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Brominated flame retardants in U.S. biosolids from the EPA national sewage sludge survey and chemical persistence in outdoor soil mesocosms

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Abstract

We determined national baseline levels and release inventories of 77 traditional and novel brominated flame retardants (BFRs) in biosolids composites (prepared from 110 samples) from the U.S. Environmental Protection Agency's 2001 national sewage sludge survey (NSSS). Additionally, analyses were performed on archived samples from a 3-year outdoor mesocosm study to determine the environmental persistence of BFRs in biosolids-amended soil. The total polybrominated diphenylether (PBDE) concentration detected in biosolids composites was 9,400±960 μg/kg dry weight, of which deca-BDE constituted 57% followed by nona- and penta-BDE at 18 and 13%, respectively. The annual mean loading rate estimated from the detected concentrations and approximate annual biosolids production and disposal numbers in the U.S., of the sum of PBDEs and non-BDE BFRs was calculated to be 47,900–60,100 and 12,900–16,200 kg/year, of which 24,000–36,000 and 6,400–9,700 kg/year are applied on land, respectively. Mean concentration of PBDEs were higher in the 2001 samples compared to levels reported in EPA's 2006/7 Targeted NSSS, reflecting on-going efforts in phasing-out PBDEs in the U.S. In outdoor soil mesocosms, >99% of the initial BFRs mass in the biosolids/soil mixtures (1:2) persisted over the monitoring duration of three years. Estimates of environmental releases may be refined in the future by analyzing individual rather than composited samples, and by integrating currently unavailable data on disposal of biosolids on a plant-specific basis. This study informs the risk assessment of BFRs by furnishing national inventories of BFR occurrence and environmental release via biosolids application on land.

Keywords

Brominated flame retardants; Polybrominated diphenylether; Biosolids; Environmental persistence; Land application; Emerging contaminants

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1. Introduction

Brominated flame retardants (BFRs) are ubiquitous chemicals produced and used in large quantities worldwide in commercial and industrial products (Alaee et al., 2003; Darnerud, 2003). As a result, significant amounts of these chemicals are released to the environment, resulting in exposure and contamination of wildlife and humans (Birnbaum and Staskal, 2004; De Wit, 2002). Different groups of BFRs used in commerce include: polybrominated diphenylethers and biphenyls (PBDEs and PBBs); hexabromocyclododecanes (HBCDs); and tetrabromobisphenol A (TBBP-A) (Alaee et al., 2003). All have been shown to persist and accumulate in the environment, even in remote regions like the arctic (Birnbaum and Staskal, 2004; Covaci et al., 2003; Darnerud, 2003; De Wit, 2002; Ikonomou et al., 2002; Law et al., 2006). Furthermore, BFRs can get transformed to other toxic substances such as brominated dioxins and furans (Br-D/F) (Weber and Kuch, 2003). Following these concerns, the European Union (EU) banned the use of penta- and octa-BDE formulations in 2002; whereas in the U.S. these congener formulations were voluntarily phased-out by 2005 (Cox and Efthymiou, 2003; U. S. EPA, 2013). The use of deca-BDE was banned in electrical and electronic applications within the EU in 2008 and is currently being phased-out in the U.S., with all sales expected to cease by the end of 2013 (Covaci et al., 2011; U. S. EPA, 2013).

With the ban and phase-out of these major BFRs, alternative or ‘novel’ BFRs (NBFRs) have increased in usage (Covaci et al., 2011). These include decabromodiphenyl ethane (DBDPE), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), hexabromobenzene (HBB), pentabromoethylbenzene (PBEB) and other formulations. NBFRs have also been detected in various environmental matrices, wherein they have been shown to persist and bioaccumulate (Ismail et al., 2009; Qiu et al., 2007; Shi et al., 2009; Verreault et al., 2007; Wu et al., 2011).

The fate and occurrence of traditional BFRs in the environment has been studied in detail over the past decade and has been critically reviewed (Birnbaum and Staskal, 2004; Covaci et al., 2003; Covaci et al., 2011; Darnerud, 2003; de Wit, 2002; Law et al., 2006; Sellström et al., 2005; Shi et al., 2009; Sjödin et al., 2003; Watanabe and Sakai, 2003). BFRs are hydrophobic and persistent chemicals with a tendency to partition to solids (such as sediments and sewage sludge) and persist and accumulate in the environment upon release. Concentrations of total PBDEs as high as 2290 μg/kg dry weight (dw) of sewage sludge have been reported in U.S. sewage sludges (Hale et al., 2003). It was also shown that concentrations of PBDEs in sewage sludges from the U.S. were substantially higher than those from Europe (Hale et al., 2003). One potential, environmental exposure pathway for humans is from land application of processed sewage sludge (biosolids) on agricultural soil. One study showed significant persistence of PBDEs in Swedish farm soil 20 years after the last use of PBDEs (Sellström et al., 2005). In the U.S., more than 50% of the produced sewage sludges are applied on agricultural land, which motivated the present work to determine BFRs loadings and trends in U.S. sewage sludges on a nationwide scale.

