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Influence of different types of coals and stoves on the emissions of parent and oxygenated PAHs from residential coal combustion in China[☆]

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ABSTRACT

To evaluate the influence of coal property and stove efficiency on the emissions of parent polycyclic aromatic hydrocarbons (pPAHs) and oxygenated PAHs (oPAHs) during the combustion, fifteen coal/stove combinations were tested in this study, including five coals of different geological maturities in briquette and chunk forms burned in two residential stoves. The emission factors (EFs) of pPAHs and oPAHs were in the range of 0.129–16.7 mg/kg and 0.059–0.882 mg/kg, respectively. The geological maturity of coal significantly affected the emissions of pPAHs and oPAHs with the lower maturity coals yielding the higher emissions. The chunk-to-briquette transformation of coal dramatically increased the emissions of pPAHs and oPAHs during the combustion of anthracite, whereas this transformation only elevated the emissions of high molecular weight PAHs for bituminous coals. The influence of stove type on the emissions of pPAHs and oPAHs was also geological-maturity-dependent. High efficiency stove significantly reduced the emissions of PAHs from those relatively high-maturity coals, but its influences on low-maturity coals were inconstant.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of the toxic organic pollutants of heightened concern all over the world. The derivatives of parent PAHs (pPAHs), such as nitrated PAHs (nPAHs) and oxygenated PAHs (oPAHs), are also persistent and mobile in environment and tend to be equally or even more toxic or mutagenic than pPAHs (Albinet et al., 2008; Wang et al., 2011; Shen et al., 2012). nPAHs and oPAHs are mainly formed from primary fuel combustion and/or through the reactions of pPAHs with atmospheric oxidants (Wang et al., 2011).

Coal combustion is considered as one of the most important sources of pPAHs, nPAHs, and oPAHs in the developing countries (Shen et al., 2012), such as in China. Although, the Chinese government is trying to change the energy consumption patterns, coal combustion was still the primary energy consumption accounting for ~66% of the total consumption in 2013 based on the China Statistical Yearbook of 2014. Coal combustion is also an important source of indoor pollutants for their widely usage for cooking and heating in the residence. Domestic coal combustion produced approximately 19.6% of the total PAH emissions in China (Xu et al., 2006), and contributed significantly to severe indoor air pollution and exposure risk in China as well (Zhang and Smith, 2007; Zhang

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et al., 2009; Shen et al., 2012).

To estimate the emissions of PAHs and their derivatives, the emission factors (EFs) are needed. EF is the mass of emitted pollutant per unit energy consumed. It varies with the fuel properties (type, rank, size, shape, and moisture), combustion facilities (residential or industrial stoves), burning conditions (combustion temperature or efficiency), and experimental methods (laboratory or field measurements) (Jenkins et al., 1996; McDonald et al., 2000; Johansson et al., 2004; Shen et al., 2011b). Chen et al. (Chen et al., 2005) studied the impact of geological maturity to the emission factors (EFs) of PAHs from coal combustion and found that the combustion of bituminous coal with vitrinite reflectance (R_O, a measure of the geological maturity of coal) around 0.9% produced the highest EFs of particulate matter, elemental carbon, organic carbon, and PAHs. Shen et al. (Shen et al., 2013a) studied the influence of volatile matter (VM) content on the emissions of PAHs and found that medium volatile bituminous coal emitted relatively large quantities of PAHs in comparison with low and high volatile bituminous coals. Meanwhile, the studies of Simoneit (Simoneit, 2002) and Shen et al. (Shen et al., 2013a) suggested that the fast burning of low moisture biomass fuel forms an oxygen deficient atmosphere yielding high pollutant emissions, whereas the burning of high moisture fuel requires extra energy to vaporize water reducing combustion temperature and efficiency, and hence increased emissions of incomplete combustion products, such as PAHs and their derivatives. However, the mechanism of the effects of coal properties on the production and emission of PAHs are still not well understood. Moreover, few studies (Zhang and Smith, 1999; Shen et al., 2013b) have drawn specific attention to the influence of different types of domestic stove on the emissions of PAHs and their derivatives. Their results showed that the emissions of contaminants were dependent not only on the fuel type but also on the stove type and the improved stove caused more emissions than the traditional stove. Studies (Liu et al., 2009; Shen et al., 2011a, 2013abib_Shen_et_al_2013a) on the emission of pPAHs and their derivatives from the residential combustion of coals with different shapes, such as honeycomb briquettes and raw chunk coals, are also limited.

