Emission characteristics for polycyclic aromatic hydrocarbons from solid fuels burned in domestic stoves in rural China

Guofeng SHEN[1,2], **Shu TAO**[1,*], **Yuanchen Chen**[1], **Yanyan Zhang**[1], **Siye Wei**[1], **Miao Xue**[2], **Bin Wang**[1], **Rong WANG**[1], **Yan LV**[1], **Wei LI**[1], **Huizhong SHEN**[1], **Ye HUANG**[1], and **Han CHEN**[1]

[1]Laboratory of Earth Surface Processes, College of Urban and Environmental Sciences, Peking University, Beijing, 100871, China

[2]Jiangsu Key Laboratory of Environmental Engineering, Jiangsu Academy of Environmental Sciences, Nanjing 210036, China

Abstract

Emission characterization of polycyclic aromatic hydrocarbons (PAHs) from residential combustion of crop residues, woody material, coal, and biomass pellets in domestic stoves in rural China are compared in term of emission factors (EFs), influencing factors, composition profiles, isomer ratios and phase distributions. The EFs of PAHs vary by two orders of magnitude among fuel types suggesting that a detailed fuel categorization is useful in the development of an emission inventory and potential in emission abatement of PAHs by replacing dirty fuels with relatively cleaner ones. The influence of fuel moisture in biomass burning is non-linear. Biofuels with very low moisture display relatively high emissions as do fuels with very high moisture. Bituminous coals and brushwood yield relatively large fractions of high molecular PAHs. The emission factor of Benzo(a)pyrene equivalent quantity for raw bituminous coal is as high as 52 mg/kg, which is 1–2 orders of magnitude higher than the other fuels. For source diagnosis, high molecular weight isomers are more informative than low molecular weight ones and multiple ratios could be used together whenever possible.

Introduction

Solid fuels are extensively used for daily cooking and heating in developing countries. Globally, annual residential consumptions of coal and biomass fuels were 2.99×10^{15} and 3.67×10^{16} Joules in 2007, of which over 93% occurred in developing countries.[1] Because of relatively low efficiencies of residential solid fuel combustion,[2–3] large quantities of incomplete combustion byproducts such as carbon monoxide, fine particulate matter (PM) and polycyclic aromatic hydrocarbons (PAHs) are emitted. It was estimated that 63% of global emissions of PAHs in 2007 were derived from use of solid fuels in homes, and in China as a whole residential solid fuel combustion contributed approximately 62% of the total.[4]

Relatively high pollution levels of PAHs have been reported in rural households in China and other developing countries, [5–7], and residential fuel combustion is the likely cause. For

example, it was reported that daily mean PAH concentration could be as high as 7500 ng/m^3 in the rural household kitchen when solid fuels were combusted.[5] PAHs, especially those with high molecular weights, are usually toxic and carcinogenic.[8–10] It was previously reported that PAHs inhalation exposure in 2003 caused 1.6% of lung cancer morbidity in Chinese population.[11] Exposure to severe indoor PAHs from the solid fuel combustion was also thought to be associated with the increased risks of neural tube defects in Shanxi, China.[12]

As typical long-range transport pollutants, PAHs are included in the Convention on Long Range Transboundary Air Pollution Protocol on Persistent Organic Pollutants.[13] To understand emission, transport, fate, source-receptor relationship, and ecological and health impacts of PAHs, source characterization is critical. According to a number of PAH emission inventories developed recently,[4, 14] uncertainties in emission factors (EFs) of PAHs (EF$_{PAHs}$) are the dominant contributor to the overall uncertainty in the emission inventory, and the diversities of stove models, fuel types, fuel properties, and even fire maintenance are key factors leading to that high uncertainty. [15–18]

The relatively small number of measurements, especially in developing countries are also a source of biases in emission inventories. In our previous studies, emissions of PAHs from the combustions of agricultural crops, wood, and coals in domestic stoves were measured,[19–23] which are important in filling the data gap in PAH emissions in China. The main objective of this study is to compile these data and to compare the EFs, composition profiles, isomer ratios, gas-particle partitioning, and size distributions of particle-bound PAHs among different fuel types. It is hoped that these efforts will lead to a better understanding of PAH emissions from the residential sources in China.

Methods

Recent PAH emission measurements for rural residential solid fuel combustion have been compiled for data analysis. The data are limited to the measurements under the same experimental conditions, i.e. fuel combustion practice, sampling methods, and analytical procedures used in our previous study, [19–23] and compared with the results reported by others.[18, 24–54] Fuels including crop residues, [19] wood, [21] coals, [20, 23] and biomass pellets[22] were tested. Ordinary biomass fuels (crop residues and woody materials) were burned in an improved brick cooking stove with a chimney. Coals were burned in a movable iron stove purchased from the local market. Pelletized biomass fuels were combusted in a modern pellet burner. The combustion experiments were conducted following the common practice in rural households. Pre-weighed fuels were inserted into the stove chamber in batches. The flue exhaust entered into the mixing chamber (about 4.5 m^3) with a built-in fan. No further dilution with clean gas was conducted in our present study which was aimed to avoid the alterations in PM mass loading and size distribution,[55] even though dilution systems are sometimes used in other studies and the dilution ratio and rate are critical factors affecting the emissions.[56–57] Measured smoke temperature and relative humidity in the sampling chamber were 20–40°C and 30–70% (TM184, Tenmars), respectively. Gaseous and particulate phase PAHs were collected using polyurethane foam plugs and quartz fiber filters, respectively, then analyzed in the laboratory with GC-MS after solvent extraction. The detailed information about the fuels, stoves, sampling and analysis can be found in the previous papers, and provided in the Supporting Information (S1).

Emission performance often varies dramatically depending on not only fuel types, but also stove designs. It would be, therefore, preferable to report emission factors for specific fuel-stove combinations. However, the stove-specific data are very limited so far in the literature.[58] Thus, in data comparison, emission factors are described as fuel-specific rather

than fuel-stove combination specific. It is realized that even dirty fuels may burn relatively cleanly in certain stoves, conversely, clean fuels may also produce relatively large pollutants under poor combustion conditions. Hence, for evaluating options for emission reduction in the future, emission factors only fuel-specific should be used with caution. These fuels are classified into nine categories: crop residue, fuel wood log, brushwood, anthracite briquette, bituminous briquette, raw anthracite, raw bituminous coal, corn straw pellet, and pine wood pellet. It is accepted that the emissions for different wood species vary greatly. In this comparative study, woody materials are classified into two categories of wood log and brushwood since these are two distinct forms of woody materials commonly found in rural households and significant differences in emission factors have been reported. [58–59] The different emissions among different species types could be partly attributed to different fuel moisture. Besides the EFs, this study collects and compiles composition profiles, some isomer ratios, gas-particle partitioning, size distribution of particle-bound PAHs, fuel moisture, and modified combustion efficiency (MCE, defined as $CO_2/(CO_2+CO)$ (molar basis)).

Fifteen PAH compounds were studied: acenaphthene (ACE), acenaphthyleme (ACY), fluorene (FLO), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benzo(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenz(a,h)anthracene (DahA), indeno(l,2,3-cd)pyrene (IcdP), and benzo(g,h,i)perylene (BghiP). The EF_{PAHs} for the total of the 15 PAHs is denoted as EF_{P15}. Naphthalene, which is also included in U.S. EPA priority PAHs, is not considered because of relatively low recovery and consequent high analytical errors, as well as low toxic effect into consideration (toxicity equivalency factor is only 0.001).[60] Although the omission would cause the change in absolute values of the EF_{PAHs} and calculated mass percents of individuals, it has negligible effects on the comparison and interpretation of influencing factors, PAH isomer ratios, and size distribution of particle-bound PAHs among different fuel types, because NAP is mainly present in gaseous phase and is not included in the selected isomer ratios.