The U.S. Environmental Protection Agency (U.S. EPA) has performed several national sewage sludge surveys to evaluate the need for regulating trace contaminants, thereby leading national efforts for a comprehensive survey on contaminant occurrence in these abundant, byproducts of wastewater treatment (U.S. EPA, 2009). As part of the 2006/7

Targeted National Sewage Sludge Survey (TNSSS), the U.S. EPA reported concentrations of 11 PBDEs in processed sewage sludge sampled from 74 U.S. wastewater treatment plants (WWTPs). In the present study, the unused samples from the EPA's 2001 survey were analyzed for 77 traditional and NBFRs and were compared to levels detected in the 2006–07 survey. This was performed in order to understand the occurrence trends and release inventories of BFRs in U.S. sewage sludges on a national scale. Additionally, archived samples of outdoor mesocosms were analyzed to investigate the persistence of BFRs over three years in agricultural soil amended with sewage sludge. Mesocosm samples originated from a study conducted from 2005 to 2008 in Baltimore, Maryland. The approach of analyzing archived sewage sludge composites and mesocosm samples has been validated previously in studies of other emerging contaminants performed to evaluate their nationwide occurrence in sewage sludges and fate in sewage sludge-amended soils (Chari and Halden, 2012; McClellan and Halden, 2010; Venkatesan and Halden, 2013a; Venkatesan and Halden, 2013b; Walters et al., 2010). The present work employed a similar methodology to analyze for BFRs with the goal of providing: (i) the national inventory and occurrence trends of these compounds in U.S. sewage sludges; (ii) estimates of national loading of BFRs to soils as a result of sewage sludge land application; and (iii) the environmental persistence of BFRs in soils amended with sewage sludges.

2. Methods

2.1. Biosolids composites

Biosolids samples analyzed in the present study were originally collected by U.S. EPA as part of the 2001 National Sewage Sludge Survey (NSSS). After completion of 2001 NSSS, the samples were acquired by our laboratory and stored in amber glass jars (500 mL) at −20°C for further analysis. The WWTP facilities were selected by the U.S. EPA to obtain unbiased national estimates of chemical contaminants in U.S. sewage sludges that are disposed of primarily by land application. The samples were collected between February and March 2001 according to an established protocol, only from facilities that included secondary treatment. Representative samples were collected in 500 mL glass or polyethylene jars from 94 WWTPs in 32 U.S. States and the District of Columbia. Information on specific sampling locations is available in peer-reviewed literature (McClellan and Halden, 2010; Venkatesan and Halden, 2013b). Samples were collected from only processed sewage sludges intended for disposal. The biosolids composites analyzed in this study constitute a representative sample (94 facilities) of the more than 16,000 WWTPs in the U.S. Of the 94 WWTPs, 89 had a single system (either aerobic or anaerobic digestion) and five of them had two systems for sludge treatment (both aerobic and anaerobic digestion). Samples were collected from each treatment systems. In addition, duplicate samples were collected from 14 facilities amounting to a total of 113 biosolids samples. Three of these samples were excluded from analysis due to broken containers. From the rest of the 110 biosolids samples, approximately 1 g of dry weight from each sample were pooled together to obtain five composites, each containing solids from between 21 and 24 individual samples (McClellan and Halden, 2010).

2.2. Soil/biosolids time-series samples

Biosolids for the mesocosm study were obtained from a full-scale activated sludge treatment plant located in the mid-Atlantic region of the U.S. (Back River WWTP in Baltimore, MD). The plant serves about 1.3 million people and is designed to treat 680 million liters per day. The major portion of the raw wastewater is from domestic sources with only minor contribution from industry (1.9%). About 75% of U.S. wastewaters are treated by systems similar to the Baltimore plant (Halden and Paull, 2005). Agricultural soil was obtained from the United States Department of Agriculture -Agricultural Research Service (USDA-ARS) Beltsville Agricultural Research Center (BARC), from plots at a depth of 0–20 cm. Larger objects like plant debris and rocks were removed before use. The soil consisted of 20% clay, 27% silt, 53% sand, organic carbon content of 1.7% and a pH of 5.6. Biosolids and soil were mixed at a volumetric ratio of 1:2, which is high compared to the typical land application rate of biosolids (e.g., 1:10 after mixing), but lower than the application rate of pure biosolids in forestry (1:1). This application rate was chosen to enable the potential observation of multiple half-lives of biosolids-borne compounds in soils and to facilitate the detection of degradates of relatively low abundance. Biosolids/soil mixtures and control soils were seeded with tomatoes, bell peppers, and green salads in plastic containers made from polyvinyl chloride 25 cm in depth, 30 cm in width and 30 – 80 cm in length. The containers were exposed to outdoor ambient weather conditions in Baltimore, Maryland without providing shelter or artificial irrigation. Mesocosms were seeded one time and left fallow after harvesting of crops at the end of the first growing season. Precipitation and temperature variation for Baltimore, Maryland during the course of the experiment between years 2005 and 2008 have been provided previously elsewhere (Walters et al., 2010). The 3-year average monthly precipitation was 91 mm and the 3-year average air temperature was 14°C. Moisture content of the soils varied between 14.6 and 35.1% from random sampling over the course of the experiment. The bottom of the containers was perforated to allow drainage of excess water; as in many other studies concentrating on chemical half-lives in soil, no attempts were made to collect the leachate from these vessels during long-term incubation (ChaIneau et al., 1995; Schlüsener and Bester, 2006; Wild et al., 1990). Samples were collected from the top 20 cm using a soil coring device, on days 57, 115, 520, 859, and 995 and were archived at −20°C until the chemical analysis was performed. More information on sampling locations, sampling techniques, and experimental setup are available in peer-reviewed literature (Venkatesan and Halden, 2013a; Walters et al., 2010).

2.3. Sample analysis

The samples were analyzed in collaboration with the commercial laboratory (AXYS Analytical Services Ltd., Sydney, British Columbia, Canada) that had developed EPA Method 1694 for pharmaceuticals and personal care products (PPCPs), and that specializes in the analysis of traditional and emerging contaminants. All concentrations are reported on a dry weight (dw) basis. Analytes were extracted and analyzed for BFRs as described hereafter.

