Aerosol and Air Quality Research, 11: 282–289, 2011

ISSN: 1680-8584 print / 2071-1409 online
doi: 10.4209/aaqr.2010.11.0098

Fate and Distribution of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans in a Woodchip-fuelled Boiler

Wei-Sheng Chen[1,2], Yun-Hwei Shen[1*], Ting-Yu Hsieh[2,3], Chang-Wen Lin[2], Lin-Chi Wang[4,5*], Guo-Ping Chang-Chien[4,5]

[1] *Department of Resources Engineering, National Cheng Kung University, 1, University Road, Tainan 70101, Taiwan, R.O.C.*
[2] *Sustainable Environment Research Center, National Cheng Kung University, 1, University Road, Tainan 70101, Taiwan, R.O.C.*
[3] *Department of Environmental Engineering, National Cheng Kung University, 1, University Road, Tainan 70101, Taiwan, R.O.C.*
[4] *Department of Chemical and Materials Engineering, Cheng Shiu University, 840, Chengching Road, Kaohsiung 833, Taiwan, R.O.C.*
[5] *Super Micro Mass Research and Technology Center, Cheng Shiu University, 840, Chengching Road, Kaohsiung 833, Taiwan, R.O.C.*

ABSTRACT

As yet, very little is known about the PCDD/F fate and distribution in the woodchip-fuelled boilers. In this study, the feeding woodchips, stack flue gases and the ashes in different units of a woodchip-fuelled boiler are sampled to investigate their PCDD/F characteristics. The PCDD/F contents in the bottom residues and fly ashes ranged from 18.9 to 66.3 ng I-TEQ/kg, which are below the Taiwanese PCDD/F regulation for reutilization of bottom residues, but still higher than PCDD/F limitations on soils for agricultural use (10 ng I-TEQ/kg), which are adopted by several countries. From the PCDD/F output/input ratios, we found that combustion of woodchips in the boiler system is more favourable for the formations of PCDFs by de novo syntheses, especially for lower chlorinated PCDF congeners. Although about half of the input PCDD/Fs mass are destroyed in the combustion, the output PCDD/Fs toxicity are 6.9 times higher than the inputs. Fly ashes exhibited the highest PCDD/F distributions among the woodchip-fuelled boiler. Still 21.4% of total PCDD/F mass and 18.0% of total PCDD/F toxicity were emitted from the stack flue gases due to the lack of control devices for gaseous phase PCDD/Fs. Decreasing de novo syntheses among the boiler systems, deploying control devices for gaseous phase PCDD/Fs, and proper management on the reutilization of fly ashes will ensure woodchip-fuelled boilers as a sustainable and renewable biomass energy.

Keywords: Dioxin; Wood; Boiler; Ash; Stack flue gases.

INTRODUCTION

Burning woodchips in power plants belongs to biomass power which is recognized as one of the major renewable energy systems (Turner, 1999). Utilizing wood as fuel can reduce carbon dioxide into the atmosphere by replacing fossil fuels, and thus help fight global warming and climate change. Consequently, wood could be a more important source of energy over fossil fuels in the future. In addition, the bottom ashes generated from a complete combustion of wood can be mixed with the cement and/or via the vitrification processes to produce slag, which is environmental friendly (Li *et al.*, 2003; Li *et al.*, 2007a; Chen *et al.*, 2009). Nevertheless, burning wood like most combustion also produce toxic pollutants, such as polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) (Preto *et al.*, 2005; Tame *et al.*, 2005; Shih and Lee, 2008), polychlorinated biphenyls (PCBs) (Atkin *et al.*, 2010), polybrominated diphenyl ethers (PBDEs) (Wang *et al.*, 2010b), PAHs and metals (Lavric *et al.*, 2004; Choosong *et al.*, 2010; Ruttanachot *et al.*, 2011).

PCDD/Fs are semi-volatile organic compounds, which are similar to PAHs, PCBs and PBDD/Fs and exited in both gas and particle phases in the ambient air and in the stack flue gases (Lee *et al.*, 1996a, b; Sheu *et al.*, 1996; Lai

---

[*] Corresponding author. Tel.: +886-7-7310606 ext. 3045; Fax: +886-7-7332204
E-mail address: lcwang@csu.edu.tw (L.C. Wang); yhshen@mail.ncku.edu.tw (Y.H. Shen)

et al., 2007; Wang *et al.*, 2010f). PCDD/F emissions are serious issues in many countries (Lin *et al.*, 2010a) because of their toxicological effects and associated adverse health implications. The important sources of PCDD/Fs have been reported as the waste incinerators (Wang *et al.*, 2007; Wang and Chang-Chien, 2007; Wang *et al.*, 2010d), iron ore sintering (Wang *et al.*, 2003c), power plants (Lin *et al.*, 2007; Lin *et al.*, 2010b; Wu *et al.*, 2010; Wang *et al.*, 2010e), coal-fired power plants (Lin *et al.*, 2007), electric arc furnaces (EAFs) (Lee *et al.*, 2004, 2005; Li *et al.*, 2008; Wang *et al.*, 2010c; Chiu *et al.*, 2011), secondary aluminum smelters (ALS) (Lee *et al.*, 2005; Li *et al.*, 2007b), crematories (Wang *et al.*, 2003a), vehicles (Chuang *et al.*, 2010a, b) and open burning of rice straw (Lin *et al.*, 2007). PCDD/F emissions from woodchip-fuelled boilers are seldom investigated relatively (Preto *et al.*, 2005; Tame *et al.*, 2005). Due that certain PCDD/F congeners were mutagenic, carcinogenic and easily to accumulated in the food (Lee *et al.*, 2009; Wang and Lee, 2010), PCDD/Fs were always concerned by the people.

