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Emissions of Parent, Nitro, and Oxygenated Polycyclic Aromatic Hydrocarbons from Residential Wood Combustion in Rural China

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Abstract

Residential wood combustion is one of the important sources of air pollution in developing countries. Among the pollutants emitted, parent polycyclic aromatic hydrocarbons (pPAHs) and their derivatives, including nitrated and oxygenated PAHs (nPAHs and oPAHs), are of concern because of their mutagenic and carcinogenic effects. In order to evaluate their impacts on regional air quality and human health, emission inventories, based on realistic emission factors (EFs), are needed. In this study, the EFs of 28 pPAHs (EF_{PAH28}), 9 nPAHs (EF_{PAHn9}) and 4 oPAHs (EF_{PAHo4}) were measured for residential combustion of 27 wood fuels in rural China. The measured EF_{PAH28}, EF_{PAHn9}, and EF_{PAHo4} for brushwood were 86.7±67.6, 3.22±1.95×10⁻², and 5.56±4.32 mg/kg, which were significantly higher than 12.7±7.0, 8.27±5.51×10⁻³, and 1.19±1.87 mg/kg for fuel wood combustion ($p < 0.05$). Sixteen U.S. EPA priority pPAHs contributed approximately 95% of the total of the 28 pPAHs measured. EFs of pPAHs, nPAHs, and oPAHs were positively correlated with one another. Measured EFs varied obviously depending on fuel properties and combustion conditions. The EFs of pPAHs, nPAHs, and oPAHs were significantly correlated with modified combustion efficiency and fuel moisture. Nitro-naphthalene and 9-fluorenone were the most abundant nPAHs and oPAHs identified. Both nPAHs and oPAHs showed relatively high tendencies to be present in the particulate phase than pPAHs due to their lower vapor pressures. The gas-particle partitioning of freshly emitted pPAHs, nPAHs and oPAHs was primarily controlled by organic carbon absorption.

Introduction

PAHs are among the toxic organic pollutants of highest concern in developing countries. Global total emissions of 16 U.S. EPA priority PAHs was 520 Gg/year in 2004, with over 80% of these emissions coming from developing countries.¹ Globally, biomass combustion contributes more than half of the total PAH emissions and this is particularly true for

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Supporting Information available

The following materials are provided in the supporting information: measured EFs of pPAHs, nPAHs and oPAHs (Tables S1–S4), correlation between individuals, derivatives and their corresponding pPAHs (Tables S5–S8), relationships between OC and pPAHs and between OC and PAH derivatives, composition profiles of pPAHs in gaseous and particulate phases, and comparison between K_p of PAH derivatives and their corresponding parent PAHs. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

developing countries.¹ In China, severe PAH pollution has been reported in both urban and rural areas.^{2–4} It has been estimated that the total consumption of wood in rural areas was 182 Tg in 2007,⁵ producing approximately 21–34 % of the total PAH emissions in China.^{6–7} Together with the emissions from other solid fuels, residential wood burning contributes significantly to severe indoor air pollution and exposure risk in China.^{4, 8–9}

PAH emissions can be estimated based on fuel consumption and emission factors (EFs). EFs, defined as the mass of a pollutant emitted per unit energy consumed, are affected by a number of factors, including fuel properties (bulk density, size, and moisture), combustion facilities (residential and industrial, old and modern stoves), fire management, and experimental methods (laboratory vs. field measurements).^{10–17} As a result, the measured EFs often vary by several orders of magnitude, leading to high uncertainty in emission estimation.^{18–19} On the other hand, average EFs are commonly used for inventory development, resulting in a bias of the total estimations. Because the field measurement of PAH EFs from residential wood combustion in China is very limited, the emission estimates for PAHs from wood burning have not been accurate.

The derivatives of parent PAHs (pPAHs), including nitrated PAHs (nPAHs) and oxygenated PAHs (oPAHs), are equally or more toxic than pPAHs and are direct acting mutagens.^{20–22} Although nPAHs and oPAHs contributed only 8% to the total PAH concentration of Beijing particulate matter (PM) during the summer, the direct acting mutagenicity of Beijing PM was 2 times higher than the indirect acting mutagenicity.²² nPAHs and oPAHs are formed from direct emission during combustion and/or through the reactions of pPAHs with atmospheric oxidants.^{20–22} To our knowledge, nPAH EFs for wood combustion have not been published and there are few reports of oPAH EFs for wood.^{23–28} Because of this lack of data, it is impossible to calculate the emissions of nPAHs and oPAHs from wood combustion.