2.3.1. Polybrominated Diphenyl Ether (PBDE) Analysis—A selected suite of PBDEs (40 congeners) were analyzed according to the protocol described in EPA method 1614 with minor modifications. Samples (biosolids composites and biosolids/soil mixtures)

were spiked with isotopically labeled BDE surrogate standards and dried by mixing with sodium sulfate. The dried solids were extracted with dichloromethane using a Soxhlet extraction apparatus, spiked with a cleanup standard ($^{13}C_{12}$-BDE-139), and cleaned up on a series of chromatographic columns that included layered acid/base silica, Florisil and alumina columns. Final extracts then were spiked with isotopically labeled internal standards prior to instrumental analysis. Analysis of BDE was performed using a Micromass Autospec Ultima magnetic sector high-resolution mass spectrometer (HRMS) (Waters, Milford, MA) equipped with a Hewlett-Packard 6890 gas chromatograph (GC). A DB-5HT capillary column (30 m, 0.25 mm i.d. × 0.1 μm film thickness) was coupled to the MS source. Two masses from the molecular ion cluster were used to monitor each of the target analytes (Table S1). Four additional non-BDE BFRs (PBEB, HBB, BTBPE, and DBDPE) were analyzed by the same method by introducing additional native, labeled surrogates, and calibration standard solutions (Table S1).

2.3.2. Polybrominated biphenyl (PBB) analysis—PBB concentrations were determined in a mega composite sample created by blending of the five biosolids composites. About 1 g (dry) of the sample was spiked with ^{13}C-labeled polychlorinated biphenyl (PCB) congeners to enable quantification standards and Soxhlet-extracted with dichloromethane. Extracts were cleaned up using acid/base silica, Florisil and Alumina chromatography columns. Purified extracts were concentrated and spiked with recovery standards prior to analysis by high resolution GC/HRMS (Table S2).

2.3.3. Hexabromocyclododecane (HBCD)—About 1.5 g (dry) sample (mega-composite biosolids) was spiked with ^{13}C-labelled surrogate standards and Soxhlet-extracted with dichloromethane (Table S3). Extracts were cleaned up using Florisil columns. Purified extracts were concentrated and spiked with recovery standards and were separated by Waters (Milford, MA) 2795 high performance liquid chromatography (HPLC) using a reversed-phase C_{18} column and analyzed using a Micromass Quattro Ultima triple quadrupole tandem mass spectrometer (Waters, Milford, MA).

2.4. Quality assurance

Analysis batches consisted of a maximum of 20 samples, one procedural blank and one spiked matrix sample for ongoing precision and recovery (OPR) determination. Clean sand was used as the matrix for procedural blanks and OPR. A duplicate was analyzed for every analysis batch that had to agree to within ±20% of prior measurements on identical samples. All reported data met the established acceptance criteria for PBDE analysis (Table S4). Ion ratios had to fall within ±15% of the theoretical values for positive identification of all target analytes. The minimum signal-to-noise ratio was 10:1. In addition to these standard procedures, a duplicate of composite biosolids sample # 1 was prepared to serve as a blind (unknown) duplicate to the commercial laboratory and was shipped along with the other composites. This sample served to evaluate analysis precision of the method in addition to the laboratory's QA/QC protocol. Precision between samples and duplicates was expressed as relative percent difference (RPD), which was calculated using the following expression.

$$RPD[\%]=\frac{|C_{sample}-C_{duplicate}|*100}{\frac{C_{sample}+C_{duplicate}}{2}} \quad (1)$$

Where, C_{sample} and $C_{duplicate}$ are the concentration detected in the original sample and in its duplicate, respectively.

2.5. Modeling annual load of chemicals in biosolids

Annual load was estimated for all detected analytes based on the annual biosolids production of 5.1–6.4 million metric dry tonnes (5.6–7 million dry U.S. tons) estimated for the year 2001 in the U.S. (NEBRA, 2007; Jones-Lepp and Stevens, 2007; National Research Council, 2002).

$$\text{Annual load}=(\text{mean analyte concentration in biosolids})\ \mu\text{g/kg}*(10^{-9}\ \text{kg}/\mu\text{g})*(5.1-6.4\times10^{9}\ \text{kg of biosolids/year}) \quad (2)$$

2.6. Statistical Analysis

Statistical analyses were performed using version 19 of the IBM SPSS software package (IBM, Armonk, New York, U.S.). The BFRs dataset was evaluated for normality by application of Shapiro-Wilk test. In order to determine the interrelations in the analytical dataset of detected BFRs and various physicochemical properties of the analytes, a principal component analysis (PCA) was performed.

3. Results and Discussion

3.1. Method performance

Method detection limits (MDLs) for PBDEs ranged between 0.009 and 2.47 μg/kg dw (Table 1). MDL for PBBs, HBCD, and other non-BDE BFRs ranged between 0.0002 and 4 μg/kg dw. Recoveries from matrix spike experiments for the various analytes ranged between 88 and 134% in sewage sludge, and from 69 to 155% in biosolids/soil mixture (Tables S5–S6). Due to the effects of extremely high levels of native BDE-209 in biosolids and biosolids/soil mixture samples, the labeled analog (^{13}C- BDE-209) was not quantifiable. To bring the area response of BDE-209 into the instrument calibration range and lessen its effects on nona-BDEs, extracts for these samples were further diluted and re-fortified with ^{13}C-labeled quantification standards (specifically, $^{13}C_{12}$-BDE-209 for BDE-209 and $^{13}C_{12}$-BDE-197 for nona-BDEs). BDE-209 and all nona-BDEs are reported from the analysis of the re-fortified extracts. As ^{13}C-BDE-209 data are not available in the original extract, BDE-209 concentrations were not recovery-corrected. Concentrations of all nona-BDEs have been recovery-corrected using ^{13}C-BDE-197 recovery data obtained from extracts before re-fortification. Trace amounts of BDE-203, 206, 207, 208 and 209 (0.007 to 0.5 μg/kg dw) were observed in the lab blank. As concentrations of these analytes in all biosolids and soil samples were greater by more than four orders of magnitude than those in lab blank, sample data were not impacted by the variances (Table S6). Similar detection of BDEs and non-BDEs in lab blanks has been reported in past studies (Hites et al., 2004; Huwe et al., 2002; Stapleston et al., 2008). Analysis precision, expressed as RPD, for non-

