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$PM_{2.5}$-Bound Polycyclic Aromatic Hydrocarbons (PAHs), Oxygenated-PAHs and Phthalate Esters (PAEs) inside and outside Middle School Classrooms in Xi'an, China: Concentration, Characteristics and Health Risk Assessment

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ABSTRACT

In China, the exposure of children to particulate toxics, like organics, has been poorly investigated mainly due to the technical challenges in sampling and analysis. This article reports indoor and outdoor concentrations of $PM_{2.5}$-bound polycyclic aromatic hydrocarbons (PAHs), oxygenated-PAHs (OPAHs) and phthalate esters (PAEs) monitored for 13 days in May 2012 in two classrooms, A and B, of a middle school at Xi'an, China. Outdoors, the average $PM_{2.5}$ mass was 96.9 μg m^{-3}, while indoor concentrations ranged between 154.7 μg m^{-3} (A) and 120.2 μg m^{-3} (B). Total PAEs, dominated by bis(2-ethylhexyl)phthalate (DEHP) and di-n-butyl phthalate (DBP), were found at much higher concentrations than PAHs and OPAHs, and their outdoor versus indoor distribution followed that of $PM_{2.5}$, ranging from 622.0 ng m^{-3} outdoors, to 808.6 (A) and 864.7 ng m^{-3} (B) indoors. Concentrations of total PAHs were about 50 ng m^{-3} outdoors and indoors, while OPAHs were observed at concentrations of 17.7 outdoors and 15.9 (A) and 19.8 ng m^{-3} (B) indoors. High molecular weight PAHs (i.e., 4-ring, 5-ring and 6-ring) generally accounted for about 80%. Variations of PAHs levels indoors were closely associated with the ventilation and the occupancy rate of the classrooms. Activities on the playground also influenced the indoor organic pollutant concentrations. Intense PAEs sources were evidenced, but outdoor sources also influenced the I/O ratios. Both the PAHs and PAEs inhalation risk estimations demonstrated that there is a non-negligible potential cancer risk for children in their school environment.

Keywords: Indoor/Outdoor; PAHs/OPAHs/PAEs; $PM_{2.5}$; Schoolchildren; Health risks.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) and phthalate esters (PAEs) are two classes of abundant and ubiquitous organic pollutants in the ambient air. They are both linked to adverse health effects and studies have showed that PAHs are toxic, mutagenic, and carcinogenic for humans. Lots of studies also demonstrated that human exposure to PAEs can induce DNA damage for human sperm, change the human semen parameters, and affect reproductive hormones levels (Duty *et al.*, 2003a, b, 2005) and DEHP has been listed as a possible carcinogen to humans (group 2B) by the International Agency for Research on Cancer (IARC, 1982) and U.S. National Toxicology Program (NTP, 1983).

For their negative environmental and health effects, PAHs and PAEs have attracted attention worldwide in the past few years. PAHs mainly originate from the processes of incomplete coal combustions, biomass burning and motor vehicle emissions in ambient air. Studies also showed that ship emissions in port and firework displays during festivals

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contributed for PAHs emissions (Pongpiachan *et al.*, 2015a, 2017). Apart from this, indoor smoking, cooking and gas-fired appliances also emit PAHs. Oxygenated-PAHs (OPAHs) are derivatives of PAHs, and can be directly emitted together with PAHs, or formed through secondary reactions (Keyte *et al.*, 2013). OPAHs can produce reactive oxygen species, which toxicity for humans have been evidenced (WHO, 2003; Chung *et al.*, 2006; Benbrahim-Tallaa *et al.*, 2012; Barrado *et al.*, 2013). PAEs are widely applied in the production of plastics, especially plasticized polyvinylchloride (PVC), but also in building materials, medical devices, personal care products, clothing, food packing, children's toys and so on (Škrbic *et al.*, 2016, Yao *et al.*, 2016). Study also has showed that DEHP is the most used PAEs in China (Meng *et al.*, 2014). Because PAEs are not covalently bound to the products, they can easily release into the environment during the manufacture, use and after disposal. Thus human exposure to PAEs increases with their consumption (Wormuth *et al.*, 2006; Hankett *et al.*, 2014, Gao and Wen, 2016). Moreover, due to their low vapor pressure, PAEs can easily be adsorbed onto aerosols, but also onto indoor surfaces (e.g., furniture) (Weschler and Nazaroff, 2010; Bu *et al.*, 2016). For that latter reason, they have been extensively studied in indoor environments (Weschler, 1980, 1984; Langer *et al.*, 2010). Similarly, indoor PAHs have attracted a large attention from researchers (Maertens *et al.*, 2004; Ong *et al.*, 2007; Mannino and Orecchio, 2008).

Human exposure to these toxics inside the buildings is a key issue with respect to their increasing levels (Guo *et al.*, 2010; Song *et al.*, 2015) and their long dwelling time indoors (Xu *et al.*, 2015). Recent studies have payed attention to human exposure to these indoor pollutants (Wang *et al.*, 2013; Zhang *et al.*, 2014; Song *et al.*, 2015; Wang *et al.*, 2015b). But few studies focused on children, who are more sensitive to respiratory pathologies than adults owing to their immature respiratory system (Kulkarni and Grigg, 2008; Langer *et al.*, 2010) and some studies have assessed the exposure of toxic organics compounds for preschool and school children (Wichmann *et al.*, 2010; Krugly *et al.*, 2014; Pongpiachan *et al.*, 2015b). Out of the home, children spend most of their time at school environment. Therefore air quality at school is expected to affect their body health (Mohamad *et al.*, 2016). The construction year, ventilation facilities, building and decoration materials, the number of students at per school and per classroom, the types of activities, etc., must be considered in the characterization of any school air quality (Xu *et al.*, 2015).

Most of the research works investigating $PM_{2.5}$ exposure in school environments were developed in Europe and the USA, where fine aerosol concentrations are 5 to 10 times lower. For instance, Zhang *et al.* (2012) reported $PM_{2.5}$ levels observed in five schools in South Texas, USA, ranging from 2.8 to 23.2 μg m^{-3}. Wichmann (2010) monitored $PM_{2.5}$, soot, NO_2 and the air exchange rate between outdoors and indoors during winter and summer in six schools and ten preschools in Stockholm, Sweden. They reported average indoor $PM_{2.5}$ levels in schools and preschools of 8.1 and 6.1 μg m^{-3}, while the outdoor $PM_{2.5}$ levels were 9.7 and 7.6 μg m^{-3}, respectively. Similarly, relative low concentrations of $PM_{2.5}$ were obtained in schools from the Netherlands, Italy, Belgium, or in Athens, Greece (Janssen *et al.*, 2001, Diapouli *et al.*, 2008; Stranger *et al.*, 2008; Gatto *et al.*, 2014; Romagnoli *et al.*, 2014). In China, the investigations in the field of outdoor and indoor particulate matter and health indicated that short-term exposure in Shanghai results in increased levels of given circulating biomarkers of inflammation, coagulation/thrombosis, and vasoconstrictions, which intensity increases as particles are finer (Chen *et al.*, 2015). In Beijing, during heavy smog periods, Chen *et al.* (2013) evidenced a statistically significant increase in hospital visits. In Taiyuan, the same group demonstrated that indoor air pollution were determinant in the occurrence of high school pupils' respiratory symptoms (Zhao *et al.*, 2008).

