JOURNAL OF ENVIRONMENTAL SCIENCES XX (2015) XXX-XXX



Available online at www.sciencedirect.com

ScienceDirect



www.elsevier.com/locate/jes

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

Q2 Xiaoyang Yang¹, Chunmei Geng^{1,*}, Xuesong Sun², Wen Yang¹, Xinhua Wang¹, Jianhua Chen¹

1. State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China. E-mail: gengcm@craes.org.cn

2. Beijing Municipal Research Institute of Environmental Protection, Beijing 100037, China

ARTICLE INFO

Article history: Received 10 June 2015 Revised 25 August 2015 Accepted 11 September 2015 Available online xxxx

Keywords:

Polycyclic aromatic hydrocarbons Industrial grade biomass boiler Emission factor Diagnostic ratio Potential toxicity risk

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 spectrometer (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.

© 2015 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.

46 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 57 properties, because they are semi-volatile organic com- 58 pounds. However, carcinogenic 5- and 6-ring PAHs are mostly 59 associated with particulate matter (Bamford and Baker, 2003; 60 Araki et al., 2009). 61

The energy consumption in China has kept rapidly 62 increasing in the past decades. China has become the largest 63 consumer of energy in the world, with the primary energy 64 consumption accounting for 22.4% of the world in 2013. 65 Currently, in China, coal is the biggest energy contributor, 66 accounting for 67.4% of the total consumption in 2013 67

* Corresponding author. E-mail: gengcm@craes.org.cn (Chunmei Geng).

http://dx.doi.org/10.1016/j.jes.2015.09.010

1001-0742/© 2015 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.

Please cite this article as: Yang, X., et al., Characteristics of particulate-bound polycyclic aromatic hydrocarbons emitted from industrial grade biomass boilers, J. Environ. Sci. (2015), http://dx.doi.org/10.1016/j.jes.2015.09.010

100

101

102

103

104

105

106

107

108

109

110

111

(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 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 113inventories are often compiled based on the strengths of 114 emission activities and EFs. Generally, EFs will vary depending 115on fuel category, fuel origin, stove type, combustion condi-116 tions, dilution technologies and so on. Some studies have 117 reported the PAH EFs for some domestic coal and biomass 118 under particular combustion conditions (Chen et al., 2005; Tao 119 et al., 2006). However, reports concerning the biomass 120combustion from industrial boilers in China are rare. 121

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 131 specially designed for biomass combustion, while others are 132 retro-fitted from original coal or oil burning boilers. In this 133 study, two biomass boilers were selected, one of which was 134 retro-fitted from an oil-fired boiler (BB1) and another was 135 specially designed (BB2). For comparison, emission from a 136 coal-fired boiler (CB) with similar power was also investigated. 137 The detailed information of these boilers is listed in Table 1. 138 These boilers operated intermittently according to the re- 139 quirements of heat supply or hot water supply. In the case of 140 heat supply, the boilers usually are used from 15th November 141 to 15th March of the next year, and the average working time 142 is about 10 h/day.

1.2. Fuel

Two kinds of biomass fuels were purchased from a local 145 market: wood pellets and straw pellets. The shape of 146 the pellets was stick-form with diameter of 0.6-0.8 cm and 147 length of 3–5 cm. The same wood pellets were used as the test 148 fuel for the burning experiments of both BB1 and BB2. A 149 bituminous coal (Datong, Shanxi Province) with block-form 150 and less than approximately 4 cm in size was also tested 151 for comparison. Analytical characteristics of the tested 152 fuels are shown in Table 2. The proximate and elemental 153 analyses were conducted at China Coal Research Institute. 154 The proximate analysis was conducted according to the 155 Chinese national standard methodologies (GB/T212-, 2008) 156 and the elemental analysis was conducted using an elemental 157 analyzer (CE-440, Exeter Analytical Inc., USA) for each test. 158 Compared with coal, the tested biomass fuels showed higher 159 percentages of volatile compounds and oxygen but lower 160 moisture, heating value, carbon content and sulfur content. 161

162

1.3. Sampling

Sampling was undertaken in January 2010. The dilution 163 sampling system used in this study has been reported in 164 detail elsewhere (Geng et al., 2013) and is briefly summarized 165 here. Gases were first extracted and two-stage diluted from 166 the flue by a dilution system (FPS 4000, Dekati Ltd., Finland) 167 which is widely used (Giechaskiela et al., 2005; Mathis et al., 168 2004; Vaaraslahti et al., 2004). The temperature of flue gas 169 could be subsequently cooled to room temperature (about 170 20 °C) and the dilution ratio was controlled at 14 to 20. Then 171 PM₁₀ samples were collected by a double-channel cyclone PM 172 sampler on quartz fiber filters (47 mm diameter, Advantec, 173 Japan) for the boilers at normal operation conditions. The 174 sampling time duration was about 150 min for each sample 175 and a total of 4 samples were collected. In order to evaluate 176 particulate matter (PM) removal rate, PM₁₀ samples were 177 respectively collected before and after precipitation, and a 178 good removal rate was confirmed (Geng et al., 2013). On the 179 other hand, PAHs in the samples collected after precipitation 180 were analyzed and are reported in this paper. 181