blinded duplicates of biosolids and biosolids/soil mixtures ranged from 0.3 to 26% and 5 to 36%, respectively (Table S7–S8). RPD for blinded duplicates of biosolids averaged at 39% (varying from 5 to 107%). The observed notable variance in PBDE concentrations could be as a result of either the extremely high concentrations of PBDEs (especially BDE-209) detected in biosolids that might have interfered with quantification, and/or the non-homogeneity of the sewage sludge samples analyzed. High RPDs (average of 42%) have been observed previously in PBDE analysis of sewage sludge samples from the 2006/7 EPA TNSSS (U.S. EPA, 2009). This limitation is considered minor, as the analytes featuring high RPD values, specifically BDE-100 (85%), BDE-153 (101%) and BDE-154 (107%), contributed only 1.6% of the total loading of PBDEs in biosolids; hence, overall mass estimates were not impacted by these atypical variances.

3.2. PBDEs in U.S. biosolids

A total of 32 PBDEs were detected in the biosolids composites, of which 94% of the PBDEs were consistently detected in all the samples analyzed (Table 1). The dataset was evaluated for normality by application of Shapiro-Wilk test; 94% of the analytes' concentration values were normally distributed ($p > 0.05$) (Table S5). BDE-209 was the most abundant PBDE with a mean concentration of 5360 ± 5163 μg/kg dw, followed by BDE-99 and BDE-47 at 1005 ± 448 and 789 ± 318 μg/kg dw respectively. Mean concentration of the remaining 29 PBDEs varied between 0.06 and 663 μg/kg dw. The total PBDE concentration detected in the biosolids composites was 9388 ± 7778 μg/kg, of which deca-BDE constitutes 57% followed by nona- and penta-BDE at 18 and 13%, respectively. In 2001, total market demand for PBDEs in the Americas comprised of 74% technical deca-BDE followed by penta-BDE and octa-BDE at 11 and 6%, respectively (ATSDR, 2004). The relative abundance of the various congeners detected in nationally representative sewage sludge samples mimicked the production volume of PBDEs. BDE-209, 47 and 99 were shown to be the major congeners that constitute deca- and penta-BDE-based technical products (La Guardia et al., 2006); as a result, these were detected as the most abundant PBDEs in the biosolids composites.

The samples analyzed in the present study were collected in 2001 prior to the phase-out of major congeners of PBDEs in the U.S. In contrast, the samples analyzed for the EPA's TNSSS were collected between August 2006 and March 2007, a few years after the voluntary phase-out of penta- and octa-BDE formulations (2004) in the U.S. This enabled a comparison of concentrations of 11 PBDEs reported in TNSSS to their respective occurrence levels in this work using samples collected in 2001 (Figure 1). Though the concentrations are not significantly different, the mean concentrations of most of the PBDEs (10 out of 11), including the major congeners in the technical grade penta-BDE products (BDE-47, 99, 100) were higher in 2001 than those reported for the 2006/7 samples. The mean total concentration of the 11 studied PBDEs accounted for 7,600 and 4,080 μg/kg dw in 2001 and 2006–07 samples, respectively. Interestingly, though deca-BDE production is only currently being phased-out in the U.S., the mean concentration of BDE-209 is about 57% lower in the 2006/7 samples compared to the 2001 samples. Similar downward trends of ΣPBDEs in U.S. sewage sludge have been reported for samples collected between 2006

and 2010, indicating the desirable impact of ongoing efforts in phasing-out PBDEs in the U.S. (Davis et al., 2012).

3.3. Non-BDE BFRs in U.S. biosolids

Out of the 28 non-BDE BFRs (21 PBBs, 3 HBCD and 4 NBFRs) analyzed, 9 chemicals (2 PBBs, 3 HBCD and 4 NBFRs) were detected in biosolids. The production volume of HBCD was much lower compared to PBDEs during sample collection (2001); whereas PBBs were banned in the U.S. since 1973 (ATSDR, 2004; U.S. EPA, 2010). Hence, PBBs and HBCD were analyzed only in a mega-composite biosolids sample (mixture of solids from the five composites originally prepared) to be economical with the available samples while still enabling a baseline estimate of their abundance in U.S. biosolids. BTBPE was the most abundant non-BDE BFR detected at a mean concentration of 1,960 ± 3,970 μg/kg dw, followed by DBDPE and PBB-153 at 480±830 and 49.1 μg/kg dw, respectively (Table 1). PBEB, HBB and total HBCD (α, β, γ) were detected at 1.6±0.7, 0.5±0.4 and 19.8 μg/kg dw, respectively. PBBs are no longer produced or used in the U.S. and hence their low detection in the present study may result from chemicals or products still lingering in the environment (ATSDR, 2004). One study reported levels of total HBCD in U.S. sewage sludge samples collected between 2002 and 2008 that was several orders of magnitude higher than the levels reported in the present study (2001 samples). The higher levels in the study preceding this work were attributed to an automotive interior parts-manufacturing plant discharging to the WWTP sampled (La Guardia et al., 2010). Currently, the U.S. EPA is working towards finding alternatives for HBCD, due to its various potential concerns (U.S. EPA, 2010).

