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# Emission factors, ozone and secondary organic aerosol formation potential of volatile organic compounds emitted from industrial biomass boilers

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ABSTRACT

To evaluate the potential benefits of biomass use for air pollution control, this paper identified and quantified the emissions of major reactive organic compounds anticipated from biomass-fired industrial boilers. Wood pellets (WP) and straw pellets (SP) were burned to determine the volatile organic compound emission profiles for each biomass-boiler combination. More than 100 types of volatile organic compounds (VOCs) were measured from the two biomass boilers. The measured VOC species included alkanes, alkenes and acetylenes, aromatics, halocarbons and carbonyls. A single coal-fired boiler (CB) was also studied to provide a basis for comparison. Biomass boiler 1 (BB1) emitted relatively high proportions of alkanes (28.9%–38.1% by mass) and alkenes and acetylenes (23.4%–40.8%), while biomass boiler 2 (BB2) emitted relatively high proportions of aromatics (27.9%–29.2%) and oxygenated VOCs (33.0%–44.8%). The total VOC (TVOC) emission factors from BB1 (128.59–146.16 mg/kg) were higher than those from BB2 (41.26–85.29 mg/kg). The total ozone formation potential (OFP) ranged from 6.26 to 81.75 $mg/m^3$ with an average of 33.66 $mg/m^3$ for the two biomass boilers. The total secondary organic aerosol potential (SOAP) ranged from 61.56 to 211.67 $mg/m^3$ with an average of 142.27 $mg/m^3$ for the two biomass boilers. The emission factors (EFs) of TVOCs from biomass boilers in this study were similar to those for industrial coal-fired boilers with the same thermal power. These data can supplement existing VOC emission factors for biomass combustion and thus enrich the VOC emission inventory.


## Introduction

Biomass is considered to be a renewable energy source and is widely used in the world. As an energy source or an alternative to fossil-based feedstock, the usage of biomass has received much attention (Chen et al., 2017; Evtyugina et al., 2014; Limousy et al., 2013; Liu et al., 2008a; Kecorius et al., 2017; Wang et al., 2018; Xu et al., 2018; Yan et al., 2016). However, the emission characterizations of biomass fuel burning are still not well researched (Schauer et al., 2001; Xu et al., 2016; Zhang et al., 2013).

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Emissions from the combustion of biomass fuels comprise both gases and particles. These particles are defined as particulate matter (PM), and gases include carbon monoxide (CO), carbon dioxide ($CO_2$), oxides of nitrogen (NOx), volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs). These pollutants have significant adverse impacts on air quality and human health (Bari et al., 2010; Caseiro et al., 2009; Guo et al., 2004, 2006; Jin et al., 2005; Reche et al., 2012). VOCs in the atmosphere also play a significant role in the formation of secondary organic aerosol (SOA) and ground-level ozone ($O_3$) (Calvert, 1976; Duan et al., 2008; Johnson et al., 2006; Kansal, 2009; Shao et al., 2009). Increases in biomass combustion from a variety of use types, including domestic to large-scale power generation or heat generation, are likely to change the current air composition of the considered airshed. This change would have an impact on air quality, which may increase with time to an extent that is currently unknown.

In China, biomass burning has emitted large amounts of total volatile organic compounds (TVOCs). For example, biomass burning was estimated to contribute >50% of the total VOC emissions in the Chengdu-Chongqing Region of Western China (Bo et al., 2008; Zhang et al., 2009). The contribution of local biomass combustion to atmospheric VOCs was estimated at 14.3% at Xinken in the Pearl River Delta, China (Liu et al., 2008b). A recent estimate of ozone and SOA formation from anthropogenic VOC emissions in China showed that biomass stoves, paints used for industrial protection and buildings, and application of adhesives were key individual sources for ozone and SOA formation (Wu et al., 2017). Therefore, VOC emissions from biomass burning are considered significant and should not be neglected.

Biomass pelleting is an attractive approach as a crop residue processing method, as it can increase the heating values of biomass and make its transportation more convenient. Some studies have focused on the atmospheric pollutants emitted from residential biofuel stoves (Xu et al., 2016) and low-temperature water boilers (Kraszkiewicz et al., 2015). However, little research has been conducted regarding VOC emissions from pelletized biomass-fired industrial boilers. We selected two biomass-fired industrial boilers to study the emission characteristics of air pollutants, in addition to a single coal-fired industrial boiler for comparison. The emission factors of $PM_{10}$ and $PM_{2.5}$ have been published previously (Geng et al., 2013). In this article, the VOC emission concentrations, emission factors and chemical profiles, ozone formation potential (OFP) and secondary organic aerosol potential (SOAP) were analyzed. The results of this study are valuable for a better understanding of the VOC emission characteristics from biomass-fired industrial boilers. Furthermore, this study can supplement existing VOC emission factors for biomass combustion and thus enrich the VOC emission inventory.

