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Emissions of parent, nitrated, and oxygenated polycyclic aromatic hydrocarbons from indoor corn straw burning in normal and controlled combustion conditions

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Abstract

Emission factors (EFs) of parent polycyclic aromatic (pPAHs), nitrated PAHs (nPAHs), and oxygenated PAHs (oPAHs) were measured for indoor corn straw burned in a cooking brick stove in both normal and controlled burning conditions. EFs of total 28 pPAHs, 6 nPAHs and 4 oPAHs were 7.9 ± 3.4 , $6.5 \pm 1.6 \times 10^{-3}$, and $6.1 \pm 1.4 \times 10^{-1}$ mg/kg, respectively. By controlling the burning conditions, it was found that the influence of fuel charge size on EFs of the pPAHs and derivatives was insignificant. Measured EFs increased significantly in a fast burning mainly because of the oxygen deficient atmosphere formed in the stove chamber with a small volume. In both restricted and enhance air supply conditions, EFs of pPAHs, nPAHs and oPAHs were significantly higher than those measured in normal burning conditions. Though EFs varied in different burning conditions, the composition profiles and calculated isomer ratios were similar without significant differences. The results from the stepwise regression model showed that fuel burning rate, air supply amount, and modified combustion efficiency were three most significant influencing factors, explaining 72–85% of the total variations.

Keywords

polycyclic aromatic hydrocarbons; PAH derivatives; emission factor; influencing factor; indoor crop straw burning

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are of wide concern due to their abundance in the environment and adverse health effects. Exposure to polycyclic aromatic hydrocarbons (PAHs) has been widely documented to be associated with the increased risks of various diseases including lung cancer and neural tube defects (Armstrong et al., 2004; Boström et

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al., 2002; Mumford et al., 1987; Ren et al., 2011). The dose-response relationship between placental PAH levels and the risk of neural tube defects in rural residents was reported in the literature (Ren et al., 2011). It was estimated that the inhalation exposure to ambient total U.S.A. Environmental Protection Agency 16 priority PAHs in China caused an over population attributable fraction for lung cancer in the range of 0.91 to 2.6% (with mean of 1.6%), which corresponded to an excess cancer incidence rate of 0.65×10^{-5} (Zhang et al., 2009). In addition to 16 priority PAHs, more and more studies also pointed out that some other parent PAHs, especially those molecular weight 302, could yield high risk and be paid high attention (Wang et al., 2012; Jia et al., 2011; Shen et al., 2012a). For example, it was reported that in comparison to the estimated excess cancer risk for only 12 priority PAHs, the ignoring of 5 PAHs with molecular weight at 302 could result in an underestimation of about 23% (Jia et al., 2011). Beside parent PAHs (pPAHs), some derivatives, like nitrated PAHs (nPAHs), oxygenated PAHs (oPAHs), and hydroxyl-PAHs (HO-PAHs), are also of growing concern since it was generally believed that these derivatives were more toxic than the parent ones (Albient et al., 2007, 2008; Andreou and Rapsomanikis, 2009; Bolton et al., 2000; Durant et al., 1996; Li et al., 2003; Reisen and Arey, 2005; Walgraeve et al., 2010). Exposure to oPAHs was though to be directly related the formation of reactive oxygen species (Chung et al., 2006; Lundstedt et al., 2007; Walgraeve et al., 2010). It was reported that direct acting mutagenicity of PM induced by nPAHs and oPAHs was about 2 times of pPAHs induced indirect acting mutagenicity in Beijing during the summer time, though the concentration of former two derivatives were only 8% of the total PAHs (Wang et al., 2011). Currently, reports of these derivatives, either in ambient air or from the emission sources, are still limited (Allen et al., 1997; Ding et al., 2012; Hattori et al., 2007; Shen et al., 2011a, 2012a, 2012b; Simoneit et al., 2007; Tang et al., 2005; Wang et al., 2007; Wang et al., 2011; Xu et al., 1982).

It is generally accepted that PAHs are produced from the incomplete combustion processes, while oPAHs and nPAHs can be emitted from the primary source, or formed secondary from the radical reactions with pPAHs and/or other precursors (Albient et al., 2007; Fitzpatrick et al., 2007; Lundstedt et al., 2007; Shen et al., 2011a; Walgraeve et al., 2010). Global total emission of EPA 16 priority PAHs was estimated at about 520 Gg/year, of which about 80% emitted from developing countries (Zhang and Tao, 2009). Among various sources of PAHs, residential solid fuel (mainly biomass and coal) combustion under low burning efficiency is a larger emitter. The situation is especially true in developing countries where large amount of biomass fuels were combusted in rural area. Globally, biomass combustion contributed about 57% of total PAHs emitted, and the proportion was as high as 66% in China (Zhang and Tao, 2009). To our knowledge, the emission inventories of PAH derivatives have not been developed so far.

