

Protecting Our Water Environment



Metropolitan Water Reclamation District of Greater Chicago

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DEPARTMENT***

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***EVALUATION OF THE FATE OF POLYBROMINATED DIPHENYL
ETHERS IN BIOSOLIDS, BIOSOLIDS-AMENDED
SOILS, AND UPTAKE IN CORN***

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EVALUATION OF THE FATE OF POLYBROMINATED DIPHENYL ETHERS IN
BIOSOLIDS, BIOSOLIDS-AMENDED SOILS, AND UPTAKE IN CORN

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BACKGROUND

Synthetic organic chemicals are commonly used in domestic, commercial, and industrial applications. As a result, they occur in wastewater and the more hydrophobic ones preferentially partition into organic solids, such as sewage sludge and biosolids. Biosolids, i.e., treated and stabilized sewage sludges, have been increasingly utilized in the United States (U.S.) as soil amendments as they contain substantial amounts of organic carbon and nutrients (such as nitrogen and phosphorus) required for plant growth. If chemicals resist degradation, they will remain in biosolids and subsequently enter the soil upon land application. Polybrominated diphenyl ether (PBDE) flame retardants have recently emerged as contaminants of concern in North America (Hale et al., 2003). They are common additives to plastics and textiles used in car interiors, furniture, carpeting and electronics. PBDEs have been detected at increasing levels in the tissues of humans and wildlife. The pathways responsible for their dissemination are still under investigation. In terms of human exposure, it appears that ingestion and inhalation of indoor dust play a major role (Wu et al., 2007). Food is also a likely component of the exposure pathway.

PBDEs have also been detected at mg per kg (on dry weight basis) levels in biosolids generated at U.S. wastewater treatment plants (Hale et al., 2001). Nonetheless, there remains a lack of data on PBDE fate in the context of agricultural utilization of biosolids. PBDEs are environmentally persistent and lipophilic in nature and thus may accumulate in the food chain. Of the three PBDE formulations, decabrominated diphenyl ether (DecaBDE) constituted about 74 percent of the total North American demand in 2001, the last year for which production data are publicly available (Hale, et al., 2003). Pentabrominated diphenyl ether (PentaBDE) represented 21 percent and octabrominated diphenyl ether (OctaBDE) represented only about 5 percent of the North American PBDE market in 2001. In December 2004, production of the two less brominated PBDE mixtures, PentaBDE and OctaBDE, ceased. However, as all three PBDE formulations have been employed in long-lived commercial products, continued releases to waste streams and the environment is expected. The constituents of PentaBDE are the most environmentally mobile and bioaccumulative. DecaBDE remains in high use today, in part as it has been assumed to exhibit low mobility, bioavailability and toxicity. However, DecaBDE's major constituent, BDE-209, has been recently detected at surprisingly high levels in humans and some wildlife, e.g. birds of prey (Chen et al., 2008). Evidence of biotically and abiotically-mediated dehalogenation of DecaBDE to less brominated congeners has been observed (La Guardia et al., 2007). These congeners may be more mobile, bioaccumulative, and toxic. Hence, an assessment of the PBDE congener profile, including BDE-209, is important. Principal toxicological effects of PBDEs center on the endocrine system, e.g. thyroid function.

PROJECT OVERVIEW

Due to the lack of data regarding the fate and accumulation of biosolids-associated PBDEs following agricultural application, PBDEs were analyzed in biosolids, soil and tissue samples of corn grown on biosolids-amended soils.

The Metropolitan Water Reclamation District of Greater Chicago (District) initiated a field project on two farm fields in fall 2004 to evaluate potential effects of Class B biosolids application to farmland. The project was designed to compare six rates of biosolids application (0 to 200 percent of conventional agronomic application rates) on soil fertility, corn (*Zea mays*) yield, and subsurface water quality. The project design and treatments were also appropriate for investigating the fate of PBDEs in biosolids-amended soils.

Site Description and Sample Collection

The farm fields to which biosolids were applied were comprised of a heavy-textured clay (Will County, IL [W]) soil and a light-textured sandy soil (Kankakee County, IL [K]). The sites received six rates of biosolids application (W: 0, 20, 30, 40, 50 and 80 wet ton/ac/yr; K: 0, 10, 20, 30, 40 and 60 wet ton/ac/yr) for three consecutive years. The mean solids contents in the biosolids samples received was 26.4 percent.

Surface soil samples were collected in the summer of 2007 by compositing five subsamples from 0 to 8-inch depth from each of the treatments from both farm sites, following three annual applications of biosolids (6 treatments [control and 5 biosolids rates] x 2 replicates x 2 sites = 24 samples). Corn tissue samples (grain, stover [stalks and leaves] and roots) were also collected and analyzed. Briefly, corn stover samples from the two highest biosolids rate plots and the control plot (3 treatments x 2 replicates x 2 sites = 12) were collected to assess plant uptake of PBDEs. Corn grain samples were collected from all 5 biosolids plots and the control plot (6 treatments x 2 replicates x 2 sites = 24). Corn root samples were taken from the five biosolids-amended plots only (5 treatments x 2 sites = 10). Corn stover and grains were ground by the District prior to shipment to Virginia Institute of Marine Sciences (VIMS). Aliquots of the original Stickney Water Reclamation Plant (WRP) biosolids (Class B biosolids) that were applied at both sites were also analyzed for PBDEs (six samples: one from each year and applied to each site). After collection and initial preparation, 76 samples were shipped to the VIMS and stored at 0°C until analysis.

Polybrominated Diphenyl Ether Laboratory Analysis

Analytical methods used for PBDE analysis at VIMS have been previously published (La Guardia et al., 2007). Samples (1 - 2 g biosolids, 12 g soil, 2 - 5 g corn stover, 2 - 3 g corn roots and 10 - 12 g corn grain on dry weight basis) were extracted by enhanced solvent extraction (Dionex ASE 200, Sunnyvale, CA) with methylene chloride. Analytical blanks (NaSO_4) were also extracted and analyzed with each sample batch. A surrogate standard containing

2,3,4,4',5,6-hexabromodiphenyl ether (BDE-166; Ultra Scientific, North Kingstown, RI) was added to each sample prior to the extraction. Each extract was purified by size exclusion chromatography, (SEC, Envirosep-ABC, 350 x 21.1 mm column; Phenomenex, Torrance, CA). Extracts were eluted with methylene chloride. The post-SEC fraction of interest was reduced in volume, added to a 2 g silica glass column (Isolute, International Sorbent Tech., Hengoed Mid-Glamorgan, UK) and eluted with 3.5 mL hexane, followed by 6.5 mL of 60:40 hexane/dichloromethane. The second fraction, containing the PBDEs, was reduced in volume and solvent exchanged to hexane.

Decachlorodiphenyl ether (DCDE; Ultra Scientific, North Kingstown, RI) was added as an internal quantitation standard to the purified extracts. PBDE concentrations determined in the samples were corrected based on surrogate (BDE-166) recoveries. The following PBDE congeners were determined in the purified extracts: BDE-47, 49, 66, 85, 99, 100, 153, 154, 183, 196, 197, 206, 208, 207 and 209. These were separated by gas chromatography (GC; 6890N, Agilent Tech., Palo Alto, CA) equipped with a pressure pulse split/splitless injector and a 15-m DB-5HT column (0.25 mm i.d., 0.1 μ m film, J&W Scientific, Agilent). The target analytes were detected and quantified by electron-capture negative chemical ionization (EC-NCI), scanning from m/z 10 to 1000. Five-point quantification curves were generated by analyzing dilutions of a PBDE standard (Wellington Laboratories Inc., Ontario, Canada) and the internal standard. The predominant ions generated in EC-NCI spectra of PBDEs are 79 and 81 m/z. However, cleaving at the ether bond has also been observed for hepta-, octa-, nona-, and deca-PBDEs. These produced spectra with ion clusters centered around 328 and 330 m/z for $[C_6Br_3H_2O]^-$, 408 m/z for $[C_6Br_4HO]^-$ and 486 and 488 m/z for $[C_6Br_5O]^-$. For PBDE identification, bromine distributions between the two benzene rings can be determined for hepta- through deca-PBDEs by examining these fragments.