Statistical analysis was performed using Statistica (v5.5, Statsoft). Since pollutant emission factors usually follow the log-normal distribution, [61] data are log-transformed in the analysis of variance (ANOVA) and multiple comparisons.

Results and Discussion

Difference among fuel types

The means and standard deviations of EF_{P15} for various fuels are shown in Figure 1. EFs of individuals for each fuel type are provided in **S2** in detail (Table S2 and S3). The results of ANOVA and multiple comparisons (**S3**-Table S4) suggest that these fuels can be classified into four categories of G1 (wood pellets, corn pellets, wood log, and anthracite briquette), G2 (crop residue), G3 (brushwood, bituminous briquette, and raw anthracite) and G4 (bituminous coal). EF_{P15} values vary from several mg/kg for G1 to about 200 mg/kg for G4, showing a variation of almost two orders of magnitude. The "dirtiest" fuel among all, raw bituminous coal is still extensively used in residential sector in China due to its low cost.[25, 28] It is believed that significant environmental and health benefits can be achieved by eliminating its use. On the other hand, the lowest EF_{P15} is found for the wood pellet, implying the potential of emission abatement of PAHs, as well as other incomplete combustion byproducts by promoting the use of pelletized biomass fuels. However, as mentioned above, emissions for stove-fuel combinations are more meaningful than fuel-specific only data, and therefore, comparative results based on current fuel-specific data should be used with caution in the future when evaluating options for emission reductions. In most PAH emission inventories, wood is always taken as a single fuel type [14, 61] and the

majority of EF_{PAHs} for wood reported in the literature were measured from combustion experiments using wood logs.[31, 34–42] Since the EF_{P15} for the brushwood is more than five times higher than that for the fuel wood log, and the former is extensively used in rural China, [62] the emission from the residential wood combustion might be considerably underestimated whenever brushwood is not distinguished from fuel wood.

Emissions of PAHs from residential solid fuel combustion in China have seldom been measured. Some laboratory chamber studies have been conducted to measure PAHs emitted from crop straw burning.[24, 27, 30] The results varied dramatically. For example, EF_{P15} for the wheat straw was reported at 234 mg/kg by Zhang *et al.,* (2008), [24] but in another study, [27] EF_{P15} values for the rice, corn, and wheat straws were only 3.5, 1.3 and 1.1 mg/kg, respectively. When the combustion temperature increased from 200 to 700 °C, EF_{P15} increased from 5.8 to 17 mg/kg for wheat and 2.2 to 29 mg/kg for bean straw.[30] The average EF_{P15} for crop residue measured in the chamber study was 23 mg/kg, slightly lower than 30 mg/kg in our study. For wood combustion, only one study reported EF_{P15} values for wood burned in traditional and improved stoves at 34 and 4.3–8.3 mg/kg, respectively. [29] The latter was close to that for the fuel wood log in our study. In one study, Chen *et al.,* (2004) [25] reported the EF_{P15} of 0.046 and 0.11 mg/kg for anthracite briquette and chunk anthracite, respectively, in a typical portable stove and in their another study, [26] EFs of 13 parent PAHs (without NAP, ACY and ACE) were reported to be 0.12 mg/kg for the anthracite briquette and 66–152 mg/kg for the bituminous briquette. Zhang *et al.,* (2008) [28] measured particulate phase PAHs for anthracite, bituminous and briquette coal combustion in residential stoves with the EF_{P15} of 16, 92 and 28 mg/kg, respectively. The results are generally lower than the EFs for coal in the present study. Many factors, including differences in fuel properties, stove types, air supply, and experimental methods affect the combustion and emission and subsequently lead to varied EF_{PAHs}.

For EF_{PAHs} measured outside of China, PAHs emitted from burning straw were generally measured in laboratory chamber studies, and some of these studies only quantified the particulate phase PAHs. [31–33, 43–44] The EF_{P15} ranges from 0.46 to 73 mg/kg, with a geometric mean of 9.1 mg/kg, which is much lower than 30 mg/kg for the crop residue in our study. It is not surprising to see much larger variation in EF_{PAHs} for coal, ranging from 2.0 (anthracite) to 8021 mg/kg (bituminous).[45–48] EF_{P15} for woody materials measured in other countries are mainly for wood logs burned in laboratory chambers, [31, 39, 44, 47] woodstove [18, 36, 38–41, 45–46, 49–51, 54] or fireplace. [18, 34–35, 37, 52–53] Reported EF_{P15} values for wood logs burned in laboratory chambers, wood stoves, and fireplaces range from 5.4–35, 1.5–63, and 0.32–332 mg/kg, with geometric means of 15, 8.0, and 16 mg/kg, respectively. EF_{P15} for the wood log measured in our study was 6.8 mg/kg, close to that for wood burned in woodstoves as measured abroad. Because of the significant differences in the measured EFs among countries, locally measured EFs are preferred in the development of an emission inventory and emission criterion. For woody material, EFs from combustion in wood stoves should be distinguished from those in fireplaces. Currently, there is relatively large uncertainty in the PAH emission inventory, primarily due to large variations in EFs for various activities and insufficient measurements on EFs. Extensive field measurements are needed in the future to develop reliable emission inventories.

Factors affecting EF_{PAHs}

Pollutant emissions from biomass burning are often found to be affected by fuel moisture and MCE.[63–66] However, the influence of moisture is complicated, and can be either negative [30], positive [63–64], or insignificant.[55] When data for crop residues and wood are grouped together (Figure 2A), the difference between the crop residue and wood can be partly explained by moisture. The EF_{P15} decreases as fuel moisture increases from 1.4% to

15%, and increases slightly when moisture increases from 15% to 42%. The similar result was also reported by Korenaga *et al*. [43] It is believed that low moisture biomass fuels burn fast and form an oxygen deficient atmosphere yielding high pollutant emissions, while the burning of fuel with high moisture requires extra energy to vaporize water, leading to reduced combustion temperature and efficiency, and hence increased emissions of incomplete combustion products.[52, 67] Based on the data collected in this study, the non-linear relationship can be quantified either by a piecewise function with two linear equations for low and high moisture ranges, respectively or by a binomial equation covering the entire experimental moisture range. In our study, biomass fuels (crop residues and woody materials) were burned in the same brick stove. It is interesting to see the significant impact of fuel moisture on EF_{PAHs}. The derived equations are useful in explaining how the moisture affects the emission, however, they are not suitable for predicting the emission since the fuel-stove combinations and burning conditions may differ dramatically from our combustion circumstances. Unlike moisture, the relationship between the EF_{P15} and MCE appears to be different between the crop residue and firewood, which could not be described by a single expression (Figure 2B). Both show significantly negative dependence of EF_{P15} on MCE. The overall dependence of the EF_{P15} on fuel moisture (*M*) and MCE can be quantified by a bivariate regression model: $logEF_{P15} = 0.0014 \, M^2 - 0.07 \, M - 8.08 \, MCE + 9.01$ ($R^2=0.675$). The calculated log-transformed EF_{P15} generally agreed well with the observed values (**S4**-Figure S2).