Emission estimation is usually developed based on the emission factors and the activity levels. Lack of EF data, especially for residential combustion source in rural area, is a big cause of uncertainties and bias in the current emission inventories (Bond et al., 2004; Lei et al., 2011; Xu et al., 2006; Zhang and Tao, 2009). Emission factors (EFs), defined as the mass of target organics emitted for per mass or energy unit of fuel consumed, can be measured from the experimental measurements or derived from other surrogate and the relationship between the target and surrogate. EFs can be influenced by a number of factors,

and reported EFs in the literature usually vary dramatically in orders of magnitude because of the differences in fuel property, stove design, burning conditions, fire management, and even experimental methodology (Chen et al., 2012; Jenkins et al., 1996; Jetter et al., 2012; Li et al., 2009; McDonald et al., 2000; Shen et al., 2011; Zhang et al., 2008a, 2008b, 2011). The measurement of EFs can be done in field, or in laboratory chamber or simulated stove burning (Chen et al., 2012). Field measurements are preferable to get more realistic EFs, however, the field study also requires relatively high labor intensity and cost. On the other hand, simulated burning experiments, either in laboratory chambers or in real stoves, are also widely adopted to measure EFs for a variety of fuel and stove combinations (Chen et al., 2009; Bhattacharya et al., 2002; Fine et al., 2004; Gullett et al., 2003; Kim Oanh et al., 1999, 2002, 2005; Venkataraman and Rao, 2001; Zhang et al., 2000). One important advantage of the simulated burning experiment is that it can be used to investigate the influencing factors of the burning processes by controlling combustion conditions (Grandesso et al., 2011; Lu et al., 2009; Shen et al., 2012c; Xie et al., 2007). For example, Lu et al., (2009) investigated the influences of fuel moisture, combustion temperature and oxygen amount on the emissions of PAHs from crop straw burning in a laboratory chamber. So far, most of controlled burning experiments were conducted in a chamber in laboratory rather than real cooking stoves.

In this study, emission factors of pPAHs, oPAHs and nPAHs were measured for corn straw burned in a residential cooking stove in normal combustion condition. One main objective of this study is to investigate the influence of fuel charge size, burning rate and air supply conditions on the emission factors of these target organics by conducting controlled burning experiments. In addition to the measured EFs, the composition profiles, isomer ratios and relationship among these co-emitted pollutants are also discussed.

1. Materials and methods

1.1 Fuel, stove and combustion experiments

The burning experiments were conducted in a new built stove in a rural kitchen. The kitchen and stove were built previously to simulate the residential biomass burning and measure emission factors of PM and PAHs from the combustion (Shen *et al.*, 2010a, 2011b). The stove used was a typical brick one that can be commonly found in rural China. The smoke from the stove chamber passed through a heating bed (“Kang” in Chinese) and then emitted into the outdoor air through a chimney. The exhaust from the fuel combustion entered into a mixing chamber where the smoke was mixed and cooled by a built-in fan. All sampling was done in the mixing chamber.

Corn straw with the moisture of 7.02% was tested in this study. The fuel was first burned in a normal combustion condition. The burning process was conducted to repeat rural residents’ burning practice as possible as we can. 550 g corn straw was inserted into the stove chamber in about 15-20 batches. Calculated fuel burning rate was about 0.045 kg/min. In addition to the normal burning, controlled burning experiments were done to investigate the influences of fuel charge size, burning rate and air supply on emissions for corn straw (Shen et al., 2012c). Three different fuel charge sizes of 275, 550, and 1100 g were tested in this study. To measure emissions from the burning of different combustion rates, we

changed the amount of fuel added per batch to achieve different burning lasting time, resulting in different burning rates. Calculated burning rates in these man-induced slower and faster burnings were 0.020 kg/min and 0.119 kg/min, respectively. To investigate the impacts of air supply, corn straw burning was also done in an enhanced air supply using an additional blower resulting a higher ventilation rate of about 19.0 m³/h, and a restricted air supply burning condition by covering part of the grate air inlet area from 0.09 m² to 0.04 m², beside the NC in which the air supply was estimated at about 9.0 m³/h (Wei, 2012). For each condition, triplicate burning experiments were done.

