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Field Measurement on the Emissions of PM, OC, EC and PAHs from Indoor Crop Straw Burning in rural China

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Abstract

Field measurements were conducted to measure emission factors of particulate matter (EF_{PM}), organic carbon (EF_{OC}), elemental carbon (EF_{EC}), 28 parent polycyclic aromatic hydrocarbons ($EF_{28pPAHs}$), and 4 oxygenated PAHs (EF_{4oPAHs}) for four types of crop straws burnt in two stoves with similar structure but different ages. The average EF_{PM} , EF_{OC} , EF_{EC} , $EF_{28pPAHs}$, and EF_{4oPAHs} were 9.1 ± 5.7 (1.8 – 22 as range), 2.6 ± 2.9 (0.30 – 12), 1.1 ± 1.2 (0.086 – 5.5), 0.26 ± 0.19 (0.076 – 0.96), 0.011 ± 0.14 (1.3×10^{-4} – 0.063) g/kg, respectively. Much high $EF_{28pPAHs}$ was observed in field compared with the laboratory derived EFs and significant difference in $EF_{28pPAHs}$ was identified among different crop residues, indicating considerable underestimation when laboratory derived EFs were used in the inventory. The field measured EF_{PM} , EF_{OC} , and EF_{EC} were significantly affected by stove age and the EFs of carbonaceous particles for the 15-year old stove were approximately 2.5 times of those for the 1-year old stove.

Keywords

Indoor crop straw burning; field measurement; carbonaceous particulate matter; polycyclic aromatic hydrocarbons; influencing factor

1. Introduction

High quality emission inventory is essential for the assessment of environmental fates and effects of air pollutants and for the development of abatement strategies (Anenberg et al., 2013; U.S. EPA, 2006). The major uncertainty of the emission inventories developed so far is from large variations in emission factors (EFs), and this is particularly true in residential sector (Bond et al., 2004; Pouliot et al., 2012; Wang et al., 2012; Zhang et al., 2011). EFs for residential fuel combustion are affected by many factors such as fuel property, stove design,

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fire management, and even experimental methods (Bhattacharya et al., 2002; Chen et al., 2012; Dhammapala et al., 2007; Jenkins et al., 1996; Jetter et al., 2012; McDonald et al., 2000; Shen et al., 2010a, 2010b).

EFs of residential fuel combustion can be measured in either laboratory or in field (Chen et al., 2012; Jetter et al., 2012). In most laboratory studies, either real stoves (Shen et al., 2010a; Zhang et al., 2000, 2008a) or chambers (Bhattacharya et al., 2002; Dhammapala et al., 2007; Jenkins et al., 1996; Jetter et al., 2012; McDonald et al., 2000; Zhang et al., 2011) were used to determine EFs. However, it is generally accepted that the combustion conditions and subsequent emissions of air pollutants differ obviously between laboratory and field tests (Dhammapala et al., 2007; Chen et al., 2012). Emissions could also be different between burning in real stoves and laboratory chambers (Jetter et al., 2012; Zhang et al., 2000). Although the laboratory test under controlled conditions is essential for understanding emission mechanism and kinetics, and assessing factors affecting the emission (Grandesso et al., 2011; Jetter et al., 2012; Shen et al., 2013a; Zhang et al., 2000), it is believed that field measurements can provide more realistic EFs since a variety of fuel/stove combinations under random conditions in real environment can be covered and fire management behaviors are real. As such, the field measured EFs are crucial in emission inventory development (Christian et al., 2010; Johansson et al., 2008; Kar et al., 2012; Roden et al., 2009; Tissari et al., 2007). Emission measurements in field are usually more difficult in sampling and financially expensive compared with the laboratory tests. Most EFs reported in the literature so far are from laboratory studies. Moreover, the majority of these data were measured in developed countries. The data gap in the field measurements in developing countries including China is one of the most important sources of uncertainty in emission inventories.