Relative high levels of PAHs were reported by Zivkovic *et al.* (2015) from Serbia in an urban school influenced by traffic air pollutants (421.9 vs. 1017 ng m^{-3} in indoor and outdoor), and in a rural school (271.6 indoors vs. 132.3 outdoors). Krugly *et al.* (2014) investigated that $PM_{2.5}$ bound PAHs were from 20.3 to 131.1 ng m^{-3} in 5 primary schools in Lithuania during heating seasons, which were much higher than that from the schools in Rome and Portugal (Gatto *et al.*, 2014; Romagnoli *et al.*, 2014; Oliveira *et al.*, 2016). In China, works about PAHs in a school environment have been investigated by Xu *et al.* (2015) according to different aerosol size fractions.

Fine particle-bound OPAHs studies have been reported in France (Ringuet *et al.*, 2012), Portugal (Souza *et al.*, 2014) and Greece (Andreou and Rapsomanikis, 2009), at levels comparable to those observed in Beijing and the industrial regions of Northeast China (Lin *et al.*, 2015; Li *et al.*, 2015). Research works provide figures for PAEs in urine samples of schoolchildren in Taiwan, Korea, and Germany (Kasper-Sonnenberg *et al.*, 2014; Kim *et al.*, 2014; Bao *et al.*, 2015). In China, PAEs levels were reported in urine, as well as in $PM_{2.5}$ and PM_{10} in Tianjin (Gu *et al.*, 2010; Kong *et al.*, 2013; Wang *et al.*, 2013; Zhang *et al.*, 2014; Song *et al.*, 2015).

The aims of the this study was to assess the concentrations of indoor and outdoor $PM_{2.5}$ and its bound PAHs, OPAHs, and PAEs in two classrooms of a middle school in Xi'an, that suffers from serious air pollution (Gao *et al.*, 2015). Original indoor/outdoor (I/O) ratios and their variations of PAHs and PAEs are also discussed, and the associated potential health risks for children are finally presented.

MATERIALS AND METHOD

Site and Sampling

The samples were collected in a middle school, located at the southwestern part of Xi'an China and the detailed description of the school is provided by Xu *et al.* (2015). There are no obvious emission sources around the school. Indoor samples were collected inside two neighboring classrooms, similar in design, located at the first floor, and hereafter defined as Indoor A and Indoor B. The sampler was installed on a desk at about 1.2 m at the back of the classrooms, and the outdoor sampling set up was located on rooftop of the same teaching building, 10 m above

ground level and 10 m away the indoor sampling site, in an attempt to minimize the influence from the playground. Five large windows, which were 1.9 m × 1.8 m was open during school hours for ventilation in each classroom, but closed after school time. In addition to the five large windows, there were no other ventilations. There were about 49–51 students aging from 12 to 14 years occupied in each classroom and the school time ranged from 8:00 to 11:30 a.m. and 1:30 to 5:30 p.m. during the sampling time.

Daily $PM_{2.5}$ samples were collected by a $PM_{2.5}$ Mini-Volume sampler (Airmetrics, Springfield, OR, USA) at a flow rate of 5 L min^{-1}, loading on pre-fired (780°C) 47-mm quartz filters (QM/A®, Whatman Inc., U.K.) from 16th May to 30th May 2012. A total of 33 effective samples were collected in this study, which included two blank samples. It stopped sampling at 24th and 25th May for the mid-term examinations. Actually, because of the noises from the sampling pump, which affected the learning efficiency for the students in daytime, it is difficult to assess the long-time exposures for students.

Meteorological Condition

Temperature (T) and relative humidity (H) were got from the National Oceanic and Atmospheric Administration (NOAA), while data of horizontal wind (U) were from the China Meteorological Data websites (http://data.cma.gov.cn) and mixed layer height (MLH) were obtained from European Centre for Medium-Range Weather Forecasts (http://apps.ecmwf.int/datasets/), respectively. Ventilation coefficient (VC) was estimated by multiplying MLH by U, as it corresponds to the transport or dispersion degree of the pollutants (Kompalli *et al.*, 2014; Wang *et al.*, 2016).

PM Gravimetric and Chemical Analyses

$PM_{2.5}$ samples were weighted by an electronic microbalance (Sartorius ME 5-F) purchased from Germany, with a sensitivity of ± 1 μg. The samples were equilibrated in a constant temperature & humidity chamber at 20–23°C and keep relative humidity at 35–45% for at least 24h at before and after sampling. The absolute errors between duplicate weights were ≤ 0.015 and 0.020 mg for blank filters and samples, respectively. Then they were stored in a freezer at < –20°C before analysis. Previous studies provide the appropriate details about aerosol gravimetric (Wang *et al.*, 2015a, 2016).

The organic species PAHs, OPAHs, and PAEs were analyzed by in-injection port thermal desorption (TD) coupled with gas chromatography/mass spectrometry (GC/MS) (Ho *et al.*, 2008; Wang *et al.*, 2015a, 2016). Details regarding the in-injection port TD-GC/MS method are available in Wang *et al.* (2015a).

Quality Assurance and Control (QA/QC)

During sampling periods, the aerosol sampler was checked every day, and field blank filters were collected. Chrysene-d_{12} ($C_{18}D_{12}$) (98%, Sigma-Aldrich, Bellefonte, PA, USA), phenanthrene-d_{10} ($C_{14}D_{10}$) (98%, Aldrich, Milwaukee, WI, USA) and *n*-tetracosane-d_{50} (*n*-$C_{24}D_{50}$) (98%, Aldrich, Milwaukee, WI, USA) were added to each samples as internal standards (IS). The concentrations of PAH and OPAH, and PAEs were quantified by a five-point calibration that was from 1–10 ng, and 20–200 ng (Sigma-Aldrich, Bellefonte, PA, USA), respectively. Replicate samples were analyzed for each ten samples, and the relative standard deviation was from 1.3 to 8.5% for PAHs, OPAHs, and PAEs. The Standard Reference Material 1649a Urban Dust from National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) was used to validate the accuracy of equipment analysis.

