Thermochemical Formation of Polybrominated Dibenzo-*p*-Dioxins and Dibenzofurans Mediated by Secondary Copper Smelter Fly Ash, and Implications for Emission Reduction

Mei Wang,^{†,‡} Guorui Liu,^{*,†,‡} Xiaoxu Jiang,^{†,‡} Minghui Zheng,^{†,‡} Lili Yang,^{†,‡} Yuyang Zhao,^{†,‡} and Rong Jin^{†,‡}

[†]State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China

[‡]University of Chinese Academy of Sciences, Beijing 100049, China

S Supporting Information

ABSTRACT: Heterogeneous reactions mediated by fly ash are important to polychlorinated dibenzo-*p*-dioxin and dibenzofuran (PCDD/Fs) formation. However, the formation of polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) through heterogeneous reactions is not yet well understood. Experiments were performed to investigate the thermochemical formation of PBDD/Fs at 150–450 °C through heterogeneous reactions on fly ash from a secondary copper smelter. The maximum PBDD/F concentration was 325 times higher than the initial PBDD/F concentration in the fly ash. The PBDD/F concentration after the experiment at 150 °C was five times higher than the initial concentration. PBDD/Fs have not previously been found to form at such a low temperature. Secondary-copper-smelter fly ash clearly promoted PBDD/F formation, and this conclusion was supported by the low activation energies that were found in Arrhenius's law calculations. Thermochemical formation of PBDD/Fs mediated by fly ash deposited in industrial facilities could explain "memory effects" that have been found for PCDD/Fs and similar compounds released from industrial facilities. Abundant polybrominated diphenyl ethers (PBDEs) that were formed through fly ash-mediated reactions could be important precursors for PBDD/Fs also formed through fly ash-mediated reactions. The amounts of PBDEs that formed through fly ash-mediated reactions suggested that secondary copper smelters could be important sources of reformed PBDEs.

INTRODUCTION

Heterogeneous reactions on fly ash are widely recognized as being the dominant mechanisms through which polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) form during industrial thermal processes. These reactions can occur because carbon-containing residues and catalytic metal particles are abundant in fly ash.^{1–4} Copper compounds are some of the most efficient catalysts of the formation of PCDD/Fs.^{1,5–8}

The catalysis of the formation of PCDD/Fs and other chlorinated organic contaminants by copper compounds (copper oxides and copper chlorides) under different combustion conditions has been investigated in numerous studies.^{4,6,9,10} Olie et al. reviewed the catalysis of PCDD/F formation by several metals during the incineration of municipal waste, and they found that copper has the strongest catalytic effect.¹¹ Stieglitz et al. found that copper(II) ions catalyze reactions on the surfaces of carbon particles in the presence of oxygen, promoting the oxidation of the carbon to CO₂ and the formation of chlorinated aromatic compounds.¹² Nganai et al. investigated the formation of PCDD/Fs through

pyrolysis mediated by copper oxide, and they found that divalent copper oxides increased the PCDD/F yield to a remarkable extent.⁷ The studies mentioned above showed that copper compounds are effective catalysts for the formation of PCDD/Fs during waste incineration processes.

Polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) are the brominated analogs of PCDD/Fs, and are also toxic.¹³ PBDD/Fs have recently attracted much attention because higher PBDD/F toxic equivalents (TEQs) than PCDD/F TEQs have been found in some environmental matrices.^{14,15} Controlling PBDD/F emissions should be prioritized so that the amounts of PBDD/Fs present in the environment and to which humans are exposed will decrease. PBDD/Fs and PCDD/Fs have similar sources, including waste incinerators, secondary nonferrous smelting processes, and iron

Received: April 28, 2016

Revised: June 17, 2016

Accepted: June 27, 2016

Published: June 27, 2016

and steel making processes. Secondary copper smelting (SCu) processes have been found to be important sources of PBDD/Fs, and PBDD/Fs have been found at higher concentrations in stack gases produced during SCu processes (2.5 ng Nm^{-3}) than in stack gases produced during the incineration of waste (0.025 ng Nm^{-3}), steelmaking using electric arc furnaces (1.5 ng Nm^{-3}), and other processes.^{16,17}

The underlying reason for PBDD/F emissions during SCu processes being higher than emissions during other processes has not yet been determined. Copper compounds are found at much higher contents in SCu systems than in waste incinerators and other industrial systems.¹⁸ The raw materials (recycled metal wire) used in secondary copper smelters normally contain plastic and cable residues that contain polybrominated diphenyl ethers (PBDEs) or other brominated flame retardants (BFRs). These BFR residues are widely recognized as being important sources of organic bromine for the formation of PBDD/Fs. Metal bromides in fly ash could also act as sources of bromine for the formation of PBDD/F, as has been reported previously.^{19,20} The large amounts of copper compounds present during SCu processes may catalyze thermochemical reactions between bromine (inorganic or organically bound) and carbon in organic material in scrap metal, allowing PBDD/Fs to form. Heterogeneous PBDD/F formation reactions mediated by fly ash with a high copper compound content could contribute to larger amounts of PBDD/Fs being emitted during SCu processes than during other processes. However, no attempt has yet been made to quantitatively evaluate the potential for PBDD/Fs forming through heterogeneous reactions mediated by real fly ash from SCu processes.

In this study, thermochemical experiments were performed to allow the potential for the formation of PBDD/Fs mediated by real fly ash from a SCu process to be quantified. The primary objective of the study was to gain, for the first time, insights into the extent to which real fly ash promotes the formation of PBDD/Fs during SCu processes. The results of this study will help characterize the role fly ash plays in the formation of PBDD/Fs, and this will help in the development of techniques for controlling PBDD/F emissions.

