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Concentrations, sources and health effects of parent, oxygenated- and nitrated- polycyclic aromatic hydrocarbons (PAHs) in middle-school air in Xi'an, China

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ABSTRACT

Indoor and outdoor concentrations of polycyclic aromatic hydrocarbons (PAHs), oxygenated-PAHs (OPAHs), and nitro-PAHs (NPAHs) associated with PM_{2.5} particles were monitored in a middle-school classroom from 8 to 22 March 2012 in Xi'an, China. The total PAHs ranged from 49.6 to 140.0 ng/m³ in outdoors and 50.3 to 111.6 ng/m³ in indoors, while OPAHs and NPAHs showed averages of 19.1 and 16.4 ng/m³, 0.1039 and 0.0785 ng/m³ for outdoor and indoor air, respectively. Strong correlations were found between indoor (I) and outdoor (O), and the I/O ratios were < 1 for almost all the species, indicating that outdoor air was the dominant influence on indoor air. Diagnostic ratios and Positive Matrix Factorization (PMF) analysis indicated that biomass burning, coal combustion, and motor vehicle emissions were the main sources for PAHs (which accounted for 30%, 27.4% and 26%, respectively, by PMF), but, secondary particle formation was important for the OPAHs and NPAHs. Inhalation cancer risks associated with outdoor and indoor particles were 6.05×10^{-5} and 5.44×10^{-5} , respectively, and so higher than the cancer risk guideline of 10^{-6} . Although the cancer risk of NPAHs is negligible for its lower concentrations, their potential for direct mutagenic effects should not be ignored.

Keywords: Indoor/outdoor air pollution; PAHs; OPAHs; NPAHs; Classroom; Health effects

1. Introduction

The negative effects of particulate matter (PM) on the human health are well documented, and the concerns are especially great for PM with aerodynamic diameters $\leq 2.5 \mu\text{m}$ (i.e. $\text{PM}_{2.5}$) (Bandowe et al., 2014). Polycyclic aromatic hydrocarbons (PAHs) are a common class of chemicals that can be toxic, mutagenic, and carcinogenic for humans (Lin et al., 2015). These pollutants have been detected in many areas (Li et al., 2015; Huang et al., 2014a; Wang et al., 2015), and China in particular has shown higher pollution levels compared with most developed countries. Size distributions and different functional areas of these pollutants were also discussed somewhere (Ren et al., 2017; Alves et al., 2016; Gao et al., 2016). The haze in China has complex sources and the formation mechanism was different (Wang et al., 2016a; Huang et al., 2014a). Huang et al. (2014a) pointed that a large extent of secondary aerosol formation, which contributed for 30 to 77% and 44 to 71% of $\text{PM}_{2.5}$ and organic aerosol, respectively, drive to the haze. On the other hand, the sulfate production was the key formation of persistent severe haze in China (Wang et al., 2016a). Previous studies have shown that as much as 1.6% of lung cancer cases can be attributed to the inhalation of PAHs from polluted air (Bandowe et al., 2014; Zhang et al., 2009). Oxygenated-PAHs (OPAHs) and nitro-PAHs (NPAHs) are derivatives of PAHs, and these are frequently more harmful than their corresponding parent-PAHs. Indeed, some studies have shown that OPAHs and NPAHs can act directly as mutagens, and they also can produce reactive oxygen species that are responsible for highly toxic (Barrado et al., 2013; Benbrahim-Tallaa et al., 2012;

Bolton et al., 2000; Chung et al., 2006; WHO, 2003) Unlike PAHs, which mainly originate from the incomplete combustion of coal biomass and motor vehicle emissions, OPAHs and NPAHs can be directly emitted together with PAHs, or they can form through secondary reactions with OH and NO₃ radicals or through homogeneous and heterogeneous reactions with NO₂ (Atkinson et al., 1990; Keyte et al., 2013; Ringuet et al., 2012). Studies of source apportionments and transformations for OPAHs and NPAHs have become hot topics recently, and field experiments have been conducted for monitoring OPAHs and NPAHs in various countries. However, almost all of the research has focused on outdoor environments, and little attention has been given to indoor environments which may be particularly useful for uncovering possible health effects.

People spend most of their time indoors (Brauer et al., 2000; Castro et al., 2011; Mentese et al., 2015), and because of this, indoor air pollution has recently been recognized as a key public health concern. Indeed, air pollution can not only be causative agent for chronic and acute respiratory diseases but also affect the medical prognosis of pre-existing diseases and conditions (Chen et al., 2004). Children are especially at risk from air pollutants because their respiratory systems have not yet fully developed (Kulkarni and Grigg, 2008; Xu et al., 2015a), and exposure during their time spent in classrooms is a serious concern because schools are in session for 175-250 days per year around the world. The indoor air quality in schools can be affected by many factors, such as the locations of the buildings, especially their proximity to emission sources; paint and decorations on and in the buildings; the

design and operation of heating, cooling, ventilation, and air filtration systems. The numbers of students and staff in the classrooms and their types of activities (e.g., physical, cleaning, and teaching activities), etc. also can influence the health risks (Alshitawi and Awbi, 2011; Guo et al. 2010; Heudorf et al. 2009; Lee and Chang, 2000; Oliveira et al., 2015; Zhang and Zhu, 2012).

There is growing concern that elevated PM concentrations in classrooms can have significant adverse effects on children's health and their overall performance (Dorizas et al., 2015; Mendell and Heath 2005; Tran et al. 2012). In Europe, some guidelines concerning school air quality already have been developed; for example, in Norway an indoor guideline for PM_{2.5} has been established (20 µg/m³ averaged over 24 h), and in Belgium an indoor guideline is 15 µg/m³ averaged over the course of a year while the proposed EU annual ambient guideline is 35 µg/m³ (Stranger et al., 2008). However, in China, there is little information available on specific toxic organic compounds in indoor air from classrooms (SINPHONIE project).

For this study, outdoor and indoor filter samples were collected from a school in Xi'an, China, a city that all too often suffers from serious air pollution (Gao et al., 2015). The carbonaceous fractions of PM_{2.5} and potentially toxic organic species (PAHs, OPAHs, and NPAHs) were quantified, and the indoor/outdoor ratios and characteristics of target compounds are discussed. Possible sources of PAHs, OPAH, and NPAHs were identified, and potential risks assessed for students' exposure to PAHs, OPAH, and NPAHs in the classrooms. Results of the study show an urgent need to cut the emissions of these potentially toxic substances and reduce classroom

exposures.

2. Materials and method

2.1. Sampling

The environment of the middle school was described in the previous study (Xu et al., 2015b). The middle school where the sampling took place is located approximately 5 km south of Xi'an city center in a commercial and residential area. There were no direct influences from industrial emissions, and the building is ~300 m away from the main road. Indoor sampling was set up in a classroom located on the second floor, ~ 8 m above ground level. It was occupied by the same 30 students, aged 12 and 14, from Monday to Friday, 8:00 am to 12:00 am and 1:30 pm to 5:30 pm local time. Indoor samplers were located in the back of the classroom and their inlets were set up 1.2 m above the ground. A matching sampling package was set up outdoors, at the end of the corridor passing alongside the sample classroom, ~6 m away from the indoor sampling site. The location of the outdoor site was chosen to sample ambient air from the schoolyard and not the air from the street. The classroom was ventilated manually by two large windows, each 1.8 × 1.5 m in size, located on two sides of the classroom. One side was connected to a small street and the other one to an inner corridor. Windows remained opened during school hours but were closed after school and during the weekends.

