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Polybrominated Diphenyl Ethers in U.S. Sewage Sludges and Biosolids: Temporal and Geographical Trends and Uptake by Corn Following Land Application

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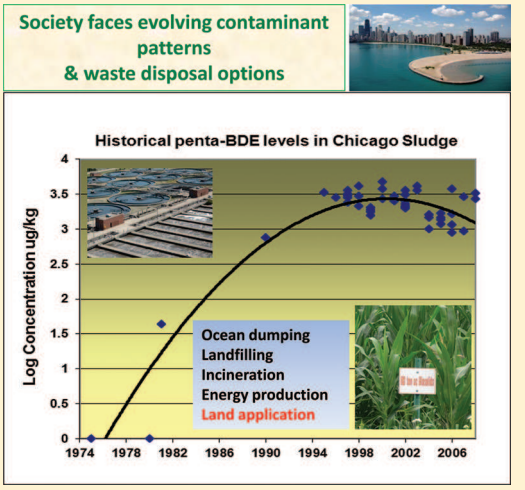
Supporting Information

ABSTRACT: Polybrominated diphenyl ethers (PBDEs) have been used extensively to flame-retard polymers and textiles. These persistent chemicals enter wastewater streams following manufacture, use, and disposal, concentrating in the settled solids during treatment. Land application of stabilized sewage sludge (known as biosolids) can contribute PBDEs to terrestrial systems. Monitoring sludge/biosolids contaminant burdens may be valuable in revealing trends in societal chemical usage and environmental release. In archived Chicago area sludges/biosolids from 1975 to 2008, penta-BDE concentrations increased and then plateaued after about 2000. Penta-BDE manufacture in the United States ended in December 2004. Deca-BDE concentrations in biosolids rose from 1995 to 2008, doubling on a 5-year interval. Evaluation of U.S. Environmental Protection Agency Targeted National Sewage Sludge Survey data from 2006 to 2007 revealed highest penta-BDE biosolids levels from western and lowest from northeastern wastewater treatment plants (2120 and 1530 μg/kg, respectively), consistent with patterns reported in some recent indoor dust and human blood studies. No significant regional trends were observed for deca-BDE concentrations. Congener patterns in contemporary Chicago biosolids support the contention that BDE-209 can be dehalogenated to less brominated congeners. Biosolids application on agricultural fields increased PBDE soil concentrations. However, corn grown thereon did not exhibit measurable PBDE uptake; perhaps due to low bioavailability of the biosolids-associated flame retardants.



INTRODUCTION

For centuries society has used water to transport wastes from human population centers. Initially, untreated wastes were dispersed directly into surface waters, often with negative environmental consequences. Alternatively, wastewater may be directed to wastewater treatment plants (WWTPs). In addition to degradative processes, WWTPs separate hydrophobic pollutants by partitioning to solids and subsequent sedimentation. In the United States, 75% of citizens are served by centralized wastewater treatment, producing 29 kg/person dry sludge annually.[1] Using current U.S. census figures of 310 million people leads to an estimated annual sludge production of 6.8 million metric tons (MT) per annum. This is comparable to the 7.8 million MT estimated for the European Union (EU) for 2000.[1] To reduce putrefiable materials and pathogen content, sludges may be further subjected to anaerobic digestion, liming, composting, or high-temperature treatments. The term "biosolids" has been coined to denote such stabilized solids. Biosolids contain substantial nitrogen, phosphorus, and organic carbon, making them attractive soil amendments and crop fertilizers. Bans on ocean dumping of sewage sludges and escalating landfilling and incineration costs have further incentivized land application. Today, about 60% of biosolids produced in the United States are land-applied.[2] Recipients include environmentally compromised industrial sites (i.e., "brownfields"), as well as farmland, forests, and public lands. In the European Union, the extent of land application varies

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greatly, ranging from zero in The Netherlands to 62% in the United Kingdom.[1]

Pollutants in land-applied biosolids, particularly chemicals resistant to degradation, are an environmental concern. While thousands of chemicals may enter wastewater, the U.S. Environmental Protection Agency (U.S. EPA) examined only 411 in its 1988 National Sewage Sludge Survey.[2] Those results were used in the development of an initial risk assessment in support of the 1993 Title 40 Code of Federal Regulations Part 503 rule governing land application. That assessment assumed that use of persistent organic pollutants (POPs) in the United States had ceased, that existing sludge concentrations were not toxicologically significant, and that levels would decrease further over time. However, since the 1990s, several new POPs in wastewaters have been discovered, for example, brominated flame retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs). Commercial PBDE use is thought to have begun in the 1970s and one product, deca-BDE, remains a high production volume chemical. Originally presumed to be retained within treated plastics and textiles, it was later observed that PBDEs may volatilize from or be released following fragmentation of finished products[3−5] and contribute to the milligram per kilogram levels observed in indoor dust and sewage sludge. The status of the PBDEs within the sludge, that is, contained within small plastic fragments or sorbed to the surface of organic-rich particles, will influence their subsequent bioavailability. To date, limited research has examined the fate and bioavailability of PBDEs in biosolids-amended soils. Duarte-Davidson and Jones[6] prioritized chemicals therein with the greatest potential for transfer into the food chain. Factors of concern included chemical persistence, groundwater leachability, plant root retention, translocation within the plant, and foliar uptake from the air. Ironically, these authors noted that brominated aromatics were not evaluated in their model as they had not yet been reported in sewage sludges.