In this study, the EFs of 28 pPAHs, 12 nPAHs, and 4 oPAHs were measured from residential wood combustion in a rural Chinese cooking stove. The impacts of fuel properties and combustion conditions, as well as the relationship between the pPAH compounds and their derivatives, were investigated.

Method

Fuels, Stove, and Combustion Experiment

The experimental set-up was the same as those in a previous study on PM emissions from residential wood combustion²⁹. In brief, 27 fuels, including 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.*), oak (*Quercus mongolica*), paulownia tomentosa (*P. tomentosa* (Thunb.) Steud.), toon (*Ailanthus altissima*), white birch (*Betula platyphylla* Suk), willow (*Salix babylonica*), locust (*Robinia pseudoacacia* L.), bamboo (*Phyllostachys heterocycla* (Carr.)), ribbed birch (*Betula dahurica* Pall.), paulownia elongata (*P. elongata* S. Y. Hu), black poplar (*Populus nigra* L.), aspen (*Populus adenopoda* Maxim.), chinaberry (*Melia azedarach*), the tree of jujube (*Ziziphus jujuba* Mill.), persimmon (*Diospyros kaki* Thunb.), mulberry (*Morus alba* L.), peach (*Prunus persica*), and 3 brushwood of lespedeza (*Leapedeza bicolor* Turcz), holly (*Buxus megistophylla* Lévl) and buxus sinica shrubs (*Buxus sinica* (Rehd. et Wils.) Cheng), were burned in a typical brick stove used by more than 175 million rural residences in Northern China³⁰. The fuel properties, including bulk density, moisture, elemental composition (C, H, N, and O), volatile matter, fixed carbon, ash content, and heating values, were measured. It was recognized that fuel composition is an important factor affecting

combustion and emissions and more measurements will be considered on fuel characterization in our future studies.

In the combustion experiments, pre-weighed (~ 1.0 kg) fuel wood pieces ($10 \sim 15 \text{ cm}^2 \times 10 \sim 20$ cm in length) were ignited and inserted into the stove chamber in 15–20 batches, simulating what residents do in daily cooking practices. The brushwood was broken into 20–30 cm sections. The combustion processes lasted for 40–60 minutes. The combustion experiments were conducted in triplicate for each fuel type. Before exit into the ambient air through the chimney, the smoke from the stove entered into a mixing chamber (4.5 m^3) with a small fan built-in¹³. The mixing chamber was used to allow deposition of larger particles, cooling down of the high smoke temperature, thorough mix of the flue air, and easy sampling. All sampling and on-line measurements were conducted in the mixing chamber. It was recognized that sampling in the mixing chamber would result in the difference from real stove in the field that are totally open to air. In addition, there are also some other types of stoves used for residential cooking and heating. Different fuel/stove combinations should be taken into consideration in future studies, especially in field measurements.

Sample Collection, Extraction, and Clean-up

Sample collection, extraction, and cleanup followed the same procedures used in a previous study on the emissions from crop residue burning.¹⁴ An active sampler with a flow rate of 1.5 L/min was used in pPAH, nPAH, and oPAH sampling. Gaseous and particulate phase samples were collected on polyurethane foam plugs (PUF, 22 mm diameter $\times$ 7.6 cm, 0.024 g/cm³) and quartz fiber filters (QFFs, 22 mm in diameter) respectively. The PUFs were Soxhlet extracted using 150 ml of dichloromethane for 8 h. A microwave accelerated system (CEM Mars Xpress, USA) was used to extract the PAHs from the PM collected on QFFs using 25 ml of a hexane/acetone mixture (1:1, v/v) at 1200 W (100%). The temperature was increased to 110°C over 10 min and held for an additional 10 min. Both PUF and QFF extracts were concentrated to 1 ml and then transferred to a silica/alumina gel column for cleanup (12 cm alumina, 12 cm silica gel and 1 cm anhydrous sodium sulfate from bottom to top). The column was eluted with 20 ml hexane, followed by 70 ml hexane/dichloromethane (1:1, v/v). The hexane/dichloromethane eluate was concentrated to 1 ml and spiked with deuterated internal standards (J&W Chemical Ltd., USA).