EXPERIMENTAL SECTION

Thermochemical Experiment Design. The fly ash that was used as a matrix for the formation of PBDD/Fs through heterogeneous reactions was collected from a bag filter in a typical SCu plant. This fly ash was used to simulate, as closely as possible, the active surfaces of fly ash produced during thermochemical processes.³ The SCu fly ash had a particularly high copper concentration, $260 \pm 2.0 \text{ mg/g}$, which was determined using an inductively coupled plasma-optical emission spectrometer.^{21,22} The fly ash had a bromine content of 0.3%, determined using a scanning electron microscope with energy dispersive X-ray analysis.²² The porosity and specific surface area of the fly ash were determined using a Brunauer–Emmett–Teller analytical system.²² The specific surface area of the SCu fly ash was $3.5 \text{ m}^2 \text{ g}^{-1}$ (Supporting Information (SI) Table S3). The high surface area of the SCu fly ash could have allowed the surface and external reactants involved in reactions to easily come into contact with each other.

The thermochemical experiments were performed in a temperature-controlled quartz horizontal laboratory furnace that had an internal diameter of 45 mm and was 600 mm long. Synthetic air was passed through the furnace at a constant flow

rate of 50 mL/min to simulate the conditions in an open SCu smelter system. A 200-mg sample of SCu fly ash in a uniform layer in a porcelain boat was placed in the furnace, then the furnace was heated to the desired temperature. Experiments were performed at 150, 200, 250, 350, and 450 °C. The set temperature in each experiment was held for between 10 and 240 min. The experiments were performed to allow the potential for PBDD/Fs to be formed at different temperatures to be quantified. The gas phase reaction products that were evolved in an experiment were trapped by passing the gas leaving the furnace through two ice-cooled impingers containing toluene. After each experiment, the quartz tube and the fittings and connecting tubes were rinsed three times with toluene to recover any products that had been deposited on the surfaces. The gaseous products of the thermochemical experiments were therefore in two solutions, the cleaning solution (the toluene used to rinse the apparatus) and the absorption solution (the toluene in the impingers). The toluene solutions and the solid residue that remained after each thermochemical experiment had been completed were stored at around 4 °C until they were analyzed.

Analytical Procedure. The PBDD/F congeners of interest were identified and quantified using isotope-dilution high-resolution gas chromatography (HRGC) combined with high-resolution mass spectrometry (HRMS). PBDEs, which could act as PBDD/F precursors, were also determined using isotope-dilution HRGC/HRMS. The analytical technique and the methods used have previously been described in detail.^{17,23} Briefly, each solid residue sample was spiked with known amounts of $^{13}\text{C}_{12}$ -labeled PBDD/F and PBDE internal standards (EDF-5408 and EO-5403; Cambridge Isotope Laboratories, Andover, MA, USA). The sample was then digested in hydrochloric acid, filtered, rinsed with distilled water, dried, and Soxhlet extracted with 250 mL of toluene for about 24 h. Each gas phase sample (i.e., each cleaning solution and each absorption solution) was spiked with known amounts of the $^{13}\text{C}_{12}$ -labeled PBDD/F and PBDE internal standards. Each extract was evaporated to a small volume using a rotary evaporator, then subjected to a series of cleanup steps, including passing the extract through a multilayer silica gel column and a basic alumina column. After the cleanup steps had been completed, the PBDD/Fs and PBDEs were separated by passing the extract through an activated carbon column, which was eluted with 80 mL of dichloromethane/hexane (5/95, v/v) to elute the PBDEs and then 250 mL of toluene to elute the PBDD/Fs. Each fraction was evaporated to about 20 μL using a rotary evaporator and then under a gentle stream of N_2 . A $^{13}\text{C}_{12}$ -labeled PBDD/F injection standard (EDF-5409; Cambridge Isotope Laboratories) was added to the PBDD/F fraction and a $^{13}\text{C}_{12}$ -labeled PBDE injection standard (EO-5404; Cambridge Isotope Laboratories) was added to the PBDE fraction before the fractions were analyzed by HRGC/HRMS. The injection standards were used to allow the recoveries of the internal standards to be calculated.

The HRGC/HRMS instrument was a Trace GC Ultra coupled to a double focusing mass spectrometer with an electron impact ion source (Thermo Fisher Scientific, Waltham, MA). A DB-5MS fused-silica column that was 15 m long (with a 0.25 mm i.d. and a 0.10- μm film; Agilent Technologies, Santa Clara, CA) was used to separate the PBDD/Fs and decabromodiphenyl ether, using the splitless/surge injection technique (using an injection port temperature of 280 °C and a glass transfer line temperature of 280 °C). A DB-5MS fused-

Figure 1. Polybrominated dibenzo-*p*-dioxin (PBDD) and polybrominated dibenzofuran (PBDF) concentrations (bars and left y-axis) and the number of times higher than the concentration in the original fly ash the concentration was (factor; points and right y-axis) after the experiments (A) at different temperatures and (B) for different periods of time.

silica column that was 30 m long (with a 0.25 mm i.d. and a 0.10- μ m film; Agilent Technologies) was used to separate the mono- to nona-brominated PBDE congeners (using an injection port temperature of 300 °C and a glass transfer line temperature of 280 °C). The HRMS instrument was operated at a resolution of approximately 10 000, in selected ion monitoring mode, and with an electron energy of 45 eV.

Quality Assurance and Quality Control. The reproducibility of the experimental runs was evaluated. The relative standard deviations of the PBDD/F concentrations in the samples produced in duplicate runs were 1%–19%, indicating that the experimental system and analytical procedure gave an acceptable level of reproducibility. Experimental blanks were produced in thermochemical experiments using a porcelain boat containing no SCu fly ash. A few of the target compounds, including octabromodibenzo-*p*-dioxin (OBDD) and octabromodibenzofuran (OBDF) were detected in the experimental blanks, but the concentrations were less than 0.1% of the concentrations in the samples produced in the experiments using SCu fly ash.