Elucidation of temporal patterns of PBDE usage and environmental release has been hampered by the lack of publicly available production data. This has been a particular issue in the United States, where such statistics have been shielded from public scrutiny by confidentiality provisions. However, some North American BFR demand data were released for 2001. Corresponding penta- and deca-BDE demands were 95% and 44% of the global total, respectively.[7] However, U.S. penta-BDE production ended after 2004. Recent data indicated that deca-BDE usage in the European Union has remained fairly constant over the past decade,[8] but the trajectory of U.S. usage is uncertain. Deca-BDE use in the United States is, however, scheduled to cease after 2012. Nonetheless, large BFR reservoirs will remain in in-use and discarded products. These will continue to release PBDEs into wastewater streams and the environment for an extended period.

While determination of levels of persistent contaminants in sewage sludge/biosolids may be valuable for assessing societal chemical usage patterns and predicting environmental release trends, this approach has seldom been exploited. PBDEs were not included in the U.S. EPA national sludge surveys conducted in 1982, 1988, or 2001. However, the 2006−2007 EPA Targeted National Sewage Sludge Survey (TNSSS) included 11 PBDE congeners present in the commercial penta-BDE (BDEs 28, 47, 66, 85, 99, 100, 138, 153, and 154), octa-BDE (BDE-183), and deca-BDE (BDE-209) mixtures.[9] Sludges/biosolids were collected from 74 WWTPs in 35 U.S. states. While contaminant data and treatment strategies could not be linked to specific WWTPs in the report, the regions of the contributing facilities were identified.

The goals of the current research were to (1) assess temporal trends of PBDE concentrations in municipal wastewater sludge/biosolids from a major U.S. city, Chicago, over a 30+ year period; (2) compare PBDE concentrations in contemporary Chicago biosolids to those reported in the 2006−2007 U.S. EPA TNSSS; (3) examine geographical trends in PBDE concentrations by use of available EPA TNSSS data; (4) evaluate PBDE congener profiles in contemporary biosolids and biosolids-amended soils for evidence of degradation; and (5) assess the accumulation of PBDEs in corn grown on biosolids-amended soils.

EXPERIMENTAL SECTION

Historical Trends of PBDEs in Chicago Sewage Sludge/Biosolids. Forty-eight historical and recent sludge/biosolids samples, including those from the farmland application study described below, were provided by the Metropolitan Water Reclamation District of Greater Chicago (MWRDGC). These were generated by several publicly owned WWTPs operating in the Chicago area between 1975 and 2008, using different wastewater treatment and solids stabilization approaches. Samples preceding in time the field application study had been air-dried and stored at room temperature in the dark. These storage conditions are consistent with those recommended by the National Institute of Standards and Technology for its freeze-dried Standard Reference Materials certified for semivolatile contaminants, including PBDEs (e.g., SRM 1944 sediment). All samples were examined for a range of PBDE congeners and the polybrominated biphenyl (PBB) congener PBB-153.

PBDEs in Agricultural Soils Amended with Contemporary Chicago Biosolids and in Corn Grown Thereon. Biosolids used in the farmland application study were generated at the MWRDGC Stickney WWTP between 2004 and 2007. This WWTP serves 2.4 million people and has a treatment capacity of 4.5 billion L/day, making it one of the largest in the world. Class B biosolids were generated by an activated sludge process, followed by anaerobic mesophilic digestion and dewatering by centrifugation. Mean moisture content of the biosolids received was 73.6% (standard deviation, SD, 3.7%). Biosolids were applied via common agricultural practices to two Illinois farm fields possessing heavy textured clay soil in Will County and a light-textured sandy soil in Kankakee County. Initially, biosolids were applied with a spreader and incorporated to a depth of 15−20 cm by plowing and discing. Plots at both sites received different rates of biosolids application (clay soil, 0, 2.1, 3.2, 4.3, 5.3, and 8.5 dry MT/hectare; sandy soil, 0, 1.1, 2.1, 3.2, 4.3, and 6.4 dry MT/hectare biosolids per year) for three consecutive years. Additional descriptions of the soils are available elsewhere.[10]

Aliquots of the biosolids applied at the two sites were analyzed for PBDEs (six samples, one per year and site). Surface soil samples were collected after the third annual biosolids application in the summer of 2007, by compositing five subsamples (taken with an auger from 0 to 15 cm depth) from each of the treatment plots. Corn (*Zea mays*) was grown in the soils by conventional agricultural practices. Corn stover (leaves and stalks) from the two highest biosolids rate plots and the nonamended plot (3 treatments × 2 replicates × 2 sites =