Measurement of Parent PAHs, nPAHs, and oPAHs

Parent PAHs were measured 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 m $\times$ 0.25 mm $\times$ 0.25 μm) was used, and the oven temperature was held 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. Helium was used as the carrier gas. PAHs were identified based on retention time and qualifying ions of standards in selected ion monitoring mode. Twenty-eight parent PAHs were measured in this study, 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). Five deuterated PAHs (Nap-*d*₈, Ace-*d*₁₀, Ant-*d*₁₀, Chr-*d*₁₂, and Perylene-*d*₁₂) were used as internal standards in PAH quantification.

Nitro-, and oxygenated PAHs were also analyzed using a GC-MS using a HP-5MS capillary column, but in a negative chemical ionization mode. The oven temperature was programmed at 60°C, increased to 150°C at a rate of 15°C/min, and then to 300°C at 5°C/min held for 15 min. High-purity helium and methane were used as the carrier and reagent gas, respectively. nPAHs and oPAHs were identified and quantified based on the retention times and selected ions of the standards (J&W Chemical, USA). 12 nPAHs and 4 oPAHs were quantified, including 1-nitro-naphthalene (1N-NAP), 2-nitro-naphthalene (2N-NAP), 5-nitro-acenaphthene (5N-ACE), 2-nitro-fluorene (2N-FLO), 9-nitro-anthracene (9N-ANT), 9-nitro-phenanthrene (9N-PHE), 3-nitro-phenanthrene (3N-PHE), 3-nitro-fluoranthene (3N-FLA), 1-nitro-pyrene (1N-PYR), 7-nitro-benzo[a]anthracene (7N-BaA), 6-nitro-chrysene (6N-CHR), 6-nitro-benzo[a]pyrene (6N-BaP), and 9-fluorenone (9FO), anthracene-9,10-dione (ATQ), benzanthrone (BZO), and benzo[a]anthracene-7,12-dione (BaAQ). Two deuterated nitro-PAHs (1-nitroanthracene-*d*₉ and 1-nitropyrene-*d*₉, J&W Chemical Ltd., USA) were used as the internal standards.

Quality Control and Data Analysis

The preparation of PUFs, filters, silica/alumina, reagents and glassware were previously described.¹⁴ All filters were baked at 450°C for 6 hours and equilibrated in a desiccator. PUF were pre-extracted with acetone and dichloromethane, followed by hexane for 8 h each. After sampling, the PUFs and QFFs were packed in aluminum foil. Procedural blanks were measured and the PAH concentrations in the blanks subtracted from the samples.

Instrumental detection limits (IDLs) for the pPAHs ranged from 0.13 ng (ACY) to 0.92 ng (BghiP). Laboratory analysis method detection limits (MDLs) ranged from 0.23 ng/mL (NAP) to 1.42 ng/mL (BghiP) for gaseous phase PAHs and from 0.53 ng/mL (PHE) to 1.32 ng/mL (BghiP) for particulate phase PAHs. Recoveries of the spiked standard PAHs ranged from 70 to 121% for gaseous and 68 to 120% for particulate phase compounds. IDLs ranged from 0.12 to 0.49 ng for nPAHs and 0.06 to 0.24 ng for oPAHs. MDLs for gaseous and particulate phase nPAH ranged from 0.18 to 0.58 and 0.12 to 0.53 ng/mL, respectively. Recoveries of the spiked standards were 78±6 to 92±10% and 93±19 to 124±30% for gaseous and particulate phase nPAH, respectively. MDLs for oPAHs were 0.32 to 0.60 ng/mL and 0.11 to 0.44 ng/mL for gaseous and particulate phase PAHs, respectively. Recoveries of the spiked oPAH standards were 72±4 to 96±14 % for gaseous phase and 82±26 to 125±10% for particulate phase.

