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# Characterization and Inventory of PCDD/Fs and PBDD/Fs Emissions from the Incineration of Waste Printed Circuit Board

Huabo Duan and Jinhui Li\*

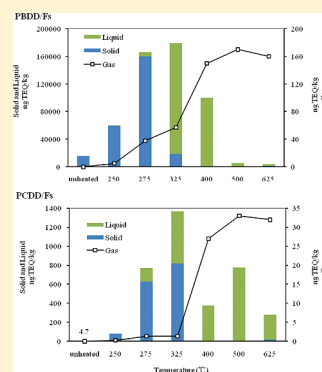
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**S** Supporting Information

**ABSTRACT:** Many developing countries have not significantly changed their course with regard to electronic waste contamination, and they are still facing the specter of mountains of hazardous electronic waste, with serious consequences for both the environment and public health. An efficient and stable analytical method was developed to determine the inventory and emission factors of polybrominated dibenzo-*p*-dioxin and dibenzofurans (PBDD/Fs) and polychlorinated dibenzo-*p*-dioxin and dibenzofurans (PCDD/Fs) formed from the incineration of scrap printed circuit boards (PCBs). Both PBDD/Fs and PCDD/Fs have been found in all experimental sections with a maximum formation rate at temperatures between 250 and 400 °C. The amounts tended first to increase and then began to decrease as the temperature rose. When subjected to a heating temperature of 325 °C, the total content of twelve 2,3,7,8-substituted PBDD/Fs congeners (tetra- through octabromo-) gathered from three outputs was the largest, at 19 000, 160 000, and 57 ng TEQ/kg in solid, liquid, and gaseous fractions, respectively; the total content of seventeen 2,3,7,8-substituted PCDD/Fs congeners (tetra- through octachloro-) was 820, 550, and 1.4 ng TEQ/kg. The formation of PCDD/Fs was remarkably less than that of PBDD/Fs because bromine concentrations considerably exceeded chlorine concentrations. The ingredients and conditions necessary to form PCDD/Fs or PBDD/Fs were definitely present, such as products of incomplete combustion, halogenides, an oxidizing atmosphere, and a catalyst—Cu salts being the most effective, significantly increasing the yields of PCDD/Fs and PBDD/Fs and decreasing the optimum temperature range.



## INTRODUCTION

Electronic waste (e-waste), or waste electrical and electronic equipment (WEEE), refers to loosely discarded, surplus, obsolete, or broken electrical or electronic devices. E-waste is one of the fastest growing segments of the global waste stream,<sup>1,2</sup> and the unregulated and informal recycling of e-waste has been recognized as a global problem. Guiyu in Shantou, Luqiao in the Taizhou region of China, Delhi and Bangalore in India, and the Agbogbloshie site near Accra, Ghana are sites where e-waste processing takes place.<sup>3,4</sup> Although a number of laws, rules, and regulations have been passed which are designed for the proper collection and treatment of these scraps, the effectiveness of these regulatory initiatives does not seem promising, as the stream of pollution from e-waste does not seem to be appreciably abating. Many developing countries have not significantly changed their course with regard to e-waste contamination, and they are still facing the specter of mountains of hazardous e-waste, with serious consequences for both the environment and public health.<sup>4,5</sup>

Among multiple types of electronic devices, scrap printed circuit boards (PCBs), cathode ray tube (CRT) monitors, and flame-retardant housing polymeric materials are very prone to emitting or producing toxic substances during the recycling processes if improperly handled. These processes include dismantling, mechanical

recycling, thermal processing, chemical separation and extraction, and the ultimate disposal of residues, such as open burning and dumping in landfills.<sup>7–10</sup>

Environmental groups claim that the recovery and disposal of e-waste is one of the largest potential contributors to the emission of dioxins.<sup>11</sup> High levels of dioxin contamination in e-waste dismantling areas, including polychlorinated dibenzo-*p*-dioxin and dibenzofurans (PCDD/F),<sup>6,12–14</sup> polybrominated dibenzo-*p*-dioxin and dibenzofurans (PBDD/F),<sup>15</sup> have repeatedly been reported. Although pyrolysis and combustion in the presence of bromine and chlorine compounds, such as brominated flame retardants (BFRs), wires/cables, TV housing plastic, and PCBs bare board, is thought to be their main source,<sup>16–19</sup> most studies have focused on high-temperature pyrolysis experiments in quartz reactors with feedstock consisting of only a few materials. In all of these experiments, priority has been given only to the formation of PCDD/Fs, while the quantitative emissions of PBDD/Fs from the incineration of waste PCBs have seldom been studied.

