	9-NA	50.4±33.1	8.59±3.33	32.0±30.2
	1-NP	27.7±14.9	38.9±24.8	38.1±27.8
	4-NP	2.65±2.10	2.06±1.51	4.04±5.70
	6-NC	37.9±18.7	13.3±4.60	59.1±39.8
	7-NBaA	71.8±52.9	12.3±2.95	54.9±64.5
	6-NBaP	4.20±2.57	1.67±0.27	6.67±4.95
	1-NPer	0.86±0.97	0.33±0.05	0.76±1.01
	1,6-DNP	0.03±0.03	0.02±0.04	0.12±0.09
	1,8-DNP	0.33±0.32	0.07±0.03	0.35±0.26
	1,3-DNP	0.78±0.69	0.60±0.14	0.75±0.77
	Total NPAHs	344±178	162±42.7	405±293
				133±33.6

<sup>a</sup>Number of samples.

ings suggest the difference in the sources and atmospheric behavior of PM and PAHs and NPAHs. 4-ring PAHs, such as Flu and Pyr, and 3-ring NAPHS, such as 2-NF and 9-NA, have a higher vapor pressure (Araki *et al.*, 2009) and are more easily volatilized from the particle surface in the warm period with higher ambient temperatures (24.8–26.1°C, obtained from the National Climatic Data Center, NOAA, <http://www.ncdc.noaa.gov/>). Moreover, weather conditions in warm seasons are more conducive to photochemical degradation of PAHs and NPAHs (Tang *et al.*, 2013). In contrast, low temperatures (6.6–18.7°C) and weak high pressures above the ground (1010.4–1025.8 hPa) in the cold period caused unfavorable dilution conditions (Bandowe *et al.*, 2014) and made PAHs and NPAHs more prone to accumulate in PM<sub>2.1</sub>. It is worth mentioning that the concentrations of PM<sub>2.1</sub>, PAHs and NPAHs had large SD in the cold period, which was caused by their high concentrations from Mar. 23 to 25. According to the results of backward trajectories (Fig. 2), there were air masses that migrated from the industrial cities located in south of Shanghai on Mar. 23 and transported long distances

from northern China on Mar. 24 and 25. Due to heavy energy consumption and air pollution in the cold season in northern China (Tang *et al.*, 2013), the polluted air masses that transported to Shanghai were partly responsible for the higher concentration values and SD of PM<sub>2.1</sub>, PAHs and NPAHs in the cold period.

During both sampling periods, the proportion of 5- and 6-ring PAHs was higher than that of 4-ring PAHs, showing the feature of high-temperature combustion process (such as vehicle engines), which was consistent with the previous report (Tang *et al.*, 2013). Meanwhile, this composition highlights the higher health risks (Hayakawa, 2016). BgPe was the most abundant compound in PAHs, followed by BbF and IDP, with no difference in sampling site or period. In different periods, the dominant NPAH homolog was 2-NF, a possible carcinogen to humans (IARC, 2019), accounting for 42.8%–51.8% and 51.3%–65.6% of NPAHs at CY and BL, respectively. The remaining NPAHs showed composition variations between different sampling periods. For example, the contents of 9-NA and 7-NBaA in NAPHS increased from the cold period to the warm

**Table 2.** Diagnostic ratios of (a) PAHs and NPAHs at CY and BL during the sampling periods and (b) different sources reported in previous studies.

(a)

Diagnostic ratio	CY		BL	
	Cold	Warm	Cold	Warm
[Flu]/([Pyr] + [Flu])	0.54	0.51	0.53	0.51
[BaA]/([Chr] + [BaA])	0.35	0.27	0.34	0.35
[BbF]/([BbF] + [BkF])	0.77	0.75	0.74	0.73
[BaP]/[BaP] + [BgPe])	0.21	0.19	0.28	0.29
[IDP]/([BgPe] + [IDP])	0.37	0.37	0.38	0.38
[1-NP]/[Pyr]	0.06	0.19	0.08	0.13
[6-NBaP]/[BaP]	0.007	0.01	0.01	0.005

The ratios were calculated using molar concentration of each compound.

