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Emission and Size Distribution of Particle-bound Polycyclic Aromatic Hydrocarbons from Residential Wood Combustion

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Abstract

Emissions and size distributions of 28 particle-bound polycyclic aromatic hydrocarbons (PAHs) from residential combustion of 19 fuels in a domestic cooking stove in rural China were studied. Measured emission factors of total PAHs were 1.79 ± 1.55 , 12.1 ± 9.1 , and 5.36 ± 4.46 mg/kg for fuel wood, brushwood, and bamboo, respectively. Approximate 86.7, 65.0, and 79.7% of the PAHs were associated with fine particulate matter with size less than $2.1 \mu\text{m}$ for these three types of fuels. Statistically significant difference in emission factors and size distributions of particle-bound PAHs between fuel wood and brushwood was observed, with the former had lower emission factors but more PAHs in finer PM. Mass fraction of the fine particles associated PAHs was found to be positively correlated with fuel density and moisture, and negatively correlated with combustion efficiency. Low and high molecular weight PAHs segregated into the coarse and fine PM, respectively. The high accumulation tendency of the PAHs from residential wood combustion in fine particles implies strong adverse health impact.

Keywords

polycyclic aromatic hydrocarbon; residential wood combustion; size distribution; cooking stove

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of pollutants mainly produced from incomplete combustion. They are well known for their mutagenic and carcinogenic potential and are among the toxic organics of growing concern in many countries. Personal exposure to PAHs was suggested to associate with the increased risk of lung cancer [1–2]. It was estimated that exposure to ambient air PAHs contributed to approximately 1.6% of lung cancer cases in China [2].

Total global emission of PAHs was estimated to be 520 Gg in 2004, among which 80% were from developing countries and 57% were from biomass fuel burning [3]. Emission of such a

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Appendix A. Supplementary material

The following material: a picture of the brick cooking stove used in this study, the calculation of emission factors, and the composition profiles of PAHs in PM of different diameters, can be found in supplementary material free of charge via the internet.

large amount of PAHs into the environment results in severe contamination at both regional and global scale. Ubiquitous PAH pollutions in various environmental media and foodstuffs have been reported in the literature [4–8]. In China, the pollution was much more serious due to higher emissions from incomplete combustions under lower burning efficiencies [9–11].

PAHs in ambient air or emission smoke are in either gaseous or particulate phase [4, 12], and absorption and/or adsorption to particulate matter (PM) were the main governance mechanism(s) of particle-bound PAHs [13–15]. It is believed that adverse health effects of PM were strongly size dependent [13, 16]. Different effects of coarse, fine and ultra-fine PM on respiratory and cardiovascular diseases have been documented in both laboratory toxicology experiments and epidemiological studies [17–27]. Though the mechanism of PM induced toxicity was not fully understood at this stage, chemical composition, including metals and toxic organics, like PAHs, is recognized as one of the key factors. It is expected that various PAH compounds attend to associate with PM of different size, leading to different toxic effects to human health, and PAHs in finer PM may produce higher toxic effect since fine particles can penetrate deep into the lung region [19–20].

Residential wood combustion (RWC) is one of the major sources of PAHs emitted, especially in developing countries due to large consumption and low combustion efficiency [28–32]. In China, RWC contributed 20 to 35% of the total PAH emissions [33, 34]. PM from RWC is primarily soot related with small size and contains high levels of organics including PAHs [35–41]. However, information on the size distribution of particle-bound pollutants was limited which prevents us from full understanding the health effects of these RWC emitted PM and PAHs.

In this study, size resolved particle-bound PAHs from RWC in a typical cooking stove in rural China were measured. The impacts of fuel property and combustion efficiency on the size distribution of particulate phase PAHs were investigated. In addition, composition profiles of PAHs in PM of different diameters are discussed.