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Because the formation of dioxin is especially likely at around 300 °C, this temperature range has been the focus of studies of waste incinerators. Besides the open burning of PCBs scrap (which almost has been banned), the processes employed in current recycling activities (including solder-opening dismantling, mechanical recycling, thermal processing, chemical separation and extraction, and the ultimate disposal of residues) invariably consist of low-temperature pyrolysis (250–300 °C). Said thermal processing is also highly suspected of producing toxic byproduct through the decomposition of flame-retardant resins. However, there has been relatively little empirical research devoted to identifying the favorable temperature conditions which lead to the generation of chlorinated and brominated and chlorinated dioxin, especially on the thermal processing of PCBs mounted with electronic components—a category which comprises a large, heterogeneous group of compounds. As yet, very little is known about how the metals in PCB waste affect the emissions of halogenated pollutants subjected to incineration.

The initial focus of this study, therefore, was to develop an efficient and stable analytical method for determining the characterization and inventory of PBDD/Fs and PCDD/Fs formed from the incineration of scrap PCB assemblies (motherboards) subjected to various temperature conditions, in the range of 250 to 625 °C. To study the effects of air atmosphere (using 20 vol % O<sub>2</sub> + 80 vol % N<sub>2</sub> mixture), incineration experiments were conducted in an electric-resistant tube furnace. Hence the behavior and causes of PCDD/Fs and PBDD/Fs formation could be comparably investigated. The results will help to determine (in quantity) whether the contributors to dioxin contamination in these areas are similar to or different from those associated with “suspected” environmental sources.

## ■ EXPERIMENTAL SECTION

**Characteristics of the Samples.** Printed circuit boards mounted with electronic components (motherboards), which had been separated from the control units of waste personal computers, were selected for studying, as they presented a multicomponent complex system. The motherboards contained the resistors, capacitors, transformers, mass storage interfaces, serial and parallel ports, expansion slots, and all the controllers required to interface with standard peripheral devices, but the expansion boards, such as video cards, batteries, and memory, were removed. The whole-board samples were ground into particles through a 1-mm sieve for further examination. The major polymer derived from PCB is epoxy resin (>20 wt %), which is mainly from the laminated board. Other polymers with small fractions include phenolic resin, nylon, polyether sulfone (PES), and polyphenylene sulfide (PPS), which are used for the housing unit of electronic components and slots. The filler is fiber glass as reinforced materials.

The elemental analysis was performed using a CE-440 Instruments CHNO analyzer. The bromine and chlorine content of the samples were determined by EPA9056A (EPA method 5050). The metals were examined by XRF (X-ray fluorescence). The average elemental composition (wt %) of the PCB samples was C, 23.89; H, 1.95; N, 0.75; O, 6.08; Cl, 0.096; and Br, 5.78, indicating the presence of BFRs. The composition (wt %) of major metals was Cu, 6.16; Al, 3.62; Fe, 0.31; and Ba, 0.50.

