Polybrominated diphenyl ethers in sewage sludge and treated biosolids: Effect factors and mass balance

M. Kim, P. Guerra, M. Theocharides, K. Barclay, S.A. Smyth, M. Alaee*

Science and Technology Branch, Environment Canada, 867 Lakeshore Rd., P.O. Box 5050, Burlington, ON L7R 4A6, Canada

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Abstract

Polybrominated diphenyl ether (PBDE) flame retardants have been consistently detected in sewage sludge and treated biosolids. Two hundred and eighty-eight samples including primary sludge (PS), waste biological sludge (WBS) and treated biosolids from fifteen wastewater treatment plants (WWTPs) in Canada were analyzed to investigate the factors affecting accumulation of PBDEs in sludge and biosolids. Factors examined included environmental/sewershed conditions and operational parameters of the WWTPs. PBDE concentrations in PS, WBS and treated biosolids were 230–82,000 ng/g, 530–8800 ng/g and 420–6000 ng/g, respectively; BDE-209, -99, and -47 were the predominant congeners. Concentrations were influenced by industrial input, leachate, and temperature. Several examinations including the measurement of BDE-202 indicated minimal debromination during wastewater treatment. Estimated solids-liquid distribution coefficients were moderately correlated to hydraulic retention time, solids loading rate, mixed liquor suspended solids, solids retention time, and removal of organic solids, indicating that PBDE partitioning to solids can be optimized by WWTPs’ operational conditions. Solids treatment type strongly affected PBDE levels in biosolids: 1.5 times increase after solids digestion, therefore, digestion efficiency could be a potential factor for variability of PBDEs concentration. In contrast, alkaline treatment reduced PBDE concentrations in biosolids. Overall, mass balance approaches confirmed that PBDEs were removed from the liquid stream through partitioning to solids. Variability of PBDE levels in biosolids could result in different PBDEs burdens to agricultural land, and different exposure levels to soil organisms.

1. Introduction

One of the most highly prioritized topics in environmental science is water quality. Wastewater treatment plants (WWTPs) play an important role in converting used water from households and industry into environmentally acceptable water by removing biodegradable carbon, nitrogen and phosphorous compounds, and microorganisms. Biosolids are a major by-product of wastewater treatment as a result of solids separation from influent wastewater and the generation of excess biomass during biological treatment. The term biosolids refers to the treated stabilized product of sewage sludge treatment obtained for further use, such as land application (Madan, 2009). Biosolids are also sent to a landfill...
or incinerated. Due to their nutrient and organic carbon content, biosolids contribute positively to recycling nutrients, soil properties and fertility (Clarke and Smith, 2011). In Canada annual production of biosolids is more than 660,000 tonnes (Bonte-Celok, 2012) and a third of the biosolids are used for land application (UN-HABITAT, 2008). However, land-applied biosolids may be contaminated with organic compounds that were not removed during wastewater treatment (WEAO, 2010).

Polybrominated diphenyl ether (PBDE) flame retardants are organic compounds that can enter the environment through biosolids land application (Clarke and Smith, 2011). PBDEs have low water solubility and high lipophilicity (Environment Canada, 2006; USEPA, 2010a); they have been detected worldwide in humans, wildlife and environmental media (USEPA, 2010a). In addition, PBDEs are identified as bioaccumulative, persistent and toxic chemicals (Environment Canada, 2006; USEPA, 2010a). Three commercial mixtures of PBDEs were used in commerce: Penta-, Octa- and Deca-BDEs (Alaee et al., 2003), by 2004 there was significant changes in the global production and use of Penta- and Octa-BDEs through various regulatory and voluntary initiatives. In addition, by 2013 USA companies will phase out the production and use of Deca-BDEs (USEPA, 2010a).

PBDEs make their way to WWTPs through the disposal of wash water from contaminated indoor dust, leachate from landfilled PBDE-containing products, and discharge from industrial sites processing PBDE containing material (USEPA, 2010a). Therefore, PBDE levels in wastewater can vary with different geographical uses and industrial discharges. In North America, some of the highest concentrations of PBDEs were measured in sewage sludge and biosolids at concentrations exceeding the low ng/g dry weight (dw) range (<10^3 ng/g) (USEPA, 2009). Since sewage sludge and biosolids are complex sample matrices, few studies have focused on these matrices. However, information on the fate of PBDEs in the solid stream is needed to generate mass balances and fully understand chemical partitioning, transformation, and persistence of PBDEs during wastewater treatment. The few mass balances that have been completed in the past have shown that PBDEs are largely associated with biosolids (>96%) (Clarke et al., 2010; North, 2004). These studies indicated that partitioning to sludge was the predominant mechanism of PBDE removal in WWTPs. However, to the best of our knowledge, no studies have analyzed the effect of different WWTP operational conditions on the fate of PBDE in sludges and biosolids. Considering that biosolids are produced from raw sludge through physical, chemical and biological processes, it is necessary to investigate the potential effect of the applied treatment on PBDE levels. Moreover, to understand the sorption mechanism of PBDEs in WWTPs, the distribution of PBDEs in the solids-liquid stream need to be delineated. It is also important to determine mass loading to terrestrial environments via land application of biosolids. This information will help determine their chemical loading to streams and soils receiving treated effluents and biosolids, respectively (Heidler and Halden, 2008).