PM_{2.5} samples were collected on pre-fired (780°C) 47 mm quartz filters (QM/A®, Whatman Inc., U.K.) both indoors and outdoors from 8 to 22 March 2012 over 24-h

periods beginning at 8:00 am local time. Mini-Volume PM_{2.5} samplers (Airmetrics, Springfield, OR, USA) were used to collect the samples, and they operated at a flow rate of 5 L/min. The samplers were calibrated using a Defender 510 Volumetric Primary Flow Standard (Bios international Corporation, Butler, NJ, USA) and the variance in flow was approximately $\pm 2\%$. A total of 26 samples were collected for the study. All of the samples were stored in a freezer at -20°C before analysis to prevent or minimize any storage artifacts.

2.2. Meteorological condition

The meteorological records of temperature (T) and relative humidity (RH) were obtained from the National Oceanic and Atmospheric Administration (NOAA) and horizontal wind data were taken from the website of China Meteorological Data, <http://data.cma.gov.cn>. The boundary layer heights were obtained from the European Center for Medium-Range Weather Forecasts, <http://apps.ecmwf.int/datasets/>.

2.3. PM Gravimetric and Chemical analyses

Our previous studies have included detail descriptions of the methods used for PM gravimetric analysis (Wang et al., 2016b, 2015). Briefly, the PM samples were weighed with the use of a Sartorius ME 5-F electronic microbalance with $\pm 1 \mu\text{g}$ sensitivity (Sartorius, Germany). Before and after sampling, the samples were equilibrated for 24 h at $20\text{-}23^{\circ}\text{C}$ and $35\text{-}45\%$ relative humidity; the absolute errors between duplicate weights were less than 0.015 mg for blank filters and 0.020 mg for samples. After weighing, the filters were stored in a refrigerator at $< -4^{\circ}\text{C}$ prior to

chemical analysis to prevent the evaporation of volatile components.

Organic and elemental carbon (OC and EC) were measured using a Desert Research Institute (DRI) Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, CA, USA) following the IMPROVE-A (Interagency Monitoring of Protected Visual Environment) thermal/optical reflectance (TOR) protocol. The IMPROVE-A protocol defines TC as OC + EC, OC as OC1 + OC2 + OC3 + OC4 + OP, and EC as EC1 + EC2 + EC3 - OP. The method has been described in detail elsewhere (Bandowe et al., 2014; Cao et al., 2004).

Twenty-five parent PAHs and three OPAHs in the filter samples were quantified using in-injection port thermal desorption (TD) unit coupled to a gas chromatography/mass spectrometer (GC/MS) (Ho et al., 2011, 2008; Ho and Yu, 2004; Wang et al., 2016b, 2015). Details of the in-injection port TD-GC/MS method have been described in a previous publication (Wang et al., 2015).

In preparation for the instrumental analyses, half of the filter samples were put into clean glass bottles and then placed in an ultrasonic water bath where they were extracted three times using 5 mL mixtures of dichloromethane (DCM) and methanol (MeOH) each time: the volume:volume (V:V) ratio for DCM : MeOH was 3:1. Prior to the ultrasonic extractions, three deuterated-NPAHs (2-nitrofluorene-D₉, 3-nitrofluoranthene-D₉, and 6-nitrochrysene-D₁₁) were added to the bottles as internal standards. After the extractions, anhydrous sodium sulfate was added to removal any water from the sample. The samples were then concentrated to about 1-2 mL by

rotary evaporator and then transferred to cell bottles and concentrated by soft nitrogen blowing. Samples finally spiked with 1-nitronaphthalene-D₇ which served as a recovery standard for the deuterated internal standards spiked to the filters before instrumental analysis.

Eight NPAHs were quantified using a model 7890B gas chromatograph (Agilent Technologies, Santa Clara, CA, USA) coupled to an Agilent 5977A mass selective detector. The system was operated in the negative chemical ionization mode with CH₄ as the ionization gas. The further details regarding GC-MS procedures have been given in Bandowe et al. (2014) and Bezabeh et al. (2003).

2.3. *Quality assurance and control (QA/QC)*

Previous studies that used the same procedures as in this study have detailed the QA/QC procedures, including the methods used for sampling, OC/EC, and organic species analysis (Wang et al., 2015; Wei et al., 2015). In brief, the aerosol samplers were checked and calibrated regularly, and field blank filters were collected to correct for backgrounds. All glassware used during sample preparation and analysis was rinsed, machine washed and baked at 450°C to remove contaminants. For the TD-GC/MS, National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) SRM 1649a urban dust was used to validate the accuracy of the PAH analyses. Internal standards (IS) were added to each sample and these included chrysene-d₁₂ (C₁₈D₁₂) (98%, Sigma-Aldrich, Bellefonte, PA, USA), *n*-tetracosane-d₅₀ (*n*-C₂₄D₅₀) (98%, Aldrich, Milwaukee, WI, USA), and phenanthrene-d₁₀ (C₁₄D₁₀)

(98%, Aldrich, Milwaukee, WI, USA). A five-point calibration over a concentration range of 1–10 ng was established for each PAH and OPAH (obtained from Sigma-Aldrich, Bellefonte, PA, USA). The correlation coefficients (R^2) for linear regressions of the calibration curves were > 0.99 in all cases. For each group of ten samples, one replicate analysis was done; the relative standard deviations of these replicates were from 1.6 to 8.2% for PAHs, from 3.2 to 9.8% for OPAHs. For the NPAH analyses, spiked target NPAHs in test filters were extracted and concentrated using the same methods as used for the samples. The recoveries and relative standard deviations were calculated as an indication of the accuracy and precision for the complete methods. Method blanks also were analyzed to evaluate potential sample contamination during laboratory analysis, and we applied the same analytical procedures as described above to determine the concentrations of our target compounds in them. Target compounds were either not detected in the blanks or the detected amounts were much lower than in the samples. The recoveries of the target compounds were from 46.2 to 109.5% and the recoveries of the inter standards were from 56.6 to 117.0%.

3. Results and discussion

3.1. Concentration levels of target compounds

The $PM_{2.5}$ mass concentrations and those of OC, EC, and organic species in the outdoor and indoor classroom samples from Xi'an are summarized in Table 1 and Fig.

1. The arithmetic means \pm standard deviations for the $PM_{2.5}$ mass concentrations were

167.8 ± 59 outdoors and 141.8 ± 42 µg/m³ indoors. Outdoors, the OC concentrations ranged from 12.0 to 43.0 µg/m³ and EC from 2.6 to 16.0 µg/m³ while indoors, the corresponding ranges for OC and EC were 14.0 to 27.8 and 3.33 to 12.0 µg/m³, respectively. The total PAHs ranged from 49.6 to 140.0 ng/m³ outdoors and from 50.3 to 111.6 ng/m³ indoors. The OPAHs and NPAHs had much lower levels, with averages of 19.1 and 16.4 ng/m³, 0.1039 and 0.0785 ng/m³ for the outdoor and indoor samples, respectively. The pollutants in the outdoor air samples from our study were comparable with those reported in other studies of ambient air in Xi'an (Wang et al., 2015; Wei et al., 2015).