Health Risk Assessment Model

Both PAHs and PAEs have been associated with negative human health effects (Škrbic *et al.*, 2016; Wang *et al.*, 2016). Individuals are generally exposed to the $PM_{2.5}$-bound organic species through inhalation, ingestion, or dermal contact (Yu *et al.*, 2015; Yao *et al.*, 2016). The inhalation cancer risk assessments of $PM_{2.5}$-bound PAHs have been evaluated by the carcinogenic potency of the components in PAHs mixtures and its derivatives (Luo *et al.*, 2015; Xia *et al.*, 2013). The human exposures to PAEs through their indoor gas phase, dust or particle have been recently investigated (Zhang *et al.*, 2014; Bu *et al.*, 2016). In this study, the BaP_{eq} was calculated by toxicity equivalency factors from Nisbet and Lagoy (1992). The daily inhalation levels were calculated as:

$$E_I = BaP_{eq} \times IR \quad (1)$$

Then the incremental lifetime cancer risk (ILCR) was used to assess the inhalation risks for students. And it was defined as:

$$\mathrm{ILCR} = (E_I \times SF \times E_D \times cf \times EF)/(AT \times BW) \quad (2)$$

where E_I (ng person^{-1} day^{-1}) is the daily inhalation levels; IR (m^3 d^{-1}) is the inhalation rate, which is 15.2 m^3 d^{-1} for 11–16 years old adolescents; SF is the cancer slope factor of BaP, which was 3.14 (mg kg^{-1} $d^{-1})^{-1}$ for inhalation exposure (Chen and Liao, 2006, Collins *et al.*, 1991); EF (day year^{-1}) represents the exposure frequency (252 day year^{-1}) (USEPA, 2001); E_D (year) acts as the exposure duration, which is 7 for adolescents; cf is a conversion factor (10^{-6}); AT (days) means the lifespan of carcinogens (25,550 days) (USEPA, 2001); and BW is the body weight for target population, with 50.2 kg in this study .

The average daily dose of PAEs in air was calculated by ADD (ng kg^{-1} d^{-1}):

$$\mathrm{ADD} = \frac{C \times IR}{BW} \quad (3)$$

where C is the concentrations of the target pollutants in air (ng m^{-3}), IR and BW are same as the above described (Pei *et al.*, 2013).

The carcinogenic risk (CR) for PAEs was assessed by DEHP, which is identified as a possible carcinogen to humans by the IARC (IARC, 1982; Li *et al.*, 2016).

$$CR = q \times ADD \quad (4)$$

q, the carcinogenic slope factor for DEHP, is 0.014 $(mg\ kg^{-1}\ d^{-1})^{-1}$ (EPA, 1997).

RESULTS AND DISCUSSIONS

Mass Concentrations

The $PM_{2.5}$ mass and concentrations of organic species (19 PAHs, 3 OPAHs, and 7 PAEs) at outside and inside the classrooms are summarized in Table 1 and Fig. 1. Outdoors, $PM_{2.5}$ mass was 96.9 μg m^{-3} on average, and varied from 42.4 to 207.0 μg m^{-3}. Indoors, $PM_{2.5}$ varied over a similar range but with much higher average concentrations (A: 60.4–283.7 μg m^{-3}, average 154.7 μg m^{-3}; 74.6–213.9 μg m^{-3}, average 120.2 μg m^{-3}). There were no obvious differences for two classrooms, as the independent-sample t-test was found above 0.05 (sig. 0.319) (Table S1). Total PAHs did not display significant changes in concentrations between outdoors (52.2 ± 18.0 ng m^{-3}) and indoors (A: 49.7 ± 16.3 ng m^{-3}; B: 50.8 ± 27.8 ng m^{-3}). The t-test for each PAHs congener also displayed that there were no differences between outdoor and indoor classrooms. The OPAHs concentrations, which were found at 17.7 (outdoors), 15.9

Table 1. $PM_{2.5}$ bounded PAHs, OPAHs, and phthalate esters (PAEs) in indoor and outdoor of two classrooms in Xi'an, China.

Pollutants (abbreviation)	Unit	Indoor A (I)[a]	Indoor B	Outdoor (O)
$PM_{2.5}$	μg m^{-3}	154.7 ± 85.1	152.5 ± 80.4	96.9 ± 45.8
acenapthene (ACE)	ng m^{-3}	1.2 ± 0.3	1.3 ± 0.3	1.2 ± 0.4
fluorene (FLO)		1.6 ± 0.4	1.6 ± 0.5	1.6 ± 0.4
phenanthrene (PHE)		3.9 ± 1.2	3.9 ± 1.0	3.6 ± 0.9
anthracene (ANT)		1.5 ± 0.3	1.6 ± 0.2	1.5 ± 0.3
fluoranthene (FLU)		2.8 ± 1.4	2.6 ± 1.5	2.9 ± 1.6
pyrene (PYR)		2.5 ± 1.2	2.4 ± 1.5	2.7 ± 1.5
benzo[a]anthracene (BaA)		2.3 ± 0.6	2.2 ± 0.7	2.3 ± 0.7
chrysene (CHR)		3.2 ± 1.6	3.1 ± 1.8	3.4 ± 1.7
benzo[b]fluoranthene (BbF)		5.1 ± 2.1	5.2 ± 2.6	5.5 ± 2.3
benzo[k]fluoranthene (BkF)		3.6 ± 1.3	3.8 ± 2.0	3.9 ± 1.7
benzo[a]fluoranthene (BaF)		0.8 ± 0.	0.8 ± 0.5	0.8 ± 0.4
benzo[e]pyrene (BeP)		2.6 ± 1.0	2.7 ± 1.4	2.8 ± 1.2
benzo[a]pyrene (BaP)		3.1 ± 1.0	3.1 ± 1.4	3.3 ± 1.2
perylene (PER)		1.2 ± 0.2	1.3 ± 0.3	1.3 ± 0.2
indeno[1,2,3-cd]pyrene (IcdP)		4.6 ± 1.5	4.9 ± 2.0	5.0 ± 1.7
benzo[ghi] perylene (BghiP)		4.6 ± 1.6	4.9 ± 2.3	4.9 ± 1.8
dibenzo[a,h]anthracene (DahA)		2.9 ± 0.6	3.0 ± 0.6	2.9 ± 0.6
coronene (COR)		0.9 ± 0.3	1.0 ± 0.4	1.0 ± 0.3
dibenzo[a,e]pyrene (DaeP)		1.5 ± 0.4	1.5 ± 0.5	1.5 ± 0.4
ΣLMW-PAHs[b]		8.2 ± 2.0	8.3 ± 1.7	7.9 ± 1.7
ΣHMW-PAHs[b]		41.5 ± 14.7	42.5 ± 19.2	44.3 ± 16.8
ΣComb-PAHs[b]		37.6 ± 13.2	38.6 ± 17.3	40.2 ± 15.1
ΣPAHs[a]		49.7 ± 16.3	50.8 ± 27.8	52.2 ± 18.0
9-fluorenone (9FLO)	ng m^{-3}	5.0 ± 1.0	5.5 ± 0.6	5.0 ± 1.2
anthraquinone (ANTQ)		9.2 ± 2.5	12.5 ± 2.2	10.9 ± 2.0
benz[a]anthracene-7,12-dione (BaAQ)		1.7 ± 0.4	1.8 ± 0.5	1.7 ± 0.4
ΣOPAHs[b]		15.9 ± 3.2	19.8 ± 2.3	17.7 ± 3.2
dimethylphthalate (DMP)	ng m^{-3}	30.8 ± 6.7	34.1 ± 3.3	34.5 ± 9.0
diethylphthalate (DEP)		80.1 ± 29.9	56.2 ± 8.8	41.4 ± 11.4
di-n-butyl phthalate (DBP)		255.2 ± 35.9	309.4 ± 47.0	186.9 ± 40.5
benzyl butyl phthalate (BBZP)		42.5 ± 7.8	43.5 ± 6.6	41.4 ± 7.8
bis (2-ethyl(hexyl))phthalate (DEHP)		318.6 ± 230.8	337.8 ± 241.5	236.4 ± 206.3
di-n-octyl phthalate (DNOP)		34.9 ± 6.7	35.4 ± 5.9	33.8 ± 6.5
bis(2-ethylhexyl)adipate (DEHA)		46.5 ± 20.1	48.3 ± 17.9	47.5 ± 15.7
ΣPAEs		808.6 ± 284.8	864.7 ± 293.2	621.9 ± 228.3

