



Source, health risk and composition impact of outdoor very fine particles (VFPs) to school indoor environment in Xi'an, Northwestern China



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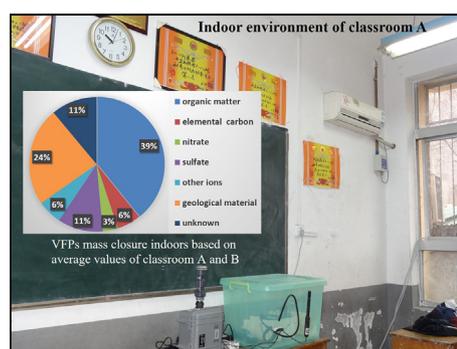
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HIGHLIGHTS

- Organic matter, SO_4^{2-} and geological material were the major components of VFPs.
- Particle resuspension and chalk dust increased the classroom VFPs concentrations.
- High temperature and suspension time of VFPs indoors lead to secondary pollution.
- Pb and Mn non-cancer and PAHs cancer risk at school require action from government.

GRAPHICAL ABSTRACT



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ABSTRACT

Very fine particles (VFPs, $\text{PM}_{0.25}$) are able to travel deeply into the respiratory tract and can produce adverse health effects, especially to children. Information on the VFPs in schools is generally lacking. We investigated the chemical compositions, sources and health risks of VFPs in a junior secondary school of Xi'an, China, during May 16th to 30th, 2012. The results showed that organic matter (37% and 39%), SO_4^{2-} (13% and 11%) and geological material (20% and 24%) were the major components of VFPs both outdoors and indoors. The VFP species indoors, such as SO_4^{2-} and elemental carbon, are mainly from outdoor origins, e.g. coal burning and traffic emissions. But particle resuspension by student activities, chalk dust and import from outdoors of soil dust also contributed to deteriorate air quality in the classroom. By contrast to outdoors, several indoor factors, like higher room temperature, limited volume and longer suspension time of classroom particles, can even lead to significant secondary pollutant production. Heavy metals (mainly from outside) bound to indoor VFPs are supposedly associated to non-cancer health risks, especially Pb through ingestion pathway and Mn through dermal contact. Outdoor VFPs may be associated to PAHs cancer health risks via inhalation way. This study confirms that both indoor and outdoor sources had contributions to indoor VFPs, and that VFPs health risk should be of higher concern in urban areas of Northwestern China.

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1. Introduction

China has undergone a rapid economic development together with epidemiological changes over the past few decades. Ambient air pollution and household air pollution ranked the fourth and the fifth causes of death in China in 2010 (Yang et al., 2013). Nowadays, haze, which is mainly caused by particulate matter (PM), is a major air pollution problem throughout much of Northern China. Xi'an is a large industrial city in Northwestern China, located in the middle of the Yellow River valley and in the center of the Guanzhong Plain, where is subjected to high concentrations of PM for much of the year (Cao et al., 2005a; Shen et al., 2009a; Xu et al., 2016a).

Very fine particles (VFPs, $PM_{0.25}$, PM with equivalent aerodynamic diameters $\leq 0.25 \mu\text{m}$) in the atmosphere is the most important fraction of $PM_{2.5}$ (PM with equivalent aerodynamic diameters $\leq 2.5 \mu\text{m}$). VFPs can represent the most important fraction of $PM_{2.5}$, like PAHs (Xu et al., 2015). VFPs are able to travel deeply into the respiratory tract, reaching the pulmonary alveoli and participating blood circulation in human body. Compared to total suspended particulate (TSP) and $PM_{2.5}$, the longer atmospheric residence time of VFPs make them able to be transported over longer distances, thus spreading over their health hazard (Mazaheri et al., 2014). Typical toxic chemical compounds, such as heavy metals and polycyclic aromatic hydrocarbons (PAHs) can be attached on VFPs, which would cause various health problems for humans, especially for children (WHO, 1998; Kumar et al., 2014; Xu et al., 2015). For example, Pb is neuro-developmental heavy metal at low exposure dose through kinds of exposure routes, affecting children health and mental development seriously (USEPA, 2006). Some of PAHs can be cytotoxic, mutagenic, teratogenic or carcinogenic for humans, and the association between specific PAHs and lung carcinogenesis, child development has already been confirmed (WHO, 1998; Tang et al., 2008).

Ambient PM is considered to be an important indicator of outdoor air quality (Fromme et al., 2008). It is generally accepted that one of the major factors influencing indoor PM concentrations is the outdoor emission source. The school environment is normally absence of combustion sources in the classroom, but the particularity—many children in a limited space over a period of several hours—makes serious indoor air quality problem. Exposure to classroom PMs, especially to VFPs can result in potential health threat to children, who represent a sensitive group, which respiratory system is non-fully developed (Tran et al., 2012). Therefore, the exposure to VFPs in schools should be a major health concern. However, the high concentrations in the classroom do not necessarily result in higher health risks to students, because the sources and the compositions of PMs in indoor ambient air may differ from those outdoors (Schwarze et al., 2006).

Up to now, only a few studies have investigated the VFPs chemical compositions inside schools, and little is known regarding the concentration and health impact from the outdoor environment. It is of importance to determine the sources of indoor particles and to examine to what degree indoor particles are affected by outdoor PMs. Therefore, the aim of the present study is to characterize the chemical properties of VFPs and their interrelation inside the classrooms and outside, and to determine the impact of the outdoor sources and indoor human activities, as well as the VFPs health risks on students by the U.S. EPA health risk assessment model.

2. Materials and methods

2.1. Site description

The junior middle school surveyed is located in the southwest part of Xi'an urban area, China, distant by about 100 m from the main roads. There are chemical factories and several residential communities around the school, but the main source of pollution is expected to be from traffic exhaust, cooking emissions. VFPs ($PM_{0.25}$) samples were

collected from May 16th to 30th, 2012 for two grade-one classes (fifty 12 to 14 years old students in each class, named classroom A and B, respectively), and for one outdoor sampling, synchronously. The outdoor sampling site was set up 1.2 m above the ground outside, in the vicinity of the classrooms. It hence reflects the average school outdoor air or Xi'an ambient atmospheric conditions. Two sets of indoor instrumental package were located on the classroom desk 1.2 m above the ground in the back of the classroom, a height consistent with the level of student breathing in the two adjacent classrooms. The classrooms investigated in this study were installed traditional blackboards in the front and back of the classroom.

