

Deca-Brominated Diphenyl Ether Destruction and PBDD/F and PCDD/F Emissions from Coprocessing deca-BDE Mixture-Contaminated Soils in Cement Kilns

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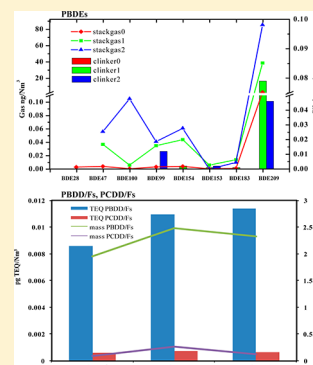
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S Supporting Information

ABSTRACT: The disposal of soil contaminated with polybrominated diphenyl ether (PBDE) was studied using an industrial coprocessing cement kiln. Two tests, Test 1 and Test 2, studied the destruction, removal, and emissions of PBDE in soils with PBDE concentrations of 4160 and 25 000 mg/kg, respectively. Emissions of polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) were also quantified. The PBDE destruction and removal efficiencies for Tests 1 and 2 were 99.9997% and 99.9998%, respectively. PBDE stack gas concentrations were 39.1 and 85.9 ng/Nm³ for Tests 1 and 2, respectively. The mean PBDD/F TEQ stack gas concentrations related to Tests 1 and 2 were 11.0 and 11.4 pg/Nm³, and PBDFs contributed 60.0–64.2% of the total PBDD/F concentrations. 2,3,7,8-TeBDD made the greatest contribution to the total PBDD/Fs, 40%, of all the homologues. The mean PCDD/F TEQ stack gas concentrations in Tests 1 and 2 were 0.74 and 0.65 pg/Nm³. The total PBDE, PBDD/F, and PCDD/F TEQ at the kiln outlet was 0.006% and 0.001% of the feed material TEQ. Therefore, coprocessing heavily PBDE-contaminated soils in a cement kiln is a highly efficient and environmentally sound treatment technology.



INTRODUCTION

In recent years, polybrominated diphenyl ethers (PBDEs) have raised concern because of their persistence, bioaccumulation, and potential adverse effects on wildlife and humans.¹ Extremely high concentrations of PBDEs have been reported in soil from e-waste recycling areas in China and other developing countries such as India, the Philippines, and Vietnam.^{1–6} E-waste is transported in massive quantities to these countries.⁷ Consequently, many large e-waste recycling sites have soils that are heavily polluted with PBDEs. According to Zou,⁵ the Pearl River Delta in China alone contains an estimated total of 48.38 tons of total PBDEs in soils. The figure is believed to be larger in areas such as Guiyu, Taizhou,⁴ and Qingyuan.³

In addition to e-waste recycling sites, soils from PBDE production sites are heavily polluted due to the release of PBDEs to the environment which can occur during synthesis and incorporation into products.⁸ Previous investigations into PBDE contamination of soils at production sites located in Shangdong and Jiangsu provinces showed PBDE soil concentrations of roughly 215 $\mu\text{g/g}$.⁹ So far, there are still many PBDEs production factories in China and other PBDEs producing countries. It will take a few years before they are

completely phased out. Traditional and primitive technology and unconsolidated management will probably increase the pollution of PBDEs in the factories and surrounding soils.^{8,10} Therefore, there are and will continue to be considerable quantities of soils contaminated with PBDE that need to be treated.

Currently, there are several combustion and noncombustion technologies that have been reported for the destruction of persistent organic pollutants (POPs) or the decontamination of polluted media. The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal technical guidelines suggest 12 technologies that are suitable for the environmentally sound destruction and disposal of POPs.¹¹ Of these technologies, the four which involve hazardous waste incineration and incineration in cement kilns also have the largest capacity. The remaining eight technologies, some of which are still at the laboratory scale,

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are technically sophisticated and currently are not affordable in many developing countries.¹²

There have been relatively few studies of treatments for soils contaminated with PBDE specifically. In one study, Fu et al.¹³ reported an optimal temperature of 400 °C for the disposal of these soils using thermal desorption technology and achieved a removal rate greater than 99%. The disadvantages of this technology are that it is limited to laboratory and pilot studies, requires special equipment at a high cost, and leaves PBDEs separated from the soil requiring further treatment.

Cement kilns possess inherent features that make them suitable for the treatment of soils containing POPs. These features include high temperatures and long residence times (greater than 1200 °C for several seconds), surplus oxygen during and after combustion, good turbulence and mixing conditions, and no generation of byproducts such as slag, ashes, or liquid residues.^{14–16} Test cement kiln burns using POP waste including PCB-oil, obsolete pesticides,^{17,18} and soils contaminated with POPs (DDT, aldrin, dieldrin, and pentachlorobenzene) have been conducted in Europe, North America, and some developing countries including China.^{19,20} These tests have shown that if adequate procedures are implemented, cement kiln coprocessing of POP waste and contaminated soils is an affordable and sustainable treatment option for POPs available in most countries.¹⁸ Given these successes, it is likely that this technology is also suitable for the treatment of PBDE-contaminated soils. Despite this likelihood, no existing studies have investigated the feasibility of treating PBDE-contaminated soils in cement kilns at any scale.

The main concern of coprocessing of hazardous waste, including POPs, in cement kilns is increased emissions of air pollutants including PCDD/Fs and heavy metals.^{17,20–23} It is well-known that polymers containing PBDEs are a precursor of polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs), but PBDD/Fs have received little attention in previous studies on pollutant emissions from cement kiln waste coprocessing. PBDD/Fs have properties and environmental toxicities similar to PCDD/Fs because they are structural analogues with chlorine atoms substituted by bromine atoms.^{24,25} Given that, more attention should be paid to PBDD/Fs. In fact, the thermal treatment of organic pollutants, especially bromine-containing pollutants (i.e., brominated flame retardants), has been shown to lead to the emission of PBDD/Fs in laboratory, pilot-scale, and industrial studies.^{26–32} Coprocessing of PBDEs in cement kilns may produce considerable quantities of PBDD/Fs, and these potential emissions should be of concern.