This study investigated the effects of operational conditions on PBDE concentrations in raw sludge and the effects of solids treatment on PBDE levels in biosolids. Overall 288 solid samples, consisting of 107 primary sludge (PS), 75 waste biological sludges (WBS) and 106 biosolids samples, were collected from 15 Canadian WWTPs, reflecting differences in seasons, community size, contributions from the industrial sector, and various wastewater and solids treatment types. The obtained data was integrated with information on PBDEs in the liquid stream of WWTPs (Kim et al., 2013). This study provides a comprehensive understanding of PBDE levels and fate during sewage and sludge treatment in relation to operational parameters in WWTPs using the largest number of samples reported to date.

2. Materials and methods

2.1. Sampling

A total of 15 WWTPs (4 chemically-assisted primary treatment, 1 gravity primary treatment, 8 secondary biological treatment, and 2 advanced biological nutrient removal treatment) participated in this study. Grab samples of PS, WBS and biosolids were collected from the underflow of the primary clarification tanks, the underflow of secondary clarification and after solids treatment/dewatering, respectively. The use of grab samples of sludge and biosolids is adequate because clarifier underflow and digester retention times at WWTPs reduce variability in sludge characteristics and produce a more homogeneous mixture. Accordingly, for short-term period sampling, a grab sample can be comparable to a composite (USEPA, 1988). However, it should also be noted that among different solids types, the composition of PS is subject to a higher degree of fluctuation since it is generated from solids in influent wastewater that is highly variable (Metcalfe and Eddy, 2003). Grab samples were collected for 3 consecutive days to provide a measure of the variability in the sampling and analytical system. The sampling campaign was done twice a year (winter and summer) and moreover, four WWTPs i.e. plants B, C, R, L were sampled during two consecutive project years to study annual variation. Samples were collected using 8 L stainless steel buckets; then, collected samples were transferred to 500 mL Amber Glass jars (Systems Plus etc. Baden, ON), and kept at 4 °C while being transported to AXYS Analytical Services (Sidney, BC, Canada) on ice, by overnight courier, for analysis. Details of WWTP operational conditions such as sludge treatment, digestion type, community size and biosolids production rate are shown in Table 1.

2.2. Sample and data analysis

PBDEs were analyzed according to USEPA method 1614A (USEPA, 2010b). A detailed description of sample and data analysis is presented in the Supporting Information. To examine the influence of sampling and analytical system variability on PBDE levels, the three results from each sampling point at every sampling campaign were treated as triplicates. Median relative standard deviation (RSD) of the concentrations in PS was 28% (3–76%, n = 36) across all congeners at all WWTPs with six instances exceeding an RSD of 50%. Less variability was found in WBS concentrations, with a
median RSD of 11% (2–79%, n = 25) across all samples and congeners. Treated biosolids also showed less variability with a median RSD of 10% (1–33%, n = 35) across all samples and congeners. Thus, PBDE levels in WBS and biosolids samples were much less variable than levels in PS. It may be presumed that interfering compounds were reduced during treatment and accordingly the matrix effect was less prominent in WBS and biosolids. The matrix effect could be associated with a shorter retention time, making PS a more heterogeneous mixture than WBS and biosolids. Additionally, the larger variability in PS than WBS and biosolids was likely ascribed to the variability of influent compositions (Metcalf and Eddy, 2003). PS probably contains higher levels of interferences such as lipids and surfactants. These interferences can be evident at all stages of the analytical method; thus, it is crucial to remove them from the sample extracts using clean-up procedures (Diaz-Cruz et al., 2009). Nevertheless, variations in different types of samples shows that three-day consecutive sampling reflects the influence of the matrix, which may be overlooked when sampling singly (Ort et al., 2010).

Examining annual variations in biosolids, by comparing collected data between two years in each of the four revisited plants (Figure S1), no statistical differences were observed (Mann–Whitney test, p > 0.05). Therefore, the annual variability in measurement of PBDEs in biosolids is relatively low.