2.2. VFPs collection and gravimetric analysis

The aerosol samples were collected with a Sioutas Personal Cascade Impactor (SKC Inc., Eighty Four, CA, USA), which uses a cyclone to separate five different particle sizes and was operated at a flow rate of 10.0 L min^{-1} . This study is built on the collection of the finest particles on the last stage of the impactor. According to the impactor specifications, their aerodynamic diameter is $<250 \text{ nm}$ or $0.25 \mu\text{m}$, which defines the term “very fine particles” (VFPs) hereafter used. Pre-fired ($780 \text{ }^\circ\text{C}$, 3 h) 47 mm Whatman quartz micro-fibre filters (QM/A, Whatman Inc., U.K.) were used to collect samples in a 47-mm filter-holder fixed at the bottom of the impactor. In order to avoid particle samples overloading and sampler blockage, the samplers were controlled by an electrical timer, which allowed them to run for 12 h every 24 h (half an hour every one hour). All filters were changed every day at 8:00 am local time. A total of 33 samples and 12 field blanks were collected, i.e. 11 samples (collected on Monday to Friday, school day) and 4 field blanks (collected on Saturday and Sunday, non-school day) for each sampling site during the study period. All of the data analysis and discussion were based on the school days results. The indoor concentrations of VFPs and chemical components were extremely low owing to no student in the classroom and the closed windows and doors. Therefore, the non-school days results were only used as background environment concentrations for reference, excluding from the discussion.

VFP samples were analyzed gravimetrically for mass concentrations with a Sartorius ME 5-F electronic microbalance (sensitivity $\pm 1 \mu\text{g}$, Sartorius, Germany). Filters were weighed before and after sampling after equilibration for 24 h at $20\text{--}23 \text{ }^\circ\text{C}$ and RH of 35%–45%. The absolute errors between duplicate weights were $<0.010 \text{ mg}$. The exposed samples and field blanks were tightly air sealed and stored in a refrigerator at less than $-20 \text{ }^\circ\text{C}$ until chemical analysis.

2.3. Chemical analysis

2.3.1. Carbon analysis

Organic carbon (OC) and elemental carbon (EC) were measured on a 0.526 cm^2 filter punch using a Desert Research Institute (DRI) Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, CA, USA) with IMPROVE_A (Interagency Monitoring of Protected Visual Environment) thermal/optical reflectance (TOR) protocol (Chow et al., 2005, 2007, 2011; Cao et al., 2013). The method yielded four OC thermal fractions (OC1, OC2, OC3, and OC4 in a non-oxidizing helium (He) atmosphere at $140 \text{ }^\circ\text{C}$, $280 \text{ }^\circ\text{C}$, $480 \text{ }^\circ\text{C}$, and $580 \text{ }^\circ\text{C}$, respectively), one OP fraction (pyrolyzed carbon determined when the reflected laser light attained its original intensity after O_2 was added to the combustion atmosphere), and three EC fractions (EC1, EC2, and EC3 in an oxidizing atmosphere of 2% oxygen (O_2) in a balance of 98% He at $580 \text{ }^\circ\text{C}$, $780 \text{ }^\circ\text{C}$, and $840 \text{ }^\circ\text{C}$, respectively). The IMPROVE_A protocol defines total carbon (TC) as $\text{OC} + \text{EC}$, OC as $\text{OC1} + \text{OC2} + \text{OC3} + \text{OC4} + \text{OP}$, and EC as $\text{EC1} + \text{EC2} + \text{EC3} - \text{OP}$.

2.3.2. Inorganic water-soluble ions analysis

Five cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}) and three anions (Cl^- , NO_3^- and SO_4^{2-}) in aqueous extracts of the filters were determined by an

ion chromatograph (IC) analyzer (Dionex-600, Sunnyvale, CA, USA), which was equipped with an AS11-HC anion column and a CS12A cation column for separation. Details of the method and QA/QC have been described in Shen et al. (2009a, 2009b) and Zhang et al. (2011).

2.3.3. Elemental analysis

The elemental concentrations of Ti, Mn, Fe, Ni, Zn, Ba and Pb in VFPs were determined by Energy Dispersive X-Ray Fluorescence (ED-XRF) spectrometry (the PANalytical Epsilon 5 ED-XRF analyzer, PANalytical, the Netherlands) (Watson et al., 1999; Cao et al., 2013). National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 2783 was employed to validate the accuracy of the instrument. Replicate analysis (five times) yielded an analytical precision between 3.9%–10.5%. Details of the ED-XRF measurements and QA/QC have been described in Xu et al. (2012, 2016a, 2017) and Brouwer (2003).

2.3.4. PAHs analysis

An in-injection port thermal desorption (TD) - gas chromatograph/mass spectrometry (GC/MS) procedure as used in this study (Ho and Yu, 2004; Chow et al., 2007; Ho et al., 2008, 2011; Xu et al., 2013, 2015, 2016b; Chen et al., 2014). Sixteen PAHs identified and quantified in this study, including fluorine (FLO, 3-ring), phenanthrene (PHE, 3-ring), anthracene (ANT, 3-ring), fluoranthene (FLU, 4-ring), pyrene (PYR, 4-ring), benzo[a]anthracene (BaA, 4-ring), chrysene (CHRY, 4-ring), benzo[b]fluoranthene (BbF, 5-ring), benzo[k]fluoranthene (BkF, 5-ring), benzo[a]fluoranthene (BaF, 5-ring), benzo[e]pyrene (BeP, 5-ring), benzo[a]pyrene (BaP, 5-ring), perylene (PERY, 5-ring), indeno[1,2,3-cd]pyrene (IcdP, 6-ring), dibenzo[a,h]anthracene (DahA, 5-ring) and benzo[g,h,i]perylene (BghiP, 6-ring). Details of this method and QA/QC have been described in previous studies (Ho and Yu, 2004; Ho et al., 2008, 2011; Xu et al., 2013; Chen et al., 2014).

2.3.5. Health risk assessment model

Based on the previous literatures (Hu et al., 2012; Sun et al., 2014; Liu et al., 2015; Jedrychowski et al., 2015), we picked four heavy metals (Mn, Ni, Zn and Pb) and all PAH species measured in this study to determine VFPs health risk here. The carcinogenic and non-carcinogenic health risks of VFPs were calculated according to the U.S. EPA health risk assessment model (USEPA, 2004, 2011). The average daily exposure dose (D) of VFPs via inhalation (D_{inh}), ingestion (D_{ing}) and dermal contact (D_{derm}) were estimated to assess the risks by the Eqs. (1)–(3) as follows, respectively:

$$D_{inh} = (C_{inh} \times R_{inh} \times EF \times ED) / (BW \times AT) \quad (1)$$

$$D_{ing} = (C_{ing} \times R_{ing} \times EF \times ED \times CF) / (BW \times AT) \quad (2)$$

$$D_{derm} = (C_{derm} \times SA \times AF \times ABS \times EF \times ED \times CF) / (BW \times AT) \quad (3)$$

definition and recommended values of parameters are shown in Table S1.

