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

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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, 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; Rutmanachot 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

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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., 2011; Lin et al., 2011b; Wu et al., 2010; Wang et al., 2010e), coal-fired power plants (Lin et al., 2007), electric arc furnaces (EAFs) (Lee et al., 2007), aluminum smelters (ALS) (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 Nm3. 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. 10 g 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 woodchips 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 approximately to 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 $^{35}$Cl$_{6}$-2,3,7,8-TCDD, $^{13}$C$_{12}$-1,2,3,4,7,8-HxCDF, $^{13}$C$_{12}$-2,3,4,7,8-PeCDF, $^{13}$C$_{12}$-1,2,3,4,7,8-HxCDD 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 result 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 ng/kg, respectively. These have the potential to be sources of PCDD/Fs in the atmosphere. The PCDD/F contents in the feeding woodchips, bottom residues, cyclone ashes, bag filter ashes and stack flue gases of the wood-fuelled industrial boiler are listed in Table 1.

**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 | 77.3 | 3.46 | 118  | 21.9 | 238  | 41.0 | 0.0345 | 0.0106 |
| 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.](image-url)
example, the emission factors were calculated using the following equation:

$$\text{EF} = \frac{C \times F_v}{I_w}$$

(1)

**EF**: Emission factor, ng I-TEQ per kg-woodchip burned  
**C**: I-TEQ concentration in stack flue gases (ng I-TEQ/Nm³)  
**F_v**: Volumetric flue gas flow rate (Nm³/hr)  
**I_w**: 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).

**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 toxicity. 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.

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 woodchips | bottom residues | cyclone ashes | Output bag filter ashes | stack flue gases | total | Output/Input ratio |
|---------|-----------------|-----------------|--------------|------------------------|-----------------|-------|------------------|
| 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 |
| 1,2,3,4,7,8-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-HpCDF | ND | 0.000547 | 0.00347 | 0.0156 | 0.00704 | 0.0267 | NA |
| 1,2,3,4,7,8-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
Conclusions

The mean PCDD/F concentrations in the stack flue gases of the wood-fuelled industrial boiler was 0.00537 ng I-TEQ/Nm³, 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/Nm³. 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 PCDF regulation for reutilization of bottom residues, but still higher than PCDF 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.

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### 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                |
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