The EFs were calculated using the carbon mass balance method with the assumption that the carbon burned³¹. EFs was released in the forms of CO₂, CO, total gaseous hydrocarbons, and carbonaceous carbon in PM of PAHs can be calculated from the EFs of CO₂ and mass emission ratios of PAHs to CO₂¹³. In this study, CO₂ and CO were measured every 2 seconds using an on-line non-dispersive infrared sensor. The instrument (GXH-3051, Technical Institute, China) was calibrated using a span gas before each combustion experiment (CO 1.00%; CO₂ 5.00%) and zero checked after each experiment. Two parameters, modified combustion efficiency (MCE, CO₂/(CO₂+CO) on a molar basis) and fuel burning rate were calculated to quantitatively describe the combustion conditions. Statistical analysis was conducted using Statistica (v5.5, StatSoft) at a significance level of 0.05.

Results and Discussion

EFs of pPAHs, nPAHs, and oPAHs

The measured EFs for pPAHs varied widely among the different fuels tested, likely due to the differences in fuel properties and combustion conditions. The detailed results are provided in the Supporting Information as means and standard deviations of the triplicate

experiments. EFs were given in both fuel mass (mg/kg) (Table S1 and S2) and combusted carbon mass units ($\mu\text{g/gC}$) (Table S3). Measured total EFs for the 28 pPAHs (EF_{PAH28}) in the gaseous and particulate phases were significantly higher ($p < 0.05$) for brushwood (55.8 ± 43.7 and 30.9 ± 24.3 mg/kg) than for fuel wood (9.07 ± 5.18 and 3.66 ± 3.00 mg/kg) and bamboo (26.0 ± 18.2 and 7.58 ± 1.61 mg/kg). Relatively high emissions of CO and PM from brushwood combustion, compared to fuel wood combustion, have been previously reported.^{29, 32} Total EFs of the 16 U.S. EPA priority PAHs (EF_{PAH16}) for fuel wood, brushwood, and bamboo were 12.1 ± 6.7 , 79.7 ± 60.4 , and 31.4 ± 16.6 mg/kg, respectively, accounting for approximately $95 \pm 3\%$ of the EF_{PAH28} . Although the 12 non-U.S. EPA priority PAHs contributed only a small fraction to the EF_{PAH28} , it is worth noting that most of these PAHs are carcinogenic.³³

In a previous study¹⁴, EF_{PAH16} for crop residues burned in the same stove used in this study were 62.7 ± 35.2 mg/kg. This EF_{PAH16} was comparable to 79.7 ± 60.4 mg/kg for brushwood ($p > 0.05$) and 5 times higher than 12.1 ± 6.7 mg/kg for fuel wood ($p < 0.05$). These differences are seen for both the gaseous and particulate phases (Figure 1). The EFs for PM (EF_{PM}) from fuel wood and brushwood combustion were 1.5 ± 0.6 and 3.8 ± 1.4 g/kg, respectively²⁹, and much lower than EF_{PM} for crop residue (8.2 ± 4.3 g/kg)¹³. The differences in EF_{PAH16} between tree wood and crop residues were larger than those for EF_{PM} and likely due to the differences in particle-bound PAH mass fractions (0.41 ± 0.14 , 0.60 ± 0.43 , and $0.16 \pm 0.06\%$ from the combustion of crop residues, brushwood, and fuel wood, respectively).

The EF_{PAHs} reported in the literature for firewood varied from 0.06 to 4180 mg/kg, depending on many factors, such as fuel properties (e.g. moisture and bulk density), combustion facility (fireplace vs. woodstove), combustion conditions (e.g. oxygen supply and fuel/air mixing status), and the PAHs measured^{10–12, 15–17, 34–40}. For example, the EFs of the sum of 17 PAHs (PAH16 and BeP) were 12 to 38 and 66 to 114 mg/kg for wood burned in a Chinese clay stove and in several stoves in other Asian countries^{38–39}. EFs of the sum of 22 PAHs were 79.8, 74.7, and 167 mg/kg for softwood and hardwood combusted in a fireplace and for hardwood burned in a woodstove in the U.S.¹². EFs of the sum of 27 PAHs for wood burned in the old and modern boilers in Sweden were 247 to 1216 and 2.66 to 57.0 mg/kg, respectively¹⁵. Jenkins *et al.* measured 19 PAHs from wood burning in a wind tunnel and reported total EFs of 12.3 to 69.6 mg/kg¹⁰. Because different PAH compounds were measured in these different studies, the EFs were directly compared across different studies. However, the ratios of the total mass of PAHs over the co-emitted PM in our study ($0.05 \sim 1.7\%$) (Figure 1) is comparable to previous studies ($0.12 \sim 3.2\%$).^{10–12, 15–17, 36}