## 1. Experiments

### 1.1. *Industrial boilers*

Two biomass-fired industrial boilers were selected. Biomass boiler 1 (BB1) was retrofitted from an oil combustion boiler, and Biomass boiler 2 (BB2) was originally designed for biomass combustion. A coal-fired industrial boiler (CB) with similar thermal power (1.4–2.1 MW) was also selected for comparison. Detailed information about these boilers is listed in Table S1. These boilers operated intermittently as determined by heat or hot water supply requirements. Under normal circumstances, the boilers were used throughout the entire winter season, or from about November 15 to March 15, with an average working time of approximately 10 hr per day.

### 1.2. *Fuel*

The biomass used in this study included wood pellets (WP) and straw pellets (SP) purchased from a market. The biomass pellets were cylinder-shaped with a diameter of 0.6–0.8 cm and a length of 3–5 cm. Bituminous coal (BC) originated from Datong, Shanxi Province, China. The proximate and elemental analyses were conducted in the China Coal Research Institute, according to the Chinese national standard methodologies (GB212-91) using an Elemental Analyzer (CE-440, Exeter Analytical Inc., USA). Analytical results are shown in Table S2. Compared with coal, biomass has a higher proportion of volatile compounds and oxygen, and lower fixed carbon, heating values, carbon and sulfur content.

### 1.3. *Sampling system*

A dilution system (FPS 4000, Dekati Ltd., Finland) was employed to extract and dilute the flue gas in this study. The dilution sampling system has been reported in detail elsewhere (Geng et al., 2013; Yang et al., 2016) and is briefly summarized here. The design of two-stage dilution in this system can decrease the temperature of flue gas from above 100°C to the ambient air temperature (approximately 20°C). The dilution ratio was controlled at 14–20 during the sampling.

After dilution, the sample gas was collected in two ways. For non-methane volatile organic compounds (NMVOCs), the gas sample was collected into a silanized stainless steel canister (3.2 L, Entech Corporation, USA). A flow-limiting valve was used for constant-speed sampling, and the sampling time was 20 min. A particle filter was added before the flow-limiting valve. For the carbonyl compounds, a gas sample was collected in two silica cartridges in serial connection coated with 2,4-dinitrophenylhydrazine (DNPH) (Agela Technologies, China) at a flow rate of approximately 1 L/min. A KI ozone scrubber was added before the DNPH-silica cartridges to prevent interference from ozone (Wang et al., 2011).

### 1.4. *VOC analysis*

Canister samples were concentrated using a cryogenic pre-concentrator (Model 7100, Entech Instruments, Inc., CA) and then analyzed by a GC system (HP-7890A, Hewlett Packard Co., USA) equipped with a quadrupole MS detector (MSD, HP-5975C, Hewlett Packard Co., USA) and an FID. Carbonyl compounds collected in the DNPH cartridges were eluted with 5 mL of acetonitrile (ACN) and then analyzed by high-pressure liquid chromatography (HPLC) using a Diamonsil C18 column (150 mm × 4.6 mm, 5 μm) with a UV detector. Detailed information on the VOC analysis has been reported in several previous studies (Liu et al., 2008c; Wang et al., 2010; Wang et al., 2013; Yuan et al., 2010).

This study applied an internal standard method for GC/MS quantification of VOCs, and the $R^2$ values for calibration curves were >0.99 for all VOC compounds. TO-15 and PAMs were used as standard gases.

In total, more than 100 VOC species were quantified in this study. Based on functional groups, we classified these VOC species into five categories: alkanes (including cycloalkanes), alkenes and acetylenes, oxygenated VOCs, aromatics and halogenated hydrocarbons. The various VOC species quantified in this study are listed in Table 1.