The purpose of this study was to assess the feasibility and performance of the treatment of soils contaminated with PBDEs and similar pollutants in cement kilns. A test burn with artificially contaminated soils in an industrial cement kiln was carried out. The destruction and removal efficiency (DRE) of PBDEs was calculated, and PBDD/F and PCDD/F emissions were measured. The main objective was to determine whether the total toxicity of PBDEs, PBDD/Fs, and PCDD/Fs was significantly reduced by coprocessing in cement kilns.

■ EXPERIMENTAL SECTION

Preparation of deca-BDE Contaminated Soils. deca-BDE-contaminated soils were artificially prepared by mixing commercial decabromodiphenyl ether (deca-BDE) with unpolluted soils. The unpolluted soils were taken from farmland in Yanjiao, Hebei Province, China. Soil from 5–40 cm deep

was collected, air-dried for 15 days after the removal of gravel, and then stored. The soil properties are shown in Supporting Information (SI) Table S1.

Commercial deca-BDE (96.99% BDE209) was purchased from the Star-Better Chemical Material Co. (Beijing, China). Two doses (50 and 300 kg) of commercial deca-BDE were added to two separate batches of 12 tons of unpolluted soil, making Soil 1 and Soil 2, respectively. A preliminary manual blend was performed three times using shovels. Mechanical mixing, also three times, was then conducted to ensure the contaminated soils were homogeneous. The resulting soil samples had PBDE concentrations of 4160 mg/kg and 25 000 mg/kg for Soil 1 and Soil 2, respectively. Comprehensive results listing PBDE homologues concentrations in the contaminated soils are shown in SI Table S2. The BDE209 concentration in Soil 1 was close to the U.S. EPA Regional Screening Level for Chemical Contaminants in industrial soil at superfund sites of 4100 mg/kg for the ingestion pathway.³³ The PBDE concentration in Soil 2 was close to concentrations previously found in wastes (printed circuit board 19 500 mg/kg).

Characteristics of the deca-BDE Contaminated Soils, Coal, and Raw Materials for Cement Production. The PBDD/F concentrations of 310 and 1600 ng TEQ/kg dry in Soils 1 and 2, respectively, were relatively high compared with PCDD/F concentrations. The PBDD/F may have originated from impurities in the commercial deca-BDE³⁴ as a result of photolysis.³⁵ The PCDD/F concentrations in Soils 1 and 2 were 2.3 ng TEQ/kg dry and 1.3 ng TEQ/kg dry, respectively. PBDE, PBDD/F, and PCDD/F congener concentrations in the soils, coal, and raw materials are provided in SI Tables S2, S3, and S4.

Cement Plant and Preparation for the Test. The test burn was conducted in a cement plant in Hebei Province, China. The plant has two dry-process kilns, each equipped with a five-stage single string suspension preheating tower. The main fuel is coal. The plant is equipped with state-of-the-art process control equipment, including the latest air pollution control technology: electrostatic precipitators (ESPs) and bag-house filters. All dust collected using the air pollution control devices was recovered in the process. The rotary kilns were 58 m long, 3.5 m in diameter, and have a production capacity of 2000 t of clinker per day.

To allow the soils to be transferred to the fuel gas chamber at the kiln inlet through a sludge pump, the deca-BDE-contaminated soils were mixed with twice their mass of tap water at the plant. The technical conditions and the process chemistry were evaluated prior to the test and were considered suitable for carrying out a test burn with soil. The processes of receiving, handling, storage, and feeding of soil, as well as the power and water supplies, were stable, safe, and adequate.

Test Burn. To conduct the test burn, the cement clinker manufacturing conditions could not be affected. The test was carried out over 3 days and each test was conducted once. The blank test (Test 0) occurred on the first day; no soil mixture was added in order to measure the kiln emissions at baseline conditions. After the blank test was complete, Test 1 was begun with Soil 1 fed into the fuel gas chamber at the kiln inlet through a sludge pump at a rate of 1.5 t/h. The test lasted for 12 h, and a total of 18 t of the soil mixture (including 12 t of soil and 6 t of tap water) was fed into the kiln. Test 2 began 24 h after Test 1 was complete using Soil 2 also fed at 1.5 t/h for

Table 1. Parameters Used in the Coprocessing Tests

test	date (duration)	feed	feed point	feed rate (tons/hour)	feed point temperature (°C)
Test 0 (blank test)	Nov. 25 0:00 (24 h)	none			1000–1050
Test 1	Nov. 26 0:00 (12 h)	Soil 1	fuel gas chamber	1.5	980–1030
pause interval	Nov. 26 12:00 (24 h)	none			1000–1050
Test 2	Nov. 27 12:00 (12 h)	Soil 2	fuel gas chamber	1.5	975–1035

12 h. A schematic diagram and major test parameters are shown in SI Figure S1 and Table 1.

Stack Gas and Clinker Sample Collection. The soils were fed into the kiln 4 h before stack gas sampling and clinker sampling started in order to ensure stable conditions during sampling. Stack gas samples were collected isokinetically (sampling time more than 2 h) from the stacks following Chinese National Guidelines for PCDD/F Emission Analysis of Ambient and Waste Gas (HJ77.2).³⁶ Two stack gas samples were collected every 2 h during each test. Soil and clinker sampling was performed following Chinese National Guidelines for PCDD/F Analysis of Solid Waste (HJ77.3),³⁶ with samples collected once every 30 min. Sampling details are provided in SI Table S5 including sampling time, frequency, and conditions.

Gas samples were collected using an automatic isokinetic sampling system (Isostack Basic, TCR Tecora, Milan, Italy), which included a heated titanium-lined sampling probe, a quartz-filter unit, a water-cooled condenser, and an XAD-2 sorbent trap. The gaseous phase sample was collected by the XAD-2 resin and condensed water, and the particulate phase was collected by the quartz-fiber filter. All samples were stored in the dark and taken to the laboratory within 1 week. Stack gas flow rates and oxygen contents were recorded simultaneously; details are in SI Table S5.

