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Emissions of particulate PAHs from solid fuel combustion in indoor cookstoves

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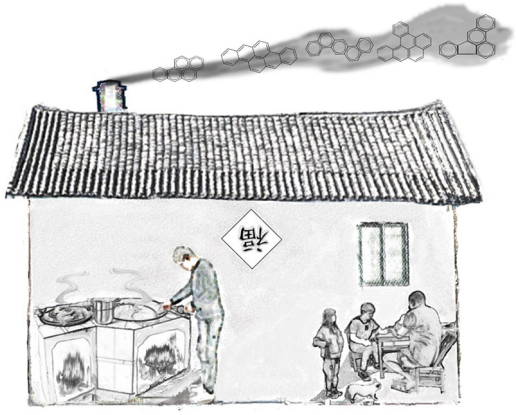
HIGHLIGHTS

- Particulate PAHs emissions from 14 fuel-stove combinations in field conditions
- Stronger influences of fuel types than stove difference in determining PAHs emission variations
- Larger intra-fuel variations in PAHs composition profiles from coal combustion
- More emission factors from the field conditions compared with the lab tests
- Highly variable isomer ratios used in PAHs source apportionment

GRAPHICAL ABSTRACT



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ABSTRACT

Residential solid fuel combustion is a major emission source of PAHs (polycyclic aromatic hydrocarbons) in most developing countries, including China; however, accurate estimates of PAH emissions are often challenged by limited real-world emission factors (EFs) under field conditions, which can hardly be repeated in laboratory-controlled tests. In this study, a series of field measurements was conducted to determine the emissions of 28 PAHs from different fuel-stove combinations. A total of 14 fuel-stove combinations were studied. The total EFs of 28 PAHs (EF_{PAH28}), on the basis of fuel mass, ranged from 20.7 to 535 mg/kg, with relatively lower EFs for coal than for biomass. Biomass burning in gasifier stoves had lower PAH EFs and fewer toxic PAH species than biomass burning in traditional brick stoves. Fuel type was a significant factor affecting PAH emissions, while stove difference had a relatively smaller influence. Much higher EFs were found from these field tests than from the idealized laboratory tests, which indicated significant underestimation in inventories based on the laboratory-based EFs. Biomass and coal had different profiles, with larger intra-fuel variations in coal than

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Emission factors
Composition profile
Isomer ratio

those in biomass. Highly variable values of some, though not all, commonly used isomer ratios indicated substantial biases in source apportionment relying on single or simple ratios without correction, and the MCE was found to be significantly corrected with some ratios.

1. Introduction

Due to rapid socioeconomic development, clean energies, such as electricity and LPG (liquid petroleum gas), are used by more families (Sun et al., 2018; Tao et al., 2018); however, solid fuel still plays an important role in household energy consumption, especially in rural areas. It was estimated that the proportions of residents relying on solid fuels for daily cooking and heating in 2012 were 29.5% and 43.4%, respectively, and were higher in rural areas (40.4% and 60.1%) (Duan et al., 2014). Owing to the relatively low combustion efficiencies of household stoves and the lack of pollution control measures (Du et al., 2017; Bond et al., 2002), the incomplete combustion of solid fuels can emit many pollutants into air, such as carbon monoxide, particulate matter (PM), and polycyclic aromatic hydrocarbons (PAHs). PAHs have attracted worldwide public attention, as they are carcinogens and mutagenic to humans (IARC, 2010; Wang et al., 2015; Wincent et al., 2016). In addition, PAHs with more condensed rings might be important contributors to atmospheric brown carbon (BrC) (N. Lin et al., 2016). Decadal efforts have been made to investigate PAH pollution from household combustion and its impact on both human health and ambient air quality (Shen et al., 2015; B. Wang et al., 2016). For instance, H.Z. Shen et al. (2013) reported that 62% of the total PAHs in China were emitted from residential solid fuel burning. Du et al. (2018a) measured the indoor level of BaP, which is considered the predominant carcinogenic individual PAH (Zosima et al., 2016) and could be as high as 81 ± 42 ng/m^3 in rural homes. Due to indoor PAH exposure by inhalation from residential solid fuel usage, the ILCR (incremental lifetime cancer risk) could be up to 2.3×10^{-4} for the populations in northern China, which exceeds the accepted level of 10^{-6} by nearly two orders of magnitude (Du et al., 2018a).

Among the various sources of air pollution, the residential sector is significantly underappreciated and often associated with high uncertainties in its emission estimates (Krumal et al., 2019; G.F. Shen et al., 2013). In addition to the limitation of uncommercial biomass consumption data, variations in emission factors (EFs, defined as pollutant emission amounts per unit fuel burned) are another source of uncertainty (Shen et al., 2015). Some studies measured the EFs of PAHs from residential solid fuel combustion (Chen et al., 2005, 2015; Krugly et al., 2014; Y. Wang et al., 2016; Y. Zhang et al., 2021), but most combustion experiments were simulated in laboratory-controlled conditions; field-based experiments on EFs from the real world are rarely carried out (Du et al., 2018a; Shen et al., 2015). EFs determined by field-based experiments can better capture the real-world burning and emission status than those determined by lab tests and thus are often preferable in emission inventory development (Du et al., 2020; Wei et al., 2014). However, field-based emission measurements are often challenged due to labor- and cost-intensive field work and limited manpower resources in field sampling (Wei et al., 2014). Recently, there has been growing interest in field-based emission studies, but to date, most studies have primarily reported PM emissions with little other air pollutant emission information in the real world (Du et al., 2017; Eilenberg et al., 2018; Liu et al., 2018; Thompson et al., 2019; Shen et al., 2015; Zhang et al., 2020; Y. Zhang et al., 2021; L. Zhang et al., 2021). Fuel-stove combinations vary greatly around the world, and even within one country, spatial differences in fuel use and stove types can produce significant differences in PAH emissions. It is believed that EFs for fuel-stove combinations can reflect household emissions better than those for fuel-specific combinations (Du et al., 2020; G.F. Shen et al., 2013). Therefore, the EFs of PAHs for real-world fuel-stove combinations along with recognized spatial differences are highly needed but unfortunately scarce so far.

In this study, a series of field tests were conducted in four different provinces in China (Shanxi, Guizhou, Hubei and Sichuan) to evaluate the EFs of PM_{10}-bound PAHs from indoor solid fuel combustion. A total of 14 stove-fuel combinations were studied. The influences of fuel types and stove differences were discussed. Daily pollutant emissions with spatial variations were further calculated based on measured EFs and fuel consumption amounts determined from the fuel-weighing survey.

2. Material and methods

2.1. Description of study sites, stoves and fuels

Field measurements were conducted at four sites, including Taigu City (Shanxi Province), Anshun City (Guizhou Province), Nanchong City (Sichuan Province) and Enshi City (Hubei Province). Taigui City is located in northern China, while the other three cities are located in southern China (Fig. S1). Eight commonly used fuels were investigated in this study, including coal (honeycomb briquettes and coal chunks) and biomass fuels (fuel wood, brushwood, bamboo, maize straw, bean straw and corncobs). Coal was burned in iron stoves, while biomass fuels were burned in built-in-place brick stoves or gasifier wood stoves (Fig. S2). Built-in-place brick stoves are hard to test in the laboratory because of their large size and lack of availability on the market. Gasifier wood stoves are improved biomass stoves with secondary air supplies to increase the burning efficiency and are expected to reduce air pollutant emissions. Detailed information on the fuels, stoves and stove-fuel combinations is summarized in Table S1.

2.2. Emission tests

Field emission measurements followed the procedures used in previous field campaigns (Shen et al., 2015). Briefly, emission exhausts were sampled during a regular cooking period. Local residents operated their stoves and managed fires during the sampling period. A stainless-steel sampling port was placed near the center of the chimney. Sampling covered the whole period of a cooking event from fire ignition to the end of burning, lasting for approximately 30–40 min per test.

A cascade impactor (PEM, SKC, PA, USA) equipped with an active pump (SKC, PA, USA) was used to collect particles (with aerodynamic diameters equal to or less than 10 μm) on QFFs (quartz-fiber filters, Tissuquartz 2500QAT-UP, PALL Corporation, USA) that were prebaked at 450 °C for ~6 h to remove organic background.