RESULTS AND DISCUSSION

Three commercial PBDE mixtures (PentaBDE, OctaBDE and DecaBDE) have been used as flame retardant additives for polymers in North America. Therein, they constitute several percent by weight of many finished polymer products. These mixtures, as a function of their components, differ in their physical properties and the types of polymers in which they are utilized. PBDE congeners exhibit low water solubilities and limited vapor pressures, which decrease with increasing bromination (de Wit, 2002). Typically, these are lower than correspondingly halogenated polychlorinated biphenyls. Accordingly, transport of PBDEs dissolved in water or volatilized in air is low. PBDEs sorb preferentially to solids when released to the environment and during the wastewater treatment process (Hale et al., 2006). Hence, transport via particles is the mode of greatest concern. Strong sorption and low water solubilities would be expected to reduce uptake by plants as well. This would be most pronounced in the case of the fully brominated congener, BDE-209, present in the greatest concentration in most biosolids/sewage sludges in the U.S.

PBDEs appear to be relatively resistant to degradation. However, some debromination has been observed in biological systems and as a result of photolysis (La Guardia et al., 2007). Debromination is viewed as an important process, particularly for BDE-209, because the resulting products may show greater toxicity, persistence and bioaccumulation potential.

Quality Control

Sodium sulfate blanks were run with the samples to monitor for possible lab contamination of samples. No PBDEs were detected in these lab blanks. All samples extracted were amended with BDE-166 (a congener absent from commercial PBDE products (La Guardia et al., 2006) to monitor analyte recovery. BDE-166 recoveries were acceptable: biosolids 86.8 ± 14.0 percent, K soil 102 ± 4.5 percent, W soil 99.6 ± 15.4 percent, corn roots 93.5 ± 14.2 percent, corn stover 104 ± 10.6 percent, and corn grain 109 ± 19.2 percent. PBDE congener concentrations in individual samples were corrected based on BDE-166 recovery. Replicate samples of all soils were taken and analyzed. PBDE concentrations determined between these generally agreed well.

Polybrominated Diphenyl Ethers in Biosolids

Biosolids were applied annually for three consecutive years at two field locations. [Table 1](#) provides the concentrations of the major PBDE congeners detected in the six Stickney WRP biosolids samples analyzed. The mean of total PBDEs was $7,796 \mu\text{g}/\text{kg}$ (on dry weight basis). Values ranged from $5,998$ to $9,880 \pm 1552 \mu\text{g}/\text{kg}$. The mean total PBDEs in the biosolids applied to the K and W soils were $9,061 \pm 929 \mu\text{g}/\text{kg}$ and $6,531 \pm 597 \mu\text{g}/\text{kg}$, respectively. [Figure 1](#) illustrates the concentrations of total PBDEs in the biosolids samples analyzed, as well as totals for congeners commonly associated with the PentaBDE, OctaBDE and DecaBDE commercial mixtures. [Figure 2](#) depicts mean contributions of individual congeners relative to total PBDEs detected.

TABLE 1: CONCENTRATIONS¹ OF VARIOUS POLYBROMINATED DIPHENYL ETHER CONGENERS IN STICKNEY BIOSOLIDS APPLIED TO RESEARCH PLOTS IN KANKAKEE (2005 – 2007) AND WILL COUNTY (2004 – 2006)

PBDE Congener ²	Lab Blank	Kankakee County			
		2005	2005R ³	2006	2007
BDE-17	ND	ND	ND	ND	ND
BDE-28	ND	ND	ND	ND	ND
BDE-49	ND	20.9	20.8	20.5	14.9
BDE-47	ND	392	359	345	299
BDE-66	ND	26.5	25.9	17.4	14.0
BDE-100	ND	208	186	180	120
BDE-99	ND	385	355	351	318
BDE-85	ND	50.7	48.9	39.4	27.5
BDE-154	ND	121	107	86.9	58.2
BDE-153	ND	157	144	110	73.1
BDE-183	ND	24.1	21.9	17.4	15.8
BDE-202	ND	ND	5.4	3.8	5.8
BDE-201	ND	12.0	9.3	10.9	9.3
BDE-197	ND	15.9	15.8	16.0	13.0
BDE-203	ND	23.3	25.9	23.8	15.1
BDE-196	ND	35.2	26.6	27.8	22.4
BDE-208	ND	111	144	126	111
BDE-207	ND	265	300	255	243
BDE-206	ND	789	709	603	682
BDE-209	ND	6,613	7,085	5,817	7,838
BDE-166 Recovery	64.0%	75.0%	74.1%	78.9%	77.7%
Penta-(\sum BDE-17 to 153)	<2	1,362	1,247	1,150	925
Octa-(\sum BDE-183 to 196)	<2	111	105	100	81.4
Deca-(\sum BDE-208 to 209)	<10	7,779	8,238	6,802	8,874
Total (\sum BDE-17 to 209)	<10	9,251	9,589	8,051	9,880

TABLE 1 (Continued): CONCENTRATIONS OF VARIOUS POLYBROMINATED DIPHENYL ETHER CONGENERS IN STICKNEY BIOSOLIDS APPLIED TO RESEARCH PLOTS IN KANKAKEE (2005 – 2007) AND WILL COUNTY (2004 – 2006)

PBDE Congener	Will County			Mean ⁴	Std. Dev. ⁴
	2004	2005	2006		
BDE-17	ND	ND	ND	-	-
BDE-28	ND	ND	ND	-	-
BDE-49	17.1	20.6	16.6	18.4	2.6
BDE-47	325	351	282	332	39.5
BDE-66	13.1	20.8	12.6	17.4	5.4
BDE-100	139	169	113	155	36.9
BDE-99	338	349	301	340	29.3
BDE-85	32.7	43.8	27.3	36.9	9.4
BDE-154	60.4	94.4	56.2	79.5	26.0
BDE-153	79.5	117	72.3	101	33.3
BDE-183	14.9	22.1	20.4	19.1	3.7
BDE-202	4.3	3.3	2.8	4.0	1.1
BDE-201	7.3	7.7	7.2	9.1	2.0
BDE-197	12.0	16.1	14.7	14.6	1.7
BDE-203	16.3	17.7	16.5	18.8	3.8
BDE-196	16.7	21.1	19.3	23.8	6.7
BDE-208	88	65	79	96.7	23.0
BDE-207	161	136	157	203	57.4
BDE-206	353	297	362	514	204
BDE-209	5,497	4,246	4,858	5,812	1,281
BDE-166 Recovery	85.5%	90.9%	113.0%	86.8%	14.0%
Penta-(\sum BDE-17 to 153)	1,005	1,165	881	1,081	179
Octa-(\sum BDE-183 to 196)	71.4	88.0	80.9	88.6	14.2
Deca-(\sum BDE-208 to 209)	6,099	4,745	5,456	6,626	1,523
Total (\sum BDE-17 to 209)	7,176	5,998	6,418	7,796	1,552

¹µg/kg, on dry weight basis. Values were corrected based on BDE-166 surrogate recoveries. Quantitation limits were 10 µg/kg for BDE-209 and 2 µg/kg for all other congeners.

²PBDE = Polybrominated diphenyl ether.

³Replicate of K-BS-05 sample.

⁴Excludes blank and replicate.

ND = Not detected.