Generally speaking, three kinds of wood have been investigated for their emitted PCDD/F characteristics during power or heat productions (Wunderli *et al.*, 2000), including waste wood (wood from construction activities and house demolition, impregnated wood and salt-laden wood) (Luthe *et al.*, 1998; Wunderli *et al.*, 2000), residual wood products (wood products which have been processed such as chipboard and wood dust from machining) (Sinkkonen *et al.*, 1995) and nature wood (wood without any treatment, including saw dust, shavings and bark) (Schatowitz *et al.*, 1994; Wunderli *et al.*, 2000). Waste and residual wood often containing various types of contaminants such as chromated copper arsenate, pentachlorophenol, creosote, adhesives, paint, PVC and other surface coatings, could lead to higher emissions of PCDD/Fs, PAHs and metals (Lavric *et al.*, 2004). Preto *et al.* (2005) conducted a series of combustion tests in a pilot-scale fluidized bed combustor by mixing hog fuel (produced from bark stripped from salt-laden wood, chlorine content: 1.25%) with wood pellets (chlorine content: 0.0049%) to evaluate the influence of the chlorine on PCDD/F formations. The PCDD/F emissions were observed increased with increasing chlorine content in the feed (Wang *et al.*, 2003b). The PCDD/F emission factors of the stack flue gases from wood burning could range several orders of magnitudes (0.001 to 6655 ng TEQ/kg-wood), but generally demonstrate that untreated nature wood emit much less PCDD/Fs (0.001 to 1.9 ng TEQ/kg-wood for wood fireplaces and stoves) (Tame *et al.*, 2007).

Not only flue gases but also solid residues from wood combustions need to be carefully managed. The solid residues (bottom residues and fly ashes) from wood combustion can be reutilized as soil improvement material, in construction of roads and as supplementary material such as concrete production or filler material or must be disposed of in waste dumps (Sinkkonen *et al.*, 1995; Wunderli *et al.*, 2000). PCDD/F contents in the multi-cyclone ashes of the salt-laden wood steam boilers could range from 0.0978 to 20.9 ng I-TEQ/g (Luthe *et al.*, 1998). Consequently, PCDD/F contents in the ashes from wood combustions must be evaluated before further considering their reutilizations.

Fates of PAHs, PCDD/Fs and PBDD/Fs in the thermal processes have been investigated by the previous studies (Kuo *et al.*, 2003; Lai *et al.*, 2007; Li *et al.*, 2007c). As yet, very little is known about the fates of PCDD/Fs in the woodchip-fuelled boilers. In this study, the stack flue gases and the ashes in different units of a woodchip-fuelled boiler are sampled to investigate their PCDD/F characteristics. Furthermore, the formations and depletions of PCDD/Fs in the boiler system were also clarified. With better understanding their PCDD/F fate and distribution, appropriate control strategies to decrease PCDD/Fs emitted from woodchip-fuelled boilers can be adopted when utilizing the renewable biomass energy.

MATERIALS AND METHODS

Basic Information Concerning the Boiler

The boiler investigated in this study utilizes woodchips as fuel. Woodchips can be used in almost all combustion systems (i.e. shaft, underfeed, stokerfired and fluidized bed furnaces). Preparation into the form of woodchips is the standard technology for woody biomass types (Spliethoff, 2010). The woodchips in this study are collected from chipping or shredding wood for the productions of furniture with chlorine content smaller than 1 mg/kg, water content of 6.08%, ash content of 5.67%, combustible content of 88.3% and heat content of 4559 kcal/kg. They vary in size and moisture content, typically ranging from 25% to 55% (Atkin *et al.*, 2010).

The investigated boiler in this study is a grate furnace boiler for the production of steam without power generator. The woodchip feeding rate of the intermittently operating boiler was 730 kg/hour, and the mean steam generation rate is 2.51 ton/hr. Its air pollution control devices include cyclone and bag filter with a flue gas oxygen content of 15.7%. The output rates of the bottom residues, cyclone ashes and bag filter ashes are 0.38, 3.2 and 3.4 kg/hour, respectively.

PCDD/F Samplings

All the stack flue gas samplings as well as chemical analyses in this study were carried out in 2010 by our accredited laboratory, which specializes in PCDD/F samplings and analyses in Taiwan. The stack flue gases of the boiler were collected isokinetically following U.S. EPA Modified Method 23 (U.S. EPA, 2001b) using U.S. EPA Modified Method 5 (U.S. EPA, 2001a) sampling trains. The sampled flue gas volumes were normalized to the dry condition of 760 mmHg and 273 K, and denoted as Nm^3. The collection time for each stack flue gas sample lasted for about three hours, although in other study (Liu and Liu, 2005), it lasted for 8 hours. To obtain representative samples, the feeding woodchips, bottom residues, and fly ashes from the cyclone and bag filter were sampled simultaneously with the stack flue gas samples.

After the coarse solids were ground to particles with a diameter of less than 1 mm, the ash samples were well-mixed and diagonal sectioned. 10g of woodchips, 5 g of bottom residues, and 2 g of the fly ashes were sampled for PCDD/F analyses. The detailed PCDD/F sampling procedures are given in our previous work (Wang *et al.*, 2010a).

Analytical Procedures

Analyses of the flue gas samples were performed following U.S. EPA Modified Method 23 (U.S. EPA, 2001b), while those of the woodchip and ash samples conformed to the U.S. EPA Modified Method 1613 (U.S. EPA, 1994). Prior to analysis, each collected sample was spiked with a known amount of the $^{13}C_{12}$-labeled internal standard to the extraction thimble. Toluene was added to fill the reservoir approximately 2/3 full, and the heat source was adjusted to cause the extractor to cycle three times per hour. After being extracted for 24 hours, the extract was concentrated and treated with concentrated sulfuric acid, and this was followed by a series of sample cleanup and fractionation procedures, including multilayer silica gel column, alumina column and activated carbon column. The eluate was concentrated to approximately 1 mL and transferred to a vial. The concentrate was further concentrated to near dryness using a stream of nitrogen. Immediately prior to analysis, the standard solution for recovery checking was added to the sample.