Once a daily exposure dose is calculated, a hazard quotient (HQ) for non-cancer risk can be obtained from Eq. (4):

$$HQ = D / RfD \quad (4)$$

the threshold value of RfD indicates whether there is an adverse health effect during a certain period. Hazard index (HI) can be obtained by summing up the individual HQ to estimate the total non-cancer risks, including multiple-element and multiple-exposure route. If the HI < 1, then non-carcinogenic effect is impossible; HI ≥ 1, adverse health effect might likely appear (Hu et al., 2012).

The incremental lifetime cancer risk (ILCR) of heavy metals or PAHs in VFPs via inhalation can be calculated by multiplying the cancer slope factor (CSF_{inh}) of heavy metals or PAHs with D as Eq. (5):

$$ILCR = D \times CSF_{inh} \quad (5)$$

for cancer risk, the value of 1×10^{-6} is an internationally accepted as the precautionary or threshold value above which the risk is unacceptable (Sun et al., 2014; Jedrychowski et al., 2015).

It is worth noting that, among the sixteen PAHs, BaP has been used as an indicator of PAHs carcinogenicity (Wang et al., 2006). The carcinogenic health risk of sixteen PAH species can be assessed by $[BaP]_{eq}$ instead (Yassaa et al., 2001) by Eq. (6):

$$\Sigma[BaP]_{eq} = \Sigma(C_i \times TEF_i) \quad (6)$$

definition and recommended values of the parameters in Eqs. (4)–(6) and the values of RfD through the three exposure ways, as well as the CSF_{inh} used in this study, are shown in Table S1 and Table S2, respectively.

3. Results and discussion

3.1. VFPs chemical characteristics

Table 1 summarizes the average concentrations of VFPs ($PM_{0.25}$) and different chemical compositions on school days during the sampling period. Average VFP mass concentrations were at similar levels outside and inside classroom A and B, because the investigated classrooms were naturally ventilated through five large windows (1.9 m × 1.8 m each window), which were only closed out of school hours. There is no regulatory standard or guideline for $PM_{0.25}$ in China or other organization/country. All samples exceeded the 24-hour WHO $PM_{2.5}$ guideline of $10 \mu g m^{-3}$.

Although TC concentrations and percentages in VFPs (one third approximately) were similar at three sampling sites, OC and EC ratios (OC/EC) varied significantly, ranging from 3.8 ± 1.5 outdoors to 5.3 ± 0.9 in classroom A. The OC/EC has been used to determine the emission and transformation characteristics of carbonaceous aerosols. OC/EC exceeding 2.0 indicates the presence of secondary organic carbon (SOC) (Gray et al., 1986; Cao et al., 2005a). In this study, either for indoor or outdoor samples, the average OC/EC values were higher than 2.0, thus suggesting the presence of SOC at school environment in Xi'an urban area. The higher average OC/EC ratio was observed in the indoor environment (4.9 ± 1.4) than outdoors (3.8 ± 1.5), indicating that SOC can be produced in a semi closed environment due to the long reaction time (the PMs were disturbed by school students during the school time) and the stable atmospheric factors (lower air exchange rate in indoors than outdoors) in the classroom (Sarwar et al., 2003), as well as organic precursor emitted from the detergent in indoor environment reaction with O_3 (Morawska et al., 2009).

Eight thermal carbon fractions of OC and EC differ by sources and have been used for the source apportionment of carbonaceous aerosol (Kim and Hopke, 2004; Cao et al., 2005a). The average percentages for eight carbon fractions outdoors and indoors of VFPs are shown in Fig. 1. The average abundances of OC1, OC2, OC3, OC4, OP, EC1-OP, EC2 and EC3 outdoors were 7.7%, 22.4%, 37.3%, 10.2%, 1.8%, 16.2%, 4.4% and 0.0%, respectively. The corresponding percentages for the indoor samples paralleled those obtained from the outdoor samples, implying that the major contributing sources were similar for carbonaceous aerosols in both indoor and outdoor school environments. Noticeably, the motor vehicle exhausts marker EC1 as EC1-OP in Fig. 1 (Cao et al., 2005a; Xu et al., 2016a) accounted for 16.2%, 12.6% and 14.5% in outside and classroom A and B respectively, suggesting that the contribution from the motor vehicle exhausts contributed more to outdoors than indoors.

Total ions accounted for 25.1%, 20.7% and 25.8% of VFPs in outdoor and classroom A and B, respectively. SO_4^{2-} , NO_3^- and Ca^{2+} were the most abundant ions, accounting for 78%–82% of total measured ions and 16%–21% of VFP mass concentrations. The total concentrations of 7 elements measured in this study were 0.53, 0.68 and $0.63 \mu g m^{-3}$ in classroom outdoor and classroom A and B during the measured period,

Table 1
Summary of VFPs mass concentrations and chemical compositions during the sampling period.