**Experiment.** A laboratory-scale fixed-bed tubular reactor, connected to a smoke capture unit, cooling unit, filter, and XAD-2 resins (0.65 mm in diameter, 25 g), was chosen to conduct the thermal decomposition runs (Supporting Information). The

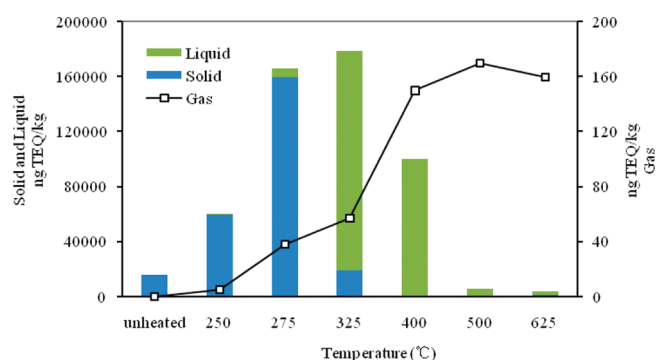
thermal experiments were carried out with 80 g of samples according to the volume of the combustion boat, which was placed in the center of a cylindrical quartz tube. The mixture gas (using 20 vol % O<sub>2</sub> + 80 vol % N<sub>2</sub> mixture) was then passed through at a flow rate of 200 mL min<sup>-1</sup>, and the system was heated at a rate of 10 °C min<sup>-1</sup> to the appointed temperature, and maintained there for 5 min.

Throughout the run, exposure to light was extremely restricted, and the vapor leaving the reactor flowed to a series of cooled gas-to-liquid separators where the liquids were condensed and collected. The uncondensed products were either vented to the smoke capture unit or captured by an adsorption unit of XAD to collect the gaseous part of the dioxin. Solid and liquid yields were determined in each experiment by weighing the amount of each obtained, and calculating the corresponding percentage, while the gas yields were determined by subtraction.

**Analytical Procedure.** Samples were pretreated in a certified laboratory in Beijing to analyze tetra- through octabromodibenzo-*p*-dioxins and furans (PBDD/Fs) and tetra- through octachlorodibenzo-*p*-dioxins and furans (PCDD/Fs). These compounds were analyzed in an HRGC–HRMS and quantified with the isotope dilution method. The steps were as follows: addition of internal standards, toluene extraction, sulfate acid treatment, silica gel cleanup, active carbon cleanup, concentration, addition of a syringe spike, and analysis by HRGC–HRMS.

All organic solvents used for extraction and cleanup were of pesticide residue analysis grade or HPLC grade, and purchased from J. T. Baker (New Jersey). Silica gel (0.100–0.210 nm) was obtained from Kanto Chemicals Co., Inc. (Tokyo, Japan). <sup>13</sup>C<sub>12</sub>-labeled and unlabeled native standard solutions of PBDD/Fs and PCDD/Fs were purchased from Cambridge Isotope Laboratories (Cambridge, MA) and Wellington Laboratories (Ontario, Canada).

Internal standards of <sup>13</sup>C<sub>12</sub>-labeled PBDD/F and PCDD/Fs were added to every sample prior to extraction. The internal standards allowed quantification of the native PBDD/Fs and PCDD/Fs in the sample. Extraction of PBDDs/Fs and PCDD/Fs from solid and resin samples was performed separately by means of Soxhlet extraction with toluene (16 h). The smoke capture unit and the XAD-2 absorption unit were extracted in toluene together to gauge the dioxins in gaseous fraction. All raw extracts were concentrated using a rotary evaporator (EYELA, Japan). The extracts of solid and resin samples and liquid samples were treated with sulfate acid, and fractionated using a multilayer silica gel column chromatograph and a carbon column chromatograph. Concentrations of PBDD/F and PCDD/Fs were determined by HRGC–HRMS analysis. Quantification and identification were performed with Agilent 6890N gas chromatography coupled with JEOL JMS-800D mass spectrometer. An autosampler (Agilent 7683B automatic liquid sampler) was used for injection (1 L, splitless). An SLB-5 ms (Supelco, 15 m × 250 μm i.d. × 0.10 μm film thickness) column was used. The HRMS was operated in an electron impact (38 eV and 500 μA current) selective ion monitoring (SIM) mode at resolution *R* > 10000 MU (5% valley). The GC oven temperature for PBDDs/Fs analysis was programmed as follows: 120 °C for 2 min, 20 °C/min to 220 °C for 0 min, 10 °C/min to 330 °C for 10 min. The GC oven temperature for PCDDs/Fs analysis was programmed as follows: 130 °C for 1 min, 15 °C/min to 210 °C for 0 min, 3 °C/min to 310 °C for 0 min, 5 °C/min to 320 °C for 10 min. The carrier gas (helium) had a constant pressure of 25.4 psi for analysis. One μL of the extract was injected under splitless mode for PBDD/Fs and



**Figure 1.** Gas, liquid, and solid residue fractions of TEQ content of PBDD/Fs from the incineration of printed circuit board scraps at various temperatures.