For PAHs, the ΣLMW-PAHs were much lower than ΣHMW-PAHs and the average ratio of ΣHMW-PAHs/ΣLMW-PAHs in outdoor and indoor were 8.3 and 8.9, respectively. The 4-ring, 5-ring and 6-ring were the dominant compounds, which accounting for 84.5% of PAHs. This was associated with the higher vapor pressure for lower molecular weight PAHs, which tend to occur in gaseous phase, and the high molecular weight components mostly bound with particulate. Benzo[b]fluoranthene (BbF) was the most abundant species. Indeno[1,2,3-cd]pyrene (IcdP), benzo[ghi]perylene (BghiP), chrysene (CHR), and benzo[k]fluoranthene (BkF) were also abundant.

For the OPAHs, anthraquinone (ANTQ) was the most abundant (12.8 and 10.7 ng/m³ in the outdoor and indoor samples, respectively), and the next most abundant OPAH species were 9-fluorenone (9FLO), and Benz[a]anthracene-7,12-dione (BaAQ). This pattern is consistent with a prior field monitoring study conducted in Shaan'xi

(Shen et al., 2013). The concentrations of the NPHAs at our site were not high compared with previous study in Guangzhou (Huang et al., 2014b). 3-Nitrofluoranthene (3Nflt) showed the highest abundances of the NPAHs, with averages of 0.0577 and 0.0338 ng/m³ outdoors and indoors, respectively.

Until now, there has been little or no research that has focused on OPAHs and NPAHs in classrooms, and indeed, there is very limited information on PAHs in schools. Furthermore, comparisons between studies are hampered by differences study designs, which include the particle-size fractions sampled, the gaseous compounds studied, and number of PAHs analyzed. We summarized the readily available data for PM_{2.5} and PM_{2.5} bound PAHs in the outdoor and classroom samples in Table 2. Most of the research to date has been conducted in Europe, and primary schools have attracted the most attention. For example, Stranger et al. (2008) assessed the indoor air quality of 27 primary schools in urban areas and suburbs of Antwerp, Belgium during the winter and summer of 2003. The average indoor and outdoor PM_{2.5} levels were from 54 to 72 µg/m³ and 27 to 72 µg/m³, respectively. Similar levels of PM_{2.5} were found in seven primary schools in Athens, Greece (Diapouli et al., 2008) while relatively lower PM_{2.5} concentrations have been reported for schools in Sweden, the Netherlands, and the USA (Janssen et al., 2001; Wichmann et al., 2010; Zhang and Zhu, 2012).

Krugly et al. (2014) reported the concentrations of PAHs bound to PM_{2.5} and gaseous PAHs in indoor air from five primary schools in various urban settings in Lithuania. The PAHs in PM_{2.5} ranged from 20.3 to 131.1 ng/m³, which is much

higher than that in schools from Rome (Gatto et al., 2014; Romagnoli et al., 2014). Oliveria et al. (2016) measured the PM_{2.5} mass loadings and associated PAH concentrations in a private and a public school in Portugal and found that the PM_{2.5} mass in the public school was lower, but the PAHs levels showed the opposite pattern. Schools in different types of representative locations in Serbia were sampled (Kovacevic et al., 2015; Zivkovic et al., 2015), and very high levels of PAHs were found in an urban/traffic school during the heating season (421.9 ng/m³ indoors vs. 1017 ng/m³ outdoors) while a rural school had its highest levels (271.6 and 132.3 ng/m³ indoors and outdoors, respectively) during the non-heating season (Zivkovic et al., 2015).

Few studies have investigated the air quality in Chinese schools, but relatively high levels of pollutants were found in our study. As noted above, there are no data from China that we can use to compare with our OPAH and NPAH concentrations in the classroom, but the levels of OPAHs in Xi'an were higher than reported in most previous studies conducted in France, Brazil, and Greece, however, comparable with those found a study conducted in Beijing and industrial regions of several cities northeastern China (Andreou and rapsomanikis, 2009; Li et al., 2015; Lin et al., 2015; Ringuet et al., 2012; Souza et al., 2014). The size distributions of PAHs and OPAHs also developed in Xi'an and Guangzhou during winter and summer in 2013 comparing with 2003, which have showed that 5-ring OPAHs were dominated. 3-Ring PAHs and OPAHs increased along with the particle sizes and > 90% were loaded at largest particles (> 9µm), but the fine particles are more toxic than coarse particles

(Ren et al., 2017). Though different NPAHs species and species numbers were quantified in different reports, for Σ NPAHs, it has comparable levels with that in urban particle in France and a traffic location in Qingyuan of China, but was lower than the studies developed rural particle in Sao Paulo and rural and urban particle northern China cities such as Taiyuan, Yantai, Dezhou and so on (Ringuet et al., 2012; Wei et al., 2014; Souza et al., 2014; Li et al., 2015; Lin et al., 2015). Much higher levels were got in kitchen air in Zhuanghu in China (Ding et al., 2012). The concentrations of PAHs, OPAHs, and NPAHs in particles of different regions worldwide are summarized in Table S1.

The results plotted in Fig. 1 also showed that while almost all of the pollutants exhibited their highest outdoor levels on 17 March low loadings were found indoors on that day, and that indoor/outdoor difference was likely due to a low ventilation coefficient (VC) (Kompalli et al., 2014), which is calculated by the boundary layer height (MLH) multiply the horizontal wind speed (U), and is used as a direct measure to characterize the degree of transport/dispersion of the pollutants taking place within convective boundary layer. The effects of the meteorological conditions and correlations between pollutants were displayed in supporting reference (Table S2). The concentrations of the outdoor $PM_{2.5}$ and PAHs have significant correlations with temperature (R^2 was 0.687 for $PM_{2.5}$ when $P < 0.01$ and 0.614 for PAHs when $P < 0.05$) and RH (R^2 was -0.628 for $PM_{2.5}$ and -0.556 for PAHs when $P < 0.05$). Concentrations of PAHs also have significant correlations with VC ($R^2 = -0.597$, when $P < 0.05$). The PAHs also showed significant ($p < 0.01$) positive correlations with $PM_{2.5}$ mass and

OC concentrations (R^2 was 0.952 and 0.864, respectively).