	Outdoor	Classroom A	Classroom B
No. of samples	11	11	11
VFPs mass ($\mu\text{g m}^{-3}$)	35.4 ± 14.9^a	35.4 ± 14.0	34.3 ± 12.3
Routine composition ($\mu\text{g m}^{-3}$)			
OC	9.5 ± 3.7	10.0 ± 3.9	9.7 ± 3.4
EC	2.5 ± 1.1	1.9 ± 0.6	2.2 ± 1.1
OC1	0.92 ± 0.61	1.09 ± 0.76	0.94 ± 0.43
OC2	2.67 ± 0.98	2.83 ± 0.93	2.63 ± 0.81
OC3	4.45 ± 2.14	4.52 ± 1.55	4.54 ± 1.48
OC4	1.22 ± 0.69	1.36 ± 0.61	1.26 ± 0.76
OP	0.22 ± 0.30	0.21 ± 0.13	0.33 ± 0.72
EC1	2.16 ± 1.17	1.71 ± 0.53	2.05 ± 1.57
EC2	0.52 ± 0.17	0.43 ± 0.23	0.47 ± 0.22
EC3	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
Total carbon	12.0 ± 4.4	11.9 ± 4.4	11.9 ± 4.3
SO_4^{2-}	4.64 ± 2.83	3.60 ± 1.94	4.07 ± 2.86
NO_3^-	1.34 ± 1.21	0.94 ± 0.57	1.65 ± 1.39
NH_4^+	0.21 ± 0.33	0.20 ± 0.25	0.54 ± 0.49
Cl^-	0.46 ± 0.23	0.42 ± 0.42	0.41 ± 0.32
Na^+	0.52 ± 0.27	0.52 ± 0.39	0.55 ± 0.45
K^+	0.19 ± 0.19	0.12 ± 0.07	0.20 ± 0.21
Ca^{2+}	1.27 ± 0.96	1.26 ± 0.78	1.16 ± 0.78
Mg^{2+}	0.25 ± 0.08	0.26 ± 0.09	0.26 ± 0.10
Total ions	8.90 ± 5.35	7.32 ± 3.43	8.84 ± 5.65
Ti	0.01 ± 0.01	0.02 ± 0.02	0.01 ± 0.01
Mn	0.01 ± 0.01	0.02 ± 0.02	0.02 ± 0.02
Fe	0.28 ± 0.13	0.36 ± 0.19	0.31 ± 0.13
Ni	0.01 ± 0.00	0.01 ± 0.01	0.01 ± 0.01
Zn	0.07 ± 0.06	0.10 ± 0.07	0.11 ± 0.04
Ba	0.13 ± 0.08	0.14 ± 0.08	0.15 ± 0.13
Pb	0.03 ± 0.02	0.04 ± 0.02	0.03 ± 0.01
Total elements	0.53 ± 0.19	0.68 ± 0.27	0.63 ± 0.20
Non-routine composition-PAHs (ng m^{-3})			
Fluorine (FLO)	16.2 ± 15.1	10.6 ± 7.7	11.8 ± 9.6
Phenanthrene (PHE)	15.4 ± 18.3	9.3 ± 7.8	10.3 ± 9.2
Anthracene (ANT)	2.1 ± 2.0	1.4 ± 1.1	1.6 ± 1.3
Fluoranthene (FLU)	2.6 ± 3.0	1.6 ± 1.6	1.9 ± 2.0
Pyrene (PYR)	2.1 ± 2.1	1.2 ± 1.3	1.5 ± 1.7
Benzo[a]anthracene (BaA)	0.7 ± 0.7	0.4 ± 0.4	0.6 ± 0.9
Chrysene (CHRY)	1.5 ± 1.9	0.9 ± 1.0	1.3 ± 1.7
Benzo[b]fluoranthene (BbF)	4.0 ± 4.9	2.5 ± 2.4	3.3 ± 4.7
Benzo[k]fluoranthene (BkF)	2.6 ± 2.8	1.8 ± 1.6	2.2 ± 2.7
Benzo[a]fluoranthene (BaF)	0.3 ± 0.4	0.2 ± 0.3	0.3 ± 0.5
BENZO[e]pyrene (BeP)	6.5 ± 6.8	4.2 ± 4.0	5.1 ± 6.3
Benzo[a]pyrene (BaP)	2.4 ± 2.9	1.6 ± 1.9	2.2 ± 3.5
Perylene (PER)	0.4 ± 0.5	0.3 ± 0.3	0.4 ± 0.6
Indeno[1,2,3-cd]pyrene (IcdP)	2.4 ± 3.0	1.6 ± 1.8	2.4 ± 3.2
Dibenzo[a,h]anthracene (DahA)	0.3 ± 0.3	0.2 ± 0.2	0.2 ± 0.3
Benzo[ghi]perylene (BghiP)	2.7 ± 3.0	1.9 ± 2.1	2.7 ± 3.3
Total PAHs	59.1 ± 54.2	38.2 ± 32.9	45.2 ± 41.5

^a Arithmetic mean (\pm standard deviation).

accounting for 1.5%, 1.9% and 1.8% of VFPs, correspondingly. Fe and Ba were found to be the dominant ones (accounting for ~75%) among all the measured elements.

The total PAHs accounted for 1.1%–1.7% of VFPs. FLO was the most abundant PAH, followed by PHE and BeP. The average FLO concentration was 12.9 ng m^{-3} , accounting for up to approximately 27% of the total measured PAHs (Fig. 2). The total quantified PAHs average concentration outdoors was 1.5 times and 1.3 times higher than in classroom A and B, which did not follow the same concentration variation trends as VFPs and other main species mentioned above. Similarly, the individual PAHs concentrations outdoors were higher than those indoors. This can be ascribed to the fact that 1) a large number of and intensive PAHs sources exist outdoors; 2) the abundances of outdoor PAHs in VFPs can be shielded by the wall of classroom and the windows and doors to some extent (when they were closed out of school hours) (Anderson et al., 1999; Guo et al., 2008). According to the diagnostic ratios of FLU/(FLU + PYR) vs. ANT/(ANT + PHE) in classroom A, B and outdoors

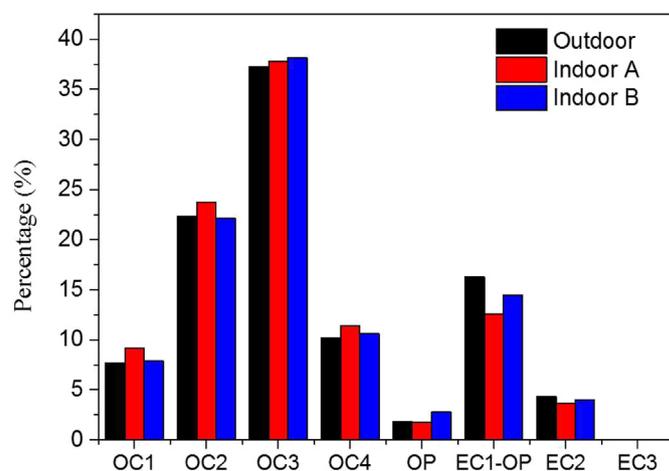


Fig. 1. Carbon fraction contribution (%) to the total carbon in VFPs.

(Fig. S1), the indoor and outdoor PAHs were basically contributed from grass, wood or coal combustion in this study.

