

## Persistence of Polybrominated Diphenyl Ethers in Agricultural Soils after Biosolids Applications

NATASHA A. ANDRADE,<sup>†</sup> LAURA L. MCCONNELL,<sup>‡</sup> ALBA TORRENTS,<sup>\*,†</sup> AND  
 MARK RAMIREZ<sup>§</sup>

<sup>†</sup>University of Maryland, Department of Civil and Environmental Engineering, 1153 Martin Hall  
 University of Maryland, College Park, Maryland 20742-3021, <sup>‡</sup>United States Department of Agriculture,  
 Agricultural Research Service, Environmental Management and Byproduct Utilization Laboratory,  
 Beltsville, Maryland 20705, and <sup>§</sup>District of Columbia Water and Sewer Authority,  
 Washington, DC 20002

This study examines polybrominated diphenyl ethers (PBDE) levels, trends in biosolids from a wastewater treatment plant, and evaluates potential factors governing PBDE concentrations and the fate in agricultural soils fertilized by biosolids. The mean concentration of the most abundant PBDE congeners in biosolids ( $\Sigma$ BDE-47, BDE-99, and BDE-209) generated by one wastewater treatment plant was  $1250 \pm 134 \mu\text{g}/\text{kg}$  d.w. with no significant change in concentration over 32 months ( $n = 15$ ). In surface soil samples from the Mid-Atlantic region, average PBDE concentrations in soil from fields receiving no biosolids ( $5.01 \pm 3.01 \mu\text{g}/\text{kg}$  d.w.) were 3 times lower than fields receiving one application ( $15.2 \pm 10.2 \mu\text{g}/\text{kg}$  d.w.) and 10 times lower than fields that had received multiple applications ( $53.0 \pm 41.7 \mu\text{g}/\text{kg}$  d.w.). The cumulative biosolids application rate and soil organic carbon were correlated with concentrations and persistence of PBDEs in soil. A model to predict PBDE concentrations in soil after single or multiple biosolids applications provides estimates which fall within a factor of 2 of observed values.

**KEYWORDS:** Polybrominated diphenyl ethers; biosolids; soil

### INTRODUCTION

Solids generated from wastewater treatment plants (WWTPs), sometimes termed biosolids, may be applied in soil remediation efforts and as soil amendments in agriculture production fields. Land application of biosolids is generally considered a sustainable practice; however, concerns exist with respect to the fate of persistent organic pollutants present in biosolids and their bioavailability. In the United States, the application of biosolids to land is regulated by 40 CFR Part 503 (1), which includes requirements for pathogen control and limits on heavy metal content. These regulations do not include limits on organic pollutants, although the inclusion of some polychlorinated biphenyls (PCBs), polychlorinated dioxins, and polychlorinated furans to Part 503 has been discussed (2). The latest survey found that, in 2004, 55% of the seven million tons (dry weight) of biosolids produced in the U.S. were land applied (3).

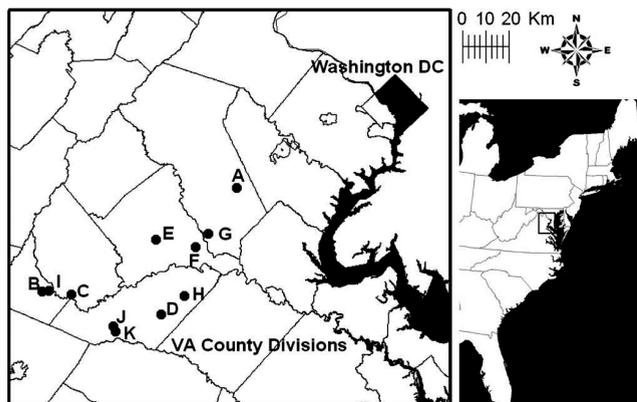
Polybrominated diphenyl ethers (PBDEs) are brominated flame retardants (BFRs) that have been used globally in hundreds of products, like foam mattresses, televisions, computers, plastics, and textiles (4). PBDEs have been produced in three commercial formulations: penta-BDE, octa-BDE, and deca-BDE; however, only the deca-BDE is currently in production.

Recent studies illustrate that levels of PBDEs in biosolids have increased over the past two decades (5–7). In a recent study,

11 wastewater treatment plants in Germany had total PBDE levels from 110 to 2500  $\mu\text{g}/\text{kg}$  d.w. (6). In Spain, biosolids samples collected at five WWTPs had concentrations between 197 and 1180  $\mu\text{g}/\text{kg}$  d.w. (7). Researchers in Kuwait analyzed biosolids samples from three WWTPs and reported mean concentrations ( $\Sigma$ PBDEs) in the range of 5.7–1600  $\mu\text{g}/\text{kg}$  d.w. (8). In Australia, 16 WWTPs were surveyed for PBDEs, and the average biosolids concentration was 1140  $\mu\text{g}/\text{kg}$  d.w. (9). In the U.S., Hale et al. (10) reported PBDEs levels in biosolids in 11 samples from WWTPs in Virginia, Maryland, New York, and California ranging from 1100 to 2290  $\mu\text{g}/\text{kg}$  d.w. for the penta-brominated PBDEs and 85–4890  $\mu\text{g}/\text{kg}$  d.w. for the decabrominated PBDE congener (BDE-209). In California, reported total PBDE concentrations from one plant ranged from 61 to 1440  $\mu\text{g}/\text{kg}$  d.w. (11). PBDEs have also been reported in biosolids from Wisconsin (12) where the mean was 1680  $\mu\text{g}/\text{kg}$  d.w. for the sum of BDE-47, BDE-99, and BDE-209 (complete PBDE chemical names listed in Table S1, Supporting Information). These studies suggest that PBDE levels in the U.S. are higher than in other parts of the world.

Concentrations of PBDEs in soil samples usually present a high level of variability, and this variability tends to increase if the soil has been impacted by human activities. A study completed in United Kingdom and Norway (13) found that in remote areas, background soil concentrations for total PBDEs were in the range of 0.6–2.5  $\mu\text{g}/\text{kg}$  d.w., with a maximum concentration of 12  $\mu\text{g}/\text{kg}$  d.w. Harrad and Hunter (14) collected soil samples in a transect across the West Midlands of the UK (also representing

\*Corresponding author. phone: 01-301-405-1979; fax: 01-301-405-2585; e-mail: alba@eng.umd.edu.



