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# Energy Recovery and Emissions of PBDD/Fs and PBDEs from Co-combustion of Woodchip and Wastewater Sludge in an Industrial Boiler

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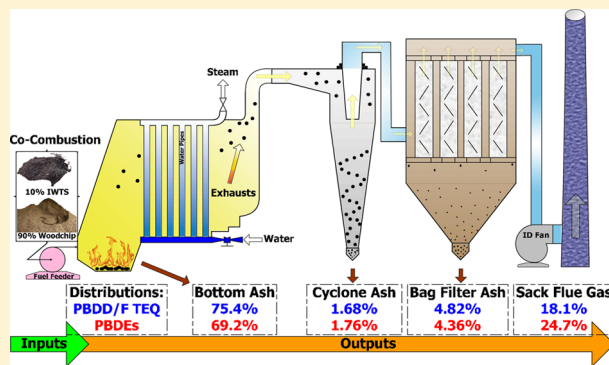
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## Supporting Information

**ABSTRACT:** The emissions of polybrominated dibenzo-*p*-dioxins, dibenzofurans (PBDD/Fs), and polybrominated diphenyl ethers (PBDEs) from trial combustion of 10 wt % dried industrial-wastewater-treatment sludge (IWTS) and 90 wt % woodchip in an industrial boiler were investigated and compared to that from woodchip combustion. The PBDD/F toxic equivalent (TEQ) and PBDE emissions increased from 0.121 pg TEQ Nm<sup>-3</sup> and 2260 pg Nm<sup>-3</sup>, respectively, of the woodchip combustion to 0.211 pg TEQ Nm<sup>-3</sup> and 4200 pg Nm<sup>-3</sup>, respectively, of the trial combustion. PBDD/F and PBDE congener profiles of inputs and outputs of the same type of combustion were similar; they also show similarity between woodchip and trial combustions, revealing that the destruction pathway was little affected by the introduction of the IWTS. The fates of PBDD/Fs and PBDEs show that the indigenous pollutants in the feed were effectively depleted (>93.5%). The dominant releasing route of PBDD/F and PBDE shifted from the stack flue gas of woodchip combustion to the ashes of trial combustion. This study demonstrates that co-combustion not only handles the fast growing sludge stream but also yields a saving of 26.3% in the fuel cost and treatment fees of sludge and ashes.



## 1. INTRODUCTION

The world is currently facing a significant increase of sludge<sup>1–3</sup> produced from municipal sewage wastewater<sup>2,3</sup> and industrial wastewater, such as paper mill factory,<sup>4</sup> petroleum and oil refinery industry,<sup>5</sup> and textile processing industry.<sup>6</sup> In Taiwan, the annual sludge growth rate by quantity is 19.5% from 2001 (0.947 million tons) to 2011 (2.79 million tons).<sup>7</sup> The conventional sludge disposals, such as land-fill and agricultural application, have many constraints owing to pathogenic contents, limited land capacity, and rapid urbanization. Meanwhile, sludge incineration has shaped into a main disposal technology, especially in developed regions, due to advantages such as fast volume reduction, pathogen and organic contaminants detoxification, and energy recovery.<sup>2</sup> However, incinerating high moisture containing sludge is energy consuming.

Usually, drying sludge relies on a fuel-burning furnace as a heat source, which is not an economic option. In an energy-tight

age, using waste heat from exhausts for sludge drying can be beneficial. The temperature of flue gas in boilers is around 100–200 °C, which is too low for generating electricity and is usually discharged into the ambient air directly. Therefore, there are some heat sources, such as exhausts of gas turbines, flue gases of biogas, landfill gas, and wood fuelled boiler, which have been proposed to be used in sludge drying.<sup>8,9</sup> Using the waste heat from flue gases of a woodchip fuelled boiler is feasible. In fact, the moisture content in the sludge could be reduced from 78% to less than 30% by this method.<sup>10</sup> The dried sludge then can be a substitute fuel for woodchip.

To further reduce the moisture content in the sludge, woodchip can be blended with the dried sludge. The fibers of

Received: July 2, 2013

Revised: September 10, 2013

Accepted: October 1, 2013



woodchip can help absorb the residue water in the dried sludge to allow easier separation and subsequent evaporation.

The disadvantage of sludge cocombustion is the emissions of inorganic pollutants such as heavy metals and organic pollutants including polycyclic aromatic hydrocarbons (PAHs)<sup>11,12</sup> and polychlorinated dibenzo-*p*-dioxin and dibenzofuran (PCDD/F).<sup>13</sup> De novo synthesis has been identified to be the major mechanism after combustion that occurs under certain temperature range via heterogeneous catalytic reactions to form PCDD/Fs. Heavy metals in sludge, such as Cu and Fe, could catalyze PCDD/F formations.<sup>14,15</sup> Besides the foresaid pollutants, concerns about the polybrominated dibenzo-*p*-dioxins/dibenzofurans (PBDD/Fs) and polybrominated diphenyl ethers (PBDEs) have recently increased since they were found in the stack flue gases of many combustion sources even though some of the feedstock contained no brominated flame retardants (BFRs).<sup>16–19</sup> Wang et al.<sup>18</sup> observed a highly correlated PBDE concentrations with PCDD/Fs in the above sources revealed that PBDEs are possibly generated through similar PCDD/F formation routes.