3.2. VFPs mass closure and reconstruction

Mass closure for particles is an effective method to analyze aerosols for source discrimination, quality assurance and mitigation efforts with a high degree of confidence that major factors have not been ignored (Ma et al., 2001; Chow et al., 2006). VFPs can be classified into seven major types: organic matter (OM), EC, NO_3^- , SO_4^{2-} , other ions (NH_4^+ , Cl^- , Na^+ , K^+ , Ca^{2+} and Mg^{2+}), geological material (GM) and unknown. For OM, since the chemical composition of the aerosol organic fraction is largely unknown, conversion factor 1.4 (1.4 corrects the organic carbon mass for other constituent associated with the organic carbon molecule) is generally used (Turpin and Lim, 2001; Guinot et al., 2007; Cozic et al., 2008) to shift OC to OM by Eq. (7):

$$\text{OM} = 1.4 \times \text{OC} \quad (7)$$

based on the Eq. (7), OM accounted for 39%, 40% and 40% of VFPs mass outside and inside classroom A and B, respectively. In addition, Fe has been widely used to estimate the upper limit of GM (Taylor and McLennan, 1986; Cao et al., 2005b). Fe constitutes about 4.0% of the Earth's crust in loess plateau (National Environmental Protection Agency, 1990). The amount of GM is calculated by Eq. (8):

$$\text{GM} = (1/4.0\%) \times \text{Fe} \quad (8)$$

based on the Eq. (8), it is found that GM contributed 20%, 25% and 22% to VFPs in outdoor and classroom A and B, respectively.

OM, EC, NO_3^- , SO_4^{2-} , other ions (NH_4^+ , Cl^- , Na^+ , K^+ , Ca^{2+} and Mg^{2+}) and GM were used to attempt a reconstruction of VFP mass concentrations in this study (Fig. 3) (Chow et al., 2015). The correlation coefficient (R^2) between the weighed and reconstructed VFP mass concentrations was 0.986 ($N = 33$, $p < 0.001$). The reconstructed mass accounted for 88.3% of the weighed VFPs in Xi'an in this study; and the slope was 0.87. We can see that the gravimetric measurement of filter samples (weighed VFP mass concentration) matched the sum of the masses of the individually identified chemical species (VFP mass concentration).

According to the chemical species classification and estimation method mentioned above (Cozic et al., 2008; Shen et al., 2009b), Fig. 4 exhibits the mass closure results of VFPs, the sums of all included components were 87%–90% of VFPs among the three sites. On average, the major components of VFPs were OM (37% and 39%), SO_4^{2-} (13% and 11%) and GM (20% and 24%) both outdoors and indoors. OM and GM showed the higher proportions in classroom indoor than outdoor,

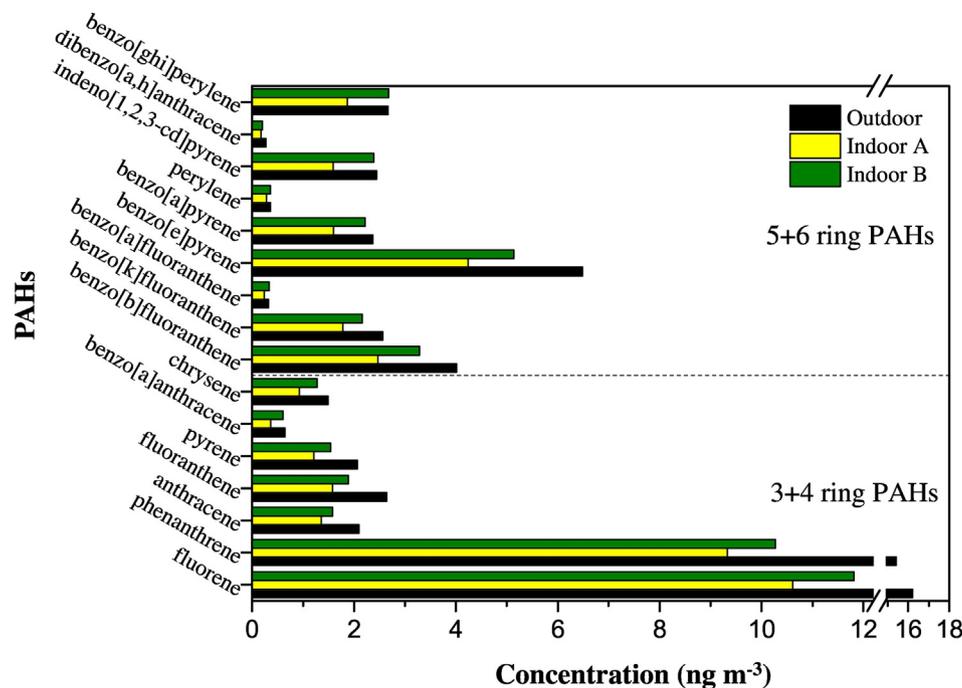


Fig. 2. Individual PAHs found in VFPs outdoors and indoors.

indicating that there were indoor sources or disturbance factors to VFPs OC and elements in classrooms. On the contrary, percentages of coal burning marker- SO_4^{2-} and vehicle exhaust marker-EC in VFPs indoors were less than those outdoors, suggesting that SO_4^{2-} and EC were dominated by outdoor origins (Xu et al., 2015, 2016a).

To the best of our knowledge, VFPs chemical composition inside the classrooms has not been reported in the literature. Thus, we compared those results with the previous studies about $\text{PM}_{1.0}$ (PM with equivalent aerodynamic diameters $\leq 1.0 \mu\text{m}$). In a previous study in Xi'an (Shen et al., 2009b), the relative contributions of chemical species to $\text{PM}_{1.0}$ mass in winter showed that OM, SO_4^{2-} and NO_3^- were the major chemical species and they attributed to 24.5%, 18.1% and 9.1% of $\text{PM}_{1.0}$, respectively. Soil dust and other undetermined fractions represented 34.2%, which is comparable to our results. Tao et al. (2012) reported the relative contributions of chemical species to $\text{PM}_{1.0}$ mass in winter in 2009 to 2010 in Guangzhou, which showed that $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 , OM and EC accounted for 30.7%, 9.7%, 22.6% and 9.7% of

$\text{PM}_{1.0}$, respectively. OM and EC attributed to 32.3% of $\text{PM}_{1.0}$ mass. Soil dust and other undetermined fractions represented $\sim 25\%$, which is lower than the figures found in Xi'an, due to Guangzhou's relatively humid atmospheric environment and the original topography of this typical southeast coastal city. Moreover, for seven consecutive 24-h periods of $\text{PM}_{1.0}$ samples collection during winter and summer 2010 in Edmonton, Canada (Bari et al., 2015), nine sources contributing to both indoor and outdoor $\text{PM}_{1.0}$ concentrations were identified. Soil contributed to $>20\%$ (indoors: 23.8%; outdoors: 19.6%) of the $\text{PM}_{1.0}$ mass, consistent with the results mentioned above in this study.