### 1.5. Estimation of OFP and SOAP

To evaluate the capacity of the identified VOCs to produce $O_3$ and SOA, the ozone formation potential (OFP) and secondary organic aerosol potential (SOAP) were used (Dong et al., 2014; Mo et al., 2017; Yan et al., 2017). The OFP (mg/m$^3$) and SOAP (mg/m$^3$) are calculated using the following equations:

$$\mathrm{OFP} = \sum_{i=1}^{n} C_i \times \mathrm{MIR}_i \quad (1)$$

where *Ci* (mg/m$^3$) is mass concentration of species i and MIRi is the maximum incremental reactivity (MIR) value of species i, as cited by Carter (2008, 2010).

$$\mathrm{SOAP} = \sum_{i=1}^{n} C_i \times \mathrm{SOAP}_i \quad (2)$$

where *Ci* (mg/m$^3$) is mass concentration of species i and SOAPi is the SOA formation potential value of species i, as cited by Derwent et al. (2010).

## 2. Results and discussion

### 2.1. VOC emission concentrations

The concentrations of total VOCs (TVOCs) emitted from biomass-fired and coal-fired industrial boilers were calculated. The TVOC concentrations of BB1 (WP: 24.58 mg/m$^3$; SP: 13.09 mg/m$^3$) were higher than those of BB2 (WP:2.01 mg/m$^3$; SP:3.81 mg/m$^3$) and CB (DT: 11.99 mg/m$^3$). Details of each VOC species can be found in Fig. 1. The VOC species resulting from biomass burning were mainly C2–C4 alkanes, alkenes, acetylenes, and oxygenated VOCs as well as aromatics. Methyl

**Table 1 – The VOC species quantified in this study.**

| No | Alkanes (28) | No | Alkenes & acetylenes (15) | No | Aromatics (16) | No | Oxygenated VOC(23) | No | Halocarbons(25) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Ethane | 29 | Ethylene | 44 | Benzene | 60 | Formaldehyde | 83 | CCl2F2 |
| 2 | Propane | 30 | Propene | 45 | Toluene | 61 | Acetaldehyde | 84 | CHClF2 |
| 3 | i-Butane | 31 | 1-Butene | 46 | Ethylbenzene | 62 | Acrolein | 85 | C2Cl2F4 |
| 4 | n-Butane | 32 | iso-Butene | 47 | m/p-Xylene | 63 | Acetone | 86 | CH3Cl |
| 5 | i-Pentane | 33 | 1,3-Butadiene | 48 | o-Xylene | 64 | Propanal | 87 | CH3Br |
| 6 | n-Pentane | 34 | trans-2-Butene | 49 | Styrene | 65 | Crotonaldehyde | 88 | CH3CH2Cl |
| 7 | 2,2-Dimethylbutane | 35 | cis-2-Butene | 50 | i-Propylbenzene | 66 | Methyl vinyl Ketone | 89 | CCl3F |
| 8 | 2,3-Dimethylbutane | 36 | 3-Methyl-1-butene | 51 | n-Propylbenzene | 67 | Methacrolein | 90 | C2Cl3F3 |
| 9 | 2-Methylpentane | 37 | 1-Pentene | 52 | m-Ethyltoluene | 68 | 2-Butanone | 91 | 1,1-Dichloroethene |
| 10 | Cyclopentane | 38 | trans-2-Pentene | 53 | p-Ethyltoluene | 69 | Butanal | 92 | CH2Cl2 |
| 11 | 3-Methylpentane | 39 | 2-Methyl-1-butene/cis-2-Pentene | 54 | 1,3,5-Trimethylbenzene | 70 | Benzaldehyde | 93 | 1,1-Dichloroethane |
| 12 | n-Hexane | 40 | 2-Methyl-2-butene | 55 | o-Ethyltoluene | 71 | i-Valeraldehyde | 94 | CHCl3 |
| 13 | 2,4-Dimethylpentane | 41 | 1-Hexene | 56 | 1,2,4-Trimethylbenzene | 72 | Valeraldehyde | 95 | 1,1,1-Trichloroethane |
| 14 | Methylcyclopentane | 42 | Ethyne | 57 | 1,2,3-Trimethylbenzene | 73 | o-Tolualdehyde | 96 | CCl4 |
| 15 | 2-Methylhexane | 43 | Isoprene | 58 | m-Diethylbenzene | 74 | m,p-Tolualdehyde | 97 | C2HCl3 |
| 16 | 2,3-DimethylPentane | | | 59 | p-Diethylbenzene | 75 | Hexanal | 98 | 1,2-Dichloropropane |
| 17 | Cyclohexane | | | | | 76 | 2,5-Dimethylbenzaldehyde | 99 | CHCl2Br |
| 18 | 3-Methylhexane | | | | | 77 | Heptanal | 100 | trans-1,3-Dichloropropene |
| 19 | 2,2,4-Trimethylpentane | | | | | 78 | Octanal | 101 | 1,1,2-trichloroethane |
| 20 | n-Heptane | | | | | 79 | Nonanal | 102 | C2Cl4 |
| 21 | Methylcyclohexane | | | | | 80 | Decanal | 103 | Chlorobenzene |
| 22 | 2,3,4-Trimethylpentane | | | | | 81 | Glyoxal | 104 | CHBr3 |
| 23 | 2-Methylheptane | | | | | 82 | Methylglyoxal | 105 | m-Dichlorobenzene |
| 24 | 3-Methylheptane | | | | | | | 106 | p-Dichlorobenzene |
| 25 | n-Octane | | | | | | | 107 | o-Dichlorobenzene |
| 26 | n-Nonane | | | | | | | | |
| 27 | n-Decane | | | | | | | | |
| 28 | n-Undecane | | | | | | | | |