For coal, volatile matter (VM) content is often identified as one of the key factors governing emissions of various air pollutants. [25–26, 68] Relatively high emission from bituminous coal compared with anthracite can be partially explained by a large difference in VM content. Emissions of incomplete combustion products generally increase with the increase of coal VM content. However, bituminous coal can be classified into three groups of low, medium, and high volatile bituminous (LVB, MVB and HVB, respectively) coals with volatile matter contents at 14–22, 22–31, and >31%, respectively. [69] Several studies revealed that the MVB may emit relatively large quantities of incomplete combustion pollutants in comparison with the LVB and HVB.[70–72] For example, the emission of elemental carbon for the MVB coal burned in the form of honeycomb briquette was measured at 0.25 g/kg, while for the LVB and HVB coals, they were only 0.043 and 0.060 g/kg, respectively. [73] For the raw coal chunks assessed in this study, a peak EF_{P15} of 1100 mg/kg is also found for MVB from Shanxi with VM content of about 22%. EF_{P15} values of most coals with VM content either lower or higher than 22% are significantly lower ((**S5**-Figure S3). A notable exception is the bituminous chunk used in rural Beijing with VM of 32% having the EF_{P15} of 1435 mg/kg. It is believed that, in addition to the VM content, other factors like ash content and coal calorific values influence the combustion and emission process significantly, leading to orders of magnitude variation in pollutant emission factors. A workable model for predicting EF_{P15} for coals will not be ready until all major factors are identified and quantified based on a large number of measurements on the EFs, coal properties, and combustion conditions.

Composition profiles and potential health impact

PAH composition profiles are important to assess health effects since some high molecular weight PAHs, like BaP and DahA, are often carcinogenic.[8–10, 74] The normalized composition profiles in emissions from different fuel types are shown in the Figure S4. In general, the overall emission profiles are similar to one another with the dominance of PHE, ACY, FLA, and PYR. Such profiles are similar to those observed in indoor air in rural Chinese households that use solid fuels for cooking and heating.[5] Surveys on ambient air PAHs in rural China found the predominance of these compounds,[75–76] confirming that residential solid fuel combustion is one of the most important sources of PAHs in China.[4, 14]

Still, some important differences among the fuels can be observed. For example, combustion of anthracite chunk coal releases relatively large amounts of FLO and ACE (22 and 28%). Emissions of FLA and PYR from biomass fuel burning (12–17 and 10–15%, respectively) are higher than those from coal combustion (4.4–8.9 and 3.5–7.2%, respectively). The squared Eulerian-distance based cluster analysis (**S7**) indicated that these fuels could be classified into two groups: A) brushwood, bituminous chunk, and bituminous briquette and B) all others.

With respect to the impact on human health, the compounds of most concern are carcinogens with relatively high molecular weights.[74, 77] The difference in emission toxicity among the fuels is evaluated by calculating mass percentage of the eight carcinogenic PAHs with molecular weight larger than 228 (F_{228}) from BaA to BghiP.[4] On average, these eight compounds account for 16% of the total PAHs. It appears that F_{228} values for bituminous briquettes (48%), raw bituminous chunk (31%), and brushwood (26%) are significantly higher ($p < 0.05$) than those for the other fuels (6.2–19%), which distinguished them in the squared Eulerian-distance based cluster analysis (**S8**). It is noted that the EF_{P15} of these three fuels (G3 or G4 in Figure 1) are also significantly higher than those of others. The combination of high EF_{P15} and relatively high F_{228} make the three fuels much more toxic than the others. Such a combined effect can be quantified by calculating BaP equivalent EFs (EF_{BaPeq}), defined as the emission of BaP equivalent quantity[77] per unit fuel mass. It is interesting to see that the calculated EF_{BaPeq} (**S9**) vary by three orders of magnitude for the fuels studied. The highest EF_{BaPeq} is 52 mg/kg for the raw bituminous chunks, followed by 41 mg/kg for the bituminous briquettes. Although the brushwood ranked the third, the mean EF_{BaPeq} is only 3.1 mg/kg, which is more than one order magnitude less toxic than the bituminous coal. For the other fuels studied, mean EF_{BaPeq} values range from 0.089 (wood pellets) to 0.90 (crop residues) mg/kg. Not only the emission amount of total PAHs, but also the contributions of carcinogenic compounds should be taken into consideration in the evaluation of environmental and health impacts of various fuels. It will be interesting to directly compare the toxicities of the emissions from various fuel combustions using either *in vitro* screening tests or *in vivo* animal tests, and to assess health risks of indoor exposure to emissions from various sorts of fuel combustion.

Isomer ratios as source signature

PAH isomer ratios are often used as diagnostic signatures for source apportionment by assuming that the paired isomers are diluted to a similar extent during transport, and the ratios remain constant *en route* from sources to receptors.[78–79] For source diagnostics using PAH isomer ratios, significantly different signatures among source types and consistent signatures within source types are required. Also, accurate and robust source signatures are critical. ANT/(ANT+PHE), FLA/(FLA+PYR), BaA/(BaA+CHR), IcdP/(IcdP+BghiP), BbF/(BbF+BkF), and BaP/(BaP+BghiP) are commonly used isomer ratios.[78–81] For example, based on the measured ratios of FLA/(FLA+PYR) and IcdP/(IcdP+BghiP), Liu *et al.* (2007) found that the dominant source of ambient PAHs in Northern China Plain is solid fuel combustion.[75] Using similar methods, motor vehicle emissions were found to be a major source of PAHs in the Chesapeake Bay Region of the USA.[80] Based on the EFs collected in this study, these isomer ratios are calculated for various solid fuels (Table 1), to evaluate the potential use of these ratios for source identification. Significant differences among individual fuels are found for all ratios according to the results of ANOVA ($p < 0.05$), except for FLA/(FLA+PYR) ($p = 0.11$). The results of multiple comparisons among different fuels for each isomer ratio are listed in the supporting material (**S10**).

An ANT/(ANT+PHE) ratio of 0.1 is often applied to distinguish between petrogenic (< 0.1) and pyrogenic (> 0.1) sources.[78–79] The ANT/(ANT+PHE) ratios for most fuels in the

present study are higher than 0.1, supporting the 0.1 criteria, although there are a few exception in individual measurements for briquette coals and wood pellets (**S10**). Among the individual fuels, ANT/(ANT+PHE) for the coal and the brushwood are generally higher than that for the others. The high value for the bituminous chunk (0.24±0.08) if validated in future may be used specifically for the identification of this source.

It is generally accepted that the ratio of FLA/(FLA+PYR) is above 0.4 in emissions from coal and biomass burning.[78–79] This is well supported by the calculated FLA/(FLA+PYR) in our study, varying narrowly from 0.52±0.02 (brushwood) to 0.56±0.02 (anthracite chunk). The three insignificant groups of FLA/(FLA+PYR) overlap considerably, suggesting that this ratio is not specific among the studied biomass and coal fuels.

The BaA/(BaA+CHR) ratio varies widely from 0.32±0.07 (bituminous briquettes) to 0.56±0.04 (brushwood) and can be divided into four well-defined insignificant groups. Unfortunately, the four groups are not governed by fuel type, making it difficult to use as a potential source indicator. The ratio of 0.32 for the bituminous briquettes is even lower than 0.35, a commonly suggested criterion for distinguishing coal combustion from other sources.[78–79]

An IcdP/(IcdP+BghiP) ratio of 0.5 is usually recommended as a criterion separating coal (> 0.5) and biomass (< 0.5) burning,[78–79] which, however, is not supported by the ratios calculated in this study. The IcdP/(IcdP+BghiP) ratios are as low as 0.28±0.05 and 0.29±0.04 for the bituminous briquette and the raw anthracite, respectively. In fact, very low IcdP/(IcdP+BghiP) ratios for bituminous briquette have been reported in the literature.[25, 28] Moreover, the ratios of the two pellet fuels found in our study are also lower than 0.5.

BbF/(BbF+BkF) ratios of 0.48 and 0.79 were suggested as criteria for distinguishing emissions from wood and coal combustion, respectively.[80] However, the calculated BbF/(BbF+BkF) ratios in this study are significantly higher than 0.48 for the biomass fuels, and significantly lower than 0.79 for the coals. Moreover, the ratios for bituminous coals and wood pellets are not significantly different from 0.57, a reference value for automobile emission.[80]

The BaP/(BaP+BghiP) ratio has been used to distinguish traffic sources (> 0.38) from non-traffic contributions (< 0.38).[79] However, among the tested fuels, the only fuel with a ratio less than 0.38 is the bituminous briquette (0.37±0.03), while the others are way above this value (0.47 – 0.69). Hence, the application of this ratio of 0.38 to distinguish traffic and non-traffic sources is inadvisable.