Among the 12 nPAHs and 4 oPAHs measured, the concentrations of 7N-BaA, 6N-CHR, and 6N-BaP were below the detection limit in most samples (~ 0.05 $\mu\text{g/kg}$). However, 5N-ACE, 2N-FLO, and 1N-PYR were measured in several fuels, and 6 nPAHs (1N-NAP, 2N-NAP, 9N-ANT, 9N-PHE, 3N-PHE, and 3N-FLA) and 4 oPAHs (9FO, ATQ, BZO, and BaAQ) were measured in all samples (Table S3 and Table S4). Therefore, the EFs for the total of 9 nPAHs (EF_{PAHn9}) and 4 oPAHs (EF_{PAHo4}) are reported. For fuel wood and brushwood, the EF_{PAHn9} was 8.27 ± 5.51 and 32.2 ± 19.5 $\mu\text{g/kg}$, respectively, and EF_{PAHo4} was 1.19 ± 1.87 and 5.56 ± 4.32 mg/kg, respectively. 1N-NAP and 2N-NAP were the two dominant nPAHs identified. For oPAHs, the EFs for two ketones (9FO and BZO) were much higher than those for two quinones (ATQ and BaAQ). Like pPAHs, EF_{PAHn9} and EF_{PAHo4} from brushwood burning were significantly higher than those from fuel wood combustion ($p < 0.05$).

EFs of nPAHs were approximately 3 orders of magnitude lower than those of pPAHs. Lower contents of N in the fuels (0.08–1.37%) and difficult incorporation of ambient N₂ in air were likely the reason for the lower nPAHs formation. In a study on indoor air PAH contamination conducted in a rural household in northern China, the measured indoor nPAH air concentrations in the kitchen where fuel wood and crop residues were burned for cooking, were significantly lower than those of pPAHs and oPAHs⁴. This difference in concentrations was explained by the direct emissions of both pPAHs and oPAHs from combustion⁴. This hypothesis is further confirmed by our results.

oPAH EFs were on the same order of magnitude as pPAH EFs. oPAH EFs from crop residue burning reported in the previous study⁴¹ were comparable to oPAH EFs from brushwood burning, and about 2 to 5 times higher than that from fuel wood burning. The individual oPAH EFs measured in this study were comparable to those measured using woodstoves^{27–28}, but lower than those measured using fireplaces^{23–26}. For example, average EFs for particle-bound 9FO, ATQ, and BZO were 0.841 (0.132 to 3.42), 0.612 (0.053 to 4.19), and 0.670 (0.150 to 2.09) mg/kg for wood combustion in fireplaces, respectively^{23–26, 28}, and were 0.625 (0.189 to 2.64), 0.256 (0.077 to 0.438), and 0.444 (0.091 to 1.01) mg/kg for wood burned in woodstoves, respectively^{27–28}. Relatively low emissions of fine PM and pPAHs from woodstoves, compared to fireplaces, were also observed and can be explained by differences in combustion conditions, including temperature, oxygen supply, residence time, and turbulent mixing of combustion gases²⁷.

There were statistically significantly positive correlations among EFs for nitrated and oxygenated PAH individuals measured in this study (Tables S5). Moreover, there were also statistically positive correlations between individual nPAHs and the corresponding pPAHs EFs ($r = 0.465 \sim 0.890$, $p < 0.05$) and between oPAHs and pPAHs EFs ($r = 0.599 \sim 0.916$, $p < 0.05$) (Tables S6). With the exceptions of RET, 5N-ACE, 2N-FLO, and 1N-PYR, all individual pPAHs, nPAHs, and oPAHs EFs were significantly correlated ($p < 0.05$) with each other.