3.2. Indoor and outdoor difference

Indoor/outdoor (I/O) concentration ratios were used as a measure of the differences between the outdoor and corresponding indoor aerosol loadings. Hence the indoor and outdoor ratio can be viewed as an indicator of the relative strengths of the indoor versus outdoor sources (Kovacevic et al., 2015; Xu et al., 2015a). That is, if the I/O ratio were > 1 , one might conclude that the indoor sources were stronger than those outdoor, and contrarily, if it were < 1 , the indoor sources would be thought to be weaker (Crist et al., 2008). Previous studies have reported that the indoor sources included: children activities and classroom cleaning. On some occasion, birthday celebrations took place in the classroom also elevated PAHs levels. Especially for heavy molecular PAHs are usually emitted from outdoor source (Oliveira et al., 2016). In this study, it is regret that the gas phase samples were not collected, and during the sampling time, there were no obvious source emission and other student activities such as the painting, wax melting, candles combustion and so on. There was no student cafeteria in the school. The I/O ratios for each analyte in our study are shown in Table 1. Except for some NPAHs, the I/O ratios for $PM_{2.5}$ mass, OC, EC, PAHs, and OPAHs were ~ 0.9 and generally < 1 during the monitoring program, indicating that the indoor sources were relatively weak (Diapouli et al., 2010).

The interpretation of the I/O ratios presented above supports the idea that the

concentrations of the organic substances indoors are mainly affected by the ambient atmosphere. And our results are consistent with a study in Serbia, which found that I/O ratios of individual PAHs and Σ PAH at all sampling sites were < 1 during the heating season. Higher outdoor PAHs levels in that study were attributed to higher PAH emissions from combustion sources during the heating season, and during the non-heating season the I/O ratios for Σ PAHs were > 1 (Zivkovic et al., 2015). There were no regular patterns for the I/O ratios in previous studies of schools, but that is likely due to differences in the locations of the schools. More generally, that is, under most common conditions, the I/O ratios for $PM_{2.5}$ and various substances have been found to be ≤ 1 , especially during heating periods (Wichmann et al., 2010).

In this study, a significant correlation between the indoor and outdoor PM concentrations ($R^2 = 0.84$) was observed, and this can be explained by the exchange of outdoor air (Diapouli et al., 2010; Kovacevic et al., 2015). This explanation is in agreement with the results of study by Guo et al. (2010) of indoor and outdoor $PM_{2.5}$ mass concentrations during winter in primary school in Brisbane, Australia; the results of that study led to the conclusion that indoor $PM_{2.5}$ levels were mainly affected by the outdoor $PM_{2.5}$ ($r = 0.68$, $p < < 0.01$). Interestingly, no significant difference in I/O ratios for $PM_{2.5}$ was observed between occupied and unoccupied classrooms in this study during the sampling site, that might due to the relative short sampling time and the weather conditions influence the enrichment of pollutants (Lower boundary layer in the unoccupied time) in this study.

3.3. Source apportionment

In order to identify the possible sources of PAHs, OPAHs, and NPAHs in $PM_{2.5}$ diagnostic ratios and indices of PAHs, OPAHs, and NPAHs were calculated, and the results are summarized in Table 3. Statistical tests showed that there were no differences ($t > 0.05$) between indoor and outdoor air. The anthracene (ANT)/(ANT+phenanthrene (PHE)) ratio varied from 0.22 to 0.34, and this ratio is indicative of a pyrogenic source. The ratio of benzo[a]anthracene (BaA)/(BaA + CHR) was > 0.2 and most often between 0.27 and 0.39, which is suggestive of emissions from coal combustion and motor vehicles. Most of the fluoranthene (FLU)/(FLU+ pyrene (PYR)) ratios were > 0.5 , and the IcdP/(IcdP+BghiP) ratios were between 0.2 and 0.5, and this is evidence that biomass burning was the main source for the PAHs. The benzo[a]pyrene (BaP)/(BaP + benzo[e]pyrene (BeP)) ratio was < 0.5 , showing that particle aging had occurred.

For the next step in analyses, selected chemical data for all the samples were input into Positive Matrix Factorization (PMF) (EPA PMF 3.0 version) model for the identification of sources and quantification of the impacts though the samples were not so many. The data for eighteen PAHs and three OPAHs were input in the model, including both their concentrations and uncertainties. PMF has been widely used in atmospheric source characterization and details of the methodology have been described elsewhere (Lin et al., 2015; Ma et al., 2010; Moon et al., 2008; Okuda et al., 2010). The profiles of each factor obtained from the model and their contributions are summarized in Figure 3.

Factor 1 was heavily loaded with the high MW PAHs (5- to 6-ring PAHs, such as

coronene (COR), BghiP, IcdP, dibenzo[a,h]anthracene (DahA)). This factor can be interpreted as one representing motor vehicle emissions (Wang et al., 2015; Wang et al., 2009), and it accounted for 26% of the total organic-compound mass loadings. Factor 2 (27.4% of the mass loadings), appears similar in composition to emissions from coal-fired power plants because it was heavily loaded with FLU, PYR (Chen et al., 2014). Benzo[a]fluoranthene (BaF), BaP, and BkF were also abundant in Factor 2. Factor 3 accounted for 30% of the mass, and it was highly loaded with 3-ring PAHs (i.e., fluorene (FLO), acenaphthene (ACE), PHE, and ANT), and so it is similar to profiles from biomass burning (Lin et al., 2015; Wang et al., 2015). The OPAHs also were abundant in Factor 3, and this supports impacts from biomass burning because these emissions are known to be important sources for OPAHs (Shen et al., 2013).

Factor 4 was heavily loaded with CHR and BbF, and the OPAHs also were abundant, especially by ANTQ. This might be a signal of the cooking emissions or secondary transformations, but the source can't be identified with confidence with the available data. A previous study showed that that biomass burning was a significant pollution source for PAHs in Xi'an during the heating period and that there also were influences of coal combustion and vehicle emissions (Wang et al., 2016c). These combustion sources also were responsible for other types of pollutants in Xi'an; for example, coal combustion and motor vehicle emissions were concluded to be the main sources for Pb, and coal combustion has found to have a heavy impact on the concentrations of water-soluble ions (Xu et al., 2012; Zhang et al., 2011). In any case, reducing these emission sources would have great benefits in terms of improving the

air quality in Xi'an. Such as Alves et al. (2016) that monitored the PAHs, OPAHs, and NPAHs in size particles emitted at urban road tunnel in Portugal, putted forward that improve of vehicle technologies and the application of environmental-friendly energy sources are possible solutions to decreased the pollutants emission and improve the air quality. The study during Asian Youth Games (AYG) in Nanjing, China at 2013 reported that 24 % of PAHs were decreased comparing with those at the pre-AYG periods (Li et al., 2016).

OPAHs are produced as direct emissions and through secondary formation (Lin et al., 2015), and the ratios of 9FLO vs FLO, ANT vs ANTQ, and BaAQ vs BaA typically have different values than those is primary emissions. This can be explained by differences in their rates of secondary formation or degradation as well as their partitioning between the particle and gas phases. Congeners with low molecular weights and high volatilities are predominantly in gaseous phase while high molecular-weight and low volatility species tend to associate with particle phase. Previous studies have demonstrated that the values for R_o (an oxygenation rate) were 0.40 ± 0.18 , 0.89 ± 0.41 , and 0.16 ± 0.05 for 9FLO/FLO, ANTQ/ANT, and BaAQ/BaA, respectively, from crop residue burning while the corresponding values for coal combustion were 0.25 ± 0.25 , 0.14 ± 0.08 , and 0.03 ± 0.02 . The R_o values were 2.06 ± 0.84 , 0.79 ± 0.23 , and $6.6 \pm 7.5 \times 10^{-2}$ for 9FLO/FLO, ANTQ/ANT, and BaAQ/BaA in samples of residential fuel wood and brushwood combustion (Shen et al., 2013, 2012, 2011).