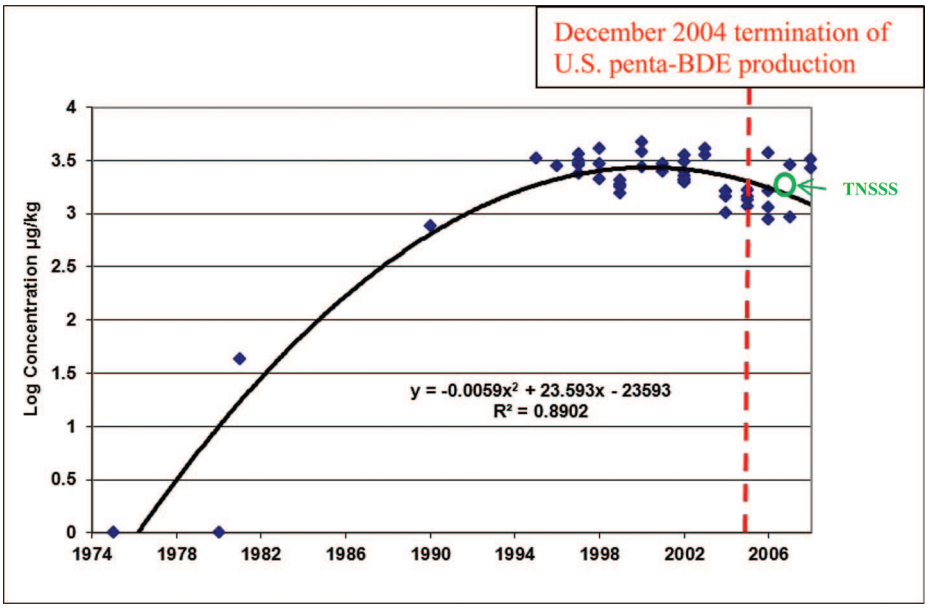

Figure 1. ∑Penta-BDE concentrations in Chicago WWTP sludge/biosolids generated between 1975 and 2008. For comparison, the mean ∑penta-BDE concentration from the 2006−2007 U.S. EPA TNSSS was 1760 μg/kg, consistent with values observed in contemporaneous Chicago sludge/biosolids.

12 samples) were collected to assess PBDE uptake. Grain was collected from all five biosolids-applied plots and the nonamended plot (6 treatments × 2 replicates × 2 sites = 24 samples). Roots, to a depth of 15 cm, were sampled from the five biosolids-applied plots only (5 treatments × 2 sites = 10 samples).

PBDE Analysis Methods. Details of the PBDE analytical methods are provided in the Supporting Information. Briefly, samples were lyophilized, spiked with a surrogate standard (BDE-166), and subjected to accelerated solvent extraction. Extracts were purified by size exclusion and silica gel liquid chromatography. An internal standard (decachlorodiphenyl ether) was added and the final extracts were analyzed by gas chromatography/mass spectrometry (GC/MS) with electron-capture negative chemical ionization (EC-NCI). Quantitation was accomplished by use of five-point quantification curves and authentic standards. The following PBDE congeners were determined: BDEs 17, 28, 47, 49/71, 66, 85, 99, 100, 153, 154, 183, 196, 197, 201, 202, 203, 206, 207, 208, and 209. PBB-153 was analyzed separately by GC/MS in the electron impact ionization mode.

Study Quality Control. Sodium sulfate lab blanks were analyzed with each sample set to monitor for potential laboratory contamination. No PBDEs were detected in the blanks. Method quantitation limits varied by matrix type, as a function of their densities and the amounts extracted. These limits were 1−2 μg/kg for soil, 2−10 μg/kg for biosolids, and 1−5 μg/kg for corn samples (less brominated congeners and BDE-209, respectively). BDE-166 surrogate recoveries from the samples were as follows: biosolids 86.8% (SD 14.0%), sandy soil 102% (SD 4.5%), clay soil 99.6% (SD 15.4%), corn roots 93.5% (SD 14.2%), stover 104% (SD 10.6%), and grain 109% (SD 19.2%). PBDE concentrations in replicate samples agreed well. Three biosolids were also spiked with ^{13}C-labeled BDE-209 and BDE-166. Mean recoveries of these surrogates were similar, 108% and 106%, respectively.

RESULTS AND DISCUSSION

Environmental media such as sediments and archived biological samples (e.g., human sera and wildlife) have been widely utilized[11−14] to establish contaminant temporal trends. However, sediments must be dated by ancillary techniques and can be disturbed by physical and biological perturbations. Contaminant burdens in organisms may be influenced by gender, age, biotransformation, and migratory behaviors. Sediments and wildlife sampled are often distant from sources. Thus, contaminant burdens therein may be low and slow to respond to changes in societal chemical releases. Analysis of rapidly responding WWTP sludge/biosolids provides an avenue for early detection of the release of problematic chemicals. This provides an opportunity to implement pre-emptive strategies to stem further environmental dissemination. However, it should be noted that, over time, treatment strategies at WWTPs may change and this could alter POP sequestration in sludges/biosolids. Also, in general, sludge/biosolids must be collected at the time produced; although examination of POPs in sludge-only landfill samples has been suggested.[15]

Temporal Trends in Legacy POPs and PBDEs in Chicago Biosolids. The utility of sludge/biosolids analysis as a tool for identifying contaminant temporal trends is illustrated by examining burdens of PBBs, PBDEs, and polychlorinated biphenyls (PCBs). PBBs became notorious after their accidental introduction into livestock feed in Michigan in 1974. This led to a ban on U.S. production of the hexa-PBB product, in which PBB-153 was the major constituent congener. While this event is well-known, it is noteworthy that the total U.S. PBB production for the period 1970−1976 was only 6000 MT.[16] This is less than the North American penta-BDE demand for 2001 alone, that is, 7100 MT. Our analysis of archived Chicago WWTP sludges revealed PBB-153 levels in the 1975, 1980, and 1990 samples of 177, 41, and 67 μg/kg, respectively. PBB-153 was not quantifiable in later sludge samples. Zhu and Hites[14] noted a 1980 peak in

