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ABSTRACT

This study describes polychlorinated dibenzo-p-dioxin and dibenzofuran (PCDD/F) behavior during the incineration of laboratory waste, including combustible laboratory solid waste (LSW), laboratory plastic waste (LPW), and organic laboratory liquid waste (LLW). Stack flue gas (SFG), input materials, bottom ash (BTA), first quenching tower ash (FQA), secondary quenching tower ash (SQA), and baghouse ash (BHA) were sampled and analyzed using high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) assay and bioassay. The PCDD/F concentration of SFG met the standard in Taiwan. The Cl levels of LPW and LLW were roughly equivalent to that of municipal solid waste (MSW). Therefore, the SFG concentration, content of fly ash, and distribution behavior of PCDD/Fs are reasonably similar to those of MSW incinerators. The LSW had an extremely high Cl level (11.4%). The emission factor of the whole incineration system was 888 µg I-TEQ/ton-waste, which is 10-fold higher than that of MSW. The PCDD/F was mainly in BTA (31.6 wt.%) and fly ash (63.1 wt.%), resulting in higher PCDD/F level of ashes compared with that of MSW ashes. Both HRGC/HRMS analysis and bioassay results show similar PCDD/F emission characteristics during the incineration of LW. In addition, the linear regression between the values acquired using these two methods show a good relation (R² > 0.84), indicating that Ad-DR bioassay is a promising fast-screen method for determining PCDD/F levels.

Keywords: Air pollution control devices; Fly ash; Incinerator; Dioxin-like compounds.

INTRODUCTION

Laboratory waste (LW) is inevitably generated during experiments. The amount of LW generated in a given experiment is usually tiny due to the small scale of the tests. At present, LW is temporarily stored in the laboratory and then transported to a LW treatment plant when an adequate amount has accumulated. Due to the complex composition and varying quality of LW, it is much more difficult to treat LW than it is to treat other industrial waste. The Ministry of Education has thus financially supported the Sustainable Environment Research Center (SERC) of National Cheng Kung University to build a LW treatment plant to dispose of university LW in Taiwan. There are three major systems, namely a physical and chemical treatment system, an incineration system, and a plasma melting system, in the LW treatment plant. The physical and chemical system treats inorganic laboratory liquid waste (LLW), which may contain acid, heavy metals, cyanide, and alkali compounds. The targets of the incinerator are combustible laboratory solid waste (LSW), laboratory plastic waste (LPW), and organic LLW. LPW is mainly plastic containers for LLW and is composed of polyethylene, polypropylene, or other Cl-free materials. LSW includes combustible waste for medical or biochemical experiments, which usually has high levels of Cl. The plasma melting system is used to dispose of hazardous residues, including sludge, toxic ash, or other waste from the two former systems. After vitrification,
hazardous materials are transformed into stable slag, and the slag can be further remade composite with polyester resin (Kuo et al., 2011).

In Taiwan, incineration is the main method for treating combustible solid waste, which totaled 6,404,987 tons (including municipal solid waste (MSW) and general industrial solid waste) in 2011 (TEPA, 2011). Previous studies reported that persistent organic pollutants, including polybrominated diphenyl ethers (PBDEs), polybrominated dibenzo-p-dioxins and dibenzofurans (PBB/D/Fs), and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), are generated during the incineration process (Du et al., 2013; Thacker et al., 2013). For waste with high Cl content, a large amount of PCDD/Fs are generated during the incineration process (Hatanaka et al., 2005). Flue gas may have a high PCDD/F concentration and cause secondary air pollution (Coutinho et al., 2006). Even with good removal efficiency via air pollution control devices (APCDs), the PCDD/F content of fly ash waste medical incinerators is often much higher than that from MSW incinerators (Gidaros et al., 2009; Wu et al., 2011). PCDD/Fs are nonpolar, poorly water-soluble, lipophilic, stable chemicals that are produced as byproducts and released into the environment in ultra-trace amounts from various combustion processes. PCDD/Fs is a class of endocrine disrupting chemicals to induce several adverse health effects including disruption of steroid sex hormones (Wang et al., 2006), delay growth and thyroid function (Su et al., 2010), interference with human reproduction (Chao et al., 2007; Su et al., 2012), increase internal dose of the breastfed infants (Chao et al., 2004; 2005), and increment of diabetes or cancer incidences (Wang et al., 2008). The levels of atmospheric PCDD/Fs depend on human industrial and domestic activities. PCDD/Fs accumulate in the tissues and milk of livestock, providing an entry into the food chain (Chao et al., 2012). PCDD/Fs' toxic effects are activated by binding to the intracellular aryl hydrocarbon receptor (AhR). This leads to changes in thyroid metabolism and may ultimately result in chronic stimulation of the thyroid and potentially to thyroid cancer (Chao et al., 2006).