Please cite this article as: Yang, X., et al., Characteristics of particulate-bound polycyclic aromatic hydrocarbons emitted from industrial grade biomass boilers, J. Environ. Sci. (2015), http://dx.doi.org/10.1016/j.jes.2015.09.010

JOURNAL OF ENVIRONMENTAL SCIENCES XX (2015) XXX-XXX

Table 1 – Information of	boilers.				
	Model	Power (MW)	Precipitator	Fire grate	Application
Biomass-fired boiler 1 (BB1)	DZW2.1-0.7/95/70-M	2.1	Bag filter	Reciprocating bar	Heat supply for residential or office building
Biomass-fired boiler 2 (BB2)	CDZL1.4-0	1.4	Water film scrubber	Chain grate	Heat supply for office building or vegetable greenhouses
Coal-fired boiler (CB)	IRZL-2.0-0	2.0	Water film scrubber	Chain grate	Heat or hot water supply for office building

182 1.4. PAH analysis

Since only particle samples were collected in this study, some 2-183 or 3-ring PAHs that mainly exist in the gas phase were not 184 appropriate for the discussion in this study. Therefore, ten PAH 185species having relatively lower saturated vapor pressure were 186analyzed and investigated (Table 3). The pretreatment and 187 analysis were conducted by Beijing Center for Physical & 188 Chemical Analysis, according to methods EPA-610 and EPA-189TO13A and described briefly here. The PM₁₀ filter samples were 190 extracted ultrasonically three times with 150 mL of dichloro-191 methane (DCM), and each extraction lasted 30 min. Surrogate 192deuterated PAHs (chrysene-d₁₂, pyrene-d₁₂, SUPELCO, USA) were 193 194 added prior to the extraction. The extracts were concentrated 195 on a rotary evaporator and fractionated using silica-alumina 196 column chromatography. The PAH fractions were then concen-197 trated and an internal standard (hexa-methylbenzene, SUPELCO, 198 USA) was added for quantification of individual PAHs by gas chromatography-mass spectrometer (GC-MS) (Varian GC-431 199coupled with Varian 240-MS, USA). 200

201 1.5. Calculation of emission factors

The fuel-mass based PAH-EF is expressed in units of milligrams (mg) of PAH emitted per kilogram (kg) of fuel burned. The EF (mg/kg) of species X on a fuel-mass basis can be calculated using the following equation:

$$EF_{X} = \frac{[X] \times D \times Q \times T}{M}$$
(1)

t2.1 t2.2	Table 2 – Analytical characte (air-dried basis).		ristics o	of the	tested fuels
t2.3 +2.4			Bion	nass	Coal
t2.4 t2.5			Wood pellet	Straw pellet	Bituminous
t2.6	Proximate	Moisture (%)	2.6	2.6	3.8
t2.7	analysis	Volatile matter (%)	75.8	57.0	31.4
t2.8	(air dry basis)	Ash (%)	5.2	25.2	10.6
t2.9		Fixed carbon (%)	16.3	15.2	54.1
t2.10		Higher heating value (MJ/kg)	20.3	14.4	26.5
t2.11		Lower heating value (MJ/kg)	19.1	13.5	25.6
t2.12	Elemental	Carbon (%)	46.9	35.8	66.9
t2.13	analysis	Hydrogen (%)	5.5	4.2	3.9
t2.14	(air dry basis)	Nitrogen (%)	0.1	0.9	0.8
t2.15		Oxygen (%)	39.5	31.1	13.1
t2.16		Sulfur (%)	0.1	0.1	0.9

where, [X] (mg/m^3) is the concentration of species X on the 20% sample filter, Q (m^3/min) is the flow rate of the flue gas in 208 stack, T (min) is the sampling time, D is the dilution factor and 209 M (kg) is the weight of fuel burned during the sampling time. 210

1.6. Quality assurance and quality control 211

Quartz-fiber filters were baked at 800 °C in an oven for 2 h to 212 remove organic materials adsorbed on them. A laboratory 213 blank sample was processed with the same procedure as the 214 real samples and no detectable PAHs were present. Field 215 blanks were analyzed and no significant contamination was 216 found. The relative correlation for the standard curve (stan- 217 dard solution including six concentration levels: 0, 10, 50, 100, 218 500 and 1000 ng/mL) was higher than 0.995 and the relative 219 standard deviation of the response factor was less than 15%. 220