A high-resolution gas chromatograph/high-resolution mass spectrometer (HRGC/HRMS) was used for PCDD/Fs analyses. The HRGC (Hewlett Packard 6970 Series, CA, USA) was equipped with a DB-5MS fused silica capillary column (L = 60 m, ID = 0.25 mm, film thickness = 0.25 µm) (J&W Scientific, CA, USA), and with a splitless injection. Helium was used as the carrier gas. The oven temperature was programmed with an initial temperature of 150°C (held for 1 min), followed by 30 °C/min ramping to 220°C (held for 12 min), followed by a 1.5 °C/min ramping to 240°C (held for 5 min), then to 310°C (held for 20 min). The HRMS (Micromass Autospec Ultima, Manchester, UK) was equipped with a positive electron impact (EI+) source. The analyzer mode of the selected ion monitoring (SIM) was used with resolving power at 10,000. The electron energy and source temperature were specified at 35 eV and 250°C, respectively. The detailed instrumental analysis parameters of PCDD/Fs are given in our previous works (Wang *et al.*, 2003a; Wang *et al.*, 2010b).

Quality Assurance and Quality Control (QA/QC)

Prior to sampling, XAD-2 resin was spiked with PCDD/F surrogate standards pre-labeled with isotopes, including $^{37}Cl_4$-2,3,7,8-TCDD, $^{13}C_{12}$-1,2,3,4,7,8-HxCDD, $^{13}C_{12}$-2,3,4,7,8-PeCDF, $^{13}C_{12}$-1,2,3,4,7,8-HxCDF and $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF. The recoveries of PCDD/F surrogate standards were 100%–125%, which met the criteria of 70%–130%. To ensure the free contamination of the collected samples, one trip blank and one field blank were also taken during the field sampling was conducted. The recoveries of PCDD/F internal standards for the tetra- through hexa-chlorinated homologues were between 82% and 109%, and met the criteria within 40%–130%, while that for the hepta- and octachlorinated homologues were between 68% and 108%, and met the criteria within 25%–130%.

RESULTS AND DISCUSSION

PCDD/F Contents (Concentrations) in the Feeding Woodchips, Ashes and Stack Flue Gases

Table 1 listed PCDD/F contents (concentrations) in the feeding woodchips, bottom residues, cyclone ashes, bag filter ashes and stack flue gases of the wood-fuelled industrial boiler. The mean PCDD/F contents of the woodchips based on mass and toxicity were 8.38 ng/kg and 0.0730 ng I-TEQ/kg, respectively, which are close to that (2 ng/kg) in the tree barks sampled in urban area (Di Lella *et al.*, 2006), but much lower than that (22.8 ng I-TEQ/kg) in the tree barks collected in the polluted area (Wen *et al.*, 2009).

The mean PCDD/F concentrations in the stack flue gases of the wood-fuelled industrial boiler was 0.00537 ng I-TEQ/Nm^3, which is much lower than the Taiwanese PCDD/F regulation for boilers of 1.0 ng I-TEQ/Nm^3. The reported PCDD/F concentrations from the burning of natural wood or wood with low chlorine or metal contents are at the same level with our findings (Lavric *et al.*, 2004; Tame *et al.*, 2007), however, waste wood treated with copper-based preservatives or chlorinated organics could resulted in the elevated PCDD/F concentrations with 3 orders higher (Tame *et al.*, 2007).

The PCDD/F contents measured in the bottom residues, cyclone ashes and bag filter ashes were 18.9, 20.5 and 66.3

Table 1. PCDD/F contents (concentrations) in the feeding woodchips, bottom residues, cyclone ashes, bag filter ashes and stack flue gases of the wood-fueled industrial boiler

PCDD/Fs	feeding woodchips (n = 2)		bottom residues (n = 2)		cyclone ashes (n = 2)		bag filter ashes (n = 2)		stack flue gases* (n = 3)	
	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
PCDDs	7.34	1.80	77.3	3.46	118	21.9	238	41.0	0.0345	0.0106
PCDFs	1.04	0.0495	77.2	0.495	156	24. 8	370	31.1	0.029	0.00355
PCDFs/PCDDs ratio	0.146	0.0425	1.00	0.0384	1.33	0.0369	1.57	0.139	0.886	0.228
Total PCDD/Fs (ng/kg)	8.38	1.75	154	3.54	273	46. 7	608	72.1	0.0635	0.0137
Total I-TEQ (ng I-TEQ/kg)	0.0730	0.00212	18.9	1.69	20.5	0.636	66.3	1.77	0.00537	0.00101

* The unit of PCDD/F concentrations in the stack flue gases is ng/Nm^3.

ng I-TEQ/kg, respectively. The higher PCDD/F contents in the bag filter ashes than those in the cyclone ashes attributed to finer fly ashes containing higher PCDD/Fs. Although the PCDD/F contents in the ashes are below the Taiwanese PCDD/F regulation for reutilization of bottom residues (< 100 or 1000 ng I-TEQ/kg depending on the purposes of the reutilization), their PCDD/F levels are still higher than PCDD/F limitations on soil for agricultural use (10 ng I-TEQ/kg), which are adopted by several countries. Consequently, before conducting the reutilizations of the ashes from wood combustions, their PCDD/F contents and appropriate management strategy must be evaluated.

Huang *et al.* (1995) reviewed more studies regarding the formation mechanisms of PCDD/F and concluded that the "de novo synthesis" can produce PCDD/Fs with the characteristic of "PCDFs/PCDDs ratio > 1", while the "precursor formation" produce PCDD/Fs with "PCDFs/PCDDs ratio << 1". In the feeding woodchips, the PCDF/PCDD ratio was smaller than 1, but after the combustion, the PCDF/PCDD ratio in bottom residues, cyclone ashes and bag filter ashes were all larger than 1, revealing combustion of woodchips in the boiler system would be more favorable for the formations of PCDFs by the de novo syntheses.