Three quality-control criteria were used to identify a target compound: (a) the HRGC retention time had to match the retention time of the corresponding $^{13}\text{C}_{12}$ -labeled standard

compound; (b) the signal-to-noise ratio had to be >3 ; and (c) the quantification to qualification ion ratio had to be within $\pm 15\%$ of the theoretical value. The recoveries of the $^{13}\text{C}_{12}$ -labeled tetra- to hepta-brominated PBDD/F internal standards were 23–128%, and the recoveries of the $^{13}\text{C}_{12}$ -labeled OBDD and OBDF internal standards were 20%–65% (SI Table S1). The recoveries of the $^{13}\text{C}_{12}$ -labeled PBDE internal standards were 43–124% (SI Table S2). The isotope dilution HRGC/HRMS method therefore gave satisfactory recoveries of the PBDD/Fs and PBDEs.

RESULTS AND DISCUSSION

Potential for PBDD/Fs Forming through Thermochemical Reactions Mediated by SCu Fly Ash. The products of the thermochemical reactions that took place in each experiment were present in the solid residue and the gas phase (captured by the impingers or in the cleaning solution). The relative amounts of the PBDD/Fs that were produced at different temperatures in the solid residue and gas phase samples are shown in SI Figure S1. The PBDD/Fs formed at 150 °C were mainly (64% of the total amount) found in the solid residue. Larger amounts of the PBDD/Fs formed during the experiments would have been transferred from the solid

Figure 2. Polybrominated dibenzo-*p*-dioxin (on the left) and dibenzofuran (on the right) homologue profiles in the original fly ash and after the thermochemical reaction experiments at different temperatures had been performed (BDD = bromodibenzo-*p*-dioxin, BDF = bromodibenzofuran, Te = tetra, Pe = penta, Hx = hexa, Hp = hepta, O = octa).

matrix to the gas phase at higher temperatures. It can be seen from SI Figure S1 that the PBDD/Fs formed were predominantly found in the gas phase at 200–450 °C (87% of the total at 200 °C, 95% at 250 °C, and >99% at 350–450 °C). This indicates that increasing the temperature increased the proportion of the PBDD/Fs formed that entered the gas phase. The sum of the PBDD/F concentrations found in the two phases (solid residue and gas phase) in each test were used in the subsequent assessments of the formation of PBDD/Fs.

The promotion of the formation of PBDD/Fs by SCu fly ash during the thermochemical experiments at 150–450 °C for between 10 and 240 min was evaluated. The PBDD/F concentrations in the SCu fly ash after the experiments at different temperatures and for different periods of time had been performed are shown in Figure 1. The PBDD to PBDF ratios were in the range 0.4–0.8, indicating that larger amounts of PBDFs than PBDDs were formed in the experiments. The influence of the temperature on the formation of PBDD/Fs was assessed by performing 30 min experiments at 150, 200, 250, 350, and 450 °C. The results of these experiments are shown in Figure 1A.

It is widely accepted that unintentionally produced persistent organic pollutants (POPs) can be formed at between 250 and 450 °C^{24–26} but that temperatures below 250 °C do not favor the unintentional formation of POPs. However, it is not yet clear whether PBDD/Fs can form below 250 °C. It can be seen from Figure 1 that the PBDD/F concentration after the experiment at 200 °C was 8.8 ng/g, which was about 34 times higher than the initial PBDD/F concentration in the SCu fly ash (0.26 ng/g). The PBDD/F concentration after the experiment at 150 °C was 1.3 ng/g, about five times higher than the initial concentration. PBDD/Fs have not previously been found to form at temperatures as low as 150 °C. These results indicate that SCu fly ash clearly promoted the formation of PBDD/Fs even at low temperatures.

Extremely high PBDD/F concentrations (58–325 times higher than the initial PBDD/F concentrations in the SCu fly ash) were found after the experiments at 250–450 °C. The highest concentration (325 times higher than the initial PBDD/F concentration) was found after a 30 min experiment at 450 °C. These results indicate that the SCu fly ash strongly promoted the formation of PBDD/Fs at 250–450 °C.

The PBDD/F concentrations found after experiments lasting different lengths of time are shown in Figure 1B. Thermochemical experiments were performed at 350 °C for

10, 30, 60, 120, and 240 min. The PBDD/F concentration had increased dramatically, to 72 times higher than the concentration in the original SCu fly ash, after a reaction time of 10 min. It can be seen from Figure 1B that the PBDD/F concentration increased slightly as the reaction time increased. The PBDD/F concentration increased from 18.7 ng/g after 10 min to 30.3 ng/g after 240 min.

Toxic equivalent factors (TEFs) for PBDD/Fs and mixed brominated/chlorinated dibenzo-*p*-dioxins and dibenzofurans relative to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (the TEF of which was assigned a value of 1.0) have recently been determined. These TEFs allow the TEQs of PBDD/Fs and mixed brominated/chlorinated dibenzo-*p*-dioxins and dibenzofurans in environmental matrices to be estimated.^{13,27–29} The PBDD/F TEQ concentrations were calculated using TEF values (shown in SI Table S4) determined by Behnisch et al.¹³ and the concentrations of the individual PBDD/F congeners. The TEQ concentrations of PBDD/Fs formed during the thermochemical reactions were 0.18–4.33 ng TEQ/g (as shown in SI Table S5), and the maximum TEQ value was about 144 times higher than the initial PBDD/F TEQ concentration in the SCu fly ash (0.03 ng TEQ/g). Fly ash is normally recycled by adding it to the raw materials during the feeding–fusion stages, or fly ash is simply thermally treated during the smelting process. Taking into consideration the increases in the PBDD/F TEQ concentrations during the thermochemical reactions, fly ash needs to be disposed of safely rather than simply being recycled by adding it to the raw materials or being thermally treated in SCu and other metallurgical plants.