2. Results and discussion

EFs of the identified 10 PAHs in particulate samples were 224 calculated on a fuel-weight basis and are shown in Table 4. 225 The total EFs of PAHs ranged from 0.0064 to 0.0380 mg/kg, 226 with an average of 0.0225 mg/kg, for the biomass boiler 227 emission samples. The total PAH EFs for the tested coal-fired 228 boiler was 1.8 times lower than the average value of biomass 229 boiler. The difference in the values between PAH EFs for the 230 biomass and coal may be due to the different volatile contents 231 of the fuels. The volatile content of biomass was 75.8% (wood 232 pellets, air dried basis) and 57.0% (straw pellets, air dried 233 basis) while that for coal was only 31.4% (Table 2). At the same 234 time, the total PAH EFs for BB1 with wood pellets was 3.6 235 times higher than that of BB1 with straw pellets (Table 4). 236

Tabi (PAI	le 3 – Investigated po Hs).	lycyclic aroma	tic hydı	rocarbons	t3.1 t3.2
No	Name	Abbreviation	Rings	Formula	t3.3 t3.4
1	Fluoranthene	FLA	4	C ₁₆ H ₁₀	t3.5
2	Pyrene	PYR	4	$C_{16}H_{10}$	t3.6
3	Benz(a)anthracene	BaA	4	$C_{18}H_{12}$	t3.7
4	Chrysene	CHR	4	$C_{18}H_{12}$	t3.8
5	Benzo(b)fluoranthene	BbF	5	$C_{20}H_{12}$	t3.9
6	Benzo(k)fluoranthene	BkF	5	$C_{20}H_{12}$	t3.10
7	Benzo(a)pyrene	BaP	5	$C_{20}H_{12}$	t3.11
8	Indeno(1,2,3-cd)pyrene	IcdP	6	$C_{22}H_{12}$	t3.12
9	Dibenz(a,h)anthracene	DahA	5	$C_{22}H_{14}$	t3.13
10	Benzo(g,h,i)perylene	BghiP	6	$C_{22}H_{12}$	t3.14

Please cite this article as: Yang, X., et al., Characteristics of particulate-bound polycyclic aromatic hydrocarbons emitted from industrial grade biomass boilers, J. Environ. Sci. (2015), http://dx.doi.org/10.1016/j.jes.2015.09.010

222

223

t4.1 t4.2	Table 4 – PA coal-fired bo	AH emissio biler (based	n factors f on fuel ma	or biomass ss) (units: r	s boiler and ng/kg).
t4:3 t4:4		BB1 wood pellet	BB1 straw pellet	BB2 wood pellet	CB bituminous
t4.5	FLA	0.0062	0.0013	0.0001	0.0044
t4.6	PYR	0.0061	0.0012	0.0001	0.0014
t4.7	BaA	0.0011	0.0004	0.0096	0.0006
t4.8	CHR	0.0015	0.0006	0.0154	0.0011
t4.9	BbF	0.0017	0.0008	0.0079	0.0022
t4.10	BkF	0.0013	0.0006	0.0028	0.0007
t4.11	BaP	0.0009	0.0004	0.0012	0.0006
t4.12	IcdP	0.0007	0.0002	0.0001	0.0003
t4.13	DahA	0.0013	0.0002	0.0006	0.0003
t4.14	BghiP	0.0025	0.0008	0.0003	0.0013
t4.15	Sum (10-PAH)	0.0231	0.0064	0.0380	0.0128
t4.10	PAH: polycycli	c aromatic h	ydrocarbon.		

Additionally, the volatile content was found to be 1.3 times 237higher in the tested wood than that in the tested straw 238(Table 2). High volatile content usually leads to incomplete 239 combustion, which results in more PAH emission (Chen et al., 240241 2005). Therefore, the different PAH EFs for BB1 with wood 242 pellets and BB1 with straw pellets, which were tested in the 243same boiler, may also be due to the different percentages of 244 volatile content between the two tested biomass fuels.

245The concentrations of benzo(a)pyrene (BaP) from the tested biomass fuels were 0.86 µg/m³ (BB1 with wood pellets), 2460.38 μ g/m³ (BB1 with straw pellets) and 1.24 μ g/m³ (BB2 with 247wood pellets). In Beijing, the standard maximum concentra-248 tion limit of BaP is $0.3 \,\mu\text{g/m}^3$ (DB11/501-2007). The BaP 249 concentration from the emission of the studied biomass 250burning was 0.3 to 3.1 times higher than the standard value, 251which indicated that the pollution of biomass combustion 252from the industrial boiler to the atmosphere was serious. 253Therefore, a more efficient precipitation system should be 254employed to reduce PAH emissions. In addition, the concen-255tration of BaP from the tested bituminous coal emission was 2560.56 μ g/m³, which was at the same level as the biomass 257emission. 258

As shown in Fig. 1, good correlation between the BaP EFs and total PAH EFs was observed ($R^2 = 0.9991$). This finding was probably due to the similar generation mechanism for the tested PAH species. Therefore, the EFs of the total PAHs can be derived from the EFs of BaP by multiplying by the slope in 263 Fig. 1, which can be used to estimate the total PAH EFs when 264 the BaP value is available. 265