FIGURE 1: CONCENTRATIONS OF TOTAL POLYBROMINATED DI-PHENYL ETHERS, AS WELL AS CONGENERS COMMONLY ASSOCIATED WITH THE PentaBDE, OctaBDE and DecaBDE COMMERCIAL MIXTURES, IN THE STICKNEY WATER RECLAMATION PLANT BIOSOLIDS APPLIED TO THE WILL AND KANKAKEE COUNTY PLOTS OVER THE THREE-YEAR PERIOD

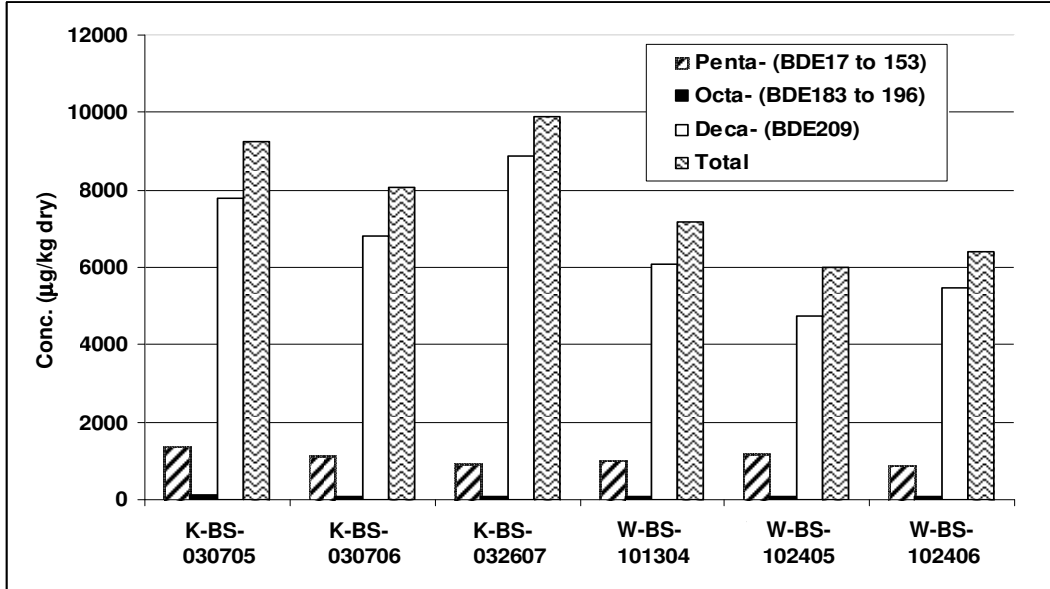
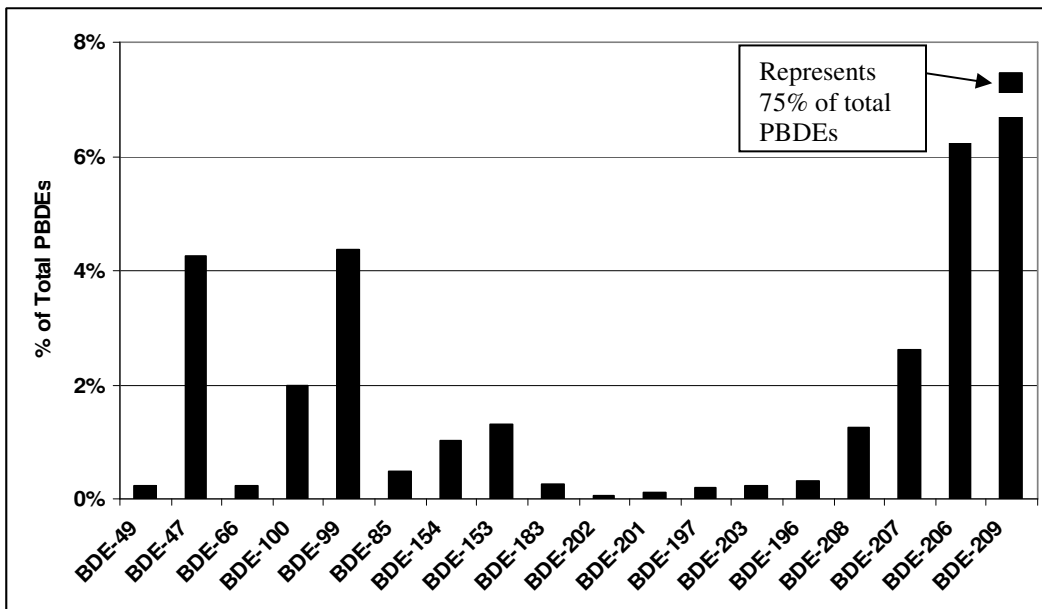


FIGURE 2: DISTRIBUTION OF INDIVIDUAL POLYBROMINATED DI-PHENYL ETHER CONGENERS IN THE STICKNEY WATER RECLAMATION PLANT BIOSOLIDS APPLIED TO THE WILL AND KANKAKEE COUNTY PLOTS.



The data in [Figures 1](#) and [2](#) demonstrate that BDE-209 (major component of DecaBDE) and BDE-99 and 47 (major congeners of the PentaBDE mixture) occurred in the highest concentrations. The quantitation limit (QL) for individual non-BDE-209 congeners in biosolids was 2 µg/kg. The QL for BDE-209 was 10 µg/kg.

While the major constituent congeners differ in the three commercial mixtures, there is an overlap in some minor congeners. BDE-209 dominated in the biosolids, constituting on average 75 percent of the total PBDEs and ranging from 4,246 to 7,838 µg/kg. The sum of BDE-206, 207, 208, and BDE-209, shows that the concentration of the total DecaBDE-related contribution is 85 percent of the total PBDEs. In a 2001 publication on U.S. biosolids, BDE-209 was reported to range between 84.8 and 4,890 µg/kg (Hale et al., 2001). In the Chicago biosolids, relative to BDE-209, BDE-206, 207 and 208 contributed approximately 8.6 percent, 3.5 percent, and 1.7 percent, respectively. Previously, it was reported that BDE-206, 207, and 208 constituted only 2.19 percent, 0.24 percent and 0.06 percent, respectively, of the major U.S. DecaBDE commercial mixture Saytex 102E (La Guardia et al., 2006). The greater contributions of these congeners in biosolids may represent some modest debromination of BDE-209. Alternatively, it may represent greater release from polymer products and subsequent transport of these less brominated congeners to the treatment plant. Stapleton and Dodder (Stapleton and Dodder, 2008) recently observed the production of less brominated congeners from BDE-209 associated with house dust, primarily nona-brominated congeners. They estimated that 35 percent of BDE-209 loss was attributable to the production of less brominated congeners, while the remainder of BDE-209 loss was not quantified, suggesting production of other degradates.

In District biosolids, the mean PentaBDE contribution (sum of BDE-17 to 154) was 1,081 µg/kg (SD 179). This is at the low end of the range of Penta-like PBDEs previously noted in U.S. biosolids, 1,100–2,290 µg/kg (Hale et al., 2001). The December 2004 cessation of commercial PentaBDE production, predating the generation of these biosolids, may have contributed to the lower concentration in the District biosolids.

In the biosolids, OctaBDE constituents (BDE-183 to BDE-207) contributed only 1.1 percent to total PBDEs, less than the 4.5 percent suggested by the 2001 production figures.

Polybrominated Diphenyl Ethers in Biosolids-Amended Soil

Will County Plots. Soil amended with biosolids exhibited evidence of increased PBDE concentrations with increasing biosolids loading. Soil concentrations increased as a function of biosolids loading ([Table 2](#)). For the Will County plots, the increase was linear ($r^2 = 0.8658$) with increasing biosolids application rate ([Figure 3](#)), reaching a maximum total PBDE concentration of 565 µg/kg (on dry weight basis). As in the case of the biosolids themselves, the major congener detected was BDE-209, constituting 67 percent to 100 percent of the total PBDEs detected. The maximum total PentaBDE (sum of constituent congeners) detected was 93.5 µg/kg. The QL for BDE-209 and non-BDE-209 congeners in soil was about 0.5 µg/kg. Low levels of total PBDEs were also detected in the Will County Control plots that did not receive any biosolids (replicates: 12.3 and 43.4 µg/kg). The congeners observed consisted of >90 percent BDE-209, which suggests potential contamination during sample handling in the laboratory.