Wunderli *et al.* (2000) reported the solid residues from the incineration of native wood are below 10 ng I-TEQ/kg. Nevertheless, the fly ashes from the cyclone of the salt-laden wood steam boilers could reach 97.8–20900 ng I-TEQ/kg (Luthe *et al.*, 1998). The degree of carbon burnout (Wunderli *et al.*, 2000), contamination levels (chlorine, copper and chlorinated organics contents) in the feeding wood (Tame *et al.*, 2007), combustion conditions and temperature trends of the flue gases (Wang *et al.*, 2010a) are influential factors affecting the PCDD/F contents in the ashes.

PCDD/F Congener Profiles

The PCDD/F congener profiles in the feeding woodchips, bottom residues, cyclone ashes, bag filter ashes and stack flue gases are illustrated in Fig. 1. OCDD is the most prominent congener in the woodchip samples. The PCDD/F congener profile of the stack flue gases is more dominant with OCDD (> 30%) followed by 2,3,7,8-TeCDF and 1,2,3,4,6,7,8-HpCDD, showing close similarity with that of the other woodchip-fuelled boiler (Wang *et al.*, 2010b), and that of burning of the tree bark samples (Ferrario *et al.*, 2000). The PCDD/F congener profiles of the ash samples are generally similar to that of the stack flue gases, especially for bottom residues, but with the increase of PCDD/F contents, 2,3,7,8-TeCDF possesses higher fraction. Wunderli *et al.* (2000) also observed comparable PCDD/F congener profiles to this present study in the grate ashes and bag filter ashes of grate burner fuelled with waste wood.

Emission Factors and Output/Input Ratio of PCDD/Fs

The emission factor of PCDD/Fs is calculated as the PCDD/F emission mass or toxicity per wet woodchip combustion. There are three routes for the boiler to release their substances containing PCDD/Fs to the environment, including bottom residues, fly ashes and stack flue gas. Taking PCDD/F emission factor of stack flue gases for

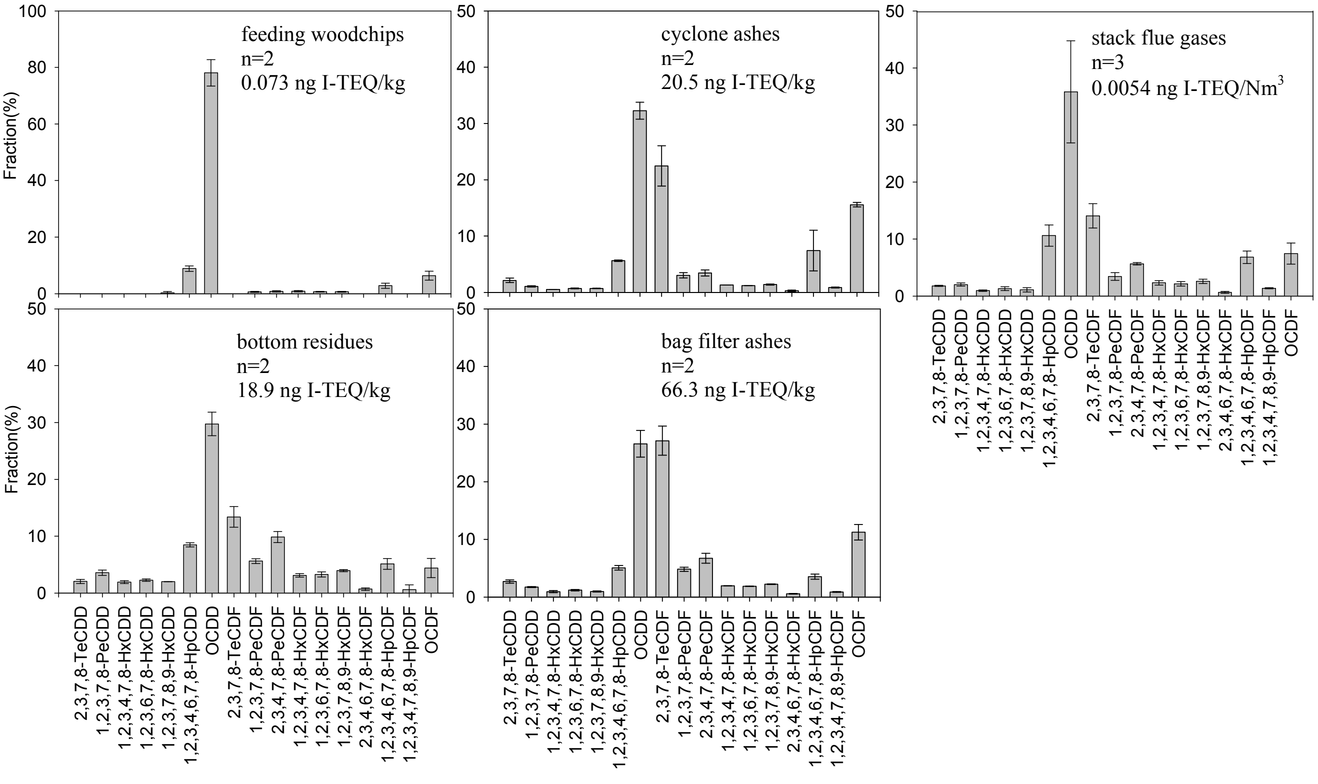

Fig. 1. PCDD/F characteristics in the feeding wood, the bottom ash, the fly ash of cyclone, the fly ash of bag filter, and the stack flue gases of the wood-fueled industrial boiler.

example, the emission factors were calculated using the following equation:

$$EF = C \times Fv/Iw \quad (1)$$

EF: Emission factor, ng I-TEQ per kg-woodchip burned
C: I-TEQ concentration in stack flue gases (ng I-TEQ/Nm^3)
Fv: Volumetric flue gas flow rate (Nm^3/hr)
Iw: Average woodchip incineration rate (kg/hr)

Table 2 lists the mean PCDD/F emission factors of the three routes and the whole boiler systems. The mean emission factor of the stack flue gases is 0.0899 ng I-TEQ/kg-woodchip, smaller than that of the other woodchip-fuelled boiler equipping cyclone and bag filter (2.99 ng I-TEQ/kg-woodchip) (Wang *et al.*, 2010b). The PCDD/F emission factors of the stack flue gases from wood burning could range several orders of magnitudes (0.001 to 6655 ng TEQ/kg-wood), but generally demonstrate that untreated nature wood emit much less PCDD/Fs (0.001 to 1.9 ng TEQ/kg-wood for wood fireplaces and stoves) (Tame *et al.*, 2007).