chloride, a typical species that results from biomass burning (Liu et al., 2008a), was also detected in all samples.

Fig. 2 shows the proportions of five categories of VOCs emitted from straw, wood biomass and coal combustion in industrial boilers. The proportions of alkanes and alkenes and acetylenes in VOC emissions from BB1 were 28.9%–38.1% and 23.4%–40.8%, respectively. These values were higher than those from BB 2 (13.6%–20.2% for alkanes and 4.5%–6.2% for alkenes and acetylenes). High proportions of alkanes and alkenes and acetylenes in VOC emissions indicated insufficient oxidation of volatile components released from the fuel. In contrast, BB2 emitted relatively high proportions of aromatics (27.9%–29.2%) and oxygenated VOCs (33.0%–44.8%). For the coal-fired industrial boiler, the proportions of VOC categories were similar to those of the two biomass boilers.

The major chemical species detected in this study are comparable to those identified in earlier studies. Wang et al. (2009) observed a high percentage of alkenes and alkynes and aromatics in VOC emissions from biomass burning in cooking stoves (24.3%–25.2% and 39.1%–49.9%, respectively). Wang et al. (2013) studied the emissions from straw pellets in residential stoves, and found high proportions of alkenes and alkynes (27.6%) and aromatics (14.4%). For aromatics, the value (4.7%–10.6%) in our study on biomass boilers was lower than those in the studies cited above. Combustion efficiency was significantly affected by combustion conditions, such as fuel density, oxygen supply, combustion temperature, and other factors (Chen et al., 2017; Wang et al., 2005). For BB1, the excess air coefficients were 5.36 (WP) and 3.72 (SP) (Geng et al., 2013) respectively, which was more than twice the regulatory value of 1.8 (DB11/501-2007). High excess air coefficients suggest that excessive air entered the furnace and was emitted into the atmosphere, which would decrease the temperature in the furnace, and result in the loss of a large amount of heat. For BB2, the excess air coefficients were 1.76 (WP) and 1.87 (SP) (Geng et al., 2013) respectively, which were similar to the regulatory values. Thus, the high proportions of alkanes and alkenes and acetylenes in VOC emissions from BB1 are likely to be due to the relatively low temperature in the furnace. The design of the boiler should be improved to be more appropriate for biomass fuel combustion with high volatile matter content.

### 2.2. Emission factors

The total VOC emission factors of BB1 (128.59 mg/kg for WP, 146.16 mg/kg for SP) were much higher than those of BB2 (41.26 mg/kg for WP, 85.29 mg/kg for SP). Sixty important VOC species, listed in Table S3, accounted for more than 90% of the total VOC emission factors. The most abundant species included ethane, propane, i-pentane, ethylene, propene, ethyne, benzene, toluene, formaldehyde, acetaldehyde, and acetone. The major chemical species detected in this study were similar to those found in earlier studies. Liu et al. (2008a) observed high percentages of ethylene, propylene, ethane, propane, benzene, and toluene in the air 1 m downwind of the chimney of a typical residential stove, which used biomass fuel, at a Chinese farmer's house. Wang et al. (2009) observed high percentages of benzene, propylene, acetone, toluene, and acetaldehyde for different biofuel-stove combinations, and the contribution of each species varied from 6.5% ± 7.3% to 17.3% ± 8.1%. Schauer et al. (2001)