**Figure 1.** Location of soil sample collection sites. Black lines indicate county boundaries in Virginia, USA. Lettered circles represent farms where several fields were sampled.

background concentrations) and reported total concentrations ( $\Sigma$ BDE-28, 47, 99, 100, 153, 154) in the range of 0.07–3.9  $\mu\text{g}/\text{kg}$  d.w. For soils that received biosolids applications, a study in Spain reported PBDE levels ranging from 21 to 690  $\mu\text{g}/\text{kg}$  d.w. (7). Hale et al. (15) reported a concentration (sum of BDE-47, 99, 100) of 76  $\mu\text{g}/\text{kg}$  d.w. in soil near a foam production facility in the U.S. Mid-Atlantic region. Wang et al. (16) analyzed soil samples collected in the area surrounding an electronic waste disposal and recycling facility in China, and the average total PBDE concentration was approximately 1100  $\mu\text{g}/\text{kg}$  d.w. Wang's study represents a worst case scenario, where the soils received daily PBDE loads.

Since PBDEs are released into wastewaters from consumer products, and since these chemicals are hydrophobic in nature, they are effectively removed with organic solids during the treatment process. Therefore, PBDE residues are present in biosolids as the material is applied to soils. The potential effects on ecosystem health and the long-term fate of the PBDEs in soil are generally unknown (17). No large-scale studies have been carried out in the U.S. to examine PBDE concentrations and persistence in agricultural soils where detailed information on application rates and timing is known. The objectives of this study were to determine if biosolids applications increase the levels of PBDEs in soil; to examine the most important factors governing PBDE concentrations in agricultural fields receiving biosolids; and to estimate the soil half-life of PBDE congeners. This paper provides the first detailed reporting of PBDE concentrations in agricultural soils as a function of the number of biosolids application and amount of biosolids applications where information on the timing and application rates are known. This study also includes a multiyear survey of PBDE biosolids concentration data from a source WWTP, and a spatial analysis of PBDE concentrations across the 30 fields included in this experiment. Research gaps regarding the availability of aged PBDE residues in soil for exchange with other environmental compartments are identified. This work represents a benchmark for PBDE concentrations in agricultural soils and biosolids in the Mid-Atlantic region of the U.S. which may be used for comparison in future studies to assess PBDE fate on a global scale.

## MATERIALS AND METHODS

**Experimental Design.** Dewatered and limed biosolids grab samples (average = 28% solids) were collected from a large mid-Atlantic WWTP every two months between July 2005 and March 2008 for a total of 15 biosolids samples.

Surface soil samples were collected between March 20 and April 1 of 2006 from 11 farms in Virginia (Figure 1). A total of 30 agricultural fields

were targeted for sample collection. Three types of sites were selected: 10 fields with zero biosolids applications; 10 fields that had received one biosolids application in the past 3.5 years; and 10 fields that had received more than one biosolids application in the past 5–15 years (Table S2, Supporting Information).

All fields, except for two (MA2 and ZH12, which were planted with corn), were pasture fields for cattle. Soils in this region are generally loam type soils (Nason, Elioak, Chewacla, Lloyd, Dyke, Unison, Bucks, Rapidan, Altavista, Catlett, Zion, Penn, Iredell, Tatum, Fluvanna, Appling, and Cecil) with organic carbon content ranging from 1.58% to 3.33% (Table S2, Supporting Information). All fields with one application received biosolids from the same wastewater treatment plant where biosolids samples were collected. Fields with multiple applications received biosolids from the sampled WWTP and other WWTPs (all WWTPs are located in Virginia, with the exception of one that is located in Maryland). Although this introduces some uncertainty in the data analysis for these fields, the level of detailed access to applicator records in this project was extremely helpful and is normally not available. Fields that received biosolids from multiple plants received on average 53.3% of the application rate from our source WWTP.

Biosolids are applied by commercial spreaders that deliver the cake on top of the soil in a mixture of various sizes of chunks of biosolids. The process does not deliver a homogeneous layer of material on top of the soil but rather an extremely heterogeneous and random layer. However, the rate of material fall throughout the field is approximately constant during application. Biosolids were applied by licensed applicators at agronomic rates determined by soil testing following state regulations for buffers around waterways and wells (18).

Sample collection points were geolocated and recorded using a field global positioning system (GPS) instrument (model GeoXT Trimble, Westminster, CO). Collection sites were selected using a spatial relationship according to the size and shape of the field and ranged from 5 to 14 samples per field, with an average of 1 sample per 1350  $\text{m}^2$  (duplicates were collected in 13 of the 30 fields sampled). Spatial analysis was performed using ArcMap (ESRI GIS and Mapping Software, Vienna, VA). Satellite imagery was obtained from the USDA Geospatial Data Gateway (19).

**Sample Collection.** Biosolids grab samples for PBDE and dry weight analysis were collected using a long-handled beaker from the solids processing facility of the WWTP at the end of the dewatering and liming process just before the material entered the biosolids temporary storage area. Samples were immediately transferred to clean, 250-mL, amber, wide-mouth jars with Teflon-lined lids and were kept frozen ( $-20\text{ }^\circ\text{C}$ ) until processing. Surface soil samples were collected at a 7.60 cm depth [light disking of the field (plowing of a field usually to a depth of 7.62 cm) usually occurs after land application of biosolids] using a N-2 Handle (JMC Soil Samplers, Newton, IA, JMC N-2 Handle PN003) sampler with attached zero-contamination tube. Soil samples were a composite of three cores collected in a 30 cm diameter area around the collection site. Samples were stored temporarily on ice then transferred to a freezer ( $-20\text{ }^\circ\text{C}$ ) and were kept frozen until processing.

**Sample Processing.** The laboratory lights were covered with a light filter that blocks light with wavelengths below 620 nm and the windows were kept covered to minimize photodegradation of PBDEs. Samples were thawed in a refrigerator ( $4\text{ }^\circ\text{C}$ ) overnight and then allowed to reach room temperature just before processing. All solvents used in sample processing were chromatographic grade, all chemical standards were analytical grade of 99.8% purity or greater, and all glassware was precleaned with detergent, distilled water, and acetone and then baked at  $300\text{ }^\circ\text{C}$  for 4 h prior to use. Soil samples were then sieved to 2 mm to remove grass, rocks, and insects. A 10-g aliquot of soil from each sample was ground with approximately 30 g of anhydrous sodium sulfate (J.T. Baker, Phillipsburg, NJ) using a clean mortar and pestle to dry the sample. Dried samples were transferred to 50 mL volume Teflon centrifuge tubes and were extracted twice with 25 mL of dichloromethane (DCM) (99.9%, Acros, Morris Plains, NJ). The method applied is a modified QuEChERS (Quick Easy Cheap Effective and Safe) method (20). The extraction procedure was performed by vigorous mixing of soil and solvent using a vortex mixer (Fisher Scientific, Fairlawn, NJ) at a speed of 2500 rpm for a total of 2 min per extraction. Sonication extractions has been reported to produce low recoveries for BDE-209 in standard reference materials (sediment in this case), but all the authors have confidence in the recoveries of the