TABLE 2: CONCENTRATIONS¹ OF VARIOUS POLYBROMINATED DIPHENYL ETHER CONGENERS IN SOIL SAMPLES COLLECTED ON OCTOBER 31, 2007, FROM THE WILL COUNTY RESEARCH PLOTS

PBDE Congener ²	BLANK	CTRL-R1	CTRL-R2	1BS-R1
BDE-49	ND	ND	ND	ND
BDE-47	ND	ND	ND	6.3
BDE-66	ND	ND	ND	ND
BDE-100	ND	ND	ND	1.6
BDE-99	ND	ND	1.0	7.7
BDE-85	ND	ND	ND	ND
BDE-154	ND	ND	ND	0.7
BDE-153	ND	ND	ND	1.0
BDE-183	ND	ND	ND	ND
BDE-197	ND	ND	ND	ND
BDE-203	ND	ND	ND	ND
BDE-196	ND	ND	ND	ND
BDE-208	ND	ND	ND	1.4
BDE-207	ND	ND	ND	ND
BDE-206	ND	1.3	ND	ND
BDE-209	ND	42.1	11.3	93.1
BDE-166 Recovery	85%	105%	95.8%	99.4%
Penta-(\sum BDE-49 to 153)	ND	ND	1.0	17.3
Octa-(\sum BDE-183 to 196)	ND	ND	ND	ND
Deca-(\sum BDE-208 to 209)	ND	43.4	11.3	94.4
Total PBEs	ND	43.4	12.3	112

TABLE 2 (Continued): CONCENTRATIONS OF VARIOUS POLYBROMINATED
DIPHENYL ETHER CONGENERS IN SOIL SAMPLES COLLECTED ON
OCTOBER 31, 2007, FROM THE WILL COUNTY RESEARCH PLOTS

PBDE Congener	1BS-R2	2BS-R1	2BS-R2	3BS-R1
BDE-49	ND	ND	ND	ND
BDE-47	ND	8.1	8.8	17.7
BDE-66	ND	ND	ND	ND
BDE-100	ND	2.3	2.1	5.0
BDE-99	ND	9.7	9.3	20.2
BDE-85	ND	ND	ND	ND
BDE-154	ND	ND	0.8	1.7
BDE-153	ND	0.8	1.0	2.1
BDE-183	ND	ND	ND	ND
BDE-197	ND	ND	ND	ND
BDE-203	ND	ND	ND	ND
BDE-196	ND	ND	ND	ND
BDE-208	ND	ND	ND	ND
BDE-207	ND	ND	2.6	3.2
BDE-206	ND	3.6	3.8	8.0
BDE-209	50.5	112	120	262
BDE-166 Recovery	108%	94.0%	114%	110%
Penta-(\sum BDE-49 to 153)	ND	20.9	22.0	46.5
Octa-(\sum BDE-183 to 196)	ND	ND	ND	ND
Deca-(\sum BDE-208 to 209)	50.5	115	126	273
Total PBDEs	50.5	136	148	75320

TABLE 2 (Continued): CONCENTRATIONS OF VARIOUS POLYBROMINATED DIPHENYL ETHER CONGENERS IN SOIL SAMPLES COLLECTED ON OCTOBER 31, 2007, FROM THE WILL COUNTY RESEARCH PLOTS

PBDE Congener	3BS-R2	4BS-R1	4BS-R2	5BS-R1	5BS-R2
BDE-49	ND	1.5	2.1	ND	ND
BDE-47	21.5	25.2	26.3	36.2	33.1
BDE-66	ND	ND	ND	ND	ND
BDE-100	5.8	7.5	6.7	8.6	7.9
BDE-99	21.8	29.5	31.0	40.5	36.6
BDE-85	1.6	ND	1.1	1.9	3.0
BDE-154	1.9	2.5	2.5	2.5	3.4
BDE-153	3.0	4.0	4.3	3.9	3.1
BDE-183	ND	60.6	ND	ND	ND
BDE-197	ND	ND	ND	ND	ND
BDE-203	ND	ND	ND	ND	ND
BDE-196	ND	ND	ND	ND	ND
BDE-208	2.0	1.6	ND	3.6	1.7
BDE-207	4.6	4.6	4.0	6.7	5.4
BDE-206	9.8	9.7	12.0	13.2	11.0
BDE-209	317	303	356	448	377
BDE-166 Recovery	109%	125%	87.8%	77.0%	71.4%
Penta-(\sum BDE-49 to 153)	55.6	70.1	74.0	93.5	87.0
Octa-(\sum BDE-183 to 196)	ND	61	ND	ND	ND
Deca-(\sum BDE-208 to 209)	333	319	372	472	395
Total PBDEs	389	450	446	565	482

¹µg/kg, on dry weight basis. Values were corrected based on BDE-166 surrogate recoveries. Quantitation limits were 5 µg/kg for BDE-209 and 0.5 µg/kg for all other congeners.

²PBDE = Polybrominated diphenyl ether.

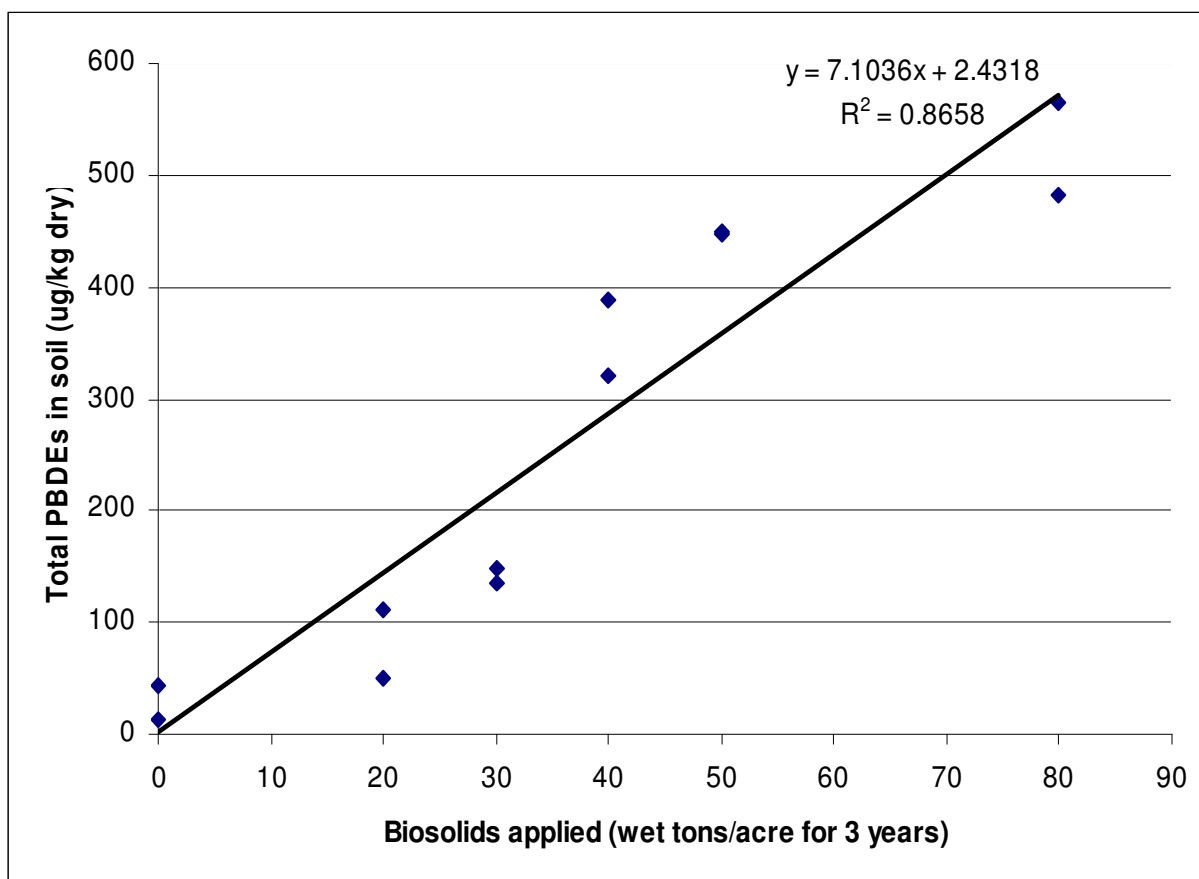
CTRL = control.

R1 and R2 = Replicate 1 and 2.

1BS, 2BS, 3BS, 4BS, and 5BS = 20, 30, 40, 50, and 80 wet ton biosolids/ac/yr, respectively.

ND = Not detected.