Stack Gas and Clinker Sample Preparation. Samples were pretreated in a certified laboratory in Beijing for the analysis of PBDD/Fs, PCDD/Fs, and PBDEs.^{29,30} PBDD/Fs and PCDD/Fs were analyzed following the HJ/77.2 and HJ77.3 standards,³⁸ respectively. The filter and XAD-2 resin were extracted from stack gas samples in a Soxhlet apparatus for 24 h. Cement clinker and soil were treated with HCl_(aq) and filtered. The liquid was extracted and the glass fiber filter was freeze-dried and extracted in a Soxhlet apparatus for 24 h. The extracted solutions were then concentrated and treated with concentrated H₂SO_{4(aq)}. Extracts were cleaned, and the PBDD/Fs and PCDD/Fs were separated from the PBDEs. This was accomplished by passing the extracts through multilayer silica columns and active carbon-impregnated silica columns, eluting PBDD/Fs and PCDD/Fs from PBDEs with toluene. PBDE analyses followed U.S. EPA Method 1614. The detailed procedure is provided in SI S5.

Instrument Analysis. PBDD/Fs and PCDD/Fs were analyzed with an Agilent 6890N gas chromatograph (Agilent Technologies Inc., Santa Clara, CA, USA) coupled with a JEOL JMS-800D high resolution mass spectrometer (JEOL Ltd., Tokyo, Japan). Separation was achieved using an SLB-5 ms column (15 m, 0.25 mm i.d., 0.10 μ m film thickness; Supelco, Bellefonte, PA, USA). The mass spectrometer was operated in electron impact (38 eV, 500 μ A) selective ion monitoring mode at a resolution greater than 10 000 (5% valley). The helium carrier gas was kept at a constant 25.4 psi. In splitless mode, 1 μ L of the extract was injected. Blank runs were conducted. The analysis and quality control details and the tentative analytical method for PBDD/Fs are described in Japan's JIS method for PCDD/Fs.

For PBDEs, an Agilent 6970 gas chromatograph was equipped with a DB-5HT capillary column (15 m, 0.25 mm i.d., 0.1 μ m film thickness, Agilent J&W Scientific, Santa Clara, CA, USA). The column oven temperature program was initially set at 100 °C, held for 4 min, raised 40 °C/min to 200 °C and held for 3.5 min, then raised 10 °C/min to 325 °C and held for 2.5 min. The helium carrier gas flow rate was 1.0 mL/min. The high-resolution mass spectrometer (Micromass Autospec Ultima, Manchester, UK) used a positive electron impact (EI⁺) source, selected ion monitoring mode, and a resolution of 10 000.

Quality Assurance and Quality Control (QA/QC). Each sample was spiked with ¹³C-labeled PCDD/F, PBDD/F, and BDE-209, and unlabeled BDE-118 standards to evaluate the performance of the sampling and cleanup procedures. The recovery of the sampling standards ranged from 98% to 118%, and the mean recovery of the cleanup standards ranged from 85% to 103% for PCDD/Fs, and from 95% to 122% for PBDD/Fs. The mean precision and recovery of the standards ranged from 73% to 121% for PBDD/Fs and from 78 to 112% for PCDD/Fs. The PBDE recoveries ranged from 85% to 118% for ¹³C-BDE-209 and from 78% to 104% for BDE-118. The recovery of the PBDE internal standards ranged from 75% to 130%.

PCDD/F TEQ values were calculated using international toxic equivalency factors (I-TEF). Because research on the toxic effects of PBDD/Fs is incomplete, PBDD/Fs were assigned the TEFs of their PCDD/F equivalents.³⁷

RESULTS AND DISCUSSION

PBDE Emissions and Destruction. Figure 1 shows the mean total PBDE concentrations in the Test 1 and Test 2 stack

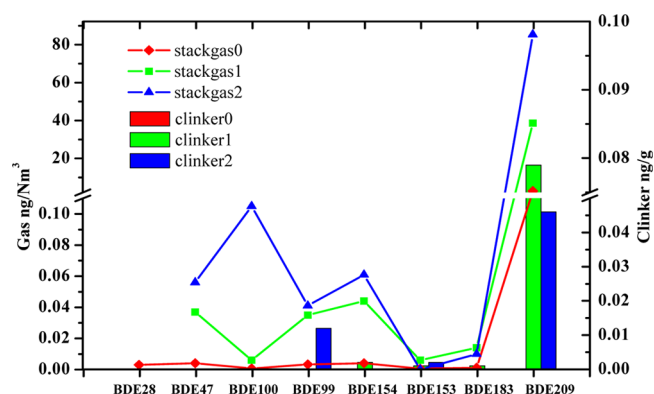


Figure 1. Concentrations of PBDE homologues in stack gases and clinkers from the cement kiln.

gases of 39 and 86 ng/Nm³, respectively. These values were about 15 and 30 times higher, respectively, than during Test 0 (2.7 ng/Nm³). The PBDE concentrations in resulting cement clinkers 1 and 2 were 0.083 and 0.060 ng/g, respectively. BDE-

209 was the dominant congener, contributing an average of 99% to the total PBDE emission.

PBDE emissions from cement kilns are not normally regulated and emission data in the public domain is very limited. Therefore, the stack gas PBDE concentrations could only be compared with concentrations derived from other sources. The stack gas PBDE concentrations were higher than concentrations in ambient air in an e-waste dismantling area³⁸ and the Guangzhou industrial zone (maximum 7.8 ng/Nm³),³⁹ but were lower than those in municipal waste incineration stack gas (109 ng/Nm³).⁴⁰ The low PBDE concentrations in our stack gas compared to municipal waste incineration stack gas can be attributed to the PBDEs being almost completely destroyed in the kiln. The kiln had a gas-phase temperature range of 1200–2000 °C, contained surplus oxygen, and had a sufficient gas residence time for efficient PBDE destruction.²⁶ Considering that the kiln was operated at parameters sufficient to destroy PBDE, the PBDE homologue concentrations in the stack gases and clinkers were very low (Figure 1). The fact that BDE-209 dominated the PBDE congener profile shows that virtually no lower PBDEs were formed from the incineration of DBDE in the cement kiln.