In general, little overlap among insignificant groups can be found for the ratios of high molecular weight isomers, which are more specific in source diagnosis. For the specific purpose of distinguishing certain sources, combinations of more than one ratio can be used to provide a multi-dimensional basis for diagnoses of sources. For example, significant differences in both BaA/(BaA+CHR) and BaP/(BaP+BghiP) may help to identify biomass pellets made from corn straw or woody material, and also distinguish between emissions from fuel wood log and brushwood combustions. Similarly, when coal briquettes are burned, the ratios of BaA/(BaA+CHR) (0.47±0.08 *vs.* 0.32±0.07), IcdP/(IcdP+BghiP) (0.54±0.20 *vs.* 0.28±0.05), and BbF/(BbF+BkF) (0.69±0.09 *vs.* 0.37±0.03) can provide information to reveal if the briquette is made of anthracite or bituminous coal. It is noted that the one-to-one correlation among these isomer ratios between each other varies for different fuels (**S11**). Thus, if multiple isomer ratios were used in source apportionment, co-linearity should be taken into consideration.

Although isomer ratios have been extensively used for PAH source diagnosis, the ratios are subject to various errors. For example, existing residential stoves vary widely in size, configuration, and operational performance.[46, 58, 82] Types and properties of biomass fuel or coal change almost infinitely.[73, 83–84] Different operators who manage the fire during the measurement can behave very differently.[15, 85–86] The sampling and analysis procedures are also subjected to errors. Moreover, subtle differences in physicochemical properties between the paired PAH isomers may cause change in these ratios during the transport.[87–88] Therefore, the isomer ratios should be used carefully in evaluating sources. Simultaneous application of more than one ratio may help to reduce the errors. If possible, changes in isomer ratios from sources to receptors should be taken into consideration [88] and a range of distributions, rather than single values, of isomer ratios are preferred in source apportionment calculation.

With limited data available, we can only conclude that there is potential for using these ratios for source apportionment among coals and biomass fuels. More data, especially field measurements, should be collected to reach robust conclusions. Since PAH isomer ratios vary widely under different combustion operations, not only fuel type, but also different combustion conditions should be taken into the consideration. The ratios should also be evaluated together with the data from other sources such as traffic emission. In addition, measurements on other PAHs not just the U.S. EPA priority PAHs, may add more detailed information to the source characterization. For instance, the use of alkyl-PAHs and oxy-PAHs can also be exploited. It has been reported that emissions of some oxy-PAHs, like fluorenone and benzanthrone from both biomass and coal combustions can be at the same level as parent PAHs.[89–91]

Phase partition and size distribution

Atmospheric lifetime and long range transport potential of PAHs depend on their partition between gaseous and particulate phases, degradation, and dry/wet depositions.[92–94] For data used in this study, the mass fraction of particulate phase PAHs is positively correlated ($p <$ 0.05) with the EF of co-emitted PM (Figure 3A), indicating that under higher PM emissions, there are higher percents of PAHs bound in PM. For the crop residues, which have relatively high EF of PM (7.0±4.3 g/kg) in comparison with the other fuels, more than 70% of total PAHs are in the particulate phase, while in the combustion of the anthracite chunk, gaseous PAHs make up to 92±5% of the total PAHs (**S12**). For the other fuels, the fraction of particulate phase PAHs is approximately 43±7%.

In emissions from residential solid fuel combustion, particle-bound PAHs are supposed to be largely present in the fine PM fraction. [19–20, 26, 95] The results from our study show that approximately 80% of particle-bound PAHs are associated with fine $PM_{2.5}$ (PM with diameter less than 2.5 Rm), and over 65% in $PM_{1.0}$ (PM with diameter less than 1.0 Rm) (**S13**). In addition to the impact on lifetime, gas-particle partition and size distribution of PAHs significantly affect their detrimental human health impacts, since fine and ultrafine particles are able to penetrate deeper into the lung. It is interesting to see that the mass fractions of very fine PM (like $PM_{0.4}$ in this study,) bound PAHs to total particle-bound PAHs are negatively correlated with the mass percent of particle-bound PAHs to total PAHs (Figure 3B). This suggests that some fuels, although having a low EF_{PM} and a relatively low fraction of PAHs in PM, still may have a relatively high health impact because of a larger fraction of PAHs in very fine particles.

Implication and limitation

Large overall uncertainties in PAH emission inventories originate mainly from the uncertainties in EFs. In addition to the fact that EF_{PAHs} are affected by many factors like the

design and condition of combustion facilities and the manner of operation, a wide variety of detailed fuel types is also one of the most important reasons leading to relatively high variations. Residential biomass fuels are often classified into only two categories of crop residues and wood in most emission inventories. However in reality, almost anything combustible is a potential fuel in rural households. Based on the above discussions, it is recommended that solid fuels should be separated into narrow groups in a PAH emission inventory in the future. Dealing with brushwood and wood log individually will be necessary to distinguish their significantly different

In addition to the implication on the development of an emission inventory, detailed information on emission variances among various solid fuels can help us to better understand the effects of emissions on air quality and subsequently health impacts, because the emission is closely related to air quality. For example, a previous study[5] on the air quality of a rural household in Northern China reported that when the wood logs were burned, the concentrations of total 15 PAHs in the kitchen were 2685–6240 ng/m^3, whereas when the corn straw was burned, the concentrations of total 15 PAHs were as high as 5208–10084 ng/m^3. In a study conducted in a Swedish residential area, it was found that daily BaP concentration in the household having residential wood combustion (0.63 ng/m^3) was significantly higher than that without wood burning (0.16 ng/m^3).[96] There should be interest in measuring and comparing indoor and outdoor PAH concentrations during the combustion of different solid fuels, and compare with those using relatively cleaner fuels, like natural gas (NG) and liquefied petroleum gas (LPG). Regarding this, more field measurements are urgently required in the future. Air modeling studies focusing on dynamic change of indoor and outdoor PAH concentrations under variable fuels and emission scenarios are also of interest.

In China, the majority of PAHs are from the residential sector, so without effective control of residential sources, it will be difficult to reduce the total emissions of PAHs. The most effective approach may be to encourage use of alternative fuels or clean cooking stoves. In most rural areas, raw chunk coals are still commonly burned. Thus, an effective but not expensive way is to promote the use of coal briquettes, and deploy high efficiency stoves. Bituminous coal should be banned in household use. It is expected that biomass fuels will continue to be an important energy source in rural areas of developing countries for years to come because of easy access and very low cost. Ordinary biomass fuels should be replaced with biogas or pelletized biomass. In fact, during the past thirty years, household coal consumption has decreased continuously due to the popularity of LPG and NG and promotion of centralized heating systems.[97–98] It is estimated that residential coal and NG consumptions in China in 2020 will be 13000 and 79000 ktoe (thousand tonnes of oil equivalent),[99] which would be 0.26 and 5.3 times of those consumed in 2009, respectively.[100] Use of these alternatives depends very much on economic development and improvement of the living standard of rural residents.[101] The government can surely help to promote these desirable changes by providing economic incentives and technical assistance.