Belonging to the BFR family, PBDEs have been extensively used in furniture, electronic goods, and other consumer items. PBDEs are presumably released from the products and further enter waste streams. In wastewater treatment plants, PBDEs are easily sequestered on sludge to several thousand ppb ( $\mu\text{g kg}^{-1}$ ).<sup>20</sup> Once the PBDE contaminated sludge is burned under incomplete combustion, this may not only be an important route of PBDE environmental dispersal but be a precursor of PBDD/Fs.<sup>21–23</sup> PBDD/Fs are structurally similar with PCDD/Fs,<sup>14</sup> which may also form through two pathways: de novo synthesis after combustion and condensation directly from precursors. However, by thermal treatment (850–1200 °C) having great combustion condition, brominated aromatics are supposed to be destroyed, resulting in less PBDD/F emissions from precursor condensation. Meanwhile, there is no sufficient study providing clear formation mechanism or destruction pathway of PBDD/F and PBDE from combustion sources.

To date, there is no study characterizing the emissions of PBDD/Fs and PBDEs and their formation mechanisms from cocombustion of sludge with other fuel. In this study, the effects of cocombusting woodchip and industrial-wastewater-treatment sludge (IWTS) on the emissions of both PBDD/Fs and PBDEs from a boiler were assessed. The concentrations (or contents) of PBDD/Fs and PBDEs in the input and outputs and the boiler efficiency were measured for the following fuel schemes: woodchip combustion (scheme 1), and cofiring woodchip and IWTS loaded with PBDEs (scheme 2). The fates of both PBDD/Fs and PBDEs in the boiler between two fuel schemes were compared. With a better understanding of the characteristics of PBDEs and PBDD/Fs during the cofiring processes, appropriate control strategies to decrease their emissions from combustors can be developed.

## 2. MATERIALS AND METHODS

**2.1. Fuel Properties and Research Boiler.** The woodchip in this study is a high quality heating fuel from residues of sawmills. It was a mixed conifer (pines, firs, larch, hemlock, etc.) with a maximum chip size of 4 inches. The IWTS was collected from the discharge of a thin-film-transistor liquid-crystal-display (TFT LCD) production plant in southern Taiwan. IWTS generated from those processes is loaded with widely used BFRs and other brominated chemicals in TFT LCD production. After mechanical dewatering, the sludge was dried to moisture

content at about 20% by stack flue gas from a boiler. The dried sludge was further blended with the woodchip prior to trial combustion. Table 1 shows the exhaustive characterization of

**Table 1. Properties of Woodchip and IWTS**

property	woodchip	IWTS <sup>a</sup>
proximate anal. (wt %)		
moisture	6.08	1.17
ash	5.67	19.7
combustible	88.3	79.2
lower heating value ( $\text{MJ kg}^{-1}$ )	19.1	18.1
element anal. (wt %)		
C	50.1	42.6
H	7.00	2.79
O	41.8	38.1
N	0.140	14.8
S	0.014	1.36
Cl	ND	0.350
heavy metal ( $\text{mg kg}^{-1}$ )		
Cu	981	
Fe	3685	
PBDD/F TEQ ( $\text{ng TEQ kg}^{-1}$ )	0.0641	4.92
PBDEs ( $\text{ng kg}^{-1}$ )	5220	159 000

<sup>a</sup>Dry matter basis.

the woodchip and the IWTS (in dry matter basis). The mean gross heating value of the woodchip and IWTS were 19.1 and 18.1  $\text{MJ kg}^{-1}$ , respectively. IWTS had higher contents of ash, nitrogen, sulfur, chlorine, copper, and ferrum than woodchip.

The boiler was fuelled by woodchip for steam production at an hourly rate of 3.6 mt ( $\sim 3.5 \text{ MPa}/300^\circ\text{C}$ ). Two fuel schemes were designed, depending on the type of fuel to be combusted in the boiler, that is, the woodchip only (scheme 1) versus a mixture of 90 wt % woodchip and 10 wt % IWTS (scheme 2). Co-combustion of excessive sludge with coals and woodchips might cause slagging problem that results in reduced accessibility and performance of the combustion chamber.<sup>24,25</sup> Therefore, 10 wt % sludge blended ratio was chosen in this study according to the slagging is still acceptable at 8 wt % sludge blended with pellet wood.<sup>24</sup>

As seen in Table 2, their respective feeding rates were  $\sim 730 \text{ kg h}^{-1}$  and  $\sim 670 \text{ kg h}^{-1}$  for scheme 1 and scheme 2. These two combustion conditions were quite comparable in terms of the generated steam pressure (3.5 and 3.1 bar, respectively) and oxygen content in the stack flue gas ( $\sim 15\text{--}16\%$  for both). A cyclone and a bag filter (Figure S1, Supporting Information) were used as the air pollution control devices (APCDs) of the boiler. The output rates of bottom ash (BA), cyclone ash (CA), and bag filter ash (BFA) and the flow rate of stack flue gas were separately recorded and are listed in Table 2. As expected, scheme 2 showed a higher ash output rate than scheme 1.