As a main renewable biomass resource, crop residue contributes about 30 – 45% of total energy consumption in rural China (Zeng et al., 2007). Total consumption of crop residue in rural China in 2007 was 340 Tg (NBSC). Because of the low combustion efficiency in cooking stoves, emission factors of a series of incomplete products, like particulate matter (PM), organic carbon (OC), elemental carbon (EC), and parent polycyclic aromatic hydrocarbons (pPAHs), from residential stove burning are usually much higher than those from industrial combustions (Bond et al., 2004; Wang et al., 2012; Zhang et al., 2008b). It was estimated that residential crop straw burning emitted 13 and 24% of total black carbon and pPAHs in China, respectively (Shen et al., 2013b; Wang et al., 2012). As a result, both ambient and indoor air qualities in rural residential areas are strongly affected by residential biomass burning (Ding et al., 2012; Jiang et al., 2008; Zhang et al., 2007). For example, it was reported that kitchen PM_{10} concentration in a rural kitchen using crop straws for cooking was $202 \pm 294 \mu g/m^3$, significantly higher than that of $67.0 \pm 32.6 \mu g/m^3$ in the household using natural gas (Jiang et al., 2008). The personal exposure levels for the former cookers were 5.4 times higher than the later cookers. In a rural household, daily mean concentrations of total PAHs in kitchen were measured at 3300, 1500 and 1400 ng/m^3 , respectively, when crop straw, wood and liquid petroleum gas were used for cooking (Ding et al., 2012).

In this study, EFs of PM, OC, EC, parent PAHs, and oxygenated PAHs (EF_{PM} , EF_{OC} , EF_{EC} , EF_{pPAHs} , and EF_{oPAHs} , respectively) for indoor crop residue burning were measured in the field. The results were compared with the literature reported EFs determined in laboratory. The effects of crop residue type and stove age were investigated.

2. Material and Methods

2.1 Study Site and Stoves

The field measurements were conducted in rural area of Nantong, Jiangsu ($120^{\circ}12' - 121^{\circ}55'$ E, $31^{\circ}41' - 32^{\circ}43'$ N) in the Yangtze River Delta region in south China. A typical rural household was selected, where the kitchen layout, stove model, and household fuel use are similar to the others in this region. Rice, wheat, cotton, and rape are main crops in this area. The annual yield of crop residues in this area was estimated to be 3.9 Tg in 2011 (SIN, 2011; Zeng et al., 2007). A large fraction of these crop residues were used as residential fuels for cooking. An improved two-pot brick stove with a chimney is commonly used in this area by most households. A relatively new stove of 1-year old and an old stove of 15-year old were selected in this study to compare the emissions from stoves of different ages. The pictures of the stoves are shown in Figure S1.

2.2 Sample Collection and On-site Measurements

Samples were collected during regular cooking time and the residents were asked to conduct fuel burning activities as normal. It is believed that the exhaust smoke was naturally diluted by the ambient air during the initial few seconds. The emitted smoke was sampled directly with the sampling probes placed close to the exit center of the chimney. An active sampler (XQC-15E, Tianyue, China) was used to collect PM and gaseous PAHs using quartz fiber filters (QFF, 22 mm in diameters) and polyurethane foam plugs (PUFs, 22 mm diameter $\times$ 7.6 cm), respectively. The flows were calibrated using a primary flow calibrator (Bios. Defender 510, USA). CO and CO₂ were measured using an on-line analyzer with two non-dispersive infrared sensors (GXH-3051, Technical Institute, China). The instrument was calibrated using a span gas in the laboratory, and zero-checked in the field tests before and after each sampling period. The probe of CO/CO₂ analyzer was also placed near the chimney center. As the EFs were calculated based on the carbon mass balance method, the probe position was flexible (Zhang et al., 2000). The sampling process lasted for 20 min for each sample and triplicate samples were collected for each experimental treatment. Sampling dilution systems are often used for emission measurements from stationary combustion sources in laboratory (Ge et al., 2001; Hildemann et al., 1989; Lipsky et al., 2005; Roden et al., 2006; Schauer et al., 1999). Unfortunately, relatively large size and complexity of these equipments render them not to be widely used in field studies (Lipsky et al., 2005; Roden et al., 2006). The situation is especially true in rural areas in developing countries, where transportation, installation, and operation of these complicate facilities are usually not practical (Christian et al., 2010; Kar et al., 2012; Tissari et al., 2007).