An important criterion for environmentally sound destruction and irreversible transformation of pollutants is to achieve a sufficient destruction efficiency (DE) or destruction and removal efficiency (DRE).¹² The DRE of this test was calculated as the difference between the mass of PBDEs fed into the kiln and the mass of PBDEs remaining in the stack emissions, using eq 1. Note that the DE calculation is provided in SI S6.

$$\text{DRE} = \frac{(W_i - W_o)}{W_i} \times 100\% \quad (1)$$

where W_i is the mass of the sum of the PBDEs (Σ PBDEs) entering the kiln and W_o is the mass of Σ PBDEs exiting in the stack gas. The mean mass of the Σ PBDEs in the stack gas from Tests 1 and 2, calculated from the Σ PBDE concentrations, the stack gas flow rate, and the stack diameter, were 26 and 65 mg (corrected for background emission), which gave DRE values of 99.9997% for Test 1 and 99.9998% for Test 2. At present, there are no explicit regulations for the PBDE disposal DRE, but the PBDE DRE in the test burn was better than the U.S. EPA regulations requirement of a DRE of at least 99.99% for insecticide disposal.⁴¹

PBDD/F and PCDD/F Concentrations in the Stack Gas.

PBDD/F and PCDD/F concentrations in the cement clinker samples were below the detection limit, so only concentrations in the stack gases are discussed here. The average PBDD/F and PCDD/F concentrations in the stack gases from each test are shown in Figure 2.

The mean TEQ concentrations of PBDD/Fs related to Tests 1 and 2 were both 1.1 pg TEQ N m⁻³, and the corresponding mass concentrations were 2.5 and 2.3 ng N m⁻³. The calculated emission factors were 0.85 and 1.1 ng/kg soil for Tests 1 and 2, respectively. The emission concentrations and factors were much lower than those for other reported thermal treatments of waste containing PBDEs such as printed circuit boards and flame-retardant plastic materials.^{26,28} These very low PBDD/F emissions from the cement kiln can primarily be attributed to the high temperatures and long residence times within the kiln, the presence of exit gas coolers,¹⁵ and the main operational mode. In the main operational mode, the hot exit gas is ducted

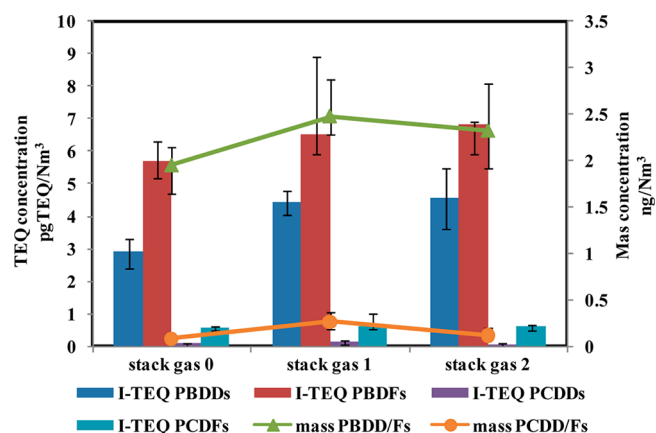


Figure 2. PBDD/F and PCDD/F mass concentrations and TEQ concentrations in stack gases from the cement kiln.

from the kiln and the preheater through the raw-mill dryer to heat the raw materials before it enters the air pollution control devices and the stack. This operating mode both reduces the exit gas temperature and appears to cause the absorption of PBDD/Fs. In addition, PBDD/F emissions may be reduced from coal-fired coal.^{42,43} Sulfur from the coal may interfere with PBDD/F formation due to SO₂ depletion of Br₂ and by SO₂ poisoning of copper catalysts, both preventing the synthesis of aromatic compounds.^{42,44}

Incinerating soils contaminated with PBDEs in the cement kiln led to an increase in PBDD/F emissions, which increased the ratios in Test 1 and Test 2 to 21.9% and 32.3%, respectively. Despite the increase in PBDD/F emissions, the total PBDD/F TEQ concentrations were an order of magnitude lower than the emission limits for PCDD/Fs specified in the U.S. EPA and European Union standards for cement kiln coprocessing of hazardous waste of 0.17 and 0.1 ng TEQ N m⁻³, respectively. There is currently no emission limit for cement kilns coprocessing hazardous waste due to incomplete research on the toxic effects of PBDD/Fs. However a scientific consensus has assigned PBDD/Fs the TEFs of their PCDD/F equivalents.³⁷ Therefore, the emission levels of PBDD/Fs were compared with the PCDD/F limits.

The PBDD/F TEQ concentrations in Tests 1 and 2 were similar, which suggests that variations in the mass of PBDEs entering the kiln in this study had only a slight effect on PBDD/F emissions. This phenomenon is similar to the results of PCDD/F test burn studies, which clearly showed that adding waste such as tires, organochlorine-contaminated soil, and industrial solvents had only a slight effect on PCDD/F emissions.^{17,18} This was probably because organic pollutants in the kiln were completely destroyed and the operational mode limited the PBDD/F and PCDD/F formation.¹⁵

Figure 2 shows that the mean total PCDD/F mass concentrations in the stack gases from Tests 1 and 2 were 0.27 and 0.13 ng N m⁻³, respectively, and the corresponding TEQ concentrations were 0.74 and 0.65 pg N m⁻³. The total PCDD/F TEQ concentrations were 2–3 orders of magnitude lower than the PCDD/F emission limits specified by the U.S. EPA and the European Union for cement kiln coprocessing of hazardous waste. The PCDD/F stack gas concentrations from Tests 1 and 2 were similar to the Test 0 concentration, which demonstrates that coprocessing soils contaminated with PBDE in the cement kiln had only a slight effect on PCDD/F emissions. PBDD/F emissions were clearly higher than PCDD/F

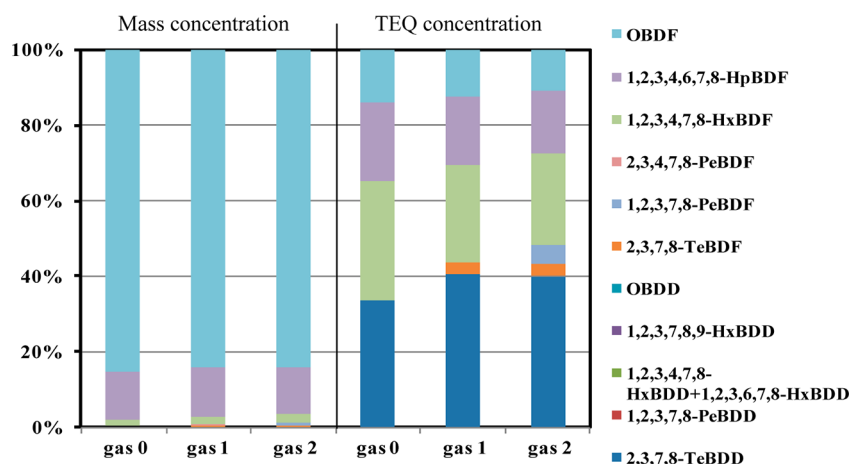


Figure 3. Congener compositions of the total mass and TEQ PBDD/F concentrations in stack gases generated by the cement kiln.