A comparison of studies reporting 10-PAH EFs and BaP EFs 266 for each tested fuel is shown in Table 5, with some data cited 267 from other reports. The BaP EFs for the tested fuels in this 268 study were at a similar level compared with the data obtained 269 from a study on the coal burning emission from the industrial 270 boiler and power plant boiler (Cui et al., 1993). Also, both the 271 10-PAH EFs and BaP EFs were much higher in the emission 272 from the residential stoves than those from the industrial 273 boiler, regardless of the fuel types, which was because the 274 precipitation systems installed after the industrial boiler can 275 effectively precipitate the emitted dust. Another reason is that 276 the oxygen supply during the burning process of a residential 277 stove is much more insufficient than that of a boiler, which 278 leads to much higher amounts of incomplete combustion 279 byproducts such as PAHs. Additionally, Shen et al. (2013) 280 reported that the PAH EFs of wood pellet burning were lower 281 than those of straw pellets, which was similar to the result 282 obtained in this study. 283

2.2. PAH diagnostic ratio

284

A number of PAH diagnostic ratios, including FLA/(FLA + PYR), 285 BaA/(BaA + CHR), IcdP/(IcdP + BghiP) and BbF/(BbF + BkF) 286 (FLA, PYR, BaA, CHR, IcdP, BghiP, BbF, and BkF refer to 287 Table 3), are often used as source-specific indicators for PAH 288 source identification (Watson, 1984; Yunker et al., 2002; 289 Galarneau, 2008; Katsoyiannis et al., 2007; Zhang et al., 2008). 290 For example, it was reported that IcdP/(IcdP + BghiP) larger 291 than 0.5 indicated emission from coal combustion, while 292 a ratio smaller than 0.5 indicated petroleum combustion 293 (Yunker et al., 2002). Four frequently-used PAH diagnostic 294 ratios were calculated and shown in Table 6, compared with 295 some results from the literature. Each of the four PAH 296 diagnostic ratios showed similar levels for wood pellets and 297 straw pellets in this study, and similar characteristics were 298 also found in Shen et al. (2013). However, the ratios of 299 IcdP/(IcdP + BghiP) for both wood pellets and straw pellets 300 were lower than those of the reference data in Table 6 for the 301 two biomass fuels, which were at a similar level compared to 302 the value for coal in this study. Therefore, IcdP/(IcdP + BghiP) 303 can probably be used as one of the reference indicators to 304 discriminate between the exhausts of industrial boilers and 305



Fig. 1 - Correlation of benzo(a)pyrene emission factors (BaP EFs) with the total polycyclic aromatic hydrocarbon (PAH) EFs.

Please cite this article as: Yang, X., et al., Characteristics of particulate-bound polycyclic aromatic hydrocarbons emitted from industrial grade biomass boilers, J. Environ. Sci. (2015), http://dx.doi.org/10.1016/j.jes.2015.09.010

IOURNAL OF ENVIRONMENTAL SCIENCES XX (2015) XXX-XXX

Table 5 – Comparis	on of PAH emission factors (EFs) with some	e reported	values.		
Boiler/stove	Fuel	Size	PAH EF	s (mg/kg)	References
			10-PAH	BaP	
BB1	Wood pellet	PM_{10}	0.0231	0.0009	This study
BB1	Straw pellet	PM_{10}	0.0064	0.0004	
BB2	Wood pellet	PM_{10}	0.0380	0.0012	
CB	Bituminous coal	PM_{10}	0.0128	0.0006	
Industrial boiler	Blended bituminous coal	PM _{2.5}	-	0.0002-0.0097	Cui et al., 1993
Power plant boiler	Blended bituminous coal and coal briquette	PM _{2.5}	-	0.0003	
Residential stove	Anthracite coal	PM _{2.5}	-	0.32-20	
Residential stove	Bituminous coal and honeycomb briquette	PM_{10}	69.00-160.00	1.05-2.46	Geng et al., 2014
Residential stove	Bituminous coal	TSP	398	34.9	Liu et al., 2009
Residential stove	Wood pellet	TSP	1.71	0.04	Shen et al., 2013
	Straw pellet	TSP	2.7	0.11	

10-PAH refers to the sum of FLA, PYR, BaA, CHR, BbF, BkF, BaP, IcdP, DahA and BghiP. TSP: total suspended particulate matter; PAH: polycyclic aromatic hydrocarbon; FLA: fluoranthene; PYR: pyrene; BaA: benz(a)anthracene; CHR: chrysene; BbF: benzo(b)fluoranthene; BkF: benzo(k)fluoranthene; BaP: benzo(a)pyrene; IcdP: indeno(1,2,3-cd)pyrene; DahA: dibenz(a,h)anthracene; BghiP: benzo(g,h,i)perylene.

residential stoves. Additionally, the diagnostic ratios for 306 the tested coal sample were generally comparable to those 307reported in Shen et al. (2011), although in our study FLA/ 308 (FLA + PYR) was a little higher than the maximum value in the 309 310 reference.