Emissions of PCDD/Fs from many industrial thermal sources have been found to increase significantly as the bag filters or other facilities increase in age, and this phenomenon is normally called the “memory effect”. It has been suggested that the memory effect in waste incinerators is caused by POPs being adsorbed and later desorbed.³⁰ The memory effect includes the “sorption and desorption memory effect” (which is caused by POPs being absorbed by amorphous materials or adsorbed onto the installation walls or onto deposits of materials in the installation) and the “de novo memory effect” (in which soot deposited in some parts of a system act as a raw material in the de novo synthesis of POPs).³¹ Sorption and desorption may not fully explain the significant increases (by one to 2 orders of magnitude) in the amounts of PBDD/Fs that have been found to form in secondary metal smelting plants over time. Fly ash can be deposited in a facility or in a bag filter

over time. Our results indicate that the “de novo memory effect” (the thermochemical formation of pollutants mediated by fly ash deposited within a facility) might be the underlying cause (in addition to sorption and desorption) of significant increases in the amounts of PBDD/Fs that are formed in secondary metal smelting plants over time.

Congener Patterns of the PBDD/Fs Formed during Fly Ash-Mediated Thermochemical Reactions. The concentrations of the different PBDD/F homologues after experiments at different temperatures had been performed are shown in Figure 2. Very different tetra- to octa-brominated PBDD/F homologue patterns were found after experiments at different temperatures. It can be seen from Figure 2 that the tetrabromodibenzofuran (TeBDF) concentration reached a maximum at 200 °C, the tetrabromodibenzo-*p*-dioxin (TeBDD) concentration reached a maximum at 250 °C, and the TeBDF and TeBDD concentrations decreased as the temperature increased further. The more-brominated PBDD/F homologues were more dominant than the less-brominated PBDD/Fs at 350–450 °C. The hepta- and octa-brominated PBDD/Fs were the dominant homologues, together contributing 56–83% of the total PBDD/Fs, at 350–450 °C. The change from the less-brominated homologues dominating at lower temperatures to the more-brominated homologues dominating at higher temperatures indicated that bromination reactions may have occurred at higher temperatures. The curves of the TeBDD and TeBDF profiles in Figure 2 were different from the curves of the other congeners, and an explanation for this is given below. The TeBDD and TeBDF activation energies were much lower than the highly brominated congener activation energies, as shown in Table 1. TeBDD and TeBDF

trations will therefore slightly decrease when the temperature increases, and the highly brominated congener concentrations will increase at relatively high temperatures.

The PBDD/F congener profiles in the SCu fly ash and in the products of the experiments at different temperatures are shown in Figure 3. Three tetra-brominated congeners (2,4,6,8-TeBDF, 2,3,7,8-TeBDF, and 2,3,7,8-TeBDD) made small contributions (6.9%, 5.8%, and 6.7%, respectively) to the total PBDD/F concentration in the original SCu fly ash. The PBDD/F congener profiles in the products and the SCu fly ash were different. The 2,3,7,8-TeBDD contributions increased until the temperature reached 250 °C, then decreased as the temperature increased further. The 2,4,6,8-TeBDF and 2,3,7,8-TeBDF contributions clearly decreased once the temperature became higher than 200 °C. The more-brominated congeners (including 1,2,3,4,6,7,8-heptabromodibenzo-*p*-dioxin (HpBDD), OBDD, 1,2,3,4,6,7,8-heptabromodibenzofuran (HpBDF), and OBDF) clearly increased as the temperature increased. OBDF was the most abundant congener after the experiment at 450 °C, contributing 31% of the total PBDD/F concentration. The next most abundant congeners (in decreasing order of contribution) were 1,2,3,4,6,7,8-HpBDF (contributing 29% of the total), OBDD (12%), and 1,2,3,4,6,7,8-HpBDD (11%). These four more-brominated congeners together contributed 83% of the total PBDD/F concentration after the experiment at 450 °C. These results indicated that the formation of highly brominated congeners was favored at relatively high temperatures.

The Arrhenius equation, shown below, describes the dependence of the rate constant (k) of a chemical reaction on the absolute temperature T (in Kelvin). In the equation, k is the rate constant for the formation of PBDD/F congeners involved in the thermochemical reactions, A is a pre-exponential factor, E_a is the activation energy, and R is the universal gas constant.

$$k = Ae^{-E_a/(RT)}$$

The Arrhenius equation was used to calculate, from the PBDD/F congener formation rates, the activation energy and pre-exponential factor for each PBDD/F congener during the thermochemical reactions. These calculations were performed with the aim of improving our understanding of the thermochemical behaviors of the PBDD/F congeners. The activation energies and pre-exponential factors that were calculated are shown in Table 1. As can be seen in Figure 3, the formation of the more-brominated PBDD/F congeners was found to be very strongly thermodynamically favored at higher temperatures. This would have been why we found that larger amounts of the more-brominated PBDD/F congeners were formed in our experiments at higher temperatures. It can be seen from Table 1 that the activation energies of the hexa- and octa-brominated PBDD/F congeners (38.7–54.7 kJ/mol) were higher than the activation energies of the tetra- to penta-brominated PBDD/F congeners (8.6–35.2 kJ/mol). This supported our conclusion that larger amounts of the more-brominated PBDD/Fs would be produced at higher temperatures. Ortuno et al. studied the de novo synthesis of PBDD/Fs using model mixtures of active carbon and CuBr₂.³² They found activation energies for the de novo synthesis of PBDD/Fs of 78.7–158.4 kJ/mol, which are higher than the activation energies of 8.6–54.7 kJ/mol that we found for the formation of PBDD/Fs when SCu fly ash was used as the matrix for thermochemical reactions. This further supports our conclusion

Table 1. Arrhenius Formulae for the Thermochemical Reactions Involved in the Formation of Polybrominated Dibenzo-*p*-Dioxins and Dibenzofurans on Secondary Copper Smelter Fly Ash at Between 423 and 723 K^a

congener	arrhenius formula
OBDD	$k = 2.82 \times 10^{-10} \exp(-39.2/RT)$
OBDF	$k = 5.99 \times 10^{-10} \exp(-38.7/RT)$
1234678-HpBDD	$k = 6.84 \times 10^{-10} \exp(-44.9/RT)$
1234678-HpBDF	$k = 6.62 \times 10^{-10} \exp(-44.8/RT)$
123478/123678-HxBDD	$k = 3.21 \times 10^{-10} \exp(-46.9/RT)$
123789-HxBDD	$k = 6.71 \times 10^{-10} \exp(-50.5/RT)$
123478-HxBDF	$k = 1.53 \times 10^{-9} \exp(-54.7/RT)$
12378-PeBDD	$k = 2.41 \times 10^{-11} \exp(-35.2/RT)$
23478-PeBDF	$k = 2.18 \times 10^{-11} \exp(-34.3/RT)$
12378-PeBDF	$k = 2.98 \times 10^{-13} \exp(-13.8/RT)$
2378-TeBDD	$k = 1.51 \times 10^{-11} \exp(-23.1/RT)$
2378-TeBDF	$k = 4.75 \times 10^{-13} \exp(-8.6/RT)$