Data on occurrence levels of NBFRs in U.S. sewage sludge samples are still scarce. The use of NBFRs are expected to increase due to the banning and phase-out of traditional BFRs (especially PBDEs). Conversely, the limited data on BTBPE, DBDPE and HBB suggest a decreasing trend in sewage sludge samples collected between 2002 and 2010 from five U.S. WWTPs (Davis et al., 2012; La Guardia et al., 2010). One study associated the decreasing trend with the relocation of an automotive interior-parts-manufacturing plant that contributed waste to the sampled WWTP (La Guardia et al., 2010). Levels of BTBPE (4816 μg/kg dw in 2002 and 1687.5 μg/kg dw in 2005) and DBDPE (2856 μg/kg dw in 2002 and 1840 μg/kg dw in 2005) reported in the latter study (La Guardia et al., 2010) is within the range of concentrations reported in the present study for nationally representative samples collected in 2001. The average concentration of the four NBFRs screened in this study (2450 μg/kg dw) were similar to the total concentration of major congeners in the penta- and octa-BDE formulations (2,200 μg/kg dw). These significant concentrations of NBFRs observed in 2001 samples shows that they were manufactured and used prior to the phase-out of PBDEs, and that levels has increased since.

3.4. Annual loading of BFRs to U.S. biosolids and agricultural land

The annual mean loading rate of total PBDEs and non-BDE BFRs in 2001 biosolids were estimated at 47,900–60,100 and 12,900–16,200 kg/year, respectively, using Equation 2 (Table 1). The most abundant compound was BDE-209 at 27,300–34,300 kg/year, followed by BTBPE and BDE-99 at 10,000–12,600 and 5,100–6,500 kg/year, respectively. Based on the estimated percentage of total sewage sludges applied on land (50–60%) (NEBRA, 2007;

Jones-Lepp and Stevens, 2007; National Research Council, 2002), the mean loading rate of total PBDEs and non-BDE BFRs to agricultural soil were estimated here to be 24,000–36,000 and 6,400–9,700 kg/year, respectively. This significant load of BFRs is applied selectively to less than one percent of the nation's agricultural land (U.S. EPA, 2012). A significant amount of BFRs were also estimated to go to incinerators (ΣPBDEs: 9,600–12,000 kg/year; non-BDE BFRs: 2,600–3,200 kg/year) and landfills (ΣPBDEs: 8,100–10,200 kg/year; non-BDE BFRs: 2,200–2,700 kg/year) as an alternative disposal route for unwanted sewage sludge (Table 1). The presence of BFRs in sewage sludge poses an additional concern due to the potential formation of brominated dioxins and furans (Br-D/F) in incinerators (Dumler et al., 1989; North, 2004). One study reported a total Br-D/F concentration of 1,803 μg/m^3 in stack emissions from sewage sludge incinerators (North, 2004). BFRs have also been detected in leachate from landfills (Odusanya et al., 2009; Osako et al., 2004). The significant load of BFRs in biosolids and the associated concerns suggests the need to regulate these chemicals in biosolids.

3.5. Persistence of BFRs in biosolids/soil mesocosms

Out of the 40 PBDEs and four NBFRs analyzed, 32 PBDEs and three NBFRs were detected in the biosolids/soil mixtures. It must be noted that the biosolids samples for the mesocosm experiment originated from the Back River wastewater treatment plant in Baltimore, and thus are different from the composites analyzed previously to determine the national inventories of BFRs in U.S. biosolids. Control samples of soil that did not receive sewage sludge showed background levels of 12 PBDEs (BDE-15, 47, 49, 66, 99, 100, 183, 203, 206, 207, 208, and 209) at levels ranging from 0.0007 to 13.8 ng/g of dry soil. However, these background levels represent only 0.02 – 1.4% of the initial levels of the respective BFRs detected in the biosolids/soil mixtures, indicating that the majority of BFRs levels in mesocosms originated from biosolids amendment. The most abundant BFRs was BDE-209 detected at a level of 17,100 μg/kg dw of biosolids/soil mixture, followed by BDE-206 and BDE-207 at 4,350 and 3,330 μg/kg dw of biosolids/soil mixture, respectively. The initial concentration of BDE-209 is more than an order of magnitude higher in the mesocosm sample compared to the mean national baseline level detected in the 2001 composite biosolids sample (5360 ± 5163 μg/kg dw). The biosolids for the mesocosm study was collected in 2005, a year after the phase-out of penta- and octa-BDE formulations and when the flame retardant market dominated by deca-BDE products. This could be the reason why BDE-209 was higher in the mesocosm study, while BDE-47, 99 and 100 were lower in the mesocosm study compared to the 2001 biosolids samples (67, 60, and 18 μg/kg dw in mesocosms compared to 789 ± 318, 1005 ± 448 and 1790 ± 62 μg/kg dw in biosolids composites, respectively).

Out of the 35 BFRs detected in the mesocosms, only ten compounds featured a loss from soil during the course of three years (Table S8; Figure S1). These include four di-BDE, four tri-BDE, and two tetra-BDE congeners. The estimated first-order half-lives for these compounds ranged between 224 and >990 days in the biosolids/soil mesocosms (Table S8; Figure S1). However, these ten PBDEs contributed only 0.3% of the total ΣBFRs load in the biosolids/soil mixtures at the beginning of the experiment. The remaining 25 BFRs persisted throughout the course of three years. Figure 2 shows the concentrations over time of NBFRs

and various congeners of PBDEs (grouped together according to the degree of bromination) in biosolids/soil mixtures. Compounds featuring lower degree of bromination (di-, tri- and tetra-BDEs) feature a loss from soil, while higher brominated compounds (penta- through deca-BDE) persisted throughout the course of the experiment. The four studied NBFRs also persisted over a period of three years in the mesocosm. Similar observation were reported in studies conducted in Spain and Sweden, where they showed persistence of PBDEs in soil even after four and 20 years after the last application of sewage sludge, respectively (Eljarrat et al., 2008; Sellström et al., 2005).