The mean PCDD/F emission factor of the whole boiler systems is 0.499 ng I-TEQ/kg-woodchip. Compared to the PCDD/F contents in the feeding woodchips (PCDD/F inputs), the PCDD/F output/input ratios are obtained and listed in Table 2. The output/input mass ratios of all PCDF congeners are larger than unity, and lower chlorinated PCDF congeners have higher ratio values, revealing combustion of woodchips in the boiler system would be more favourable for the formations of PCDFs by de novo syntheses (Wang *et al.*, 2003b). For PCDDs, the output/input mass ratios of the highly chlorinated PCDD congeners (1,2,3,4,6,7,8-HpCDD and OCDD) are less than unity, while the others are larger than unity. The phenomena may attribute to the formations of the lower chlorinated PCDD congeners by dechlorinating the highly chlorinated PCDD congeners, or by precursor mechanisms (Wang *et al.*, 2003b).

The PCDD/F output/input ratios based on mass and toxicity are 0.6 and 6.9, respectively. Although about half of the input PCDD/Fs mass are destroyed in the combustion, the output PCDD/Fs toxicity are 6.9 times higher than the inputs. The above results indicated that more amount of higher molecular weight PCDD/F congener like OCDD and OCDF were decomposed, but certain fraction of lower molecular weight PCDD/Fs like 2.3.7,8-TCDD and 2.3.7,8-TCDF with a higher toxicity equivalent factor were formed due to de novo synthesis and therefore elevated the output toxicity.

PCDD/F Distributions in the Boiler System

Table 3 lists the PCDD/F distribution (%) among the different ashes and the stack flue gases of the woodchips-fuelled boiler, which was obtained from each emission factor of ashes and stack flue gas divided by the total emission factors of the boiler. Bag filter ashes exhibited the highest distributions of PCDD/F mass and

Table 2. PCDD/F emission factors of the bottom residues, cyclone ashes, bag filter ashes and stack flue gases of the wood-fueled industrial boiler.

PCDD/Fs	Input	Output					Output/ Input ratio
	woodchips	bottom residues	cyclone ashes	bag filter ashes	stack flue gases	total	
2,3,7,8-TeCDD	ND	0.00164	0.0251	0.0755	0.0194	0.122	NA
1,2,3,7,8-PeCDD	ND	0.00288	0.0126	0.0489	0.0229	0.0873	NA
1,2,3,4,7,8-HxCDD	ND	0.00154	0.00632	0.0262	0.0106	0.0447	NA
1,2,3,6,7,8-HxCDD	ND	0.00182	0.00851	0.0332	0.0141	0.0576	NA
1,2,3,7,8,9-HxCDD	0.0220	0.00160	0.00847	0.0270	0.0123	0.0494	2.2
1,2,3,4,6,7,8-HpCDD	0.733	0.00682	0.0671	0.144	0.116	0.334	0.5
OCDD	6.59	0.0240	0.388	0.760	0.414	1.59	0.2
2,3,7,8-TeCDF	ND	0.0108	0.265	0.764	0.153	1.19	NA
1,2,3,7,8-PeCDF	0.0510	0.00452	0.0358	0.136	0.0370	0.213	4.2
2,3,4,7,8-PeCDF	0.0650	0.00792	0.0408	0.189	0.0633	0.301	4.6
1,2,3,4,7,8-HxCDF	0.0690	0.00250	0.0160	0.0550	0.0246	0.0981	1.4
1,2,3,6,7,8-HxCDF	0.0570	0.00263	0.0142	0.0527	0.0246	0.0941	1.7
1,2,3,7,8,9-HxCDF	0.0540	0.00317	0.0167	0.0634	0.0282	0.111	2.1
2,3,4,6,7,8-HxCDF	ND	0.000547	0.00347	0.0156	0.00704	0.0267	NA
1,2,3,4,6,7,8-HpCDF	0.226	0.00414	0.0930	0.101	0.0757	0.274	1.2
1,2,3,4,7,8,9-HpCDF	ND	0.000485	0.0103	0.0249	0.0141	0.0498	NA
OCDF	0.519	0.00355	0.187	0.321	0.0809	0.592	1.1
PCDDs	7.34	0.0403	0.518	1.11	0.607	2.28	0.3
PCDFs	1.04	0.0402	0.684	1.72	0.510	2.95	2.8
Total PCDD/Fs (ng/kg-woodchip)	8.38	0.0802	1.20	2.83	1.12	5.23	0.6
PCDDs I-TEQ	0.0160	0.00366	0.0347	0.111	0.0370	0.186	12
PCDFs I-TEQ	0.0570	0.00620	0.0548	0.198	0.0581	0.317	5.6
Total I-TEQ (ng I-TEQ/kg-woodchip)	0.0730	0.00985	0.0899	0.309	0.0950	0.504	6.9

ND: not detectable; NA: not available

Table 3. PCDD/F distribution (%) among the different ashes and the stack flue gases of the woodchips-fuelled boiler.