2.3 Sample Analysis and Data Analysis

Procedures for analyzing PM, EC, OC, pPAHs, and oPAHs followed those in a previous study (Shen et al., 2012a, 2012b). Briefly, PM gravimetric analysis was conducted using a

high precision digital balance (0.01 mg). EC and OC were measured using a Sunset EC/OC analyzer (RT-4, Sunset Lab.). The temperature protocol was: increased to 600, 840, and 550 °C in a pure helium atmosphere for OC detection, and then 550, 650, and 870 °C in an oxygen/helium atmosphere for EC detection.

Soxhelt extraction and a microwave extraction system (CEM Mars Xpress, USA, 1200 W, increased to 110°C in 10 min and then held for another 10 min) were used to extract gaseous pPAHs and oPAHs in PUFs (150 mL dichloromethane) and particle-bound PAHs in QFFs (25 mL hexane/acetone mixture (1:1, v/v)), respectively. A silica/alumina gel column (pre-eluted by 20 mL hexane) was used for cleanup of the extracts and PAHs were eluted with 70 mL hexane/dichloromethane mixture (1:1, v/v). The elution was then rotary evaporated to 1 mL, and spiked with deuterated internal standards (J&W Chemical Ltd.).

For analysis of pPAHs, a gas chromatograph (GC, Agilent 6890) coupled with a mass spectrometer (MS, Agilent 5973) in electron ionization mode and a HP-5MS capillary column (30 m × 0.25 mm × 0.25 µm) was used. The oven temperature was held at 50°C for 1 min, increased to 150°C at a rate of 10°C/min, to 240°C at 3°C/min, and then to 280°C for another 20 min. For oPAH analysis, negative chemical ionization mode (GC 6890 - MS 5975) was applied and the oven temperature was increased from 60 to 150°C at a rate of 15°C/min, to 300°C at 5°C/min, and then held for 15 min. High-purity helium was used as the carrier gas. The reagent gas in oPAH analysis was methane. pPAHs and oPAHs were identified based on the retention time and qualitative ions of the standards in selected ion mode.

28 pPAHs including naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLO), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), retene (RET), benzo [c] phenanthrene (BcP), cyclopenta [c, d] pyrene (CPP), benzo (a) anthracene (BaA), chrysene (CHR), benzo (b) fluoranthene (BbF), benzo (k) fluoranthene (BkF), benzo (a) pyrene (BaP), benzo (e) pyrene (BeP), perylene (PER), dibenz (a, h) anthracene (DahA), indeno (1, 2, 3-cd) pyrene (IcdP), benzo (g, h, i) perylene (BghiP), dibenzo [a, c] pyrene (DacP), dibenzo [a, l] pyrene (DalP), dibenzo [a, e] fluoranthene (DaeF), Coronene (COR), dibenzo [a, e] pyrene (DaeP), dibenzo [a, i] pyrene (DaiP), and dibenzo [a, h] pyrene (DahP), and 4 oxygenated PAHs including 9-fluorenone (9FO), anthracene-9, 10-dione (ATQ), benzanthrone (BZO), and benzo [a] anthracene-7, 12-dione (BaAQ), were quantified. Blanks were measured and the results were subtracted from the samples.

The carbon mass balance method (S1 in Supporting Information) was adopted to calculate EFs (Zhang et al., 2000). It was assumed that the total carbon emitted from the fuel burning is in the forms of either gaseous compounds (CO, CO₂, and total hydrocarbons) or carbon in PM (Zhang et al., 2000). Total gaseous hydrocarbon was not measured here, which could cause a relatively small error (Roden et al., 2006). The burning efficiency was characterized by modified combustion efficiency (MCE), defined as CO₂/(CO+CO₂) (molar basis). It is accepted that the difference between MCE and combustion efficiency is very small, and the former is commonly adopted (Janhäll et al., 2010; McMeeking et al., 2009). Statistical

analysis was conducted using *Statistica* (v5.5, StatSoft) and a significance level of 0.05 was applied.