In comparison, the average ratios of 9FLO/FLO, ANTQ/ANT, and BaAQ/BaA in

the present study were 2.7, 7.7, and 0.65, respectively in the outdoor samples. This associated with most studied developed in filed researches (Shen et al., 2011; Wang 2010). The OPAH to PAH ratios in the outdoor samples from our study were much higher than those for freshly emitted compounds from typical combustion processes (R_o), and these high ratios suggest that secondary formation process of OPAHs play an important role in determining the kinds of compounds found in Xi'an.

The ratio $(2Nflt+3Nflt)/1NP$ has often been used to assess the sources of NPAHs: when the ratios are < 5 , primary emissions are indicated, but ratios > 5 are taken as evidence of secondary formation (Huang et al., 2014b). In our study, 2Nflt was not quantified, but the average ratios of $3Nflt/1NP$ were 18 outdoors and 17.8 indoors, and these high values implicate secondary formation as an important source for the particulate NPAHs. Furthermore, the highest $3Nflt/1NP$ ratios during the study occurred on hazy days; that is, 14 March showed a high value outdoors and indoor air showed its highest value on 15 March. Similarly, 17 March, another hazy day, had the highest ratio outdoors corresponding with the high indoor value (Fig. 1). Hazy weather does not promote the dispersion of pollutants, but rather it likely enhanced the formation and accumulation of secondary pollutants.

3.4. Health risk assessment

Several approaches involving $PM_{2.5}$ -bound PAHs have been used to evaluate the carcinogenic potential of mixtures of PAHs and their derivatives (Huang et al., 2014b; Pongpiachan et al., 2015). The most widely-used method is the calculation of toxicity equivalency factors (TEFs) which are based on the measured concentrations of BaP.

The risk of cancer for PAHs also has been estimated through relative potency factors (RPF) developed by the US EPA (U.S. EPA, 2010), and calculations of potential equivalency factors (PEF) (OEHHA, 2005) of three NPAHs are yet another approach that has been used in some studies. Here, the inhalation cancer risk for the pollutants was calculated from the following:

$$\text{Cancer Risk} = \sum \text{BaP}_{\text{eq}} \times \text{UR}_{\text{BaP}}$$

in which $\sum \text{BaP}_{\text{eq}}$ is the total BaP_{eq} concentration and UR_{BaP} is the BaP unit risk, which was assumed to be $1.1 \times 10^{-6} (\text{ng}/\text{m}^3)^{-1}$ (OEHHA, 2005).

The BaP equivalent concentrations and inhalation cancer risks of the individual compounds and Σ PAHs and Σ NPAHs are presented in Table 4, and time-series plots of cancer risks are shown in Fig. 4. The total BaP_{eq} was $55.08 \text{ ng}/\text{m}^3$ outdoors and 49.45 indoors. The three NPAHs contributed 0.07% and 0.06% to the outdoor and indoor total toxicity although they accounted for only 0.02% of total concentrations of the measured toxicants. As note previously, the Σ NPAHs in this study were much lower than the previous study of air quality in Guangzhou simply because fewer species measured here (Huang et al., 2014b), and therefore, the overall health risks are almost surely underestimated. DahA had the highest carcinogenic potency of the PAHs (66% and 67% outdoors and indoors, respectively), and this was largely a consequence of its high PEF (10). This is consistent with some previous studies (Oliveira et al., 2015; Zhang et al., 2012), but different from another study conducted in Shimizu, Japan, which found that naphthalene (NAP) was the dominant indoor carcinogen, accounting for 63% and 56% of the carcinogenicity risk in summer and

winter, respectively (Ohura et al., 2003).

The overall inhalation cancer risks calculated for outdoor and indoor PAHs and derivatives bound to PM_{2.5} in this study were 6.05×10^{-5} and 5.44×10^{-5} , respectively; these are both higher than the cancer risk guideline value of 10^{-6} (US EPA, 1989; Zhang et al., 2012). It also should be emphasized that risks associated with gas-phase species were not considered here; and the gas/particle partitioning of relatively volatile species such as NAP was not considered. If those additional factors were considered, the aggregate risks would have been much higher.

A comparison of day-to-day variations also is informative; for example, 10 and 17 March, which were both weekends (samples collected by 48 h), showed strikingly different results. On both of those days, the students were taking practice tests, and their activities were less than on typical school days. The highest loadings of most outdoor pollutants were recorded on 17 March while low levels both indoors and out were found on 10 March (Figure 1). So the differences of the occupied and unoccupied periods were not discussed here. This displayed that the cancer risks showing in indoor air was much relative with the outdoor levels, and the student's activities might played minor roles.

4. Conclusions

The levels of PM_{2.5}-bound PAHs in the air of a classroom in Xi'an, China were relatively high compared with most of the schools that have been tested in Europe. Indoor air quality apparently was determined by the concentrations of pollutants in the outdoor air, and secondary formation was an important source for both OPAHs and

NPAHs. Biomass burning, vehicle emissions, and coal combustion were the main sources for PAHs, which accounted for 83.4% of the total PAHs. The cancer risk assessment showed significant health risks for the students, but overall, the risks were higher outdoors, and the student's activities played minor roles.

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Figure Captions

Figure 1. Variations of meteorological variables and concentrations of PM_{2.5}, organic carbon (OC), elemental carbon (EC), polycyclic aromatic hydrocarbons (PAHs), oxygenated-PAHs (OPAHs), and nitrated-PAHs (NPAHs) in PM_{2.5} in air from a middle school classroom from Xi'an, China.

Figure 2. Concentrations and indoor (I)/outdoor (O) (I/O) ratios of polycyclic aromatic hydrocarbons (PAHs), oxygenated-PAHs (OPAHs), and nitrated-PAHs (NPAHs) in PM_{2.5} from a middle school classroom from Xi'an. See Table 1 for abbreviations.

Figure 3. Positive matrix factorization (PMF) model results: (a) profiles of four PAH factors and (b) pie chart of contributions of the four factors to PM_{2.5} mass.

Figure 4. Variations of benzo[a]pyrene (BaP) equivalent concentrations and inhalation cancer risks of PAHs and NPAHs in PM_{2.5} from outdoor air and air from a middle school classroom in Xi'an.