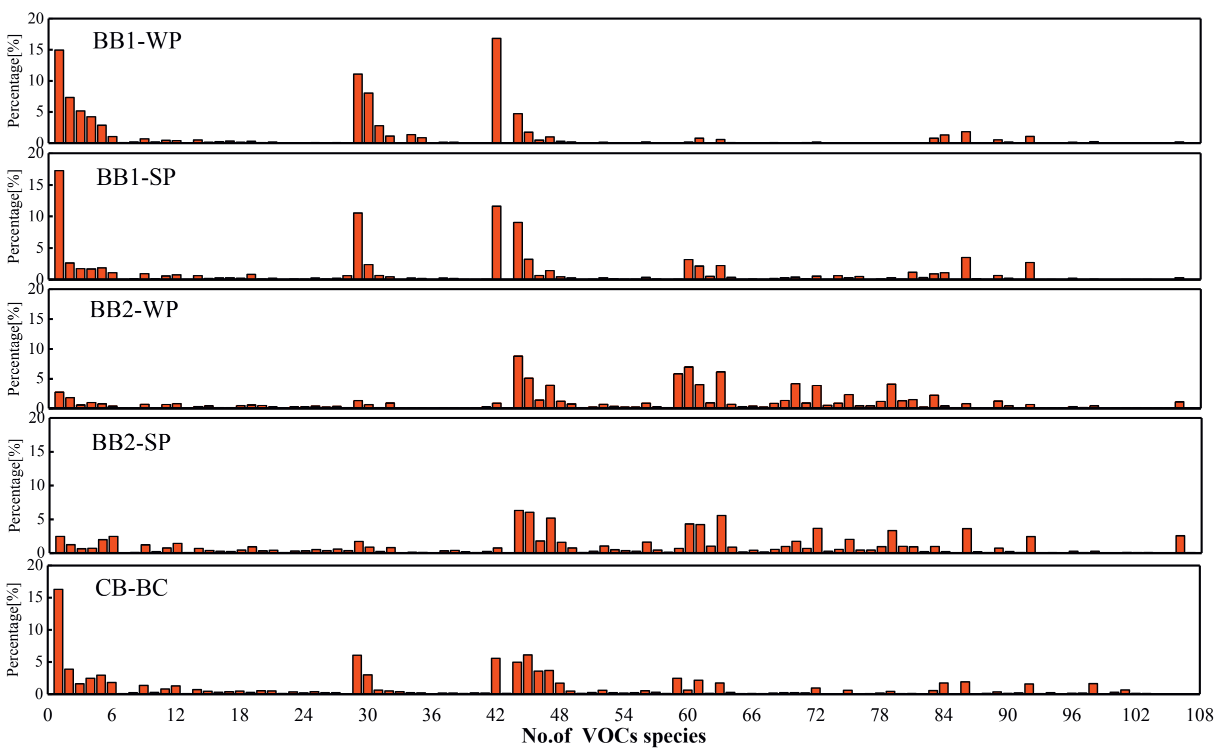


**Fig. 1 – VOC source profiles from biomass-fired and coal-fired industrial boilers.**

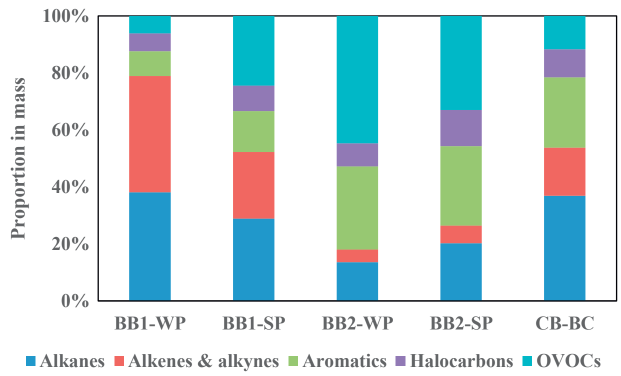


**Fig. 2 – Mass proportions of VOCs emitted from biomass and coal combustion in industrial boilers.**

reported the abundance of acetaldehyde, formaldehyde, ethylene, acetylene, acetone, glyoxal, methylglyoxal, benzene, and naphthalene in flue gas from the fireplace combustion of pine wood.