FIGURE 3: TOTAL POLYBROMINATED DIPHENYL ETHER LEVELS IN SOIL SAMPLES FROM THE WILL COUNTY PLOTS VERSUS CUMULATIVE AMOUNT OF WET BIOSOLIDS APPLIED OVER THE THREE-YEAR PERIOD



Kankakee County Plots. The Kankakee County plots amended with biosolids also exhibited evidence of accumulation of PBDEs (Table 3). The soil PBDE burdens relative to the amount of biosolids applied are shown in Figure 4. Overall, the major congener detected in the soils was BDE-209, constituting 66 percent to 87 percent of the total PBDEs detected. The maximum sum of congeners associated with PentaBDE detected in soil was 232 µg/kg. The ratio of relative contributions of the less brominated congeners (i.e. BDE-47, -99 and -100) in soil was very similar to that reported in DE-71 (La Guardia et al., 2006), the commercial PentaBDE product used in North American polyurethane products. This was true for the W soil samples as well. DE-71 was produced and distributed in the U.S. by Great Lakes Chemical Company, now part of Chemtura. BDE-99 and -47 dominated, with lesser contributions of -100, -153 and -154.

The ratios of the contributions of BDE-206, BDE-207 and BDE-208 to BDE-209 in the biosolids-amended plots from the Will and Kankakee County sites did not exceed the ratios observed in the biosolids.

There are limited published data on PBDEs in agricultural soils following application of stabilized sewage sludge. Eljarrat et al. (2008) recently examined the soil levels of PBDEs at several Spanish agricultural sites receiving sludge applications. PBDEs in sludges applied ranged from 197 to 1,185 µg/kg (dry weight). The bulk of the total PBDE detected was BDE-209. PentaBDE has been used on a more limited basis in the European Union than in North America and, hence, would be expected to make a smaller contribution to total PBDEs. Total PBDE concentrations in Spanish soils, receiving biosolids at a rate of 15 to 25 dry metric tonnes per hectare (~35 to 55 wet tons per acre), ranged from 30 to 689 µg/kg. Annual applications occurred for two or three years, and thus the amount of sludge applied were roughly comparable to some of the Will and Kankakee County sites. However, the Spanish sludge PBDE content was several times lower than the levels found in the Stickney WRP biosolids. The authors concluded that PBDEs (including BDE-209) were persistent in soils even years after sludge application. They did not address the issue of PBDE bioavailability. Spanish soil that received no sludge exhibited a total PBDE concentration of 20.7 µg/kg, 71.0 percent of which was BDE-209.

Polybrominated Diphenyl Ethers in Biosolids-Fertilized Corn

Corn stover (Table 4), roots (Tables 5 and 6) and grain (Table 7) were also analyzed. Quantitation limits for non-BDE-209 congeners were 1 to 2 µg/kg and BDE-209 congeners were 5 to 10 µg/kg on a dry weight basis.

PBDEs, with one exception, were not detected in the corn-tissue samples. One stover sample (K-Ctrl-2) unexpectedly exhibited 299 µg/kg of BDE-209 (Table 4). However, its accompanying replicate (K-Ctrl-2) did not exhibit detectable PBDE concentrations. The Control-2 extract was re-injected onto GC/MS and BDE209 was again detected, indicating that it was not related to possible GC injector carry-over. The soil plot on which this corn was grown

TABLE 3: CONCENTRATIONS¹ OF VARIOUS POLYBROMINATED DIPHENYL ETHER CONGENERS IN SOIL SAMPLES COLLECTED ON OCTOBER 31, 2007, FROM THE KANKAKEE COUNTY RESEARCH PLOTS

PBDE Congener ²	BLANK	CTRL-R1	CTRL- R2	1BS-R1
BDE-49	ND	ND	ND	ND
BDE-47	ND	ND	ND	13.1
BDE-66	ND	ND	ND	ND
BDE-100	ND	ND	ND	2.9
BDE-99	ND	ND	0.8	15.3
BDE-85	ND	ND	ND	0.7
BDE-154	ND	ND	ND	3.0
BDE-153	ND	ND	ND	3.9
BDE-183	ND	ND	ND	ND
BDE-197	ND	ND	ND	ND
BDE-203	ND	ND	ND	ND
BDE-196	ND	ND	ND	ND
BDE-208	ND	ND	ND	9.0
BDE-207	ND	ND	ND	15.3
BDE-206	ND	ND	ND	15.0
BDE-209	ND	6.7	4.9	429
BDE-166 Recovery	90.3%	99.6%	95.8%	98.8%
Penta (\sum BDE-49 to 153)	ND	ND	0.8	39.0
Octa (\sum BDE-183 to 196)	ND	ND	ND	ND
Deca-(\sum BDE-208 to 209)	ND	6.7	4.9	468
Total PBDEs	ND	6.7	5.6	507

TABLE 3 (Continued): CONCENTRATIONS OF VARIOUS POLYBROMINATED DI-PHENYL ETHER CONGENERS IN SOIL SAMPLES COLLECTED ON OCTOBER 31, 2007, FROM THE KANKAKEE COUNTY RESEARCH PLOTS

PBDE Congener	1BS-R2	2BS-R1	2BS-R2	3BS-R1
BDE-49	ND	ND	ND	ND
BDE-47	12.0	10.8	9.0	23.8
BDE-66	ND	ND	ND	ND
BDE-100	2.8	2.6	2.2	5.9
BDE-99	14.3	13.3	11.7	26.6
BDE-85	ND	ND	ND	1.4
BDE-154	3.1	2.7	2.3	6.3
BDE-153	4.2	3.5	3.2	8.8
BDE-183	ND	ND	ND	ND
BDE-197	ND	ND	ND	ND
BDE-203	ND	ND	ND	ND
BDE-196	ND	ND	ND	ND
BDE-208	4.9	2.8	7.6	6.7
BDE-207	9.3	5.6	15.9	13.3
BDE-206	14.3	8.6	16.0	23.4
BDE-209	417	297	472	542
BDE-166 Recovery	99.8%	96.6%	109.8%	107.6%
Penta (\sum BDE-49 to 153)	36.5	33.0	28.4	72.7
Octa (\sum BDE-183 to 196)	ND	ND	ND	ND
Deca- (\sum BDE-208 to 209)	446	314	511	586
Total PBDEs	482	347	540	658

TABLE 3 (Continued): CONCENTRATIONS OF VARIOUS POLYBROMINATED DIPHENYL ETHER CONGENERS IN SOIL SAMPLES COLLECTED ON OCTOBER 31, 2007, FROM THE KANKAKEE COUNTY RESEARCH PLOTS

PBDE Congener	3BS-R2	4BS-R1	4BS-R2	5BS-R1	5BS-R2
BDE-49	ND	ND	ND	ND	ND
BDE-47	20.9	20.2	26.9	45.6	56.9
BDE-66	ND	ND	ND	ND	ND
BDE-100	5.4	4.5	7.9	19.4	31.3
BDE-99	22.9	21.2	31.5	45.9	55.4
BDE-85	1.3	1.1	2.4	4.9	7.9
BDE-154	2.7	2.3	9.6	20.9	35.3
BDE-153	7.8	6.5	11.6	27.5	45.5
BDE-183	ND	ND	ND	5.2	ND
BDE-197	ND	ND	ND	2.4	3.9
BDE-203	ND	ND	1.3	3.7	6.6
BDE-196	ND	ND	1.3	4.4	7.4
BDE-208	7.2	6.5	10.9	29.7	55.4
BDE-207	13.5	12.7	21.1	56.4	116.6
BDE-206	22.2	19.4	36.8	95.6	188.8
BDE-209	504	421	734	758	1,193
BDE-166 Recovery	100.6%	108%	101.8%	102.6%	101.6%
Penta (\sum BDE-49 to 153)	60.9	55.9	89.8	164	232
Octa (\sum BDE-183 to 196)	ND	ND	2.6	15.7	18.0
Deca- (\sum BDE-208 to 209)	547	460	802	939	1,554
Total PBDEs	608	516	895	1,119	1,805

¹ μ g/kg, on dry weight basis. Values were corrected based on BDE-166 surrogate recoveries. Quantitation limits were 5 μ g/kg for BDE-209 and 0.5 μ g/kg for all other congeners.

CTRL = control.