3. Results

The measured EF_{PM} , EF_{OC} , EF_{EC} , EFS , and EF_{40PAH} are listed in Table 1 as means and standard deviations for each fuel/stove combination. For all stove-fuel combinations, arithmetic means and standard deviations of EF_{PM} , EF_{OC} , and EF_{EC} were 9.1 ± 5.7 , 2.6 ± 2.9 , and 1.1 ± 1.2 g/kg, respectively, which were higher than the corresponding median values, indicating right-skewed frequency distributions. In fact, log-normal distributions of EFs are often reported for residential coal and biomass burning (Zhang et al., 2007).

Similarly, EF_{28pPAH} and EF_{40PAH} were also right-skewed since arithmetic means are higher than median. Average EF of the total 16 U.S. EPA priority PAHs, which are often reported in the literature, was 252 ± 185 mg/kg. Table S1 shows EFs for individual pPAH and oPAH compounds. Compound profiles of PAHs for the two stoves tested are shown in Figure 1 as means of the four crop residues. It appears that the composition profiles of the two stoves were very similar to each other (Kolmogorov test, $p > 0.05$). In fact, the composition profiles of EF_{p28PAH} and EF_{40PAH} for the individual crop residues were also very much alike. For parent PAHs, the emissions were dominated by NAP ($39 \pm 8\%$), ACY ($16 \pm 3\%$) and PHE ($14 \pm 2\%$), followed by FLA ($6.5 \pm 1.5\%$) and PYR ($7.7 \pm 2.0\%$). The total contribution of the 20 high molecular weight parent PAHs (mw ≥ 228) contributed merely 9.0% of the total. The calculated means of several commonly used isomer ratios, including ANT/(ANT+PHE), FLA/(FLA+PYR), BaA/(BaA+CHR), IcdP/(IcdP+BghiP), BbF/(BbF+BkF), BaP/(BaP+BghiP), and BeP/(BeP+BaP), were 0.16 ± 0.01 , 0.46 ± 0.02 , 0.46 ± 0.03 , 0.58 ± 0.01 , 0.74 ± 0.02 , 0.78 ± 0.02 , and 0.36 ± 0.03 , respectively. Insignificant differences were observed for these isomer ratio values among the four fuel types and the two stoves ($p > 0.05$). Among the 4 oxygenated PAHs, EFs of 9FO and ATQ were higher than the other two oPAHs, contributing to 54 ± 28 and $26 \pm 16\%$ of the total oPAHs, respectively.

The EFs for all the target contaminants varied widely even though only two stoves and four crop residues were tested. The calculated coefficients of variations (CVs) for EF_{PM} , EF_{OC} , EF_{EC} , EF_{28pPAH} , and EF_{40PAH} were as high as 63, 114, 113, 73, and 130%, respectively. Such high variations of EFs were not surprising since a variety of factors, such as crop type, stove design, burning temperature, air supply, fueling and fire management behaviors (Chen et al., 2012; Jetter et al., 2012), can affect the combustion and emission. It is suggested that more field campaigns under various conditions are needed to collect more data to reduce the uncertainty in emission estimation.

4. Discussion

4.1 Comparison with EFs reported in the literature

There were a few studies, either in field or laboratory, investigated emissions of PM and PAHs from indoor crop residue burning in China. It is interesting to compare our results with those reported in the literature. To do so, EF_{PM} , EF_{OC} , EF_{EC} , EF_{16pPAH} , and EF_{40PAH} derived in the present study are shown in Figure 2 together with those previously by others

measured in field (Li et al., 2007, 2009), using real stoves but in a simulated kitchen (Shen et al., 2011a, 2011b; Zhang et al., 2000), or biomass burning in chambers (Cao et al., 2008; Lu et al., 2009).