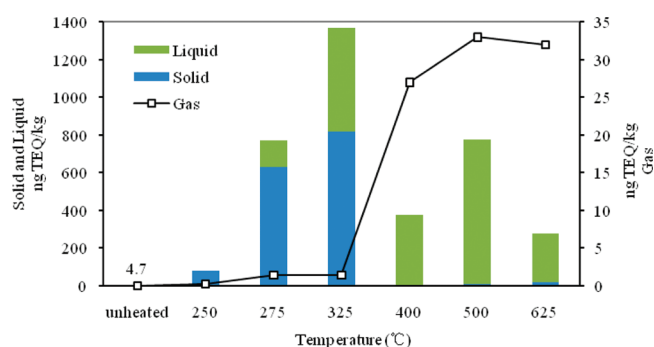
PCDD/Fs. The injection port temperature was set at 260 and 300 °C for PBDD/Fs and PCDD/Fs, respectively. A blank run was conducted. Details of MS analysis and quality control are described by Japan's JIS method for PCDD/Fs and tentative analytical method for PBDD/Fs. Whereas the recoveries for the twelve individual 2,3,7,8-PBDD/Fs congeners ranged from 0% to 412%, the recoveries for the seventeen individual 2,3,7,8-PCDD/Fs congeners ranged from 28% to 119%, falling within the requirement of the standard limit.

PCDD/F TEQ values were calculated based on World Health Organization suggested Toxic Equivalency Factor (WHO-TEF, Supporting Information). WHO recommends the use of the same TEF values for PBDD/Fs as described for the chlorinated analogues. Because research on the toxic effects of PBDD/Fs is incomplete, PBDD/F TEFs were assigned as those of their PCDD/F equivalents.<sup>20</sup>

## RESULTS AND DISCUSSION

**PBDD/F and PCDD/F Concentrations.** The heating experiment was conducted to capture and analyze the products formed in the incineration of the PCBs. These processes resulted in the generation of three outputs under an air atmosphere: gaseous, liquid, and solid residues. Increasing percentages of 1.22%, 1.78%, 11.29%, 22.59%, 26.64%, and 29.98% of mass loss were produced at 250, 275, 325, 400, 500, and 625 °C, respectively, of which a proportion of 0.56%, 1.14%, 4.36%, 8.16%, 4.66%, 6.09% of weight was held and separated as liquid product, respectively. Actually, incomplete combustion happened at all heating temperatures due to both the excess over feedstock and the deficiency of residence time. Thus, some liquid blended with solid residue was categorized as solid output, particular under the low-temperature conditions. Generally, as reaction temperature increases, char production yield decreases but the yield of noncondensable gas increases, because degradable organics decompose and gas production increases at higher temperatures.

Figures 1 and 2 summarize the total TEQ PBDD/Fs and PCDD/Fs content per kilogram of waste PCBs, expressed as fractions, from the incineration runs under the various experimental conditions. The formation of dioxin is generally considered to occur only rarely below 300 °C. However, extremely large amounts of PBDD/Fs were obtained at temperatures of 250 and 275 °C, even without heating. For the unheated PCBs, the total PBDD/Fs concentration reached 4.3 mg/kg (16 000 ng TEQ/kg, WHO-TEF), showing that either the assembly processing, the