LW usually contains high levels of CI because chlorides are common reagents in laboratories. Therefore, the incineration of LW has a high potential of generating PCDD/Fs. However, few studies have focused on the treatment of LW. The present study investigates the operation characteristics of LW incineration in two parts. Part 1 investigates the emission characteristics and distribution of PCDD/Fs for the whole incineration process. Part 2 focuses on the PCDD/F profiles of output materials, characteristics of ash, and the influence of Cl content. In this study, the PCDD/F concentration of input and output materials was analyzed. The PCDD/F mass distributions among output materials were investigated. In general, PCDD/F analysis takes about 2 weeks or longer, which may not reflect the real-time operational situation. Therefore, a highly sensitive recombinant hepatoma cell method (adenoviral vector-dioxin response (Ad-DR) bioassay), which takes much less time, was also adopted to analyze the PCDD/F concentration of specimens. Ad-DR bioassay has been demonstrated as a possible screening tool and has been shown to produce results consistent with those of high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) (Chao et al., 2010, 2012; Lin et al., 2013). This study confirms the feasibility of this quick method for ash samples.

METHODS

Processes of Incineration System

The LW treatment plant of SERC is located in Tainan, Taiwan. The capacity of the incineration system is 120 kg/hr. The process flow diagram is shown in Fig. 1. Solid input materials are fed using the feeding unit and organic LLW is directly injected into the incinerator. The operation temperatures of the primary and secondary combustion chambers are 900°C and 1150°C, respectively. The secondary combustion chamber is equipped with a diesel combustor to destroy persistent organics, carbon monoxide (CO), and unburned residues in the flue gas. The flue gas passes through a series of APCDs, including the first quenching tower, secondary quenching tower, baghouse filter with injection of activated carbon, and scrubber, and is then emitted to the ambient air through a stack. The first and secondary quenching towers quench the flue gas rapidly to 600°C and 160°C, respectively, to avoid the formation of PCDD/Fs. The activated carbon is injected to adsorb persistent organic gaseous pollutants and is trapped with particulates by a baghouse filter, which is the most popular process for removing PCDD/Fs. Before being emitted into the ambient air, the flue gas is heated to 120°C to avoid the formation of white smoke. The APCDs in the incineration systems have been proven to remove heavy metals effectively (Chang et al., 2012).

![Fig. 1. Process flow of incineration system.](image-url)
This study focused on PCDD/F emission characteristics during incineration. To investigate the influence of input materials, incineration tests with three input materials, namely LPW, LLW, and LSW (run-1 to run-3), were conducted. The average feeding rates of the solid and liquid waste were 120 and 240 kg/hr, respectively. Ashes and flue gas were sampled and analyzed for the three runs.

Sampling of Flue Gas and Solid Specimens

The stack flue gas (SFG) sampling followed the standard sampling procedure of PCDD/Fs in stack flue gas, NIEA A807.74C, which was issued by Environmental Analysis Laboratory EPA in Taiwan. The flue gas was collected isokinetically and the sampling probe was cleaned with acetone, dichloromethane, and toluene sequentially before sampling. In the experiments, the sampling train, assembled by train parts, used no sealing grease, which meets the requirements of U.S. EPA Modified Method 5. Prior to sampling, about 20-40 g of adsorbent (Amberlite XAD-2®) was loaded in the cartridge and then spiked with PCDD/F surrogate standards pre-labeled with isotopes 37Cl4-2,3,7,8-TCDD, 13C12-1,2,3,4,7,8-HxCDD, 13C12-2,3,4,7,8-TeCDF, 13C12-1,2,3,4,7,8-HxCDF, and 13C12-1,2,3,4,7,8,9-HpCDF. After the sampling procedures, samples were preserved and transported to the laboratory at temperatures under 10°C for further analysis.

Solid specimens, including bottom ash (BTA), first quenching tower ash (FQA), secondary quenching tower ash (SQA), and baghouse ash (BHA), were collected from the bottom ash pit and APCD units of the incineration systems. The solid specimens were dried and ground for further analysis.