3.3. Outdoor VFPs impact on indoor VFPs

3.3.1. Inter-correlations of chemical species in VFPs

OC, EC and PAHs have many common origins, such as coal combustion and diesel/gasoline exhaust (Cao et al., 2005a; Liu et al., 2011). Relationships between PAHs measured in this study with OC or EC in classroom outdoor and indoor are examined in Table 2. In general, OC and PAHs correlations and EC and PAHs correlations were both higher outdoors than indoors. Between EC and PAHs, the nine highest correlations ($R^2 > 0.65$) of PAHs with EC consisted in BaA, CHRY, BbF, BkF, BaF, BeP, BaP, PER and IcdP (range of R^2 : 0.661–0.751) outdoors. The same nine PAH species led to low R^2 values (0.365–0.464) indoors. The good correlations observed outdoors may result from the similarity of their sources and the open (well-mixed) environment compared to indoors. In addition, Table 2 displays weak correlations between OC and PAHs (outdoors: $0.066 < R^2 < 0.180$; indoors: $0.001 < R^2 < 0.049$), suggesting different origins for those species. The possible explanation is that SOC is an important contributor to OC, but PAHs are only emitted from primary sources (Xu et al., 2013, 2015).

Moreover, low temperature carbon fractions, such as OC1–OC3, had higher positive correlations in both classroom outdoor and indoor, with low molecular weight PAHs (LMW, 3- and 4-ring PAHs), while the high temperature carbon fractions, like OC4, EC1 and EC2, showed the stronger positive correlations with high molecular weight PAHs (HMW, 5- and 6-ring PAHs), owing to the consistent volatilization and similarity of origins (The correlations of carbon fractions and PAHs were omitted in Table 2).

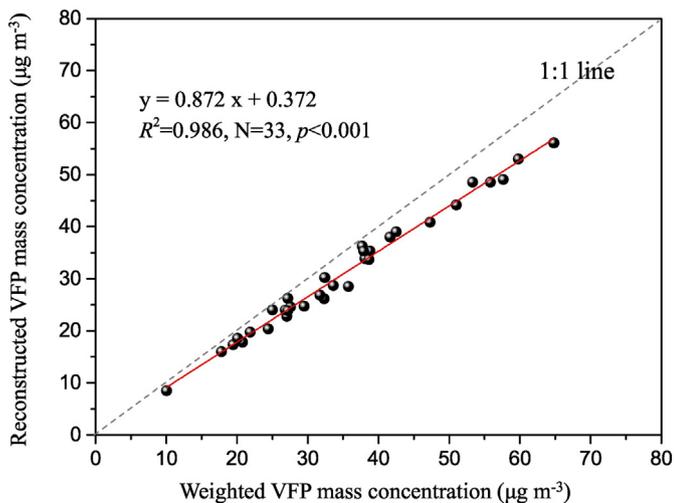


Fig. 3. Weighed versus reconstructed VFP mass concentrations.

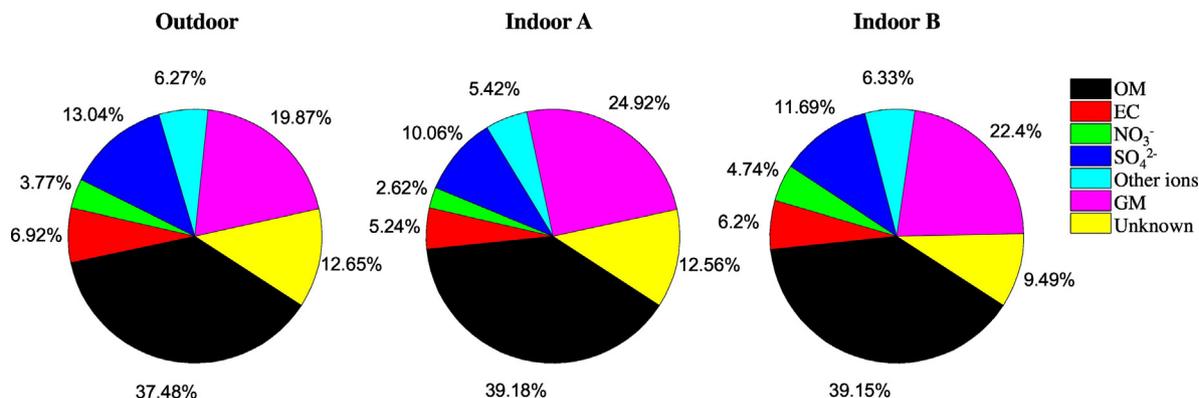


Fig. 4. VFPs mass closure outdoors and indoors (classroom A and B).

3.3.2. VFPs species outdoor/indoor ratio classification

The outdoor/indoor ratio (O/I) can be viewed as a convenient indicator of the relative intensities of the indoor versus outdoor sources, and thus can be used to estimate the impact of VFPs onto the indoor environment at school (Huang et al., 2007; Zhu et al., 2010). For each of the classrooms A and B, the main chemical components of VFPs were categorized according to their outdoor/indoor ratios. Fig. 5 displays the three resulting groups: (I) O/I is always below 1.0 for classroom A and B (within green circle); (II) O/I is always above 1.0 for classroom A and B (within blue circle); and (III) O/I shows an uncertain interactive relationship with 1.0 for classroom A and B (within black circle). Furthermore, Group III is divided into two sub areas - III1 and III2 for discussion.

As shown in Fig. 5, Group I accounted for almost all the trace elements, indicating that elemental concentrations in both classrooms were higher than outdoors. This showed that there were obvious indoor sources: use of chalk or disturbance factors, such as student activities (Thatcher and Layton, 1995; Almeida et al., 2011). Interestingly, Group II samples were enriched in almost all PAHs, suggesting that outdoor sources dominated the PAHs fingerprint observed inside the classrooms, while indoor PAH sources were light or inexistent. Moreover, the average LMW PAHs O/I ratios were 1.7 for classroom A and 1.3 for classroom B, while HMW PAHs O/I ratios were 1.5 and 1.1 for classroom A and B, respectively. As you see that HMW PAHs in the classrooms were much closer to the levels of HMW PAHs outside. HMW PAHs in VFPs outside could more easily enter the classroom by attached

dust than LMW PAHs, or LMW PAHs in the classrooms volatilized easily from VFPs because of the thermodynamics (Xu et al., 2015). As we know, HMW PAHs are more harmful to human health than LMW PAHs (Nisbet and Lagoy, 1992; Xu et al., 2013). The associated health risks of PAHs inside and outside the classrooms are discussed in next section.

III1 and III2 corresponded to OC and EC, respectively, implying that OC and EC had different transportation ways and sources. OC is constituted by primary and secondary organic carbon fractions, while EC is only from primary sources (Cao et al., 2007), similarly to PAHs. The sampling period occurred in May with bright sunshine and high air temperature. The relatively lower O/I_A and O/I_B ratios for OC than those for EC suggest that outside OC was transported into the classrooms, possibly attached to the geological material brought in by the students. It then remained suspended in such a small volume for relatively long time, while a series of photochemical reactions could take place, resulting in high concentrations of SOC in the classrooms, which was consistent with the SOC estimation mentioned above.