Influence of Fuel Moisture and Combustion Efficiency

Because of limited data for brushwood, the analysis on the influence of fuel properties and relationship between EFs of PAHs and EFs of co-emitted pollutants in the following discussion was only conducted for fuel wood. As shown in Figure 2A, significantly negative correlations ($p < 0.05$) were observed between MCE and pPAHs, oPAHs, and nPAHs EFs. MCE for *Paulownia elongata* was only $88.4 \pm 0.7\%$, much lower than those of others ($92.2 \sim 96.2\%$), which was likely due to the highest moisture content ($41.8 \pm 2.0\%$) of it. MCE can be influenced by various factors, including fuel moisture content, oxygen supply, and fire management^{11, 16}. Significantly positive correlations between EFs and fuel moisture ($p < 0.05$) were observed in this study (Figure 2B), likely because an appreciable amount of energy is needed to vaporize the water which can reduce the combustion temperature and lead to reduced combustion efficiencies and enhanced pollutant emissions^{23, 42}. Similar effect of moisture on PAH emission from wood combustion was also reported in the literature^{16, 43}. The other factors measured in this study, including density, heating value, and volatile matter content, were not significantly correlated with EFs ($p > 0.05$).

pPAHs, oPAHs, and nPAHs EFs were all significantly positively correlated ($p < 0.05$) to EF_{PM} simultaneously measured²⁹ (Figure 3A and 3B). In addition to EF_{PM}, positive correlations (Figure 3C and 3D) were also found between EFs of pPAHs and their derivatives and EFs of CO (EF_{CO}), which is also a by-product of incomplete combustion. Similar relationships between EF_{PAHs} and EF_{PM} and between EF_{PAHs} and EF_{CO} have been reported^{43–45}. The EFs of particle-bound PAHs (pPAHs, nPAHs, and oPAHs) and EFs of

organic carbon were also positively correlated (Figure S1). PAHs are an important, though not dominant, component of PM organic matter^{27, 46}.

PAH Composition Profiles and Isomer ratios

Of the 28 pPAHs measured in this study, most of their EFs were positively correlated ($p < 0.05$) with each other, especially those with similar molecular size (Table S7). Positive correlations among individual pPAHs are often observed in field measurements of pPAHs concentrations^{22, 47}. In this study, only RET EFs were the exception likely because it is mainly formed from the thermal degradation of abietic acid in conifer wood⁴⁸.

The composition profile of pPAHs from wood combustion was dominated by 2 and 3 ring PAHs (from NAP to ANT), accounting for 73.6% of the total PAHs. The predominant individual pPAHs were NAP ($41.0 \pm 12.6\%$) and PHE ($16.9 \pm 5.6\%$), followed by FLA ($9.1 \pm 3.4\%$) and PYR ($7.8 \pm 2.9\%$) (Figure 4). PHE ($20.0 \pm 9.7\%$), FLA ($23.9 \pm 3.8\%$), and PYR ($20.9 \pm 3.4\%$) were also predominant individual pPAHs in the particulate phase (Figure S2). A number of PAH isomer ratios, including ANT/(ANT+PHE), FLA/(FLA+PYR), BaA/(BaA+CHR), IcdP/(IcdP+BghiP), BbF/(BbF+BkF), and BaP/(BaP+BghiP), are often used as source specific indicators for PAH source apportionment⁴⁹, though their application were sometimes suspected^{50–51}. For wood in this study, calculated isomer ratios (means and standard derivations) for these six pairs were 0.12 ± 0.02 , 0.54 ± 0.02 , 0.50 ± 0.04 , 0.55 ± 0.03 , 0.51 ± 0.03 , and 0.62 ± 0.04 . They were within the previously reported ranges of 0.10 to 0.30, 0.43 to 0.74, 0.39 to 0.56, 0.16 to 0.69, 0.35 to 0.51, and 0.38 to 0.78 for ANT/(ANT+PHE), FLA/(FLA+PYR), BaA/(BaA+CHR), IcdP/(IcdP+BghiP), BbF/(BbF+BkF), and BaP/(BaP+BghiP), respectively.^{14, 36–40, 44}