^a k is the rate constant for the formation of the PBDD/F congener of interest during a thermochemical reaction, the first term in parentheses after exp is the activation energy (E_a in kJ/mol), R is the universal gas constant, and T is the temperature (in K). BDD = bromodibenzo-*p*-dioxin, BDF = bromodibenzofuran, Te = tetra, Pe = penta, Hx = hexa, Hp = hepta, O = octa

will therefore be much more easily formed than highly brominated congeners at relatively low temperatures. Increasing the temperature could increase the formation rates of highly brominated congeners and cause TeBDD and TeBDF to be transformed into highly brominated congeners through bromination reactions. The TeBDD and TeBDF concen-

Figure 3. (Top) Polybrominated dibenzo-*p*-dioxin and (bottom) polybrominated dibenzofuran congener patterns in the original fly ash and after the thermochemical reaction experiments at different temperatures had been performed (BDD = bromodibenzo-*p*-dioxin, BDF = bromodibenzofuran, Te = tetra, Pe = penta, Hx = hexa, Hp = hepta, O = octa).

that SCu fly ash is a strong catalyst for the formation of PBDD/Fs.

The different congener patterns found after different reaction times are shown in Figure 4. The contributions of 2,3,7,8-TeBDD, 2,4,6,8-TeBDF, and 2,3,7,8-TeBDF to the total PBDD/F concentration decreased as the reaction time increased. The contributions of the more-brominated congeners, including 1,2,3,4,6,7,8-HpBDD, OBDD, 1,2,3,4,6,7,8-HpBDF, and OBDF, clearly increased as the reaction time increased. These trends indicated that the 2,3,7,8-TeBDD, 2,4,6,8-TeBDF, and 2,3,7,8-TeBDF formation reactions tended to reach equilibrium more quickly than the 1,2,3,4,6,7,8-HpBDD, OBDD, 1,2,3,4,6,7,8-HpBDF, and OBDF formation reactions. A longer reaction time would therefore favor the formation of the more-brominated congeners.

Formation of PBDEs during Fly Ash-Mediated Thermochemical Reactions and the Relationship between the Formation of PBDEs and the Formation of PBDD/Fs. Extensive use of brominated flame retardants, especially PBDEs, in the past means that more brominated precursors of PBDD/Fs are now present in the raw materials used in secondary metal smelting than would have previously been the case.³³ The likelihood of PBDD/Fs forming during industrial thermal processes is therefore higher than it would previously have been.^{34–36} High PBDD/F yields have been found when PBDEs have been thermally treated.^{33,37,38} We therefore measured the PBDE concentrations in the products of the experiments and in the SCu fly ash to allow the relationship between the formation of PBDEs and PBDD/Fs to be investigated.

It is widely accepted that PBDEs are important precursors of PBDD/Fs formed during industrial thermal processes.^{19,35,39} The PBDE concentrations in the original fly ash and in the

products of the experiments are presented in Figure 5. The PBDE concentration in the original fly ash was 0.08 $\mu\text{g/g}$. It can be seen from Figure 5 that the PBDE concentration increased significantly after the SCu fly ash had been thermally treated. The PBDE concentrations were 3.4–5.3 $\mu\text{g/g}$ after 30 min experiments at 250–450 $^{\circ}\text{C}$ had been performed. The highest PBDE concentration (5.3 $\mu\text{g/g}$, more than 67 times higher than the PBDE concentration in the original fly ash) was found after the SCu fly ash had been heated to 350 $^{\circ}\text{C}$ for 30 min. The considerably higher PBDE concentrations after the fly ash had been heated than in the original fly ash indicated that large quantities of PBDEs were formed on the SCu fly ash through thermochemical reactions. It has been found that de novo synthesis of unintentionally produced POPs, including PCDD/Fs, polychlorinated naphthalenes, and other halogenated organic compounds, from carbon sources can be catalyzed by compounds of copper or other metals.^{20,40,41} It has also been suggested that de novo synthesis of PBDEs from organic residues (acting as carbon sources) produced by plastics and cables in the raw materials used in SCu processes can occur,⁴² and that this is catalyzed by copper compounds.

The PBDE to PBDD/F concentration ratios for the experiments performed under different conditions are shown in Figure 5. It can be seen that the PBDE concentrations were 41–328 times higher than the PBDD/F concentrations. Vetter et al. found that about 0.5% of the decabromodiphenyl ether present could be transformed into PBDD/Fs when complex matrices containing decabromodiphenyl ether were heated.³⁸ The PBDE to PBDD/F ratios found by Vetter et al.³⁸ were similar to the PBDE to PBDD/F ratios for our experiments. Altarawneh et al. performed a detailed mechanistic and kinetic study of the formation of PBDD/Fs from PBDEs, and their theoretical calculations indicated that the loss of a Br or H atom

Figure 4. (Top) Polybrominated dibenzo-*p*-dioxin and (bottom) polybrominated dibenzofuran congener patterns in the original fly ash and after the thermochemical reaction experiments with different reaction times had been performed (BDD = bromodibenzo-*p*-dioxin, BDF = bromodibenzofuran, Te = tetra, Pe = penta, Hx = hexa, Hp = hepta, O = octa).