1.2 Sampling, laboratory analysis and quality control

Sampling, laboratory analysis and quality control procedures were the same as those in the previous study (Shen et al., 2012a). Briefly, gaseous and particulate phase parent PAHs and PAH derivatives were collected on polyurethane foam plugs (PUFs) and quartz fiber filters (QFFs), respectively. The pump flow rate was about 1.5 L/min, calibrated using a flow meter (Bios, Defender 510, USA). The filters used were pre-baked at 450°C for 6 h and equilibrated in desiccators. PUF were pre-extracted with acetone, dichloromethane and hexane in sequence. The PUFs and QFFs after sampling were packed in clean aluminum foil, stored under -20°C and then transported back to the laboratory.

Soxhelt extraction using 150 mL dichloromethane and microwave accelerated extraction (CEM, Marx Xpress, USA) were used to extracted the organics in PUFs and QFFs, respectively. The temperature protocol in the microwave accelerated extraction was: increased to 110°C in 10 min and then held for another 10 min. The extracts were concentrated to 1 mL using a rotary evaporator (Eyela, Japan). A silica/alumina gel column filled with 12 cm alumina, 12 cm silica gel, and 1 cm anhydrous sodium sulfate from bottom to top was used to clean up the extracts. The column was pre-eluted with 20 mL hexane, followed by 70 mL hexane/dichloromethane. The later was collected, concentrated to 1 mL, spiked with internal standards and analyzed.

Parent PAHs and their derivatives were all analyzed using a gas chromatograph (GC, Agilent 6890) connected to a mass spectrometer equipped with a HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm). For parent PAHs, the electron ionization mode was used while for their derivatives, the negative chemical mode using methane as reagent gas was used. The oven temperature program for the analysis of pPAHs was: 50°C held for 1 min, increased to 150°C at a rate of 10°C/min, to 240°C at 3°C/min, and then finally to 280°C held for 20 min. For oPAHs and nPAHs analysis, the oven temperature was, increased to 150°C from 60°C at a rate of 15°C/min, and finally to 300°C at 5°C/min held for another 15 min. The carrier gas was high purity helium. Chemicals were identified based on the retention time and qualified ions of the standards in selected ion mode. 28 parent PAHs including naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLO), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), retene (RET), benzo[c]phenanthrene (BcP), cyclopenta[c,d]pyrene(CPP), benzo(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), benzo(e)pyrene (BeP), perylene (PER), dibenz(a,h)anthracene (DahA), indeno(1,2,3-cd)pyrene (IcdP), benzo(g,h,i)perylene (BghiP), dibenzo[a,c]pyrene

(DacP), dibenzo[a,l]pyrene (DalP), dibenzo[a,e]fluoranthene (DaeF), Coronene (COR), dibenzo[a,e]pyrene (DaeP), dibenzo[a,i]pyrene (DaiP), and dibenzo[a,h]pyrene (DahP), 4 oPAHs including 9-fluorenone (9FO), anthracene-9,10-dione (ATQ), benzantrone (BZO), and benzo[a]anthracene-7,12-dione (BaAQ), and 6 nPAHs including 1-nitro-naphthalene (1N-NAP), 2-nitro-naphthalene (2N-NAP), 9-nitro-anthracene (9N-ANT), 9-nitro-phenanthrene (9N-PHE), 3-nitro-phenanthrene (3N-PHE), and 3-nitro-fluoranthene (3N-FLA) were analyzed. Five deuterated parent PAHs (NAP-*d*₈, ANT-*d*₁₀, ACE-*d*₁₀, CHR-*d*₁₂, and PER-*d*₁₂, J&W Chemical Ltd., USA) and 2 deuterated nitro-PAHs (1-nitroanthracene-*d*₉ and 1-nitropyrene-*d*₉, J&W Chemical Ltd., USA) were used as the internal standards for the analysis of parent PAHs and their derivatives, respectively. All glassware was ultrasonically cleaned and baked at 500 °C for about 10 h. Instrumental detection limit, method detection limit, recoveries of the spiked standards were also determined for each target, and can be found elsewhere in detail (Shen et al., 2012a). The recoveries of spiked samples were 70-121 and 68-125% for gaseous and particulate phase compounds, respectively, which were within the acceptable range. Blank samples were also analyzed and the results were subtracted.