**Table 1.** PBDE Congener and Total Concentration in Biosolids Samples ( $n = 2$  for Each Collection Date)

collection date	concentration ( $\mu\text{g}/\text{kg}$ d.w.)								total
	BDE 28	BDE 47	BDE 100	BDE 99	BDE 154	BDE 153	BDE 183	BDE 209	
07/20/2005	28.5	165	69.5	176	55.7	55.5	BQL	792	1350
09/19/2005	56.1	238	92.6	245	67.9	71.2	BQL	948	1730
01/05/2006	51.0	173	75.8	183	59.3	61.8	BQL	891	1500
03/06/2006	52.8	149	72.4	158	58.7	60.4	BQL	861	1420
05/25/2006	54.4	175	78.3	184	61.8	64.1	BQL	901	1520
07/25/2006	48.1	163	71.8	176	55.7	58.0	BQL	825	1400
09/28/2006	48.6	153	69.7	158	55.6	56.9	BQL	862	1410
11/28/2006	49.7	147	69.9	160	55.7	57.2	BQL	826	1370
01/29/2007	48.9	136	66.0	144	54.2	55.4	31.8	854	1390
03/30/2007	49.5	144	67.7	146	55.0	56.6	BQL	963	1490
05/30/2007	58.6	188	83.8	196	66.3	68.6	BQL	1070	1740
08/10/2007	BQL	138	64.8	152	51.3	52.9	BQL	883	1360
10/02/2007	47.9	170	72.0	173	55.9	57.4	BQL	1030	1610
12/03/2007	26.9	128	61.4	128	50.3	51.3	BQL	873	1330
03/13/2008	64.7	152	80.1	160	69.4	70.4	BQL	1220	1820

method presented here (21). Just prior to extraction, an extraction surrogate, 40 ng of 2,2',3,3',4,4',5,5',6,6'-dechlorobiphenyl (PCB-209) was added as an extraction surrogate (PCB-209 was chosen as a surrogate because it is cheaper than a  $^{13}\text{C}_{12}$  labeled compound and it is not expected to be found in great amounts in environmental samples analyzed in this study). The samples were centrifuged for a total of 5 min per extraction at the speed of 5000 rpm, and the solvent was decanted and reduced to 0.5 mL using a gentle stream of  $\text{N}_2$ . The extract was cleaned up using a 2-g alumina Superclean N-alumina (Supelco, Bellefonte, PA) solid phase extraction cartridge, and PBDEs were eluted using 6 mL of DCM; the final extract was reduced to 0.5 mL and transferred to hexane (HPLC grade, Fisher Scientific, Fair Lawn, NJ). An internal standard ( $^{13}\text{C}_{12}$  2,2',3,4,4',5'-hexachlorobiphenyl ( $^{13}\text{C}_{12}$  PCB 138)) was added to the final extract. The carbon content of the soil was determined using a carbon–nitrogen analyzer (TruSpec CN, LECO, Corp., St. Joseph, MI). Biosolids extractions were carried out in one batch and they were processed in duplicate. Soil extractions were carried out in batches by field. Along with samples, three spike samples were included: one blank sand sample spiked with 10 ng of  $^{13}\text{C}_{12}$  BDE 209 (Cambridge Isotope Laboratories, Inc., Andover, MA), a second blank sand spiked with an unlabeled mixture of the target PBDEs, and one duplicate soil sample was spiked with the unlabeled PBDE mixture to examine potential matrix effects on PBDE recoveries. One lab duplicate soil sample was processed for each field, and 43% of the fields had one field duplicate sample. All BDE and PCB congener standards were obtained from Cambridge Isotope Laboratories, Inc. (Andover, MA).

**Sample Analysis.** Eight PBDE congeners were selected as target analytes ranging from the tribrominated BDE-28 to the deca-brominated BDE-209 (Table S1, Supporting Information). Samples extracts were analyzed using an Agilent 6890 gas chromatograph (GC) coupled with an Agilent 5975 mass selective detector (MSD) in negative chemical ionization mode with methane as the ionization gas. The Agilent capillary column used (DB-5-MS) had a length of 15 m, diameter of 0.25 mm, and film thickness of 0.1  $\mu\text{m}$  (J&W Scientific, Folsom, CA). This column was preceded by a fused silica capillary deactivated column (5 m, 0.25 mm i.d.). The carrier gas used was helium with a constant flow of 1.6 mL/min. The oven temperature program was as follows: 48  $^\circ\text{C}$  for 3 min, 20  $^\circ\text{C}/\text{min}$  to 210  $^\circ\text{C}$ , 25  $^\circ\text{C}/\text{min}$  to 310  $^\circ\text{C}$ , 310  $^\circ\text{C}$  for 5 min. The injection volume was 1  $\mu\text{L}$ . A programmable temperature vaporizing (PTV) inlet was used with the following temperature program: 48  $^\circ\text{C}$  for 0.45 min and then ramped at a rate of 600  $^\circ\text{C}/\text{min}$  to 300  $^\circ\text{C}$  and held for 23 min. The GC-MS interface was kept at a temperature of 300  $^\circ\text{C}$ . Sample concentrations were quantified using the internal standard method with a five point calibration curve. We monitored each compound using at least two ions (Table S1, Supporting Information). Blanks presented peaks only for BDE-47 and BDE-99, but they were all well below MDL values. For biosolids samples, the PCB-209 surrogate had a mean percent recovery value of  $112 \pm 14\%$  ( $n = 30$ ), and recovery for all BDE congeners analyzed (BDE-28, BDE-47, BDE-99, BDE-100, BDE-154, BDE-153, BDE-183, and BDE-209) averaged 52% to 68% recovery for one sand spike (Table S1, Supporting

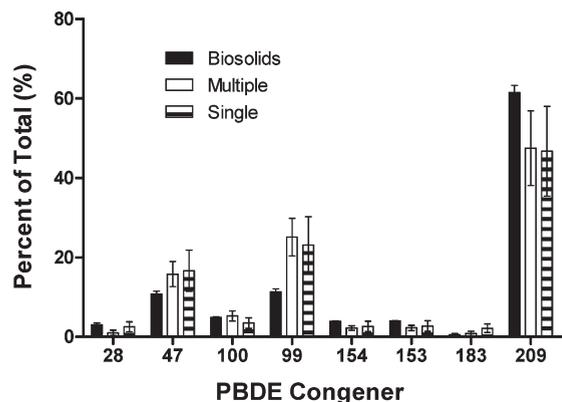
Information). In soil, surrogate recoveries (PCB-209) averaged  $73 \pm 16\%$  ( $n = 338$ ) in soil samples and in sand blanks. In soil samples, BDE mean congener recoveries ranged from 61 to 92% ( $n=30$ ) (Table S1, Supporting Information). Labeled BDE-209 mean recovery in soil was  $107 \pm 46\%$  ( $n = 30$ ). Final concentration values were not adjusted for recovery values. The method detection limits were calculated using EPA 40 CFR Part 136 Appendix B (22) with sand as a matrix and ranged from 0.380 to 6.02  $\mu\text{g}/\text{kg}$  (Table S1, Supporting Information). Laboratorial duplicates averaged a 9.55% difference and field duplicates had an average 8.96% difference.