Figure 5. Polybrominated diphenyl ether concentrations (bars and left y-axis) after thermochemical reaction experiments at different temperatures had been performed, and the polybrominated diphenyl ether to polybrominated dibenzo-*p*-dioxin and dibenzofuran concentration ratios (factor; points and right y-axis).

from the *ortho* position of a PBDE then a ring-closure reaction is the most accessible PBDF-production pathway with modest reaction barriers.³⁹ Weber and Kuch found that PBDD/Fs can

be formed from PBDEs through the simple intramolecular elimination of HBr.¹⁹ The large amounts of PBDEs formed during fly ash-mediated thermochemical reactions could

therefore provide abundant brominated PBDD/F precursors, allowing PBDD/Fs to be formed on SCu fly ash through thermochemical reactions. Weber and Kuch summarized the possible pathways for PBDD/Fs to be formed from brominated flame retardants.¹⁹ The results of our study on the formation of PBDD/Fs during SCu processes supported the mechanisms Weber and Kuch suggested for the formation of PBDD/Fs from PBDEs.¹⁹ The possible pathways through which PBDD/Fs can be formed from PBDEs during thermochemical processes were determined from our results and the results of the study performed by Weber and Kuch,¹⁹ and the pathways are shown schematically in SI Figure S3.

Environmental Implications and Strategies for Decreasing PBDD/Fs Emissions. Fly ash is normally recycled by adding it to the raw materials used in a smelter or simply by thermally treating it during the smelting process.⁴³ The significant increases in PBDD/F concentrations caused by fly ash-mediated thermochemical reactions mean that fly ash must be disposed of safely rather than simply recycled by adding it to the raw materials or by thermally treating it in SCu plants and other metallurgical plants.

Air pollution control devices that are used to decrease particle emissions from industrial facilities efficiently decrease emissions of PCDD/Fs and similar compounds to the atmosphere because the devices remove particles containing the pollutants.^{44,45} APCDs are normally operated below 200 °C because PCDD/Fs and similar compounds are not generally formed below 200 °C. However, PBDD/Fs clearly formed on fly ash at below 200 °C in our study, suggesting that PBDD/Fs could form in APCDs in industrial plants, particularly in secondary nonferrous smelting plants, even when the APCDs are operated at temperatures below 200 °C.

The promotion of PBDD/F formation by fly ash allows us to suggest a novel way of controlling the formation and emission of unintentionally produced POPs. Fly ash deposited in a smelting facility and APCDs could contribute to significant increases in the amounts of PBDD/Fs formed during SCu processes. Therefore, periodically removing fly ash deposited in a smelting facility and APCDs can directly and effectively decrease the amounts of PBDD/Fs formed during industrial processes.

The intentional production of PBDEs for use as brominated flame retardants has been banned because PBDEs have been added to Annex A of the Stockholm Convention.⁴⁶ POPs that can be unintentionally produced during industrial thermal processes (e.g., PCDD/Fs, polychlorinated biphenyls, polychlorinated naphthalenes, hexachlorobenzene, and pentachlorobenzene) are included in Annex C of the Stockholm Convention, which requires measures aimed at decreasing unintentional emissions of these compounds to be taken. PBDE emissions from some industrial thermal processes have been explained by the incomplete destruction of PBDEs (present as impurities) in the raw materials.^{47,48} No direct experimental evidence is available to support the reformation of PBDEs during industrial thermal processes, especially during SCu processes. Our results indicate that significant amounts of PBDEs can be formed through fly ash-mediated thermochemical reactions, suggesting that SCu processes could be important sources of PBDE emissions. This indicates that unintentional emissions of PBDEs must be considered (in addition to the production and release of PBDEs used as brominated flame retardants) when compiling a PBDE inventory.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b02119.

Tables S1–S5 and Figures S1–S3 (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +86 10 6284 9356; fax: +86 10 6284 9355; e-mail: glliu@rcees.ac.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge support from the National 973 program (2015CB453100), the National Natural Science Foundation of China (21477147), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB14020102), and the Youth Innovation Promotion Association Chinese Academy of Sciences (2016038).

■ REFERENCES

- (1) Altarawneh, M.; Dlugogorski, B. Z.; Kennedy, E. M.; Mackie, J. C. Mechanisms for formation, chlorination, dechlorination and destruction of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs). *Prog. Energy Combust. Sci.* **2009**, 35 (3), 245–274.
- (2) Liu, G.; Jiang, X.; Wang, M.; Dong, S.; Zheng, M. Comparison of PCDD/F levels and profiles in fly ash samples from multiple industrial thermal sources. *Chemosphere* **2015**, 133, 68–74.
- (3) Addink, R.; Olie, K. Mechanisms of formation and destruction of polychlorinated dibenzo-p-dioxins and dibenzofurans in heterogeneous systems. *Environ. Sci. Technol.* **1995**, 29 (6), 1425–1435.
- (4) Fujimori, T.; Takaoka, M.; Takeda, N. Influence of Cu, Fe, Pb, and Zn Chlorides and Oxides on Formation of Chlorinated Aromatic Compounds in MSWI Fly Ash. *Environ. Sci. Technol.* **2009**, 43 (21), 8053–8059.
- (5) Hinton, W. S.; Lane, A. M. Effect of zinc, copper, and sodium on formation of polychlorinated dioxins on MSW incinerator fly ash. *Chemosphere* **1992**, 25 (6), 811–819.
- (6) Takaoka, M.; Shiono, A.; Nishimura, K.; Yamamoto, T.; Uruga, T.; Takeda, N.; Tanaka, T.; Oshita, K.; Matsumoto, T.; Harada, H. Dynamic change of copper in fly ash during de novo synthesis of dioxins. *Environ. Sci. Technol.* **2005**, 39 (15), S878–S884.
- (7) Nganai, S.; Lomnicki, S. M.; Dellinger, B. Formation of PCDD/Fs from the copper oxide-mediated pyrolysis and oxidation of 1,2-dichlorobenzene. *Environ. Sci. Technol.* **2010**, 45 (3), 1034–1040.
- (8) Fujimori, T.; Tanino, Y.; Takaoka, M. Coexistence of Cu, Fe, Pb, and Zn oxides and chlorides as a determinant of dioxin generation in municipal solid waste incinerator fly ash. *Environ. Sci. Technol.* **2013**, 48 (1), 85–92.
- (9) Ryu, J.-Y.; Mulholland, J. A.; Chu, B. Chlorination of dibenzofuran and dibenzo-p-dioxin vapor by copper (II) chloride. *Chemosphere* **2003**, 51 (10), 1031–1039.
- (10) Chin, Y. T.; Lin, C.; Chang-Chien, G. P.; Wang, Y. M. PCDD/Fs formation catalyzed by the copper chloride in the fly ash. *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.* **2011**, 46 (5), 465–470.
- (11) Olie, K.; Addink, R.; Schoonenboom, M. Metals as catalysts during the formation and decomposition of chlorinated dioxins and furans in incineration processes. *J. Air Waste Manage. Assoc.* **1998**, 48 (2), 101–105.
- (12) Stieglitz, L.; Zwick, G.; Beck, J.; Bautz, H.; Roth, W. Carbonaceous particles in fly ash - a source for the de-novo-synthesis of organochlorocompounds. *Chemosphere* **1989**, 19 (1–6), 283–290.