R1 and R2 = Replicate 1 and 2.

1BS, 2BS, 3BS, 4BS, and 5BS = 10, 20, 30, 40, and 60 wet ton biosolids/ac/yr, respectively.

² PBDE = Polybrominated Diphenyl Ether.

ND = Not detected.

FIGURE 4: TOTAL POLYBROMINATED DIPHENYL ETHER LEVELS IN SOIL SAMPLES FROM THE KANKAKEE COUNTY PLOTS VERSUS CUMULATIVE AMOUNT OF WET BIOSOLIDS APPLIED OVER THE THREE-YEAR PERIOD

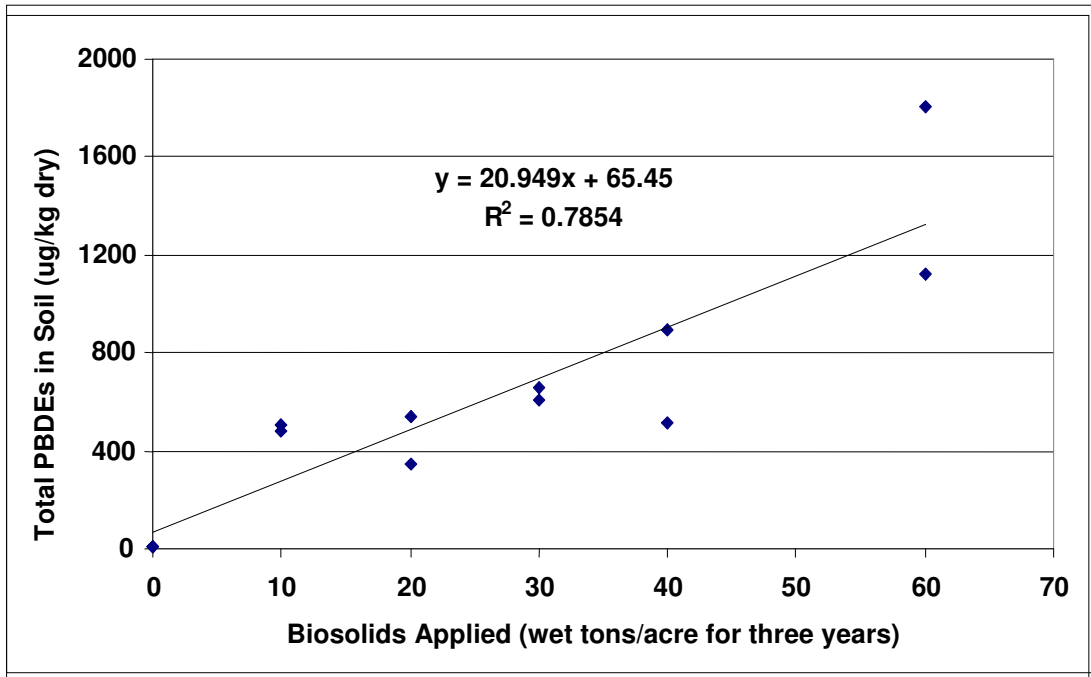


TABLE 4: CONCENTRATIONS¹ OF VARIOUS POLYBROMINATED DIPHENYL ETHER CONGENERS IN CORN STOVER (STALKS AND LEAVES) COLLECTED ON OCTOBER 31, 2007, FROM CONTROL AND PLOTS RECEIVING BIOSOLIDS IN KANKAKEE AND WILL COUNTY

PBDE Congener ²	K-CTRL-R1	K-CTRL-R2	K-4BS-R1
BDE-49	ND	ND	ND
BDE-47	ND	ND	ND
BDE-66	ND	ND	ND
BDE-100	ND	ND	ND
BDE-99	ND	ND	ND
BDE-85	ND	ND	ND
BDE-154	ND	ND	ND
BDE-153	ND	ND	ND
BDE-183	ND	ND	ND
BDE-197	ND	ND	ND
BDE-203	ND	ND	ND
BDE-196	ND	ND	ND
BDE-208	ND	ND	ND
BDE-207	ND	ND	ND
BDE-206	ND	ND	ND
BDE-209	ND	299	ND
BDE-166 Recovery	109%	74.5%	105%
Total PBDEs	ND	299	ND

TABLE 4 (Continued): CONCENTRATIONS OF VARIOUS POLYBROMINATED DI-PHENYL ETHER CONGENERS IN CORN STOVER (STALKS AND LEAVES) COLLECTED ON OCTOBER 31, 2007, FROM CONTROL AND PLOTS RECEIVING BIOSOLIDS IN KANKAKEE AND WILL COUNTY

PBDE Congener	K-4BS-R2	K-5BS-R1	K-5BS-R2	W-CTRL
BDE-49	ND	ND	ND	ND
BDE-47	ND	ND	ND	ND
BDE-66	ND	ND	ND	ND
BDE-100	ND	ND	ND	ND
BDE-99	ND	ND	ND	ND
BDE-85	ND	ND	ND	ND
BDE-154	ND	ND	ND	ND
BDE-153	ND	ND	ND	ND
BDE-183	ND	ND	ND	ND
BDE-197	ND	ND	ND	ND
BDE-203	ND	ND	ND	ND
BDE-196	ND	ND	ND	ND
BDE-208	ND	ND	ND	ND
BDE-207	ND	ND	ND	ND
BDE-206	ND	ND	ND	ND
BDE-209	ND	ND	ND	ND
BDE-166 Recovery	106%	102%	101%	112%
Total PBDEs	ND	ND	ND	ND

TABLE 4 (Continued): CONCENTRATIONS OF VARIOUS POLYBROMINATED
DIPHENYL ETHER CONGENERS IN CORN STOVER (STALKS AND LEAVES)
COLLECTED ON OCTOBER 31, 2007, FROM CONTROL AND PLOTS
RECEIVING BIOSOLIDS IN KANKAKEE AND WILL COUNTY

PBDE Congener	W-4BS-R1	W-4BS-R2	W-5BS-R1	W-5BS-R2
BDE-49	-	ND	ND	ND
BDE-47	ND	ND	ND	ND
BDE-66	ND	ND	ND	ND
BDE-100	ND	ND	ND	ND
BDE-99	ND	ND	ND	ND
BDE-85	ND	ND	ND	ND
BDE-154	ND	ND	ND	ND
BDE-153	ND	ND	ND	ND
BDE-183	ND	ND	ND	ND
BDE-197	ND	ND	ND	ND
BDE-203	ND	ND	ND	ND
BDE-196	ND	ND	ND	ND
BDE-208	ND	ND	ND	ND
BDE-207	ND	ND	ND	ND
BDE-206	ND	ND	ND	ND
BDE-209	ND	ND	ND	ND
BDE-166 Recovery	111%	106%	119%	103%
Total PBDEs	ND	ND	ND	ND

¹µg/kg, on dry weight basis. Values were corrected based on BDE-166 surrogate recoveries. Quantitation limits were 5 µg/kg for BDE-209 and 1 µg/kg for all other congeners.

²PBDE = Polybrominated diphenyl ether.

K-4BS and K-5BS = 40 and 60 wet ton biosolids/ac/yr.

R1 and R2 = Replicate 1 and 2.

W-4BS and W-5BS = 50 and 80 wet ton biosolids/ac/yr.

ND = Not detected.