The term half-life used above represents the overall loss of chemical from soil that may include various loss mechanisms like degradation, volatilization, leaching, plant uptake and so on. Photolysis of higher brominated PBDEs by UV-light and sunlight have been observed in the past with formation of lower brominated congeners through sequential debromination (Hua et al., 2003; Söderström et al., 2004). Microbial debromination of deca- and octa-BDEs have also been observed under anaerobic conditions (He et al., 2006; Lee and He, 2010). PBDEs have low mobility and generally are considered non-leachable from soils; however, trace amounts of these chemicals have been detected in leachate tests under laboratory conditions (Kim et al., 2006; Litz, 2002). Plant uptake of PBDEs has also been observed from contaminated soils, suggesting potential human exposure risks (Huang et al., 2009; Huang et al., 2011; Mueller et al., 2006). Leachate and plants samples from the mesocosm study were not analyzed, which hampers pinpointing the mechanism by which the lower brominated PBDEs were lost from the soil.

To obtain a perspective on the interrelations in the analytical dataset, a PCA was performed in clustering mode based on the analyte concentrations in biosolids/soil time series samples and their respective physical/chemical properties (octanol-water partition coefficient, solubility, molecular weight, and vapor pressure) (Figure 3; Table S9). The first two principal components explained the highest amount of variance in the dataset and when combined accounted for 97% of the total observed variability. The PCA plot reveals that major congeners of technical deca-BDE products cluster together, suggesting a correlation in their occurrence and fate in soil. Similarly, major congeners of technical penta- and octa-BDE formulations cluster together. Interestingly, all minor congeners of commercial penta- and octa-BDE formulations group together in the PCA plot. The observed correlation for these minor congeners could be as a result of their trace levels in commercial products and/or their formation as debromination products from higher brominated BDE congeners. In case of NBFRs, the occurrence and fate of BTBPE and HBB in biosolids/soil mixtures correlate with each other.

3.6. Study limitations

In this work, a proven composite sample approach was pursued (McClellan and Halden, 2010; Venkatesan and Halden, 2013a; Venkatesan and Halden, 2013b) to obtain a reasonable mean baseline concentration for the target analytes in an economical, and scientifically defensible fashion. However, pooling of samples is not well suited to capture the variation in concentrations among individual WWTPs, which may show inter-plant variability in loadings and removal efficiencies. It is also possible for minor contaminants to

become diluted during mixing. Extrapolation of these average concentrations to total sewage sludge production in the U.S. carries potential risks. Some of the uncertainties in the estimates of chemical loads provided are listed below.

i. The biosolids production volume of individual WWTPs sampled in this study is unknown. Hence the exclusion of the biosolids volumes per plant in our load calculations introduces inaccuracies into the estimate.

ii. The amount of biosolids applied on land varies by WWTP, with some plants contributing zero and others 100% of their produced biosolids to land application. Hence, not accounting for these variations in our calculation introduces further error in our estimation of BFRs releases to U.S. soils.

iii. The average concentration reported in the present study provides robust baseline values for these chemicals in biosolids. However, the mass loads of BFRs may significantly vary from plant to plant depending on the sources, treatment processes and population served by the WWTP.

While this approach cannot determine the variability of concentrations between the large numbers of WWTPs studied, it is suitable for identifying major BFRs contaminants and determining their average concentrations in U.S. biosolids. The National Sewage Sludge Survey conducted by the U.S. EPA is by far the most comprehensive survey of U.S. sewage sludges, as it contains 94 samples from 32 U.S. States and the District of Columbia. Given the large number of samples analyzed and their selection by the government agency with the purpose of providing a good representation of the more than 16,000 American WWTPs, the obtained national loading estimates are expected to be fairly robust. Additionally, the nationwide inventories of several congeners of PBDEs and NBFRs are reported for the first time in this study making the results a unique and valuable contribution to the literature, despite their inherent limitations.

The primary purpose for the mesocosm experiment performed in Baltimore, Maryland in 2005–2008 was to understand the fate of pharmaceuticals and personal care products (PPCPs) in biosolids-amended soils (Walters et al., 2010). After analysis of PPCPs, the remaining samples were stored at −20°C for future analysis. Hence, the number and volume of samples for this work were limited and replicate samples were not always available for each sampling event. Additionally, storage of the samples for extended periods of time prior to analysis may have allowed chemical degradation of labile chemicals. Therefore, results from the present study are conservative with respect to both detection frequencies and concentrations of BFRs monitored.

4. Conclusions

BFRs are widespread in the environment and contribute a significant fraction to the annual loading of emerging contaminants contained in U.S. biosolids as shown in the present work. Subsequent land application of biosolids during this period might result in a significant accumulation of BFRs in U.S. soils, thereby increasing opportunities for environmental dispersion of these compounds and associated human exposure risks. Mesocosm experiments showed BFRs to persist in soil for years with little attenuation observable (<1%

in 3 years). Though PBDEs are being phased-out in the U.S., the replacement chemicals (NBFRs) have similar structural properties. As these substitutes share undesirable properties of traditional BFRs, such as environmental persistence and accumulation potential, they similarly may require regulations to protect human health and the environment.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Highlights

- We provide nationwide inventories of 77 brominated flame retardants in U.S. biosolids
- Deca-bromo diphenyl ether constituted 57% of the total BFRs load in biosolids
- Estimated 30–46 tonnes of BFR releases to U.S. soils via biosolids land application
- >99% of initial BFR mass persisted over three years in biosolids amended soil