PCDD/F Analysis

The PCDD/F analysis was conducted following the procedure given in U.S. EPA Modified Methods 23 and 1613. The samples were spiked with the 13C12-labeled internal standard. A series of steps, including 24-hr Soxhlet extraction, nitrogen blowing, cleanup and fractionation procedure, and nitrogen blowing, were conducted before instrumental analysis. The finally concentrated eluate (about 1 mL) was analyzed using HRGC (Hewlett Packard 6970 Series gas chromatograph, CA, USA) and HRMS (Micromass Autospec Ultima, Manchester, UK) to measure the PCDD/F concentration. Details of the procedure can be found in a previous study (Wang and Chang-Chien, 2007).

PCDD/F Measurement Using Bioassay

All specimens, including ash and flue gas, were divided into two parts for two PCDD/F measurement methods. One part was used for chemical analysis (HRGC/HRMS) and the other part was used for the dioxin bioassay (Ad-DR bioassay). The Ad-DR bioassay was technically supported by Dr. Tsou of National Health Research Institutes (NHRI). The dioxin bioassay (Ad-DR bioassay) used rat hepatoma cells (H4IIE cells) infected with AdEasy virus expressing TATA-4 × DRE-Luc (a luciferase reporter gene driven by a promoter with four copies of dioxin-responsive element (DRE)). Ad-DR bioassay with the virus construct has been proven to be useful for the quantitative analysis of dioxins and dioxin-like compounds (Lin et al., 2013). Details of the bioassay procedure can be found elsewhere (Lin et al., 2013). The luciferase activity was expressed as relative light units (RLUs)/well. The values of the sigmoid semi-logarithmic TCDD dose-response calibration curve were fitted using the Hill equation (Chao et al., 2011). According to a previous study, PCDD/F levels in the AhR reporter gene assay can be expressed as bio-analytical equivalents (BEQs) (Kojima et al., 2011).

RESULTS AND DISCUSSION

PCDD Composition of Input and Output Materials

The characteristics of the three input materials are shown in Table 1. The PCDD/F content in LPW, LLW, and LSW was 0.12, 0.002, and 0.088 ng I-TEQ/g, respectively. The Cl levels for LPW, LLW, and LSW were 2,470, 202, and 114,000 mg/kg, respectively. Table 2 shows the PCDD/F concentration of flue gas for three runs. The total PCDD/F concentrations were 2.09, 2.26, and 3.07 ng/Nm³ in run-1 to run-3, respectively. The international toxic equivalent PCDD/F concentrations were 0.358, 0.420, and 0.491 ng I-TEQ/Nm³ in run-1 to run-3, respectively, all of which meet the standard of 0.5 ng I-TEQ/Nm³ (TEPA, 2005).

### Table 1. Characteristics of input materials.

<table>
<thead>
<tr>
<th>Run</th>
<th>Input material</th>
<th>PCDD/F content (ng/g)</th>
<th>Cl content (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Total concentration</td>
<td>I-TEQs</td>
</tr>
<tr>
<td>1</td>
<td>LPW</td>
<td>2.36</td>
<td>0.120</td>
</tr>
<tr>
<td>2</td>
<td>LLW</td>
<td>0.224</td>
<td>0.002</td>
</tr>
<tr>
<td>3</td>
<td>LSW</td>
<td>1.23</td>
<td>0.088</td>
</tr>
</tbody>
</table>

### Table 2. PCDD/F concentration of flue gas for three input materials.

<table>
<thead>
<tr>
<th>Total concentration (ng/Nm³)</th>
<th>I-TEQs (ng I-TEQ/Nm³)</th>
<th>BEQs (ng BEQ/Nm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LPW</td>
<td>2.09</td>
<td>0.358</td>
</tr>
<tr>
<td>LLW</td>
<td>2.26</td>
<td>0.420</td>
</tr>
<tr>
<td>LSW</td>
<td>3.07</td>
<td>0.491</td>
</tr>
<tr>
<td>Taiwanese standard</td>
<td>N.A.</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Fig. 2 shows the PCDD/F content of ash. Overall, the PCDD/F level of ash in run-3 was much higher than those in the other two runs. The PCDD/F level profiles obtained using two different methods were all similar. There was almost no BTA generated in the incineration of LLW; thus, PCDD/F content data was not available. The PCDD/F content was 0.02 ng I-TEQ/g and 1.86 ng I-TEQ/g in run-1 and run-3, respectively. In comparison with that of BTA of MSW incinerators (0.0138–0.0787 ng I-TEQ/g) from a previous study, the result of run-1 was roughly equivalent but the result of run-3 was much higher (Wang et al., 2010). According to the statistical data in annual reports of TEPA, the Cl content in MSW ranged from 800 to 2,500 mg/kg (average value = 1520 mg/kg) from 1999 to 2011. The Cl level in LPW was 2,470 mg/kg, which is roughly equal to the average value in MSW. The PCDD/F content of BTA in run-3 is reasonably close to that of MSW incinerators. However, the PCDD/F content of BTA in run-1 was about two orders higher. A previous study reported that increased Cl content in the input materials highly increased the formation of PCDD/Fs (Aurell et al., 2009), supporting this result. The high PCDD/F level in ash is due to the formation of metal chloride or other chlorinated aromatic compounds (Lu et al., 2007).