2.3. Laboratory PAH analysis

A microwave accelerated extraction system (CEM, Mars Xpress, USA) was used to extract PAHs from the QFFs using 25 mL of a mixture of n-hexane/acetone (1:1, V/V). The temperature protocol was to increase the temperature to 110 °C within 10 min and then hold for another 10 min. The extract was further cleaned using a silica/alumina gel column that was pre-eluted with 20 mL of hexane. The final concentrates (~l mL) 110 were spiked with 200 ng of deuterated internal standards (naphthalene-d8, acenaphthene-d10, anthracene-d10, chrysene-d12, and peperylene-d12, J&W Chemical, USA) and analyzed for targets.

Gas chromatography-mass spectrometry (GC–MS, Agilent GC 6890, MS 5973, USA) in electron ionization mode was used for PAH analysis.

The column was a HP-5MS capillary column. The programmed temperature of the oven was held at 50 °C for 1 min, heated to 150 °C at 10 °C per min, then increased to 240 °C at a rate of 3 °C per min, heated to 280 °C at 20 °C per min and maintained for another 20 min. A 1 μL sample was injected in splitless mode, and the carrier gas was high-purity helium. The targeted parent PAHs measured in this study included 16 US EPA priority PAHs and 12 nonpriority parent PAHs. In this study, PAH_{28}, PAH_{16} and PAH_{12} indicated a total of 28 parent PAHs, 16 priority PAHs and 12 nonpriority PAHs, respectively. The PAH lists and the TEF (toxic equivalent factor) values for each individual are provided in Table S2.

2.4. Quality control and data analysis

Before and after sampling, the pump was calibrated using a primary flow calibrator (Bios Defender 510, USA). Known amounts of authentic standards were spiked in the sampling media to quantify the recoveries of PAHs, which ranged from 87%–114%. The recoveries of individual PAHs as well as the instrument detection limits and method detection limits are provided in Table S2. Additional information on the instrument detection limit, method detection limit, and recoveries of the target PAHs was added to Table S2. Field blanks were measured and subtracted from the results.

The fuel mass-based EFs of the PAHs were calculated using the carbon mass balance method (Zhang et al., 2000). To better compare the emissions of different fuels and stoves, per fuel energy-based EFs (EF_C and EF/Hi, where Hi (MJ/kg) is the calorific value of fuel *i*) and useful energy delivered-based EFs (EF_E and EF/Hi/η, where η (%) is the thermal efficiency, which were usually measured by water boiling tests) were also calculated (Shen, 2016; Zhang et al., 2000) (Table S3). Unfortunately, the calorific values of solid fuels and stove thermal efficiencies were not measured in this study; therefore, literature-reported results were adopted. The modified combustion efficiency (MCE), defined as CO/(CO + CO2), was used as a surrogate for the combustion conditions (Zhang et al., 2000). BaPeq (BaP equivalent EF) was used as a proxy of the toxicity of PAH emissions and calculated by the following equation:

$$\mathrm{BaPeq} = \sum_{i=1}^{n=28} \mathrm{TEF_{PAHi}} \times \mathrm{EF_{PAHi}} \quad (1)$$

where *PAHi* represents PAH congener i and TEF_{PAHi} is the toxicity equivalency factor of PAH i. The results are expressed as median and interquartile range values. SPSS 21.0 (IBM Corporation, Armonk, NY, USA) was used for the statistical analysis, and a significance level of 0.05 was adopted.

3. Results and discussion

Fig. 1 compares the EFs of PAH_{16} and PAH_{28}, as well as the mass fraction of PAH_{28} in PM_{10} and BaPeq of the PAH_{28} of the PM_{10} from the 14 stove-fuel combinations in this study. EFs varied by over one magnitude for the different combinations. The lowest EFs of PAH_{16} and PAH_{28}, which were 18.3 ± 22.8 and 20.7 ± 26.1 mg/kg, respectively, were observed for honeycomb briquettes burning in iron stoves (Shanxi Province). Bean straw burning in brick stoves (Sichuan) had the highest EFs of PAH_{16} and PAH_{28} of 429 ± 384 and 535 ± 489 mg/kg, respectively. The EFs based on fuel energy and useful energy delivered for different fuel-stove combinations tested are listed and compared in Table S3, which confirmed the low emissions from coal combustion. For example, the EF of PAH_{16} from coal chunk burning was 2.2 ± 1.9 mg/MJ, which was significantly lower than that of PAH_{16} from corncob burning (4.3 ± 3.0 mg/MJ) ($p < 0.05$). On the basis of useful energy delivered, the EF_E of PAH_{28} from fuel wood burning in gasifier stoves (4.6 ± 4.0 mg/MJ_d) was expectedly significantly lower ($p < 0.05$) than that from burning in traditional built-in brick stoves (10.0 ± 3.1 mg/MJ_d).

The mass fraction of PAH_{28} in PM_{10} ranged from 2.6‰ (corncob burning in brick stoves, Shanxi) to 19.6‰ (Bamboo burning in brick stoves, Guizhou), with an arithmetic mean of 9.8‰. This was close to the results in literature studies (Shen et al., 2012; Zosima et al., 2016), but the low mass fractions of PAHs might cause the considerably high toxic potentials of the particles emitted. A statistically significant positive correlation was observed between EF_{PAH28} and the mass fraction of PAH_{28} to PM_{10} ($p < 0.05$), suggesting that higher PAH emissions from solid fuel burning would be accompanied by a higher toxicity potential of particles. PAH emissions were significantly negatively correlated with the MCE ($p < 0.05$), as seen in past studies (Shen et al., 2011; G.F. Shen et al., 2013). As pollutants from the incomplete combustion process, PAH emissions were positively correlated with other products, such as CO and PM (Fig. 2).

From all tests performed here, PAH_{16} contributed to over 80% of the total 28 PAHs targeted; however, the BaPeq of PAH_{16} only accounted for 49.5% of the BaPeq based on the 28 PAHs, since some nonpriority PAHs have higher toxic potentials. The proportion of BaPeq attributed to

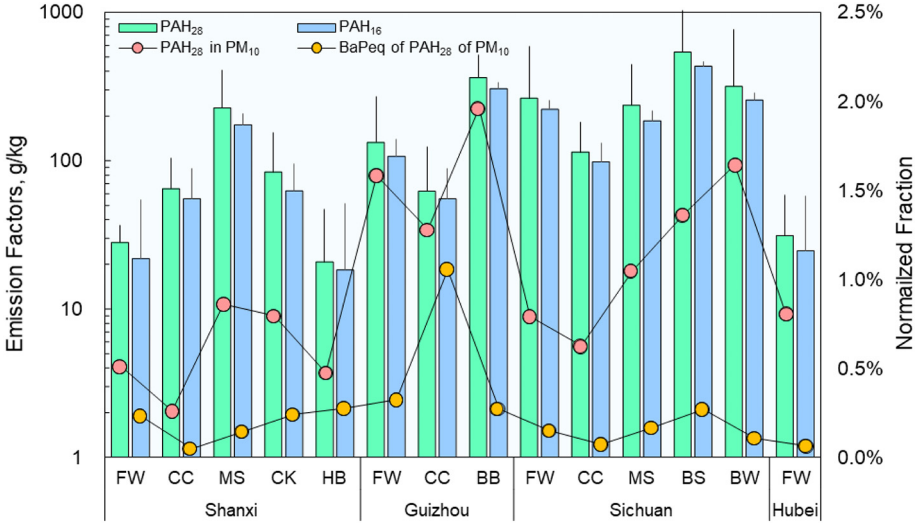

Fig. 1. The EFs of PM_{10}-bound PAH_{28} and PAH_{16}, as well as fraction of PAH_{28} in PM_{10} and BaPep of PAH_{28} of PM_{10} from different fuel types in different regions. In the picture, FW, CC, MS, CK, HB, BB, BS and BW represent fuel wood, corncob, maize straw, coal chunk, honeycomb briquette, bamboo, brushwood, bean straw, respectively.

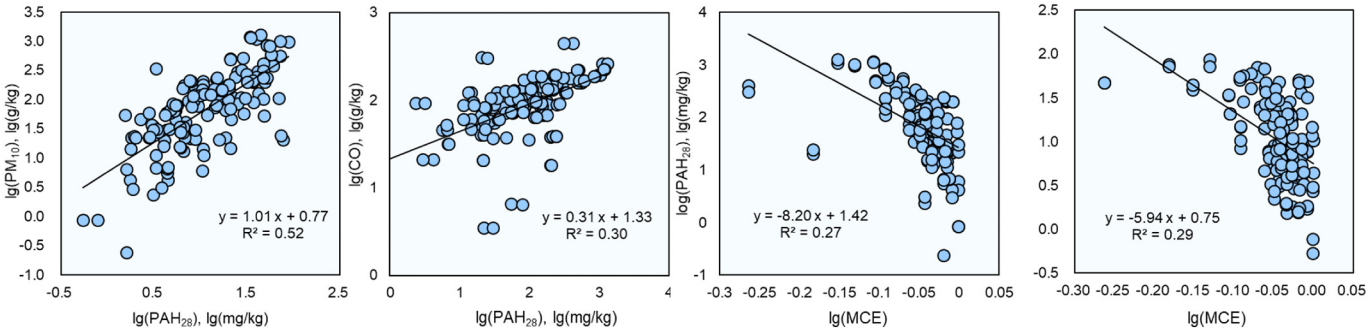

Fig. 2. Correlations between EFs of PM_{10}, PAH_{28} and MCE (data were log transformed).