[a] Arithmetic mean ± SD; [b] ΣLMW-PAHs is sum of acenapthene, fluorine, phenanthrene, anthracene. ΣHMW-PAHs is sum of fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, perylene, indeno[1,2,3-cd]pyrene, benzo[ghi] perylene, dibenzo[a,h]anthracene, coronene, dibenzo[a,e]pyrene. ΣComb-PAHs is the ΣHMW-PAHs minus pyrene, dibenzo[a,e]pyrene. ΣPAHs is sum of the ΣLMW-PAHs and ΣHMW-PAHs mentioned above. ΣOPAHs is sum of the three detected OPAH: 9-fluorenone, anthraquinone, benz[a]anthracene-7,12-dione. ΣPAEs is sum of dimethylphthalate, diethylphthalate, di-n-butyl phthalate, benzyl butyl phthalate, bis(2-ethyl(hexyl))phthalate, di-n-octyl phthalate, and bis(2-ethylhexyl)adipate.

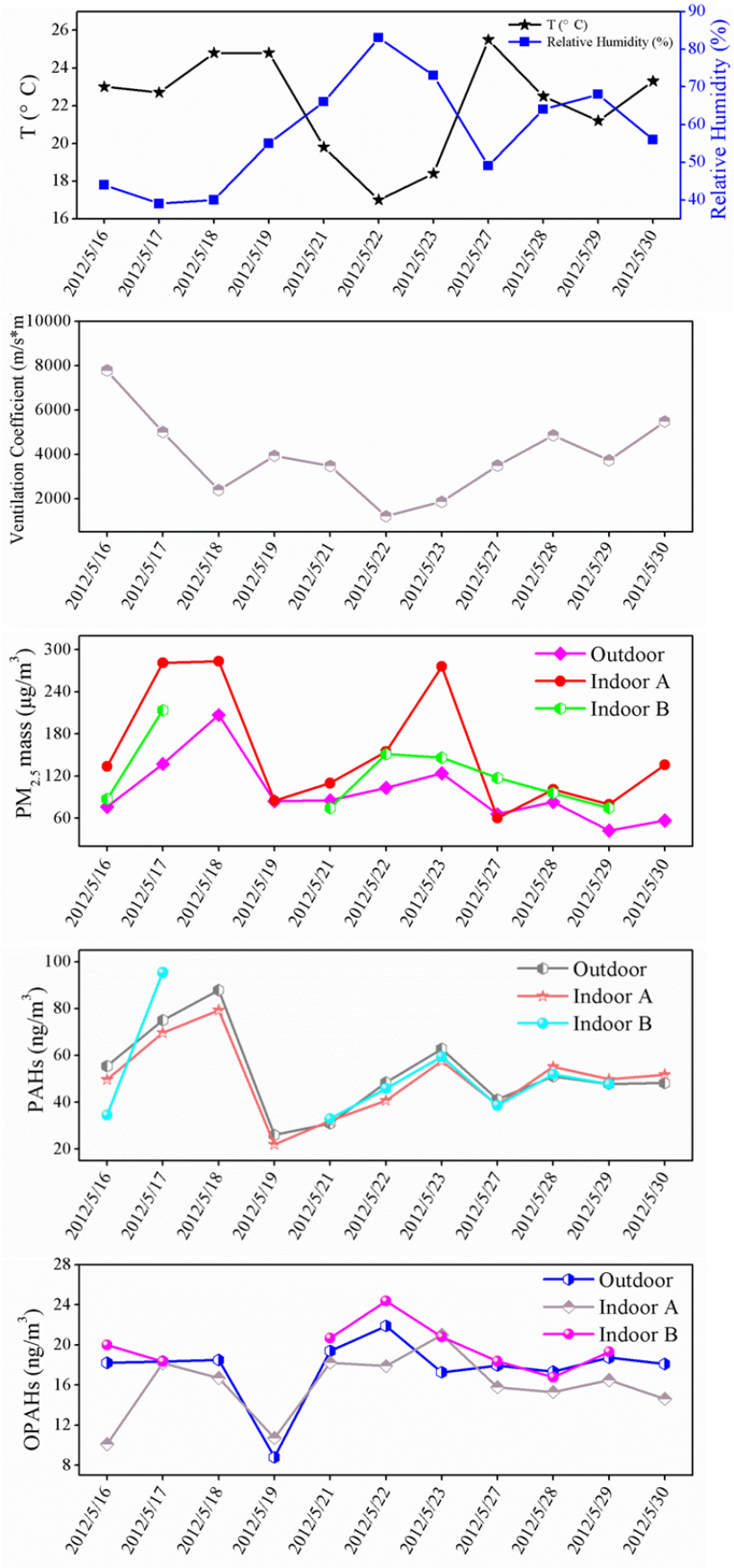

Fig. 1. The variations of climate parameters and concentrations of PAHs, OPAHs, and phthalate esters in $PM_{2.5}$ in two classrooms of middle school in Xi'an.