(b)

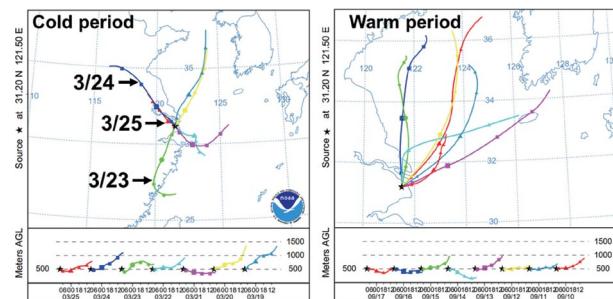
Source	Gasoline-engine	Diesel-engine	Coal stove
[Flu]/([Pyr] + [Flu])	0.4 <sup>a</sup>	0.60–0.70 <sup>b</sup>	0.36–0.53 <sup>c</sup>
[BaA]/([Chr] + [BaA])	0.22–0.55 <sup>d</sup>	0.38–0.64 <sup>b</sup>	0.18–0.38 <sup>c</sup>
[BbF]/([BbF] + [BkF])	0.52–0.60 <sup>e</sup>		0.81–0.95 <sup>c</sup>
[BaP]/[BaP] + [BgPe])		0.23–0.28 <sup>f</sup>	0.47–0.86 <sup>g</sup>
[IDP]/([BgPe] + [IDP])	0.21–0.22 <sup>h</sup>	0.35–0.70 <sup>b</sup>	0.14–0.32 <sup>c</sup>

<sup>a</sup>Rogge *et al.*, 1993. <sup>b</sup>Sicre *et al.*, 1987. <sup>c</sup>Huang *et al.*, 2014. <sup>d</sup>Simcik *et al.*, 1999. <sup>e</sup>Dickhut *et al.*, 2000. <sup>f</sup>Masclet *et al.*, 1987. <sup>g</sup>Daisey *et al.*, 1979. <sup>h</sup>Khalili *et al.*, 1995.

period, which can be attributed to the enhanced volatility of 9-NA and photochemical activity of 7-NBaA in the warm season (Hayakawa, 2016). On the contrary, the proportions of 1-NP and 4-NP in the total NPAHs were higher in the warm period (22%–24% for 1-NP, 1.2%–1.3% for 4-NP) than in the cold period (8.1%–9.4% for 1-NP, 0.77%–1.0% for 4-NP), probably due to the faster photochemical conversion of their precursors in the warm season (Hayakawa, 2016).

### 3.3 Main Sources

The composition of produced PAHs and NPAHs varies with combustion processes, thus the characteristic ratios between PAH and NPAH in airborne particles contribute to distinguish their main sources (Tang *et al.*, 2017). In this study, seven diagnostic ratios were used to determine the primary sources of PAHs and NPAHs at CY and BL during the sampling periods, and the results are presented in Table 2a. The PAH ratios at CY and BL were consistent and showed no variation between different periods. Compared with the source-ratio correspondence reported in previous studies (Table 2b), the [Flu]/([Pyr] + [Flu]) and [BbF]/([BbF] + [BkF]) ratios indicated emission from coal stoves (Huang *et al.*, 2014), the [BaP]/(BaP) +



**Fig. 2.** Back trajectories at 500 m above Shanghai during the sampling periods by using HYSPLIT-WEB model provided by the Air Resources Laboratory, NOAA. (A).

[BgPe]) and [IDP]/([BgPe] + [IDP]) ratios indicated emission from diesel engines (Masclet *et al.*, 1987; Sicre *et al.*, 1987), while the [BaA]/([Chr] + [BaA]) ratio showed the mixed characteristics of coal stove and gasoline engine emissions (Huang *et al.*, 2014; Simcik *et al.*, 1999). These results suggest that PAHs at both schools were subject to a mixture of vehicle emissions and coal combustion in the cold and warm periods.