PCDD/Fs	bottom residues (%)	cyclone ashes (%)	bag filter ashes (%)	stack flue gases (%)
PCDDs	1.77	22.8	48.8	26.7
PCDFs	1.36	23.1	58.3	17.2
Total PCDD/Fs	1.53	22.9	54.2	21.4
Total I-TEQ	1.97	18.0	61.9	18.0

TEQ, which are 54.2% and 61.9%, respectively. Together with the cyclone ashes, the distributions of PCDD/F mass and TEQ of the fly ashes reach 77.1% and 79.9%, respectively. Still 21.4% of total PCDD/F mass and 18.0% of total PCDD/F toxicity were emitted from the stack flue gases. Much higher PCDD/F distribution in the fly ashes (> 90%), and much lower PCDD/F distribution in the stack flue gases (< 1%) had been observed in the waste incinerators (Wang *et al.*, 2010a) and fly ash treatment plant (Lin *et al.*, 2008), because they deploy activated carbon injection to adsorb gaseous phase PCDD/Fs into particulate phase PCDD/Fs (fly ashes). However, before the fly ash treatment plant adopting activated carbon to control PCDD/Fs, 66.7% of total PCDD/F toxicity was emitted from the stack flue gases (Lin *et al.*, 2008).

CONCLUSIONS

The mean PCDD/F concentrations in the stack flue gases of the wood-fuelled industrial boiler was 0.00537 ng I-TEQ/Nm^3, which is at the same level from the burning of natural wood or wood with low chlorine or metal contents, and much lower than the Taiwanese PCDD/F regulation for boilers of 1.0 ng I-TEQ/Nm^3. The PCDD/F contents in the bottom residues and fly ashes ranged from 18.9 to 66.3 ng I-TEQ/kg. The PCDD/F levels are below the Taiwanese PCDD/F regulation for reutilization of bottom residues, but still higher than PCDD/F limitations on soil for agricultural use (10 ng I-TEQ/kg), which are adopted by several countries. The output/input mass ratios of all PCDF congeners are larger than unity, revealing that combustion of woodchips in the boiler system is more favourable for the formations of PCDFs by de novo syntheses, especially for lower chlorinated PCDF congeners. For the lower chlorinated PCDD congeners, they are formed by dechlorinating the highly chlorinated PCDD congeners, or by precursor mechanisms. Still 21.4% of total PCDD/F mass and 18.0% of total PCDD/F toxicity were emitted from the stack flue gases due to the lack of control devices for gaseous phase PCDD/Fs.

REFERENCES

Atkin, A., Bignal, K.L., Zhou, J.L. and Cazier, F. (2010). Profiles of Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls from the Combustion of Biomass Pellets. *Chemosphere* 78: 1385–1392.

Chen, C.C., Lee, W.J., Shih, S.I. and Mou, J.L. (2009). Reduction of Carbon Content in Waste-tire Combustion Ashes by Bio-thermal Treatment. *J. Environ. Sci. Health A.* 44: 1430–1440.

Chiu, J.C., Shen, Y.H., Li, H.W., Lin, L.F., Wang, L.C. and Chang-Chien, G.P. (2011). Emissions of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans from an Electric Arc Furnace, Secondary Aluminum Smelter, Crematory and Joss Paper Incinerators. *Aerosol Air Qual. Res.* 11: 13–20.

Choosong, T., Chomanee, J., Tekasakul, P., Tekasakul, S., Otani, Y., Hata, M. and Furuuchi, M. (2010). Workplace Environment and Personal Exposure of PM and PAHs to Workers in Natural Rubber Sheet Factories Contaminated by Wood Burning Smoke. *Aerosol Air Qual. Res.* 10: 8–21.

Chuang, S.C., Chen, S.J., Huang, K.L., Chang-Chien, G.P., Wang, L.C. and Huang, Y.C. (2010a). Emissions of Polychlorinated Dibenzo-p-dioxin and Polychlorinated Dibenzofuran from Motorcycles. *Aerosol Air Qual. Res.* 10: 533–539.

Chuang, S.C., Chen, S.J., Huang, K.L., Wu, E.M.Y., Chang-Chien, G.P. and Wang, L.C. (2010b). Gas/Particle Partitioning of Dioxins in Exhaust Gases from Automobiles. *Aerosol Air Qual. Res.* 10: 489–496.

Di Lella, L., Loppi, S., Protano, G. and Riccobono, F. (2006). Toxic Trace Elements and Organic Compounds in the Ambient Air of Kabul, Afghanistan. *Atmos. Environ.* 40: 225–237.

Ferrario, J., Byrne, C. and Cleverly, D. (2000). 2,3,7,8-Dibenzo-p-dioxins in Mined Clay Products from the United States: Evidence for Possible Natural Origin. *Environ. Sci. Technol.* 34: 4524–4532.

Huang, H. and Buekens, A. (1995). On the Mechanisms of Dioxin Formation in Combustion Processes. *Chemosphere* 31: 4099–4117.

Kuo, Y.M., Lin, T.C., Tsai, P.J., Lee, W.J. and Lin, H.Y. (2003). Fate of Polycyclic Aromatic Hydrocarbons during Vitrification of incinerator ash in a Coke Bed Furnace. *Chemosphere* 51: 313–319.

Lai, Y.C., Lee, W.J., Li, H.W., Wang, L.C. and Chang-Chien, G.P. (2007). Inhibition of Polybrominated Dibenzo-p-dioxin and Dibenzofuran Formation from the Pyrolysis of Printed Circuit Boards. *Environ. Sci. Technol.* 41: 957–962.

Lavric, E.D., Konnov, A.A. and De Ruyck, J. (2004). Dioxin Levels in Wood Combustion - A Review. *Biomass Bioenergy.* 26: 115–145.

Lee, W.J., Lewis, S.J.L., Chen, Y.Y., Wang, Y.F., Sheu, H.L., Su, C.C. and Fan, Y.C. (1996a). Polychlorinated Biphenyls in the Ambient air of Petroleum Refinery, Urban and Rural areas. *Atmos. Environ.* 30: 2371–2378.