1.3 EF calculation and data analysis

The carbon mass balance method was adopted to calculate the EFs of pPAHs, oPAHs and nPAHs. It assumed that total carbon from the fuel burning was emitted in the forms of gaseous CO, CO₂, total hydrocarbon (THC) and carbon in particulate matter (Zhang et al., 2000; Dhammapala et al., 2007). Because the method did not require to collect all the exhaust smoke, and the position of sampling probe was not very critical, the carbon method has been widely used in the EF measurement. The detailed calculation process can be found elsewhere (Zhang et al., 2000; Shen et al., 2010a). In this study, CO and CO₂ were determined using an online non-dispersive infrared sensor (GXH-3051, China) and recorded automatically every 2 seconds. The instrument was calibrated using the span gas and zero checked before the combustion experiment. THC was not measured in the present study which may lead to an error in 4% (Roden et al., 2006). Total carbon in particulate matter was measured using the Sunset EC/OC analyzer (Sunset RT-4, USA). Modified combustion efficiency (MCE), defined as CO₂/(CO₂+CO), was used to characterize the burning. Since most of the carbon was emitted into the forms of CO and CO₂, the difference between MCE and combustion efficiency was very small. Statistica (v5.5, StatSoft) was used in data statistical analysis and a significant level of 0.05 was adopted.

2. Results and Discussion

2.1 Emission factor

Measured EFs of total 28 pPAHs, 4 oPAHs, and 6 nPAHs (EF_{28pPAHs}, EF_{4oPAHs}, and EF_{6nPAHs}, respectively) for corn straw burned in normal combustion condition were 7.9±3.4, 6.1±1.4×10⁻¹, and 6.5±1.6×10⁻³ mg/kg, respectively. EF of total U.S. EPA 16 priority PAHs was 7.6±3.3 mg/kg. In a previous study, EFs of 16 pPAHs and 4 oPAHs for corn straw were reported at 39±16, and 2.9±0.6 mg/kg, respectively (Shen et al., 2011b), significantly higher than those measured in this study (*p* < 0.05). Since the same stove was used, the difference here could be mainly a result of different fuel moisture. Moistures of the

corn residue measured in the previous and present study were 2.5 ± 0.6 and $7.0 \pm 0.2\%$. It was thought that fuel with relatively low moisture would burn too fast to result in an oxygen deficient atmosphere which produced much higher emissions of incomplete combustion products (Rogge et al., 1998; Simoneit, 2002). EF of total 16 pPAHs for corn straw (moisture was not reported) burned in a laboratory chamber (Zhang et al., 2011) was reported at 1.7 mg/kg, which was obviously lower than that in our study, attributing to the different fuel/stove burning conditions and difference in experimental designs.

In the controlled burnings, emissions of pPAHs, oPAHs and nPAHs were all found to be independent ($p > 0.05$) of the fuel charge size (Fig. 1). Similar results were also reported in the literature for PM and PCDD/F emissions from simulated open biomass burning (Grandesso et al., 2011). In the fast burning with a rate of 0.119 ± 0.016 kg/min, measured $EF_{28pPAHs}$, EF_{4oPAHs} , and EF_{6nPAHs} were 68 ± 55 , 3.8 ± 2.3 , and $3.8 \pm 0.76 \times 10^{-2}$ mg/kg, much higher than those from slower burnings. Under relatively higher burning rates, the air was exhausted rapidly that can cause an air-limited condition in the cooking stove with a small chamber volume, and hence produced higher emissions. High emissions of incomplete combustion products under an air deficient condition were also confirmed in the burning experiments with restricted air supply. As shown in Fig. 1, measured EFs of PAHs and their derivatives were significantly lower in the normal burning condition, and increased under both restricted (41 ± 2.5 , 2.7 ± 1.5 , and $1.9 \pm 0.51 \times 10^{-2}$ mg/kg for $EF_{28pPAHs}$, EF_{4oPAHs} , and EF_{6nPAHs} , respectively) and enhanced air supply conditions (12 ± 5.9 , 1.7 ± 0.97 , and $9.7 \pm 6.1 \times 10^{-3}$ mg/kg for $EF_{28pPAHs}$, EF_{4oPAHs} , and EF_{6nPAHs} , respectively). Increased in EFs under enhanced air supply may be attributed to the cooled combustion temperature (Johansson et al., 2003; Shen et al., 2012d.). It was accepted that adequate air supply is required for high efficient combustion emitting lower pollutants (Houshfar et al., 2011; Lu et al., 2009).