**2.2. Sampling Procedures.** The boiler system had an automatic fuel feeder, and stack sampling was conducted after the combustor had reached steady state. A steady state is that the combustor air supply changes a little under a fixed boiler loading. Usually, it took half an hour to reach steady state after fuel switching. Stack flue gas samplings and chemical analyses in this study were carried out by an accredited laboratory for PCDD/F stack flue gas samplings and analyses in Taiwan. The stack flue gas was collected iso-kinetically following the U.S. EPA Modified Method 23,<sup>26</sup> using the Modified Method 5 sampling trains. The sampled flue gas volumes were normalized

**Table 2. Operating conditions of the boiler**

	scheme 1	scheme 2
feeding fuel	woodchip	90 wt % woodchip 10 wt % IWTS
fuel feeding rate (kg h <sup>-1</sup> )	730	670
Emission Rate		
stack flue gas (Nm <sup>3</sup> h <sup>-1</sup> )	214	209
bottom ash (kg h <sup>-1</sup> )	0.38	2.24
cyclone ash (kg h <sup>-1</sup> )	3.19	9.03
bag filter ash (kg hr <sup>-1</sup> )	3.41	4.51
Combustion Characteristics		
combustion temp. (°C)	850	800
temp. of stack (°C)	98.9	93.7
O <sub>2</sub> (%)	15.4–15.5	16.2–16.4
CO <sub>2</sub> (%)	5.4–5.5	4.6–4.8
CO (ppm)	500–570	550–600
boiler efficiency (%)	53.9	50.6
heat input (MJ h <sup>-1</sup> )	13 914	12 708
heat output (MJ h <sup>-1</sup> )	7497	6433
Steam pressure (bar)	3.5	3.1

to the dry condition of 760 mmHg and 273 K and denoted as Nm<sup>3</sup>. Simultaneous with the stack flue gas sampling, the feed fuels, BA, CA, and BFA were also sampled following the Minnesota 7035.2910 for municipal incinerator.<sup>27</sup> After magnetic removal of ferrous and nonferrous metals, glasses, and stones, the ashes were grounded to a diameter less than 1 mm and were homogenized. Feeding fuels (10 g), BA (5 g), and 2 g of both CA and BFA were taken for PBDD/F and PBDE analyses.

**2.3. Analytical Procedures.** Known amounts of surrogate standards (PBDD/Fs and PBDEs) were spiked in the glass cartridge prior to the stack flue gas sampling. Samples were analyzed for twelve 2,3,7,8-substituted PBDD/F and 30 PBDE congeners following the U.S. EPA Method 1613B<sup>28</sup> and U.S. EPA Method 1614,<sup>29</sup> respectively. Internal standards (<sup>13</sup>C-labeled PBDD/Fs and PBDEs) were spiked into the samples before Soxhlet extraction with toluene in order to monitor the extraction and cleanup processes. The detailed procedures were reported previously.<sup>16,19,30–32</sup> Briefly, the concentrated extract was treated with concentrated sulfuric acid, followed by a series of sample cleanup and fractionation steps. By using a multilayered silica column, an alumina column, and an activated carbon column (ACC), PBDD/Fs and PBDEs were fractionated sequentially in the ACC by toluene and toluene/methanol/ethyl acetate/hexane (5/5/10/80, v/v/v/v), respectively. The eluate was concentrated to approximately 1 mL and stored in a vial and refrigerated prior to analyses.