F emissions, which shows that the PBDD/F emission should be paid more attention than PCDD/F when incinerating PBDE-contaminated soils in a cement kiln. More research on PBDD/F emissions will be required.

PBDD/F and PCDD/F Congener Profiles. The PBDD/F and PCDD/F congener profiles in the stack gases are shown in Figures 3 and 4, respectively ($n = 11$ for PBDD/Fs, $n = 17$ for

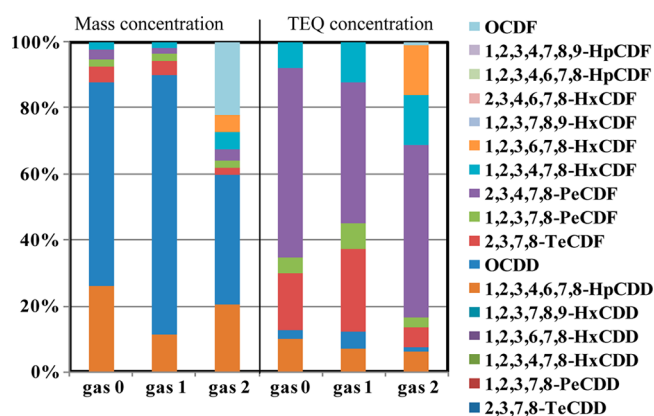


Figure 4. Congener compositions of the total mass and TEQ PCDD/F concentrations in stack gases generated by the cement kiln.

PCDD/Fs). OBDF was the largest contributor to the PBDD/F mass concentration, making up 84.2%–85.4% of the total PBDD/Fs in Figure 4. Ma et al.⁴⁵ also reported that OBDF was the predominant congener in the PBDD/F profile in samples from an e-waste recycling facility.

Four congeners, 2,3,7,8-TeBDD, 1,2,3,4,7,8-HxBDF, 1,2,3,4,6,7,8-HpBDF, and OBDF, were the greatest contributors to the total TEQ concentrations in each test, making up 40.6%, 26.0%, 18.2%, and 12.3% of the total PBDD/F TEQ in Test 1, and 40.0%, 24.6%, 16.3%, and 11.0% of the total in Test 2, respectively. 2,3,7,8-TeBDF accounted for 2.9% of the total PBDD/F TEQ in the Test 1 stack gas, and 2,3,7,8-TeBDF and 1,2,3,7,8-PeBDF accounted for 3.3% and 4.8% of the total PBDD/F TEQ in the Test 2 stack gas, respectively. 2,3,7,8-TeBDD made the largest contribution of these congeners in the test burns, which is markedly different from the PBDD/F congener profile reported from waste printed circuit board incineration and other industrial thermal processes such as waste incineration, cremation, and steel making.^{26,27} This

difference may be due to the higher temperature in the cement kiln compared with other thermal processes, and may suggest a different PBDD/F formation mechanism at different temperatures.

PBDFs were dominant in all the samples, contributing 64.2% and 60.0% to the total PBDD/F TEQ concentrations in Test 1 and Test 2 stack gases, respectively. The PBDF congener profiles in the stack gases were similar to stack gas emissions from metallurgic industrial thermal processes.²⁷ Luijk et al.⁴⁶ reported that PBDF formation predominated and that PBDD yields were considerably lower than PBDF yields during the thermal stresses involved in PBDE production and processing. Ma et al.⁴⁷ also reported that the PBDF content was significantly higher than the PBDD content in samples collected from e-waste dismantling areas.

These patterns may be attributed to the presence of a polymer matrix which serves as a hydrogen donor during thermal degradation, shifting the homologue pattern to lower brominated congeners and significantly enhancing PBDF formation.²⁶ However, the relative dominance of PBDFs produced in the cement kiln was much lower than those produced in the e-waste facility studied by Ma et al.⁴⁸ In that facility, PBDF concentrations were several orders of magnitude higher than the PBDD concentrations. This difference indicates that PBDDs are more easily generated at higher temperatures which cause the destruction on PBDEs. Although different amounts of PBDEs entered the cement kiln in the two tests, the proportions of the total TEQ attributable to the various congeners were similar in Tests 1 and 2. The four congeners, 2,3,7,8-TeBDD, 2,3,7,8-TeBDF, 1,2,3,4,7,8-HxBDF, and 1,2,3,4,6,7,8-HpBDF, together made the largest contributions to the total TEQ stack gas concentrations: 100%, 97.1%, and 96.7% in Test 0, Test 1, and Test 2, respectively.

It can be seen in Figure 4 that the largest contributor to the mass PCDD/F concentration, accounting for 39.4%–78.8%, was OCDD. Ma et al.⁴⁸ also reported that OCDD was the dominant congener in the PCDD/F profile in soils from an e-waste recycling facility. However, 2,3,4,7,8-PeCDF was found at the highest TEQ concentrations, contributing 57.5%, 43.2%, and 52.2% of the total PCDD/F TEQ in Test 0, Test 1, and Test 2, respectively. Our results differ from other reports^{20,21} that have shown that 2,3,7,8-TeCDF was usually the dominant congener produced in facilities both using and not using hazardous waste as fuel supplements. However, in those studies, the PCDD/F congener profiles were variable which

Table 2. Total TEQ at the Inlet and Outlet of the Cement Kiln in the Test Burns

	total TEQ entering kiln (ng)				total TEQ exiting kiln (ng)			
	PBDEs	PBDD/Fs	PCDD/Fs	total	PBDD/Fs	PCDD/Fs	PBDEs	total
Test 1	45,000,727	2,616	19.5	45,003,363	1,692	654	0.37	2,346
Test 2	270,001,383	81,050	66.6	270,082,500	2,178	20	0.84	2,198

may be caused by a combination of factors including the kiln design, operating conditions, and fuels and raw materials used.²⁰ In our study, the higher molecular weight congeners probably condensed onto particulates and were recycled back through the process, whereas less thermodynamically stable compounds were converted into more volatile, less chlorinated congeners. Consequently, PCDFs were dominant in all the samples, contributing 83.2% and 92.8% to the total stack gas PCDD/F concentrations in Tests 1 and 2, respectively. 2,3,4,7,8-PeCDF was the largest contributor to the total TEQ concentration, accounting for 57.5%, 60.6%, and 52.2% in Test 0, Test 1, and Test 2, respectively. In summary, the PCDD/F congener profiles were not as consistent as the PBDD/F profiles, which may imply that they had different formation mechanisms.