The ratio of a NPAH (such as 1-NP and 6-NBaP) to its parent PAH (pPAH, correspondingly Pyr and BaP) can be used to determine the relative significance of

**Table 3.** Mean and SD of BaP-equivalent toxic concentration of PAHs and NPAHs at CY and BL during the sampling periods.

Compound	TEF	CY		BL	
		Cold ( <i>n</i> =7)	Warm ( <i>n</i> =5)	Cold ( <i>n</i> =7)	Warm ( <i>n</i> =7)
Flu	0.001 <sup>a</sup>	0.48±0.34	0.18±0.07	0.62±0.51	0.21±0.06
Pyr	0.001	0.40±0.31	0.17±0.05	0.57±0.49	0.20±0.04
BaA	0.1	31.0±20.2	5.10±1.61	38.2±33.6	8.24±1.18
Chr	0.01	5.62±3.36	1.34±0.40	6.60±4.80	1.58±0.29
BbF	0.1	174±90.3	34.7±8.69	170±165	33.8±3.35
BkF	0.1	55.5±35.6	11.8±3.41	59.6±57.5	12.4±1.21
BaP	1	569±485	116±31.7	775±844	182±19.5
BgPe	0.1	206±125	54.0±11.0	195±186	50.1±5.87
IDP	0.01	12.4±8.41	3.24±0.69	11.8±11.5	3.03±0.36
Total PAHs		1060±758	227±55.6	1260±1290	291±23.3
2-NF	0.01 <sup>b</sup>	1.47±0.68	0.84±0.24	2.07±1.47	0.87±0.17
9-NA	0.0032 <sup>c</sup>	0.16±0.11	0.03±0.01	0.10±0.10	0.005±0.02
1-NP	0.1	2.77±1.49	3.89±2.48	3.81±2.78	2.98±2.37
4-NP	0.1	0.31±0.19	0.26±0.11	0.71±0.60	0.25±0.11
6-NC	10	379±187	133±46.0	591±3.98	78.7±5.69
1,6-DNP	10	0.39±0.28	0.57±0.40	1.32±0.84	0.28±0.18
1,8-DNP	0.1	0.03±0.03	0.007±0.003	0.04±0.03	0.008±0.006
Total NPAHs		384±189	138±48.2	600±403	83.0±5.81
Total		1440±929	365±96.5	1860±1640	374±22.7

<sup>a</sup>TEFs of PAHs were collected from U.S. EPA (2010). <sup>b</sup>TEFs of NPAHs were collected from OEHHA (2005). <sup>c</sup>TEF of 9-NA was collected from Durant *et al.* (1996).

vehicle exhaust and coal combustion to PAHs and NPAHs. Evidence shows that the NPAH/pPAH ratio of coal combustion is orders of magnitude lower than that of vehicle exhaust (Hayakawa *et al.*, 2018). And Tang *et al.* (2005) found 0.001 of [1-NP]/[Pyr] ratio in coal burning smoke and 0.36 in vehicle exhaust. As shown in Table 2a, the [1-NP]/[Pyr] ratio at two schools consistently suggests the higher contributions of coal combustion in the cold period and vehicle emission in the warm period. The instruction of [6-NBaP]/[BaP] ratio at CY was consistent with the [1-NP]/[Pyr] ratio, while the [6-NBaP]/[BaP] ratio at BL showed the opposite temporal trend. In addition, the promoted conversion of PAHs to NPAHs in the warm period may also lead to an increase in the NPAH/pPAH ratio, which affects the identification of primary sources (Kameda, 2018).

Due to the influence of the East Asian monsoon, air pollution in Shanghai is susceptible to external pollution sources (Wang *et al.*, 2016). As shown in Fig. 2, in the cold period, polluted air masses from industrial cities south to Shanghai and northern China were found arriving in Shanghai, which enhanced the pollution in Shanghai, as discussed in section 3.2. In the warm period, the air masses mainly came over or passed through

the sea, which had a dilution effect on air pollutants in Shanghai (Wang *et al.*, 2016). The impact of external pollution sources on PAHs and NPAHs at the two schools was greater in the cold period.