Lee, W.J., Shih, S.I. and Li, H.W. (2009). Assessment of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans Contribution from Different Media to Surrounding Duck

Farms. *J. Hazard. Mater.* 163: 1185–1193.

Lee, W.J., Su, C.C., Sheu, H.L., Fan, Y.C., Chao, H.R. and Fang, G.C. (1996b). Monitoring and Modeling of PCB Dry Deposition in Urban Area. *J. Hazard. Mater.* 49: 57–88.

Lee, W.S., Chang-Chien, G.P., Wang, L.C., Lee, W.J., Tsai, P.J., Wu, K.Y. and Lin, C. (2004). Source identification of PCDD/Fs for Various Atmospheric Environments in a Highly Industrialized City. *Environ. Sci. Technol.* 38: 4937–4944.

Lee, W.S., Chang-Chien, G.P., Wang, L.C., Lee, W.J., Wu, K.Y. and Tsai, P.J. (2005). Emissions of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans from Stack Gases of Electric Arc Furnaces and Secondary Aluminum Smelters. *J. Air Waste Manage. Assoc.* 55: 219–26.

Li, C.T., Huang, Y.J., Huang, K.L. and Lee, W.J. (2003). Characterization of Slags and Ingots from the Vitrification of Municipal Solid Waste Incineration Ashes. *Ind. Eng. Chem. Res.* 42: 2306–2313.

Li, C.T., Lee, W.J., Huang, K.L., Fu, S.F. and Lai, Y.C. (2007a). Vitrification of Chromium Electroplating Sludge. *Environ. Sci. Technol.* 41: 2950–2956.

Li, H.W., Lee, W.J., Huang, K.L. and Chang-Chien, G.P. (2007b). Effect of Raw Materials on Emissions of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans from the Stack Flue Gases of Secondary Aluminum Smelters. *J. Hazard. Mater.* 147: 776–784.

Li, H.W., Lee, W.J., Tsai, P.J., Mou, J.L., Chang-Chien, G.P. and Yang, K.T. (2008). A Novel Method to Enhance Polychlorinated Dibenzo-p-dioxins and Dibenzofurans Removal by Adding Bio-solution in EAF Dust Treatment Plant. *J. Hazard. Mater.* 150: 83–91.

Li, H.W., Wu, Y.L., Lee, W.J and Chang-Chien, G.P. (2007c). Fate of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in a Fly Ash Treatment Plant. *J. Air Waste Manage. Assoc.* 57: 1024–1031.

Lin, L.F., Lee, W.J., Li, H.W., Wang, M.S. and Chang-Chien, G.P. (2007). Characterization and Inventory of PCDD/F Emissions from Coal-fired Power Plants and other Sources in Taiwan. *Chemosphere* 68: 1642–1649.

Lin, L.F., Shih, S.I., Su, J.W., Shih, M.L., Lin, K.C., Wang, L.C. and Chang-Chien, G.P. (2010a). Dry and Wet Deposition of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans on the Drinking Water Treatment Plant. *Aerosol Air Qual. Res.* 10: 231–244.

Lin, W.Y., Wang, L.C., Wang, Y.F., Li, H.W. and Chang-Chien, G.P. (2008). Removal Characteristics of PCDD/Fs by the Dual Bag Filter System of a Fly Ash Treatment Plant. *J. Hazard. Mater.* 153: 1015–1022.

Lin, W.Y., Wu, Y.L., Tu, L.K., Wang, L.C. and Lu, X. (2010b). The Emission and Distribution of PCDD/Fs in Municipal Solid Waste Incinerators and Coal-fired Power Plant. *Aerosol Air Qual. Res.* 10: 519–532.

Liu, Y. and Liu, Y. (2005). Novel Incineration Technology Integrated with Drying, Pyrolysis, Gasification, and Combustion of MSW and Ashes Vitrification. *Environ. Sci. Technol.* 39: 3855–3863.

Luthe, C., Karidio, I. and Uloth, V. (1998). Dioxins Formation in Salt-laden Power Boilers: A Mass Balance. *Chemosphere* 36: 231–249.

Preto, F., McCleave, R., McLaughlin, D. and Wang, J.S. (2005). Dioxins/furans Emissions from Fluidized Bed Combustion of Salt-laden Hog Fuel. *Chemosphere* 58: 935–941.

Ruttanachot, C., Tirawanichakul, Y. and Tekasakul, P. (2011). Application of Electrostatic Precipitator in Collection of Smoke Aerosol Particles from Wood Combustion. *Aerosol Air Qual. Res.* 11: 90–98.

Schatowitz, B., Brandt, G., Gafner, F., Schlumpf, E., Buhler, R., Hasler, P. and Nussbaumer, T. (1994). Dioxin Emissions from Wood Combustion. *Chemosphere* 29: 2005–2013.

Sheu, H.L., Lee, W.J., Su, C.C., Chao, H.R. and Fan, Y.C. (1996). Dry Deposition of Polycyclic Aromatic Hydrocarbons in Ambient Air. *J. Environ. Eng.* 122: 1101–1109.

Shih, S.I. and Lee, W.J. (2008). Significance of Biomass Open Burning on the Levels of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in the Ambient Air. *J. Hazard. Mater.* 153: 276–284.

Sinkkonen, S., Makela, R., Vesterinen, R. and Lahtipera, M. (1995). Chlorinated Dioxins and Dibenzothiophenes in Fly-ash Samples from Combustion of Feat, Wood Chips, Refuse Derived Fuel and Liquid Packaging Boards. *Chemosphere* 31: 2629–2635.

Spliethoff, H. (2010). Power Generation from Biomass and Waste. *Power Generation from Solid Fuels*, Springer, New York, p. 361–467.