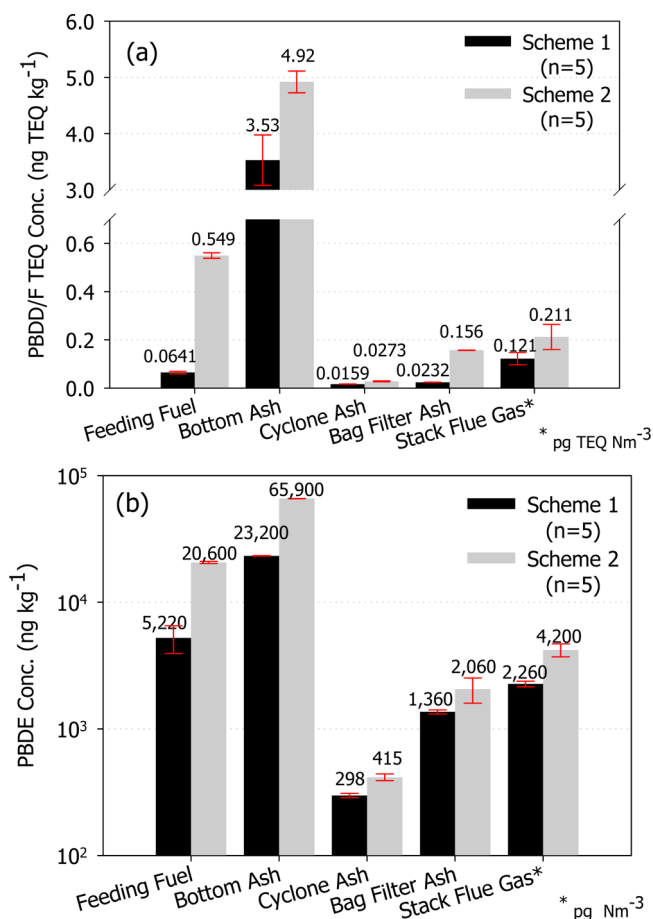
A high-resolution gas chromatograph/high-resolution mass spectrometer (HRGC/HRMS) was used for PBDD/F and PBDE analyses. For the PBDD/F analysis, the HRGC (Hewlett-Packard 6970 Series, CA, U.S.A.) was equipped with a DB-5MS fused silica capillary column ( $L = 60$  m, ID = 0.25 mm, and film thickness = 0.25  $\mu$ m) (J&W Scientific, CA, U.S.A.); for the PBDE analyses, a DB-5HT capillary column ( $L = 15$  m, ID = 0.25 mm, and film thickness = 0.25  $\mu$ m) (J&W Scientific, CA, U.S.A.) was used. Samples were injected in a splitless mode into HRGC/HRMS carried by helium gas. The HRMS (Micromass Autospec Ultima, Manchester, U.K.) was equipped with a positive electron impact (EI+) source. The analyzer mode of the selected ion monitoring (SIM) was used with a resolving power of 10 000. The electron energy and source temperature were specified at 35 eV and 250 °C, respectively. Details of the

analytical parameters of PBDEs and PBDD/Fs in the instruments were described previously.<sup>32,33</sup>

Field and laboratory blanks were carried out for each scheme. The mean total amounts of PBDD/Fs and PBDEs in the field blank samples were ND and 191 pg for the stack flue gas samples, respectively. The mean total amounts of PBDD/Fs and PBDEs in the laboratory blank samples were ND and 150 pg, respectively. All these blank samples were negligible (<5% of real samples) compared with the corresponding ash and stack flue gas samples. Recoveries of precision and recovery (PAR) and internal labeled standards of PBDD/Fs and PBDEs were within their corresponding criteria. Detailed descriptions are provided in our previous studies.<sup>16–18</sup>

### 3. RESULTS AND DISCUSSION

**3.1. PBDD/F and PBDE Characterizations in the Boiler System.** There are four routes for the boiler to release pollutants to the environment after fuel combustion, including BA, CA, BFA, and stack flue gas ( $n = 5$  for each unit). Figure 1



**Figure 1.** Concentrations of (a) PBDD/Fs and (b) PBDEs in scheme 1 and scheme 2.

shows the mean (total) PBDD/F toxic equivalent (TEQ) and PBDE concentrations/contents in the input and outputs, where the TEQ values of PBDD/Fs were calculated using the international toxic equivalency factors (I-TEF) of the corresponding PCDD/Fs.<sup>16,17,34</sup> The concentrations of each congener are listed in Tables S1 and S2 (Supporting Information). It should be noted that PBDEs were detected in the woodchip of this study, but it is in the low level of the pine



bark samples in US (989–922 000 ng kg<sup>-1</sup>).<sup>35</sup> The mean PBDD/F TEQ and PBDE contents in the fuel of scheme 2 (0.549 ng TEQ kg<sup>-1</sup> and 20 600 ng kg<sup>-1</sup>) were 85.6 and 3.95 times, respectively, higher than those of scheme 1. The significantly higher PBDD/F TEQ and PBDE contents in scheme 2 were contributed from the PBDE-contaminated IWTS (4.92 ng TEQ kg<sup>-1</sup> for PBDD/Fs and 159 000 ng kg<sup>-1</sup> for PBDEs).