PAH_{16} was lower for coal than for biomass fuels (34.8 ± 5.6% vs 51.8 ± 20.6%) ($p < 0.05$), and in emissions from the burning of bamboo and fuel wood, the proportions were as high as 66.0% and 63.2%, respectively.

3.1. Fuel and stove difference in determining PAH EFs

PAH emissions can be affected by many factors, including fuel types, combustion appliances, and combustion conditions (Shen et al., 2011; Du et al., 2017; Wei et al., 2014; Wu et al., 2015). Fuel and stove impacts are often expected and widely discussed in past studies. Studies and pollution controls expect to identify dirty fuels and eliminate their use to improve air quality and protect human health; however, the observed results between different fuels, or distinct stoves, are not always consistent because of the interaction of stove and fuel impacts and the co-impacts of other influencing factors (Dhammapala et al., 2007; Du et al., 2020). In Shanxi Province, both coal and biomass fuels are found in residents' daily lives. The emission measurements showed that honeycomb briquette combustion had lower EFs of PAHs than biomass fuel burning. However, the PAH emissions from the burning of coal chunks were higher than those from corncob and fuel wood burning, and the difference was significant between coal chunks and fuel wood ($p < 0.05$). Due to the higher calorific values of coal chunks, the fuel value-based EFs of coal chunks were lower than those of corncobs. Similar results were reported in previous studies (G.F. Shen et al., 2013; Yang et al., 2014). Honeycomb briquetting is a clean coal technology whose purpose is to hopefully reduce air pollutant emissions (Chen et al., 2015; Zhi et al., 2009). Some previous studies reported that honeycomb briquettes had lower PAH emissions than coal chunks, with a difference of approximately 2.5–40 times (Shen et al., 2010; G.F. Shen et al., 2013; Chen et al., 2004; Li et al., 2016); however, some contradictory results were also reported (Chen et al., 2015; Y. Wang et al., 2016). For example, G. Shen et al. (2013) reported that PAH emissions from the burning of honeycomb briquettes were over one magnitude lower than those from coal chunk combustion. In the study conducted by Chen et al. (2015), particulate PAH emissions from honeycomb briquette combustion were 2 times higher than those from coal chunk combustion. In the present study, the EFs of PAH_{28} from the burning of honeycomb briquettes were only a quarter of those from the burning of coal chunks (20.7 ± 26.1 vs 83.6 ± 70.3 mg/kg, respectively), suggesting significantly lower emissions from the briquettes than from the raw chunks. The lower indoor air pollution of PAHs in homes burning briquettes than in those burning raw chunks was confirmed by Chen et al. (2016). It appears that the total PAHs from both gaseous and particulate phases are lower for the briquettes than for the raw chunks; however, for individual PAHs, the difference between the chunks and briquettes might be species-specific because of the distinct formation pathways and mechanism for PAHs with different rings. In addition to the lower EFs, the BaPeq of PAH_{28} for the honeycomb briquettes was half that for the coal chunks, indicating an advisable way to replace coal chunks with honeycomb briquettes in residential combustion to reduce PAH emissions and lower human health risks.

Intra-fuel differences were also found within the biomass fuels, which ranged from 81.6 ± 58.0 (corncob) to 535 ± 489 (bean straw) mg/kg. Corncobs, accounting for 4.8% of the total cooking energy in rural China (Tao et al., 2018), have the lowest EFs of PAH_{28} among the biomass fuels, as did the BaPeq of PAH_{28}. Fuel wood had higher EFs of PAHs than corncobs, but the BaPeq values of PAH_{28} for these two fuels were similar. The EFs of PAHs and BaPeq for the brushwood were ~ 3 times higher than those for the fuel wood ($p < 0.05$). Similar results were reported by Shen et al. (2012) and G.F. Shen et al. (2013), in which the EFs of PAH_{28} for brushwood were 6–10-fold higher than those for fuel wood. Brushwood can be commonly seen and burned in many rural homes; thus, its emissions should be separated into emissions from wood logs and fuel wood to accurately estimate emissions from wood combustion. This study clearly showed that among different biomass fuels, raw crop straw had the highest PAH emissions (Ding et al., 2012; Y. Zhang et al., 2021). Bean straw produced the highest PAHs and BaPeq compared with the other biomasses. The burning of crop straw may result in severe air pollution and consequently harmful impacts on human health. Ding et al. (2012) previously reported that indoor PAH concentrations in kitchens due to crop straw combustion were 2.2 times higher than those due to fuel wood burning, which were 3300 and 1500 ng/m^3, respectively. Such high emissions in residential stoves should be controlled. Pelletization may be a way to replace the direct combustion of uncompressed straw in residential stoves and reduce emissions from straw burning, since previous studies have proven that biomass pellets can reduce the majority of pollutant emissions, including PAHs (Shen et al., 2012; Johansson et al., 2004).

In addition to fuel differences, stove structure plays an important role in combustion and pollutant emissions (Zosima et al., 2016; P. Lin et al., 2016). Improved stoves are often expected to have better thermal performance and lower air pollutant emissions (Carter et al., 2014; Jetter et al., 2012). Statistically significant differences in PAH emissions were only observed for fuel wood burning from different locations where stoves were not identical ($p < 0.05$). In addition to the difference between traditional and improved stoves, brick stove differences among the different locations also resulted in different PAH emissions. Although all stoves were made from brick, the stove inner structure of brick stoves was similar in Sichuan and Guizhou but different in Shanxi, North China (Fig. S3a). The EFs of PAH_{28} from maize straw and corncob burning in different brick stoves were similar, 229 ± 186 and 82 ± 58 mg/kg, respectively. The results obtained from two-way ANOVA showed that fuel type significantly influenced the EFs ($p < 0.05$), while the stove impacts were not statistically significant ($p > 0.05$). Gasifier wood stoves are modern stoves with lower emissions and were promoted in Hubei through a pilot project (Shen et al., 2015). The fuel mass-based EFs of PAH_{28} from fuel wood burning in gasifier wood stoves (31.2 ± 27.5 mg/kg) were much lower than those from burning in brick stoves in Guizhou and Sichuan (132 ± 138 and 262 ±

360 mg/kg, respectively) ($p < 0.05$), but the emissions were close to the results found in brick stoves in Shanxi (27.9 ± 8.6 mg/kg). This caused concerns that gasifier wood stoves might not necessarily have lower PAH EFs than built-in brick stoves. However, as mentioned before, if considering the higher thermal efficiencies of biomass wood stoves, which were approximately 2.5 times higher than those of traditional built-in-place brick stoves, the useful energy delivered-based EFs of PAH_{28} from fuel wood burning in gasifier wood stoves were lower than those from burning in brick stoves (Shanxi), which were 4.6 ± 4.0 and 10.0 ± 3.1 mg/MJ_d ($p < 0.05$), respectively. In addition, due to the improved thermal efficiency of gasifier wood stoves, less fuel consumption per cooking event was expected. The promotion of gasifier wood stoves may contribute to not only PAH emission reductions but also household energy savings. Furthermore, it is interesting to see that the BaPeq for wood burning in gasifier stoves was much lower than that in brick stoves ($p < 0.05$), indicating that in gasifier wood stoves, some highly toxic PAHs can be effectively mitigated. This reduction in high-toxicity PAHs may be attributed to high combustion efficiency。 It was previously reported that for wood combustion in stoves, the ratios of high-toxicity PAHs to the total would be lower in higher combustion efficiencies (Krumal et al., 2019).