Experiment

Fuel combustion experiments

Nineteen biomass fuels, including 15 fuel wood (Chinese white poplar (*Populus tomentosa* Carr.), water Chinese fir (*Metasequoia glyptostroboides*), Chinese pine (*Pinus tabulaeformis* Carr.), cypress (*Cupressus funebris* Endl.), elm (*Ulmus pumila* L.), fir (*Cunninghamia lanceolata*), larch (*Larix gmelini* (Rupr.) Rupr.), maple (*Acer mono Maxim.*), paulowonia tomentosa (*P. tomentosa* (Thunb.) Steud.), willow (*Salix babylonica*), locust (*Robinia pseudoacacia* L.), ribbed birch (*Betula dahurica* Pall.), paulownia elongata (*P. elongata* S. Y. Hu), black poplar (*Populus nigra* L.), and aspen (*Populus adenopoda Maxim.*)), 3 brushwood (lespedeza (*Leapedeza bicolor*. Turcz), holly (*Buxus megistophylla Lévl*), and buxus sinica shrub (*Buxus sinica* (Rehd. et Wils.) Cheng)), and 1 bamboo (*Phyllostachys heterocyclus* (Carr.)) were burned in a typical brick stove. The wok stove used in this study was 80 cm in length, 70 cm in width and 65 cm in height, with one iron pot in the middle. The chamber volume was approximately 0.20 m³. The grate to the pot bottom

distance and grate to the ground distance were 30 and 15 cm, respectively. A picture of the wok stove is shown in Figure S1. Pre-weighed wood pieces ($10 \sim 15 \text{ cm}^2 \times 10 \sim 20 \text{ cm}$ in length) were ignited and inserted into the stove in 15–20 batches. The smoke from the combustion entered into a mixing chamber (4.5 m^3), in which a build-in fan was on all the time to mix the exit smoke and minimize the influence of temperature on the sampling [42]. The samples were directly collected from the chamber without further dilution to avoid the potential impacts of dilution rates and ratios on mass load and size distribution [43–44]. Detailed information on experiment set-up, combustion procedure, and measured fuel properties (density, moisture, elemental contents, and proximate analysis results) were provided in a previous paper focusing on emission factors of PM from the residential wood combustion [45].

Sample collection and extraction

Sampling collection and extraction methods followed the procedure in a previous study on PAH emission from indoor crop residue burning [46] with a small modification. *Particle bound PAHs were collected on glass fiber filters (GFFs)* and 4 size segregated samples with PM diameters of <0.4 , $0.4\text{--}1.1$, $1.1\text{--}2.1$, and $2.1\text{--}10 \mu\text{m}$ were collected using a cascade impactor at a flow rate of 28.3 L/min (FA-3, Kangjie, China).

Particle-bound PAHs were extracted using a microwave accelerated system (CEM Mars Xpress, USA) Microwave power was set at 1200 W (100%). The temperature program was to 110°C in 10 min and then held for another 10 min. After extraction, the extracts were concentrated to 1 mL and transferred to a silica/alumina gel column for clean up. The column was packed with 12 cm alumina, 12 cm silica gel, and 1 cm anhydrous sodium sulfate from bottom up, and pre-eluted with 20 mL hexane. Target PAHs were eluted with 70 mL hexane/dichloromethane (1:1) mixture. The eluate was finally concentrated to 1 mL and spiked with deuterated internal standards (J&W Chemical, USA).

PAH analysis and quality control

PAH analysis was performed using a gas chromatograph (GC, Agilent 6890) connected to a mass spectrometer (MS, Agilent 5973) in electron ionization mode. A HP-5MS capillary column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$) was used. The oven temperature was programmed at 50°C for 1 min, increased to 150°C at a rate of 10°C/min , to 240°C at 3°C/min , and then to 280°C for another 20 min. Carrier gas was helium. Twenty eight target PAHs, including naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLO), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), retene (RET), benzo[c]phenanthrene (BcP), cyclopenta[c,d]pyrene(CPP), benzo(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), benzo(e)pyrene (BeP), perylene (Per), dibenz(a,h)anthracene (DahA), indeno(1,2,3-cd)pyrene (IcdP), benzo(g,h,i)perylene (BghiP), dibenzo[a,c]pyrene (DacP), dibenzo[a,l]pyrene (DalP), dibenzo[a,e]fluoranthene (DaeF), Coronene(COR), dibenzo[a,e]pyrene (DaeP), dibenzo[a,i]pyrene (DaiP), dibenzo[a,h]pyrene (DahP), were identified based on retention time and qualified ions of standards in selected ions mode. Five deuterated PAHs (NAP- d_8 ANT- d_{10} ACE- d_{10} CHR- d_{12} and Perylene- d_{12}) were used as internal standards for quantification.