In the present study, emission characteristics of PAHs for a variety of solid fuels measured in residential stoves in rural China are compared. It should be noted that the results are not readily generalized because the analysis is limited to data from our previous measurements, and variations in the processes of combustion experiments, sampling procedure and laboratory analysis are all subject to errors. The study provides useful information for understanding the emission processes and improving emission inventories in the future. Since factors including fuel properties, stove types, and fire management procedures, vary widely among different areas, those locally measured EFs for fuel-stove combinations in actual use are preferable for the development of high quality emission inventories.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

References

1. Wang R, Tao S, Ciais P, Shen H, Huang Y, Chen H, Shen G, Wang B, Li W, Zhang Y, Lu Y, Zhu D, Chen Y, Liu X, Wang W, Wang X, Liu W, Li B, Piao S. High resolution mapping of combustion processes and implications for CO_2 emissions. Atmos Chem Phys. 2013; 13:5189–5203.

2. Zhang J, Smith KR. Household air pollution from coal and biomass fuels in China: Measurements, health impacts, and interventions. Environ Health Perspect. 2007; 115:848–855. [PubMed: 17589590]

3. Adkins E, Tyler E, Wang J, Siriri D, Modi V. Field testing and survey evaluation of household biomass cookstoves in rural sub-Saharan Africa. Energy Sustain Develop. 2010; 14:172–185.

4. Shen HZ, Huang Y, Wang R, Zhu D, Li W, Shen GF, Wang B, Zhang Y, Chen Y, Lu Y, Chen H, Li T, Sun K, Li B, Liu W, Liu J, Tao S. Global atmospheric emissions of polycyclic aromatic hydrocarbons from 1960 to 2008 and future predictions. Environ Sci Technol. 2013; 47:6415–6424. [PubMed: 23659377]

5. 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 SLM, Tao S. Occurrence and exposure to polycyclic aromatic hydrocarbons and their derivatives in a rural Chinese home through biomass fuelled cooking. Environ Pollut. 2012; 169:160–166. [PubMed: 22209516]

6. Li Z, Sjodin A, Romanoff L, Horton K, Fitzgerald C, Eppler A, Aguilar-Villalobos M, Naeher L. Evaluation of exposure reduction to indoor air pollution in stove intervention projects in Peru by urinary biomonitoring of polycyclic aromatic hydrocarbon metabolites. Environ International. 2011; 37(3):1157–1163.

7. Masih J, Masih A, Kulshrestha A, Singhvi R, Taneja A. Characteristics of polycyclic aromatic hydrocarbons in indoor and outdoor atmosphere in the North central part of India. J Hazar Mater. 2010; 177:190–198.

8. Mastral A, Callen M. A review on polycyclic aromatic hydrocarbon (PAH) emissions from energy generation. Environ Sci Technol. 2000; 34:3051–3057.

9. Ravindra K, Sokhi R, Grieken R. Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. Atmos Environ. 2008; 42(13):2895–2921.

10. Jia Y, Stone D, Wang W, Schrlau J, Tao S, Simonich S. Estimated reduction in cancer risk due to PAH exposure if source control measures during the 2008 Beijing Olympics were sustained. Environ Health Perspect. 2011; 119:815–820. [PubMed: 21632310]

11. Zhang Y, Tao S, Shen H, Ma J. Inhalation exposure to ambient polycyclic aromatic hydrocarbons and lung cancer risk of Chinese population. Proc Natl Acad Sci U S A. 2009; 106:21063–21067. [PubMed: 19995969]

12. Ren A, Qiu X, Jin L, Ma J, Li Z, Zhang L, Zhu H, Finnell R, Zhu T. Association of selected persistent organic pollutants in the placenta with the risk of neural tube defects. Proc Natl Acad Sci U S A. 2011; 108:12770–12775. [PubMed: 21768370]

13. United Nations Economic Commission for Europe. [Accessed Jan, 2013] Convention on Long-range Transboundary Air Pollution. http://www.unece.org/env/lrtap

14. Zhang Y, Tao S. Global atmospheric emission inventory of polycyclic aromatic hydrocarbons (PAHs) for 2004. Atmos Environ. 2009; 43:812–819.

15. Chen Y, Roden C, Bond T. Characterizing biofuel combustion with patterns of real-time emission data (PaRTED). Environ Sci Technol. 2012; 46:6110–6117. [PubMed: 22533493]

16. Shen GF, Yang YF, Wang W, Tao S, Zhu C, Min Y, Xue M, Ding J, Wang B, Wang R, Shen H, Li W, Wang X, Russell AG. Emission factors of particulate matter and elemental carbon for crop residues and coals burned in typical household stoves in China. Environ Sci Technol. 2010; 44:7157–7162. [PubMed: 20735038]

17. Jetter J, Zhao Y, Smith K, Khan B, Yelverton T, DeCarlo P, Hays M. Pollutant emissions and energy efficiency under controlled conditions for household biomass cookstoves and implications for Metric useful in setting international test standards. Environ Sci Technol. 2012; 46:10827–10834. [PubMed: 22924525]

18. McDonald JD, Zielinska B, Fujita EM, Sagebiel JC, Chow JC, Watson JG. Fine particle and gaseous emission rates from residential wood combustion. Environ Sci Technol. 2000; 34:2080–2091.

19. Shen G, Wang W, Yang Y, Ding J, Xue M, Min Y, Zhu C, Shen H, Li W, Wang B, Wang R, Wang X, Tao S, Russell AG. Emissions of PAHs from indoor crop residue burning in a typical rural stove: emission factors, size distributions and gas-particle partitioning. Environ Sci Technol. 2011; 45:1206–1212. [PubMed: 21247097]

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

21. Shen G, Tao S, Wei S, Zhang Y, Wang R, Wang B, Li W, Shen H, Huang Y, Chen Y, Chen H, Yang Y, Wang W, Wang X, Liu W, Simonich S. Emissions of parent, nitro, and oxygenated polycyclic aromatic hydrocarbons form residential wood combustion in rural China. Environ Sci Technol. 2012; 46:8123–8130. [PubMed: 22765266]

22. Shen G, Tao S, Wei S, Zhang Y, Wang R, Wang B, Li W, Shen H, Huang Y, Yang Y, Wang W, Wei W, Wang X, Liu W, Wang X, Simonich S. Reductions in emissions of carbonaceous particulate matter and polycyclic aromatic hydrocarbons from combustion of biomass pellets in comparison with raw fuel burning. Environ Sci Technol. 2012; 46:6409–6416. [PubMed: 22568759]

23. Liu W, Dou H, Wei Z, Chang B, Qiu W, Liu Y, Tao S. Emission characteristics of polycyclic aromatic hydrocarbons from combustion of different residential coals in North China. Sci Total Environ. 2009; 407:1436–1446. [PubMed: 19036409]

24. Zhang Y, Dou H, Chang B, Wei Z, Qiu W, Liu S, Liu W, Tao S. Emission of polycyclic aromatic hydrocarbons form indoor straw burning and emission inventory updating in China. Ann N Y Acad Sci. 2008; 1140:218–227. [PubMed: 18991920]

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

26. Chen Y, Sheng G, Bi X, Feng Y, Mai B, Fu J. Emission factors for carbonaceous particles and polycyclic aromatic hydrocarbons from residential coal combustion in China. Environ Sci Technol. 2005; 39:1861–1867. [PubMed: 15819248]

27. Zhang H, Hu D, Chen J, Ye X, Wang S, Hao J, Wang L, Zhang R, An Z. Particle size distribution and polycyclic aromatic hydrocarbons emissions from agricultural crop residue burning. Environ Sci Technol. 2011; 45:5477–5482. [PubMed: 21615081]

28. Zhang Y, Schauer J, Zhang Y, Zeng L, Wei Y, Liu Y, Shao M. Characteristics of particulate carbon emissions from real-world Chinese coal combustion. Environ Sci Technol. 2008; 42:5068–5073. [PubMed: 18754349]

29. Wang H, Zhuang Y, Hao Z, Cao M, Zhong J, Wang X, Kim Oanh N. Polycyclic aromatic hydrocarbons from rural household biomass burning in a typical Chinese village. Science in China Series D: Earth Sciences. 2008; 51:1013–1020.