3.2. Comparing EFs with previous laboratory results

Most previous studies on PAH emissions from solid fuels are performed under well-controlled laboratory conditions (Chen et al., 2005, 2015; Cheng et al., 2019; G.F. Shen et al., 2013; Vicente et al., 2016). Unlike those from well-controlled tests, the results from the field campaigns are subjected to many unrepeated influencing factors. For example, stoves tested in the lab could be very different from those used in the real world (Oanh et al., 2005; G.F. Shen et al., 2013). The fire management and fuel burning operations conducted by residents are subject to their burning habits and cooking conditions, which can hardly be repeated in laboratory tests (Du et al., 2018b; Li et al., 2021). In addition to variations between field and lab tests, the influences of fuel properties, stoves, and fire management may also lead to large variations among different field campaigns (G.F. Shen et al., 2013; Du et al., 2018b). G.F. Shen et al. (2013) previously investigated the EFs of PAH_{28} from the burning of brush wood, fuel wood and bamboo in a simulated kitchen in rural Beijing, which were one magnitude lower than our results, at 12.1 ± 9.1, 1.8 ± 1.6 and 5.4 ± 4.5 mg/kg, respectively. Wiriya et al. (2016) measured the EFs of PAH_{16} from the burning of maize residue in a laboratory chamber, which were only 0.5 ± 0.1 mg/kg. Vicente et al. (2016) calculated the EFs of PAH_{14} (PAH_{16} except for CHR and BbF) from the combustion of fuel wood, ranging from 0.2 to 22.0 mg/kg. Cheng et al. (2019) measured the EFs of PAH_{18} (PAH_{16} and COR and BeP) from the burning of honeycomb briquettes and coal chunks via laboratory tests, which ranged from 0.4–5.4 and 0.5–219 mg/kg, respectively. Sun et al. (2017) found that the EF of $PM_{2.5}$-bound PAH_{16} from maize straw burning was only 8.2 ± 5.9 mg/kg. Chen et al. (2015) determined the EFs of PAH_{16} (bound in $PM_{2.5}$) from honeycomb briquette and coal chunk burning, which were 6.9 ± 7.9 and 2.3 ± 1.6 mg/kg, respectively. All these laboratory-based results were approximately several times to nearly 2 orders of magnitude lower than our results, even for the same type of fuel burning. Since field-based tests had much higher EF values, great underestimation would be introduced when lab-based EFs were used to develop emission inventories. In addition to biases in the estimated emissions, laboratory-controlled tests can hardly capture variations in the combustion and emission conditions observed in the field. For example, during a real-world cooking period, residents usually add fuels several times, and the frequency or amounts of fuels added are often random, resulting in variability in the emissions across the whole period (Du et al., 2018b; Li et al., 2021). Under controlled conditions, combustion events were conducted by well-trained researchers following standard test protocols (i.e., water boiling tests). In field tests, stoves were operated by local residents based on their habits and burning conditions, which were very random and uncontrollable compared to laboratory studies, as mentioned before, and fuels were reloaded several times (Roden et al., 2006, 2009; Li et al., 2021). Consequently, there were not only differences in average EF values but also large variations between laboratory and field studies (Du et al., 2018b). Furthermore, idealized laboratory tests can hardly reproduce some poor combustion moments that occur occasionally in real-world conditions but that release large quantities of incomplete combustion pollutants (Dhammapala et al., 2007; Roden et al., 2009).

3.3. Composition profiles

The composition profiles for different fuel types are exhibited in Fig. 3. In general, the overall predominant individual PAHs in emission smoke from coal combustion were ACY (13.8%), PHE (12.8%), FLA (10.8%) and PYR (10.4%), while for the burning of biomass fuels, PYR (17.5%), FLA (15.5%), PHE (12.2%) and CcdP (11.5%) were the dominant species. Significant differences in the emission profiles between the burning of coal and biomass fuels were found for PYR, BaP, PER, BeP, and DBalP ($p < 0.05$).

Large differences were observed between the emission profiles from the combustion of honeycomb briquettes and coal chunks. The predominant individual PAHs for honeycomb briquette combustion were ACY (20.6%), PHE (14.9%), and CHR (10.9%), while for the burning of raw chunks, they were FLA (14.5%), PYR (13.1%) and PHE (10.6%). Such composition profile differences were also reported in some past studies. For example, Yang et al. (2014) reported that the emissions of particle phase PAHs from honeycomb briquette combustion were dominated by PHE, BbF and FLA, whereas in a laboratory campaign, Cheng et al. (2019) observed high emissions of BbF, CHR, BeP for briquette combustion and BbF, CHR, and BaA for coal chunk burning. The large disparities between the different composition profiles for coal combustion can be partly explained by coal properties and stove designs. Previous studies reported that differences in coal properties and stove efficiency may result in variations in PAH composition profiles during combustion processes (Chen et al., 2005; B. Wang et al., 2016; Y. Wang et al., 2016).

In contrast to the intrafuel difference in coal combustion, the composition profiles for wood fuel and crop residue combustion were similar, with the predominant compounds being PHE, FLA and PYR. These predominant particulate PAHs from the burning of wood fuels and crop residues were also reported previously (Sun et al., 2018; Zhang et al., 2020). In addition, CcdP was found to be a major contributor to total PAH emissions in this study and accounted for 7.9% and 10.9% of the combustion of wood fuel and crop residues, respectively. A relatively higher contribution of CcdP was also reported for the particle-bound PAH emissions from fuel wood burning and indoor air that rely on biomass fuel for cooking (Yang et al., 2014; Du et al., 2018a). However, CcdP was not included in the 16 priority PAH lists. Many previous studies only focused on 16 priority PAHs; for example, in the research conducted by Chen et al. (2015), B. Wang et al. (2016), Y. Wang et al. (2016), and Zhang et al. (2020), nonpriority PAHs were seldom measured. This would underestimate the health impact of PAH emissions because some nonpriority PAHs had higher TEFs than priority PAHs.

Contributions of PAHs with different rings are shown in Fig. 4. Generally, for emissions from the burning of all kinds of solid fuels (biomass fuels and coal), PAHs with 2–3 rings comprised most (44.3%) of the total. For the burning of wood fuels, 4-ring PAHs were predominant in the total PAH emissions (42.2%). The 5–6-ring compounds from coal combustion contributed more to PAH emissions than biomass fuel burning; in contrast, for the BaPeq of PAHs, their contributions in coal were higher than those in biomass fuels. Even though the proportions of 5–6-ring PAHs to total PAH emissions from wood fuel and crop residue burning were close (17.4% vs 19.8%, respectively), their contributions to the BaPeq toxicity of PAHs were different (76.6% vs 86.2%, respectively). More attention should be paid to 5–6-ring PAHs since