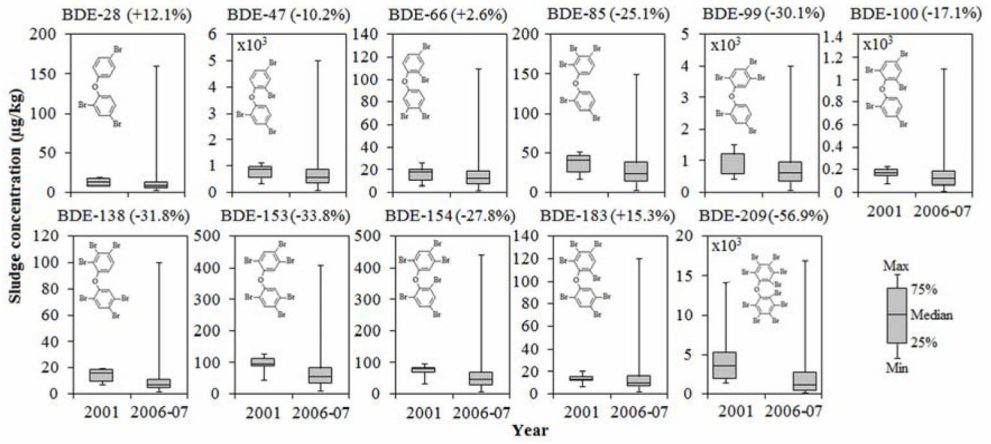

Figure 1.

Comparison of BFR levels in U.S. sewage sludges from EPA National Sewage Sludge Surveys conducted in 2001 and 2006/7. Percentage values within parenthesis represent increases (+) or decreases (−) in mean concentrations from 2001 to 2006/7. The y-axis scale for BDE-99, BDE-100, and BDE-209 is in thousands.

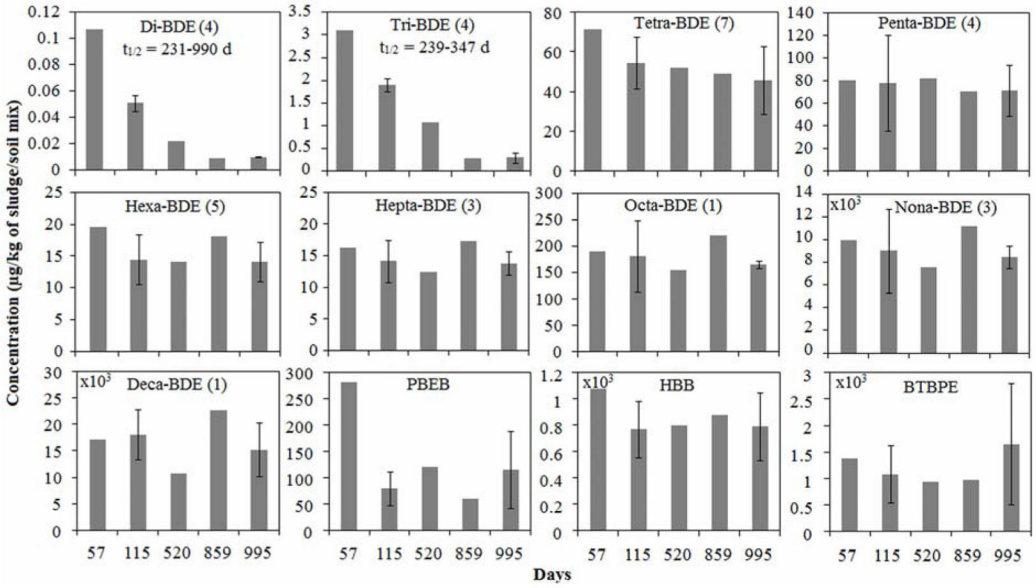

Figure 2.

Concentrations of BFRs over time in soil amended with sewage sludge. Congeners of PBDEs are grouped together according to the degree of bromination. The number within parenthesis represents the number of congeners in that group. The estimated half-life of the congeners is provided for compounds featuring a loss from soil. The y-axis scale of nona-BDE, deca-BDE, HBB, and BTBPE is in thousands. Error bars represent minimum and maximum concentrations.

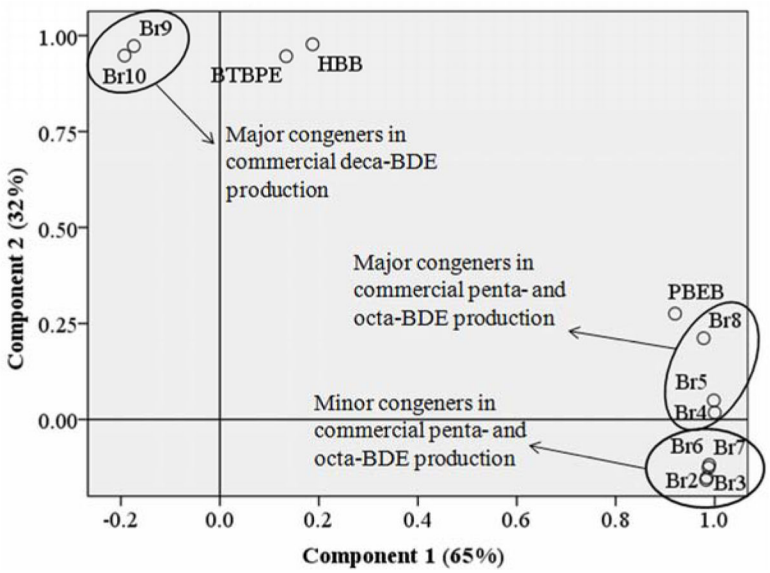

Figure 3.

Principal component analysis of BFR concentration in biosolids/soil time series samples and their physical/chemical properties (octanol-water partition coefficient, solubility, molecular weight, and vapor pressure). Congeners of PBDEs are grouped together according to the degree of bromination (Br2 – dibrominated BDE through Br10 – decabrominated BDE). The highlighted circles represent the cluster of compounds that correlate with each other.