311 2.3. Potential toxicity risk

312 To assess the potential toxicity risk to ecosystems and human beings, a sum of 7 carcinogenic PAH components 313 $(\Sigma PAH_7, BaA, CHR, BbF, BkF, BaP, IcdP and DahA$ 314 (dibenz(a,h)anthracene)), BaP-equivalent carcinogenic power 315 (BaPE), and 2,3,7,8-tetrachlorodibenzodioxin (TCDD)-based 316 total toxicity potency (TEQ) have been utilized in many 317 studies (Cecinato, 1997; Larsen and Larsen, 1998; Bosveld et 318 al., 2002; Bhargava et al., 2004; Lu et al., 2008; Liu et al., 2009). 319 At the same time, PAHs are considered to be the main cause of 320 indirect-acting mutagenicity (Gibson, 1983; Durant et al., 321 1996). We had previously assayed the indirect-acting muta-322 genicities of PAHs by the Ames test (Yang et al., 2010), and the 323 results were used for the mutagenicity evaluation in this 324 study. The original parameters for the calculation are listed in 325Table 7 and the calculated results for the potential risk of 326 PAHs in the burning emissions of the tested fuels are listed in 327 Table 8. In addition, the values listed in Table 8 for BaPE, TEQ 328

and indirect-acting mutagenicities represent the results of 329 each PAH species multiplied by each corresponding EF value. 330 In this study, BB2 with wood pellets showed the highest 331 values of Σ PAH₇, BaPE, TEQ and indirect-acting mutagenic- 332 ities among the tested fuels, while BB1 with straw pellets 333 showed the lowest toxicities. The above result was consistent 334 with the PAH EFs for each fuel. In addition, compared with 335 data from some other reports (Chen et al., 2005, 2006; Geng et 336 al., 2014), the toxicity of the PAHs for the emission from the 337 industrial boilers is much lower than that from residential 338 stoves due to the much lower amount of PAH emission. 339 However, due to their long-term operation, the PAH emission 340 from industrial biomass boilers may still be more important 341 than that from residential stoves. 342

3. Conclusions

Using a dilution system, particulate samples from industrial 345 boiler combustion with two types of biomass fuels and coal 346 were collected to analyze for 10 kinds of PAHs. The total PAH 347 EFs for the tested coal-fired boiler were lower than the average 348 value for the biomass boilers, and the EFs for BB1 with wood 349 pellets were higher than that for BB1 with straw pellets. These 350 results might be due to the different volatile contents of the 351

Table 6 – PAH diagno	ostic ratios for the t	ested fuels.				
	This stu	dy (industrial boiler	s)	Refere	nces (residential sto	oves)
	Wood pellet ^a	Straw pellet ^b	Coal ^c	Wood pellet ^d	Straw pellet ^d	Coal ^e
FLA/(FLA + PYR)	0.46	0.52	0.76	0.56	0.54	0.32-0.70
BaA/(BaA + CHR)	0.41	0.43	0.36	0.36	0.40	0.27-0.56
IcdP/(IcdP + BghiP)	0.26	0.20	0.21	0.50	0.45	0.23-0.63
BbF/(BbF + BkF)	0.66	0.59	0.76	0.53	0.55	0.60–0.89

PAH: polycyclic aromatic hydrocarbon; FLA: fluoranthene; PYR: pyrene; BaA: benz(a)anthracene; CHR: chrysene; BbF: benzo(b)fluoranthene; BkF: benzo(k)fluoranthene; IcdP: indeno(1,2,3-cd)pyrene; BghiP: benzo(g,h,i)perylene.

^a Average values of BB1 and BB2 with wood pellet.

 $^{\rm b}\,$ Value of BB1 with straw pellet.

^d Shen et al., 2013.

^e Shen et al., 2011.

^c Value of coal-fired boiler (CB).

343

Please cite this article as: Yang, X., et al., Characteristics of particulate-bound polycyclic aromatic hydrocarbons emitted from industrial grade biomass boilers, J. Environ. Sci. (2015), http://dx.doi.org/10.1016/j.jes.2015.09.010

Table 7 – Parameters	for	the	toxicity	risk	evaluation	0
each PAH species.						

PAH	BaPE	TEQ	Indirect-acting mutagenicities [*] (revertant/mg)
FLA	-	0.00000001	1.8
PYR	-	-	<0.1
BaA	0.06	0.00001	2.0
CHR	-	0.0001	<0.1
BbF	0.07	-	7.8
BkF	0.07	-	3.8
BaP	1	0.0001	16.1
IcdP	0.08	-	0.8
DahA	0.6	0.0001	5.0
BghiP	-	0.0000001	0.3

BaPE: benzo(a)pyrene-equivalent carcinogenic power for PAHs (Cecinato, 1997); TEQ: total toxicity potency for PAHs, base on 2,3,7,8-tetrachlorodibenzo-dioxin (TCDD) in vitro assays (Bosveld et al., 2002); PAH: polycyclic aromatic hydrocarbon; FLA: fluoranthene; PYR: pyrene; BaA: benz(a)anthracene; CHR: chrysene; BbF: benzo(b)fluoranthene; BkF: benzo(k)fluoranthene; BaP: benzo (a)pyrene; IcdP: indeno(1,2,3-cd)pyrene; DahA: dibenz(a,h) anthracene; BghiP: benzo(g,h,i)perylene.