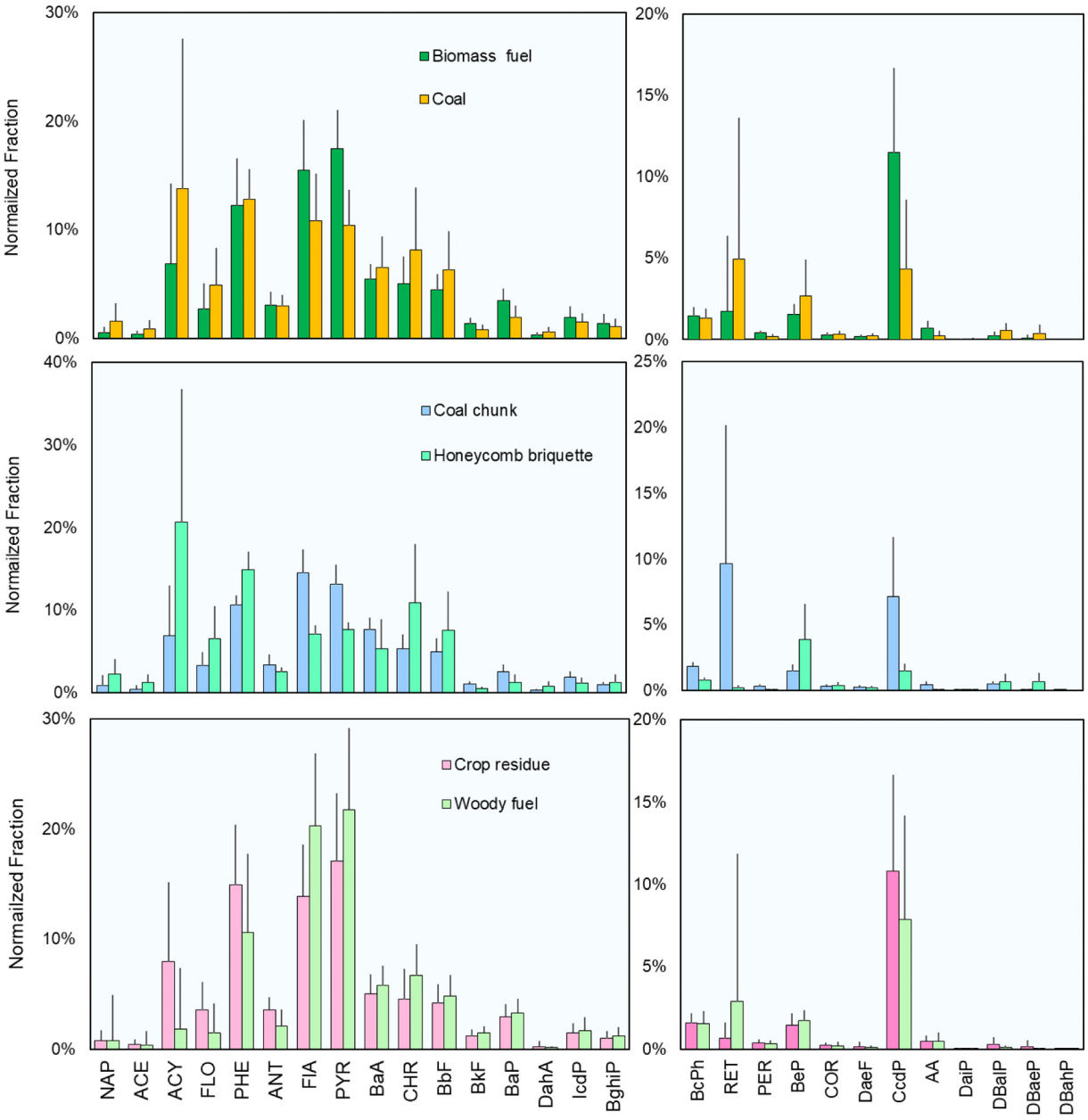

Fig. 3. Composition profiles of particle-bound PAH_{28} from solid fuel combustion.

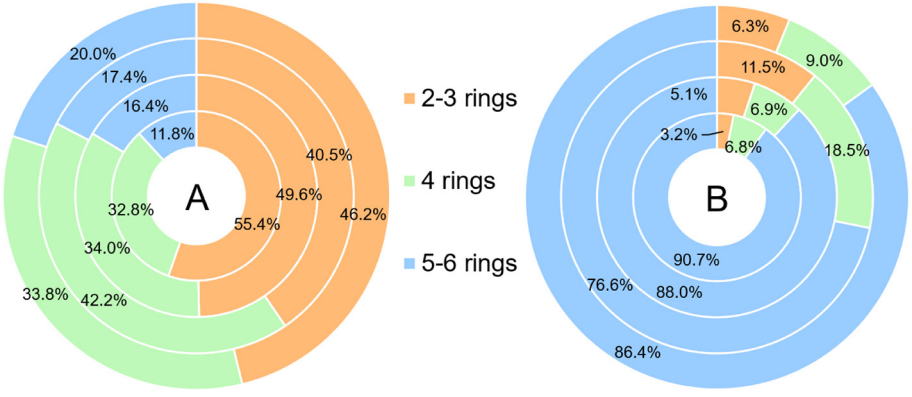

Fig. 4. Ratios of PAHs with different rings to total EFs (a) and BaPeq (b) of 28 total PAHs. The ring from inside to outside represented PAHs from the burning of honeycomb briquettes, coal chunks, woody fuels and crop residues, respectively.

Table 1
Isomer ratios from this study and reported in the literatures.

	Fuel types	ANT/(ANT + PHE)	FLA/(FLA + PYR)	BaA/(BaA + CHR)	IcdP/(IcdP + BghiP)	BbF/(BbF + BkF)	BaP/(BaP + BghiP)
This study	Biomass	0.18 ± 0.04	0.47 ± 0.05	0.51 ± 0.08	0.59 ± 0.06	0.77 ± 0.05	0.76 ± 0.06
	Coal	0.23 ± 0.08	0.50 ± 0.03	0.46 ± 0.14	0.60 ± 0.09	0.87 ± 0.06	0.64 ± 0.12
Shen et al., 2014	Biomass	0.12 ± 0.01	0.53 ± 0.01	0.45 ± 0.09	0.51 ± 0.04	0.53 ± 0.02	0.57 ± 0.05
	Coal	0.18 ± 0.04	0.54 ± 0.02	0.43 ± 0.09	0.41 ± 0.14	0.52 ± 0.05	0.51 ± 0.16
Liu et al., 2017	Fuel wood	0.29 ± 0.18	0.52 ± 0.02	0.34 ± 0.03	0.49 ± 0.05	0.82 ± 0.05	0.48 ± 0.04
	Coal	0.10 ± 0.02	0.59 ± 0.04	0.23 ± 0.01	0.51 ± 0.11	0.94 ± 0.01	0.40 ± 0.05
Shen et al., 2011	Biomass	0.12 ± 0.01	0.53 ± 0.01	0.48 ± 0.02	0.54 ± 0.02	0.55 ± 0.03	0.60 ± 0.05
Wei et al., 2014	Biomass	0.16 ± 0.01	0.46 ± 0.02	0.46 ± 0.03	0.58 ± 0.01	0.74 ± 0.02	0.78 ± 0.02

these high-molecular weight PAHs had relatively higher TEF values. In this study, 5–6-ring compounds only accounted for 17.9% of the total PAH emissions; however, they were the major contributor to the BaPeq of PAHs (82.6%).

3.4. Isomer ratios

PAH isomer ratios are often used for source apportionment by assuming that paired isomers display similar rates of degradation and/or transformation once emitted into the environment, and the ratios do not change or change slightly during transportation (Katsoyiannis et al., 2011; Yunker et al., 2002; Zhang et al., 2005). For example, Cai et al. (2017) characterized solid fuel combustion and traffic exhaust as being the main PAH sources in surface soil in the Yangtze River Delta based on the PAH isomer ratios of FLA/(FLA + PYR), IcdP/(IcdP + BghiP) and BaA/(BaA + CHR). As shown in Table 1, six commonly used isomer ratios are calculated and compared in this study.

It is suggested that the ratios FLA/(FLA + PYR) <0.4 and >0.5 and IcdP/(IcdP + BghiP) <0.2 and >0.5 designate petrogenic sources and the combustion of coal and biomass, respectively. FLA/(FLA + PYR) and IcdP/(IcdP + BghiP) are in the ranges of 0.4–0.5 and 0.2–0.5 for the sources of fossil fuel burning and petroleum combustion, respectively (Yunker et al., 2002). BaA/(BaA + CHR) values of <0.2, 0.2–0.35, and >0.35 represent petrogenic sources, coal combustion and traffic exhaust, respectively (Tobiszewski and Namiesnik, 2012). The calculated isomer ratios in this field measurement from the burning of coal and biomass fuel are demonstrated in Fig. 5, and a wider scope than the abovementioned literature ranges can be observed for these isomer ratios. The ratios of IcdP/(IcdP + BghiP) ranged from 0.37 to 0.70, with an anthracite mean of 0.59, and 93.8% of the total results were larger than the recommended criterion value of 0.5, indicating a better performance in distinguishing the source of solid fuel combustion from other sources. However, for the FLA/(FLA + PYR) and BaA/(BaA + CHR) ratios, only 24.1% and 50% of the results were in the suggested scope, respectively, indicating substantial errors when these two ratios were used for source diagnosis. The overlapping values of isomer ratios from coal and biomass combustion suggested that it is nearly impossible to separate these two sources from each other by using these ratios. In addition to the fuel difference, combustion conditions, as indicated by the MCE, can affect PAH formation, resulting in variations in the isomer ratios. For example, the values of IcdP/(IcdP+BghiP) for the corncob burned in brick stoves in Shanxi and Guizhou were 0.66 ± 0.01 and 0.48 ± 0.06, respectively ($p < 0.05$), while the corresponding MCE values were 92 ± 4% and 83 ± 13%, respectively. For PAH emissions from biomass burning, as seen in Fig. S4, a statistically positive relationship was found between FLA/(FLA + PYR) and MCE, and for other ratios, such as ANT/(ANT + PHE), BaA/(BaA + CHR), and IcdP/(IcdP +BghiP), lower ratio values under higher MCEs were revealed ($p < 0.05$). Generally, the MCE can explain 20–30% of the variation in FLA/(FLA + PYR) and 40–60% of the variation in the ratios of ANT/(ANT + PHE), BaA/(BaA + CHR), and IcdP/(IcdP+BghiP). Future studies are interesting to better examine the reasons behind the variable isomer ratios. With high uncertainty and variations in the observed isomer ratios, source apportionment by using single or simple isomer ratios should be avoided or at least corrected (Zhang et al., 2000), which unfortunately was not the case in many reports. However, in the real world, combustion conditions are subject to many factors; for example, residential stoves vary widely in ventilation, performance and inner structure (Oanh et al., 2005; Zhang et al., 2000). Fuel properties and stove operations changed greatly among different studies (B. Wang