Data were statistically evaluated by non-parametric methods such as Mann–Whitney test and Spearman coefficients using Minitab 16 Software (Minitab Inc., PA, USA) since the datasets were not normally distributed. However, a two-way ANOVA test for unequal sample size was also

<table>
<thead>
<tr>
<th>Plant code</th>
<th>Process type</th>
<th>Sludge types sampled</th>
<th>Digestion</th>
<th>Biosolid application</th>
<th>Wastewater flow rate (×1000 m³/d)</th>
<th>Population served (×1000 inhab)</th>
<th>Biosolids production rate (dry total solids tonnes/year)</th>
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</thead>
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<tr>
<td>H(H1)</td>
<td>PT</td>
<td>PS, Biosolids</td>
<td>N (H1-AS)</td>
<td>Class A material</td>
<td>61 ± 21</td>
<td>65</td>
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<td>PS, Biosolids</td>
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<td></td>
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<td>Incineration</td>
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<td>Not available</td>
<td>Not available</td>
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<tr>
<td></td>
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<td>PS, Biosolids</td>
<td>Y (MA)</td>
<td>Composted at landfill</td>
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<td>PS, WBS, Biosolids</td>
<td>Y (TA)</td>
<td>Mine reclamation. Class A product</td>
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<td>12000</td>
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<td>PS, WBS, Biosolids</td>
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<td>PS, WBS, Biosolids cothickening</td>
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<td>Incineration</td>
<td>410 ± 110</td>
<td>1000</td>
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<td>Q</td>
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<td>Land application Class A</td>
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<td>PS, WBS, Biosolids</td>
<td>N</td>
<td>Compost</td>
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<td>65</td>
<td>2600</td>
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</table>

a Chemically-assisted primary treatment used alum coagulant and anionic polymer for plant H, M, and N and ferric chloride and anionic polymer for plant U. PBDE content of the chemical products was not determined in this study.

b Y-yes, N-no (dewatering step only), AS-alkaline stabilization, MA-mesophilic anaerobic digestion, TA-thermophilic anaerobic digestion, AE-aerobic digestion.

c Class A biosolids require no detectible level of pathogens while Class B still contain detectible pathogens after treatment (USEPA, 2003).

d Plant H’s primary sludge was dewatered and combined with sludges of neighboring plants for alkaline stabilization treatment. For comparison purposes, H = dewatered primary sludge from plant H, and H1 = the product of alkaline treatment.
conducted on data fitting log normal distribution using SPSS 13 (IBM Corporation, USA) in cases where there was no equivalent statistical approach for non-parametric data.

3. Results and discussion

3.1. Overall PBDE levels in sludges and biosolids and distribution of congeners

Of the 47 analyzed congeners, 15 (BDE-10,-11,-13, 25,-30,32,-33,-77,-105,-116,-120,-126,-128,-166, and -181) showed a frequency of non detection (ND) between 50 and 100% in samples; therefore, these were not considered further. The remaining congeners were used to compute total PBDEs and the NDs were substituted by ½ of the sample detection limit (SDL) (Table S2). The SDLs were four to five orders of magnitude lower compared to the concentrations of major congeners (BDE-47,-99,-209); hence, any arbitrary values taken between zero and SDL for substitution minimally affected total PBDEs. This study adopted the ½ of SDL approach that was frequently used in the literature (Alava et al., 2012), and included as many different congeners as possible to estimate total PBDEs. The range of concentrations of PBDEs in PS, WBS and biosolids are displayed in Fig. 1A. Concentrations ranged from 230 to 82000 ng/g (median 990 ng/g), 530 to 8800 ng/g (median 1600 ng/g) and 420 to 6000 ng/g (median 1900 ng/g), in PS, WBS and biosolids, respectively.

The three most predominant congeners were BDE-209,-47 and -99, while BDE-100,-206,-207 and -208 were less predominant (Fig. 1B). In PS, the most prevalent congener was BDE-209 (median 53% of total PBDEs), followed by BDE-47 and BDE-99, both at a median of 14%. The predominance of BDE-209 could be related to the different market use of PBDE technical mixtures of those congeners. BDE-209 accounted for 98% of the Deca-BDE technical mixture while BDE-99 and -47 were 35–50% and 25–37% of the Penta-BDE mixture, respectively (USEPA, 2010a). In 2001, in North America it was estimated that the trade amount of Deca-BDE was 3.5 times larger than Penta-BDE (BSEF, 2003); currently, only the use of Deca-BDE is still allowed in North America. Since Deca-BDE was in use at higher rates, and is still legal to use, there is a higher proportion of BDE-209 in the primary solids stream than the other two congeners. In WBS, BDE-209,-47, and -99 accounted for 35, 22, and 22%, respectively, of total PBDEs (median values). Since WBS is a mixture of biomass and solids retained in the system longer than PS, the relative distribution of congeners may indicate their relative partitioning tendency to biomass. This finding is supported by a study (Langford et al., 2005) that reported a different sorption tendency of diverse congeners onto sludge. In biosolids, the median proportions of BDE-209,-99, and -47 were 47, 16 and 16% of total PBDEs. Comparing different solids, the contributions of these three congeners in PS was different in that in WBS, BDE-209 decreased while BDE-47 and -99 increased. This pattern may have occurred due to the different physical chemical properties of the congeners. On a concentration basis, the PS/WBS ratios for both BDE-47 and -99 were similar at 29:71 while BDE-209’s ratio was 45:55. BDE-209 has very low solubility in organic solvents compared to BDE-47 and -99 (ATSDR, 2004). Therefore, it is presumed that BDE-209 is mainly bond to particulates that are settled in PS while BDE-47 and -99 can be also bond to dissolved colloidal matters that are settled in WBS. Hence, the congeners had different degree of distribution between PS and WBS. This phenomenon is further discussed in Section 3.2. Biosolids are a mixture of PS and WBS; hence, the proportion of BDE-209 increased from WBS while those of BDE-47 and -99 decreased.