Indirect-acting mutagenicities of PAHs in vitro assays (Salmonella typhimurium TA100 strain with S9 mix) (Yang et al., 2010).

352 fuels, since high volatile content usually leads to incomplete 353 combustion, which results in more PAH emission. Compared 354 with the reference data, total PAH EFs were much higher in the emission of the residential stoves than those from the 355 industrial boilers whatever the fuel type, which was mainly 356 due to the installed precipitation systems for the industrial 357 boilers. The BaP concentration from the emission of the 358 studied biomass burning was 0.3 to 3.1 times higher than the 359 standard value (DB11/501-2007), indicating the environment 360 pollution risk of using industrial biomass boilers. Good 361 correlation between BaP EFs and the total PAH EFs was 362 observed, indicating the usefulness of BaP values for the 363 estimation of the total PAH amount. The investigated PAH 364 diagnostic ratio for both wood pellets and straw pellets 365 showed similar levels. However, the ratios of IcdP/ 366 (IcdP + BghiP) for the two biomass fuels in this study were 367

Table 8–Po fuels.	otential toxicity	y risk of	PAHs for	each tested
	BB1 wood pellet	BB1 straw pellet	BB2 wood pellet	CB bituminous
∑PAH ₇ (mg/k, BaPE [*] TEQ ^{**} Indirect-actin mutagenicitie (revertant/mg	g) 0.0084 0.0012 0.0003 1.6E-06 25 2)	0.0031 0.0005 0.0003 6.8E-07	0.0375 0.0026 0.0030 4.5E-06	0.0058 0.0008 0.0009 9.1E-07
∑PAH ₇ is the mutagenicitie PAHs in vitro PAHs: p benzo(a)pyrei	e sum of 7 carcin es are calculated assays. olycyclic ar ne-equivalent; TE d by BaPF	ogenic PAI by indirect omatic Q: total tox	H species; -acting mu hydroca sicity poter	indirect-acting utagenicities of rbon; BaPE ncy.

- alculated by BaPE
- Calculated by TEQ.

t8.17

lower than those of the reference data from residential stoves. 368 which can probably be used as an indicator for industrial 369 boiler and residential stove exhausts. Based on the toxic risk 370 calculation, the toxicity of the PAHs for the emission from the 371 industrial boilers was much lower than that from residential 372 stoves due to the much lower amount of PAH emission. 373

Acknowledgments

This work was supported by the National Natural Science 376 Foundation of China (Nos. 41105090, 41275135), the Interna- Q4 tional S&T Cooperation Program of China (No. 2012DFG90290), 378 the National High Technology Research and Development 379 Program (863) of China (No. 2012AA063506) and China 380 Ministry of Environmental Protection's Special Funds for 381 Scientific Research on Public Welfare (No. 20130916). 382

375

38.3

428

REFERENCES

Circumst. 13 (3), 317-324.