The purpose of this research is (i) to determine the EFs of pPAHs and oPAHs from different types of residential coal combustion, (ii) to investigate the possible reasons for the influence of coal properties, forms, and stove types on the emissions of PAHs and their derivatives. For the lack of data, the result will lead to a better understanding of PAH emissions from the residential sources in China.

2. Materials and methods

2.1. Coals and stoves

Five different types of coals from five locations, including Yulin (YL) in Shaanxi province, Cixian (CX) in Hebei province, Zhongyang (ZY) in Shanxi province, Changzhi (CZ) in Shanxi province, and Anyang (AY) in Henan province, were tested in two forms (honeycomb briquette and raw chunk coal) in this study. Each coal sample included three subsamples collected from the same batch of coal. The three subsamples were homogenized before test. Their volatile matter content (V_{daf}), ranks, and other characteristics are summarized in Table S1 in the Supporting Information (SI). Briefly, these coals cover a wide range of geological maturity and can be classified into one high-volatile bituminous coal (HVB), two medium-volatile bituminous coals (MVB), one low volatile bituminous coal (LVB), and one semi-anthracite coal (SA). The sizes of various coal chunks were similar (3–5 cm in diameter). Honeycomb briquettes for each coal were manufactured by a machine after intermixing coal powders (powdered from corresponding raw coal chunk) with clean clay (coal: clay = 2: 1 for bituminous coal and 1:1 for anthracite), and the briquettes were 16-hole (1.5 cm diameter each) columns with a height of 8 cm, a diameter of 12.5 cm, and a weight of ~300 g. The manufacturing process and the proportion of clay were identical to those of honeycomb briquettes sold on market.

Two commonly used household coal-stoves in China were selected, including a low-efficiency stove (LES) and a high-efficiency stove (HES). LES stove can only use raw coal chunk, whereas HES stove can use both honeycomb briquette and raw coal chunk. For comparison of burning efficiency of two stoves and two forms of coals, small raw coal chunks (3–5 cm in diameter) for the five coals were burned separately in the LES and HES stoves, while briquettes for the five coals were burned in the HES stove. Totally, fifteen coal/stove combinations were tested in this study. A duplicate sample was run randomly for every five coal/stove combinations to check the repeatability of this study. The relative standard deviations for these duplicate samples were <5%, which suggested that the data were reliable.

2.2. Sampling and analysis

The dilution sampling system and the emission sampling procedure has been described in detail elsewhere (Chen et al., 2005, 2015bib_Chen_et_al_2015). Briefly, the sampling system included four parts (Fig. S1, SI): a hood for gathering emissions from stoves, a long curved pipe for cooling flue gas to ambient temperature, an end pump for drawing flue gas through the sampling system at a flow rate of ~12 m^3/min, and a branched pipe upstream the end pump for ducting part of exhaust to the high-volume particle sampler (quartzfiber filter, i.e. QFF, Whatman) at a flow rate of ~65 L/min with a split ratio of ~0.005.

Before sampling, a few anthracite coals were burned to heat the inner chamber of the stove to a high temperature, and then used to ignite the experimental coal chunks or briquettes from the bottom. The sampling procedure started when briquettes or chunks were added into the stove and ignited by preburned charcoals, and ended when the coals burned out under natural conditions without any disturbance, which ensured that the entire combustion process was sampled. The flow rate was calibrated and the system was cleaned before each combustion experiment. The disturbance of background (accounting for 1–4% of coal emission) can be neglected due to the significantly high emission compared with background pollution level.

The QFF sample was spiked with the deuterium-labeled surrogate standard, consisting of naphthalene-D8, acenaphthene-D10, phenanthrene-D10, chrysene-D12, and perylene-D12, and then Soxhlet extracted with dichloromethane (DCM) for 24 h. After solvent exchange with hexane and concentration to ~0.5 mL using a rotary evaporator, each extract was cleaned by passing through a silica gel-alumina column containing baked anhydrous sodium sulfate (1 cm), neutral silica gel (3 cm, 3% deactivated), and neutral alumina (3 cm, 3% deactivated) from the top to the bottom using an eluent of 20 mL hexane/DCM (1:1, v/v). The 5 raw coal samples were also Soxhlet extracted and purified as shown above. These extracts were concentrated to approximately 0.5 mL using a gentle stream of N_2 prior to the instrumental analysis.

All samples were analyzed using an Agilent 7890GC-5975MS supplied with a DB5-MS column (30 m × 0.25 mm × 0.25 μm). The mass spectrometer was operated in electron impact ion (EI) mode for pPAHs, and electron capture negative ion (ECNI) mode for oPAHs. Sixteen pPAHs and six oPAHs were analyzed in this study. More details are provided in the SI and our previous study (Chen et al., 2015).