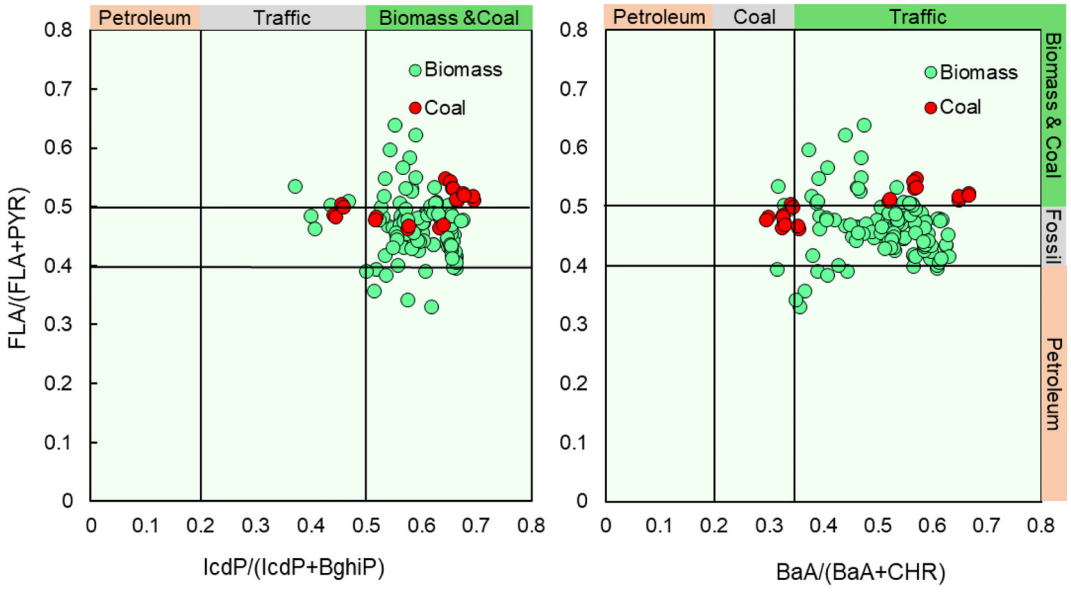

Fig. 5. Isomer rations from the combustion of coal and biomass fuels.

et al., 2016; Y. Wang et al., 2016; Shen et al., 2011; Li et al., 2021). All these factors can significantly affect these ratios. In addition, it is suggested that PAH-specific ratios from field measurements may be affected by different photodegradation rates (Tobiszewski and Namiesnik, 2012). Specific ratios should be used with caution, and the difference and variability observed in the present study call for more field tests to determine the restriction of PAH isomer ratios in the identification of different emission sources.

4. Conclusions

In this study, field measurements were carried out in four provinces in rural China to estimate PAH emissions from residential solid fuel combustion for cooking. The effects of different stoves and fuel types on PAH emissions were investigated. The results were compared with those obtained from previously performed well-controlled laboratory tests. Over an order of magnitude variations were found between the EFs of PAHs from the combustion of different fuel types under different burning conditions. Bean straw burning had the highest PAH EFs. Gasifier wood stoves, which were promoted as clean stoves, had relatively lower PAH emissions. Furthermore, the BaPeq of the PAH emissions from this stove was much lower than that from traditional brick stoves. Compared to the results originating from laboratory studies, field tests obtained much higher EF values, implying significant underestimations in the emission inventories primarily based on lab-based EFs. In addition to the EF differences, PAH composition profiles also varied significantly between the honeycomb briquettes and coal chunks. Several PAH isomer ratios commonly used in PAH source apportionment varied greatly depending on not only the fuel source but also the combustion conditions. BaPeq toxicity potentials were mainly affected by the contributions of 5–6-ring PAHs, which should be given more attention in future studies.

CRediT authorship contribution statement

Wei Du: Conceptualization, Investigation, Writing – original draft, Writing – review & editing. **Jinze Wang:** Writing – original draft, Writing – review & editing. **Shaojie Zhuo:** Investigation, Writing – review & editing. **Qirui Zhong:** Writing – review & editing. **Wei Wang:** Investigation, Writing – review & editing. **Yuanchen Chen:** Writing – review & editing. **Zhenglu Wang:** Writing – review & editing. **Kang Mao:** Writing – review & editing. **Ye Huang:** Writing – review & editing. **Guofeng Shen:** Conceptualization, Writing – review & editing, Funding acquisition, Supervision. **Shu Tao:** Writing – review & editing, Funding acquisition, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Information of fuel-stove combinations, sampling size, as well as carbon content and moisture; energy and useful energy based EFs. Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.145411.

References

Bond, T.C., Covert, D.S., Kramlich, J.C., Larson, T.V., Charlson, R.J., 2002. Primary particle emissions from residential coal burning: optical properties and size distributions. J. Geophys. Res.-Atmos. 107.

Cai, C.Y., Li, J.Y., Di, W., Wang, X.L., Tsang, D.C.W., Li, X.D., Sun, J.T., Zhu, L.H., Shen, H.Z., Tao, S., Liu, W.X., 2017. Spatial distribution, emission source and health risk of parent PAHs and derivatives in surface soils from the Yangtze River Delta, eastern China. Chemosphere 178, 301–308.

Carter, E.M., Shan, M., Yang, X.D., Li, J.R., Baumgartner, J., 2014. Pollutant emissions and energy efficiency of Chinese gasifier cooking stoves and implications for future intervention studies. Environ. Sci. Technol. 48, 6461–6467.

Chen, Y.J., Bi, X.H., Mai, B.X., Sheng, G.Y., Fu, J.M., 2004. Emission characterization of particulate/gaseous phases and size association for polycyclic aromatic hydrocarbons from residential coal combustion. Fuel 83, 781–790.

Chen, Y.J., Sheng, G.Y., Bi, X.H., Feng, Y.L., Mai, B.X., Fu, J.M., 2005. Emission factors for carbonaceous particles and polycyclic aromatic hydrocarbons from residential coal combustion in China. Environ. Sci. Technol. 39, 1861–1867.

Chen, Y.J., Zhi, G.R., Feng, Y.L., Tian, C.G., Bi, X.H., Li, J., Zhang, G., 2015. Increase in polycyclic aromatic hydrocarbon (PAH) emissions due to briquetting: a challenge to the coal briquetting policy. Environ. Pollut. 204, 58–63.

Chen, Y., Shen, G., Huang, Y., Zhang, Y., Han, Y., Wang, R., Shen, H., Su, S., Lin, N., Zhu, D., Pei, L., Zheng, X., Wu, J., Wang, X., Liu, W., Wong, M., Tao, S., 2016. Household air pollution and personal exposure risk of polycyclic aromatic hydrocarbons among rural residents in Shanxi, China. Indoor Air 26, 246–258.

Cheng, Y., Kong, S.F., Yan, Q., Liu, H.B., Wang, W., Chen, K., Yin, Y., Zheng, H., Wu, J., Yao, L.Q., Zeng, X., Zheng, S.R., Wu, F.Q., Niu, Z.Z., Zhang, Y., Yan, Y.Y., Zheng, M.M., Qi, S.H., 2019. Size-segregated emission factors and health risks of PAHs from residential coal flaming/smoldering combustion. Environ. Sci. Pollut. R 26, 31793–31803.

Dhammapala, R., Claiborn, C., Simpson, C., Jimenez, J., 2007. Emission factors from wheat and Kentucky bluegrass stubble burning: comparison of field and simulated burn experiments. Atmos. Environ. 41, 1512–1520.

Ding, J., Zhong, J., Yang, Y., Li, B., Shen, G., Su, Y., Wang, C., Li, W., Shen, H., Wang, B., Wang, R., Huang, Y., Zhang, Y., Cao, H., Zhu, Y., Simonich, S., Tao, S., 2012. Occurrence and exposure to polycyclic aromatic hydrocarbons and their derivatives in a rural Chinese home through biomass fuelled cooking. Environ. Pollut. 169, 160–166.

Du, W., Shen, G.F., Chen, Y.C., Zhu, X., Zhuo, S.J., Zhong, Q.R., Qi, M., Xue, C.Y., Liu, G.Q., Zeng, E., Xing, B.S., Tao, S., 2017. Comparison of air pollutant emissions and household air quality in rural homes using improved wood and coal stoves. Atmos. Environ. 166, 215–223.