To address the impacts of these factors, a stepwise regression model was used. In addition to the fuel charge size, burning rate and air supply, MCE calculated to characterize the combustion conditions was as added as the 4th independent variable. The results showed that burning rate, air supply and MCE were three significant factors influencing measured emission factors. EFs could be further predicted from these three factors, and about 78, 72, and 85% of total variations in $EF_{28pPAHs}$, EF_{4oPAHs} , and EF_{6nPAHs} could be explained by them. The predicted EFs generally agreed well with the measured EFs (Fig. 2).

2.2 Composition profile and isomer ratios

The composition profiles of pPAHs, oPAHs and nPAHs from the corn straw burning under different burning conditions were similar, though measured EFs differed among these burning experiments. For parent PAHs, NAP (35%), PHE (16%), followed by FLA (10%) and PYR (9%) were dominated PAHs (Fig. 3). PAH individuals were positively ($p < 0.05$) correlated with each other, especially those with similar molecular weight, except RET. The formation of RET is thought to be associated with the degradation of abietic acids, which is different from that for other PAHs formed through the pyrolysis and prosynthesis processes (Ramdahl et al., 1983; Simoneit, 2002; Shen et al., 2012e). The means of several commonly used isomer ratios in PAH source apportionment, including ANT/(ANT+PHE), FLA/(FLA

+PYR), BaA/(BaA+CHR), IcdP/(IcdP+BghiP), BbF/(BbF+BkF), BaP/(BaP+BghiP), and BeP/(BeP+BaP) (Katosoyiannis et al., 2011; Watson, 1984; Yunker et al., 2002), were 0.12 ± 0.02 , 0.54 ± 0.02 , 0.49 ± 0.03 , 0.54 ± 0.03 , 0.51 ± 0.03 , 0.63 ± 0.04 , and 0.42 ± 0.05 , respectively. These ratios were also independent of the different burning conditions tested in this study, and agreed with those for crop straw reported in the literature (Kim Oanh et al., 2005; Sheesley et al., 2003; Shen et al., 2011b; Yunker et al., 2002). It is noted that these ratios may change after emission into the atmosphere (Zhang et al., 2005; Wang et al., 2007), and hence, the use of them in source apportionment should be in caution (Katosoyiannis et al., 2011; Zhang et al., 2005).

9FO was the most abundant oPAHs, contributing about 61% of the total 4 oPAHs measured. In the emissions of nPAHs, approximate 30, 32, and 22% of the total nPAHs identified were 1N-NAP, 2N-NAP, and 9N-ANT (Fig. 4). EFs of the PAH derivatives were positively correlated with EFs of their corresponding parent PAHs (Fig. 5). EFs of 9FO and ATQ were within 0-1 orders of magnitude of EFs of their parent FLO and ANT, and EF of BaAQ were about 1-2 orders of magnitude lower than EF_{BaA} . EFs of nPAHs were about 2-4 orders of magnitude of EFs of those corresponding parent PAHs.

2.3 Gas-particle partitioning

The partitioning coefficient (K_p), defined as $K_p = F/(A \times PM)$ where F and A are PAH concentrations in particulate and gaseous phases (ng/m^3), respectively, and PM is the mass concentration of particulate matter ($\mu g/m^3$), is calculated to describe gas-particle partitioning of PAHs and their derivatives (Pankow, 1987). As shown in Fig. 6 (A), lg-transformed K_p generally increased with the increase of the compound molecular weight, for both parent PAHs and PAH derivatives, which is expected that high molecular weight organics tend to be present in particulate matter. In comparison with the corresponding parent PAHs, PAH derivatives had more tendencies to be associated with the particles, with higher K_p values. For example, calculated lg K_p values for 1N-NAP and 2N-NAP were -5.2 ± 0.4 , and -5.1 ± 0.5 , significantly higher ($p = 2.8 \times 10^{-6}$ and $p = 1.7 \times 10^{-6}$, respectively) than that of -6.6 ± 0.9 for NAP. The lg K_p values for 9FO and ATQ were -4.5 ± 0.5 and -3.9 ± 0.5 , respectively, also significantly higher than those of -5.6 ± 0.7 and -4.8 ± 0.6 for FLO and ANT ($p = 6.4 \times 10^{-8}$ and $p = 2.7 \times 10^{-7}$, respectively).