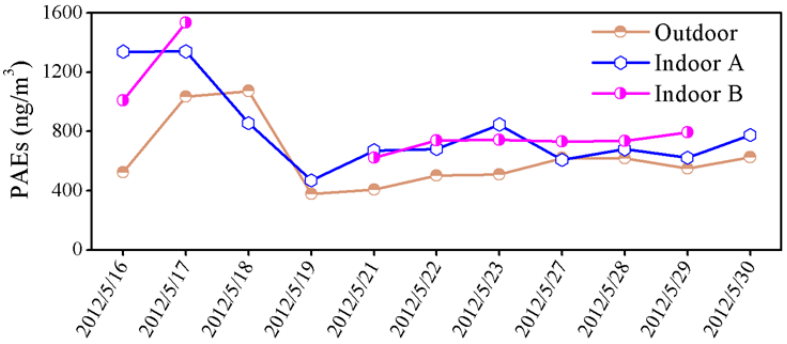

Fig. 1. (*continued*).

(Indoor A) and 19.8 ng m^{-3} (Indoor B), on average. The t-test showed that the OPAHs in indoor A and B have difference, which due to the differences of anthraquinone (ANTQ) (Table S2). But PAEs reached high concentrations at outdoors (622.0 ng m^{-3}) and, even higher levels at indoors (A: 808.6; B: 864.7 ng m^{-3}), much higher than PAHs and OPAHs. Although there were no obvious different for total PAEs, however, the concentrations of diethylphthalate (DEP) and DBP between outdoor and indoor also showed differences.

Indoor and Outdoor Sources

Previous studies indicated that the indoor/outdoor (I/O) ratios can be acted as a represent of the relative intensities of the indoor or outdoor source (Kovacevic *et al.*, 2015; Xu *et al.*, 2015). In this study, $PM_{2.5}$ mass in indoors is about 20–50% higher than in outdoors, and the I/O ratios led to ranges of 0.91–2.40, average: 1.6 (classroom A), and 0.87–1.80, average: 1.4 (classroom B). Studies conducted during heating seasons usually yield to fine aerosol I/O ratios below 1, due to the higher outdoor aerosol concentrations emitted from heating combustion sources (e.g., Zivkovic *et al.*, 2015). The relatively good correlation (R^2 = 0.71, P = 0.00105) between indoor and outdoor aerosol concentrations was assumed to be caused by the re-suspension of the particles deposited in the classrooms originally emitted from outdoor combustion processes (Diapouli *et al.*, 2010; Kovacevic *et al.*, 2015). The diagnostic ratios of ANT/(ANT + PHE), FlU/(FlU + PYR), BaA/(BaA + ChR), IcdP/(IcdP + BghiP), and BaP/BghiP can be used for tracers of possible sources (Pongpiachan, 2015). These ratios in the present study were summarized in Table S3, which demonstrated that the vehicle emission, coal combustion and biomass burning were the main sources.

The I/O ratios of ΣPAHs and ΣOPAHs were close to 1 (0.97 and 0.99, respectively), supporting the hypothesis of well-ventilated classrooms. Interestingly, the I/O ratios for ΣPAEs were from 0.80 to 2.6 (average: 1.4), underlining the predominance of indoor sources. In particular, the average I/O ratios for DEP, DEHP and DBP were all higher than 1 in both classrooms (Fig. 2). For DEHP are generally used as plasticizers in building materials, furniture and plastic toys (Schettler, 2006). DMP and DEP are used in personal care products, adhesives, inks, waxes and coatings, and varnishes (Guo and Kannan, 2013; Net *et al.*, 2015). Painting material applied on the classroom walls is a potential source for PAEs (Guidotti *et al.*, 1998). The plasticizer and the painting materials used in and on the surface of desks and chairs also might the source of PAEs in classrooms.

Chemical Composition of PAHs, OPAHs and PAEs

PAHs and PAEs mass concentrations and chemical composition are showed in Figs. 2 and 3. Total PAHs concentrations were investigated in the range 26.0–87.9 ng m^{-3} at outdoors, 22.0–79.3 ng m^{-3} (A) and 32.9–95.4 ng m^{-3} (B) at indoors. Despite slight discrepancies in their mass concentration variations, compositions of indoor and outdoor PAHs appear overall similar. The low molecular weight (ΣLMW)-PAHs (3-ring) were much lower than the high molecular weight (ΣHMW)-PAHs (4-ring, 5-ring and 6-ring) and the average ratios of ΣHMW-PAHs/ΣLMW-PAHs in outdoors, classrooms A and B were 5.5, 5.1 and 5.1, respectively. ΣHMW-PAHs were the dominant compounds, accounting for 84.0, 83.0 and 82.1% of PAHs in outdoors, and classrooms A and B, respectively. This might due to that LMW-PAHs have relatively higher vapor pressure, thus prefer to distribute in the gaseous phase, while the high molecular weight PAHs are prone to bound to particles. Benzo[b]fluoranthene (BbF) had the highest contribution, contributed about 10% of the ΣPAHs, which followed by indeno[1,2,3-cd]pyrene (IcdP) and benzo[ghi] perylene (BghiP), and they accounted for about 19% of ΣPAHs. Benzo[a]pyrene (BaP), as the indicator of carcinogenic risks, was found outdoors at 3.3 ng m^{-3}, and indoors at 3.1 ng m^{-3}. Those levels are far beyond the air quality standard of 1 ng m^{-3} set by World Health Organization (Gao *et al.*, 2012), which calls for increased attention from both researchers and authorities.

Among OPAHs, ANTQ dominates with concentrations of about 10 ng m^{-3} in all three studied environments, followed by 9-fluorenone (9FLO) (about 5 ng m^{-3}) and benz[a]anthracene-7,12-dione (BaAQ) (less than 2 ng m^{-3}), which are lower than that those reported previously in Xi'an (Wei *et al.*, 2015; Wang *et al.*, 2016). The ratios of 9FLO/fluorene (FLO), ANTQ/ anthracene (ANT), and BaAQ/ benzo[a]anthracene (BaA) provide an indication for oxidation rates for FLO, ANT, and BaA. The values were found to be similar with the results of Wang *et al.* (2016) in Xi'an ambient air. This suggested the important role of secondary formation processes for OPAHs (Shen *et al.*, 2011, 2012, 2013).