Currently, field measurement data on emissions from residential fuel combustion in China are still very scarce. To the best of our knowledge, only carbonaceous particles were measured among the few field emission studies in China, while no field studies on emission of PAHs has not been conducted before. For example, Li *et al.* (2009) measured EF_{PM} , EF_{OC} , and EF_{EC} for four stoves in rural Beijing, Shandong, Chongqing, and Henan, and found the means of EF_{PM} , EF_{OC} , and EF_{EC} for crop residue were 4.4 ± 1.9 , 1.9 ± 1.0 , and 0.43 ± 0.32 g/kg, respectively, which were similar to those we measured from the stove used for 1 year (6.1 ± 4.1 , 1.9 ± 2.4 , and 0.66 ± 0.72 g/kg, respectively). Unfortunately, the ages of the stoves tested by Li *et al.* (2009) were not provided in the published paper.

Emissions of PM and PAHs from crop straw burning had been previously measured in real stoves under controlled conditions. For example, Zhang *et al.*, (2000) measured EF_{PM} for crop residues burned in a brick stove with a chimney at 1.1–29 g/kg with a mean of 8.1 g/kg, which was similar to the results we measured for the 1-yr stove. In our previous study in a simulated kitchen, the average EF_{PM} , EF_{OC} , EF_{EC} , EF_{16pPAH} , and EF_{40pPAH} for a new brick stove were 10, 1.5, 1.7, 0.087, and 0.0059 g/kg, respectively (Shen et al., 2010a, 2011a, 2011b). For EF_{PM} , EF_{OC} and EF_{40pPAH} , there were no significant differences between this study (1-year stove) and Shen *et al.*,’s data ($p > 0.05$). However, much higher EF_{16pPAH} and lower EF_{EC} were found in the field test (1-year stove) ($p < 0.05$). It was suggested that very low combustion rate may occur occasionally and randomly in the field and such a poor combustion moment can release very large quantities of incomplete combustion products including PAHs (Dhammapala et al., 2007; Roden et al., 2009). This phenomenon can hardly be repeated in laboratory test. On the other hand, an intense flaming generated in burning under controlled conditions might be associated with formation of a large quantity of light-absorbing particle (Chen et al., 2012; Li et al., 2009; Just et al., 2013). However, the calculated MCEs of the two experiments were very close to each other ($90 \pm 4\%$ vs. $92 \pm 3\%$) and the difference in EF_{PAH} can not be solely explained by this difference. More field data should be collected before the emission process can be better understood.

Most EFs were measured in chambers other than real stoves in laboratory studies (Cao et al., 2008; Jenkins et al., 1996; Lu et al., 2009; Shen et al., 2013a; Zhang et al., 2008b, 2011). For example, EF_{PM} , EF_{OC} , and EF_{EC} for crop straws (corn, wheat, and rice) reported by Cao *et al.* (2008) were similar to those obtained for the 1-year stove in this study. For PAHs, the EFs reported for laboratory chamber test in the literature vary widely. For example, EF_{16pPAH} for wheat straw reported by Zhang *et al.* (2008b) was 343 mg/kg, which was comparable to our field test, while it was only 1.4 mg/kg in another laboratory chamber study (Zhang et al., 2011). Likewise, the measured EF_{16pPAH} for rice straw was 5.3 mg/kg (Zhang et al., 2011), whereas the EF_{16pPAH} for rice straw was also reported in the range from 9.3 to 24 mg/kg, increasing with the increase of combustion temperature, and strongly affected by fuel moisture and oxygen content (Lu et al., 2009).

In addition to the field measurements, combustion emissions have been studied in laboratory tests using real stoves or chambers. Taking different combustion conditions between the real stoves and chambers into consideration, real stoves are preferred over chambers. It appears that the EFs measured in laboratory are mostly lower than those obtained in the field and such difference is particularly true for PAHs, and the variations of EFs in field measurements are generally higher than those in laboratory tests since the random pattern of behaviors of residents in fueling and fire management could hardly be reproduced by researchers, who are well trained to repeat procedures. The diversity in stove type and variation in stove age can hardly be taken into a full consideration. It is generally accepted that emissions measured in the field are closer to the reality and are the best data source for developing emission inventories. However, it is usually difficult to collect enough data to generate representative statistics due to extremely high variations and relatively high costs and labor intensity. On the other hand, laboratory tests are less expensive and can be conducted efficiently. Moreover, Laboratory tests under controlled conditions are important in terms of understanding the emission mechanisms and factors affecting the emission and of developing quantitative models.