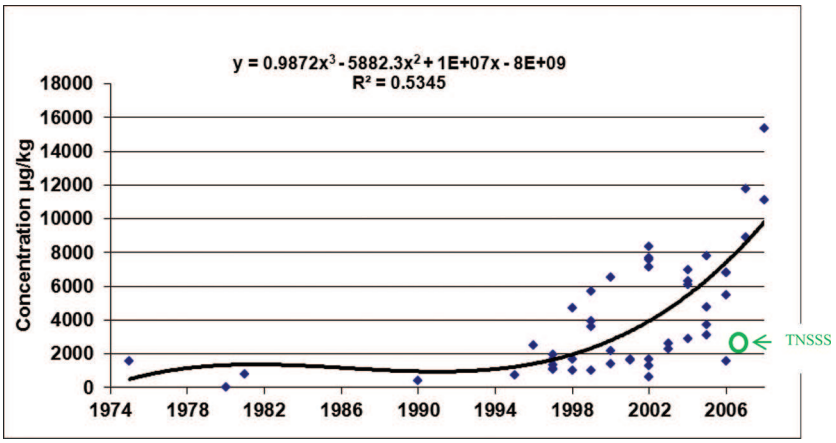

Figure 2. Concentrations of BDE-209 in Chicago sludges/biosolids from 1975 to 2008. The mean concentration in the EPA 2006−2007 TNSSS was 2310 μg/kg (standard deviation 3110).

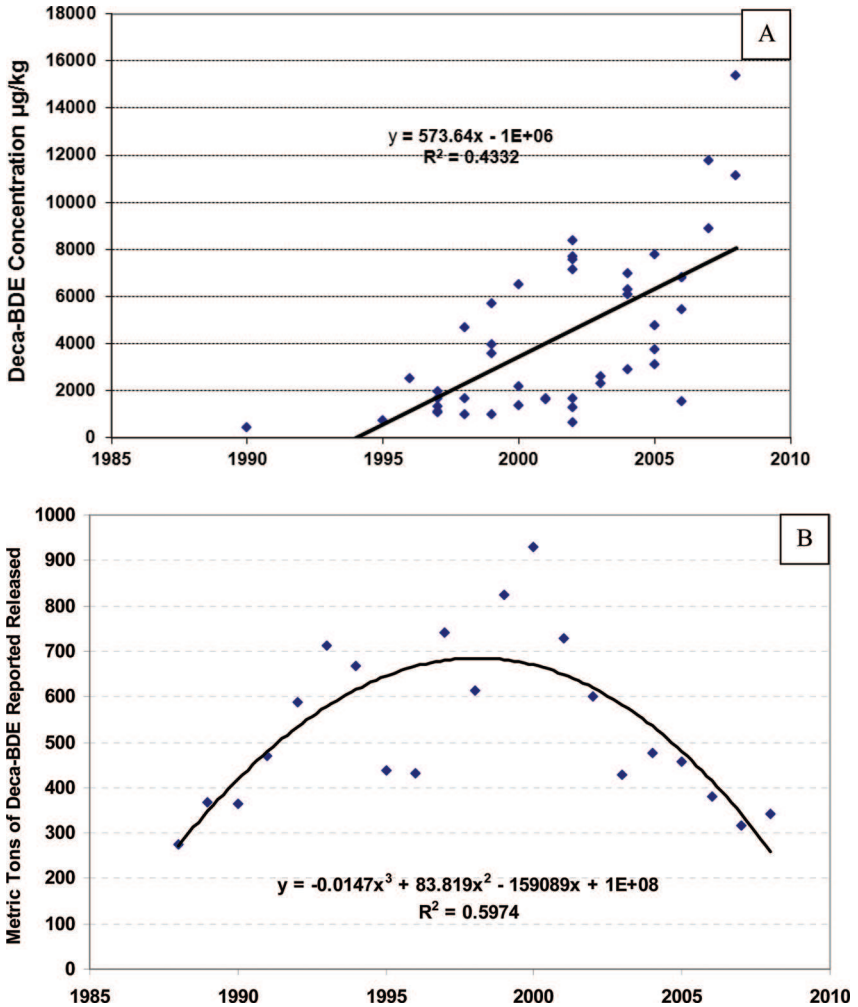

Figure 3. (A) Concentrations of deca-BDE (micrograms per kilogram) detected in Chicago wastewater sludges/biosolids (this study) from 1990 to 2008. (B) Amounts (MT) of deca-BDE reported released by U.S. industries via the U.S. EPA Toxics Reduction Inventory database from 1998 to 2008.

PBB-153 concentrations in Laurentian Great Lakes sediments, lagging the U.S. regulatory restriction on new PBB uses by 5 years. Due to their chemical similarity, PBDEs may have been marketed as a direct replacement for PBBs in many commercial applications. A mid-1970s date is also consistent with the appearance of PBDEs in dated environmental media. However, years passed between the presumed period of first usage and the initial 1981 report of PBDEs in wildlife.[17] Sludge/biosolids analysis may also reveal the reappearance of legacy chemicals in contemporary wastewater streams. For example, in 2007 substantial PCB levels were detected in samples of Milwaukee's biosolid product Milorganite.[18] The origin of the PCBs was

later identified as a shuttered metal die-cast facility. From there the PCBs are believed to have entered a sewer line and later traveled to a WWTP following pipe cleaning. Unfortunately, the chemical analysis was completed after the biosolids were applied on several city parks, triggering a soil remediation effort.