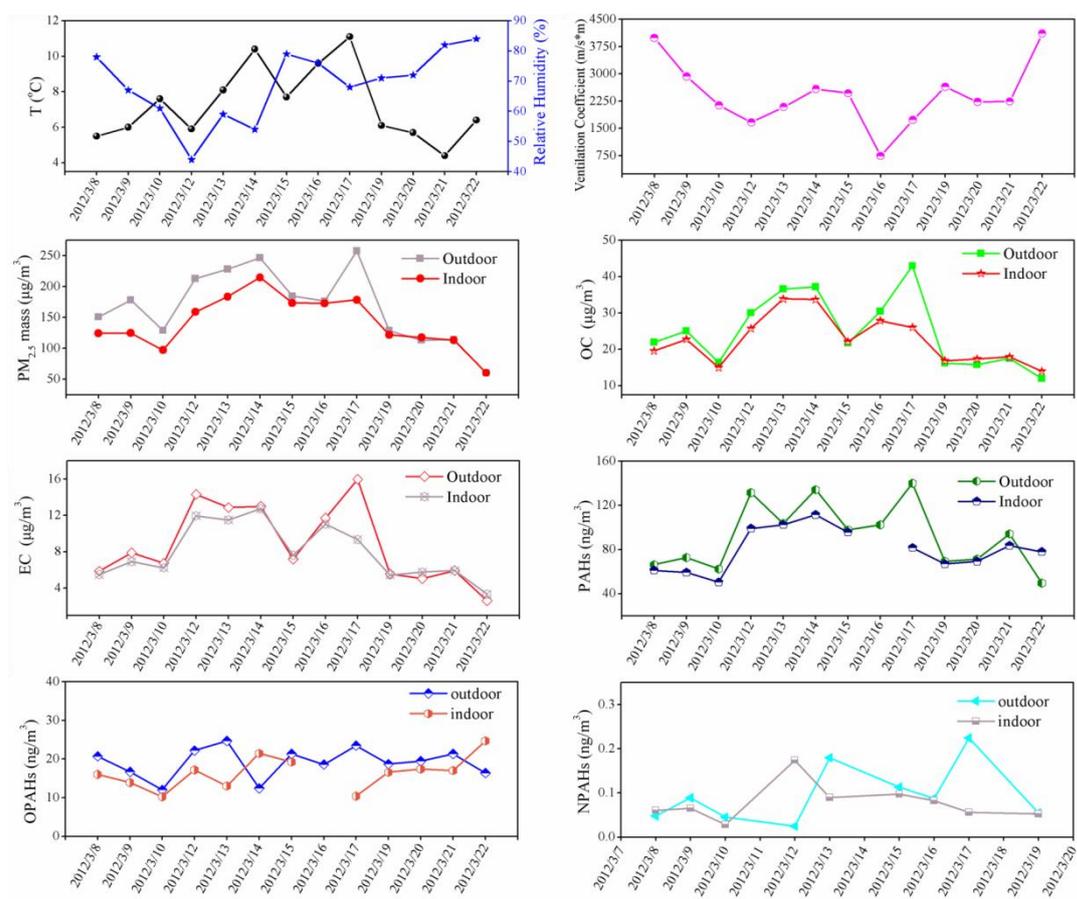


Fig. 1

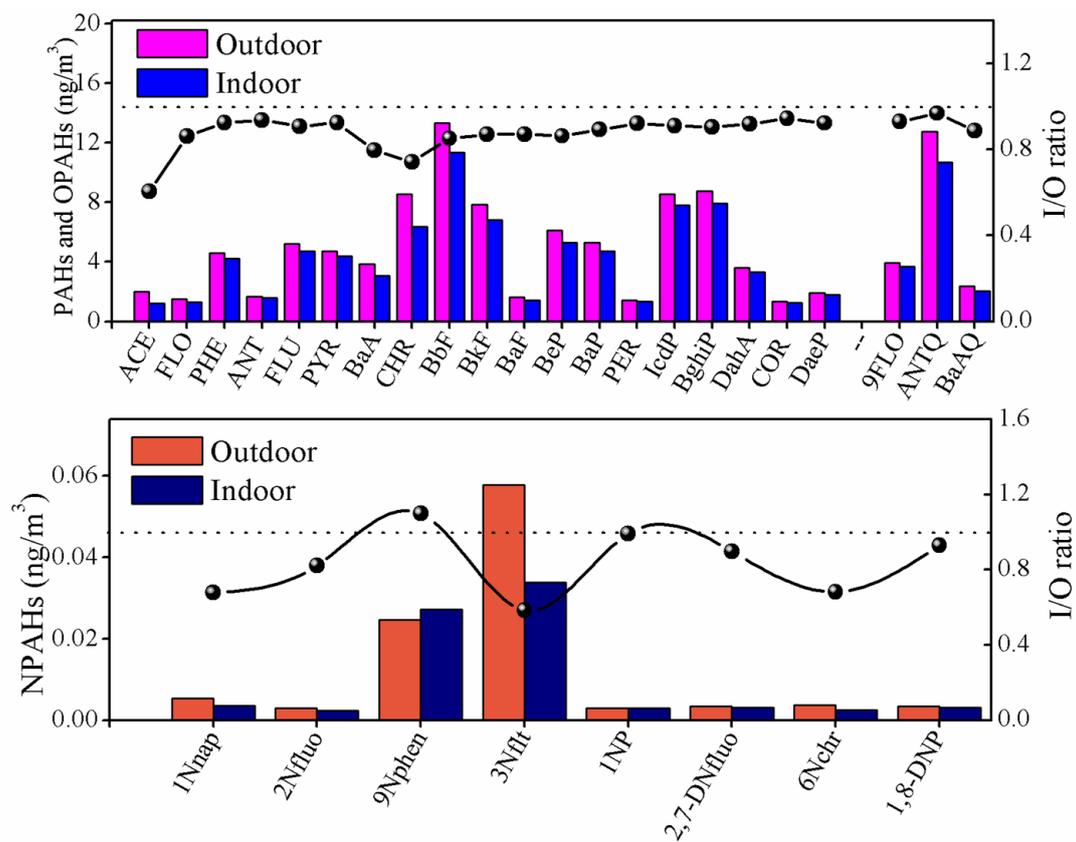


Fig. 2

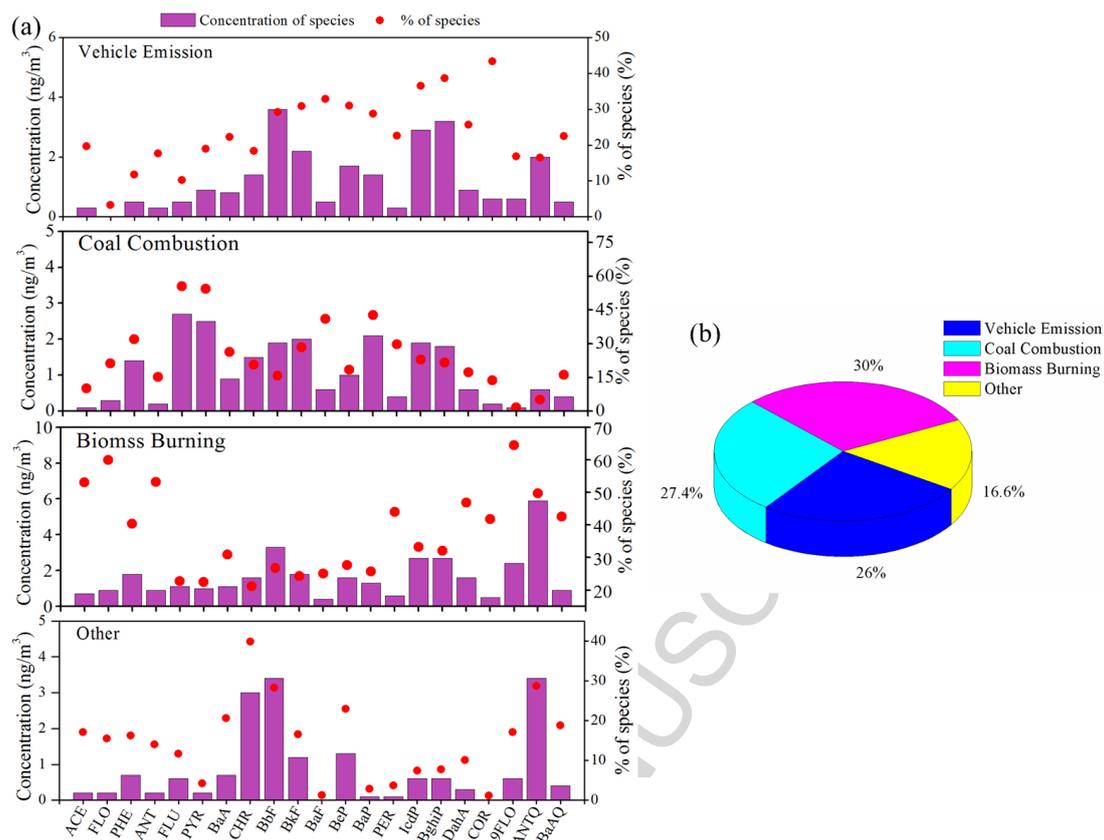


Fig. 3

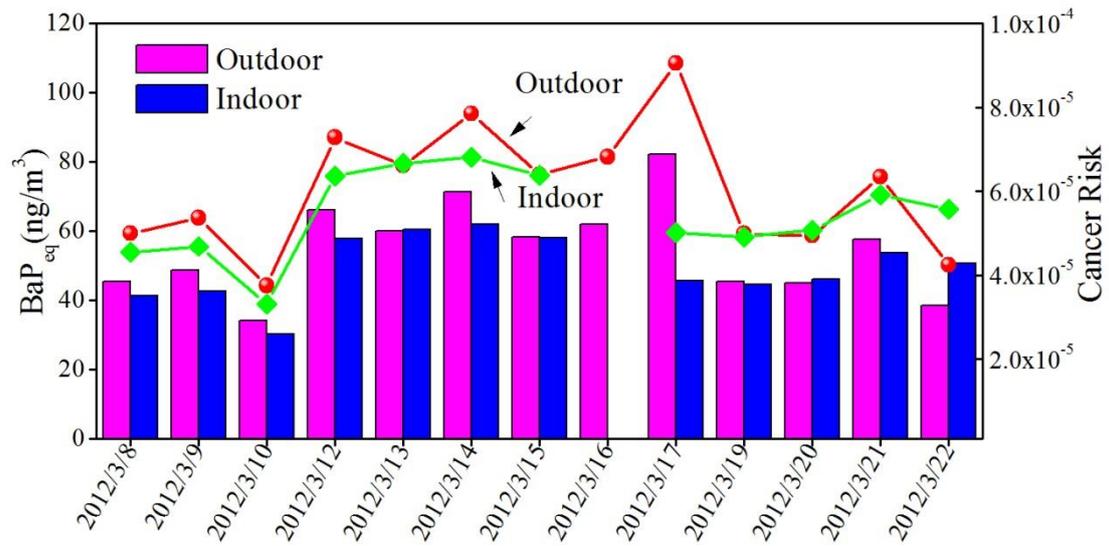


Fig. 4

Table 1 Concentrations of PM_{2.5} and selected substances in outdoor and indoor air samples from a middle school in Xi'an, China.

Pollutants (abbreviation)	Unit	Outdoor(O) ^a	Indoor(I)	I/O
PM _{2.5}	μg/m ³	167.8±59	141.8±42	0.87±0.12
OC		24.9±9.8	22.5±6.6	0.94±0.14
EC		8.8±4.2	7.9±3.0	0.96±0.16
acenaphthene (ACE)	ng/m ³	2.0±1.9	1.2±0.4	0.83±0.44
fluorene (FLO)		1.5±0.4	1.3±0.3	0.88±0.19
phenanthrene (PHE)		4.6±1.2	4.2±1.2	0.93±0.22
anthracene (ANT)		1.7±0.3	1.6±0.3	0.94±0.16
fluoranthene (FLU)		5.2±2.0	4.7±1.8	0.94±0.28
pyrene (PYR)		4.7±1.8	4.4±1.4	0.96±0.22
benzo[a]anthracene (BaA)		3.8±1.2	3.1±0.7	0.85±0.20
chrysene (CHR)		8.5±3.3	6.4±1.8	0.80±0.24
benzo[b]fluoranthene (BbF)		13.3±5.3	11.4±3.2	0.93±0.31
benzo[k]fluoranthene (BkF)		7.8±2.9	6.8±1.9	0.94±0.23
benzo[a]fluoranthene (BaF)		1.6±0.6	1.4±0.4	0.97±0.26
benzo[e]pyrene (BeP)		6.1±2.3	5.3±1.4	0.93±0.27
benzo[a]pyrene (BaP)		5.3±1.9	4.7±1.3	0.95±0.19
perylene (PER)		1.4±0.3	1.3±0.3	0.95±0.14
indeno[1,2,3-cd]pyrene (IcdP)		8.5±2.7	7.8±1.8	0.98±0.29
benzo[ghi] perylene (BghiP)		8.7±2.9	7.9±1.9	0.98±0.32
dibenzo[a,h]anthracene (DahA)		3.6±0.7	3.3±0.6	0.95±0.16