TABLE 5: CONCENTRATIONS¹ OF VARIOUS POLYBROMINATED DIPHENYL ETHER CONGENERS IN CORN GRAIN COLLECTED ON OCTOBER 31, 2007, FROM CONTROL AND PLOTS RECEIVING BIOSOLIDS IN WILL COUNTY

PBDE Congener ²	CTRL R1	CTRL R2	1BS-R1	1BS-R2
BDE-49	ND	ND	ND	ND
BDE-47	ND	ND	ND	ND
BDE-66	ND	ND	ND	ND
BDE-100	ND	ND	ND	ND
BDE-99	ND	ND	ND	ND
BDE-85	ND	ND	ND	ND
BDE-154	ND	ND	ND	ND
BDE-153	ND	ND	ND	ND
BDE-183	ND	ND	ND	ND
BDE-197	ND	ND	ND	ND
BDE-203	ND	ND	ND	ND
BDE-196	ND	ND	ND	ND
BDE-208	ND	ND	ND	ND
BDE-207	ND	ND	ND	ND
BDE-206	ND	ND	ND	ND
BDE-209	ND	ND	ND	ND
BDE-166 Recovery	91%	122%	74.1%	74.1%
Total PBDEs	ND	ND	ND	ND

TABLE 5 (Continued): CONCENTRATIONS OF VARIOUS POLYBROMINATED DI-PHENYL ETHER CONGENERS IN CORN GRAIN COLLECTED ON OCTOBER 31, 2007, FROM CONTROL AND PLOTS RECEIVING BIOSOLIDS IN WILL COUNTY

PBDE Congener	2BS-1	2BS-2	3BS-1	3BS-2	4BS-1
BDE-49	ND	ND	ND	ND	ND
BDE-47	ND	ND	ND	ND	ND
BDE-66	ND	ND	ND	ND	ND
BDE-100	ND	ND	ND	ND	ND
BDE-99	ND	ND	ND	ND	ND
BDE-85	ND	ND	ND	ND	ND
BDE-154	ND	ND	ND	ND	ND
BDE-153	ND	ND	ND	ND	ND
BDE-183	ND	ND	ND	ND	ND
BDE-197	ND	ND	ND	ND	ND
BDE-203	ND	ND	ND	ND	ND
BDE-196	ND	ND	ND	ND	ND
BDE-208	ND	ND	ND	ND	ND
BDE-207	ND	ND	ND	ND	ND
BDE-206	ND	ND	ND	ND	ND
BDE-209	ND	ND	ND	ND	ND
BDE-166 Recovery	107%	122%	115%	95.7%	125%
Total PBDEs	ND	ND	ND	ND	ND

TABLE 5 (Continued): CONCENTRATIONS OF VARIOUS POLYBROMINATED
DIPHENYL ETHER CONGENERS IN CORN GRAIN COLLECTED ON
OCTOBER 31, 2007, FROM CONTROL AND PLOTS RECEIVING
BIOSOLIDS IN WILL COUNTY

PBDE Congener	4BS-2	5BS-1	5BS-2
BDE-49	ND	ND	ND
BDE-47	ND	ND	ND
BDE-66	ND	ND	ND
BDE-100	ND	ND	ND
BDE-99	ND	ND	ND
BDE-85	ND	ND	ND
BDE-154	ND	ND	ND
BDE-153	ND	ND	ND
BDE-183	ND	ND	ND
BDE-197	ND	ND	ND
BDE-203	ND	ND	ND
BDE-196	ND	ND	ND
BDE-208	ND	ND	ND
BDE-207	ND	ND	ND
BDE-206	ND	ND	ND
BDE-209	ND	ND	ND
BDE-166 Recovery	106%	131%	99.1%
Total PBDEs	ND	ND	ND

¹µg/kg, on dry weight basis. Values were corrected based on BDE-166 surrogate recoveries. Quantitation limits were 5 µg/kg for BDE-209 and 2 µg/kg for all other congeners.

²PBDE = Polybrominated diphenyl ether.

CTRL = control.

R1 and R2 = Replicate 1 and 2.

1BS – 5BS = 20, 30, 40, 50, and 80 wet ton biosolids/ac/yr, respectively.

ND = Not detected.

TABLE 6: CONCENTRATIONS¹ OF VARIOUS POLYBROMINATED DIPHENYL ETHER CONGENERS IN CORN GRAIN COLLECTED ON OCTOBER 31, 2007, FROM CONTROL AND PLOTS RECEIVING BIOSOLIDS IN KANKAKEE COUNTY

PBDE Congener ²	CTRL-R1	CTRL-R2	1BS-R1	1BS-R2
BDE-49	ND	ND	ND	ND
BDE-47	ND	ND	ND	ND
BDE-66	ND	ND	ND	ND
BDE-100	ND	ND	ND	ND
BDE-99	ND	ND	ND	ND
BDE-85	ND	ND	ND	ND
BDE-154	ND	ND	ND	ND
BDE-153	ND	ND	ND	ND
BDE-183	ND	ND	ND	ND
BDE-197	ND	ND	ND	ND
BDE-203	ND	ND	ND	ND
BDE-196	ND	ND	ND	ND
BDE-208	ND	ND	ND	ND
BDE-207	ND	ND	ND	ND
BDE-206	ND	ND	ND	ND
BDE-209	ND	ND	ND	ND
BDE-166 Recovery	106%	118%	124%	95.2%
Total PBDEs	ND	ND	ND	ND

TABLE 6 (Continued): CONCENTRATIONS OF VARIOUS POLYBROMINATED DI-PHENYL ETHER CONGENERS IN CORN GRAIN COLLECTED ON OCTOBER 31, 2007, FROM CONTROL AND PLOTS RECEIVING BIOSOLIDS IN KANKAKEE COUNTY

PBDE Congener	2BS-R1	2BS-R2	3BS-R1	3BS-R2	4BS-R1
BDE-49	ND	ND	ND	ND	ND
BDE-47	ND	ND	ND	ND	ND
BDE-66	ND	ND	ND	ND	ND
BDE-100	ND	ND	ND	ND	ND
BDE-99	ND	ND	ND	ND	ND
BDE-85	ND	ND	ND	ND	ND
BDE-154	ND	ND	ND	ND	ND
BDE-153	ND	ND	ND	ND	ND
BDE-183	ND	ND	ND	ND	ND
BDE-197	ND	ND	ND	ND	ND
BDE-203	ND	ND	ND	ND	ND
BDE-196	ND	ND	ND	ND	ND
BDE-208	ND	ND	ND	ND	ND
BDE-207	ND	ND	ND	ND	ND
BDE-206	ND	ND	ND	ND	ND
BDE-209	ND	ND	ND	ND	ND
BDE-166 Recovery	147%	114%	133%	92%	131%
Total PBDEs	ND	ND	ND	ND	ND

TABLE 6 (Continued): CONCENTRATIONS OF VARIOUS POLYBROMINATED
DIPHENYL ETHER CONGENERS IN CORN GRAIN COLLECTED ON
OCTOBER 31, 2007, FROM CONTROL AND PLOTS RECEIVING
BIOSOLIDS IN KANKAKEE COUNTY

PBDE Congener	4BS-R2	5BS-R1	5BS-R2
BDE-49	ND	ND	ND
BDE-47	ND	ND	ND
BDE-66	ND	ND	ND
BDE-100	ND	ND	ND
BDE-99	ND	ND	ND
BDE-85	ND	ND	ND
BDE-154	ND	ND	ND
BDE-153	ND	ND	ND
BDE-183	ND	ND	ND
BDE-197	ND	ND	ND
BDE-203	ND	ND	ND
BDE-196	ND	ND	ND
BDE-208	ND	ND	ND
BDE-207	ND	ND	ND
BDE-206	ND	ND	ND
BDE-209	ND	ND	ND
BDE-166 Recovery	80.5%	115%	97%
Total PBDEs	ND	ND	ND

¹µg/kg, on dry weight basis. Values were corrected based on BDE-166 surrogate recoveries. Quantitation limits were 5 µg/kg for BDE-209 and 2 µg/kg for all other congeners.

²PBDE = Polybrominated diphenyl ether.

CTRL = control.

1BS - 5BS = 10, 20, 30 40, and 60 wet ton biosolids/ac/yr, respectively.

R1 and R2 = Replicate 1 and 2.

ND = Not detected.