Du, W., Chen, Y.C., Zhu, X., Zhong, Q.R., Zhuo, S.J., Liu, W.J., Huang, Y., Shen, G.F., Tao, S., 2018a. Wintertime air pollution and health risk assessment of inhalation exposure to polycyclic aromatic hydrocarbons in rural China. Atmos. Environ. 191, 1–8.

Du, W., Zhu, X., Chen, Y., Liu, W., Wang, W., Shen, G., Tao, S., Jetter, J.J., 2018b. Field-based emission measurements of biomass burning in typical Chinese built-in-place stoves. Environ. Pollut. 242, 1587–1597.

Du, W., Yun, X., Chen, Y., Zhong, Q., Wang, W., Wang, L., Qi, M., Shen, G., Tao, S., 2020. PAHs emissions from residential biomass burning in real-world cooking stoves in rural China. Environ. Pollut. 267, 115592.

Duan, X.L., Jiang, Y., Wang, B.B., Zhao, X.G., Shen, G.F., Cao, S.Z., Huang, N., Qian, Y., Chen, Y.T., Wang, L.M., 2014. Household fuel use for cooking and heating in China: results from the first Chinese Environmental Exposure-Related Human Activity Patterns Survey (CEERHAPS). Appl. Energy 136, 692–703.

Eilenberg, S.R., Bilsback, K.R., Johnson, M., Kodros, J.K., Lipsky, E.M., Naluwaffa, A., Fedak, K.M., Benka-Coker, M., Reynolds, B., Peel, J., Clark, M., Shan, M., Sambandam, S., L'Orange, C., Pierce, J.R., Subramanian, R., Volckens, J., Robinson, A.L., 2018. Field measurements of solid-fuel cookstove emissions from uncontrolled cooking in China, Honduras, Uganda, and India. Atmos. Environ. 190, 116–125.

IARC (International Agency for Research on Cancer), 2010. Some non-heterocyclic polycyclic aromatic hydrocarbons and some related exposures. IARC Monogr. Eval. Carcinog. Risks Hum. 92, 765–771.

Jetter, J., Zhao, Y.X., Smith, K.R., Khan, B., Yelverton, T., DeCarlo, P., Hays, M.D., 2012. Pollutant emissions and energy efficiency under controlled conditions for household biomass cookstoves and implications for metrics useful in setting international test standards. Environ. Sci. Technol. 46, 10827–10834.

Johansson, L.S., Leckner, B., Gustavsson, L., Cooper, D., Tullin, C., Potter, A., 2004. Emission characteristics of modern and old-type residential boilers fired with wood logs and wood pellets. Atmos. Environ. 38, 4183–4195.

Katsoyiannis, A., Sweetman, A.J., Jones, K.C., 2011. PAH molecular diagnostic ratios applied to atmospheric sources: a critical evaluation using two decades of source inventory and air concentration data from the UK. Environ. Sci. Technol. 45, 8897–8906.

Krugly, E., Martuzevicius, D., Puida, E., Buinevicius, K., Stasiulaitiene, I., Radziuniene, I., Minikauskas, A., Kliucininkas, L., 2014. Characterization of gaseous- and particle-phase emissions from the combustion of biomass-residue-derived fuels in a small residential boiler. Energy Fuel 28, 5057–5066.

Krumal, K., Mikuska, P., Horak, J., Hopan, F., Krpec, K., 2019. Comparison of emissions of gaseous and particulate pollutants from the combustion of biomass and coal in modern and old-type boilers used for residential heating in the Czech Republic, Central Europe. Chemosphere 229, 51–59.

Li, Q., Jiang, J.K., Qi, J., Deng, J.G., Yang, D.S., Wu, J.J., Duan, L., Hao, J.M., 2016. Improving the energy efficiency of stoves to reduce pollutant emissions from household solid fuel combustion in China. Environ. Sci. Tech. Let. 3, 369–374.

Li, T.K., Liu, B.S., Bi, X.H., Wu, J.H., Zhang, Y.F., Feng, Y.C., 2021. Size and chemical characteristics of particles emitted from typical rural biomass cookstoves in North China. Atmos. Res. 249, 105295.

Lin, N., Chen, Y.C., Du, W., Shen, G.F., Zhu, X., Huang, T.B., Wang, X.L., Cheng, H.F., Liu, J.F., Xue, C.Y., Liu, G.Q., Zeng, E.Y., Xing, B.S., Tao, S., 2016a. Inhalation exposure and risk of polycyclic aromatic hydrocarbons (PAHs) among the rural population adopting wood gasifier stoves compared to different fuel-stove users. Atmos. Environ. 147, 485–491.

Lin, P., Aiona, P.K., Li, Y., Shiraiwa, M., Laskin, J., Nizkorodov, S.A., Laskin, A., 2016b. Molecular characterization of brown carbon in biomass burning aerosol particles. Environ. Sci. Technol. 50, 11815–11824.

Liu, Y., Zhang, Y., Li, C., Bai, Y., Zhang, D., Xue, C., Liu, G., 2018. Air pollutant emissions and mitigation potential through the adoption of semi-coke coals and improved heating stoves: field evaluation of a pilot intervention program in rural China. Environ. Pollut. 240, 661–669.

Oanh, N.T.K., Albina, D.O., Ping, L., Wang, X.K., 2005. Emission of particulate matter and polycyclic aromatic hydrocarbons from select cookstove-fuel systems in Asia. Biomass Bioenergy 28, 579–590.

Roden, C.A., Bond, T.C., Conway, S., Pinel, A.B.O., 2006. Emission factors and real-time optical properties of particles emitted from traditional wood burning cookstoves. Environ. Sci. Technol. 40, 6750–6757.

Roden, C.A., Bond, T.C., Conway, S., Osorto Pinel, A.B., MacCarty, N., Still, D., 2009. Laboratory and field investigations of particulate and carbon monoxide emissions from traditional and improved cookstoves. Atmos. Environ. 43, 1170–1181.

Shen, G.F., 2016. Changes from traditional solid fuels to clean household energies - opportunities in emission reduction of primary PM2.5 from residential cookstoves in China. Biomass Bioenergy 86, 28–35.

Shen, G.F., Wang, W., Yang, Y.F., Zhu, C., Min, Y.J., Xue, M.A., Ding, J.N., Li, W., Wang, B., Shen, H.Z., Wang, R., Wang, X.L., Tao, S., 2010. Emission factors and particulate matter size distribution of polycyclic aromatic hydrocarbons from residential coal combustions in rural Northern China. Atmos. Environ. 44, 5237–5243.

Shen, G.F., Wang, W., Yang, Y.F., Ding, J.N., Xue, M.A., Min, Y.J., Zhu, C., Shen, H.Z., Li, W., Wang, B., Wang, R., Wang, L., Tao, S., Russell, A.G., 2011. Emissions of PAHs from indoor crop residue burning in a typical rural stove: emission factors, size distributions, and gas-particle partitioning. Environ. Sci. Technol. 45, 1206–1212.

Shen, G.F., Tao, S., Wei, S.Y., Zhang, Y.Y., Wang, R., Wang, B., Li, W., Shen, H.Z., Huang, Y., Chen, Y.C., Chen, H., Yang, Y.F., Wang, W., Wang, X.L., Liu, W.X., Simonich, S.L.M., 2012. Emissions of parent, nitro, and oxygenated polycyclic aromatic hydrocarbons from residential wood combustion in rural China. Environ. Sci. Technol. 46, 8123–8130.

Shen, H.Z., Huang, Y., Wang, R., Zhu, D., Li, W., Shen, G.F., Wang, B., Zhang, Y.Y., Chen, Y.C., Lu, Y., Chen, H., Li, T.C., Sun, K., Li, B.G., Liu, W.X., Liu, J.F., Tao, S., 2013a. Global atmospheric emissions of polycyclic aromatic hydrocarbons from 1960 to 2008 and future predictions. Environ. Sci. Technol. 47, 6415–6424.

Shen, G.F., Tao, S., Chen, Y.C., Zhang, Y.Y., Wei, S.Y., Xue, M., Wang, B., Wang, R., Lu, Y., Li, W., Shen, H.Z., Huang, Y., Chen, H., 2013b. Emission characteristics for polycyclic aromatic hydrocarbons from solid fuels burned in domestic stoves in rural China. Environ. Sci. Technol. 47, 14485–14494.