Some compounds such as benzene, ethylene, and acetylene are often used as tracers for motor vehicle exhaust in the urban atmosphere (Haszpra and Szilagyi, 1994; Kansal, 2009). However, the chemical profiles of VOCs emitted from biomass burning in our study and other previous studies (Liu et al., 2008a; Wang et al., 2005; Zhang et al., 2013) have proven that biomass burning also contributed to the ambient concentrations of benzene, ethylene, and acetylene. Furthermore, the contribution of vehicle emission to ambient VOCs would be overestimated if emissions related to biomass burning are not included.

Since only three boilers were analyzed in this study, we compared the emission factors calculated from this study with those of previous publications in Table 2. EFs of TVOC from the biomass boilers in this study were higher than those from a power station boiler, were similar to an industrial coal boiler, and were lower than residential coal stoves and biomass stoves.

### 2.3. OFP and SOAP for VOCs

OFP and SOAP were calculated for each boiler to evaluate the environmental impact of the combustion processes. Tables 3 and 4 list the top 10 compounds that had the greatest effect on $O_3$ and SOA formation. The OFP of the top 10 compounds accounted for more than 64% versus total compounds, while the proportion was more than 95% for SOAP.

The total OFP ranged from 6.26 to 81.75 mg/m$^3$ with an average of 33.66 mg/m$^3$ for the two biomass-fired industrial boilers. Alkenes and aldehydes were major components for BB1, while aldehydes and aromatic hydrocarbons were major components for BB2. The difference between these two biomass boilers may be due to variations in boiler combustion efficiency. As illustrated above, for BB2, the high combustion efficiency led to sufficient burning, so that low-molecular-weight compounds were combusted instead of discharging from the stack. The total OFP for the tested coal-fired industrial boiler was similar to the average value of the biomass boilers.

The total SOAP ranged from 61.56 to 211.67 mg/m$^3$ with an average of 142.27 mg/m$^3$ for the two biomass boilers. The alkenes and aldehydes were major components for both boilers. The total SOAP for the tested coal-fired industrial boiler was 1.84 times higher than the average value of biomass-fired industrial boilers.

### 2.4. Diagnostic ratio

Burning of biomass is known to give off large amounts of ethyne, ethylene, ethane, propene, propane, isoprene, 1-butene, benzene, toluene, m/p-xylene, aldehydes, and various other organics (Carmichael et al., 2003; Liu et al., 2008a; Zhang et al., 2013). These compounds have different reaction activities and life spans and various sources. Ratios of two VOC species have commonly been used to identify the VOC sources and chemical evolution (Parrish et al., 2007; Yuan et al., 2012a, 2012b). For example, the values of ethylene/ethyne, m, p-xylene/ethylbenzene, and toluene/benzene have been used to determine the differences in chemical impact between sampling sites or sampling time (Liu et al., 2008a; Mo et al., 2017), while the values of ethyne/ethane and benzene/propane have been used to identify the biomass burning source (Guo et al., 2011; Wang et al., 2005).

Five frequently used diagnostic ratios were calculated (Table 5) and compared with certain results from the literature. These ratios reflect emission ratios of the two individual VOCs in the source region. Each of the five diagnostic ratios showed similar levels for wood pellets and straw pellets in this study. In previous studies the ratios of VOCs varied within a large range, such as ethyne/ethane from 0.21 (sugarcane leaves, in a laboratory biomass burning simulation system) (Zhang et al., 2013) to 3.82 (wheat, in a typical residential stove component)

**Table 2 – Comparison of TVOC EFs in this study with previous studies.**

| | Fuel | TVOC EFs [mg/kg] | Reference |
|---|---|---|---|
| Biomass boiler | Wood pellet | 41.40–147.44 | This study |
| Biomass boiler | Straw pellet | 86.07–131.85 | This study |
| Industrial boiler | Datong bituminous coal | 152.27 | This study |
| Industrial boiler | Coal | 40.00 | Wei (2009) |
| Power station boiler | Coal | 20.00 | Wei (2009) |
| Hot water boiler | Coal | 570.00 | Wei (2009) |
| Residential stove | Coal | 4500.00 | Wei (2009) |
| Residential stove | Crop | 5380.00 | Tian et al. (2011) |
| Residential stove | Wood | 1920.00 | Tian et al. (2011) |
| Residential stove | Biomass | 180.00–26,570.00 | Wei (2009) |
| Open burning | Crop | 7000.00 | Tian et al. (2011) |
| Forest fire | / | 6900.00 | Tian et al. (2011) |
| Open burning | Crop | 15,700.00 | Streets et al. (2003) |