As for the water-soluble inorganic ions in VFPs (out of the three groups), they generally led to a great variety of O/I ratios, indicating the uncertain impact of outdoor sources to indoor ions at school. O/I ratios in classroom A and B were different for all the secondary water-soluble ions (NO₃⁻, NH₄⁺ and SO₄²⁻) and K⁺, but the values were comparable for the primary ions (Cl⁻, Na⁺, Mg²⁺ and Ca²⁺). This suggests the secondary formation of ions was dependent on the environment changes, and that their source profiles were particularly complex. Among all the primary ions measured in this study, Ca²⁺ is the only characterized by O/I ratios > 1 for both classrooms. This was attributed to the use of

Table 2

Correlations of PAHs with OC and EC outdoors and indoors. (Indoor calculations are based on average values of classroom A and B; high correlation coefficients ($R^2 > 0.65$) are in bold.)

PAHs	With OC (R^2)		With EC (R^2)	
	Outdoor	Indoor	Outdoor	Indoor
Fluorine (FLO)	0.070	0.001	0.019	0.005
Phenanthrene (PHE)	0.092	0.001	0.022	0.011
Anthracene (ANT)	0.099	0.006	0.039	0.035
Fluoranthene (FLU)	0.180	0.005	0.297	0.200
Pyrene (PYR)	0.154	0.012	0.463	0.305
Benzo[a]anthracene (BaA)	0.071	0.030	0.661	0.462
Chrysene (CHRY)	0.114	0.019	0.737	0.413
Benzo[b]fluoranthene (BbF)	0.095	0.021	0.677	0.402
Benzo[k]fluoranthene (BkF)	0.112	0.023	0.698	0.365
Benzo[a]fluoranthene (BaF)	0.147	0.031	0.751	0.442
Benzo[e]pyrene (BeP)	0.122	0.020	0.698	0.372
Benzo[a]pyrene (BaP)	0.076	0.029	0.663	0.449
Perylene (PER)	0.112	0.048	0.683	0.464
Indeno[1,2,3-cd]pyrene (IcdP)	0.080	0.007	0.680	0.395
Dibenzo[a,h]anthracene (DahA)	0.076	0.049	0.616	0.382
Benzo[ghi]perylene (BghiP)	0.066	0.004	0.631	0.342
Total PAHs	0.146	0.017	0.380	0.229

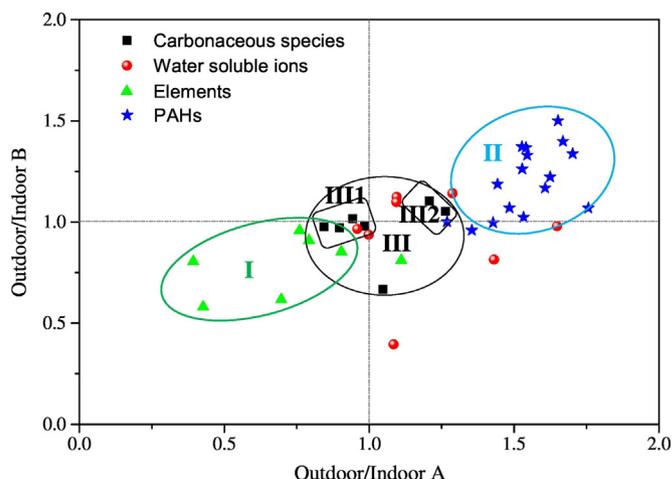


Fig. 5. Outdoor/indoor ratios of the main aerosol components in classroom A versus classroom B.

chalk during school-time (confirmed by questionnaires) and dust resuspension from indoor activities (walking, sitting and playing) (Fromme et al., 2008). Previous studies have also reported that crustal elements or crustal ions were the most abundant in PM, even finer PM (such as PM_{1.0}) inside classrooms (Gemenetzis et al., 2006; Tran et al., 2012).

In summary, the influence degree of outdoor particles on indoor VFPs varied according to different chemical aerosol components. Chalk dust, particle resuspension by student activities and import of outdoor soil dust are the most ubiquitous origins of Ca²⁺, Fe, Mn and Ti in the classrooms (Tran et al., 2012). The combined effects of relatively high temperature (owing to a high occupancy rate) and frequent suspension of VFPs (owing to student activities) in the limited volume of the classrooms can lead to more intense secondary air pollution (SOC and secondary water-soluble ions) indoors (Sarwar et al., 2003; Morawska et al., 2009; Mejía et al., 2011). The other species are mainly from outdoor origins, such as natural, traffic, coal combustion, industrial and other anthropogenic sources (Diapouli et al., 2008; Mejía et al., 2011).

3.4. VFPs health risk assessment

Non-cancer risks of four heavy metals (Mn, Ni, Zn and Pb) via three different ways (inhalation, ingestion and dermal contact) inside and outside the classrooms are shown in Table 3 and Fig. 6. Among those metals, the HQ of Pb indoors through ingestion way was the highest (1.2), which suggests that Pb non-carcinogenic risk was obvious in the classroom, well-beyond the threshold value (1.0). This result confirmed the high child blood lead level (BLL) in China (Qi et al., 2002). The urban child BLL in China ranged from 5.0 to 9.0 µg dL⁻¹, with an average level of 8.8 µg dL⁻¹ (Qi et al., 2002; Chen et al., 2006). The mean 1662 children (0–6 years old) BLL was 5.8 µg dL⁻¹ between 2010 and 2011 in Xi'an (Men and Guo, 2013), which is above the U.S. Centers for Disease Control (CDC) child BLL guideline (5 µg dL⁻¹). Except for Pb, HQs of other heavy metals either indoors or outdoors were <1.0.