Shen, G., Tao, S., Wei, S., Chen, Y., Zhang, Y., Shen, H., Huang, Y., Zhu, D., Yuan, C., Wang, H., Wang, Y., Pei, L., Liao, Y., Duan, Y., Wang, B., Wang, R., Lv, Y., Li, W., Wang, X., Zheng, X., 2013c. Field measurement of emission factors of PM, EC, OC, Parent, Nitro-, and Oxy-polycyclic aromatic hydrocarbons for residential briquette, coal cake, and wood in rural Shanxi, China. Environ. Sci. Technol. 47, 2998–3005.

Shen, G., Wei, S., Zhang, Y., Wang, B., Wang, R., Shen, H., Li, W., Huang, Y., Chen, Y., Chen, H., Tao, S., 2014. Emission and size dsitribution of particle-bound polycyclic aromatic hydrocarbons from residential wood combustion. Biomass Bioenerg 55, 141–147.

Shen, G.F., Chen, Y.C., Xue, C.Y., Lin, N., Huang, Y., Shen, H.Z., Wang, Y.L., Li, T.C., Zhang, Y.Y., Su, S., Huangfu, Y.B., Zhang, W.H., Chen, X.F., Liu, G.Q., Liu, W.X., Wang, X.L., Wong, M.H., Tao, S., 2015. Pollutant emissions from improved coal- and wood-fuelled cookstoves in rural households. Environ. Sci. Technol. 49, 6590–6598.

Sun, J., Shen, Z.X., Zeng, Y.L., Niu, X.Y., Wang, J.H., Cao, J.J., Gong, X.S., Xu, H.M., Wang, T.B., Liu, H.X., Yang, L., 2018. Characterization and cytotoxicity of PAHs in PM2.5 emitted from residential solid fuel burning in the Guanzhong Plain, China. Environ. Pollut. 241, 359–368.

Sun, J., Shen, Z., Cao, J., Zhang, L., Wu, T., Zhang, Q., Yin, X., Lei, Y., Huang, Y., Huang, R., Liu, S., Han, Y., Xu, H., Zheng, C., Liu, P., 2017. Particulate matters emitted from maize straw burning for winter heating in rural areas in Guangzhong Plain, China: current emission and future reduction. Atmos. Res. 184, 66–76.

Tao, S., Ru, M.Y., Du, W., Zhu, X., Zhong, Q.R., Li, B.G., Shen, G.F., Pan, X.L., Meng, W.J., Chen, Y.L., Shen, H.Z., Lin, N., Su, S., Zhuo, S.J., Huang, T.B., Xu, Y., Yun, X., Liu, J.F., Wang, X.L., Liu, W.X., Cheng, H.F., Zhu, D.Q., 2018. Quantifying the rural residential energy transition in China from 1992 to 2012 through a representative national survey. Nat. Energy 3, 567–573.

Thompson, R.J., Li, J., Weyant, C., Edwards, R., Lan, Q., Rothman, N., Hu, W., Dang, J., Dang, A., Smith, K.R., Bond, T.C., 2019. Field emission measurements of solid fuel stoves in Yunnan, China demonstrate dominant causes of uncertainty in household emission inventories. Environ. Sci. Technol. 53, 3323–3330.

Tobiszewski, M., Namiesnik, J., 2012. PAH diagnostic ratios for the identification of pollution emission sources. Environ. Pollut. 162, 110–119.

Vicente, E.D., Vicente, A.M., Bandowe, B.A.M., Alves, C.A., 2016. Particulate phase emission of parent polycyclic aromatic hydrocarbons (PAHs) and their derivatives (alkyl-PAHs, oxygenated-PAHs, azaarenes and nitrated PAHs) from manually and automatically fired combustion appliances. Air Qual. Atmos. Health 9, 653–668.

Wang, B., Jin, L., Ren, A.G., Yuan, Y., Liu, J.F., Li, Z.W., Zhang, L., Yi, D.Q., Wang, L.L., Zhang, Y.L., Wang, X.L., Tao, S., Finnell, R.H., 2015. Levels of polycyclic aromatic hydrocarbons in maternal serum and risk of neural tube defects in offspring (vol 49, pg 588, 2015). Environ. Sci. Technol. 49, 10754–10755.

Wang, B., Liu, Y.Y., Li, Z.J., Li, Z.W., 2016a. Association of indoor air pollution from coal combustion with influenza-like illness in housewives. Environ. Pollut. 216, 646–652.

Wang, Y., Xu, Y., Chen, Y.J., Tian, C.G., Feng, Y.L., Chen, T., Li, J., Zhang, G., 2016b. Influence of different types of coals and stoves on the emissions of parent and oxygenated PAHs from residential coal combustion in China. Environ. Pollut. 212, 1–8.

Wei, S.Y., Shen, G.F., Zhang, Y.Y., Xue, M., Xie, H., Lin, P.C., Chen, Y.C., Wang, X.L., Tao, S., 2014. Field measurement on the emissions of PM, OC, EC and PAHs from indoor crop straw burning in rural China. Environ. Pollut. 184, 18–24.

Wincent, E., Le Bihanic, F., Dreij, K., 2016. Induction and inhibition of human cytochrome P4501 by oxygenated polycyclic aromatic hydrocarbons. Toxicol. Res. 5, 788–799.

Wiriya, W., Chantara, S., Sillapapiromsuk, S., Lin, N.H., 2016. Emission profiles of PM10-bound polycyclic aromatic hydrocarbons from biomass burning determined in chamber for assessment of air pollutants from open burning. Aerosol Air Qual. Res. 16, 2716–2727.

Wu, F., Liu, X., Wang, W., Man, Y.B., Chan, C.Y., Liu, W., Tao, S., Wong, M.H., 2015. Characterization of particulate-bound PAHs in rural households using different types of domestic energy in Henan Province, China. Sci. Total Environ. 536, 840–846.

Yang, C., Su, Y., Chen, Y., Huang, Y., Liu, W., Shen, G., Duan, Y., Liu, W., Tao, S., 2014. Emission factors of particulate matter and polycyclic aromatic hydrocarbons for residential solid fuels. Asian J. Ecotoxicol. 9, 545–555 (in Chinese).

Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., Sylvestre, S., 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Org. Geochem. 33, 489–515.

Zhang, J., Smith, K.R., Ma, Y., Ye, S., Jiang, F., Qi, W., Liu, P., Khalil, M.A.K., Rasmussen, R.A., Thorneloe, S.A., 2000. Greenhouse gases and other airborne pollutants from household stoves in China: a database for emission factors. Atmos. Environ. 34, 4537–4549.

Zhang, X.L., Tao, S., Liu, W.X., Yang, Y., Zuo, Q., Liu, S.Z., 2005. Source diagnostics of polycyclic aromatic hydrocarbons based on species ratios: a multimedia approach. Environ. Sci. Technol. 39, 9109–9114.

Zhang, Y., Shen, Z.X., Sun, J., Zhang, L.M., Zhang, B., Zhang, T., Wang, J.H., Xu, H.M., Liu, P.P., Zhang, N.N., Cao, J.J., 2020. Parent, alkylated, oxygenated and nitro polycyclic aromatic hydrocarbons from raw coal chunks and clean coal combustion: emission factors, source profiles, and health risks. Sci. Total Environ. 721, 137696.

Zhang, Y., Shen, Z.X., Sun, J., Zhang, L.M., Zhang, B., Zou, H.J., Zhang, T., Ho, S.S.H., Chang, X.J., Xu, H.M., Wang, T., Cao, J.J., 2021a. Parent, alkylated, oxygenated and nitrated polycyclic aromatic hydrocarbons in PM2.5 emitted from residential biomass burning and coal combustion: a novel database of 14 heating scenarios. Environ. Pollut. 268, 115881.

Zhang, L., Luo, Z.H., Li, Y.J., Chen, Y.C., Du, W., Li, G., Cheng, H.F., Shen, G.F., Tao, S., 2021b. Optically measured black and particulate brown carbon emission factors from real-world residential combustion predominantly affected by fuel differences. Environ. Sci. Technol. 55 (1), 169–178.

Zhi, G.R., Peng, C.H., Chen, Y.J., Liu, D.Y., Sheng, G.Y., Fu, J.M., 2009. Deployment of coal briquettes and improved stoves: possibly an option for both environment and climate. Environ. Sci. Technol. 43, 5586–5591.

Zosima, A.T., Tzimou-Tsitouridou, R.D., Nikolaki, S., Zikopoulos, D., Ochsenkuhn-Petropoulou, M.T., 2016. PM10 emissions and PAHs: the importance of biomass type and combustion conditions. J. Environ. Sci. Health A 51, 341–347.