4.2 Influence of fuel type and stove age

Among many factors affecting EFs, stove age and fuel type were tested in this study. Based on the measured EFs for the target pollutants, a two-way analysis of variance was conducted for log-transformed EF_{PM} , EF_{OC} , EF_{EC} , EF_{28pPAH} , and EF_{40pPAH} . For all the pollutants, no interaction between the two factors (stove age and fuel type) was found ($p > 0.05$). Significant difference among the four fuel types was only found for EF_{28pPAH} ($p = 0.027$). EF_{28pPAH} for the 4 tested crop residues followed the trend as rape straw ($4.2 \pm 2.8 \times 10^2$ mg/kg) > rice straw ($2.2 \pm 0.9 \times 10^2$ mg/kg) ~ wheat straw ($2.2 \pm 1.3 \times 10^2$ mg/kg) > cotton straw ($1.6 \pm 0.9 \times 10^2$ mg/kg). In a previous study on PAH EFs conducted in a simulated kitchen using a real stove, the observed EF_{16pPAH} of the same four crop residues followed the same order (Shen et al., 2011b). This might be related to the distinct properties, such as bulk density and moisture, of different crop straws, and different fuel-air mixing status in the stove chamber when burning different straws. A further study is needed to explain the phenomena. It seems that the difference among the crops was not randomly occurred and it would be preferred to model individual crop residues separately in the future for developing better PAH emission inventories.

The most significant difference occurred between the two stoves with different age. With an exception of EF_{40pPAH} ($p = 0.742$), EF_{PM} ($p = 0.004$), EF_{OC} ($p = 0.090$), EF_{EC} ($p = 0.043$), and EF_{28pPAH} ($p = 0.082$) were all significant at different levels below 10%, indicating that stove age is critical in terms of emissions of carbonaceous particles and PAHs. For example, the measured EF_{PM} , EF_{OC} and EF_{EC} for the stove used for about 1 year were 6.1 ± 4.1 , 1.9 ± 2.4 , and 0.66 ± 0.72 g/kg, respectively, which was some 2.5 times lower than 12 ± 5 , 3.4 ± 3.4 , and 1.5 ± 1.5 g/kg for the stove used for approximately 15 years. It was reported that EF_{PM} for residential wood combustion in a stove used for 1 year was 50% higher than a new one of same type.²¹ The increase in EFs of carbonaceous particles in aged stoves can be explained by the stove degradation, like flue block after long time use. Such a difference in

stove age adds more complexity to the variation in emissions, which should be taken into consideration in inventory development in the future.

4.3 Relationship among co-emitted pollutants

It is generally accepted that the emissions of incomplete combustion products, including CO, carbonaceous particulate matter and PAHs, highly depend on fuel combustion efficiency. For the data collected in this study, although there are general trends of negative dependence of EFs on MCE and positive dependence of their EFs on the EF of CO, these correlations were not statistically significant ($p > 0.05$). As a main incomplete byproduct, CO was occasionally used as a surrogate for other incomplete products. However, correlation between CO and PM were not always significant (Gupta et al., 1998; Li et al., 2007; Venkataraman et al., 2004) indicating the surrogate should be used with caution.

It is interesting to see that the measured EF_{PM} , EF_{OC} , and EF_{EC} (log-transformed) in this study are well correlated. Whether the data for the two stoves are plotted separately or together (the latter is shown in Figure 3), the correlations between EF_{PM} and EF_{OC} and between EF_{PM} and EF_{EC} are all significant ($p < 0.05$) (Table S2). For both new and old stoves considered, the slopes of the regression equations were 1.18 ($R^2 = 0.748$) for EF_{PM} against EF_{OC} , and 1.15 ($R^2 = 0.713$) for EF_{PM} against EF_{EC} , respectively. It appears that when the combustion condition is favorable for the formation of these incomplete combustion byproducts, emissions of OC and EC increased together with the increase of PM emission.

