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## Characteristics of particulate-bound polycyclic aromatic hydrocarbons emitted from industrial grade biomass boilers

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### ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are carcinogenic or mutagenic and are important toxic pollutants in the flue gas of boilers. Two industrial grade biomass boilers were selected to investigate the characteristics of particulate-bound PAHs: one biomass boiler retro-fitted from an oil boiler (BB1) and one specially designed (BB2) biomass boiler. One coal-fired boiler was also selected for comparison. By using a dilution tunnel system, particulate samples from boilers were collected and 10 PAH species were analyzed by gas chromatography–mass spectrometry (GC–MS). The total emission factors (EFs) of PAHs ranged from 0.0064 to 0.0380 mg/kg, with an average of 0.0225 mg/kg, for the biomass boiler emission samples. The total PAH EFs for the tested coal-fired boiler were 1.8 times lower than the average value of the biomass boilers. The PAH diagnostic ratios for wood pellets and straw pellets were similar. The ratio of indeno(1,2,3-*cd*)pyrene/[indeno(1,2,3-*cd*)pyrene + benzo(*g,h,i*)perylene] for the two biomass boilers was lower than those of the reference data for other burning devices, which can probably be used as an indicator to distinguish the emission of biomass boilers from that of industrial coal-fired boilers and residential stoves. The toxic potential of the emission from wood pellet burning was higher than that from straw pellet burning, however both of them were much lower than residential stove exhausts.

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### Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous pollutants, and some of them are carcinogenic and/or mutagenic (Ames et al., 1975; Epstein et al., 1979). In addition to natural processes, PAHs mainly originate from coal and wood burning, petrol and diesel oil combustion, industrial processes and so on (Bamford and Baker, 2003; Chen et al., 2006; Yunker et al., 2002). In the atmosphere, the partitioning of PAHs between the particulate and gas phases depends on the vapor pressure as well as air conditions such as ambient

temperature, and nature of the aerosol such as origin and properties, because they are semi-volatile organic compounds. However, carcinogenic 5- and 6-ring PAHs are mostly associated with particulate matter (Bamford and Baker, 2003; Araki et al., 2009).

The energy consumption in China has kept rapidly increasing in the past decades. China has become the largest consumer of energy in the world, with the primary energy consumption accounting for 22.4% of the world in 2013. Currently, in China, coal is the biggest energy contributor, accounting for 67.4% of the total consumption in 2013

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(BP Statistical Review of World Energy, 2013). Biomass is organic material with intrinsic chemical energy content and is composed of a wide variety of forestry and agricultural resources, industrial processing residues, and municipal solid and urban wood residues. China is a leading agricultural nation and the amount of crop residue was found to be 802.32 million tons in 2009 (Song et al., 2014). Among the crop residue resources, process residue is an important contributor in China; the total process residue quantity in China from 2007 to 2009 was evaluated at 88.62 million tons annually, which was equivalent to 49.34 million tons of standard coal (Guo et al., 2012). Due to the large resource amount and renewable characteristics, biomass is expected to play a more important role in the energy structure of China in the future.

Much of the previous research on emission factors (EFs) in relation to coal or biomass combustion has focused on small residential stoves, mainly because of their wide usage in China. Due to the low combustion efficiency and lack of control measures, emissions from small residential stoves usually result in serious indoor and outdoor air pollution (Chen et al., 2006; Zhi et al., 2008; Yang et al., 2010; Shen et al., 2012). Bignal et al. (2008) investigated the PAH emission from a woodchip-fired 50 kW domestic boiler. Olsson and Kjällstrand (2006) reported a study on PAH concentrations relative to other organic emissions in two modes (flaming and glowing) of a 30 kW boiler. The above studies involved relatively small biomass boilers where raw fuel with high moisture content was used for burning. It was reported that high moisture content usually leads to high PAH release (Bignal et al., 2008). On the other hand, due to its higher combustion efficiency and lower emissions, the industrial grade biomass boiler has been promoted in China in recent years. Some researchers reported PAH EFs for some industrial coal-fired boilers (Yang et al., 1998; Li et al., 1999; Dyke et al., 2003), however data from industrial biomass boilers were not included. In addition, the use of processed crop residues (dry pellets) is also gradually expanding in China, which has much lower moisture than that of raw biomass fuels and is expected to have lower emissions of PAHs, as well as other incomplete combustion byproducts. Currently, data on the emission profile, especially PAHs, of industrial grade biomass boilers using local processed biomass fuels in China are scarce.