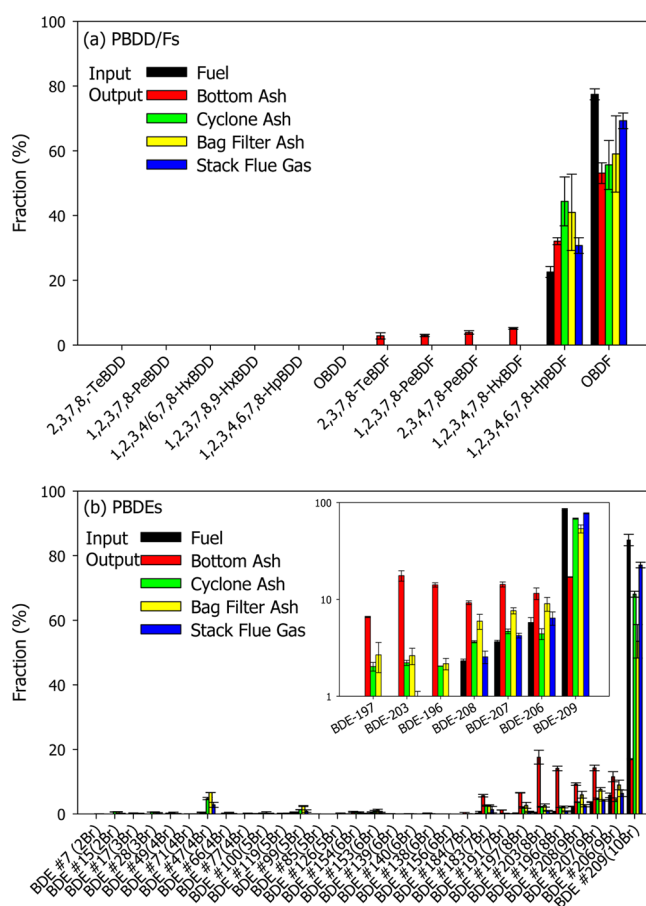
The PBDD/F TEQ and PBDE concentrations/contents in the outputs were higher for scheme 2 than for scheme 1, while both scheme 1 and scheme 2 exhibited similar trends of PBDD/F TEQ and PBDE contents in the ashes. BA contained the highest contents of PBDD/F TEQ and PBDEs for both schemes, but they dramatically decreased in the CA and BFA. The significantly higher PBDE contents in the BA compared to the feed for both schemes revealed that most of the PBDEs in the fuel were concentrated. The elevated PBDE levels in the output materials for scheme 2 compared to scheme 1 may be attributed to incomplete destruction through sludge cofiring because of their flame retardatory characteristic.

The mean total PBDD/F TEQ and PBDE concentrations in the stack flue gas were 0.121 pg TEQ Nm<sup>-3</sup> and 2260 pg Nm<sup>-3</sup>, respectively, for scheme 1, and the respective values were 0.211 pg TEQ Nm<sup>-3</sup> and 4197 pg Nm<sup>-3</sup> for scheme 2. The PBDD/F TEQ and PBDE concentrations in the stack flue gases of this study were lower than those generated by municipal waste incinerators (PBDD/Fs: 1.90–3.14 pg TEQ Nm<sup>-3</sup>; PBDEs: 26 100–109 000 pg Nm<sup>-3</sup>),<sup>17</sup> metallurgical processors (PBDD/Fs: 1.57–4.16 pg TEQ Nm<sup>-3</sup>; PBDEs: 15 700–35 200 pg Nm<sup>-3</sup>),<sup>16</sup> industrial waste incinerators (PBDEs: 26 800 pg Nm<sup>-3</sup>),<sup>18</sup> power plants (PBDEs: 47 200 pg Nm<sup>-3</sup>),<sup>18</sup> and vehicles (PBDEs: 29 100–46 700 pg Nm<sup>-3</sup>)<sup>18</sup> in Taiwan.

**3.2. PBDD/F and PBDE Congener Profiles in the Input and Output Materials.** Figures 2 and 3 show the congener profiles of PBDD/Fs and PBDEs in the inputs and outputs. Both fuels were similarly dominated by 1,2,3,4,6,7,8-HpBDF and OBDF for the PBDD/Fs and BDE-209, -206, and -207 for the PBDEs. However, the octa- and nona-BDE congeners had higher fractions in the feed for scheme 2 than scheme 1. Those higher PBDE congeners for scheme 2 were contributed from those in the PBDE contaminated IWTS.

The dominant PBDD/F and PBDE congeners of outputs for both schemes were almost similar to those of inputs. The congener profiles of ashes in this study were also generally similar to those of combustion-generated ashes.<sup>14,16,17</sup> First, the PBDD/F and PBDE congener profiles of inputs and outputs of the same scheme were very similar. Second, the comparison of the profiles in scheme 1 and scheme 2 also showed similarity. Both suggest that the PBDD/Fs and PBDEs in the outputs originated from the indigenous pollutants in the feed and decomposition pathways were little affected by the introduction of the IWTS. Only BAs showed a different pattern between the two schemes.