Although significant differences in EF_{PM} , EF_{OC} , and EF_{EC} between the two stoves tested were identified, the difference in stove age did not affect the relationship among these EFs, as suggested by the overall correlations between EF_{PM} and EF_{OC} and between EF_{PM} and EF_{EC} for the two stoves together. Such a similarity is confirmed by the result of a two-way analysis of variance, which suggests that there was no significant influence of crop type or stove age on the measured EC/OC and (EC+OC)/PM ratios. Therefore, such a relationship, if can be further confirmed in future field studies, can be used to estimate emissions of EC and OC from residential crop residue burning based on the measured PM emission.

According to the results, it was not surprising to see that there was no significant correlation between the emissions of PAHs and the emissions of carbonaceous particles ($p > 0.05$). As discussed above, the former was significantly different among crop types ($p = 0.027$) and stove ages ($p = 0.082$), while the latter depended only on stove age ($p = 0.004$, 0.090, and 0.043 for PM, OC, and EC, respectively). One possible reason is that low molecular weight PAHs, which accounted for the majority of PAHs, tended to mainly exist in gaseous phase (Lu et al., 2009; Shen et al., 2013b).

As expected, EFs of various parent PAHs were generally correlated with one another, especially for those with similar molecular weight, with an only exception of RET (Table S3). RET was considered to be a unique compound, sometimes referred as a marker of the emission from softwood (Ramdahl, 1983). The result of a principal component analysis (Figure 4) also confirmed that RET was distinct from the other parent PAHs. 81% of variance can be explained by the first principal component which was an association

(loading scores > 0.70) of all PAHs except RET, while the second principle component was a sole-variate (RET) one. It was also interesting to see that there were two distinguished groups with a group of low-median molecular weight PAHs and another group of high molecular weight ones in terms of the first component.

Similarly, the measured EFs of individual oPAH compounds correlated well with each other ($p < 0.05$), suggesting their similar formation processes. Relationship between oPAHs and their corresponding parent PAHs are shown in Figure 5. Significant correlations were identified for the 1-year stove, which was also revealed in a previous laboratory study on coal and crop straw burning emission using a new stove.⁴⁵ There was no such relationship for the old stove. It appears that the aging of stoves affected the formation and emission of pPAHs ($p = 0.082$) and oPAHs ($p = 0.742$) differently. A well explanation may rely on more studies about the formation mechanisms of parent and oxygenated PAHs in future.

It should be noted that the results in the present study are based on limited sample sizes and it should not be generalized simply. It is expected to reach a sound conclusion when more further studies available, especially field measurements. In the future study on EFs, more pollutants should be measured simultaneously. Such a multi-purpose campaign can not only improve the experiment efficiency, but also provide useful information on emission processes of these co-emitted pollutants.

5. Conclusions

In this study, emission factors of PM, OC, EC, parent PAHs and oxygenated PAHs were measured in field for the indoor crop straw burning. For all stove-fuel combinations, arithmetic means and standard deviations of EF_{PM} , EF_{OC} , EF_{EC} , EF_{pPAHs} , and EF_{oPAHs} were 9.1 ± 5.7 , 2.6 ± 2.9 , 1.1 ± 1.2 , 0.26 ± 0.19 , 0.011 ± 0.014 g/kg, respectively. Field measurement is expected to provide more reliable data for emission inventory, but it also has relatively high variances. Significantly higher emissions of PAHs measured in field suggests considerable underestimation in the inventory using laboratory derived emission factors. Emissions of carbonaceous particulate matter increased by about 2, 5 times in the old stove compared to those in the new stove, indicating the influence of stove aging on the emission performance should not be overlooked.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgement

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Appendix

Pictures of the stoves, calculation of EFs, measured EFs of individuals, and correlation coefficients for PAHs are provided in the supporting material available free of charge via the internet.

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Figure 1.