- (13) Behnisch, P. A.; Hosoe, K.; Sakai, S.-i. Brominated dioxin-like compounds: in vitro assessment in comparison to classical dioxin-like compounds and other polyaromatic compounds. *Environ. Int.* **2003**, *29* (6), 861–877.
- (14) Shaw, S. D.; Berger, M. L.; Harris, J. H.; Yun, S. H.; Wu, Q.; Liao, C.; Blum, A.; Stefani, A.; Kannan, K. Persistent organic pollutants including polychlorinated and polybrominated dibenzo-p-dioxins and dibenzofurans in firefighters from Northern California. *Chemosphere* **2013**, *91* (10), 1386–1394.
- (15) Venkatesan, A. K.; Halden, R. U. Contribution of polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs) to the toxic equivalency of dioxin-like compounds in archived biosolids from the US EPA's 2001 National Sewage Sludge Survey. *Environ. Sci. Technol.* **2014**, *48* (18), 10843–10849.
- (16) Du, B.; Zheng, M.; Tian, H.; Liu, A.; Huang, Y.; Li, L.; Ba, T.; Li, N.; Ren, Y.; Li, Y.; Dong, S.; Su, G. Occurrence and characteristics of polybrominated dibenzo-p-dioxins and dibenzofurans in stack gas emissions from industrial thermal processes. *Chemosphere* **2010**, *80* (10), 1227–1233.
- (17) Wang, M.; Liu, G.; Jiang, X.; Li, S.; Liu, W.; Zheng, M. Formation and emission of brominated dioxins and furans during secondary aluminum smelting processes. *Chemosphere* **2016**, *146*, 60–67.
- (18) Cains, P. W.; McCausland, L. J.; Fernandes, A. R.; Dyke, P. Polychlorinated dibenzo-p-dioxins and dibenzofurans formation in incineration: effects of fly ash and carbon source. *Environ. Sci. Technol.* **1997**, *31* (3), 776–785.
- (19) Weber, R.; Kuch, B. Relevance of BFRs and thermal conditions on the formation pathways of brominated and brominated-chlorinated dibenzodioxins and dibenzofurans. *Environ. Int.* **2003**, *29* (6), 699–710.
- (20) Ortuno, N.; Conesa, J. A.; Molto, J.; Font, R. De novo synthesis of brominated dioxins and furans. *Environ. Sci. Technol.* **2014**, *48* (14), 7959–7965.
- (21) Jiang, X.; Liu, G.; Wang, M.; Zheng, M. Fly ash-mediated formation of polychlorinated naphthalenes during secondary copper smelting and mechanistic aspects. *Chemosphere* **2015**, *119*, 1091–1098.
- (22) Wang, M.; Liu, G.; Jiang, X.; Xiao, K.; Zheng, M. Formation and potential mechanisms of polychlorinated dibenzo-p-dioxins and dibenzofurans on fly ash from a secondary copper smelting process. *Environ. Sci. Pollut. Res.* **2015**, *22* (11), 8747–8755.
- (23) Li, S.; Liu, W.; Liu, G.; Wang, M.; Li, C.; Zheng, M. Atmospheric emission of polybrominated dibenzo-p-dioxins and dibenzofurans from converter steelmaking processes. *Aerosol Air Qual. Res.* **2015**, *15*, 1118–1124.
- (24) Tuppurainen, K.; Halonen, I.; Ruokojärvi, P.; Tarhanen, J.; Ruuskanen, J. Formation of PCDDs and PCDFs in municipal waste incineration and its inhibition mechanisms: A review. *Chemosphere* **1998**, *36* (7), 1493–1511.
- (25) Huang, H.; Buekens, A. On the mechanisms of dioxin formation in combustion processes. *Chemosphere* **1995**, *31* (9), 4099–4117.
- (26) Xhrouet, C.; Pirard, C.; De Pauw, E. De novo synthesis of polychlorinated dibenzo-p-dioxins and dibenzofurans on fly ash from a sintering process. *Environ. Sci. Technol.* **2001**, *35* (8), 1616–1623.
- (27) Birnbaum, L. S.; Staskal, D. F.; Diliberto, J. J. Health effects of polybrominated dibenzo-p-dioxins (PBDDs) and dibenzofurans (PBDFs). *Environ. Int.* **2003**, *29* (6), 855–860.
- (28) Loganathan, B. G.; Kannan, K.; Watanabe, I.; Kawano, M.; Irvine, K.; Kumar, S.; Sikka, H. C. Isomer-specific determination and toxic evaluation of polychlorinated biphenyls, polychlorinated/brominated dibenzo-p-dioxins and dibenzofurans, polybrominated biphenyl ethers, and extractable organic halogen in carp from the Buffalo River, New York. *Environ. Sci. Technol.* **1995**, *29* (7), 1832–1838.
- (29) Ma, J.; Addink, R.; Yun, S.; Cheng, J.; Wang, W.; Kannan, K. Polybrominated dibenzo-p-dioxins/dibenzofurans and polybrominated diphenyl ethers in soil, vegetation, workshop-floor dust, and electronic shredder residue from an electronic waste recycling facility and in soils from a chemical industrial complex in eastern China. *Environ. Sci. Technol.* **2009**, *43* (19), 7350–7356.