Tame, N.W., Dlugogorski, B.Z. and Kennedy, E.M. (2005). PCDD/F Formation in Flaming Combustion, Smoldering, and Oxidative Pyrolysis of 'Eco-friendly' Treated Wood. *Proc. Combust. Inst.* 30: 1237–1243.

Tame, N.W., Dlugogorski, B.Z. and Kennedy, E.M. (2007). Formation of Dioxins and Furans during Combustion of Treated Wood. *Prog. Energy Combust. Sci.* 33: 384–408.

Turner, J. (1999). A Realizable Renewable Energy Future. *Science* 285: 687–689.

U.S. (1994). EPA Modified Method 1613. Tetra- through Octa-chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS. Office of Water Engineering and Analysis Division.

U.S. (2001b). EPA Modified Method 23.Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Stationary Sources. Code of federal Regulations, Title 40, Part 60, Appendix A.

U.S. EPA (2001a). Modified Method 5. Determination of Particulate Emission from Stationary Sources. Code of Federal Regulations, Title 40, Part 60, Appendix A.

Wang, I.C. and Lee, W.J. (2010). Polychlorinated Dibenzo-p-dioxin, Polychlorinated Dibenzofurans and Polychlorinated Biphenyls in Farmed Fish, Water, Sediment, and Feed. *J. Environ. Sci. Health A.* 45: 201–210.

Wang, L.C. and Chang-Chien, G.P. (2007). Characterizing the Emissions of Polybrominated Dibenzo-p-dioxins and Dibenzofurans from Municipal and Industrial Waste Incinerators. *Environ. Sci. Technol.* 41: 1159–1165.

Wang, L.C., Hsi, H.C., Chang, J.E., Yang, X.Y., Chang-Chien, G.P. and Lee, W.S. (2007). Influence of

Start-up on PCDD/F Emission of Incinerators. *Chemosphere* 67: 1346–1353.

Wang, L.C., Hsi, H.C., Wang, Y.F., Lin, S.L. and Chang-Chien, G.P. (2010a). Distribution of Polybrominated Diphenyl Ethers (PBDEs) and Polybrominated Dibenzo-*p*-dioxins and Dibenzofurans (PBDD/Fs) in Municipal Solid Waste Incinerators. *Environ. Pollut.* 158: 1595–1602.

Wang, L.C., Lee, W.J., Lee, W.S. and Chang-Chien, G.P. (2010b). Emission Estimation and Congener-specific Characterization of Polybrominated Diphenyl Ethers from Various Stationary and Mobile Sources. *Environ. Pollut.* 158: 3108–3115.

Wang, L.C., Lee, W.J., Lee, W.S., Chang-Chien, G.P. and Tsai, P.J. (2003a). Characterizing the Emissions of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans from Crematories and their Impacts to the Surrounding Environment. *Environ. Sci. Technol.* 37: 62–67.

Wang, L.C., Lee, W.J., Lee, W.S., Chang-Chien, G.P. and Tsai, P.J. (2003b). Effect of Chlorine Content in Feeding Wastes of Incineration on the Emission of Polychlorinated Dibenzo-p-dioxins/Dibenzofurans. *Sci. Total Environ.* 302: 185–198.

Wang, L.C., Lee, W.J., Tsai, P.J., Lee, W.S. and Chang-Chien, G.P. (2003c). Emissions of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans from Stack Flue Gases of Sinter Plants. *Chemosphere* 50: 1123–1129.

Wang, L.C., Wang, Y.F., Hsi, H.C. and Chang-Chien, G.P. (2010c). Characterizing the Emissions of Polybrominated Diphenyl Ethers (PBDEs) and Polybrominated Dibenzo-p-dioxins and Dibenzofurans (PBDD/Fs) from Metallurgical Processes. *Environ. Sci. Technol.* 44: 1240–1246.

Wang, M.S., Chen, S.J., Lai, Y.C., Huang, K.L. and Chang-Chien, G.P. (2010d). Characterization of Persistent Organic Pollutants in Ash Collected from Different Facilities of a Municipal Solid Waste Incinerator. *Aerosol Air Qual. Res.* 10: 391–402.

Wang, Y.F., Chao, H.R., Wang, L.C., Chang-Chien, G.P. and Tsou, T.C. (2010e). Characteristics of Heavy Metals Emitted from a Heavy Oil-Fueled Power Plant in Northern Taiwan. *Aerosol Air Qual. Res.* 10: 111–118.

Wang, Y.F., Hou, H.C., Li, H.W., Lin, L.F., Wang, L.C., Chang-Chien, G.P. and You, Y.S. (2010f). Dry and Wet Depositions of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in the Atmosphere in Taiwan. *Aerosol Air Qual. Res.* 10: 378–390.

Wen, S., Yang, F., Li, J., Gong, Y., Zhang, X., Hui, Y., Wu, Y., Zhao, Y. and Xu, Y. (2009). Polychlorinated Dibenzo-p-dioxin and Dibenzofurans (PCDD/Fs), Polybrominated Diphenyl Ethers (PBDEs), and Polychlorinated Biphenyls (PCBs) Monitored by Tree Bark in an E-waste Recycling Area. *Chemosphere* 74: 981–987.

Wu, Y.L., Li, H.W., Chien, C.H., Lai, Y.C. and Wang, L.C. (2010). Monitoring and Identification of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in the Ambient Central Taiwan. *Aerosol Air Qual. Res.* 10: 463–471.

Wunderli, S., Zennegg, M., Dolezal, I.S., Gujer, E., Moser, U., Wolfensberger, M., Hasler, P., Noger, D., Studer, C. and Karlaganis, G. (2000). Determination of Polychlorinated Dibenzo-p-dioxins and Dibenzo-furans in Solid Residues from Wood Combustion by HRGC/HRMS. *Chemosphere* 40: 641–649.

Received for review, November 22, 2010
Accepted, March 24, 2011