The PBDE congener profiles in the Chicago area historical sludges/biosolids we analyzed were similar to those of the penta- and deca-BDE commercial mixtures.[19] Time-trend analysis of ∑penta-BDE related congener (∑BDE 17, 28, 47, 49/71, 66, 85, 99, 100, 153, and 154) concentrations in these sludges suggest an exponential increase from the mid-1970s, peaking in the mid-1990s (Figure 1). Concentrations appeared to have leveled off ca. 2000 and may be decreasing thereafter. Octa-BDE-related congeners (mainly BDE-183) exhibited a similar temporal pattern but contributed only 2% of the total PBDEs in the sludges. Estimation of the octa-BDE contribution was confounded by overlap of congeners between the other two, more dominant commercial mixtures (e.g., BDE-207 in deca-BDE and BDE-153 in penta-BDE).[19]

Alcock et al.[20] suggested that the North American penta-BDE use may have peaked in the mid-1990s. The temporal trends we observed in sewage sludge/biosolids PBDE burdens are consistent with this. Kohler et al.[21] observed a peak in penta- and octa-BDE concentrations in Swiss lake sediments dated to the mid-1990s, while deca-BDE continued to increase. Hassanin et al.[22] reported a decrease in PBDE levels (BDE-209 was not assayed) in archived U.K. vegetation samples collected primarily between 1961 and 2004. Despite cessation of commercial penta- and octa-BDE production and efforts to restrict deca-BDE production and use, the bulk of PBDEs remain in in-service or discarded polymer products, wherein they routinely were added at percent levels. If escape from such products is a major release pathway, as has been suggested,[23] trends in environmental levels might be expected to lag changes in production.

Chicago Stickney WWTP biosolids generated between 2004 and 2007, and later applied to agricultural soils, contained mean ∑penta-BDE, ∑deca-BDE (∑BDEs 206, 207, 208, and 209), and ∑PBDE concentrations of 1080, 6630, and 7800 μg/kg, respectively. In biosolids from a mid-Atlantic U.S. WWTP, Andrade et al.[24] observed lower ∑penta-BDE (∑BDEs 28, 47, 99, 100, 153, and 154), BDE-209, and ∑PBDEs (∑BDEs 28, 47, 99, 100, 153, 154, 183, and 209) concentrations, that is, 574, 920, and 1500 μg/kg, respectively. They perceived no significant PBDE concentration changes over the short interval sampled, 2005−2008. The 2006−2007 EPA TNSSS data returned a higher mean for ∑penta-related congeners (∑BDEs 28, 66, 47, 85, 99, 100, 138, 153, and 154) for samples collected from across the United States, that is, 1760 μg/kg (SD 1510).[9] Maximum TNSSS-reported ∑penta-BDE and BDE-209 concentrations for the continental United States were 11 000 and 17 000 μg/kg, respectively. The mean BDE-209 level in the EPA TNSSS was lower than the 2004−2007 Chicago biosolids, that is, 2310 μg/kg (SD 3110). Unfortunately, BDEs 206, 207, and 208 were not determined in the TNSSS. These congeners are valuable for gauging the extent of degradation via dehalogenation. Some problems were reported during the TNSSS BDE-209 analysis that might have compromised its accurate determination.[9] Ricklund et al.[25] reported a mean BDE-209 concentration of 5240 μg/kg in five samples from U.S. WWTPs obtained from 1999 to 2000.

The trajectory of BDE-209 concentrations in the Chicago sludges/biosolids was relatively flat from 1974 to 1994 but increased thereafter (Figure 2). Log transformation of concentrations did not improve the overall trend line fit. The mean BDE-209 level in 2006−2007 Chicago biosolids was 6870 μg/kg (SD 3410), exceeding both the EPA 2006−2007 TNSSS mean and that reported in a multistate U.S. biosolids study[26] from 1999 to 2000 (mean 1010 μg/kg; SD 1400). Given that BDE-209 levels in Chicago biosolids were increasing rapidly from 1995 to 2006 (Figures 2 and 3A), the latter observation is understandable. The substantial between-sample variability observed may reflect intermittent releases or the distribution of major BFR sources, for example, textile operations. Differing industrial practices and levels of industrial product stewardship during plastics and textile manufacturing may also contribute. For example, incomplete emptying of BFR delivery containers by plastics and textile manufacturers prior to disposal was recently identified as a path for substantial releases to landfills.[8] Also, while the textile industry represents less than a third of total deca-BDE demand, it may contribute disproportionately to releases to WWTPs and surface waters.[8] Better management of aqueous waste streams could reduce that contribution.

While the temporal trajectory of BDE-209 concentrations in Chicago sludges/biosolids since 1990 (Figure 3A) was positive (doubling time 5 years), the nationwide industry-reported release of deca-BDE (based on the U.S. EPA Toxics Reduction Inventory (TRI) database)[27] peaked around 2001 (Figure 3B), coincident with rising concerns regarding PBDEs in the U.S. environment. This release estimate (to all compartments, including landfills) represented about 3% of the total reported 2001 North American deca-BDE demand of 24 500 MT. In contrast, the EU Voluntary Emissions Control Action Programme[8] reported an environmental release of only 0.1% of the total used by participating members in 2009.

Geographical Patterns of PBDEs in Sewage Sludges/Biosolids. California has the strictest flame retardancy standards in the United States. Hence, it has been postulated that PBDE usage might be more intensive in the West. Accordingly, we investigated the influence of WWTP location on sludge/biosolids ∑penta-BDE and BDE-209 concentrations by mining the EPA 2006−2007 TNSSS data.[9] The PBDE data were log-transformed to approximate normal distributions (confirmed by Shapiro Wilks tests) and then subjected to analysis of variance (ANOVA) ($p < 0.01$). Regional concentration relationships for ∑penta-BDE and BDE-209 showed different trends (see Supporting Information, Figure S1). For BDE-209, the ANOVA of regional differences was not statistically significant. However, differences might have been obscured by BDE-209 quantitation problems, as mentioned above. In contrast, ∑penta-BDE concentrations in sludges/biosolids differed statistically by region ($F_{3,74}$) = 3.46 (p 0.02). A posthoc comparison test (Newman−Keuls) indicated that ∑penta-BDE concentrations in northeastern biosolids were lower than midwestern (p 0.042) and western (p 0.01) biosolids but not southern WWTP solids (p 0.08). See Supporting Information for further details. Zota et al.[28] recently reported a similar regional ∑penta-BDE (∑BDEs 47, 99, and 100) concentration pattern (west > south > midwest > northeast) in human blood sera and higher indoor dust levels in California than other U.S. regions.