## RESULTS AND DISCUSSION

**Concentrations in Biosolids.** With the exception of BDE-183 (detected in only one sample), all eight target congeners were present in all biosolids samples. The total PBDE concentration ranged from 1320 to 1820  $\mu\text{g}/\text{kg}$  d.w. (Table 1) with a mean value of  $1500 \pm 158 \mu\text{g}/\text{kg}$  d.w. BDE-47, BDE-99, and BDE-209 together represented 82–87% of the total concentration, suggesting that the commercial formulations penta-BDE and deca-BDE were the primary PBDE sources to the WWTP. The mean concentrations of BDE-47, BDE-99, and BDE-209 in biosolids were  $161 \pm 27$ ,  $169 \pm 27$ , and  $920 \pm 112 \mu\text{g}/\text{kg}$  d.w., respectively. Biosolids PBDE concentrations from this plant are similar to those observed in other plants in the U.S. (10–12).

During the sampling period, from mid-2005 to early-2008, no significant increase or decrease could be detected in PBDE concentrations on a total ( $r^2 = 0.04$ ) or congener basis. In addition to regression analysis, a Mann-Kendall test was performed on the data for all the congeners and total concentration, and the tests results suggest that the hypothesis of trend is rejected at the 95% confidence level. There was no seasonal trend in concentration, and meteorological conditions did not appear to have a significant effect on PBDE concentration. There was no significant correlation between congener concentration and two-day average temperature (BDE-47  $r^2 = 0.231$ , BDE-99  $r^2 = 0.267$ , and BDE-209  $r^2 = 3.0 \times 10^{-4}$ ) or total weekly precipitation (BDE-47  $r^2 = 0.043$ , BDE-99  $r^2 = 0.026$ , and BDE-209  $r^2 = 0.038$ ) for the day of sample collection. At the sample collection frequency included in this study, results suggest a relatively constant source of PBDEs in wastewater, not strongly affected by environmental conditions. Frequent sampling of unprocessed wastewater entering plant would likely be required to examine environmental factors affecting PBDE concentrations.

**Concentrations in Soil.** BDE-183 and BDE-28 were below the detection limit [BDL (Table S1, Supporting Information)] in all fields with zero or one application. BDE-183 was detected in some



**Figure 2.** Average relative congener pattern in biosolids ( $n = 15$ ), soils with multiple biosolids applications ( $n = 69$ ), and one application ( $n = 68$ ) shown with standard error.

fields with multiple applications, but it was below the quantitation limit [BQL (Table S1, Supporting Information)], while BDE-28 was BDL in all multiple fields as well. As in the biosolids, the dominant congeners found in all agricultural soils were BDE-47, BDE-99, and BDE-209; however, the contribution of each congener to the total concentration varied with the number of applications that the field received. Since the contribution of these three congeners is much higher than the other congeners, the following discussion and concentrations presented will be limited to these three congeners (Table S3, Supporting Information). The contribution of BDE-47, BDE-99, and BDE-209 to the total concentration in surface soil collected from fields with zero applications was 75%, and the BDE mean concentration was  $5.01 \pm 3.01 \mu\text{g}/\text{kg d.w.}$ , slightly higher than levels found in Europe (13, 14). Fields with one application had a contribution from these congeners of 86% and an average concentration of  $15.2 \pm 10.2 \mu\text{g}/\text{kg d.w.}$  Fields with multiple applications presented a contribution of these congeners of 88% and had an average concentration of  $53.0 \pm 41.7 \mu\text{g}/\text{kg d.w.}$

As PBDEs are relatively persistent, an additive effect is expected and fields receiving multiple biosolids applications are expected to have higher soil concentrations overall than those with one application. Mean total PBDE concentrations for single and multiple application field groups were compared using an unpaired  $t$  test with a 95% confidence level. Concentrations in the multiple application group ( $n = 69$ ) were significantly higher than those in the single application group ( $n = 68$ ) ( $P = 0.012$ ). Similar findings have been reported by Eljarrat et al. (7) and also by Sellstrom et al. (23). Soil samples from three research stations and two farms in Sweden had concentration levels from 0.06 to  $3900 \mu\text{g}/\text{kg d.w.}$  for soils that were treated with biosolids, and they concluded that biosolids application increased concentrations 2- to 13-fold (23), similar to a 8-fold increase for our multiple application fields. In our study, the zero application group results were not considered in comparison with the other groups since so many of the congener concentrations were BQL.

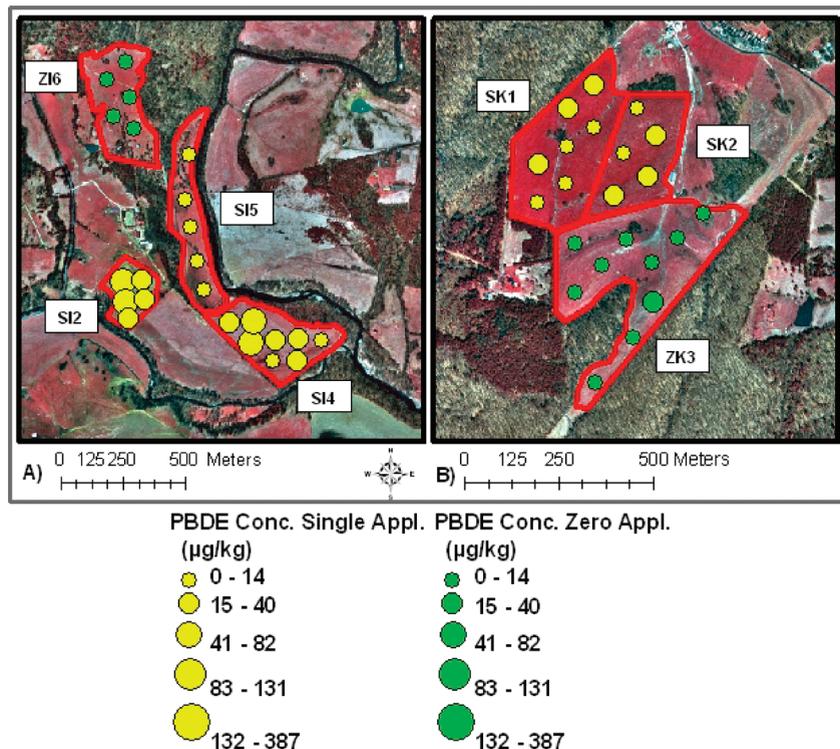
**Congener Distribution.** An examination of the congener pattern observed in soils which received biosolids as compared with that of the biosolids suggests some changes in PBDE use patterns over the past few years (Figure 2). The ratio between congeners BDE-209 and the sum of BDE-47 and BDE-99 for biosolids samples was  $2.84 \pm 0.48$ , while the same ratio for fields with multiple applications was  $1.31 \pm 0.64$  and for fields with one application was  $1.40 \pm 1.05$  [Tukey's test shows statistically significant difference between biosolids ratio from single application ( $q = 7.44$ ) and from multiple application ( $q = 6.78$ ), while