Ames, B.N., McCann, J., Yamasaki, E., 1975. Methods for	the c
detecting carcinogens and mutagens with the salmonella/	ŝ
mammalian-microsome mutagenicity test. Mutat. Res. 31 (6),	Ş
347–363.	ŝ
Araki, Y., Tang, N., Ohno, M., Kameda, T., Toriba, A., Hayakawa, K.,	ŝ
2009. Analysis of atmospheric polycyclic aromatic	ŝ
hydrocarbons and nitropolycyclic aromatic hydrocarbons in	ŝ
gas/particle phases separately collected by a high-volume air	Ş
sampler equipped with a column packed with XAD-4 resin.	ŝ
J. Health Sci. 55 (1), 77–85.	ŝ
Bamford, H.A., Baker, J.E., 2003. Nitro-polycyclic aromatic	ŝ
hydrocarbon concentrations and sources in urban and	Ş
suburban atmospheres of the Mid-Atlantic region. Atmos.	ŝ
Environ. 37 (15), 2077–2091.	ŝ
Bhargava, A., Khanna, R.N., Bhargava, S.K., Kumar, S., 2004.	ŝ
Exposure risk to carcinogenic PAHs in indoor-air during	4
biomass combustion whilst cooking in rural India. Atmos.	4
Environ. 38 (28), 4761–4767.	4
Bignal, K.L., Langridge, S., Zhou, J.L., 2008. Release of polycyclic	4
aromatic hydrocarbons, carbon monoxide and particulate	4
matter from biomass combustion in a wood-fired boiler under	4
varying boiler conditions. Atmos. Environ. 42 (39), 8863–8871.	4
Bosveld, A.T.C., de Bie, P.A.F., van den Brink, N.W., Jongepier, H.,	4
Klomp, A.V., 2002. In vitro EROD induction equivalency factors	4
for the 10 PAHs generally monitored in risk assessment studies	4
in the Netherlands. Chemosphere 49 (1), 75–83.	4
BP Statistical Review of World Energy, 2013. The Editor: BP	4
Statistical Review of World Energy, BP p.l.c, UK. bp.com/	4
statisticalreview.	4
Cecinato, A., 1997. Polycyclic aromatic hydrocarbons (PAH),	4
benz(a)pyrene (BaPY) and nitrated-PAH (NPAH) in suspended	4
particulate matter. Ann. Chim. 87, 483–496.	4
Chen, Y.J., Sheng, G.Y., Bi, X.H., Feng, Y.L., Mai, B.X., Fu, J.M., 2005.	4
Emission factors for carbonaceous particles and polycyclic	4
aromatic hydrocarbons from residential coal combustion in	4
China. Environ. Sci. Technol. 39 (6), 1861–1867.	4
Chen, Y.J., Zhi, G.R., Feng, Y.L., Fu, J.M., Feng, J.L., Sheng, G.Y., et	4
al., 2006. Measurements of emission factors for primary	4
carbonaceous particles from residential raw-coal combustion	4
in China. J. Geophys. Res. Let. 332 (20), L20815.	4
Cui, w.x., Yao, W.X., Xu, X.B., 1993. Emission regularity and	4
distribution characteristics of polycyclic aromatic	4
nydrocarbons from coal combustion sources. Acta Sci.	4

Please cite this article as: Yang, X., et al., Characteristics of particulate-bound polycyclic aromatic hydrocarbons emitted from industrial grade biomass boilers, J. Environ. Sci. (2015), http://dx.doi.org/10.1016/j.jes.2015.09.010

JOURNAL OF ENVIRONMENTAL SCIENCES XX (2015) XXX-XXX

429Durant, J.L., Busby Jr., W.F., Lafleur, A.L., Penman, B.W., Crespi, 430C.L., 1996. Human cell mutagenicity of oxygenated, nitrated and unsubstituted polycyclic aromatic hydrocarbons 431 432 associated with urban aerosols. Mutat. Res. 371 (3-4), 123-157. Dyke, P.H., Foan, C., Fiedler, H., 2003. PCB and PAH releases from 433 434 power stations and waste incineration processes in the UK. Chemosphere 50 (4), 469-480. 435Epstein, S.S., Fujii, K., Asahina, S., 1979. Carcinogenicity of a 436 composite organic extract of urban particulate atmospheric 437 438 pollutants following subcutaneous injection in infant mice. 439Environ. Res. 19 (1), 163-176. Galarneau, E., 2008. Source specificity and atmospheric processing 440 441 of airborne PAHs: implications for source apportionment. 442 Atmos. Environ. 42 (35), 8139-8149. GB/T212-2008, 2008. Proximate analysis of coal, State Bureau of 443Quality and Technical Supervision. 444 Geng, C.M., Chen, J.H., Wang, X.H., Yang, W., Yin, B.H., Liu, H.J., et 445 al., 2013. Comparative study on the particle emission 446 characteristics of biomass boiler with coal-fired industrial 447 boiler. Res. Environ. Sci. 26 (6), 666-671. 448 Geng, C.M., Chen, J.H., Yang, X.Y., Ren, L.H., Yin, B.H., Liu, X.Y., et 449 450al., 2014. Emission factors of polycyclic aromatic hydrocarbons 451 from domestic coal combustion in China. J. Environ. Sci. 26 (1), 160-166. 452453Gibson, T.L., 1983. Sources of direct-acting nitroarene mutagens in airborne particulate matter. Mutat. Res. Lett. 122 (2), 115-121. 454455Giechaskiela, B., Ntziachristosa, L., Samarasa, Z., Scheer, V., Casati, R., Vogt, R., 2005. Formation potential of vehicle 456exhaust nucleation mode particles onroad and in the 457laboratory. Atmos. Environ. 39 (18), 3191-3198. 458 459Guo, L.L., Wang, X.Y., Tao, G.C., Xie, G.H., 2012. Assessment of field crop process residues production among different provinces in 460China. J. China Agri. Univ 17 (6), 45-55. 461 462 Katsoyiannis, A., Terzi, E., Cai, Q.Y., 2007. On the use of PAH molecular diagnostic ratios in sewage sludge for the 463 464 understanding of the PAH sources. Is this use appropriate? 465Chemosphere 69 (8), 1337-1339. 466 Larsen, J.C., Larsen, P.B., 1998. Chemical carcinogens. In: Hester, R., Harrison, R. (Eds.), Air Pollution and Health. The Royal 467 468 Society of Chemistry, Cambridge, UK, pp. 33-56. Li, C.T., Mi, H.H., Lee, W.J., You, W.C., Wang, Y.F., 1999. PAH emission 469from the industrial boilers. J. Hazard. Mater. 69 (1), 1-11. 470 Liu, W.X., Dou, H., Wei, Z.C., Chang, B., Qiu, W.X., Liu, Y., et al., 471 472 2009. Emission characteristics of polycyclic aromatic hydrocarbons from combustion of different residential coals in 473 North China. Sci. Total Environ. 407 (4), 1436-1446. 474Lu, H., Zhu, L.Z., Chen, S.G., 2008. Pollution level, phase 475distribution and health risk of polycyclic aromatic 476hydrocarbons in indoor air at public places of Hangzhou. 477 China. Environ. Pollut. 152 (3), 569-575. 478479 Mathis, U., Ristimäki, J., Mohr, M., Keskinen, J., Ntziachristos, L.,