In addition to the 6 commonly used isomer ratios, BeP/(BeP+BaP) was also calculated in this study. Although BeP is not among the 16 U.S. EPA priority PAHs, it is sometimes reported in field measurements together with the 16 PAHs. The BeP/(BaP+BeP) ratio has been used as an indicator of the degree of photodegradation in ambient air because BaP degrades faster than BeP in the atmosphere^{52–53}. Measured BeP/(BaP+BeP) for residential wood combustion in this study varied from 0.29 to 0.54, with a mean and standard deviation of 0.41 ± 0.06 . This is similar to what has been reported for wood combustion in the literature (from 0.33 to 0.71 with mean and standard deviation of 0.51 ± 0.12)^{10, 23–27, 37–39, 46}.

In a previous study, significantly positive correlations were found between the EFs for pPAHs and the EFs for their derivatives from crop residue and coal combustion⁴¹. In this study, a similar relationship was found for wood burning. Figure 5 shows these relationships for NAP, FLO, ANT, and PHE, as examples. The results for all of the PAH compounds are given in Table S6. The ratios of the nPAH to the corresponding pPAH (R_N) and the oPAH to the corresponding pPAH (R_O) were calculated and shown in Figure S3. Because of very low EF_{nPAHs} values, the R_N values were as low as 1.51×10^{-4} (3N-PHE/PHE) to 4.67×10^{-3} (9N-ANT/ANT). However, because the EF_{oPAHs} values were higher, the R_O values for 9FO/FLO, ATQ/ANT, and BaAQ/BaA were 2.06 ± 0.84 , 0.792 ± 0.237 , and $6.56 \pm 7.54 \times 10^{-2}$, respectively, with no significant difference in these ratios between fuel wood and brushwood combustion ($p > 0.05$).

Ambient pPAHs, nPAHs, and oPAHs concentrations in indoor and outdoor air in a rural household burning crop residue and wood for cooking were measured by Ding *et al.*,⁴. In comparison to this study, R_N and R_O ratios in ambient air were significant higher than in emissions from wood combustion ($p < 0.05$), especially for R_N in summer. For example, the average 1N-NAP/NAP ratios in ambient air were 1.17×10^{-2} and 2.89×10^{-1} in winter and summer⁴, respectively, and both ambient air ratios were significantly higher than the same ratio of 7.88×10^{-4} measured in this study for primary wood combustion. This suggests that

nPAHs are formed from photochemical reactions following direct emission from combustion.^{21–22}

Wood combustion produced significantly higher 9FO/FLO ratios than crop residue and coal combustion, while crop residue combustion produced higher ATQ/ANT and BaAQ/BaA ratios and a lower 9FO/FLO ratio⁴⁰. Coal combustion produced the lowest R_O ratios (Figure S4). These differences in R_N and R_O ratios may be useful for distinguishing between emissions from the three types of residential solid fuels. A previous study found that R_O was positively correlated with EF_{pPAHs} for coal combustion and negatively correlated with EF_{pPAHs} for crop residue combustion⁴¹. However, we did not find a similar relationship for wood in this study ($p > 0.05$, Table S8). Although these ratios may be useful for identifying emissions from these different combustion sources, more field data is needed before it can be broadly applied in source apportionment.

Gas-Particle Partition of pPAHs, nPAHs, and oPAHs

pPAHs and their derivatives are emitted from combustion sources in the gaseous and/or particulate phase depending on their molecular weight and vapor pressure^{21, 41, 54}. Gas-particle partitioning is usually described by the partition coefficient (K_P), defined as $K_P = F/(A \times PM)$, where F and A are the particle-bound and gaseous phase concentrations, and PM is the mass concentration of co-emitted PM⁵⁴. Log-transformed K_P values for the various compounds measured in this study were calculated and plotted against molecular weight in Figure 6A, showing an increasing tendency. As shown in Figure S5, K_P of most derivatives were significantly higher than ($p < 0.05$) those of pPAHs, except 3N-FLA, 1N-PYR, and BaAQ ($p > 0.05$). These results are similar to oPAHs emitted from crop residue and coal burning⁴¹. In comparison with the corresponding pPAHs, the derivatives often have lower vapor pressures and are more likely to be present in the particulate phase²⁰.