30. Lu H, Zhu L, Zhu N. Polycyclic aromatic hydrocarbon emission from straw burning and the influence of combustion parameters. Atmos Environ. 2009; 43:978–983.

31. Jenkins B, Jones A, Turn S, Williams R. Emission factors for polycyclic aromatic hydrocarbons from biomass burning. Environ Sci Technol. 1996; 30:2462–2469.

32. Dhammapala R, Claiborn C, Jimenez J, Corkill J, Gullett B, Simpson C, Paulsen M. Emission factors of PAHs, methoxyphenols, levoglucosan, elemental carbon and organic carbon from simulated wheat and kentucky bluegrass stubble burns. Atmos Environ. 2007; 41:2660–2669.

33. Hays M, Fine P, Geron C, Kleeman M, Gullett B. Open burning of agricultural biomass: physical and chemical properties of particle-phase emissions. Atmos Environ. 2005; 39:6747–6764.

34. Fine PM, Cass GR, Simoneit BRT. Chemical characterization of fine particle emissions from fireplace combustion of woods grown in the Northeastern United States. Environ Sci Technol. 2001; 35:2665–2675. [PubMed: 11452590]

35. Fine PM, Cass GR, Simoneit BRT. Chemical characterization of fine particle emissions from fireplace combustion of woods grown in the Southern United States. Environ Sci Technol. 2002; 36:1442–1451. [PubMed: 11999049]

36. Fine PM, Cass GR, Simoneit BRT. Chemical characterization of fine particle emissions from wood stove combustion of prevalent United States tree species. Environ Eng Sci. 2004; 21:705–721.

37. Fine PM, Cass GR, Simoneit BRT. Chemical characterization of fine particle emissions from fireplace combustion of wood types grown in the Midwestern and western United States. Environ Eng Sci. 2004; 21:387–409.

38. Gullett B, Touati A, Hays M. PCDD/F, PCB, HxCBz, PAH and PM emission factors for fireplace and woodstove combustion in the San Francisco Bay region. Environ Sci Technol. 2003; 37:1758–1765. [PubMed: 12775046]

39. Hays M, Geron C, Linna K, Smith N, Schauer J. Speciation of gas--phase and fine particle emissions from burning of foliar fuels. Environ Sci Technol. 2002; 36:2281–2295. [PubMed: 12075778]

40. Hays M, Smith N, Kinsey J, Dong Y, Kariher P. Polycyclic aromatic hydrocarbon size distributions in aerosols from appliances of residential wood combustion as determined by direct thermal desorption-GC/MS. Aerosol Science. 2003; 34:1061–1084.

41. Hedberg E, Kristensson A, Ohlsson M, Johansson C, Johansson P, Swietlicki E, Vesely V, Wideqvist U, Westerholm R. Chemical and physical characterization of emissions from birch wood combustion in a wood stove. Atmos Environ. 2002; 36:4823–4837.

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

43. Korenaga T, Liu X, Huang Z. The influence of moisture content on polycyclic aromatic hydrocarbons emission during rice straw burning. Chemosphere. 2001; 3:117–122.

44. Keshtkar H, Ashbaugh L. Size distribution of polycyclic aromatic hydrocarbon particulate emission factors from agricultural burning. Atmos Environ. 2007; 41:2729–2739.

45. Kim Oanh N, Reutergardh L, Dung N. Emission of polycyclic aromatic hydrocarbons and particulate matter form domestic combustion of selected fuels. Environ Sci Technol. 1999; 33:2703–2709.

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

47. Lee R, Coleman P, Jones J, Jones K, Lohmann R. Emission factors and importance of PCDD/Fs, PCBs, PCNs, PAHs and PM10 from the domestic burning of coal and wood in the U.K. Environ Sci Technol. 2005; 39:1436–1447. [PubMed: 15819195]

48. Levendis Y, Atal A, Carlson J, Dunayevskiy Y, Vouros P. Comparative study on combustion and emissions of waste tire crumb and pulverized coal. Environ Sci Technol. 1996; 30:2742–2754.

49. Kim Oanh N, Nghiem L, Phyu Y. Emission of polycyclic aromatic hydrocarbons, toxicity and mutagenicity from domestic cooking using sawdust briquettes, wood and kerosene. Environ Sci Technol. 2002; 36:833–839. [PubMed: 11918004]

50. Lamberg H, Nuutinen K, Tissari J, Ruusunen J, Yli-Pirila P, Sippula O, Tapanainen M, Jalava P, Makkonen U, Teinila K, Saarnio K, Hillamo R, Hirvonen M, Jokiniemi J. Physicochemical characterization of fine particles from small--scale wood combustion. Atmos Environ. 2011; 45:7635–7643.

51. Pettersson E, Boman C, Westerholm R, Bostrom D, Nordin A. Stover performance and emission characteristics in residential wood log and pellet combustion. Part 2: wood stove. Energy fuels. 2011; 25:315–323.

52. Rogge W, Hildemann L, Mazurek M, Cass G, Simoneit B. Sources of fine organic aeroosl. 9. pine, oak and synthetic log combustion in residential fireplaces. Environ Sci Technol. 1998; 32:13–22.

53. Schauer J, Kleeman M, Cass G, Simoneit B. Measurement of emissiosn from air pollution sources. 3. C1–C29 organic compounds from fireplace combustion of wood. Environ Sci Technol. 2001; 35:1716–1728. [PubMed: 11355184]

54. Tissari J, Hytönen K, Lyyränen J, Jokiniemi J. A novel field measurement method for determining fine particle and gas emissions from residential wood combustion. Atmos Environ. 2007; 41:8330–8344.

55. Roden C, Bond T, Conway S, Pinel A. Emission factors and real-time optical properties of particles emitted from traditional wood burning cookstoves. Environ Sci Technol. 2006; 40:6750–6757. [PubMed: 17144306]

56. Hildemann L, Cass G, Markowski G. A dilution stack sampler for collection of organic aerosol emissions: design, characterization and field tests. Aerosol Sci Technol. 1989; 10(1):193–204.

57. Lipsky E, Robinson A. Design and evaluation of a portable dilution sampling system for measuring fine particle emissions from combustion systems. Aerosol Sci Technol. 2005; 39(6):542–553.

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

59. Shen G, Wei S, Wei W, Zhang Y, Min Y, Wang B, Wang R, Li W, Shen H, Huang Y, Yang Y, Wang W, Wang X, Wang X, Tao S. Emission factors, size distributions and emission inventories of carbonaceous particulate matter from residential wood combustion in rural China. Environ Sci Technol. 2012; 46:4207–4214. [PubMed: 22380753]

60. Mi H, Lee W, Tsai P, Chen C. A comparison on the emission of polycyclic aromatic hydrocarbons and their corresponding carcinogenic potencies from a vehicle engine using leaded and lead-free gasoline. Environ Health Perspect. 2001; 109(12):1285–1290. [PubMed: 11748037]

61. Xu S, Liu W, Tao S. Emission of polycyclic aromatic hydrocarbons in China. Environ Sci Technol. 2006; 40:702–708. [PubMed: 16509306]

62. Edwards R, Smith K, Zhang J, Ma Y. Implications of changes in household stoves and fuel use in China. Energy policy. 2004; 32:395–411.

63. Chomanee C, Tekasakul S, Tekasakul P, Furuuchi M, Otani Y. Effects of moisture content and burning period on concentration of smoke particles and particle-bound polycyclic aromatic hydrocarbons from rubber wood combustion. Aerosol Air Qual Res. 2009; 9:404–411.

64. Bignal KL, Langridge S, Zhou JL. Release of polycyclic aromatic hydrocarbons, carbon monoxide and particulate matter form biomass combustion in a wood-fired boiler under varying boiler conditions. Atmos Environ. 2008; 42:8863–8871.