The PCDD/F content of fly ash was on average higher than that of BTA in all runs, which is consistent with the results of previous studies (Lin et al., 2008; Wang et al., 2010; Zhang et al., 2012). The average PCDD/F level of quenched ash was a little lower than that of BHA. This can be explained by the venture scrubber having an average PCDD/F (in I-TEQ) removal efficiency of 44.5% (Hunsinger et al., 1998). Therefore, the PCDD/F mass is divided approximately equally into quenched ash and the ash in following units, as found in this study.

**PCDD/F Emission Factors of Output Materials**

Incinerators have three paths, namely bottom ash, fly ash, and flue gas, to discharge their pollutants to the environment. For path I (bottom ash), BTA is currently reutilized after elutriation. For path II (fly ash), FQA, SQA, and BHA are regarded as hazardous materials that need to be solidified before taken to a landfill. For path III (flue gas), FSG is directly emitted into the ambient air. Table 3 shows the PCDD/F emission factors of each path and the whole system for the three input materials. The emission factors of the whole system for LPW, LLW, and LSW were 145, 214, and 888 µg I-TEQ/ton-input-material, respectively. Previous studies reported that the emission factors for hardwood (Cl = 0.04%), coal (Cl = 0.35%), and MSW (Cl = 0.15%) were 0.2, 3.0, and 0.55 µg I-TEQ/ton-input-material (Lee et al., 2005; Wang et al., 2010). In comparison with the results in these above mentioned studies, the Cl contents of LPW and LLW were roughly equivalent, but the emission factors were much higher. This is probably due to that the composition of input materials in this study is extremely complicated. The input material also had high level of metals which may serve as catalysts to form PCDD/Fs. It was obviously that the emission factors were much lower even with roughly equivalent Cl content while combusting fuels due to the homogeneous composition. For ash, the emission factors of path II in run-1 and run-2 were 121 and 188 µg I-TEQ/ton-input-material, respectively, which are roughly equal to that in MSW incinerators (Lin et al., 2008; Wang et al., 2010). However, the emission factor of path II in run-3 was about 10-fold higher. Similar results were found for path I. The PCDD/F concentration has to be controlled to under 0.5 ng I-TEQ/Nm³ to meet the Taiwanese standard, and thus the emission factors of Path III in the three runs were about the same (TEPA, 2005). However, these emission factors are higher than that of MSW incinerators. This is due to the standard for large MSW incinerators being more stringent (0.1 ng I-TEQ/Nm³) (TEPA, 2003).
Table 3. PCDD/F emission factor of each path and whole incineration system.

<table>
<thead>
<tr>
<th>Unit: µg/ton-waste</th>
<th>Path I</th>
<th>Path II</th>
<th>Path III</th>
<th>Whole system</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BTA</td>
<td>FQA + SQA + BHA</td>
<td>Flue gas</td>
<td></td>
</tr>
<tr>
<td>Run-1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>1,240</td>
<td>125</td>
<td>1,470</td>
</tr>
<tr>
<td>I-TEQs</td>
<td>3.09</td>
<td>121</td>
<td>21.5</td>
<td>145</td>
</tr>
<tr>
<td>Bioassay</td>
<td>6.35</td>
<td>190</td>
<td>33.3</td>
<td>229</td>
</tr>
<tr>
<td>Run-2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>0</td>
<td>2,470</td>
<td>136</td>
<td>2,610</td>
</tr>
<tr>
<td>I-TEQs</td>
<td>0</td>
<td>188</td>
<td>25.2</td>
<td>214</td>
</tr>
<tr>
<td>Bioassay</td>
<td>0</td>
<td>228</td>
<td>44.0</td>
<td>273</td>
</tr>
<tr>
<td>Run-3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>10,100</td>
<td>13,300</td>
<td>184</td>
<td>23,500</td>
</tr>
<tr>
<td>I-TEQs</td>
<td>287</td>
<td>572</td>
<td>29.5</td>
<td>888</td>
</tr>
<tr>
<td>Bioassay</td>
<td>226</td>
<td>882</td>
<td>75</td>
<td>1,180</td>
</tr>
</tbody>
</table>