there is no difference between single application and multiple application ( $q = 0.39$ )]. The ratios show that BDE-209 is present in relatively greater abundance in biosolids than in soils, and that BDE-47 and BDE-99 are present in relatively greater abundance in sampled soils than in biosolids. The prevalence of BDE-209 in biosolids may be because deca-BDE is the only commercial formulation currently in use in the U.S. However, biosolids applications for some of these fields occurred before the removal of penta-BDE formulation from the market, and this may explain why the penta-BDE-related congeners are prevalent in soils that have received biosolids. Difference in the ratios may also be caused by some debromination of BDE-209 in the soil environment, differences in degradation or transport rates in different fields, or the increased difficulty to extract it from soil over time (24).

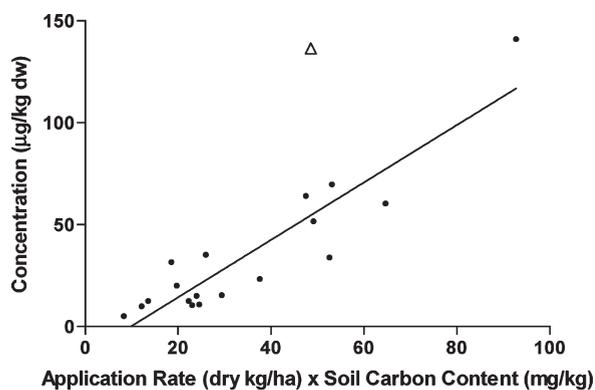
Studies like the one described here usually rely on data provided by commercial applicators and farmers. This data, while frequently accurate, may sometimes contain errors, which was observed in our case and resulted in the elimination of two fields from further examination and analysis. Examination of concentration and congener pattern data suggests that field ZK3 did actually receive biosolids application (Figure 3). The congener pattern for field ZK3 is significantly closer to the observed pattern in soils that received one biosolids application (BDE-209/(BDE-47 + BDE-99) ratio of 0.77) than other fields in the zero application group. Field ZK3 (average  $\Sigma\text{PBDE} = 10.2 \mu\text{g}/\text{kg d.w.}$ ) borders two fields that received one biosolids application: SK1 ( $10.6 \mu\text{g}/\text{kg d.w.}$ ) and SK2 ( $17.9 \mu\text{g}/\text{kg d.w.}$ ). This proximity of pattern and total concentration indicates either a recording error, where the field did receive biosolids, or there are other means of transport influencing the concentration of these nonvolatile and highly hydrophobic chemicals (estimated vapor pressure:  $\log P$  range =  $-2.9$  to  $-8.4$  (25); estimated  $\log K_{ow}$  range:  $4-10$  (26)).

The information received from the applicator on Field S15 indicated that this field received one biosolids application (Figure 3). However, our spatial analysis suggests that it is unlikely this very narrow, ditched field was appropriate for biosolids application. The PBDE concentrations found in this field were all BQL. Since there is enough evidence from this spatial analysis to dispute application information for fields ZK3 and S15, these data have been eliminated from further analysis.

**Soil Organic Carbon, Application Rate, and Time of Application.** The hydrophobic nature of PBDEs suggests they will have a strong affinity for soil organic carbon, and thus PBDEs would be highly retained in soils with moderate to high organic carbon content. The concentration of PBDEs in soils receiving biosolids applications were evaluated relative to the application rate and the carbon content of the soils (ranging from 1.58% to 3.33% carbon). The sum of all application rates received by each field was multiplied by the soil percent carbon (Figure 4). A positive correlation with the application rate (considering all fields) yielded an  $r^2 = 0.67$  and the relationship with soil percent carbon yielded an  $r^2 = 0.41$ . However, the relationship was stronger when the two variables were multiplied ( $r^2 = 0.84$ ). This approach is justified because while the application rate is of primary importance, the soil organic carbon appears to enhance the persistence of the PBDEs. Biosolids application was not found to increase the soil organic carbon concentration when compared to fields receiving no biosolids (data not shown); therefore, the effect of the soil organic matter is independent of the biosolids application rate. The relationship of the two variables multiplied for fields with one application ( $r^2 = 0.28$ ) was not as strong as the same relationship for the fields with multiple applications ( $r^2 = 0.89$ ), but this is likely due to the small range of concentration and application values in the single application



**Figure 3.** Total PBDE concentrations observed for fields with one biosolids application (yellow dots) and zero applications (green dots). (A) Field SI5 was removed from the analysis because results indicate it did not receive a biosolids application. (B) Field ZK3 (zero applications) has a concentration profile that matches neighboring fields SK1 and SK2 which have received a single biosolids application. Field ZK3 was removed from analysis because results indicate it did receive biosolids application.



**Figure 4.** Relationship between the concentrations of PBDEs in the fields that have received biosolids application with their total application rate multiplied by their carbon content. Point represented by a triangle is an outlier that was removed from the regression.

group. One outlier (field MA3) was removed from the calculations (Grubbs' outlier test,  $Q = 1\%$ , and extreme studentized deviate test (GraphPad Software, Inc., San Diego)). The strong correlation observed indicates that the amount of biosolids applied will have a direct influence on the soils PBDE concentration, but PBDEs will also likely persist longer in upper soil layers in the presence of higher soil organic carbon.