PAEs have been widely detected in indoor dust and

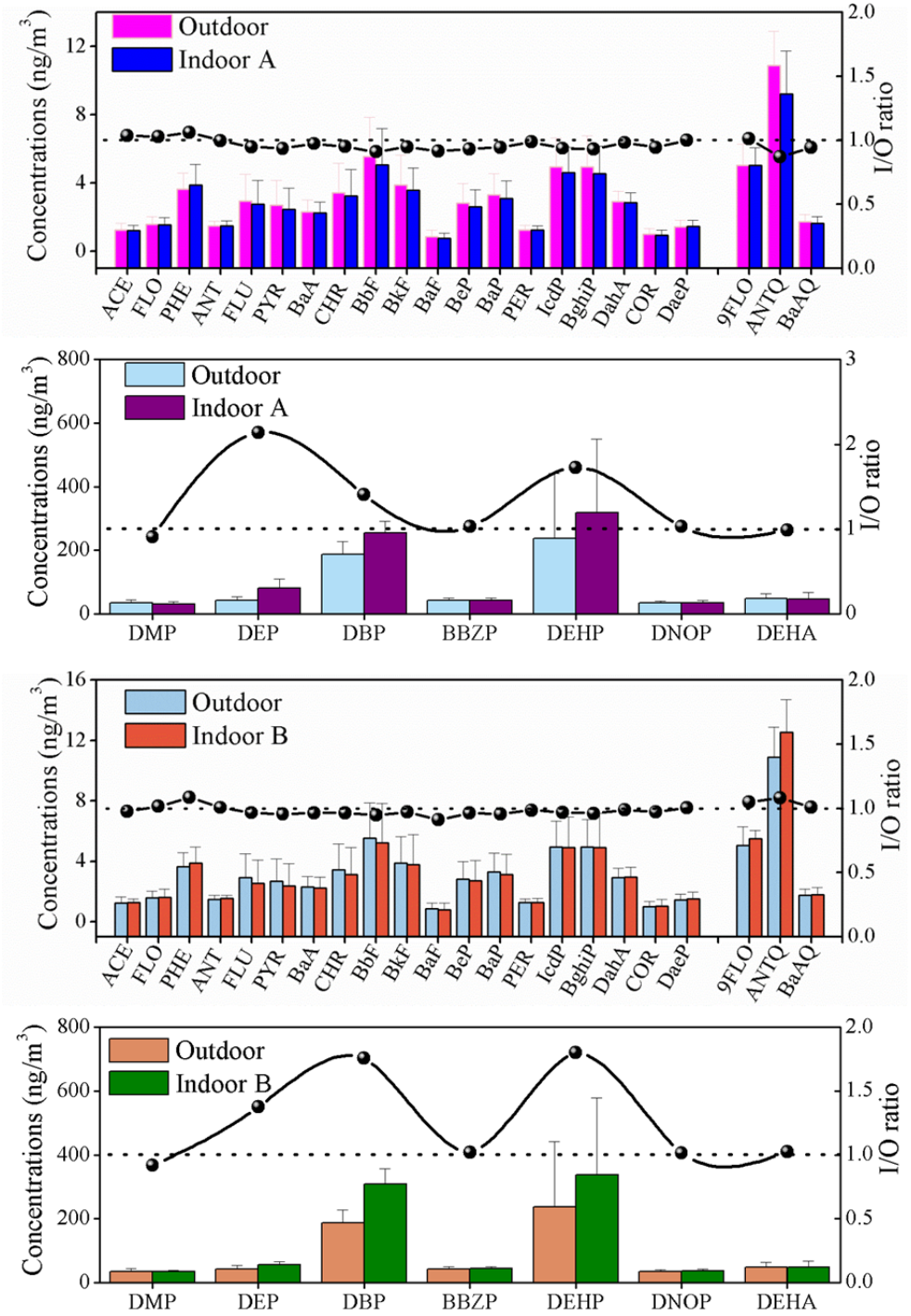

Fig. 2. The characteristics and the Indoor/outdoor (I/O) ratios of PAHs, OPAHs, and PAEs in two classrooms of middle school from Xi'an.

sewage sludge. However, few of them are reported in ambient air. ΣPAEs ranged from 376.6 to 1074 ng m^{-3} in outdoors, from 469.2 to 1341 ng m^{-3} in classroom A, and from 621.7 to 1537 ng m^{-3} in classroom B. Indoor PAEs are directly emitted from various household products that contain PAEs. As a consequence, the outdoor concentrations of PAEs might be partly attributed to the dispersion from indoor to outdoor ambient air (Weschler *et al.*, 1980; Zhang *et al.*, 2014), that they are greatly affected by the equilibrium partition between the gas and particle phases. DEHP and DBP were the dominant species and they accounted for 38.0 and 30.1% of ΣPAEs in outdoor, respectively. And in classroom A and B, they accounted for 39.4 and 31.6%, 39.1 and 35.8%. This was similar with the previous studies developed in Tianjin and Denmark (Langer *et al.*, 2010; Kong *et al.*, 2013). Classrooms A and B led to similar PAEs profiles and variability. DEHP, DBP, and DEP were found at higher concentrations indoors than outdoors, while the other