Toxicity (Equivalence) Reduction. As discussed above, a high DRE was achieved incinerating soils contaminated with PBDE in the cement kiln, and the PBDD/F, PCDD/F stack gas TEQ concentrations were below the PCDD/F emission limits specified in the relevant U.S. EPA and European Union standards. However, because of the relatively low toxicity of PBDEs and much higher toxicity of PBDD/Fs and PCDD/Fs, more attention should be paid to the change in total toxicity between before and after coprocessing PBDE-contaminated soils. The total toxicity (equivalence) entering the cement kiln in the soils and the sum of PBDEs, PBDD/Fs, and PCDD/Fs in the stack gases were evaluated.

The relative potencies and efficacies (REP EC_{5TCDD}) from the dioxin-responsive-chemical activated luciferase gene expression (DR-CALUX) test, which have been reported by Behnisch et al. and Takigami et al.,^{49,50} were used as TEFs to calculate a "TEQ" for the PBDEs because I-TEFs are not available for PBDEs. REP EC_{5TCDD} values for several PBDE homologues are shown in SI Table S6.

PBDE homologue TEQ concentrations were calculated using the following formula:

$$\Sigma \text{TEQ} = \sum_i C_i \text{REP}_i \quad (2)$$

where ΣTEQ is the PBDE homologue TEQ concentration (ng TEQ/g), C_i is the PBDE homologue mass concentration (ng/g), and REP_i is the REP EC_{5TCDD} value for the PBDE homologue. The total TEQ of the PBDE homologues, the PBDD/Fs, and the PCDD/Fs that enter and exit the cement kiln during the test burns were determined and are presented in Table 2.

As shown in Table 2, the total TEQ at the outlet was much lower than at the inlet. The decreasing ratios in Tests 1 and 2 were 99.995% and 99.999%, respectively.

Evaluation of the Feasibility and Environmental Safety of Using the Cement Kiln for Coprocessing PBDE-Contaminated Soils. The test burns indicated that the cement kiln was able to destroy PBDEs in soil effectively and in an environmentally sound manner, with low PBDD/F and PCDD/F emissions in compliance with Chinese, U.S. EPA, and European Union regulations. The DRE for highly contaminated

soil (PBDE concentrations up to 25 000 mg/kg) was above 99.999%. The selection of appropriate feed points is essential for environmentally sound coprocessing.¹⁵ In our test burns, the soil was fed into the fuel gas chamber at the kiln inlet, under conditions that were favorable for the destruction of PBDEs but unfavorable for the formation of PBDD/Fs. The feasibility of other feeding scenarios (e.g., in the raw-feedstock mill) requires further study. An accurate cost evaluation has not yet been conducted, but it is estimated that it will be more cost-efficient to use a cement kiln for coprocessing PBDE-contaminated soils than to build a special facility for waste incineration. Although extremely low PBDD/F and PCDD/F emissions were found, additional trials including the use of different technologies and devices need to be studied to attempt to reduce PBDD/F and PCDD/F emissions even further.

■ ASSOCIATED CONTENT

Supporting Information

Additional PBDE, PBDD/F, and PCDD/F concentrations in soils, coal, and raw materials, and schematic diagram of test and REP EC_{5TCDD} values for PBDE homologues. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

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■ REFERENCES

- (1) Hites, R. A. Polybrominated diphenyl ethers in the environment and in people: A meta-analysis of concentrations. *Environ. Sci. Technol.* **2004**, *38*, 945–956.
- (2) Leung, A. O. W.; Luksemburg, W. J.; Wong, A. S.; Wong, M. H. Spatial distribution of polybrominated diphenyl ethers and polychlorinated dibenzo-p-dioxins and dibenzofurans in soil and combusted residue at Guiyu, an electronic waste recycling site in southeast China. *Environ. Sci. Technol.* **2007**, *41*, 2730–2737.
- (3) Luo, Y.; Luo, X. J.; Lin, Z.; Chen, S. J.; Liu, J.; Mai, B. X.; Yang, Z. Y. Polybrominated diphenyl ethers in road and farmland soils from an e-waste recycling region in southern China: Concentrations, source profiles, and potential dispersion and deposition. *Sci. Total Environ.* **2009**, *407*, 1105–1113.
- (4) Tue, N. M.; Sudaryanto, A.; Minh, T. B.; Isobe, T.; Takahashi, S.; Viet, P. H.; Tanabe, S. Accumulation of polychlorinated biphenyls and brominated flame retardants in breast milk from women living in

Vietnamese e-waste recycling sites. *Sci. Total Environ.* **2010**, *408*, 2155–2162.

(5) Zou, M. Y.; Ran, Y.; Gong, J.; Mai, B. X.; Zeng, E. Y. Polybrominated diphenyl ethers in watershed soils of the Pearl River Delta, China: Occurrence, inventory, and fate. *Environ. Sci. Technol.* **2007**, *41*, 8262–8267.

(6) Zhao, Y. X.; Qin, X. F.; Li, Y.; Liu, M. T.; Yan, S. S.; Qin, Z. F.; Xu, X. B.; Yang, Y. J. Diffusion of polybrominated diphenyl ether (PBDE) from an e-waste recycling area to the surrounding regions in Southeast China. *Chemosphere* **2009**, *76*, 1470–1476.