**Table 3 – Top 10 VOC species contributing to ozone formation.**

| | OFP from top 10 VOCs species (mg/m$^3$) | | | | | OFP from total VOCs species (mg/m$^3$) | Sum(top10)/ Total |
|---|---|---|---|---|---|---|---|
| BB1-WP | Ethylene | Propene | 1-Butene | trans-2-Butene | Ethyne | 81.75 | 85.83% |
| | 23.55 | 22.10 | 6.41 | 4.81 | 3.77 | | |
| | cis-2-Butene | m/p-Xylene | Iso-Butene | Toluene | i-Butane | | |
| | 2.89 | 1.82 | 1.68 | 1.64 | 1.50 | | |
| BB1-SP | Ethylene | Formaldehyde | Propene | Glyoxal | Acetaldehyde | 34.15 | 76.67% |
| | 10.87 | 3.44 | 3.17 | 1.65 | 1.61 | | |
| | Toluene | Ethyne | m/p-Xylene | Benzene | 1-Butene | | |
| | 1.47 | 1.26 | 1.26 | 0.75 | 0.71 | | |
| BB2-WP | Formaldehyde | m/p-Xylene | Acetaldehyde | p-Diethylbenzene | Toluene | 6.26 | 70.58% |
| | 1.29 | 0.59 | 0.51 | 0.50 | 0.40 | | |
| | Glyoxal | Ethylene | Acetaldehyde | o-Xylene | Butanal | | |
| | 0.36 | 0.23 | 0.20 | 0.18 | 0.15 | | |
| BB2-SP | Formaldehyde | m/p-Xylene | Acetaldehyde | Toluene | Ethylene | 12.48 | 64.44% |
| | 1.59 | 1.58 | 1.08 | 0.94 | 0.61 | | |
| | 1,2,4-Trimethylbenzene | o-Xylene | Glyoxal | Propene | Acetaldehyde | | |
| | 0.56 | 0.48 | 0.46 | 0.41 | 0.35 | | |
| CB-BC | Ethylene | Propene | m/p-Xylene | Toluene | Acetaldehyde | 34.51 | 68.28% |
| | 6.30 | 4.05 | 3.32 | 2.82 | 1.63 | | |
| | o-Xylene | Ethylbenzene | p-Diethylbenzene | 1-Butene | Formaldehyde | | |
| | 1.52 | 1.26 | 1.26 | 0.71 | 0.68 | | |

(Liu et al., 2008a) and ethyne/propane from 0.80 (sugarcane leaves, in a laboratory biomass burning simulation system) (Zhang et al., 2013) to 8.3 (dry grass, from an open fire) (Wang et al., 2005). The average ratios of ethane/propane (4.44) and toluene/benzene (10.09) in this study were higher than those in previous biomass burning studies. Compared with ambient air in some cities, these ratios from biomass burning were relatively higher overall; that is, the fresh fumes from biomass burning contained abundant reactive compounds. These ratios may help to identify biomass burning; however, the ratios of a single pair of VOCs are not enough to identify biomass burning, and further study is needed.

**Table 4 – Top 10 VOC species contributing to secondary organic aerosol.**

| | SOAP from top 10 VOCs species (mg/m$^3$) | | | | | SOAP from total VOCs species (mg/m$^3$) | Sum(top10)/ Total |
|---|---|---|---|---|---|---|---|
| BB1-WP | Benzene | Toluene | m/p-Xylene | Ethylbenzene | Ethylbenzene | 211.67 | 95.59% |
| | 103.47 | 41.02 | 17.72 | 12.22 | 9.22 | | |
| | o-Xylene | Ethylene | m-Ethyltoluene | Propene | Benzaldehyde | | |
| | 6.58 | 3.40 | 3.25 | 3.03 | 2.42 | | |
| BB1-SP | Benzene | Toluene | m/p-Xylene | Benzaldehyde | Ethylbenzene | 187.48 | 96.04% |
| | 96.43 | 36.75 | 12.28 | 9.65 | 8.14 | | |
| | Styrene | o-Xylene | m-Ethyltoluene | Ethylene | n-Propylbenzene | | |
| | 6.13 | 4.71 | 3.12 | 1.57 | 1.28 | | |
| BB2-WP | Benzaldehyde | Benzene | Toluene | m/p-Xylene | Styrene | 61.56 | 97.36% |
| | 17.58 | 16.00 | 9.96 | 5.75 | 3.08 | | |
| | Ethylbenzene | o-Xylene | m-Ethyltoluene | p-Ethyltoluene | n-Propylbenzene | | |
| | 3.05 | 2.25 | 1.35 | 0.47 | 0.45 | | |
| BB2-SP | Toluene | Benzene | m/p-Xylene | Benzaldehyde | Ethylbenzene | 108.35 | 95.67% |
| | 23.62 | 22.86 | 15.33 | 14.72 | 7.85 | | |
| | Styrene | o-Xylene | m-Ethyltoluene | p-Ethyltoluene | 1,2,4-Trimethylbenzene | | |
| | 6.45 | 5.96 | 4.18 | 1.39 | 1.30 | | |
| CB-BC | Toluene | Benzene | Ethylbenzene | m/p-Xylene | o-Xylene | 261.6 | 96.39% |
| | 70.50 | 53.49 | 46.34 | 32.27 | 19.00 | | |
| | Styrene | m-Ethyltoluene | Benzaldehyde | n-Propylbenzene | o-Ethyltoluene | | |
| | 11.83 | 7.06 | 5.92 | 3.27 | 2.46 | | |