coronene (COR)		1.3±0.4	1.3±0.3	1.02±0.33
dibenzo[a,e]pyrene (DaeP)		1.9±0.4	1.8±0.4	0.97±0.23
ΣLMW-PAHs ^b		9.8±3.0	8.4±2.1	0.92±0.24
ΣHMW-PAHs ^b		82.1±27.7	71.6±17.8	0.87±0.22
ΣComb-PAHs ^b		75.5±25.7	65.4±16.3	0.93±0.25
ΣPAHs ^a		92.0±29.7	79.9±19.3	0.93±0.25

9-fluorenone (9FLO)	ng/m ³	3.9±0.68	3.7±1.0	0.93±0.18
anthraquinone (ANTQ)		12.8±3.4	10.7±3.3	0.97±0.65
benz[a]anthracene-7,12-dione (BaAQ)		2.4±0.5	2.0±0.4	0.88±0.16
ΣOPAHs ^b		19.1±3.9	16.4±4.2	0.91±0.36
1-Nitronaphthalene (1Nnap)	ng/m ³	0.0053±0.0080	0.0036±0.0030	1.2±1.1
2-Nitrofluorene (2Nflu)		0.0029±0.0032	0.0024±0.0026	0.31±0.40
9-Nitrophenanthrene (9Nphen)		0.0247±0.0120	0.0272±0.0277	2.2±4.1
3-Nitrofluoranthene (3Nflt)		0.0577±0.0477	0.0338±0.0134	1.1±1.1
1-Nitropyrene (1NP)		0.0029±0.0012	0.0029±0.0030	1.6±2.7
2,7-Dinitrofluorene (2,7-DNflu)		0.0034±0.0017	0.0030±0.0026	0.55±0.36
6-Nitrochrysene (6Nchr)		0.0036±0.0012	0.0025±0.0014	0.73±0.40
1,8-Dinitropyrene (1,8-DNP)		0.0033±0.0029	0.0031±0.0017	0.64±0.55
ΣNPAHs		0.1039±0.0674	0.0785±0.0416	1.5±2.1

^a Arithmetic mean ± SD; ^b ΣLMW-PAHs is sum of acenaphthene, 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. ΣNPAHs is sum of 1-Nitronaphthalene, 2-Nitrofluorene, 9-Nitrophenanthrene, 3-Nitrofluoranthene, 1-Nitropyrene, 2,7-Dinitrofluorene, 6-Nitrochrysene, and 1,8-Dinitropyrene.