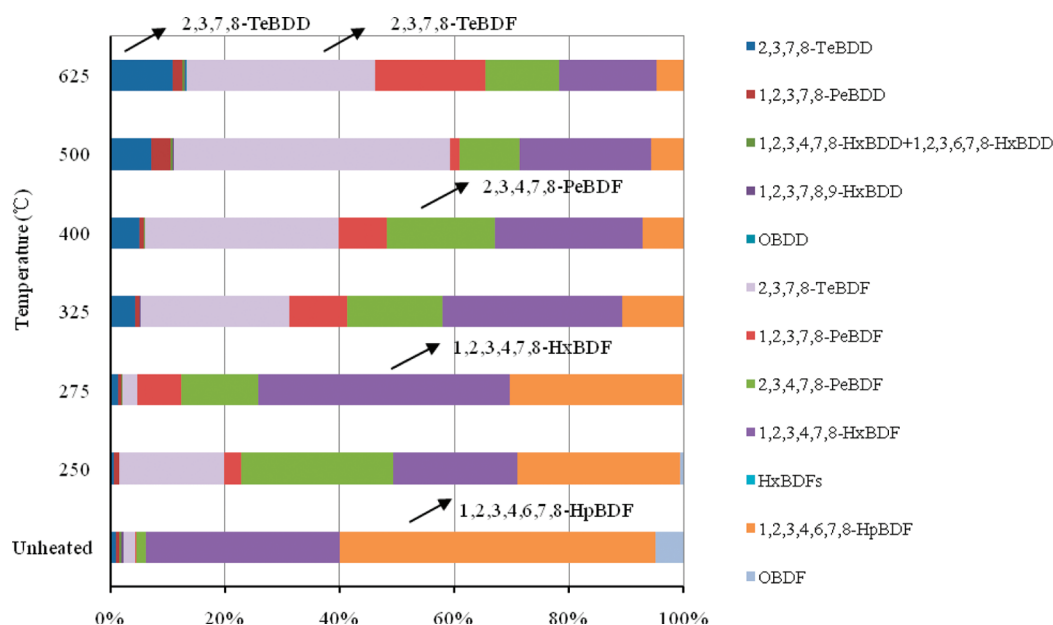
**Figure 2.** Gas, liquid, and solid residue fractions of TEQ content of PCDD/Fs from the incineration of printed circuit board scraps at various temperatures.

usage stage, or the grinding process at the end-of-life stage probably resulted in the formation due to the addition of BFRs. The total content of PBDD/Fs in solid and liquid fractions tended first to increase and then began to decrease as the temperature rose, but in amounts much higher than in unheated PCBs below the temperature of 400 °C. Whereas the quantity of PBDD/Fs contained in the solid fraction was greater than in liquid condensation below the temperature of 325 °C, on the other hand the amount of PBDD/Fs contained in liquid condensation was much higher above 325 °C. By contrast, the content of PBDD/Fs in the gas fraction kept increasing as the temperature rose, but it was still less than in the other fractions. When subjected to a heating temperature of 325 °C, the total content of twelve 2,3,7,8-substituted PBDD/Fs congeners gathered from three outputs was the largest, with 19 000, 160 000, and 57 ng TEQ/kg in solid, liquid, and gaseous fractions, respectively. At higher temperatures, the PBDD/F concentration diminished again and the compounds were almost completely destroyed at 625 °C.

Because chlorine is chemically similar to bromine, the mechanisms for the formation of PCDD/Fs are similar to those of PBDD/Fs upon thermal treatment via the pyrolysis of precursor compounds (such as halogenated aromatic compounds).<sup>21</sup> They therefore have similar physicochemical properties, toxicity, and geochemical behavior in the environment. As shown in Figure 2, the TEQ concentration of PCDD/Fs produced from the incineration of PCB scrap is significantly lower than that of PBDD/Fs, which could be explained by the high bromination level. During the incineration processes in this study, bromine concentrations considerably exceeded chlorine concentrations.