TABLE 7: CONCENTRATIONS¹ OF VARIOUS POLYBROMINATED DIPHENYL ETHER CONGENERS IN CORN ROOTS COLLECTED ON OCTOBER 31, 2007, FROM CONTROL AND PLOTS RECEIVING BIOSOLIDS IN KANKAKEE AND WILL COUNTY

PBDE Congener ²	K-BS-1	K-BS-2	K-BS-3	K-BS-4	K-BS-5
BDE-49	ND	ND	ND	ND	ND
BDE-47	ND	ND	ND	ND	ND
BDE-66	ND	ND	ND	ND	ND
BDE-100	ND	ND	ND	ND	ND
BDE-99	ND	ND	ND	ND	ND
BDE-85	ND	ND	ND	ND	ND
BDE-154	ND	ND	ND	ND	ND
BDE-153	ND	ND	ND	ND	ND
BDE-183	ND	ND	ND	ND	ND
BDE-197	ND	ND	ND	ND	ND
BDE-203	ND	ND	ND	ND	ND
BDE-196	ND	ND	ND	ND	ND
BDE-208	ND	ND	ND	ND	ND
BDE-207	ND	ND	ND	ND	ND
BDE-206	ND	ND	ND	ND	ND
BDE-209	ND	ND	ND	ND	ND
BDE-166 Recovery	85.0%	121%	109%	104%	74.8%
Total PBDEs	ND	ND	ND	ND	ND

TABLE 7 (Continued): CONCENTRATIONS OF VARIOUS POLYBROMINATED DIPHENYL ETHER CONGENERS IN CORN ROOTS COLLECTED ON OCTOBER 31, 2007, FROM CONTROL AND PLOTS RECEIVING BIOSOLIDS IN KANKAKEE AND WILL COUNTY

PBDE Congener	W-BS-1	W-BS-2	W-BS-3	W-BS-4	W-BS-5
BDE-49	ND	ND	ND	ND	ND
BDE-47	ND	ND	ND	ND	ND
BDE-66	ND	ND	ND	ND	ND
BDE-100	ND	ND	ND	ND	ND
BDE-99	ND	ND	ND	ND	ND
BDE-85	ND	ND	ND	ND	ND
BDE-154	ND	ND	ND	ND	ND
BDE-153	ND	ND	ND	ND	ND
BDE-183	ND	ND	ND	ND	ND
BDE-197	ND	ND	ND	ND	ND
BDE-203	ND	ND	ND	ND	ND
BDE-196	ND	ND	ND	ND	ND
BDE-208	ND	ND	ND	ND	ND
BDE-207	ND	ND	ND	ND	ND
BDE-206	ND	ND	ND	ND	ND
BDE-209	ND	ND	ND	ND	ND
BDE-166 Recovery	90.2%	84.3%	97.2%	88.7%	80.7%
Total PBDEs	ND	ND	ND	ND	ND

¹µg/kg, on dry weight basis. Values were corrected based on BDE-166 surrogate recoveries. Quantitation limits were 5 µg/kg for BDE-209 and 2 µg/kg for all other congeners.

²PBDE = Polybrominated diphenyl ether.

Kankakee County Plots, K-1BS, 2BS, 3BS, 4BS, and 5BS = 10, 20, 30, 40, and 60 wet ton biosolids/ac/yr, respectively.

Will County Plots, W-1BS, 2BS, 3BS, 4BS, and 5BS = 20, 30, 40, 50, and 80 wet ton biosolids/ac/yr, respectively.

ND = Not detected.

did not receive biosolids. Of the related control soil samples, BDE-209 was not detected in one and only at 6.7 $\mu\text{g}/\text{kg}$ in the other. The BDE-209 detection in stover most likely represents sample contamination that occurred sometime between field collection and final analysis. DecaBDE is commonly detected at high concentrations in the indoor environment and in indoor dust in particular (Wu et al., 2007).

Studies of chemically-similar hydrophobic organochlorines in the past have reported minimal uptake by plants, such as corn (O'Connor et al., 1990; Webber et al., 1994; Hundal et al., 2008). Plant uptake is generally mediated by concentrations dissolved in soil interstitial water. Hence, significant plant uptake of low water solubility compounds, such as PBDEs, is not expected (Hellstrom, 2000).

CONCLUSIONS

Concentrations of PBDEs in biosolids were between 5 and 10 mg/kg (on dry weight basis). The congeners detected were dominated by BDE-209. These findings are consistent with other recent U.S. studies. PBDE concentrations and congener patterns were similar to those commonly reported in indoor house dust. Modest debromination of BDE-209 may have occurred at some point during the wastewater treatment process prior to land application of biosolids. This is evidenced by greater proportions of nonabrominated congeners in biosolids versus that in the commercial DecaBDE product. However, the contributions to total PBDEs of these nonabrominated congeners were apparently lower in soil than in the source biosolids. PBDEs were detected in the soil but at a dilution greater than ten-fold compared to levels in biosolids. The maximum soil concentration of total PBDEs was 1,805 $\mu\text{g}/\text{kg}$. The results of the analyses support the hypothesis that biosolids-derived PBDEs present in agricultural soils show no observable tendency to accumulate in corn roots, stover, or grain.

REFERENCES

- Chen, D., M.J. La Guardia, E. Harvey, M. Amaral, K. Wohlfort, and R.C. Hale. "Polybrominated Diphenyl Ethers in Peregrine Falcon (*Falco peregrinus*) Eggs from the Northeastern U.S." *Environ. Sci. Technol.*, 2008, 42:7594-7600.
- DeWit, C.A. "An Overview of Brominated Flame Retardants in the Environment." *Chemosphere*, 2002, 46:583-24.
- Eljarrat, E., G. Marsh, A. Labandeira, and D. Barcelo. "Effect of Sewage Sludges Contaminated with Polybrominated Diphenylethers on Agricultural Soils." *Chemosphere*, 2008, 71:1079-1086.
- Hale, R.C., M.J. La Guardia, E. Harvey, M.O. Gaylor, T.M. Mainor, and W.H. Duff. "Flame Retardants: Persistent Pollutants in Land-Applied Sludges." *Nature*, 2001, 412:141-2.
- Hale, R.C., M. Alaei, J.B. Manchester-Neesvig, H.M. Stapleton, and M.G. Ikononou. "Polybrominated Diphenyl Ether (PBDE) Flame Retardants in the North American Environment." *Environ. Intern.*, 2003, 29:771-779.
- Hale, R.C., M.J. La Guardia, E. Harvey, M.O. Gaylor, and T. M. Mainor. "Brominated Flame Retardant Concentrations and Trends in Abiotic Media." *Chemosphere*, 2006, 64:181-186.
- Hellstrom, T. "Brominated Flame Retardants (PBDE and PBB) in Sludge-A Problem?" The Swedish Water and Wastewater Association Report No M 113 (Eng.), 2000, p. 28
- Hundal, L.S., A. Cox, T.C. Granato, and Z. Abedin. "Levels of Dioxins in Soil and Corn Tissues after 30 Years of Biosolids Application." *J. Environ. Qual.*, 2008, 37:1497-1500.
- La Guardia, M.J., R.C. Hale, and E. Harvey. "Detailed Polybrominated Diphenyl Ether (PBDE) Congener Composition of the Widely Used Penta-, Octa-, and Deca-PBDEs Technical Flame-Retardant Mixtures." *Environ. Sci. Technol.*, 2006, 40:6247-6254.
- La Guardia, M. J., R.C. Hale, and E. Harvey. "Evidence of Debromination of Decabromodiphenyl Ether (BDE-209) in Biota from a Wastewater Receiving Stream." *Environ. Sci. Technol.*, 2007, 41:6663-6670.
- O'Connor, G.A., D. Kiehl, G.A. Eiceman, and J.A. Ryan. "Plant Uptake of Sludge-Borne PCBs." *J. Environ. Qual.*, 1990, 19:113-118.
- Stapleton, H.M. and N.G. Dodder. "Photodegradation of Decabromodiphenyl Ether in House Dust by Natural Sunlight." *Environ. Toxicol. Chem.*, 2008, 27:306-312.

REFERENCES (Continued)

Webber, M.D., R.I. Pietz, T.C. Granato, and M.L. Svoboda. "Plant Uptake of PCBs and Other Organic Contaminants from Sludge-Treated Coal Refuse." *J. Environ. Qual.*, 1994, 23: 1019-1026.

Wu, N., T. Herrmann, O. Paepke, J. Tickner, R. Hale, E. Harvey, M. La Guardia, M. McClean, and T. Webster. "Human Exposure to PBDEs: Associations of PBDE Body Burdens with Food Consumption and House Dust Concentrations." *Environ. Sci. Technol.*, 2007, 41:1584-1589.