Samaras, Z., et al., 2004. Sampling conditions for the

480 533 measurement of nucleation mode particles in the exhaust of a 481 diesel vehicle. Aeros. Sci. Technol. 38 (12), 1149–1160. 482

- Olsson, M., Kjällstrand, J., 2006. Low emissions from wood burning 483 in an ecolabelled residential boiler. Atmos. Environ. 40 (6), 484 1148–1158. 485 Shen C.F. Wang W. Yang Y.F. Ding I.N. Yue M. Min Y.L. et al. 486
- Shen, G.F., Wang, W., Yang, Y.F., Ding, J.N., Xue, M., Min, Y.J., et al., 486
 2011. Emissions of PAHs from indoor crop residue burning in a 487
 typical rural stove: emission factors, size distributions, and gas-particle partitioning. Environ. Sci. Technol. 45 (4), 489
 1206–1212. 490
- Shen, G.F., Tao, S., Wei, S.Y., Zhang, Y.Y., Wang, R., Wang, B., et al., 491
 2012. Emissions of parent, nitro, and oxygenated polycyclic aromatic hydrocarbons from residential wood combustion in rural China. Environ. Sci. Technol. 46 (15), 8123–8130.
- Shen, G.F., Tao, S., Chen, Y.C., Zhang, Y.Y., Wei, S.Y., Xue, M., et al., 495
 2013. Emission characteristics for polycyclic aromatic 496
 hydrocarbons from solid fuels burned in domestic stoves in rural China. Environ. Sci. Technol. 47 (24), 14485–14494. 498
- Song, G.B., Che, L., Yang, Y.G., Lyakurwa, F., Zhang, S.S., 2014.499Estimation of crop residue in China based on a Monte Carlo500analysis. Chin. J. Popul. Res. Environ. 12 (1), 88–94.501
- Tao, S., Li, X.R., Yang, Y., Goveney, R.M., Lu, X.X., Chen, H.T., et al., 502
 2006. Dispersion modeling of polycyclic aromatic
 hydrocarbons from combustion of biomass and fossil fuels and
 production of coke in Tianjin. China. Environ. Sci. Technol. 40
 505
 (15), 4586–4591.
- Vaaraslahti, K., Virtanen, A., Ristimaki, J., Keskinen, J., 2004. 507
 Nucleation mode formation in heavy-duty diesel exhaust with 508
 and without a particulate filter. Environ. Sci. Technol. 38 (18), 509
 4884–4890. 510
- Watson, J.G., 1984. Overview of receptor model principles. J. Air511Pollut. Control Assoc. 34 (6), 619–623.512
- Yang, H.H., Lee, W.J., Chen, S.J., Lai, S.O., 1998. PAH emission from 513 various industrial stacks. J. Hazard. Mater. 60 (2), 159–174. 514
- Yang, X.Y., Igarashi, K., Tang, N., Lin, J.M., Wang, W., Kameda, T., 515 et al., 2010. Indirect- and direct-acting mutagenicity of diesel, 516 coal and wood burning-derived particulates and contribution 517 of polycyclic aromatic hydrocarbons and nitropolycyclic 518 aromatic hydrocarbons. Mutat. Res. 695 (1–2), 29–34. 519
- Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H.,
 Goyette, D., Sylvestre, S., 2002. PAHs in the Fraser River basin: a
 critical appraisal PAH ratios as indicators of PAH source and
 composition. Org. Geochem. 33 (4), 489–515.
- Zhang, Y.X., Schauer, J.J., Zhang, Y.H., Zeng, L.M., Wei, Y.J., Liu, Y., 524
 et al., 2008. Characteristics of particulate carbon emissions
 from real-world Chinese coal combustion. Environ. Sci.
 Technol. 42 (14), 5068–5073.
- Zhi, G.R., Chen, Y.J., Feng, Y.L., Xiong, S.C., Li, J., Zhang, G., et al., 528
 2008. Emission characteristics of carbonaceous particles from 529
 various residential coal-stoves in China. Environ. Sci. Technol. 530
 42 (9), 3310–3315. 531

532