Preparation of filters, silica/alumina, reagents, and glassware could be found elsewhere in details [45–46]. Filters were baked at 450°C for 6 h before use, and particle-load GFFs were stored at –20°C prior to analysis. Before and after sampling, GFFs were packed in pre-baked aluminum foil. The silica gel and alumina were baked at 450°C for 6 h, activated at 130°C for 12 h, and deactivated with deionized water (3%, w/w) prior to use. The anhydrous sodium sulfate was baked at 450°C for 8 h. All glassware were cleaned in an ultrasonic cleaner and baked at 500°C for at least 10 h. Procedure blanks were also measured and subtracted from the results. Instrument detection limits for the PAHs were 0.13 (ACY) to 0.92 ng (BghiP). Method detection limits ranged from 0.53 (PHE) to 1.32 ng/mL (BghiP). Recoveries of the spiked standard PAHs were 68 to 120%. 2-fluoro-1,1'-biphenyl and p-terphenyl-*d*₁₄ (J&W Chemical, USA) were added as surrogates to monitor the extraction and cleanup procedures and surrogate recoveries were 102±25% and 99±10%, respectively.

Results and Discussion

Emission Factors and Size Distribution of Particle-bound PAHs

PAHs from the combustions of different fuels varied obviously depending on both fuel property and burning conditions. Emission factors of 28 target PM₁₀ bound PAHs (EF_{P28}), defined as the mass of total PAHs emitted per fuel mass, were 1.79±1.55, 12.1±9.1, and 5.36±4.46 mg/kg for fuel wood, brushwood, and bamboo, respectively (see the Supporting Information for detailed calculation for emission factor). Of 28 PAHs, 16 U.S. EPA priority PAHs made up to 84–95% with their emission factors averaged at 1.64±1.43, 10.5±7.7, and 4.60±3.63 mg/kg, respectively (Table S1). Brushwood combustion produced significantly higher particle-bound PAHs than the fuel wood burning ($p < 0.05$). Kim Oanh *et al.*, (2005) reported emission factors of 16 particle phase PAHs (EF_{P16}) for wood in a Chinese clay stove at 1.62 mg/kg [47]. It was also reported that EF_{P16} for wood chips burned in domestic cooking stoves in other Asian countries ranged in 0.39–5.79 mg/kg with mean and standard derivation of 2.07±1.86 mg/kg [47–49]. The results were comparable to that for fuel wood, and obviously lower than that for brushwood in our study.

Figure 1 shows the normalized size distributions of total PAHs for three types of fuels. The size distributions were similar between fuel wood and bamboo, which were different from that of brushwood. PAHs associated with PM_{0.4–1.1} (PM with diameter between 0.4 and 1.1 μm) contributed 39.4±15.4% and 39.4±4.7% of the total for fuel wood and bamboo, respectively. The second largest size fractions were those associated with PM_{0.4} (PM with diameter less than 0.4 μm) accounting for 26.7±7.7% and 21.8±21.4% for fuel wood and bamboo, respectively. For brushwood, however, PAHs associated with PM_{0.4–1.1} was only 28.0±13.0%, much less than those for fuel wood and bamboo. Meantime, PAHs associated with course PM_{2.1–10} (diameter larger than 2.1 μm) was 35.0±7.8% for brushwood, significantly higher than those from fuel wood (13.3±7.5%) and bamboo (20.3±9.2%). Such a difference in PAH size fraction was consistent with that in the size distribution of PM, which also showed that PM emitted from fuel wood combustion was finer than those from burning of brushwood [45]. The reason of this difference is not clear at this stage. More studies on the formation mechanism of PM and PM associated pollutants emitted from the combustion of different fuels are necessary before the phenomenon can be fully understood.