65. Dhammapala R, Claiborn C, Corkill J, Gullett B. Particulate emissions from wheat and Kentucky bluegrass stubble burning in eastern Washington and northern Idaho. Atmos Environ. 2006; 40:1007–1015.

66. Grandesso E, Gullet B, Touati A, Tabor D. Effect of moisture charge size and chlorine concentration on PCDD/F emissions from simulated open burning of forest biomass. Environ Sci Technol. 2011; 45:3887–3894. [PubMed: 21469704]

67. Simoneit B. Biomass burning-a review of organic tracers for smoke from incomplete combustion. Appl Geochem. 2002; 17:129–162.

68. Bond TC, Streets DG, Yarber KF, Nelson SM, Woo J, Klimont Z. A technology-based global inventory of black and organic carbon emissions from combustion. J Geophys Res. 2004; 109:D14203.10.1029/2003JD003697

69. American Society for Testing and Materials. Standard classification of coals by rank. p. D388-12.

70. Zhi G, Chen Y, Feng Y, Xiong S, Li J, Zhang G, Sheng G, Fu J. Emission characteristics of carbonaceous particles from various residential coal-stoves in China. Environ Sci Technol. 2008; 42:3310–3315. [PubMed: 18522111]

71. Radke M, Schaffer R, Leythaeuser D, Teichmuller M. Composition of soluble organic matter in coals: relation to rank and liptinite fluorescence. Geochim Cosmoch Acta. 1980; 44:1787–1800.

72. Oros D, Simoneit B. Identification and emission rates of molecular tracers in coal smoke particulate matter. Fuel. 2000; 79:515–536.

73. Chen Y, Zhi G, Feng Y, Liu D, Zhang G, Li J, Sheng G, Fu J. Measurements of black and organic carbon emission factors for household coal combustion in China: implication for emission reduction. Environ Sci Technol. 2009; 43:9495–9500. [PubMed: 20000546]

74. Boström C, Gerde P, Hanberg A, Jernström B, Johansson C, Kyrklund T, Rannug A, Törnqvist M, Victorin K, Westerholm R. Cancer risk assessment, indicators, and guidelines for polycyclic aromatic hydrocarbons in the ambient air. Environ Health Perspect. 2002; 110(3):451–488. [PubMed: 12060843]

75. Liu S, Tao S, Liu W, Liu Y, Dou H, Zhao J, Wang L, Wang J, Tian Z, Gao Y. Atmospheric polycyclic aromatic hydrocarbons in north China: a winter-time study. Environ Sci Technol. 2007; 41:8256–8261. [PubMed: 18200848]

76. Wang W, Simonich S, Giri B, Chang Y, Zhang Y, Jia Y, Tao S, Wang R, Wang B, Li W, Cao J, Lu X. Atmospheric concentrations and air-soil gas exchange of polycyclic aromatic hydrocarbons (PAHs) in remote, rural village and urban areas of Beijing-Tianjin region, North China. Sci Total Environ. 2011; 409(15):2942–2950. [PubMed: 21669328]

77. Nisbet I, LaGoy P. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). Regul Toxicol Pharm. 1992; 16:290–300.

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

79. Katsoyiannis A, Sweetman A, Jones K. PAH molecular disgnostic ratios applied to atmospheric sources: a critical evaluation using two decades of source inventory and air concentration data from the UK. Environ Sci Technol. 2011; 45:8897–8906. [PubMed: 21859122]

80. Dickhut R, Canuel E, Gustafson K, Liu L, Arzayus K, Walker S, Edgecombe G, Gaylor M, MacDonald E. Automotive sources of carcinogenic polycyclic aromatic hydrocarbons associated with particulate matter in the Chesapeake Bay Region. Environ Sci Technol. 2000; 34:4635–4640.

81. Zuo Q, Duan Y, Yang Y, Wang X, Tao S. Source apportionment of polycyclic aromatic hydrocarbons in surface soil in Tianjin, China. Environ Pollut. 2007; 147:303–310. [PubMed: 16828945]

82. Venkataraman C, Rao GM. Emission factors of carbon monoxide and size resolved aerosols from biofuel combustion. Environ Sci Technol. 2001; 35:2100–2107. [PubMed: 11393993]

83. Demirbas A. Combustion characteristics of different biomass fuels. Progress Energy Combust Sci. 2004; 30:219–230.

84. Jenkins B, Baxter L, Miles T Jr, Miles T. Combustion properties of biomass. Fuel Process Technol. 1998; 54:17–46.

85. Johansson M, Edwards R, Frenk C, Masera O. In-field greenhouse gas emissions from cookstoves in rural Mexian households. Atmos Environ. 2008; 42(6):1206–1222.

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

87. Tobiszewski M, Namie nik J. PAH diagnostic ratios for the identification of pollution emission sources. Environ Pollut. 2012; 162:110–119. [PubMed: 22243855]

88. Zhang X, Tao S, Liu W, Yang Y, Zuo Q, Liu S. Source diagnostic of polycyclic aromatic hydrocarbons based on species ratios: A multimedia approach. Environ Sci Technol. 2005; 39:9109–9114. [PubMed: 16382931]

89. Shen G, Tao S, Wang W, Yang Y, Ding J, Xue M, Min Y, Zhu C, Shen H, Li W, Wang B, Wang R, Wang W, Wang X, Russell A. Emissions of Oxygenated Polycyclic Aromatic Hydrocarbons from indoor solid fuel combustion. Environ Sci Technol. 2011; 45:3459–3465. [PubMed: 21375317]

90. Fitzpatrick EM, Ross AB, Bates J, Andrews G, Jones JM, Phylaktou H, Pourkashanian M, Williams A. Emission of oxygenated species from the combustion of pine wood and its relation to soot formation. Process Saf Environ Protect. 2007; 85:430–440.

91. Walgraeve C, Demessere K, Dewulf J, Zimmermann R, van Langenhove H. Oxygenated polycyclic aromatic hydrocarbons in atmospheric particulate matter: Molecular characterization and occurrence. Atmos Environ. 2010; 44:1831–1846.

92. Halsall C, Sweetman A, Barrie L, Jones K. Modelling the behaviors of PAHs during atmospheric transport from the UK to the Arctic. Atmos Environ. 2001; 35:255–267.

93. Lang C, Tao S, Zhang G, Fu J, Simonich S. Outflow of polycyclic aromatic hydrocarbons from Guangdong, Southern China. Environ Sci Technol. 2007; 41:8370–8375. [PubMed: 18200865]

94. Zhang Y, Tao S, Ma J, Simonich S. Transpacific transport of benzo[a]pyrene emitted from Asia. Atmos Chem Phys. 2011; 11:11993–12006.

95. Shen G, Wei S, Zhang Y, Wang B, Wang R, Shen H, Li W, Huang Y, Chen Y, Chen H, Tao S. Emission and size distribution of particle-bound polycyclic aromatic hydrocarbons from residential wood combustion in rural China. Biomass Bioenergy. 2013; 55:141–147.

96. Gustafson R, Östman C, Sallsten G. Indoor levels of polycyclic aromatic hydrocarbons in homes with or without wood burning for heating. Environ Sci Technol. 2008; 42:5074–5080. [PubMed: 18754350]

97. National Bureau of Statistics of China. China Statistical Yearbook 2012. China Statistics Press; Beijing: 2012. http://www.stats.gov.cn/tjsj/ndsj/2012/indexch.htm [Accessed Jan. 16th, 2013]

98. You C, Xu X. Coal combustion and its pollution control in China. Energy. 2010; 35:4467–4472.

99. Gerard Adams F, Shachmurove Y. Modelling and forecasting energy consumption in China: implications for Chinese energy demand and imports in 2020. Energy Economics. 2008; 30(3): 1263–1278.