Summing up three exposure pathways, HI1 values for individual heavy metals were represented in Table 3 and Fig. 6. Pb was also observed on the highest end, with values of 0.91 and 1.2 for outside and inside the classroom, respectively. The other three metals, Mn, Zn and Ni, were all within the safety limit both outdoors and indoors. Moreover, for various exposure pathway, HI2 values for four heavy metals exhibited that ingestion (1.0 outdoors; 1.3 indoors) and dermal contact (0.29 outdoors; 0.48 indoors) resulted in a greater non-cancer risk to students compared to inhalation exposure (0.0058 and 0.0074 outdoors and indoors) (Table 3). Those results are consistent with the previous fine particle studies (Hu et al., 2012; Sun et al., 2014; Liu et al., 2015) (There is no VFPs health risk study available as we known). HI of heavy metals in airborne PM_{0.4} (PM with equivalent aerodynamic diameters ≤ 0.4 µm) via ingestion, dermal contact and inhalation exposure were 0.36, 1.11 and 0.00053 in Changsha, China, comparable with current study (Liu et al., 2015). Besides, HI2 of heavy metals inside the classroom were 1.3, 1.3 and 1.7 times higher than outside for inhalation, ingestion and dermal contact, respectively. Overall, the high HI values obtained in this study, especially associated to Pb, point out non-negligible non-cancer health risks to the students of Xi'an junior middle school.

Table 3
Non-carcinogenic health risks of heavy metals in VFPs inside and outside the classroom in Xi'an. (Indoor calculations are based on average values of classroom A and B).

	Inhalation exposure		Ingestion exposure		Dermal contact		HI1 ^a	
	Outdoor	Indoor	Outdoor	Indoor	Outdoor	Indoor	Outdoor	Indoor
Mn	2.2 × 10 ⁻³	4.0 × 10 ⁻³	2.9 × 10 ⁻²	4.8 × 10 ⁻²	2.7 × 10 ⁻¹	4.4 × 10 ⁻¹	0.30	0.50
Ni	5.5 × 10 ⁻⁴	5.2 × 10 ⁻⁴	8.2 × 10 ⁻²	4.2 × 10 ⁻²	1.1 × 10 ⁻²	1.1 × 10 ⁻²	0.094	0.054
Zn	1.0 × 10 ⁻⁴	1.1 × 10 ⁻⁴	3.7 × 10 ⁻²	4.0 × 10 ⁻²	5.2 × 10 ⁻⁴	5.7 × 10 ⁻⁴	0.038	0.041
Pb	3.0 × 10 ⁻³	2.8 × 10 ⁻³	8.9 × 10 ⁻¹	1.2	1.7 × 10 ⁻²	2.2 × 10 ⁻²	0.91	1.2
HI2 ^b	0.0058	0.0074	1.0	1.3	0.29	0.48	/	/

^a Sum of three exposure pathways (inhalation, ingestion and dermal contact).

^b Sum of four heavy metals (Mn, Ni, Zn and Pb).

The ILCR values associated to Ni and Pb both outdoors and indoors were much <1 × 10⁻⁶ (acceptable level), similar as the pervious literatures (Hu et al., 2012; Sun et al., 2014), indicating that the carcinogenic risk posed by those toxic heavy metals to children via inhalation is acceptable (Fig. 6). However, the carcinogenic risk posed by PAHs via inhalation was much higher than the threshold value (Fig. 6), with average levels of 9.7 × 10⁻⁶ and 6.1 × 10⁻⁶ outside and inside the classrooms, respectively. It demonstrates that carcinogenic PAHs are a threat to schoolchildren health, approximately 8 times of acceptance threshold. Moreover, the ILCR values of PAHs outdoors were higher than those indoors, which may result from the outdoor-indoor distribution of individual PAH concentrations owing to different volatility and transportation capacity (Xu et al., 2015).

It is concluded based on the data that different exposure pathways presented different levels of risks for different chemical species in VFPs. We must pay attention to heavy metal non-cancer health risks, especially Pb through ingestion exposure and Mn through dermal contact, as well as PAHs cancer health risk via inhalation way in Xi'an school environment.

Due to the restriction of policy, the samplings were conducted at a rather short period. The strategy might have limited the generalities of the results and increased uncertainties on the health assessments, potentially underestimating the concentrations because of no sample collection in heating period in winter. However, the consideration is a major research direction in the future.

4. Conclusions

Atmospheric VFPs were investigated in this study to determine their sources, chemical composition and associated health risk outside and inside two classrooms in a junior secondary school of Xi'an. We found that: 1) organic matter, SO₄²⁻ and geological material were the major components of VFPs both outdoors (37%, 13% and 20%, respectively) and indoors (39%, 11% and 24%, respectively); 2) EC and PAHs were predominantly of outdoor origins, from motor vehicles and coal combustion; inside the classroom, secondary formation may be an important contributor to OC and water-soluble ions, while particles resuspension by student activities and chalk dust contributed to crustal elements; 3) VFPs of outdoor origins resulted in non-cancer and cancer risks to students. Health risks associated to some individual components, like Pb and PAHs, were beyond the internationally accepted health thresholds. This study thus highlights the seriousness of the VFPs pollution and health hazards in school environment of Xi'an. The environmental protections and treatments should be conducted synchronously in schools (such as, reducing students' indoor activities and use of chalk) and outdoors to diminish the high VFPs exposure of the students in this region.

Competing financial interests

The authors declare no competing financial interests.

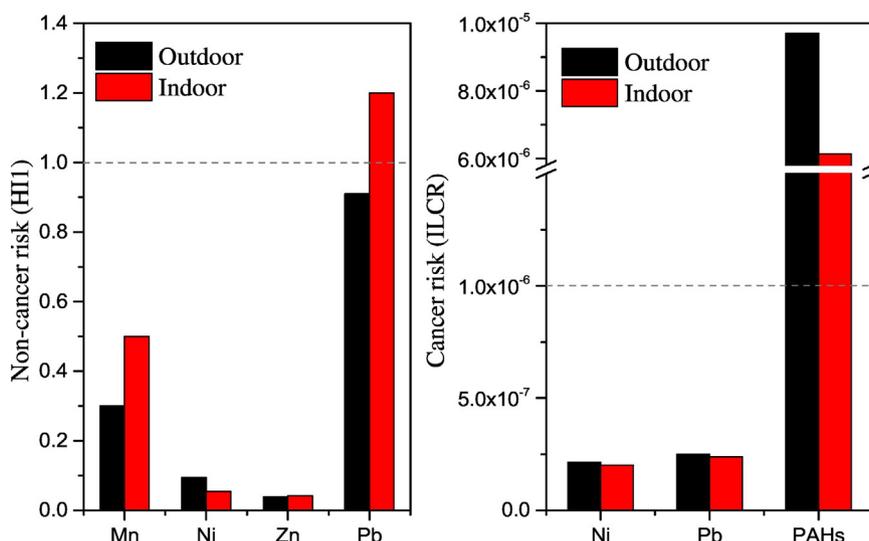


Fig. 6. Non-cancer risks and cancer risks related to heavy metals and PAHs in VFPs inside and outside the classroom in Xi'an. (Gray dot lines represent the threshold values).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2017.08.101>.

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