Calculated mass median aerodynamic diameters (MMAD, the diameter at which where 50% of the total mass are larger and the other 50% are smaller) of total PAHs for fuel wood, brushwood, and bamboo were 0.75 (0.38–1.6 as range), 1.4 (0.65–1.9) and 0.92 (0.49–1.4) μm , respectively. The difference between fuel wood and brushwood was statistically significant (Kolmogorov-Smirnov test, $p < 0.05$). The results were comparable to those for residential biomass burning reported in the literature [15, 42, 50–52]. For example, the MMAD values of PAHs from biofuel combustions in various cooking stoves in India were reported at 0.40–1.01 μm [15]. In an indoor crop residue burning experiment, the measured MMAD of PAHs was at 1.3 (0.96–1.5 as range) μm , which was not significant ($p > 0.05$) from that for brushwood [46]. In a previous study on residential coal combustion, calculated MMADs of PAHs were 0.11–0.13 and 0.95–0.98 μm for low and high caking coals, respectively [50]. It was found that MMAD values of PAHs from solid fuels were larger than those from vehicle emissions, which were reported to be 0.075–0.12 μm [53–54].

In general, majority of particle-bound PAHs were associated with fine PM. There were 86.7%, 65.0%, and 79.7% of the total PAHs were associated with $\text{PM}_{2.1}$ for fuel wood, brushwood, and bamboo, respectively. High abundance of PAHs strongly associated with fine PM was also reported for the fresh emissions from indoor crop residue and coal combustion [46, 50]. Taking the influences of the size distribution on deposition rates and health effects into consideration, the impacts of high abundance of PAHs in fine particles, especially those from fuel wood combustion, deserve more attention in risk analysis.

Influences of Fuel Property and Combustion Condition

Differences in fuel properties and combustion conditions can result in variation in size distributions of PM, consequently size distribution of particle-bound PAHs [13, 15, 55]. The impacts of fuel properties, including density, moisture, elemental (C, H, N, and O) contents, volatile matter contents, heating values, and ash content, and combustion condition described by the modified combustion efficiency (MCE) were investigated. It is believed that fine particle associated PAHs could be influenced by the combustion temperature, as high temperature often results in strong air convection and sufficient oxygen for combustion. In this study, there was no significant difference in the recorded temperature among the combustions of various fuels. Hence, the possible impact of combustion temperature was not further analyzed here. Although correlation coefficient between MCE and fuel moisture was negative, it is not significant statistically ($p > 0.05$). Besides fuel moisture, combustion efficiency can also be influenced by many other factors, like oxygen supply, combustion temperature, and fuel-air mixing status [39, 56].

As shown in Figure 2, fractions of PAHs associated with $\text{PM}_{2.1}$ were positively correlated with fuel density and moisture ($p < 0.05$), and negatively correlated with MCE ($p < 0.05$). The impacts of other factors tested in this study were not statistically significant ($p > 0.05$). The influences of fuel density, moisture, and MCE on the size distribution of particle-bound PAHs can be partly explained by the change in the size distributions of PM, to which the PAHs associated through absorption and/or adsorption [15]. In our previous study, it was found that the combustions of wood fuels with relative higher moisture under lower MCE produced higher mass percents of finer particles [45]. As a result, more PAHs in fine PM

could be expected under high moisture and low MCE. In addition, moisture can also influence the evaporation and partitioning of organics [13, 56], resulting in the mass change of these organics in PM with different sizes.

Distributions of individual PAH compound

Size distributions of individual PAHs usually follow a trend that higher molecular weight (MW) compounds tend to be present in finer particles, while lower MW ones prefer to partition to coarser PM. This pattern was reported for both freshly emitted PAHs [13, 15, 46, 50, 57] and PAHs in ambient air [53–54, 58–62]. The same tendency was also revealed in this study. For example, for fuel wood combustion, there were 24.2 ± 8.9 and $26.7 \pm 0.8\%$ of total particle-bound NAP and PHE in $PM_{0.4}$ while $PM_{0.4}$ -bound BaP and IcdP made up 32.2 ± 2.8 and $33.0 \pm 2.9\%$ of the total. MMAD values for individual PAHs varied from 0.47 to 1.0 μm , decreasing generally with the increase of PAH molecular weight.

The most important reason resulting in such phenomena is rapid temperature decrease and selective adsorption of high molecular weight PAHs on fine particles at relatively high temperature. The other explanation might be: 1) the influence of PAH diffusive ability that negatively correlates with chemical MW [58]; 2) the vaporization of low MW PAHs from smaller particles which have high partial pressures due to their curved surfaces [13–14]; 3) the difference in particle surface area and organic matter content affecting absorption/absorption [14]; 4) varied chemical composition and concentration gradients that govern the gas to particle transfer [13].