- (30) Li, H.-W.; Wang, L.-C.; Chen, C.-C.; Yang, X.-Y.; Chang-Chien, G.-P.; Wu, E. M.-Y. Influence of memory effect caused by aged bag filters on the stack PCDD/F emissions. *J. Hazard. Mater.* **2011**, *185* (2–3), 1148–1155.
- (31) Weber, R.; Sakurai, T.; Ueno, S.; Nishino, J. Correlation of PCDD/PCDF and CO values in a MSW incinerator - indication of memory effects in the high temperature/cooling section. *Chemosphere* **2002**, *49* (2), 127–134.
- (32) Ortuno, N.; Conesa, J. A.; Molto, J.; Font, R. De novo synthesis of brominated dioxins and furans. *Environ. Sci. Technol.* **2014**, *48* (14), 7959–7965.
- (33) Zhang, M.; Buekens, A.; Li, X. Brominated flame retardants and the formation of dioxins and furans in fires and combustion. *J. Hazard. Mater.* **2016**, *304*, 26–39.
- (34) D'Silva, K.; Fernandes, A.; Rose, M. Brominated organic micropollutants—igniting the flame retardant issue. *Crit. Rev. Environ. Sci. Technol.* **2004**, *34* (2), 141–207.
- (35) Sindiku, O.; Babayemi, J.; Osibanjo, O.; Schlummer, M.; Schluep, M.; Watson, A.; Weber, R. Polybrominated diphenyl ethers listed as Stockholm Convention POPs, other brominated flame retardants and heavy metals in e-waste polymers in Nigeria. *Environ. Sci. Pollut. Res.* **2015**, *22*, 1–13.
- (36) Ortuno, N.; Lundstedt, S.; Lundin, L. Emissions of PBDD/Fs, PCDD/Fs and PBDEs from flame-retarded high-impact polystyrene under thermal stress. *Chemosphere* **2015**, *123*, 64–70.
- (37) Ren, M.; Peng, P. a.; Cai, Y.; Chen, D.; Zhou, L.; Chen, P.; Hu, J. PBDD/F impurities in some commercial deca-BDE. *Environ. Pollut.* **2011**, *159* (5), 1375–1380.
- (38) Vetter, W.; Bendig, P.; Blumenstein, M.; Hägele, F.; Behnisch, P. A.; Brouwer, A. Formation of polybrominated dibenzofurans (PBDFs) after heating of a salmon sample spiked with decabromodiphenyl ether (BDE-209). *Environ. Sci. Pollut. Res.* **2015**, *22* (19), 14530–14536.
- (39) Altarawneh, M.; Dlugogorski, B. Z. A mechanistic and kinetic study on the formation of PBDD/Fs from PBDEs. *Environ. Sci. Technol.* **2013**, *47* (10), 5118–5127.
- (40) Weber, R.; Iino, F.; Imagawa, T.; Takeuchi, M.; Sakurai, T.; Sadakata, M. Formation of PCDF, PCDD, PCB, and PCN in de novo synthesis from PAH: Mechanistic aspects and correlation to fluidized bed incinerators. *Chemosphere* **2001**, *44* (6), 1429–1438.
- (41) Iino, F.; Imagawa, T.; Takeuchi, M.; Sadakata, M. De novo synthesis mechanism of polychlorinated dibenzofurans from polycyclic aromatic hydrocarbons and the characteristic isomers of polychlorinated naphthalenes. *Environ. Sci. Technol.* **1999**, *33* (7), 1038–1043.
- (42) Hu, J. C.; Zheng, M. H.; Liu, W. B.; Li, C. L.; Nie, Z. Q.; Liu, G. R.; Xiao, K.; Dong, S. J. Occupational exposure to polychlorinated dibenzo-p-dioxins and dibenzofurans, dioxin-like polychlorinated biphenyls, and polychlorinated naphthalenes in workplaces of secondary nonferrous metallurgical facilities in China. *Environ. Sci. Technol.* **2013**, *47* (14), 7773–7779.
- (43) Hu, J.; Zheng, M.; Nie, Z.; Liu, W.; Liu, G.; Zhang, B.; Xiao, K. Polychlorinated dibenzo-p-dioxin and dibenzofuran and polychlorinated biphenyl emissions from different smelting stages in secondary copper metallurgy. *Chemosphere* **2013**, *90* (1), 89–94.
- (44) McKay, G. Dioxin characterisation, formation and minimisation during municipal solid waste (MSW) incineration: review. *Chem. Eng. J.* **2002**, *86* (3), 343–368.
- (45) Kulkarni, P. S.; Crespo, J. G.; Afonso, C. A. Dioxins sources and current remediation technologies—a review. *Environ. Int.* **2008**, *34* (1), 139–153.
- (46) UNEP, Stockholm Convention on Persistent Organic Pollutants. 2015. <http://chm.pops.int/TheConvention/ThePOPs/TheNewPOPs/tabid/2511/Default.aspx>.
- (47) Wang, L.-C.; Hsi, H.-C.; Wang, Y.-F.; Lin, S.-L.; Chang-Chien, G.-P. Distribution of polybrominated diphenyl ethers (PBDEs) and polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs) in municipal solid waste incinerators. *Environ. Pollut.* **2010**, *158* (5), 1595–1602.

(48) Sakai, S.-i.; Watanabe, J.; Honda, Y.; Takatsuki, H.; Aoki, I.; Futamatsu, M.; Shiozaki, K. Combustion of brominated flame retardants and behavior of its byproducts. *Chemosphere* **2001**, *42* (5–7), 519–531.