Gas-particle partitioning is thought to be controlled by the relative importance of absorption into organic matter and adsorption onto the particle surface^{55–56}. The two different processes can be identified by plotting the K_P values plot against the sub-cooled liquid vapor pressures (P_L^0), and the slope may indicate adsorption (steeper than -1) or absorption (shallower than -0.6) governance, respectively⁵⁵. In this study on wood combustion, the calculated slope of K_P against P_L^0 is -0.39 ± 0.06 , suggesting a dominance of absorption into particles (Figure 6B). This mechanism of sorption is confirmed by the positive correlation between K_P and octanol-air partition coefficient (K_{OA}) ($r = 0.919$, $p < 0.05$) (Figure 6C)⁵⁶. A similar result was reported for crop residue and coal combustion^{14, 45, 57}.

P_L^0 and K_{OA} values were not available for the nPAHs and oPAHs. However, significantly positive correlations between EFs of pPAHs and EFs of their derivatives suggest that the partitioning mechanism for nPAHs and oPAHs is similar to that for pPAHs. In fact, both pPAHs and their derivatives were positively correlated with OC ($p < 0.05$) (Figure S1), suggesting that the absorption mechanism may be dominant for these freshly emitted PAH derivatives.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

The measured gaseous and particulate phase EF_{PAH16} (stacked bars) and ratios of EF_{PAH16} over EF_{PM} (dots) from residential brushwood and fuel wood combustions. The results are presented as arithmetic means and standard deviations. For comparison, EF_{PAH16} and EF_{PAH16}/EF_{PM} for crop residue burning are also shown¹³. Fuels: 1. White poplar, 2. Elm, 3. Locust, 4. Maple, 5. Fir, 6. Larch, 7. Water Chinese Fir, 8. Cypress, 9. Oak, 10. Chinese Pine, 11. Willow, 12. Paulownia Tomentosa, 13. Toon, 14. White Birch, 15. Ribbed Birch, 16. Paulownia Elongate, 17. Black Poplar, 18. Aspen, 19. Chinaberry, 20. Jujube tree, 21. Persimmon tree, 22. Mulberry tree, 23. Peach tree, 24. Lespedeza, 25. Buxus sinica shrubs, 26. Holly, 27. Horse bean straw, 28. Peanut straw, 29. Soybean straw, 30. Cotton straw, 31. Rice straw, 32. Wheat straw, 33. Rape straw, 34. Sesame straw, and 35. Corn straw.

Figure 2. Correlations between EFs (pPAHs (carmine), nPAHs (blue), and oPAHs (pink)) and MCE (A) and fuel moisture (B) from the residential fuel wood combustion.

Figure 3.

Relationships between EF_{PM} and EF_{PAHs} (A: pPAHs, B: nPAHs and oPAHs) and between EF_{CO} and EF_{PAHs} (C: pPAHs, D: nPAHs and oPAHs). Data shown are means and standard derivations of triplicate fuel wood experiments.

Figure 4. Composition profile of PAH emitted from residential wood combustion. Both gaseous and particulate phase PAHs are shown as pink and purple bars, respectively. Data are means and standard derivations from all wood combustion experiments. Compound: 1. NAP, 2. ACY, 3. ACE, 4. FLO, 5. PHE, 6. ANT, 7. FLA, 8. PYR, 9. RET, 10. BcP, 11. CPP, 12. BaA, 13. CHR, 14. BbF, 15. BkF, 16. BeP, 17. BaP, 18. PER, 19. IcdP, 20. DahA, 21. BghiP, 22. DacP, 23. DalP, 24. DaeF, 25. COR, 26. DaeF, 27. DaiP, 28. DahP

Figure 5. Correlations between the measured EFs PAH derivatives and EFs of the corresponding parent PAHs. The data are log-transformed. Means and standard deviations are shown.

Figure 6. Relationship between K_p of various PAHs and their molecular weight (A) and dependence of K_p on $\log P_L^0$ (B) and K_{OA} (C). K_p , P_L^0 , and K_{OA} are all log-transformed.