The gas-particle partitioning of organics were usually thought to be controlled by absorption and/or adsorption (Goss and Schwarzenbach 1998; Lohmann and Lammel 2004). Though the mechanism(s) should be complicated, it can be evaluated in practice by plotting the K_p versus the subcooled liquid-vapor pressure (P_L^0). It was suggested that a steep slope (< -1.0) may indicate that adsorption controlled the partitioning while a shallow slope (> -0.6) indicated absorption dominance, and the slope between -0.6 and -1.0 suggested both absorption and adsorption governed the partitioning (Goss and Schwarzenbach 1998).

Figure 6(B) shows the relationship between K_p and P_L^0 , and the slope was -0.43 , > -0.6 , suggested that the gas-particle partitioning of PAHs from corn straw burning was mainly controlled by absorption into the strong absorber, like organic carbon, rather than adsorption. The governance of absorption could be also confirmed by the significantly positively correlation (Fig. 6(C)) between K_p and the octanol-air partition coefficient (K_{OA})

(Lohmann and Lammel 2004). The absorption dominated partitioning of freshly emitted PAHs had also been reported in the literature for combustion sources besides crop straw burning, like wood, coal and diesel combustions (Roden et al., 2006; Spezzano et al., 2009; Shen et al., 2010b, 2012a).

3. Conclusion

In this study, emission factors of 28 pPAHs, 4 oPAHs and 6 nPAHs were measured for corn straw burned in a residential brick cooking stove. Measured $EF_{28pPAHs}$, EF_{4oPAHs} , and EF_{6nPAH} were 7.9 ± 3.4 , $6.1 \pm 1.4 \times 10^{-1}$, and $6.5 \pm 1.6 \times 10^{-3}$ mg/kg, respectively in normal burning condition. EF of total U.S. EPA 16 priority PAHs was 7.6 ± 3.3 mg/kg, contributing about 95% of total 28 pPAHs.

Controlled burning experiments were conducted investigate the impacts of fuel charge size, burning rate and air supply. It was found that the influence of fuel charge size was not significant. Measured EFs were higher at 8 ± 55 , 3.8 ± 2.3 , and $3.8 \pm 0.76 \times 10^{-2}$ mg/kg in the fast burning with the rate of 0.119 ± 0.016 kg/min, in comparison to the rate of 0.045 kg/min in normal burning. In both restricted and enhanced air combustions, EFs of pPAHs and their derivatives increased significantly. It was accepted that adequate air supply was required for high efficient combustions with lower emissions of incomplete pollutants. By using a stepwise regression model, it was shown that fuel burning rate, air supply amount and modified combustion efficiency were three most significantly factors influencing measured EFs in this study. About 78, 72, and 85% of total variations in $EF_{28pPAHs}$, EF_{4oPAHs} , and EF_{6nPAHs} could be explained by these three factors. Predicted EFs based on these factors agreed well with those measured values. Future studies are needed to investigate the formation mechanisms for both parent PAHs and their derivatives.

The composition profiles and calculated isomer ratios were similar, independent of the tested burning conditions, though measured EFs varied obviously. Low and median molecular weight PAHs, including NAP, PHE, FLA and PYR, were the most abundant species. PAH individuals correlated with each other significantly, except retene. The derivatives were positively correlated with their corresponding parent PAHs.

High molecular weight organics have more tendencies to be associated with particle. The gas-particle partitioning of freshly emitted PAHs were thought to be mainly controlled by the absorption rather than adsorption. In comparison with the parent PAHs, PAH derivatives have more tendencies to be present in particulate phase mainly due to their lower vapor pressures.

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Fig. 1.

Comparison of measured $EF_{28pPAHs}$, EF_{40PAHs} , and EF_{6nPAHs} for corn residue in controlled combustions of different fuel charge size, burning rate, and air supply conditions. EFs are lg-transformed, and data shown are means and standard deviations from triplicate measurements. The p values from ANOVA analysis are also listed.

Fig. 2. Comparison of predicted and measured $EF_{28pPAHs}$, EF_{40PAHs} , and EF_{6nPAHs} for corn residue. The prediction results were based on fuel burning rate, air supply and MCE.

Fig. 3.

Composition profiles of parent PAHs from indoor corn straw burning. Data shown are means and standard deviations of all burning experiments. Compounds listed are 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, 28. DahP.

Fig. 4.

Composition profiles of oPAHs and nPAHs from indoor corn straw burning. Data shown are means and standard deviations of all burning experiments.

Fig. 5. Correlations between the measured EFs (lg-transformed) of PAH derivatives and those of their corresponding parent PAHs.

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