Table 1

Concentrations and estimated loads of BFRs in U.S. biosolids from the 2001 EPA's national sewage sludge survey

Compounds	Detection limit (μg/kg)	Biosolids concentration (μg/kg) Avg. (Min, Max)	Detected Frequency (%)	Annual Load (kg/year)[a] (Min-Max)			
				To biosolids	To land application	To incineration	To landfills
Polybrominated diphenylethers (PBDEs)							
BDE-7	0.025	1.1 (0.2, 1.7)	100	5–7	3–4	1–1.3	1
BDE -8/11	0.029	0.2 (0.14, 0.4)	100	1–2	0.6–0.9	0.2–0.3	0.2
BDE -12/13	0.052	0.17 (0.07, 0.24)	60	0.9–1.1	0.4–0.6	0.1–0.2	0.1
BDE-15	0.010	2.6 (0.47, 7.7)	100	13–17	7–10	2–3	2.5
BDE-17/25	0.023	23.7 (8.9, 42.2)	100	121–152	60–91	24–30	20–26
BDE-28/33	0.027	13.4 (8.4, 18.6)	100	68–85	34–51	14–17	12–15
BDE-32	0.016	0.08 (0.04, 0.16)	100	0.4–1	0.2–0.3	0.1	<0.1
BDE-37	0.011	0.24 (0.16, 0.37)	100	1–2	0.6–0.9	0.2–0.3	0.2
BDE-47	0.055	789 (314, 1120)	100	4026–5052	2012–3031	805–1010	684–859
BDE-49	0.015	38.4 (7.7, 62)	100	196–246	98–148	39–49	33–42
BDE-51	0.015	2.9 (0.7, 5.1)	100	15–18	7–11	3–4	2.5–3
BDE-66	0.020	16.6 (5.7, 26.1)	100	85–106	42–63	17–21	14–18
BDE-71	0.016	9.3 (1.7, 17.8)	100	48–60	24–36	10–12	8–10
BDE-75	0.033	1.2 (0.3, 1.7)	100	6–7	3–4	1–1.5	1
BDE-77	0.016	0.06(0.05, 0.08)	80	0.3–0.4	0.1–0.2	<0.1	<0.1
BDE-85	0.009	37 (16.8, 51.9)	100	189–237	94–142	38–47	32–40
BDE-99	0.051	1004 (402, 1510)	100	5123–6429	2561–3858	1025–1286	871–1093
BDE-100	0.018	179 (75.3, 229)	100	913–1146	457–688	183–229	155–194
BDE-119/120	0.025	1.7 (1.2, 2.4)	100	9–11	4–7	1.5–2	1.5
BDE-138/166	0.032	15 (7.4, 20)	100	77–96	38–58	15–19	13–16
BDE-140	0.019	3.4 (1.7, 4.6)	100	17–22	9–13	3–4	3–4
BDE-153	0.012	103 (43.9, 138)	100	528–663	264–398	106–133	90–113
BDE-154	0.016	81.8 (34.3, 124)	100	417–523	209–314	83–105	71–89
BDE-155	0.013	4.5 (1.8, 6.6)	100	23–29	11–17	5–6	4–5
BDE-181	0.020	0.5 (0.1, 1)	100	2–3	1–2	0.5	0.4

Compounds	Detection limit (μg/kg)	Biosolids concentration (μg/kg) Avg. (Min, Max)	Detected Frequency (%)	Annual Load (kg/year)[a] (Min-Max)			
				To biosolids	To land application	To incineration	To landfills
BDE-183	0.010	14 (8.4, 20.5)	100	72–90	36–54	14–18	12–15
BDE-190	0.028	2 (0.9, 3.4)	100	10–13	5–7	2–2.5	2
BDE-203	0.040	26.8 (9.3, 59.2)	100	137–171	68–103	27–34	23–29
BDE-206	0.245	587 (149, 1420)	100	2992–3754	1496–2253	598–751	509–638
BDE-207	0.219	663 (157, 1430)	100	3381–4243	1690–2546	676–849	575–721
BDE-208	0.175	409 (112, 965)	100	2088–2620	1044–1572	418–524	355–445
BDE-209	2.470	5360 (1420, 14200)	100	27336–34304	13668–20582	5467–6861	4647–5832
Polybrominated biphenyls (PBBs)							
PBB-101[b]	0.005	4.7	-	24–30	12–18	4.8–6	4.1–5.1
PBB-153[b]	0.005	49.1	-	250–314	125–189	50.1–62.9	42.6–53.4
Other BFRs							
PBEB	0.0002	1.6 (0.77, 2.5)	100	8–10	4–6	1.6–2	1.5
HBB	0.001	0.5 (0.16, 1.3)	100	2–3	1–2	0.5	0.4
BTBPE	0.6	1964 (37.3, 9060)	100	10015–12568	5008–7541	2003–2514	1702–2137
DBDPE	4	485 (6.43, 1440)	60	2475–3105	1237–1863	495–621	421–528
alpha-HBCD[b]	0.15	6.7	-	34–43	17–26	6.9–8.6	5.8–7.3
beta-HBCD[b]	0.1	0.8	-	4–5	1.9–2.9	0.8–1	0.7–0.9
gamma-HBCD[b]	0.14	12.3	-	63–79	31.4–47.2	12.6–15.8	10.7–13.4

[a] Annual load values were calculated based on the estimated percentage of total sewage sludges use and disposal (50–60% to land application;17% to landfills; 20% to incineration). (NEBRA, 2007; Jones-Lepp and Stevens, 2007; National Research Council, 2002)

[b] These compounds were analyzed in the mega-composite sample (mixture of composites 1 through 5) and hence minima and maxima values are not available.