(7) UNEP DEWA/GRID-Europe. *E-waste, the hidden side of IT equipment's manufacturing and use*; Environment Alert Bulletin 5; UNEP: Nairobi, Kenya, 2005; http://www.grid.unep.ch/product/publication/download/ew_e-waste.en.pdf.

(8) Jin, J.; Wang, Y.; Liu, W. Z.; Yang, C. Q.; Hu, J. C.; Cui, J. Polybrominated diphenylethers in atmosphere and soil of a production area in China: Levels and partitioning. *J. Environ. Sci.* **2011**, *23*, 427–433.

(9) Niu, S. Study on pollution levels and distribution law of PBDEs in soil from production areas. Master Dissertation, Beijing University of Chemical Technology, Beijing, 2011. (In Chinese).

(10) Ma, J.; Qiu, X. H.; Zhang, J. L.; Duan, X. L.; Zhu, T. State of polybrominated diphenyl ethers in China: An overview. *Chemosphere* **2012**, *8*, 769–778.

(11) *Updated General Technical Guidelines for the Environmentally Sound Management of Wastes Consisting of, Containing or Contaminated with Persistent Organic Pollutants (POPs)*; Basel Convention, Basel, 2007; www.basel.int/meetings/sbc/workdoc/techdocs.html.

(12) *Review of the Emerging, Innovative Technologies for the Destruction and Decontamination of POPs and the Identification of Promising Technologies for Use in Developing Countries*; UNEP: Nairobi, Kenya, 2004; www.unep.org/stapgef.

(13) Fu H. H.; Huang Q. F.; Zhu X. H. Effects of temperature and residue time on remediation of decabromodiphenyl ether contaminated soil by thermal desorption technology. *Res. Environ. Sci.* **2012**, *25*, 981–986. (In Chinese).

(14) Abad, E.; Martinez, K.; Caixach, J. Polychlorinated dibenzo-p-PCDD/PCDF/polychlorinated dibenzofuran releases into the atmosphere from the use of secondary fuels in cement kilns during clinker formation. *Environ. Sci. Technol.* **2004**, *38*, 4734–4738.

(15) Karstensen, K. H. Formation, release and control of PCDD/PCDF in cement kilns – A review. *Chemosphere* **2008**, *70*, 543–560.

(16) Peng Z.; Yu Y. L.; Ding Q.; Wang K. X.; Gao X. H. Demonstration study of co-processing of DDT in a preheater/precalciner cement kiln system. *China Environ. Sci.* **2012**, *32*, 1326–1331. (In Chinese).

(17) Karstensen, K. H.; Mubarak, A. M.; Gunadasa, H. N. Test burn with PCB-oil in a local cement kiln in Sri Lanka. *Chemosphere* **2010**, *78*, 717–723.

(18) Karstensen, K. H.; Kinh, N. K.; Thang, L. B.; Viet, P. H.; Tuan, N. D.; Toi, D. T.; Hung, N. H.; Quan, T. M.; Hanh, L. D.; Thang, D. H. Environmentally sound destruction of obsolete pesticides in developing countries using cement kilns. *Environ. Sci. Policy* **2006**, *9*, 577–586.

(19) Conesa, J. A.; Gálvez, A.; Mateos, F.; Martín-Gullón, I.; Font, R. Organic and inorganic pollutants from cement kiln stack feeding alternative fuels. *J. Hazard. Mater.* **2008**, *116*, 1–8.

(20) Zemba, S.; Ames, M.; Green, L.; Botelho, M.; Gossman, D.; Linkov, I. Emissions of metals and polychlorinated dibenzo(p)dioxins and furans (PCDD/Fs) from Portland cement manufacturing plants: Inter-kiln variability and dependence on fuel types. *Sci. Total Environ.* **2011**, *409*, 4198–4205.

(21) Ames, M.; Zemba, S.; Green, L.; Botelho, M. J.; Gossman, D.; Linkov, I. Polychlorinated dibenzo(p)dioxin and furan (PCDD/F) congener profiles in cement kiln emissions and impacts. *Sci. Total Environ.* **2012**, *419*, 37–43.

(22) Conesa, J.; Gálvez, A.; Mateos, F.; Martín-Gullón, I.; Font, R. Organic and inorganic pollutants from cement kiln stack feeding alternative fuels. *J. Hazard. Mater.* **2008**, *158*, 585–592.

(23) Sikkema, J. K.; Alleman, J. E.; Ong, S. K.; Wheelock, T. D. Mercury regulation, fate, transport, transformation, and abatement within cement manufacturing facilities: Review. *Sci. Total Environ.* **2011**, *409*, 4167–4178.

(24) Birnbaum, L. S.; Staskal, D. F.; Diliberto, J. J. Health effects of polybrominated dibenzo-p-dioxins (PBDDs) and dibenzofurans (PBDFs). *Environ. Int.* **2003**, *29*, 855–860.

(25) Olsman, H.; Engwall, M.; Kammann, U. Relative differences in arylhydrocarbon receptor-mediated response for 18 polybrominated and mixedhalogenated dibenzo-p-dioxins and -furans in cell lines from four different species. *Environ. Toxicol. Chem.* **2007**, *26*, 2448–2454.

(26) Duan, H. B.; Li, J. H.; Liu, Y. C.; Yamazaki, N.; Jiang, W. Characterization and inventory of PCDD/Fs and PBDD/Fs emissions from the incineration of waste printed circuit board. *Environ. Sci. Technol.* **2011**, *45*, 6322–6328.

(27) Du, B.; Zheng, M. H.; Tian, H. H.; Liu, A. M.; Huang, Y. R.; Li, L. L.; Ba, T.; Li, N.; Ren, Y.; Li, Y. W.; Dong, S. P.; Su, G. J. Occurrence and characteristics of polybrominated dibenzo-p-dioxins and dibenzofurans in stack gas emissions from industrial thermal processes. *Chemosphere* **2010**, *80*, 1227–1233.

(28) Ebert, J.; Bahadir, M. Formation of PBDD/F from flame-retarded plastic materials under thermal stress. *Environ. Int.* **2003**, *29*, 711–716.

(29) Balabanovich, A. I.; Hornung, A.; Luda, M. P.; Koch, W.; Tumiat, V. Pyrolysis study of halogen containing aromatics reflecting reactions with polypropylene in a post treatment decontamination process. *Environ. Sci. Technol.* **2005**, *39*, 5469–5474.