The composition profiles of PAHs in PM of different diameters were similar in general (Table S2). Overall, PHE, FLA, and PYR were the dominant PAHs found in PM, contributed 21.5–29.6, 15.8–18.9, and 17.1–18.6% of the total particle-bound PAHs, respectively. As mentioned above, higher MW PAH preferentially segregated to fine PM. And hence, higher contribution of higher MW ones to the total PAHs in finer PM could be expected. PAHs with MW > 228 made up to 18, 25, 33, and 32% of the total PAHs in $PM_{2.1-10}$, $PM_{1.1-2.1}$, $PM_{0.4-1.1}$ and $PM_{0.4}$ respectively. For most individuals, the differences between PAH fractions in coarse PM ($PM_{2.1-10}$) and fine PM ($PM_{0.4}$, $PM_{0.4-1.1}$ and $PM_{1.1-2.1}$) were statistically significant (Table S3). It was recognized that such little differences could be also a result of uncertainty from PAH quantification. The utilization of these differences in health risk estimation should be in caution before more measured data available.

BaP equivalent concentrations (BaP_{eq}) for different fuels were also calculated using the toxicity equivalency factors suggested by Nisbet and Lagoy (1992) [63]. Since high molecular weight PAHs tended to occur in fine PM in comparison with low molecular weight ones and high molecular weight PAHs often had relatively high TEF values, it is expected that the size distribution of BaP_{eq} should be different from that of the total PAHs. Because the TEF values for the other 12 PAHs identified in this study were not available, the comparison includes only 16 U.S. EPA priority PAHs (P16). Figure 3 compares the normalized size distributions of P16 and calculated BaP_{eq} from fuel wood combustion. For P16, total mass concentrations in $PM_{2.1-10}$, $PM_{1.1-2.1}$, $PM_{0.4-1.1}$ and $PM_{0.4}$ made up 13.6 ± 8.1 , 21.0 ± 7.8 , 39.1 ± 17.8 , and $26.4 \pm 9.9\%$ of the total particulate phase PAHs, respectively, while

the mass percents of BaP_{eq} in these size fractions were 8.4±5.5, 17.7±6.6, 42.9±17.8, and 31.0±9.9%, respectively. The differences between mass percentages of P16 and those of BaP_{eq} in the same size fraction were statistically significant (Wilcoxon test for paired samples, $p < 0.05$).

Conclusion

Emission factors of 28 PM₁₀ bound PAHs were measured with means and standard derivations of 1.79±1.55, 12.1±9.1, and 5.36±4.46 mg/kg for fuel wood, brushwood, and bamboo, respectively. Particle-bound PAHs from residential wood combustion were mainly present in fine PM with about 86.7, 65.0, and 79.7 of the total in PM_{2.5} for these 3 types of fuels. Difference in the emission factors and size distributions of particle-bound PAHs between fuel wood and brushwood was observed. Brushwood combustion yielded higher emission factors, and more PAHs associated with coarse PM than the burning of fuel wood. Low molecular weight PAHs tended to be in coarse PM while high molecular weight preferred to segregate into fine PM. PAH mass fraction in fine PM was found to be positively correlated with fuel moisture and density ($p < 0.05$), and it was negatively correlated with combustion efficiency ($p > 0.05$). Since fine PM can penetrate deep into the lung area, high accumulation of PAHs in these fine PM, especially those high molecular weight PAHs of high toxic potential, should be paid high attention in exposure risk assessment.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgement

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Fig. 1.
e Size distributions of particle-bound PAHs from residential fuel wood, brushwood, and bamboo fuel combustions. Data shown are means and standard derivations from all combustion experiments.

Fig. 2.

e Relationship between mass fractions of PM_{2.1}-bound PAHs and fuel density (A), moisture (B), and combustion efficiency (C) from residential wood combustion. Data shown are results from fuel wood combustion.

Fig. 3.
e Size distributions of total concentration of 16 U.S. EPA priority PAHs (P16) and calculated BaPeq from residential fuel wood combustion.