For the unheated PCBs, the total PCDD/Fs concentration was 4.7 ng TEQ/kg (WHO-TEF). The total content of PCDD/Fs in solid and liquid fractions tended first to increase and then began to decrease as the temperature rose, but in amounts much higher than in unheated PCBs, at all heating temperatures. The quantity of PCDD/Fs contained in the solid fraction was greater than in liquid condensation below the temperature of 325 °C, on the other hand, the amounts of PCDD/Fs contained in liquid condensation was much higher at temperatures above 325 °C. By contrast, the content of PCDD/Fs in the gas fraction kept increasing as the temperature rose, but was still less than in other fractions. When subjected to a heating temperature of 325 °C, the total content of seventeen 2,3,7,8-substituted PCDD/Fs congeners gathered from three outputs was the largest, with 820, 550, and 1.4 ng TEQ/kg in solid, liquid, and gaseous fractions, respectively.





**Figure 3.** Composition of total TEQ PBDD/F homologues for liquid and solid outputs generated from degraded PCB samples at various temperatures.

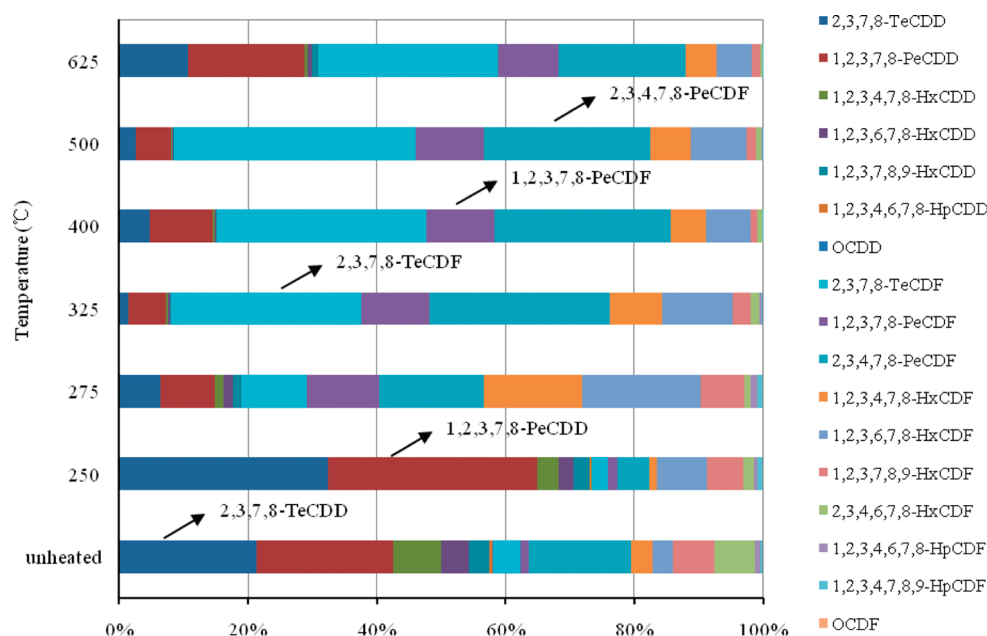
To summarize, it was quantifiably indicated that chlorinated- and brominated-dioxin were generated during the incineration of PCBs within the temperature range of 250–625 °C when subjected to air atmosphere. The formation of PCDD/Fs and PBDD/Fs takes place by catalytic-assisted coupling of precursors (chlorinated and brominated aromatic compounds derived from BFRs and miscellaneous plastic housing). Copper compounds as major metals (in mass fraction) found in PCBs, have a strong catalytic effect.<sup>22</sup> PCDD/Fs and PBDD/Fs were distributed mostly in char samples at temperatures lower than 325 °C, but later, at higher temperatures, these were predominant in oil, or liquid residue, in mass concentrations. High concentrations of PBDD/Fs were detected in three outputs of incinerated PCB scrap, which could be identified as a major contributor to the dioxin-like compounds contamination in e-waste dismantling areas. However, the considerably less quantity of PCDD/Fs generation from the incineration of PCBs scrap shows that other contributors, such as the open burning of MSW and plastic recovery processing, appear to be important sources of PCDD/Fs contamination, which require further investigation.