In order to diagnose the relative contributions of various sources and devise effective control strategies, accurate inventories are often compiled based on the strengths of emission activities and EFs. Generally, EFs will vary depending on fuel category, fuel origin, stove type, combustion conditions, dilution technologies and so on. Some studies have reported the PAH EFs for some domestic coal and biomass under particular combustion conditions (Chen et al., 2005; Tao et al., 2006). However, reports concerning the biomass combustion from industrial boilers in China are rare.

In this research, EFs of particulate-bound PAHs exhausted from two types of industrial biomass boiler were investigated. Two types of pelletized biomass fuels were tested respectively. Additionally, the PAH EFs of the emission from one industrial coal-fired boiler were also studied for comparison.

## 1. Methods

### 1.1. Biomass boilers and coal-fired boiler

Currently, in China, some of the biomass boilers are specially designed for biomass combustion, while others are retro-fitted from original coal or oil burning boilers. In this study, two biomass boilers were selected, one of which was retro-fitted from an oil-fired boiler (BB1) and another was specially designed (BB2). For comparison, emission from a coal-fired boiler (CB) with similar power was also investigated. The detailed information of these boilers is listed in Table 1. These boilers operated intermittently according to the requirements of heat supply or hot water supply. In the case of heat supply, the boilers usually are used from 15th November to 15th March of the next year, and the average working time is about 10 h/day.

### 1.2. Fuel

Two kinds of biomass fuels were purchased from a local market: wood pellets and straw pellets. The shape of the pellets was stick-form with diameter of 0.6–0.8 cm and length of 3–5 cm. The same wood pellets were used as the test fuel for the burning experiments of both BB1 and BB2. A bituminous coal (Datong, Shanxi Province) with block-form and less than approximately 4 cm in size was also tested for comparison. Analytical characteristics of the tested fuels are shown in Table 2. The proximate and elemental analyses were conducted at China Coal Research Institute. The proximate analysis was conducted according to the Chinese national standard methodologies (GB/T212-, 2008) and the elemental analysis was conducted using an elemental analyzer (CE-440, Exeter Analytical Inc., USA) for each test. Compared with coal, the tested biomass fuels showed higher percentages of volatile compounds and oxygen but lower moisture, heating value, carbon content and sulfur content.

### 1.3. Sampling

Sampling was undertaken in January 2010. The dilution sampling system used in this study has been reported in detail elsewhere (Geng et al., 2013) and is briefly summarized here. Gases were first extracted and two-stage diluted from the flue by a dilution system (FPS 4000, Dekati Ltd., Finland) which is widely used (Giechaskiela et al., 2005; Mathis et al., 2004; Vaaraslahti et al., 2004). The temperature of flue gas could be subsequently cooled to room temperature (about 20 °C) and the dilution ratio was controlled at 14 to 20. Then PM<sub>10</sub> samples were collected by a double-channel cyclone PM sampler on quartz fiber filters (47 mm diameter, Advantec, Japan) for the boilers at normal operation conditions. The sampling time duration was about 150 min for each sample and a total of 4 samples were collected. In order to evaluate particulate matter (PM) removal rate, PM<sub>10</sub> samples were respectively collected before and after precipitation, and a good removal rate was confirmed (Geng et al., 2013). On the other hand, PAHs in the samples collected after precipitation were analyzed and are reported in this paper.

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