The fraction of BDE-209 in the BA of scheme 1 (17.0%) was significantly lower than that of scheme 2 (61.6%). A similar fractions among BDE-209 (10Br), -203 (8Br), -196 (8Br), -208 (9Br), and -207 (9Br) in the BA of scheme 1 reveals that BDE-209 was debrominated to lower brominated congeners, nona- and octa-BDEs. Factors such as temperature, hydrogen donor, and presence of water affect the debromination/hydrogenation reaction for PBDEs.<sup>22</sup> Generally, debromination reaction of PBDEs is much easier at high temperature and when hydrogen donors are present. Since the gas retention time (2 s)

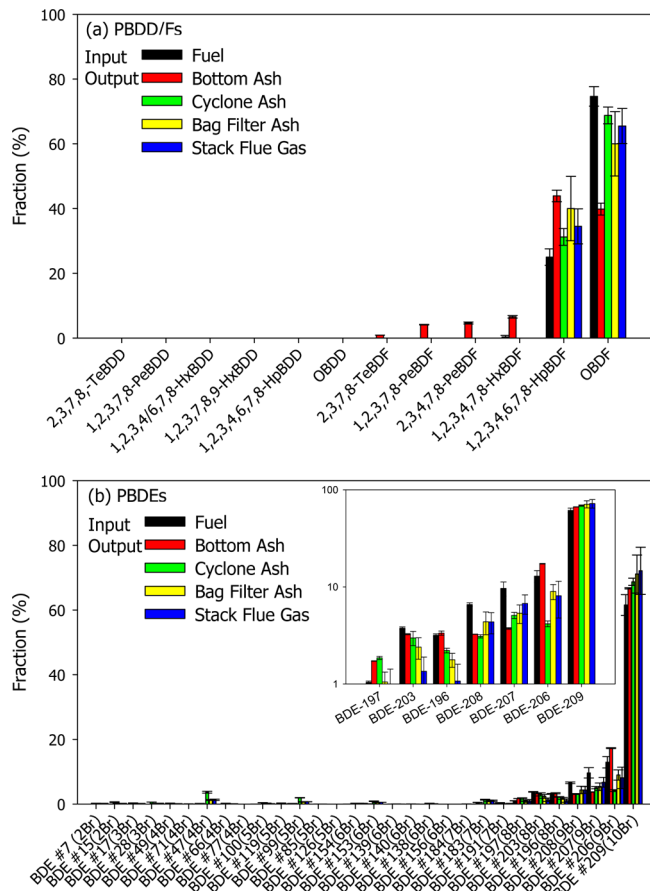


**Figure 2.** (a) PBDD/F and (b) PBDE congener profiles in the input and outputs in scheme 1.

and the feedstock retention time in the furnace of the boiler (about 15 min) are the same for both schemes, a lower PBDE debromination reaction is expected for scheme 2 owing to the lower combustion temperature and less hydrogen content of the feed compared to scheme 1.

As aforementioned, higher PBDE contents in the BA for both fuel schemes is attributed to incomplete PBDE destruction in the feeds. The detected PBDD/Fs in the outputs might come from incomplete destruction during combustion of input or form via pyrolysis and thermalysis of PBDE loaded IWTS in the boiler after combustion. However, Weber and Kuch<sup>22</sup> had reported that the formation of highly brominated substitute PBDD/Fs were not favorable from highly bromine-substituted PBDEs (e.g., BDE-209) due to “steric crowding”. Hanari et al.<sup>36</sup> reported that the abundant 1,2,3,4,6,7,8-HpBDF and OBDF in the ashes may be the impurities in the commercial deca-BDE mixture. PBDD/Fs is structurally similar to PCDD/Fs, so the formation may also be inhibited for scheme 2 by the higher sulfur content in IWTS than in woodchip.<sup>37,38</sup> Consequently, the elevated PBDD/F and PBDE contents in the output materials of both schemes are likely attributed to incomplete destruction of the indigenous compound in the fuels.

**3.3. Fates of PBDD/Fs and PBDEs in the Boiler.** Fates of both PBDD/Fs and PBDEs are evaluated by the input and output rates of masses and their corresponding toxicities, which are listed in Table 3. The PBDD/F TEQ and PBDE inputs were 46.8 ng TEQ h<sup>-1</sup> and 3970 μg h<sup>-1</sup>, respectively, for scheme 1 and 253 ng TEQ h<sup>-1</sup> and 13 800 μg h<sup>-1</sup>, respectively, for scheme 2. Sum of the outputs of PBDD/F TEQ and PBDEs from the



**Figure 3.** (a) PBDD/F and (b) PBDE congener profiles in the input and outputs in scheme 2.

industrial boiler were 3.03 ng TEQ h<sup>-1</sup> and 43.4 μg h<sup>-1</sup>, respectively for scheme 1 and 14.6 ng TEQ h<sup>-1</sup> and 213 μg h<sup>-1</sup>, respectively for scheme 2. The output-to-input (O/I) ratios of PBDD/Fs and PBDEs (Table 3) were smaller than unity for both fuel schemes, so both combustion conditions led to net PBDD/F and PBDE destructions (93.5–99.0%). The O/I ratio of PBDD/F TEQ was lower for scheme 2 (0.0577) than scheme 1 (0.0647) implying that PBDD/Fs likely did not form during