**Congener Profiles of PBDD/Fs and PCDD/Fs.** Further investigations of the PBDD/Fs and PCDD/Fs congener profiles contained in the decomposed products (a total of liquid condensate and solid residue) are shown in Figures 3 and 4.

As shown in Figure 3, PBDF was dominant in all the samples. Although the samples were subjected to various heating temperatures, the total mass proportions attributable to the various congener profiles were similar. For untreated PCB samples, the two congeners 1,2,3,4,7,8-HxBDF and 1,2,3,4,6,7,8-HpBDF exhibited the largest contributions to the total TEQ concentration, accounting for 34% and 55% of the total TEQ PBDD/Fs, respectively. As the temperature rose, however, the TEQ content of both the congeners 1,2,3,4,7,8-HxBDF and 1,2,3,4,6,7,8-HpBDF kept decreasing. Meanwhile, the TEQ content of both the congeners 2,3,7,8-TxBDF and 2,3,7,8-TxBDD exhibited steady increases, accounting for 33% and 18% of the total TEQ PBDD/Fs, respectively, at a temperature of 625 °C, followed by 1,2,3,7,8-PeBDF (19%), 1,2,3,6,7,8-PeBDF (13%), and 1,2,3,4,7,8-HxBDF (17%). The

congener profiles for the PBDFs (tetra- to penta-brominated) were similar to those observed for environmental samples, in that a wide range of PBDF congeners were observed.<sup>23</sup> Luijk and Govers<sup>24</sup> verified that PBDF formation predominated, and that PBDD yields were considerably lower compared to PBDFs during the thermal stress of BFRs (PBDE) production and processing. Ma et al.<sup>15</sup> also reported that PBDFs content was significantly higher than PBDDs in samples collected from the e-waste dismantling areas, showing a connection between the disposal of PCBs and PBDD/Fs pollution in these areas. The presence of a polymer matrix serves as hydrogen donor during thermal degradation shifting the homologue pattern to lower brominated congeners and enhancing PBDF formation significantly.

For untreated PCB samples, PCDD was dominant, and the two congeners 2,3,7,8-TeCDD and 1,2,3,7,8-PeCDD exhibited the largest contributions to the total TEQ concentration, accounting for 66% of the total TEQ PCDD/Fs. When subjected to a temperature of 250 °C, the mass proportion attributable to various congener profiles was similar to that for untreated PCBs, indicating that hardly any new PCDD/Fs were formed. However, the TEQ concentration of PCDF was much greater than that of PCDD when the heating temperature rose above 275 °C. As the temperature rose, there were only small differences among the mass fractions of the various congeners of PCDD/Fs. The TEQ content of the congeners 2,3,7,8-TeCDF and 2,3,4,7,8-PeCDF exhibited slight growth. The TEQ contents of four congeners of HxCDFs, though, showed an upward trend. At a temperature of 625 °C, the concentration of 2,3,7,8-TeCDF ranked first, accounting for 28% of the total TEQ PBDD/Fs, followed by 2,3,4,7,8-PeCDF (20%), 1,2,3,7,8-PeCDD (18%), and 2,3,7,8-TeCDD (11%). Weber and Hagenmaier<sup>25</sup> reported similar findings in their study of the formation of PCDD at temperatures below 300 °C while the onset for PCDF formation was 350 °C. Above 430 °C, PCDF was the dominant product. The formation of PCDFs is considered exclusively to be a result of the condensation of two radicals, while the formation of PCDDs principally involves radical/radical molecule/radical or molecule/molecule type coupling where the first, such as the radical/radical pathways, are kinetically favored.<sup>22</sup>



**Figure 4.** Composition of total TEQ PCDD/F homologues for liquid and solid outputs generated from degraded PCB samples at various temperatures.