PBDEs in Chicago Biosolids Applied to Illinois Agricultural Plots. Mean ∑PBDEs in the 2004−2007 Chicago (Stickney WWTP) biosolids applied to the sandy soil (Kankakee County; biosolids collected in the spring) and clay soil (Will County; biosolids collected in the fall) were

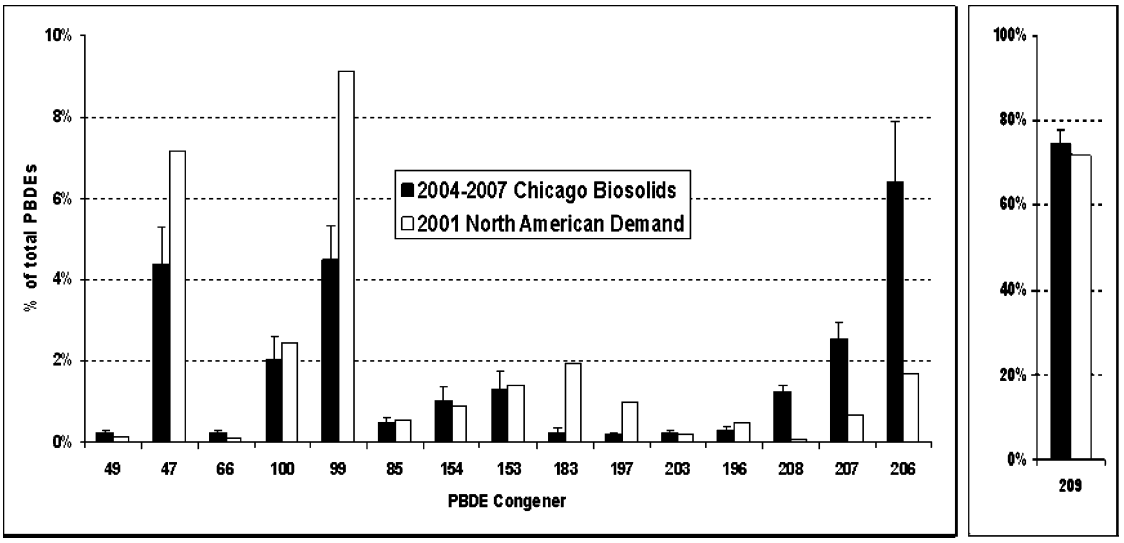

Figure 4. PBDE congener contributions in 2004−2007 Chicago-derived biosolids versus their predicted distribution based on 2001 North American PBDE demand and published commercial mixture compositions.[19] BDE-209 (right inset) is shown separately due to its large contribution.

significantly different (ANOVA, $p < 0.05$): 9060 μg/kg (SD 929) and 6530 μg/kg (SD 597), respectively. BDE-209 dominated in these biosolids, constituting on average 74% of the total PBDEs, and ranged from 4250 to 7840 μg/kg.

The congener profiles, as a percent of total PBDEs, were consistent between samples. We compared these profiles to predicted congener distributions (Figure 4) generated from the industry-reported 2001 North American market demands for the three commercial mixtures (penta-BDE, DE-71; octa-BDE, DE-79; and deca-BDE, Saytex 102E), weighted by their respective congener compositions.[19] BDE-209 (constituting 97% of the deca-BDE product Saytex 102E) dominated in these contemporary Chicago biosolids. Predicted and measured BDE-209 biosolid contributions matched well (Figure 4). Interestingly, BDE-206 was the next most abundant congener, and the levels of both BDE-206 and BDE-207 were 4-fold higher than predicted. In the Chicago biosolids, BDE-208 was 23-fold higher than we predicted. We hypothesize that these three nonabrominated congeners arise from BDE-209 degradation. Following a 238-day lab incubation, Gerecke et al.[29] reported anaerobic, microbially mediated dehalogenation of BDE-209 in sludge obtained from a mesophilic digester. A mixture of nona- and octa-BDEs was generated, with the level of BDE-208 being particularly increased. These authors commented that the presence of brominated primers enhanced the BDE-209 degradation rate by 2-fold. They noted that congener patterns in grab samples from a Swiss WWTP anerobic digestor, with a 28-day residence time, also supported BDE-209 degradation.

In the contemporary land-applied Chicago biosolids, BDEs 49, 66, 100, 85, 153, 154, 203, and 196 approximated our predicted contributions (Figure 4). In contrast, BDEs 47 and 99 (major penta-BDE congeners), as well as BDEs 183 and 197 (major octa-BDE constituents) were quantified at less than predicted levels. This might relate to decreasing releases following the December 2004 termination of U.S. penta- and octa-BDE manufacture, degradation to other constituents, or lower local usage of these products. Andrade et al.[24] also reported low contributions of BDE-183 to ∑PBDEs in mid-Atlantic U.S. biosolids collected from 2005 to 2008. This congener is often reported to be low in environmental samples. This relates to modest market demand but also perhaps to its use in electrical wiring and thermoplastics rather than in polyurethane foam (penta-BDE) and textiles (deca-BDE).