Table 2 Mass concentrations of PM_{2.5} and polycyclic aromatic hydrocarbons (PAHs) in outdoor air and indoor air from schools around the world.

Region	PM _{2.5} (µg/m ³)		PAHs(ng/m ³)		Sampling period	Reference
	Indoor	Outdoor	Indoor	Outdoor		
Netherlands	23.0	24.8	NA	NA	April 1997 -May 1998	Janssen et al., 2001
Antwerp, Belgium ^a	57,72	53,54	NA	NA	Dec. 2002	Stranger et al., 2008
Antwerp, Belgium ^a	61.54	72,27	NA	NA	June 2003	Stranger et al., 2008
Athens, Greece	82	56	NA	NA	Nov.2011-Feb.2004;Oct.-Dec.2004	Diapouli et al., 2008
Stockholm, Sweden ^b	8.1; 6.1	9.7, 7.6	NA	NA	Dec.2003-July 2004	Wichmann et al., 2010
South Texas,USA	2.8-7.9	6.5-23.2	NA	NA	Feb. 2009-Feb.2010	Zhang et al., 2012
Nis,Serbia	38.5	40.3	NA	NA	Mar.-Apr.2013	Kovacevic et al., 2015
Rome, Italy	11-27	22-34	1.8-8.3	6.3-9.5	Nov.-Dec 2011, Feb.-Mar. 2012	Romagnoli et al., 2014
Rome, Italy	12-27	9-16	0.3-1.02	0.4-1.21	May-June 2012	Romagnoli et al., 2014
Kaunas,Lithuania	NA	NA	20.3-131.1	40.7-121.2	Heating season 2011/2012	Krugly et al., 2014
Rome,Italy	20	33	6.0	9.1	Winter, 2012	Gatto et al., 2014
Rome,Italy	16	14	0.63	1.08	Spring/summer 2012	Gatto et al., 2014
Serbia ^c	12.0-51.4	22.4-131.0	88.4-421.9	201.7-1017	Dec.2011	Zivkovic et al.,2015
Serbia ^c	1.25-67	2.07-9.2	36.9-271.6	27.0-132.3	June 2012	Zivkovic et al.,2015
Portugal ^d	18.4	19.3	1.45	1.62	Apr.-June 2013	Oliveira et al., 2016
Portugal ^e	14.2	15.2	4.23	4.55	Apr.-June 2013	Oliveira et al., 2016
Xi'an, China			53.2	72.9	May 2012	Xu et al., 2015
<i>Xi'an, China</i>	<i>141.8</i>	<i>167.8</i>	<i>79.9</i>	<i>92.0</i>	<i>Mar. 2012</i>	<i>This study</i>

^a means data from schools in urban and suburbs. ^b means the school and preschool; ^c means Median; ^d means in private school; ^e means in public school.

Table 3 Diagnostic ratios and indices of PAHs, OPAHs, and NPAHs.

Ratio or Index	Outdoor	Indoor
	Average (range)	Average (range)
ANT/(ANT + PHE)	0.27 (0.22-0.34)	0.28 (0.22-0.32)
BaA/(BaA + CHR)	0.32 (0.27-0.39)	0.33 (0.27-0.38)
BaP/(BaP + BeP)	0.46 (0.40-0.50)	0.47 (0.42-0.51)
IcdP/(IcdP + BghiP)	0.50 (0.48-0.51)	0.50 (0.48-0.51)
Flu/(Flu + PYR)	0.52 (0.51-0.56)	0.51 (0.36-0.54)
9FLO/FLO	2.7(2.0-3.8)	2.8 (2.2-3.8)
ANTQ/ANT	7.7 (2.8-10.7)	6.8 (3.8-9.7)
BaAQ/BaA	0.65(0.44-0.90)	0.68 (0.58-0.81)
3Nflt/1NP	18.0(7.1-38.8)	17.8(4.0-44.2)

Table 4 BaP equivalent concentrations and inhalation cancer risk of individual PAHs and their derivatives.

Species	PEF ^a	BaP _{eq} (ng/m ³)		Cancer risk	
		Outdoor	Indoor	Outdoor	Indoor
FLU	0.08	0.42	0.38	4.58×10 ⁻⁷	4.16×10 ⁻⁷
BaA	0.2	0.77	0.61	8.46×10 ⁻⁷	6.75×10 ⁻⁷
CHR	0.1	0.85	0.64	9.40×10 ⁻⁷	6.99×10 ⁻⁷
BbF	0.8	10.7	9.1	1.17×10 ⁻⁵	1.0×10 ⁻⁵
BkF	0.03	0.23	0.20	2.58×10 ⁻⁷	2.25×10 ⁻⁷
BaP	1	5.3	4.7	5.81×10 ⁻⁶	5.19×10 ⁻⁶
IcdP	0.07	0.60	0.54	6.58×10 ⁻⁷	6.0×10 ⁻⁷
BghiP	0.009	0.08	0.07	8.66×10 ⁻⁸	7.83×10 ⁻⁸
DahA	10	36.1	33.2	3.97×10 ⁻⁵	3.65×10 ⁻⁵
ΣPAHs		54.98	49.42	6.05×10 ⁻⁵	5.44×10 ⁻⁵
	PEF ^b				
1NP	0.1	0.0003	0.0003	3.23×10 ⁻¹⁰	3.20×10 ⁻¹⁰
6Nchr	10	0.0363	0.0248	3.99×10 ⁻⁸	2.72×10 ⁻⁸
1,8-DNP	1	0.0033	0.0031	3.68×10 ⁻⁹	3.42×10 ⁻⁹
ΣNPAHs		0.0399	0.0282	4.39×10 ⁻⁸	3.10×10 ⁻⁸
Total		55.08	49.45	6.05×10 ⁻⁵	5.44×10 ⁻⁵

^a the value of potency equivalency factor (PEF) from U.S.EPA (2010). ^bValue from OEHHHA(2005)

Highlight

- PM_{2.5} bounded 19 PAHs, 3OPAHs, and 8NPAHs were monitored in a middle school in Xi'an.
- Indoor pollutants were mostly influenced by outdoor air.
- Biomass burning, coal combustion, and vehicle emission were main sources for PAHs. Secondary formation was the main source for OPAHs and NPAHs.
- Inhalation cancer risks assessment of PAHs showed that there were potential health risks for students during sampling time.