PCDD/F Distribution of Output Materials

Table 4 shows the PCDD/F distribution among output materials, namely BTA, FQA, SQA, BHA, and SFG. For low Cl content in input materials (run-1 and run-2), the PCDD/F distribution profiles were similar in the three representative ways (in total concentration, I-TEQ and BEQs). Most of the PCDD/Fs (~50% or higher) were in BHA. PCDD/Fs in quenching ash and SFG accounted for ~25% and ~20%, respectively. Less than 5% of PCDD/Fs was in BTA. For MSW incinerators, PCDD/Fs are mainly collected in BHA, but their percentage is much higher (average ~92%). The fractions of PCDD/Fs in BTA and SFG were 5% and 0.5%, respectively. The major differences in PCDD/F distribution between this incinerator and MSW incinerators are due to the different standards of the two types of incinerator. For PCDD/F concentration in SFG, the standards for incinerators with capacities of <100 tons/day and >100 tons/day are 0.5 and 0.1 ng I-TEQ/Nm³, respectively (TEPA, 2003, 2005). To meet the stringent standard of large MSW incinerators, the incinerator operators have to inject a lot of activated carbon (0.16 kg activated carbon/ton MSW) to adsorb PCDD/Fs, which are collected in the baghouse filters as BHA. In addition, the units prior to baghouse filters, such as the superheater, economizer, and dry scrubber, have no effect on the removal of PCDD/Fs. This explains why such a high fraction of PCDD/Fs (~92%) resided in BHA and an extremely small fraction (<0.5%) existed in SFG. For incinerators with capacities of <100 tons/day, the limit is less strict than that for those with capacities of >100 tons/day. In addition, the PCDD/Fs are removed by quenching processes and gather in the quenching ash. Therefore, ~25% and ~20% of PCDD/Fs were distributed in quenching ash and SFG, respectively.

For run-3, the input material had 11.4% Cl, leading to the formation of a large amount of PCDD/Fs (~30%) in BTA (see Fig. 2). According to previous data (Table 2), the PCDD/F emission factor of run-3 was about 4-fold higher than those of the other runs. Therefore, the fraction of PCDD/Fs in SFG has to be reduced to meet the standard. The percentages of PCDD/Fs in quenching ash and BHA are roughly equivalent to those in the other runs.

Comparison of Chemical Analysis and Bioassay for PCDD/F Measurement

Fig. 3 shows the relationship between I-TEQs and BEQs of the specimens in this study. For SFG samples (including gas and particulate phases), a linear regression between HRGC/HRMS assay values and the Ad-DR bioassay values of log (PCDD/Fs I-TEQs) = 0.9673 × log (BEQs) – 0.0302 (R² = 0.84, p < 0.001) was determined after regression. The linear regression for ash samples was log (PCDD/Fs I-TEQs) = 1.179 × log (BEQs) – 0.8114 (R² = 0.90, p < 0.001). According to the linear regressions, the BEQ can serve as an index of PCDD/F emission to quickly predict the approximate PCDD/F concentration for HRGC/HRMS analysis. In addition, the PCDD/F distributions for I-TEQs and BEQs have similar profiles (Chao et al. 2010, 2012; Lin et al., 2013). Therefore, Ad-DR bioassay may be a promising method for investigating PCDD/F emission behavior with reduced time and the cost.

CONCLUSION

This study investigated the incineration behaviors of
three types of LW using chemical analysis and bioassay. For LLW and LPW, the Cl level was roughly equivalent to that of MSW. Therefore, the SFG concentration, content of fly ash, and distribution behavior of PCDD/Fs were similar to those reported in previous studies. For LSW, the high Cl level (11.4%) made the emission factor of the whole system 10-fold higher (888 µg I-TEQ/ton-waste). The PCDD/Fs mainly gathered at BTA (31.6%) and fly ash (63.1%). The PCDD/F behaviors during incineration revealed by chemical analysis and bioassay were similar. In addition, the linear regression between HRGC/HRMS assay values and the bioassay values showed a good relation (R² > 0.84), indicating that bioassay may be a promising method for investigating PCDD/F behaviors.

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