Stapleton and Dodder[30] suggested that the observation in environmental samples of BDE-202 (below detection in commercial deca-BDE mixtures) or a low BDE-197/BDE-201 ratio (these two octa-BDEs were not reported present in the deca-BDE product Saytex 102E and with a ratio >20 in the commercial octa-BDE) might indicate BDE-209 degradation. Debromination may occur via abiotic (e.g., photodegradation) or biologically mediated processes. In our 2004−2007 Chicago biosolids, we detected low concentrations of BDE-202 (mean concentration of 4.2 μg/kg; SD 1.17) and a BDE-197/BDE-201 ratio of 1.7. Dehalogenation is a concern as BDE-209 is now the most abundant PBDE congener in many abiotic media (such as soils, sediments, and sludge/biosolids), substantial amounts continue to enter the environment and the less brominated congeners exhibit higher bioaccumulation potentials.

PBDE Levels and Profiles in Biosolids-Applied Soil. Biosolids land-application rates are based on the nitrogen needs of crops. They typically are not reapplied annually, as a substantial fraction of nutrients are released gradually. However, in the current project, biosolids were applied for three consecutive years to two Midwest U.S. agricultural fields (clay soil and sandy soil) below, above, and at the agronomic rate. Soils amended with biosolids exhibited increased PBDE burdens versus nonapplied control plots. Concentrations of PBDEs increased linearly with the amounts of biosolids applied for the high clay soil ($r^2 = 0.866$; Figure 5) and sandy soil plots ($r^2 = 0.785$; see Supporting Information, Figure S2). Maximum soil ∑PBDE concentrations detected were 565 and 1810 μg/kg, respectively. The ∑PBDE concentrations measured in the biosolids-amended clay soil approximated the predicted values, based on the nominal amounts applied and measured levels in representative biosolids samples. However, the PBDE values determined in the sandy soils exceeded predictions. Soil densities of 1.3 and 1.6 g/cm^3 (high clay and sandy soil) and a biosolids incorporation depth of 15 cm were used to calculate expected soil PBDE concentrations. This apparent over-application might be due to loss of traction by the biosolids

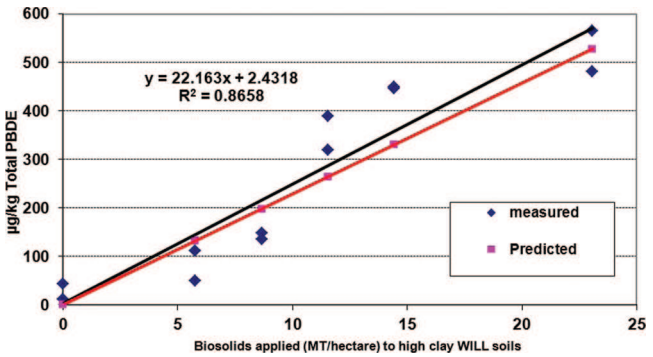

Figure 5. Measured PBDE concentrations in clay soil from the Will County site, in good agreement with predicted values, calculated from the expected biosolids application rates and PBDE concentrations determined in biosolids subsamples. This indicates PBDEs are relatively persistent and will accumulate in soils following repeated biosolids application.

spreading apparatus on the sandy soil. Indeed, Higgins et al.,[10] examining samples from the same plots, reported deviations from expected triclosan and triclocarban soil concentrations for the sandy soil plots.

As in the case of the biosolids themselves, the major congener detected in the soils was BDE-209, constituting 67−100% of the total PBDEs detected. The maximum soil ∑penta-BDE detected was 93.5 μg/kg. Low PBDE levels, mostly BDE-209, were also detected in the non-biosolids-applied clay soil control plots (replicates: 12.3 and 43.4 μg/kg).

BDE-209 was also the major congener detected in the sandy soil plots, constituting 66−87% of the total PBDEs detected. The maximum ∑penta-BDE detected in the sandy soil was 232 μg/kg. The congener distribution of the less brominated congeners (i.e., BDEs 47, 99, and 100) in both soils was similar to that reported in DE-71,[19] the dominant commercial penta-BDE product used in North America. While higher soil levels for electronic waste site soils have been reported, our PBDE concentrations were comparable to those reported by Wang et al.[31] for soil contaminated by burning of electronics waste in China.

Limited published data on PBDEs in agricultural soils following application of biosolids are available. Eljarrat et al.[32] examined soil PBDE levels after application of 15−25 dry MT of biosolids/hectare for 2 or 3 years at several agricultural sites in Spain, comparable to our higher application scenarios. The ∑PBDEs in the biosolids applied there ranged from 197 to 1185 μg/kg (dry weight). Observed soil levels ranged from 30 to 689 μg/kg. As expected, BDE-209 was the dominant congener. Spanish soil that received no intentional biosolids application exhibited a ∑PBDE concentration of 20.7 μg/kg, 71.0% of which was BDE-209. The authors concluded that PBDEs, including BDE-209, were persistent due to their continued presence in soils years after biosolids application. Andrade et al.[24] examined PBDEs in soils from 30 mid-Atlantic U.S. fields that had received varying amounts of biosolids from different WWTPs. PBDE soil burdens increased with the number of biosolids applications. They noted a lesser dominance of BDE-209 in biosolids-applied soils than in the biosolids that were applied, relative to BDEs 47 and 99. This was postulated to be due to BDE-209 degradation or higher penta-BDE burdens in the older biosolids. Likewise, Xia et al.[33] observed increasing ∑penta-BDE concentrations in U.S. soils receiving biosolids applications for 33 years. They also noted substantial accumulation of PBDEs in surface soils and minimal apparent degradation.