(30) Evans, C. S.; Dellinger, B. Formation of bromochlorodibenzo-p-dioxins and furans from the high-temperature pyrolysis of a 2-chlorophenol/2-bromophenol mixture. *Environ. Sci. Technol.* **2005**, *39*, 7940–7948.

(31) Hanari, N.; Kannan, K.; Miyake, Y.; Okazawa, T.; Kodavanti, P. R. S.; Aldous, K. M.; Yamashita, N. Occurrence of polybrominated biphenyls, polybrominated dibenzo-p-dioxins, and polybrominated dibenzofurans as impurities in commercial polybrominated diphenyl ether mixtures. *Environ. Sci. Technol.* **2006**, *40*, 4400–4405.

(32) 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*, 699–710.

(33) U. S. Environmental Protection Agency, Website; http://www.epa.gov/reg3hw_md/risk/human/rb-concentration_table/Generic_Tables/pdf/indsoil_sl_table_run_MAY2012.pdf.

(34) Ren, M.; Peng, P. A.; Cai, Y.; Chen, D. Y.; Zhou, L.; Chen, P.; Hu, J. F. PBDD/F impurities in some commercial deca-BDE. *Environ. Pollut.* **2011**, *159*, 1375–1380.

(35) Hagberg, J.; Olsman, H.; van Bavel, B.; Engwall, M.; Lindström, G. Chemical and toxicological characterization of PBDFs from photolytic decomposition of decaBDE in toluene. *Environ. Int.* **2006**, *32*, 851–857.

(36) *Ambient air and Waste gas Determination of Polychlorinated Dibenzo-p-dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) Isotope Dilution HRGC-HRMS*; HJ.2-2008, 2008; <http://www.zhb.gov.cn/info/bgw/bgg/200901/W020090107554662775660.pdf>.

(37) Van den Berg, M.; Birnbaum, L. S.; Denison, M.; De Vito, M.; Farland, W.; Feeley, M.; Fiedler, H.; Hakansson, H.; Hanberg, A.; Haws, L.; Rose, M.; Safe, S.; Schrenk, D.; Tohyama, C.; Tritscher, A.; Tuomisto, J.; Tysklind, M.; Walker, N.; Peterson, R. E. The 2005 World Health Organization reevaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. *Toxicol. Sci.* **2006**, *93*, 223–241.

(38) Li, Y. M.; Jiang, G. B.; Wang, Y. W.; Wang, P.; Zhang, Q. H. Concentrations, profiles and gas-particle partitioning of PCDD/Fs, PCBs and PBDEs in the ambient air of an E-waste dismantling area, southeast China. *Chin. Sci. Bull.* **2008**, *53*, 521–528.

(39) Chen, L. G.; Mai, B. X.; Bi, X. H.; Chen, S. J.; Wang, X. M.; Ran, Y.; Luo, X. J.; Sheng, G. Y.; Fu, J. M.; Zeng, E. Y. Concentration Levels, Compositional Profiles, and Gas-Particle Partitioning of

Polybrominated Diphenyl Ethers in the Atmosphere of an Urban City in South China. *Environ. Sci. Technol.* **2006**, *40*, 1190–1196.

(40) Wang, M. S.; Chen, S. J.; Huang, K. L.; Lai, Y. C.; Chang, G.-P.; Tsai, J. H.; Lin, W. Y.; Chang, K. C.; Lee, J. T. Determination of levels of persistent organic pollutants (PCDD/Fs, PBDD/Fs, PBDEs, PCBs, and PBBs) in atmosphere near a municipal solid waste incinerator. *Chemosphere* **2010**, *80*, 1220–1226.

(41) *National Emissions Standards for Hazardous Air Pollutants*. 40 CFR Part 60. Federal Register, 1999; <http://www.epa.gov/mats/pdfs/20111216MATSfinal.pdf>.

(42) Raghunathan, K.; Gullett, B. K. Role of sulphur in reducing PCDD and PCDF formation. *Environ. Sci. Technol.* **1996**, *30*, 18–27.

(43) Gullett, B. K.; Raghunathan, K. Observations on the effect of process parameters on PCDD/PCDF and furan yield in municipal waste and coal systems. *Chemosphere* **1997**, *34*, 10–27.

(44) Vogg, H.; Metzger, M.; Stieglitz, L. Recent findings on the formation and decomposition of PCDD/PCDF in municipal solid waste incineration. *Waste Manage. Res.* **1987**, *5*, 285–294.

(45) Ma, J.; Horii, Y. C.; Cheng, J. P.; Wang, W. H.; Wu, Q.; Ohura, T.; Kannan, K. T. Chlorinated and parent polycyclic aromatic hydrocarbons in environmental samples from an electronic waste recycling facility and a chemical industrial complex in china. *Environ. Sci. Technol.* **2009**, *43*, 643–649.

(46) Luijk, R.; Govers, H. A. J. The formation of polybrominated dibenzo-p-dioxins (PBDDs) and dibenzofurans (PBDFs) during pyrolysis of polymer blends containing brominated flame retardants. *Chemosphere* **1992**, *25*, 361–374.

(47) Ma, J.; Addink, R.; Yun, S.; Chen, J. P.; Wang, W. H.; Kannan, K. T. 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*, 7350–7356.

(48) Ma, J.; Kannan, K. T.; Chen, J. P.; Horii, Y. C.; Wu, Q.; Wang, W. H. Concentrations, profiles, and estimated human exposures for polychlorinated dibenzo-p-dioxins and dibenzofurans from electronic waste recycling facilities and a chemical industrial complex in eastern China. *Environ. Sci. Technol.* **2008**, *42*, 8252–8259.

(49) Behnisch, P. A.; Hosoe, K.; Sakai, S. Brominated dioxin-like compounds: In vitro assessment in comparison to classical dioxin-like compounds and other polyaromatic compounds. *Environ. Int.* **2003**, *29*, 861–877.

(50) Takigami, H.; Sakai, S.; Brouwer, A. Bio/chemical Analysis of Dioxin-like Compounds in Sediment Samples from Osaka Bay, Japan. *Environ. Technol.* **2005**, *26*, 459–470.