**Prediction of PBDE Concentrations in Soil.** Our analysis indicates that the main factor controlling the concentrations of PBDEs in soils is the biosolids application rate, and soil organic carbon appears to enhance the retention of PBDEs in soil. While the average concentration of PBDEs measured in biosolids in this study cannot be assumed to be identical to those applied to the agricultural fields sampled, two biosolids samples collected in

2005 when nine fields received applications differed by  $-4.9\%$  and  $+6.7\%$  from the average biosolids concentration value. To develop a prediction tool for PBDE concentration in soils, we utilized a modified version of the equation developed by Jackson and Eduljee (27). This equation assumes no degradation/dissipation after application.

$$C_{\text{pred}} \left( \frac{\mu\text{g}}{\text{kg}} \text{ d.w.} \right) = \frac{[\text{PBDE}] \times \text{application rate} \times \text{area}}{\text{soil volume} \times \rho} \quad (1)$$

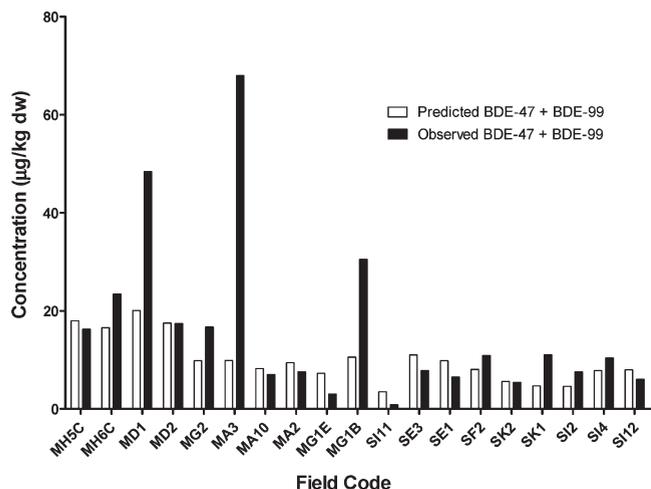
Some assumptions were made in order to perform calculations: (1) the concentration of PBDEs in biosolids applied was  $1250 \pm 130 \mu\text{g}/\text{kg}$  d.w., (2) the soil density,  $\rho$ , (28) remained constant at  $1.3 \text{ g}/\text{cm}^3$ , and (3) biosolids were incorporated to a depth of 7.6 cm. The biosolids concentration utilized represented our average observed concentration. The incorporation depth of 7.6 cm was chosen to mimic the no till practice (disking of the field usually occurs after land application of biosolids).

Calculations of predicted concentrations using the above equation for fields that received one biosolids application overestimated (average of 110% of overestimation considering all types of fields and all congeners) PBDE concentrations as compared to measured values. Different factors could contribute to lower than estimated values: (1) some dissipation is taking place, (2) a greater mixing than the depth assumed here, and/or (3) additional mixing that occurs over the years as a result of regular field usage.

To estimate this overall loss rate, we used a general disappearance equation (27):

$$C'_{\text{pred}} \left( \frac{\mu\text{g}}{\text{kg}} \text{ d.w.} \right) = C_{\text{pred}} \left( \frac{\mu\text{g}}{\text{kg}} \text{ d.w.} \right) e^{-(\ln 2/t_{0.5})t} \quad (2)$$

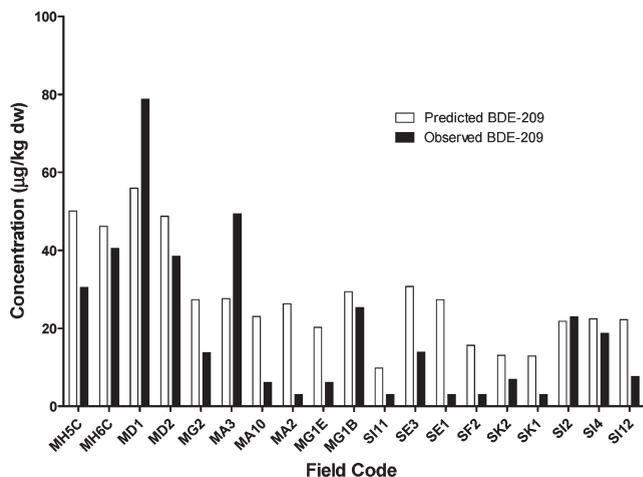
While the rate of dissipation, volatilization, or mixing is unknown, some data exist on soil half-lives for chlorinated



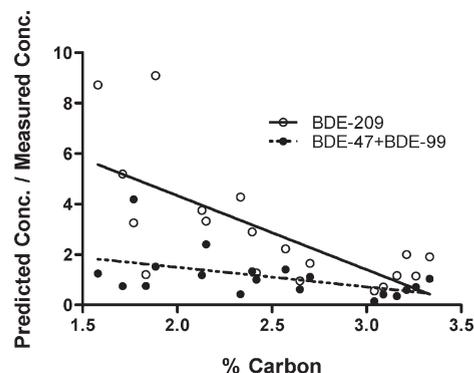
**Figure 5.** Comparison between predicted and observed concentrations for the sum of BDE-47 and BDE-99 congeners. Fields are in ascending order by date of first biosolids application.

organic pollutants. To estimate the half-life for the lower brominated congeners, we used as reference one polychlorinated biphenyl (PCB): PCB-138, which has similar  $\log K_{ow}$  values as BDE-47 and BDE-99 (26, 29). A soil half-life for PCB-138 has been estimated at 2430 days in a PCB modeling study (29) and 6870 days in a literature review (30). On the basis of these previous studies, we averaged the half-life values and assumed a half-life for BDE-47 and BDE-99 of 12.7 years, or 4650 days. To estimate the half-life of BDE-209, we used both PCB-209 and PCB-180 as reference chemicals. Even though these chemicals have a lower molecular weight than BDE-209, they represent the high end hydrophobicity of the PCBs and are suitable for comparison. A soil half-life for PCB-209 was estimated to be 8330 days in a modeling study of PCBs (29), while the estimate for PCB-180 was 13700 days was reported in a literature review (30) and 8660 days for a study using a weathered sandy loam soil (31). Considering BDE-209 stability in the environment and data compiled from literature, we assumed a half-life of 10230 days or approximately 28 years.

With these assumptions and projected half-lives, a predicted soil concentration was calculated. For single application fields, the estimate was performed using eqs 1 and 2. For multiple application fields, the estimate was performed for each application separately, taking into consideration the time between applications and the application rates for each occasion. The values of predicted concentrations were compared to the values of measured concentrations for each of the fields that received biosolids application. For BDE-47 + BDE-99, the predictions were similar to the measured concentrations ( $p = 0.10$ ) using the 12.7-year soil half-life value (Figure 5) with a median predicted/observed concentration ratio of 1.01. For BDE-209, using the 28-year half-life estimation, the predictions were 2.33 times (median) higher than measured concentrations (data not shown). By reducing the half-life estimate for BDE-209 to 12.7 years as for the other BDE congeners, the predictions were twice the value of the observed values ( $p = 0.15$ ) with a median ratio value of 2.00 (Figure 6). Since the median ratio is greater than 1, predicted concentrations are higher than the measured concentrations, suggesting that some important dissipation processes were not incorporated in the simple model used in this study or that levels of BDE-209 in biosolids applied to fields could have been lower than the assumption made. One of the limitations of the measured concentration data is that it is confined to the upper soil layer.