**Table 5 – Comparison of the VOC diagnostic ratios of biomass boiler plumes with previous studies.**

| Reference | Sampling type | Fuel | Diagnostic ratio | | | | |
|---|---|---|---|---|---|---|---|
| | | | Ethyne/ ethane | Ethyne/ propane | Benzene/ propane | Ethane/ propane | Toluene/ benzene |
| This study | Biomass boiler | Wooden pellet | 0.83 | 2.36 | 1.57 | 2.61 | 9.72 |
| | | Crop residue pellet | 0.57 | 4.27 | 2.41 | 6.28 | 10.46 |
| Zhang et al. (2013) | Biomass burning simulation system | Rice straw | 0.3 | 1.08 | 0.83 | 3.65 | 1.47 |
| | | Sugarcane leaves | 0.21 | 0.8 | 0.3 | 3.77 | 1.16 |
| Wang et al. (2005) | Open fire | Dry grass | – | 8.3 | 1.6 | – | – |
| Liu et al. (2008a) | Typical residential stove | Wheat | 3.82 | 6 | 3.57 | 1.57 | 0.28 |
| | | Corn | 0.64 | 1.6 | 1.8 | 2.5 | 0.78 |
| | | Wood | 1.33 | 4 | 2.13 | 3 | 0.53 |
| Wu et al. (2016) | Ambient air | / | 0.64 | 1.01 | 0.28 | 1.57 | 0.66 |
| Lyu et al. (2016) | Ambient air | / | 0.37 | 1 | 0.89 | 2.74 | 1.18 |
| Leuchner and Rappenglück (2010) | Ambient air | / | 0.12 | 0.09 | 0.14 | 0.75 | 2.68 |
| Na and Kim (2001) | Ambient air | / | – | – | 0.22 | 0.6 | 1.86 |

## 3. Conclusions

In this study, two types of biomass-fired industrial boilers were selected to determine the VOC emission concentrations, emission factors and chemical profiles. One coal-fired industrial boiler was also studied for comparison. More than 100 types of volatile organic compounds (VOCs) were quantified. The VOC species resulting from biomass burning were mainly C2–C4 alkanes, alkenes, acetylenes, and oxygenated VOCs as well as aromatics. The TVOC concentrations of biomass-fired industrial boilers were from 2.01 to 24.58 $mg/m^3$, while the TVOC emission factors were from 41.26 to 146.16 mg/kg. The average OFP was 33.66 $mg/m^3$ and the average SOAP was 142.27 $mg/m^3$ for the two biomass-fired industrial boilers. Five frequently used diagnostic ratios were calculated. The average ratios of ethane/propane (4.44) and toluene/benzene (10.09) were higher than those in previous biomass burning studies.

The quantities of VOC emissions from the biomass-fired industrial boilers in this study were similar to that of the coal-fired industrial boiler, rather than being cleaner. There are many types of biomass available in China, and biomass is widely used. Suitable combustion technology and instruments should be developed for use with different biomass species. Biomass burning is an important source for ambient VOCs and its usage should be well controlled.

The results obtained from this study are valuable for better understanding the VOC emission characteristics of biomass-fired industrial boilers and can provide a supplement to existing VOC emission factors for biomass-fired industrial combustion. The emission characteristics of various biomass types in different combustion instruments varied greatly. Further study is needed to perform more biomass burning tests to reduce the uncertainty.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jes.2019.03.012.

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