IWTS cofiring. The higher sulfur content in the feed of scheme 2 than scheme 1 are the formation inhibitor of PBDD/Fs.<sup>39</sup> Although PBDD/Fs could form from PBDE debromination,<sup>22</sup> which resulted in the higher PBDD/F TEQ O/I ratio for scheme 1 compared to scheme 2, the formation phenomenon was not significant for both schemes in this study according to the similar congener profiles. For the O/I ratio of PBDEs, it was elevated from 0.0109 in scheme 1 to 0.0154 in scheme 2. As aforesaid, lower combustion temperature, insufficient hydrogen content in the feed, and similar residence time with more PBDE inputs for scheme 2 resulted in slightly less destruction. The O/I ratio of Σ<sub>2–8Br</sub> BDEs for scheme 1 was higher than scheme 2 while the trend of O/I ratio of Σ<sub>9–10Br</sub> BDEs was inverted for scheme 1 and scheme 2. Both support the debromination processes occurred in BA for scheme 1, but in general, both fuel schemes had very good PBDD/F TEQ and PBDE destruction efficiencies (1 – O/I ratio) in the boiler (>93.5%). The similar trend had also been observed in a fly ash thermal treatment plants<sup>40</sup> that most of the PBDEs in the feedstock of fly ash were depleted.

However, PBDEs were also found to be formed in the combustion systems that their feedstock or fuel contains bromine, but no PBDEs, such as power plants and vehicles.<sup>18,32</sup> The thermal formation of PBDEs was further verified by heating fly ash in a laboratory furnace.<sup>41</sup> Therefore, we think that the fate of PBDEs in combustion systems is the result of the competition between formations (i.e., precursor and de novo synthesis) and destructions. The destruction of PBDEs is dominant in combustion systems with high PBDE-contained feedstock, while the formation of PBDEs is more apparent when few PBDEs exist in the feedstock. Similar phenomena could be observed on the polycyclic aromatic hydrocarbon (PAHs). The fate of PAHs is depletion in combustion systems with high PAH inputs, such as gasoline engine,<sup>42</sup> carbon black manufacturing process,<sup>43</sup> and plastic waste incineration,<sup>11</sup> while the fate of PAHs is formation in biomass open burnings.<sup>44,45</sup>

### 3.4. PBDD/F and PBDE Distributions in the Boiler.

Table 3 list the PBDD/F and PBDE distributions (%) among the different ashes and the stack flue gases for both fuel schemes, which are obtained from each emission rate divided by the sum of those in the boiler system. The PBDD/F TEQ and PBDEs had the highest distributions in the stack flue gas for scheme 1

**Table 3.** Mean Emission Rates (and Distributions) of Both PBDD/Fs and PBDEs for Scheme 1 and Scheme 2<sup>a</sup>

		inputs		output				
		fuels	bottom ash	cyclone ash	bag filter ash	stack flue gas	sum	outputs/inputs
Scheme 1								
PBDD/Fs	mass (μg h <sup>-1</sup> )	15.4	0.0410 (8.46)	0.0103 (2.11)	0.0174 (3.58)	0.416 (85.8)	0.485	0.0314
	TEQ (ng TEQ h <sup>-1</sup> )	46.8	1.34 (44.2)	0.0509 (1.68)	0.0790 (2.61)	1.56 (51.5)	3.03	0.0647
PBDEs	Σ <sub>2–8 Br</sub> BDEs (μg h <sup>-1</sup> )	131	1.20 (23.0)	0.183 (3.51)	1.11 (21.4)	2.70 (52.1)	5.20	0.0398
	Σ <sub>9–10 Br</sub> BDEs (μg h <sup>-1</sup> )	3840	7.63 (19.9)	0.767 (2.01)	3.53 (9.22)	26.3 (68.8)	38.2	0.0100
	total (μg h <sup>-1</sup> )	3970	8.82 (20.3)	0.950 (2.19)	4.64 (10.7)	29.0 (66.8)	43.4	0.0109
Scheme 2								
PBDD/Fs	mass (μg h <sup>-1</sup> )	49.8	0.293 (25.4)	0.0646 (5.59)	0.156 (13.5)	0.641 (55.5)	1.15	0.0232
	TEQ (ng TEQ h <sup>-1</sup> )	253	11.0 (75.4)	0.246 (1.68)	0.705 (4.82)	2.65 (18.1)	14.6	0.0577
PBDEs	Σ <sub>2–8 Br</sub> BDEs (μg h <sup>-1</sup> )	1280	13.3 (68.2)	0.708 (3.64)	0.925 (4.6)	4.56 (23.4)	19.5	0.0152
	Σ <sub>9–10 Br</sub> BDEs (μg h <sup>-1</sup> )	12 500	134 (69.3)	3.04 (1.57)	8.36 (4.31)	48.1 (24.8)	194	0.0155
	total (μg h <sup>-1</sup> )	13 800	148 (69.2)	3.75 (1.76)	9.28 (4.36)	52.6 (24.7)	213	0.0154