**Figure 6.** Comparison between predicted and observed concentrations for BDE-209 congener. Fields are in ascending order by date of first biosolids application.



**Figure 7.** Ratio between predicted concentrations and measured concentrations for BDE-209 and BDE-47 + BDE-99 as a function of soil organic carbon content. Fields that received one or multiple applications are plotted ( $n = 19$ ) for each congener group. Trend is a clearer for BDE-209 ( $r^2 = 0.48$ ) than for the lower brominated congeners ( $r^2 = 0.25$ ).

Therefore, physical migration of soil residues may have occurred, resulting in losses in surface soils which are unrelated to biotic or abiotic loss processes influenced by the physical/chemical properties of the PBDE congeners.

As a further examination of soil organic carbon effects, the ratio between the predicted concentrations and the measured concentration in soil were plotted against the soil organic carbon content (Figure 7). The further the ratio is from 1 indicates that some dissipation processes are not accounted for. A ratio below 1 would indicate that the congener is more stable than the model predicts. A relatively strong trend ( $r^2 = 0.47$ ) was observed for BDE-209 where the ratio value approaches 1 under higher soil organic carbon conditions. The trend was not as clear for BDE 47 + 99 ( $r^2 = 0.25$ ); however, the majority of the ratios are  $< 2$ . These results suggest that PBDEs will preferentially bind to soils with a larger content of organic carbon, and this will limit the rate of dissipation from top soils. Our analysis also suggests that BDE-209 may be more available for losses under low soil organic carbon conditions, leading to the steeper slope of the regression line.

While the above model provides a reasonable estimate of PBDE levels in soils receiving biosolids applications, a more accurate description of environmental fate should incorporate many processes that have not yet been quantified. Within the soil column, microbial degradation, volatilization, leaching, or

irreversible sorption can occur. Biological degradation is not expected to happen for higher brominated congeners in well drained top soil, where most of the PBDEs will stay, because this process is usually anaerobic (32) although aerobic degradation has been proven for some lower brominated congeners (33). A decrease in concentration may be expected during the first few months after application, especially if the material was not well incorporated into the soil. On the soil surface, photolysis may be an important loss process, high winds may move dust particles off-site, and large storm events may erode soils causing losses. If the biosolids are left on top of the soil, PBDEs would be more available for both volatilization and photodegradation loss processes. These two processes are expected to be the most important pathways for PBDEs loss in the soil environment. As the lower brominated congeners (BDE-47 and BDE-99) have a much lower molecular weight when compared to the fully brominated congener BDE-209; they may be more likely to undergo volatilization. BDE-209 is more susceptible to photodegradation, resulting in nona- and octa- brominated congeners (34). BDE-47 and BDE-99 will also undergo photolysis but at a slower rate (34), and the products will also be lower brominated congeners.

A complicating factor to assess the fate of persistent organic pollutants associated with biosolids application is the nature of the material applied to the soil. PBDEs are not applied as a liquid spray as with pesticides; the biosolids material and associated PBDEs are applied like manure to a field as a matrix rich in organic matter with a low surface area/volume ratio. Even if the biosolids are lightly incorporated into the soil, it is likely the material will remain bound together for some time before it becomes fully available for exchange with soil particles. This assimilation time from one media to another may be a critical factor controlling the fate and availability of PBDEs for various dissipation and degradation processes. The diffusion of the chemical from the interior of the biosolids chunks to the surface may also be a contributing factor for availability for both photodegradation and volatilization. Volatilization is likely to continue even after the biosolids is completely incorporated to the soil with loss rates changing with temperature; however, photodegradation is expected to be negligible since light will not reach the soil aggregates that are under the surface. Also, uptake by plants and biota cannot be discounted when predicting concentrations (23, 24). The loss processes controlling the fate of these chemicals are not fully understood, and the degradation and emission rates should vary widely depending on soil properties and meteorological conditions.

A soil environment is difficult to model and the fate of these chemicals depends on their interaction with all environmental compartments and on agricultural management practices. More controlled experiments, which would include repeated soil sampling of a field, repeated sampling of fields with different types of soil, and incorporation of sorption, biodegradation, volatilization, and photodegradation studies, are needed to better estimate the disappearance half-life of these chemicals and to better understand their disappearance in the soil environment.

This work generates many questions with respect to the bioavailability of soil PBDEs. For example, PBDE exposure to soil-dwelling organisms such as earthworms could lead to bioaccumulation by species higher in the food chain such as birds. Also, many farm fields receiving biosolids are used to grow forage crops, corn, soy beans, and other crops, and questions remain whether soil PBDEs are available for plant uptake. Evidence of initial BDE losses from soil in the first two years after application was observed, but conclusions regarding the long-term fate of BDE congeners in soil are only preliminary at present. Further

controlled experiments examining PBDE fate in soils are needed to more accurately predict the half-lives of specific BDE congeners.

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**Supporting Information Available:** Detailed compounds information; quality assurance/quality control; detailed field information; and soil concentration of PBDEs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