### 3.4 Inhalation Cancer Risk

Since the available values of TEF are limited, BaP<sub>eq</sub> concentrations of 9 PAH and 7 NPAH compounds were calculated, results are shown in Table 3. During both periods, the mean BaP<sub>eq</sub> concentration at BL was higher than that at CY. The mean BaP<sub>eq</sub> concentration in the cold period was 4 to 6 times that in the warm period at both CY and BL, indicating a relatively higher health risk in cold seasons. PAHs contributed more to BaP<sub>eq</sub> concentration than NPAHs, with a proportion of 73.3% and 62.1% at CY in the cold and warm periods, respectively, and 67.7% and 77.8% at BL in the cold and warm periods, respectively. Different from previous reports (Bandowe *et al.*, 2014; Wang *et al.*, 2011), NPAHs had a considerable contribution to BaP<sub>eq</sub> concentration in this study, accounting for 26.7% and 37.9% at CY in the cold and warm periods, and 32.3% and 22.2% at BL in the cold and warm periods. This finding suggests that NPAHs in PM<sub>2.5</sub> at both schools were the important risk factor for children health. At

CY and BL, BaP had the highest  $\text{BaP}_{eq}$  concentration among PAHs during both periods, followed by BgPe and BbF, and the most critical compound in NPAH was 6-NC. These four compounds accounted for more than 90% of the total  $\text{BaP}_{eq}$  concentration.

The inhalation CR of PAHs and NPAHs in  $\text{PM}_{2.1}$  for children during elementary period was calculated based on the exposure parameters of children aged 6 to 12 years in Shanghai (MEE, 2016) and the school schedule. The inhalation CR for children was  $1.61 \times 10^{-5}$  at CY, and was  $1.93 \times 10^{-5}$  at BL, both exceeded the acceptable level ( $10^{-6}$ ) regulated by U.S. EPA (2010), indicating that the exposure of children to PAHs and NPAHs during school time may have adverse effects on their healthy development. In addition, although the exposure length during the cold season (90 d) was half that during the warm season (180 d), concentrations of PAHs and NPAHs were higher during the cold season. Thus, the inhalation CR caused by exposure to PAHs and NPAHs during the cold season was about twice as high as during the warm season in both schools. To protect children's health from particulate PAHs and NPAHs, schools urgently need to pay attention to the exposure environment of children.

#### 4. CONCLUSION

In this study, PAHs and NPAHs in  $\text{PM}_{2.1}$  were observed at urban and suburban elementary schools in Shanghai during two samplings in cold and warm seasons in 2007. During the sampling periods, the concentrations of PAHs and NPAHs at urban and suburban schools had no significant difference ( $p > 0.05$ ) and were higher in the cold period than in the warm period. During both periods, PAHs at the two schools showed consistent composition, the main components were BgPe, BbF and IDP, and NPAHs were dominated by 2-NF. The diagnostic ratios indicate that the sources of PAHs and NPAHs at the two elementary schools were relatively stable in different sampling periods and were subject to the mixed effects of vehicle emission and coal combustion. Moreover, the results of the backward trajectory showed that PAHs and NPAHs were more susceptible to external polluted air masses in the cold period, while in the warm period, clean air flow from the sea contributed to pollutants dilution. The  $\text{BaP}_{eq}$  concentrations of PAHs and NPAHs at the two schools were consistently higher in the cold period than in the

warm period, and the key contributors were BaP, BgPe, BbF and 6-NC. In this study, NPAHs contributed more to the  $\text{BaP}_{eq}$  concentration than previous reports, suggesting that NPAHs in  $\text{PM}_{2.1}$  at both schools was an important risk factor for children health. At the urban and suburban schools, the inhalation CR of PAHs and NPAHs in  $\text{PM}_{2.1}$  for children during elementary period exceeded the acceptable risk level regulated by U.S. EPA, highlighting the adverse impact of exposure to PAHs and NPAHs on the healthy development of children.

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