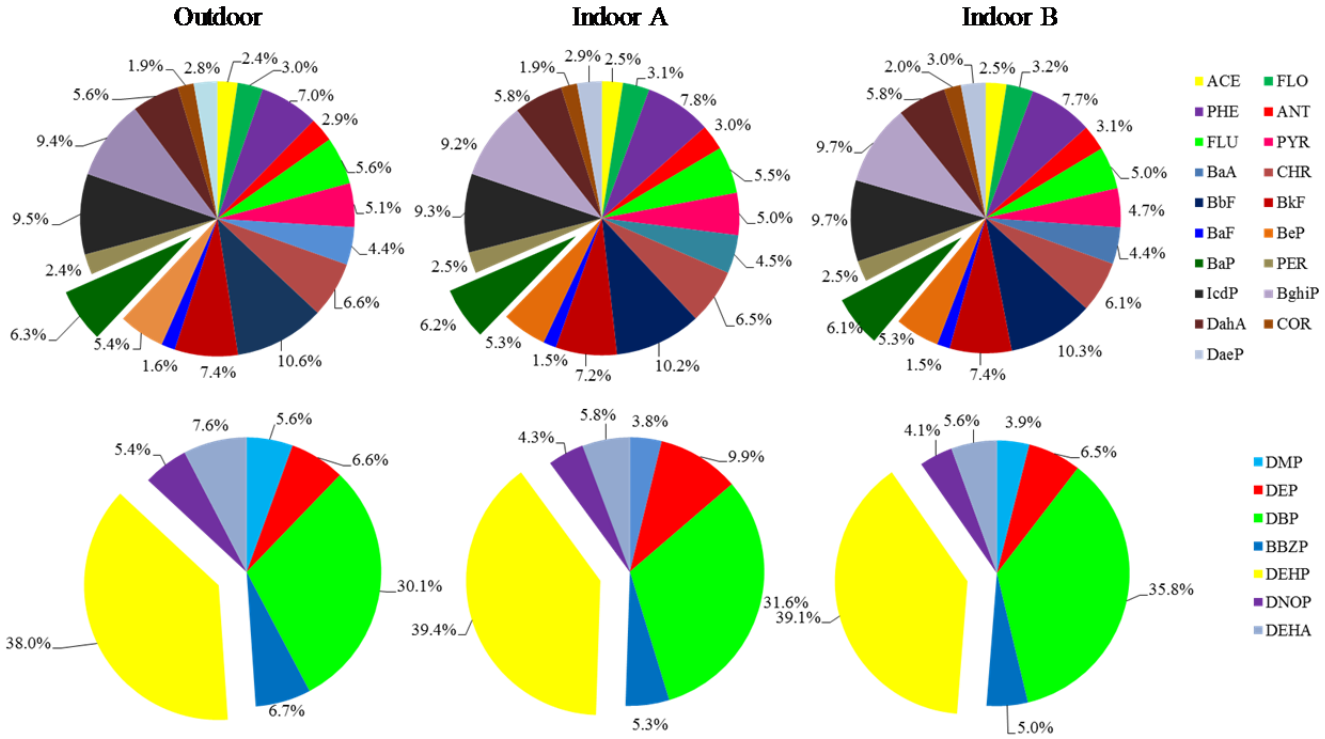

Fig. 3. The compositions of PAHs and PAEs in $PM_{2.5}$ in two classrooms of middle school from Xi'an.

species (benzyl butyl phthalate (BBZP), di-n-octyl phthalate (DNOP), and bis(2-ethylhexyl)adipate (DEHA)) were comparable between indoors and outdoors. Dimethylphthalate (DMP) was a litter higher in outdoors. This was correlated with their possible sources, and their physical and chemical properties also influence their distributions (Schettler, 2006; Guo and Kannan, 2013).

Effects from Classroom Occupancy Phases

The concentrations of PAHs, OPAHs, and PAEs during the classroom occupancy phases, defined as "occupied" for weekday samples and "unoccupied" for weekend ones, are compared in Fig. 4. Classroom B was removed for the insufficient sampling time of the weekend samples at May 19th and May 20th. Organic species in general were found at higher levels in the occupied phase (including room B). Total PAHs concentrations on weekdays were, outside the classrooms, 30.9–87.9 ng m^{-3} (average: 56.4 ng m^{-3}); and inside indoor A: 32.0–79.3 ng m^{-3} (54.0 ng m^{-3}). Whereas, on weekends, the corresponding mean concentrations were about one-third lower (outdoors: 33.6 ng m^{-3}; A: 30.4 ng m^{-3}). OPAHs, outdoors were decreased from about 18 ng m^{-3} on weekdays, to about 14 ng m^{-3} on weekends, were from 16.5 to 13.2 ng m^{-3} for weekdays and weekends in classroom A. PAEs variations describe a comparable patterns with average levels significantly lower on weekends than on weekdays (outdoors: 498.7 vs. 649.4; A: 539.1 vs. 868.5 ng m^{-3}, respectively).

PAHs are supposed to have an outdoor origin only in school environment. However, they are detected indoors as the room ventilation and/or the movements of the students and teachers in and out the classroom have an effect of re-distribution of particle-bound contaminants. Higher ventilation rate and occupancy rate can be resulted in higher indoor particle mass loadings on weekdays than on weekends, as illustrated by $PM_{2.5}$ mass concentrations (weekdays: 150.0 μg m^{-3}, weekends: 87.6 μg m^{-3}, on average). As a result, the I/O ratios of PAHs in weekdays were higher than in weekends (Fig. 4), though they were lower than 1. PAEs has the similar pattern that weekdays are also associated to higher levels than weekends, and due to their indoor origin, I/O ratios for PAEs were all higher than 1. The significant high I/O ratios in weekdays showed the mainly indoor sources, which different with the PAHs. Interestingly, an exception arose regarding for OPAHs, that the average I/O ratio in room A appears lower in weekdays than in weekends. During weekdays, almost all of the samples in outdoors were higher than indoor A, and at May 16th, the OPAHs in indoor A (10.1 ng m^{-3}) were much lower than outdoor (18.2 ng m^{-3}), which induced the much lower I/O ratios (0.55), and for the entire weekdays sample, the I/O ratio was 0.89. On the other hands, the OPAHs at the weekends of May 19th, the indoor OPAHs levels were higher in indoor A than in outdoor (10.7 vs. 8.8 ng m^{-3}), and the I/O ratio was 1.22. For these reasons, the I/O ratios for OPAHs in weekday showed higher values. This might due to that main source for OPAHs was from the secondary formation, and the different microenvironment might have different mount of pollutants.

Health Risk Assessment

The calculated results of the daily inhalation for PAHs and PAEs were displayed in Table 2. The BaP_{eq} were: outdoors: 19.7 ng m^{-3}; A: 19.1; B: 19.7 ng m^{-3}, exceeding