#### LITERATURE CITED

- (1) USEPA. The standards for the use or disposal of sewage sludge. 40 CFR Part 503. *Fed. Regist.* **1993**, *58*, 9248–9404.
- (2) Harrison, E. Z.; McBride, M. B.; Bouldin, D. R. Land application of sewage sludges: an appraisal of the U.S. regulations. *Int. J. Environ. Pollut.* **1999**, *11*, 1–36.
- (3) *A National Biosolids Regulation, Quality, End Use, and Disposal Survey Report. Final Report*; North East Biosolids and Residuals Association (NEBRA): Tamworth, NH, **2007**.
- (4) de Wit, C. A. An overview of brominated flame retardants in the environment. *Chemosphere* **2002**, *46*, 583–624.
- (5) Nylund, K.; Asplund, L.; Jansson, B.; Jonsson, P.; Litzen, K.; Sellstrom, U. Analysis of some polyhalogenated organic pollutants in sediment and sewage sludge. *Chemosphere* **1992**, *24*, 1721–1730.
- (6) Knoth, W.; Mann, W.; Meyer, R.; Nebhuth, J. Occurrence and fate of PBDE in sewage sludge from municipal waste water treatment plants. *Organohalogen Compd.* **2004**, *66*, 3749–3754.
- (7) Eljarrat, E.; Marsh, G.; Labandeira, A.; Barcelo, D. Effect of sewage sludges contaminated with polybrominated diphenylethers on agricultural soils. *Chemosphere* **2008**, *71*, 1079–1086.
- (8) Gevao, B.; Muzaini, S.; Helaleh, M. Occurrence and concentrations of polybrominated diphenyl ethers in sewage sludge from three wastewater treatment plants in Kuwait. *Chemosphere* **2008**, *71*, 242–247.
- (9) Clarke, B.; Porter, N.; Symons, R.; Marriott, P.; Ades, P.; Stevenson, G.; Blackbeard, J. Polybrominated diphenyl ethers and polybrominated biphenyls in Australian sewage sludge. *Chemosphere* **2008**, *73*, 980–989.
- (10) Hale, R. C.; La Guardia, M. J.; Harvey, E. P.; Gaylor, M. O.; Matteson Mainor, T.; Duff, W. H. Persistent pollutants in land-applied sludges. *Nature* **2001**, *412*, 140–141.
- (11) North, K. D. Tracking polybrominated diphenyl ether releases in a wastewater treatment plant effluent, Palo Alto, California. *Environ. Sci. Technol.* **2004**, *38*, 4484–4488.
- (12) Hale, R. C.; Alae, M.; Manchester-Neesvig, J. B.; Stapleton, H. M.; Ikononou, M. G. Polybrominated diphenyl ether flame retardants in the North American environment. *Environ. Int.* **2003**, *29*, 771–779.
- (13) Hassanin, A.; Breivik, K.; Meijer, S. N.; Steinnes, E.; Thomas, G. O.; Jones, K. C. PBDEs in European background soils: levels and factors controlling their distribution. *Environ. Sci. Technol.* **2004**, *38*, 738–745.
- (14) Harrad, S.; Hunter, S. Concentrations of polybrominated diphenyl ethers in air and soil on a rural-urban transect across a major UK conurbation. *Environ. Sci. Technol.* **2006**, *40*, 4548–4553.
- (15) Hale, R. C.; La Guardia, M. J.; Harvey, E.; Mainor, T. M. Potential role of fire retardant-treated polyurethane foam as a source of brominated diphenyl ethers to the US environment. *Chemosphere* **2002**, *46*, 729–735.
- (16) Wang, D.; Cai, Z.; Jiang, G.; Leung, A.; Wong, M. H.; Wong, W. K. Determination of polybrominated diphenyl ethers in soil and sediment from an electronic waste recycling facility. *Chemosphere* **2005**, *60*, 810–816.
- (17) McDonald, T. A. A perspective on the potential health risks of PBDEs. *Chemosphere* **2002**, *46*, 745–755.

- (18) HJR 118/SJR 117: Commission on the Future of Virginia's Environment, Biosolids subcommittee; <http://dls.state.va.us/pubs/legisrec/2002/hjr118a.htm>.
- (19) USDA Geospatial Data Gateway; <http://datagateway.nrcs.usda.gov/>.
- (20) Anastassiades, M.; Lehotay, S. J.; Stajnbaher, D.; Schenck, F. J. Fast and easy multiresidue method employing acetonitrile extraction/partitioning and "dispersive solid-phase extraction" for the determination of pesticide residues in produce. *J. AOAC Int.* **2003**, *86*, 412–431.
- (21) Stapleton, H. M.; Keller, J. M.; Schantz, M. M.; Kucklick, J. R.; Leigh, S. D.; Wise, S. A. Determination of polybrominated diphenyl ethers in environmental standard reference materials. *Anal. Bioanal. Chem.* **2007**, *387*, 2365–2379.
- (22) 49 CFR 43430, Oct. 265, 1984; 50 FR 694, 696, Jan. Four 1985, as amended at 51 FR 23703, June 30, 1986.
- (23) Sellstrom, U.; De Wit, C. A.; Lundgren, N.; Tysklind, M. Effect of sewage-sludge application on concentration of higher-brominated diphenyl ethers in soils and earthworms. *Environ. Sci. Technol.* **2005**, *39*, 9064–9070.
- (24) Mueller, K. E.; Mueller-Spitz, S. R.; Henry, H. F.; Vonderheide, A. P.; Soman, R. S.; Kinkle, B. K.; Shann, J. R. Fate of pentabrominated diphenyl ethers in soil: abiotic sorption, plant uptake, and the impact of interspecific plant interactions. *Environ. Sci. Technol.* **2006**, *40*, 6662–6667.
- (25) Hui-Ying, X.; Jian-Wei, Z.; Qing-Sen, Y.; Yan-Hua, W.; Jian-Ying, Z.; Hai-Xiao, J. QSPR/QSAR models for prediction of the physico-chemical properties and biological activity of polybrominated diphenyl ethers. *Chemosphere* **2007**, *66*, 1998–2010.
- (26) Braekevelt, E.; Tittlemier, S. A.; Tomy, G. T. Direct measurement of octanol–water partition coefficients of some environmentally relevant brominated diphenyl ether congeners. *Chemosphere* **2003**, *51*, 563–567.
- (27) Jackson, A. P.; Eduljee, G. H. An assessment of the risks associated with PCDDs and PCDFs following the application of sewage sludge to agricultural land in the UK. *Chemosphere* **1994**, *29*, 2523–2543.
- (28) Wolf, B. *The Fertile Triangle. The Interrelationship of Air, Water, and Nutrients in Maximizing Soil Productivity*; Food Products Press, The Haworth Press: New York, NY, 1999; p 113.
- (29) Paasivirta, J.; Sinkkonen, S. I. Environmentally relevant properties of all 209 polychlorinated biphenyl congeners for modeling their fate in different natural and climatic conditions. *J. Chem. Eng. Data* **2009**, *54*, 1189–1213.
- (30) Sinkkonen, S.; Paasivirta, J. Degradation half-life times of PCDDs, PCDFs and PCBs for environmental fate modeling. *Chemosphere* **2000**, *40*, 943–949.
- (31) Ayris, S.; Harrad, S. The fate and persistence of polychlorinated biphenyls in soil. *J. Environ. Monit.* **1999**, *1*, 395–401.
- (32) He, J.; Robrock, K. R.; Alvarez-Cohen, L. Microbial reductive debromination of polybrominated diphenyl ethers (PBDEs). *Environ. Sci. Technol.* **2006**, *40*, 4429–4434.
- (33) Robrock, K. R.; Coelhan, M.; Sedlak, D. L.; Alvarez-Cohen, L. Aerobic biotransformation of polybrominated diphenyl ethers (PBDEs) by bacterial isolates. *Environ. Sci. Technol.* **2009**, *43*, 5705–5711.
- (34) Eriksson, J.; Green, N.; Marsh, G.; Bergman, A. Photochemical decomposition of 15 polybrominated diphenyl ether congeners in methanol/water. *Environ. Sci. Technol.* **2004**, *38*, 3119–3125.

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