100. International Energy Agency. [Accessed Jan. 16th, 2013] Statistics. Energy Balance for China. 2009. http://www.iea.org/stats/balancetable.asp?COUNTRY_CODE=CN

101. Wang X, Feng Z. Study on affecting factors and standard of rural household energy consumption in China. Renew Sustain Energy Rev. 2005; 9:101–110.
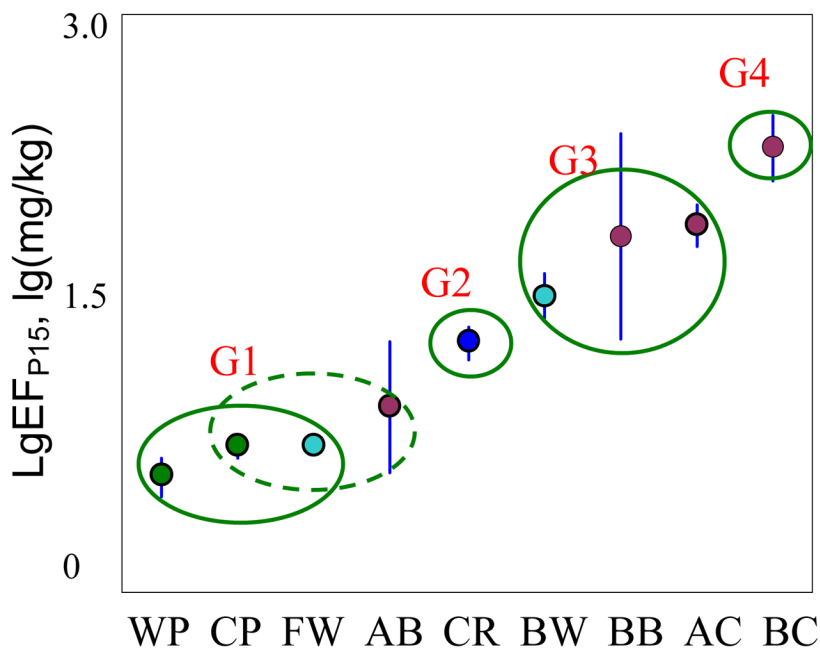
Figure 1.
Comparison of EF_{P15} among various fuel types combusted in residential stoves. Means and standard deviations of log-transformed EF_{P15} are shown. Four significant groups of G1, G2, G3, and G4 can be distinguished based on the result of ANOVA and a multiple comparison. WP, CP, FW, AB, CR, BW, BB, AC, and BC represent wood pellets (n=11), corn straw pellets (n=12), fuel wood (n=66), anthracite briquette (n=5), crop residue (n=25), brushwood (n=10), bituminous briquette (n=4), anthracite chunk (n=4), and bituminous chunk (n=11), respectively. Among the four fuels (WP, CP. FW, and AB) in G1, there was no difference among EF_{PAH} for CP, FW, and AB (a dashed ellipse), meanwhile, EF_{PAH} for WP, CP, and FW were different, but not statistically significant ($p > 0.10$).
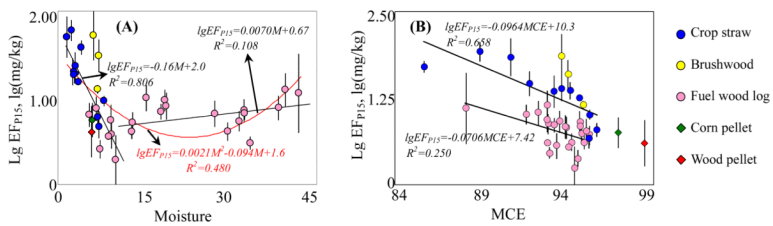
Figure 2.
Dependence of EF$_{P15}$ on moisture and MCE for biomass fuels, including fuel wood, brushwood, crop residue, and pellets. (**A**) Relationship between EF$_{P15}$ and fuel moisture. The relationship between log-transformed EF$_{P15}$ and moisture can be fitted with a piecewise function of two segments (black lines) or a binomial equation (red curve); (**B**) Relationship between EF$_{P15}$ and MCE
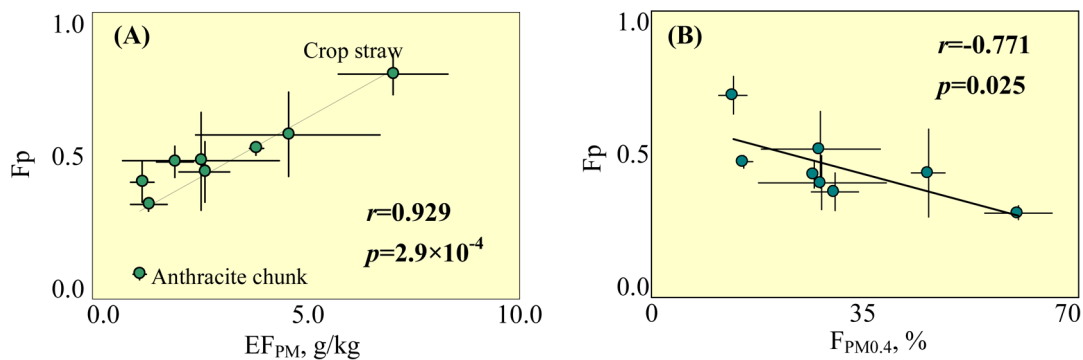
Figure 3.
Relationship (A) between mass fraction of particle-bound PAHs (Fp) and EFs of co-emitted PM, and (B) between Fp and mass percentage of particle-bound PAHs in fine $PM_{0.4}$ ($F_{PM0.4}$). Data are means and standard errors for each fuel type. contributions and avoid underestimation of PAH emissions from residential wood combustion.

Table 1

Calculated PAH isomer ratios based on the measured EFs for various solid fuels combusted in residences in China. The results are shown as means and standard deviations. Fuels are classified into several groups marked by "A", "B", "C", "D", "E", and "F", with statistically significant difference among the groups and insignificant within each group based on the results of multiple comparisons at a significance level of 0.05.

	ANT/(ANT+PHE)	FLA/(FLA+PYR)	BaA/(BaA+CHR)	IcdP/(IcdP+BghiP)	BbF/(BbF+BkF)	BaP/(BaP+BghiP)
corn pellet	0.12±0.02 A	0.53±0.04 A B	0.38±0.06 B	0.46±0.05 B	.55±0.03 C	0.49±0.08 C
wood pellet	0.10±0.02 A B	0.54±0.05 B C	0.34±0.10 A	0.48±0.05 B C	0.55±0.06 C	0.59±0.12 D
crop residue	0.12±0.02 A B	0.54±0.03 A B C	0.48±0.03 C	0.53±0.03 C D	0.55±0.04 C	0.58±0.04 D
fuel wood	0.12±0.01 A B	0.54±0.02 B C	0.49±0.04 C	0.55±0.03 D	0.51±0.04 B	0.63±0.04 E
brushwood	0.13±0.02 B C	0.52±0.02 A	0.56±0.04 D	0.54±0.01 D	0.50±0.03 B	0.56±0.02 D
anthracite briquette	0.14±0.06 B C	0.53±0.03 A B C	0.47±0.08 C	0.54±0.20 D	0.46±0.09 A	0.69±0.09 F
bituminous briquette	0.16±0.09 C D	0.53±0.06 A B C	0.32±0.07 A	0.28±0.05 A	0.57±0.01 C	0.37±0.03 A
raw anthracite	0.18±0.04 D	0.56±0.02 C	0.40±0.12 B	0.29±0.04 A	0.49±0.03 A B	*data not available*
raw bituminous	0.24±0.08 E	0.55±0.02 C	0.54±0.05 D	0.52±0.21 C D	0.55±0.07 C	0.47±0.12 B