The relative contributions of BDE-206, BDE-207, and BDE-208 compared to BDE-209 in both the biosolids-amended clay and sandy soils were higher than in the commercial deca-BDE mixture[19] but did not exceed the ratios we observed in the biosolids that were applied. This is consistent with a lack of anaerobic conditions in the soil required for microbially mediated dehalogenation.

PBDE Concentrations in Corn. Several plant uptake pathways for PBDEs exist, but few studies, especially via land-applied biosolids, have been undertaken. Semivolatiles, such as PBDEs, may volatilize from soils and later sorb to the waxy outer surfaces of leaves or bark.[34] In the case of direct soil uptake, contaminants are believed to be first solubilized into soil interstitial water and then enter the roots and pass up the xylem to the remainder of the plant. Hence, plant uptake of hydrophobic compounds is expected to be limited.[35]

The extent of association between the PBDEs and the soil or biosolids matrix will influence their bioavailability. Uptake of PBDEs by Italian ryegrass (*Lolium multiflorum*), pumpkin (*Cucurbita pepo*), and maize (*Zea mays*) from weathered electronic waste recycling site soils in China[36] was recently examined. The authors reported preferential accumulation of the less brominated congeners, consistent with their greater water solubility and mobility. Decreasing PBDE levels were observed as one progressed from roots to stems and leaves. They noted planting reduced soil PBDE concentrations but attributed this predominantly to enhanced soil degradation and volatilization, rather than accumulation by the plant. Uptake of hydrophobic contaminants may be greater when soil amendment occurs via spiking with neat compounds rather than delivered via organic-rich media such as biosolids. For example, Huang et al.[37] observed substantial BDE-209 root/soil dry weight concentration ratios, ranging from 14% to 57% in various plants. Lipid content of the plant tissue was reported to be a strong determinant of dry weight PBDE content. Mueller et al.[38] harvested radishes (*Raphanus sativus*) and zucchini (*Cucurbita pepo*), grown for 10 weeks from seeds, on soils amended with penta-BDE at 75 μg/kg. However, these plants exhibited low PBDE levels, about 1 and 4 μg/kg, respectively. Interestingly, they reported that the organic solvent extractability of soil-amended penta-BDE increased 8-fold in the presence of a mixed consortium of plant species, compared to single species or in the absence of plants. They hypothesized that this might be due to plant exudates. Nevertheless, PBDE uptake in plants was not higher in mixed than monoculture plantings. Concentrations in zucchini shoots exceeded those in roots, and BDE-100 levels exceeded those of BDEs 47 and 99.

In the only published sludge/biosolids-related plant PBDE uptake study we located, Vrkoslavová et al.[39] grew nightshade (*Solanum nigrum*) and tobacco (*Nicotiana tabacum*) directly in undiluted biosolids (∑penta-BDE, 568 μg/kg; BDE-209, 400 μg/kg) over a 6 month period. These plants accumulated up to 15.4 and 76.6 μg/kg ∑penta-BDE, respectively, with highest levels in the stems versus the roots or leaves. Tobacco leaves accumulated 68.4 μg/kg ∑penta-BDE and 117 μg/kg BDE-209. No BDE-209 was detected in the tobacco leaves or roots. Beck et al.[40] noted that uptake of semivolatiles at high levels in sludge might be mediated by soil to air versus soil to root transfer due to the hydrophobicity of these compounds and strong sorption to soil organic matter. They also noted that biosolids have higher percentages of lipoidal materials that may

bind such contaminants more strongly than natural soil organic matter.

In our study we did not detect PBDEs in any of 46 corn grain, stover, or root samples examined (except for a single, apparently compromised stover control sample; see Supporting Information). Quantitation limits for BDE-209 were 5 μg/kg (dry weight basis) and 1−2 μg/kg for non-BDE-209 congeners. Lipophilic PBDEs associate with soil organic matter.[24,36] Total organic carbon content of our biosolids was 18−20%, about 10-fold higher than typical agricultural soils. Application of dewatered biosolids cake by agricultural spreaders disperses small organic-rich conglomerates rather than a homogeneous layer of material on the soil surface. The existence of such aggregates in soil may delay plant uptake of entrained PBDEs compared to other exposure scenarios, most notably organic solvent-based lab amendment. Indeed, Andrade et al.[24] hypothesized increasing PBDE persistence with increasing soil organic matter in biosolids-applied fields. Also, if PBDEs remain associated with small fragments of the original polymer as commercially produced, their bioavailability may be low, at least in the short term.[41] Teuten et al.[42] reported that equilibrium partition coefficients for hydrophobic contaminants and polymers, such as polyethylene, are orders of magnitude greater than for these contaminants and natural organic matter. These same authors also noted that addition of clean plastic to sediments reduced the availability of hydrophobic contaminants to aquatic invertebrates.

The referenced studies and our results indicate that physicochemical factors related to the soil/chemical compartment, as well as physiological and ecological aspects of the plants themselves, may influence uptake of PBDEs. Thus, additional research on the long-term fate and bioavailability of contaminants associated with land-applied biosolids is indicated.

■ ASSOCIATED CONTENT

Supporting Information

Additional text, two tables, and two figures with more detailed descriptions of analytical methodology and results. This information is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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