<sup>a</sup>Noted: The toxicity equivalence factors (TEF) concept was applied to determine the toxicity of PBDD/Fs. The TEF of each congener present in a mixture is multiplied by the respective mass concentration and the products are summed to represent the TEQ of the mixture. The I-TEF of the PCDD/Fs was applied to determine the toxicity of corresponding PBDD/Fs.<sup>16,17,34</sup>

(51.5% and 66.8%, respectively), while only 18.1% and 24.7% of them were emitted from the stack flue gas for scheme 2, respectively. The PBDD/F TEQ and PBDE distributions for scheme 2 reveal that most of those pollutants were constrained in the BA (75.4% and 69.2%, respectively). Our previous study found that PBDE contents decreased as temperature in each APCD unit of the incinerators decreased,<sup>17</sup> which is consistent with the scheme 2 of this study.<sup>17</sup> It seems that PBDEs tend to distribute in BA of the boiler when it has a higher input amount of PBDEs.

The PBDD/F and PBDE removal efficiencies by APCDs are listed in Table 4, which were calculated as follows: removal

**Table 4. Removal Efficiencies by the APCDs for Scheme 1 and Scheme 2**

	removal efficiency (%)		
	cyclone	bag filter	total APCDs
Scheme 1			
PBDD/Fs	2.31	4.01	6.22
PBDD/F TEQ	3.01	4.82	7.69
PBDEs	2.74	13.8	16.1
Scheme 2			
PBDD/Fs	7.49	19.6	25.6
PBDD/F TEQ	6.83	21.0	26.4
PBDEs	5.71	15.0	19.8

efficiency by the cyclone (%) is  $A/(A + B + C)$  and that by the bag filter is  $B/(B + C)$ , where A, B, and C are the emission rates of the CA, BFA, and stack flue gas in the boiler, respectively. The mean PBDD/F TEQ and PBDE removal efficiencies by the APCDs (range: 7.69–26.4% and 16.1–19.8%, respectively) are not good for both schemes. It should be noted that the PBDD/F TEQ and PBDE removal efficiencies were higher for scheme 2 than for scheme 1. The dominant PBDD/F and PBDE congeners are highly brominated ones for both schemes, which are easily condensed onto particulate phase. The higher output ash in bag filter for scheme 2 might provide more surface area for condensation than for scheme 1, and therefore resulted in higher removal efficiency. However, the exact reasons need further investigation.

In this study, most of the PBDD/Fs and PBDEs in the stack flue gases were partitioning in the gaseous phase (Tables S3 and S4, Supporting Information). The APCDs in this study are designed for particulate removal; thus, the gaseous phase pollutants are easily penetrating through the APCDs. An injection of pulverized activated carbon (PAC) into bag filters is capable to increase the removal efficiency. However, the PBDD/F and PBDE concentrations in the stack flue gases of this study are lower than those from the other combustion sources. Thus, the emission control of the PBDD/Fs and PBDEs from stack flue gas via PAC injection can be considered if it is required to reduce their emissions during sludge cofiring.

**3.5. Boiler Efficiency and Cost.** The boiler efficiency is defined as the output steam energy divided by the input gross heating value of the fuel, as shown in Table 2. More ash outputs were found for scheme 2 than for scheme 1, which carried more combustion generated heat out from the boiler. Furthermore, the higher water content was introduced in the boiler in scheme 2 than in scheme 1, and the combustion peak temperature was lower for scheme 2. These contributed to a lower boiler efficiency for scheme 2 (50.6%) than for scheme 1 (53.9%). With regard to the social effects of using sludge as a cofuel, the

fuel consumption per output energy of steam (F/S) showed that scheme 2 (104 kg GJ<sup>-1</sup>) increased the fuel consumption compared to scheme 1 (97.4 kg GJ<sup>-1</sup>) on the same output energy basis. Although F/S ratio slightly increased, the woodchip consumption was replaced by IWTS. Based on the 60 USD t<sup>-1</sup> woodchip price, 50 USD t<sup>-1</sup> ash treatment fee, and 135 USD t<sup>-1</sup> waste sludge treatment fee in Taiwan, the estimated costs are 3.17 and 2.20 USD for scheme 1 and scheme 2, respectively, to produce one kilojoule output energy. As shown, the cost for scheme 2 could be 26.3% less than that for scheme 1 to produce the same output energy of steam. On the waste-to-energy prospect, cofiring IWTS with original fuel not only offers an option for disposal of the fast growing sludge stream but also yields a cost saving from energy recovery.

## ■ ASSOCIATED CONTENT

### Supporting Information

Additional tables and figure as described in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We express our deep gratitude to S. H. Wu, T. Y. Hsien, L. P. Chang, Y. F. Yeh, Y. C. Chang, L. K. Tu, and Cary T. Chiou for their technical support and offering insightful discussion. The authors also acknowledge the National Science Council of Taiwan for supporting this research work under Grant NSC 98-2221-E-230-002-MY2.

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