Composition profiles of the measured pPAHs and oPAHs for crop residue burned in the new (1 year) and old (15 years) stoves. The results are arithmetic means (bars) and standard deviations (sticks) of the four crop residues. The compounds are 28 parent PAHs (1. NAP, 2. ACY, 3. ACE, 4. FLO, 5. PHE, 6. ANT, 7. FLA, 8. PYR, 9. RET, 10. BcP, 11. CPP, 12. BaA, 13. CHR, 14. BbF, 15. BkF, 16. BeP, 17. BaP, 18. PER, 19. IcdP, 20. DahA, 21. BghiP, 22. DacP, 23. DalP, 24. DaeF, 25. COR, 26. DaeP, 27. DaiP, and 28. DahP) and 4 oxygenated PAHs (29. 9FO, 30. ATQ, 31. BZO, 32. BaAQ).

Figure 2.

Comparison of EF_{PM} , EF_{OC} , EF_{EC} , EF_{16PAH} , and EF_{40PAH} (from left to right) for indoor crop residue burning in China from (A) laboratory chamber tests, (B) stove combustions in simulated kitchens, and (C) field measurements (this study). Means and standard deviations are shown. EF_{16PAH} are shown in log-scale.

Figure 3.

Relationship between EF_{PM} and EF_{oc} (open) and between EF_{PM} and EF_{ec} (blue) for the two stoves tested in the field experiment. The two stoves were marked with either circles (1-year stove) or diamonds (15-year stove).

Figure 4.

Factor loading plot of the first two principal components derived from a principle component analysis. (1. NAP, 2. ACY, 3. ACE, 4. FLO, 5. PHE, 6. ANT, 7. FLA, 8. PYR, 9. RET, 10. BcP, 11. CPP, 12. BaA, 13. CHR, 14. BbF, 15. BkF, 16. BeP, 17. BaP, 18. PER, 19. IcdP, 20. DahA, 21. BghiP, 22. DacP, 23. DalP, 24. DaeF, 25. COR, 26. DaeP, 27. DaiP, and 28. DahP).

Figure 5.

Relationship between EFs of 9FO, ATQ, and BaAQ (from left to right) and EFs of their corresponding parent PAHs for crop straws burned in a 1-year old stove (top row) and a 15-year old stove (bottom row).

EF_{PM}, EF_{OC}, EF_{EC}, EF_{28pPAH}, and EF_{40PAH} for indoor crop residue burning in the two stoves. Arithmetic means and standard deviations from triplicate measurements are shown for individual stove-fuel combinations and overall means (standard deviations), median, and geometric means are also listed.

Table 1

Stove	Fuel	PM g/kg	OC g/kg	EC g/kg	pPAHs mg/kg	oPAHs mg/kg
Stove 1 (1-yr stove)	wheat straw	9.8±4.7	2.6±1.8	0.46±0.19	310±128	17±9.8
	rape straw	3.7±3.0	0.58±0.17	0.47±0.48	561±348	8.2±7.2
	rice straw	5.2±2.9	1.1±0.9	0.51±0.37	257±105	22±3.5
	cotton straw	5.7±4.6	3.1±4.5	1.2±1.4	122±53	2.2±2.2
	Mean of 4 straw	6.1±4.1	1.9±2.4	0.66±0.72	330±237	12±18
Stove 2 (15-yr stove)	wheat straw	17±7	4.1±1.8	1.4±0.9	122±41	7.3±6.3
	rape straw	13±5	4.9±6.5	2.7±2.4	276±88	14±11
	rice straw	8.2±2.8	1.5±0.6	0.64±0.19	166±5	6.9±6.3
	cotton straw	10±4	2.5±1.8	0.96±0.90	188±119	7.0±12
	Mean of 4 straw	12±5.5	3.4±3.4	1.5±1.5	190±92	8.7±8.4
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Mean±standard deviation		9.1±5.7	2.6±2.9	1.1±1.2	259±189	11±14
Median		7.9	1.4	0.71	176	7.1
Geometric mean		7.3	1.6	0.67	214	3.5