**Evaluation of Incineration Conditions Favorable to the Emission of PCDD/Fs and PBDD/Fs.** The formation mechanisms for PCDD/Fs and PBDD/Fs during thermal processes have been investigated during the last two decades in numerous laboratory studies and under various combustion conditions. Due to the similar properties of chlorine and bromine, the formation mechanisms of PBDD/Fs may be comparable to those of PCDD/Fs during thermal treatment. PBDD/Fs are formed (a) through *de novo* synthesis and/or (b) from precursor compounds (such as brominated aromatic compounds) during condensation or elimination reactions.<sup>21,26</sup> The former route is observed in the temperature range between 250 and 650 °C. It has been reported that the open dumping and burning of e-waste may contribute to emissions of PCDD/Fs and some other related compounds. For example, PVC-containing materials are PCDD/F precursors, and when burned, they produce PCDD/Fs—under uncontrolled combustion conditions. It has already been demonstrated that BFRs can form PBDD/Fs during combustion and pyrolysis processes. Considerable amounts of PBDD/Fs can be formed from the pyrolysis of waste PCBs which contain BFRs.<sup>19,27</sup>

The ingredients and conditions necessary to form PCDD/Fs or PBDD/Fs are (1) incomplete combustion, (2) halogenides, mainly Cl-, but also Br-, (3) an oxidizing atmosphere, and (4) a catalyst, with Cu salts being the most effective ones. In this study, incomplete combustion of halogenated-PCBs scraps occurred at all heating temperatures due to both the excess over feedstock and the deficiency of residence time. Accordingly, as can be seen in Figures 1 and 2, both PCDD/Fs and PBDD/Fs were found at the temperature of 250 °C; however, at a temperature of 325 °C they increased approximately 4 times and 11 times, respectively. The results obtained indicate that the formation of PBDD/Fs could occur from the incineration of electronic scrap and of materials containing BFRs, with a maximum formation rate between 250 and 400 °C. At higher temperatures, the PCDD/F and PBDD/F concentrations diminished again and the compounds were almost totally destroyed at 600 °C. Vogt and Stieglitz<sup>28</sup> reported similar findings in their study of the thermal behavior of

PCDD/PCDF in fly ash from municipal solid waste incinerators. However, the temperatures that led to peak amounts in this study were low compared to those in other related studies (300–500 °C).<sup>29</sup>

The experimental data on the quantitative yields of the decomposition products leads to reflection on the influence of oxygen and metals on the compounds obtained from the decomposition process. The formation of dioxin is generally considered to occur only rarely below 300 °C, and only starts to appear around 300 °C. However, extremely large amounts of PCDD/Fs were obtained in presence of oxygen and metals even at temperatures as low as 250 °C. A constant supply of oxygen with a flow rate of 200 mL/min promotes the radical halogenation reactions leading to the formation of dioxin species, because of the metals contained in PCB scrap, such as Fe and Cu. These metal oxides can catalyze the debromination/hydrogenation reaction, thereby accelerating the formation of PCDD/Fs and PBDD/Fs. This results in a temperature decrease similar to that in lab studies that indicated that the presence of a polymer matrix<sup>30,31</sup> and metals (CuO, Fe<sub>2</sub>O<sub>3</sub>, and Sb<sub>2</sub>O<sub>3</sub>)<sup>32–34</sup> increased the yield of PBDDs/PBDFs formed and decreased the optimum temperature range for their formation. The pyrolysis of crushed waste containing a high amount of chlorine (PVC) and metals (iron and copper) has been shown to result in the formation of high levels of chlorinated aromatics including PCDDs/PCDFs.<sup>35,36</sup> Divalent oxides of copper (Cu (II) O) have been shown to remarkably enhance the yield of PCDD/Fs in comparison with other metal oxides, and all copper species promote the formation of PCDD/Fs.<sup>37</sup> To disclose whether cooperative or competitive mechanisms among these factors which result in the increasing formation of PBDD/Fs requires further studies. To avoid the degradation and uncertainty during the analysis of PBDD/Fs which is present in high yields, both the sampling process and analytical procedure also deserve attention in further experiments.

## ■ ASSOCIATED CONTENT

**Supporting Information.** Additional sketch of the experimental apparatus, tables of all recoveries of PCDD/F and

PBDD/F. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

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