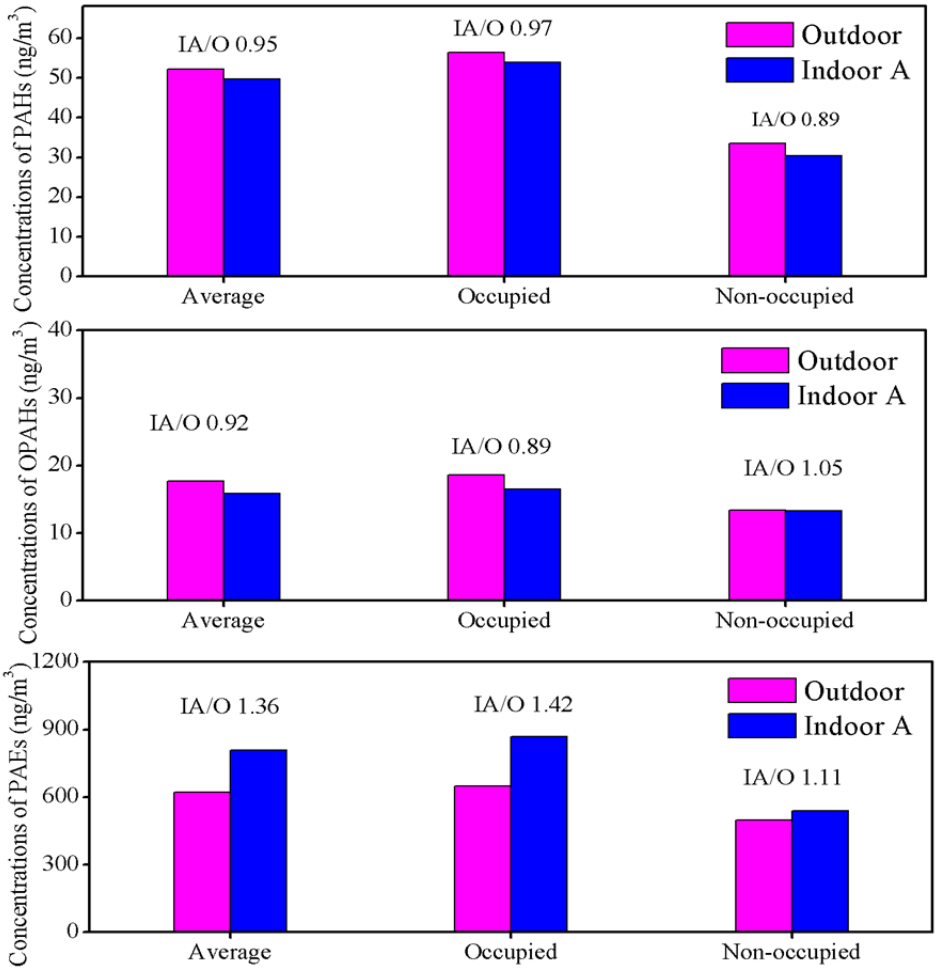

Fig. 4. The concentrations and I/O ratios of PAHs, OPAHs, and PAEs during occupied and non-occupied time in classroom A of middle school from Xi'an.

Table 2. BaP equivalent concentrations of PAHs and mean daily inhalation of PAHs and PAEs.

Species	BaP_{eq}[a] (ng m^{-3})			E_I (ng person^{-1} day^{-1})			ILCR		
	Outdoor	Indoor A	Indoor B	Outdoor	Indoor A	Indoor B	Outdoor	Indoor A	Indoor B
PAHs	19.7	19.1	19.7	299.1	289.7	299.0	1.29×10^{-6}	1.25×10^{-6}	1.29×10^{-6}
PAEs	TDI[b] (μg kg^{-1} d^{-1})	RfD[b] (μg kg^{-1} d^{-1})		ADD (ng kg^{-1} d^{-1})			CR		
				Outdoor	Indoor A	Indoor B	Outdoor	Indoor A	Indoor B
DMP				10.4	9.3	10.3			
DEP	750	800		12.5	24.2	17.0			
DBP	100	100		56.6	77.3	93.7			
BBZP	200	200		12.6	12.9	13.2			
DEHP	37	20		71.6	96.5	102.3	1.00×10^{-6}	1.35×10^{-6}	1.43×10^{-6}
DNOP		400		10.2	10.6	10.7			
DEHA				14.4	14.1	14.6			

[a] the value of toxic equivalency factor (TEFs) from Nisbet and Lagoy, 1992.
[b]TDI Value from EU CSTEE, and RfD from US EPA.

both the European Union's annual average BaP_{eq} standard (European Union, 2014) and the China National Daily BaP_{eq} standard (Ministry of Environmental Protection of the People's Republic of China, 2012), which were 1 and 2.5 ng m^{-3}, respectively. Our results were comparable with previous studies developed in Beijing, Tianjin, and Shijiazhuang (Zhang *et al.*, 2016), but much higher than in Guangzhou and Northern Thailand (Pongpiachan, 2016; Ren *et al.*, 2017). The corresponding daily inhalations ranges were: outdoors: 156.8–399.8 ng day^{-1} (average: 299.1 ng day^{-1}); A: 143.7–371.4 ng day^{-1} (average 289.8 ng day^{-1}), B: 194.5–444.3 ng day^{-1} (average 299.0 ng day^{-1}), there

were no obvious difference between outdoors and indoors. Previous reports have considered that when ILCR value was equal or higher than 10^{-4}, there were serious health risks, and when it was equal or lower than 10^{-6}, there were no health problems (Xia *et al.*, 2013; USEPA, 1980). In the present study, the ILCR values were: outdoors 1.29×10^{-6} on average; A: 1.25×10^{-6} and B: 1.29×10^{-6}. Thus, about 80% of the ILCR values were higher than 10^{-6}, reflecting high risks of cancer.

Exposure levels to ADD of DEP, DBP, BBZP, and DEHP of students were lower (Table 2) than the reference values, namely the tolerable daily intake (TDI) edited by European Scientific Communities on Toxicity, Ecotoxicity and the Environment (CSTEE), and the US EPA's reference doses (RfDs), which are 750, 100, 200, 37 μg kg^{-1} d^{-1} and 800, 100, 200, 20, 400 μg kg^{-1} d^{-1}, respectively. However, our findings did not consider the other various exposure pathways, like ingestion, dermal exposure, etc., which may increase the total risk for students. The ADD for DBP indoors were A: 77.3 and B: 93.7 ng kg^{-1} d^{-1}, which was lower than the estimated by International Program on Chemical Safety (IPCS) of indoor exposure level DBP for adults provided (120 ng kg^{-1} d^{-1}) (Kavlock *et al.*, 2002; Zhang *et al.*, 2014). Overall, our results also was lower with those of a study of teenager exposure to indoor DBP in Tokyo (150 ng kg^{-1} d^{-1}), and reported for Tianjin (Otake *et al.*, 2004; Zhang *et al.*, 2014). For the gas-phase PAEs were not analysis and calculated here. We also assessed the CR of DEHP bounded in $PM_{2.5}$, our estimation led to mean indoor CRs of A: 1.35×10^{-6} and B: 1.43×10^{-6}, while the outdoor CR was found at 1.00×10^{-6}. Both were higher than 10^{-6}, indicating a moderate inhalation risk (10^{-6}–10^{-5}) for DEHP.

CONCLUSION

Air pollution in China, which combines high background levels with intense haze episodes, leads to negative effects on human health. However, research works are still lacking to better understand the levels of exposure, especially of the susceptible populations, such as schoolchildren. In this study, $PM_{2.5}$-bound PAHs, OPAHs, and PAEs were monitored inside and outside two classrooms of a middle school in Xi'an, a Northern Chinese megacity suffering from severe air pollution. High concentrations of $PM_{2.5}$ mass and organic species are reported. Outdoor combustion sources were found responsible for emitting PAHs and OPAHs, while PAEs are mainly from indoor sources. The I/O ratios in weekdays and weekends demonstrated that the classroom occupancy phases, as well as cleaning and physical activities on the outdoor playground influenced the spatial distribution and the concentrations of the organic pollutants. Cancer risks associated to the exposure to PAHs and PAEs were estimated to stand at a moderate level. Despite the limited number of samples owing to the sampling challenges, this work brings evidence of the significant contribution of particulate organics to the health risk associated to air pollution. It suggests that design new studies in the future to characterize exposure to both particulate and gas-phase organic species over a longer time scale.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

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