Previous studies on PBDEs in WWTP solid streams were mainly focused on the analysis of biosolids (Table S1). Those investigations varied in the number of studied WWTPs (from one to 74) and number of samples (from one to 120). The total PBDE concentrations in these studies ranged from 4.5 to 35,300 ng/g dw (Clarke et al., 2008; De la Torre et al., 2011; Gevao et al., 2008; Knoth et al., 2007; USEPA, 2009; Wang et al., 2007; Yang et al., 2011), indicating variation in regions and sampling strategies. Particularly, total PBDE levels in North America including this study (Hale et al., 2001; North, 2004; Rayne and Ikonomou, 2005; USEPA, 2009) were higher than those in European countries (de Boer et al., 2003; De la Torre...
et al., 2011; Knoth et al., 2007; Ricklund et al., 2008), Australia, and Kuwait (Clarke et al., 2008; Gevao et al., 2008) by one to two orders of magnitude, reflecting greater demand and usage of PBDEs (BSEF, 2003).

For major congeners, levels ranged from 0.2 to 5000 ng/g dw for BDE-47 (Gevao et al., 2008; USEPA, 2009), <0.006 to 4000 ng/g dw for BDE-99 (USEPA, 2009; Wang et al., 2007) and <1 to 22,894 ng/g dw for BDE-209 (Peng et al., 2009; Wang et al., 2007). These three congeners were the most predominant in biosolids. BDE-209 was the highest congener regardless of regional difference. Median values of BDE-209 (or average if unavailable) in national surveys collecting samples from more than 10 WWTPs ranked China (2370 ng/g dw (Yang et al., 2011)) > USA (1163 ng/g dw (USEPA, 2009)) > Canada (891 ng/g dw (this study)) > Germany (393 ng/g dw (Knoth et al., 2007)) > Australia (320 ng/g dw (Clarke et al., 2008)) > Spain (271 ng/g dw (De la Torre et al., 2011)) > Sweden (11 ng/g ww (Öberg et al., 2002)). High levels were detected in places where Deca-BDE products are widely produced and/or imported; for example, in China, the production of this mixture was between 10,000 and 30,000 tons from 2000 to 2005 (Yang et al., 2011). In Canada, only 3000 tonnes of Deca-BDEs entered the market in 2009 (Environment Canada, 2010). This literature review showed that PBDEs in biosolids have been well studied; however, little information was found for PBDEs in PS and WBS (Song et al., 2006; Knoth et al., 2007). Therefore, in order to fully understand the behavior and fate of PBDEs in the solid stream of WWTPs their examination in PS, WBS, and biosolids is essential.

The distribution of PBDE congeners at different stages of the solids stream could be affected by the degradation of PBDEs. Knoth et al. (2007) observed changes in the ratio of BDE-99/BDE-100 in sludges as an indicator of debromination by comparing them to the 84:16 ratio present in commercial formulations (Bromkal 70-5DE). In our study, this ratio was constant at 83:17 for PS, WBS and biosolids, giving no indication of debromination. A comparison in the proportions of BDE-209, 99, and 47 between digested and non-digested biosolids was made, also showing no difference in proportions (p > 0.05). Hence, no debromination during the digestion process was observed. In order to acquire more information about potential debromination during sludge treatment, BDE-202 was analyzed as well. BDE-202’s presence is an indicator of debromination because it is not present in any PBDE commercial mixtures. It was used as a marker of debromination in several studies, where it was not found in sludge (La Guardia et al., 2007), but was reported in biota (La Guardia et al., 2007) and house dust (Stapleton and Dodder, 2008). In our study, BDE-202 was detected in 41 of 75 sludge samples, at concentrations up to 3.3 ng/g and was also detected in four of 30 influent samples at levels of 160 ± 63 pg/L. These results give no clear indication of BDE-202’s appearance due to wastewater treatment; accordingly, it was determined that debromination was insignificant and PBDE level changes due to breakdown were minimal.

### 3.2. Effect factors and distribution coefficients

![Fig. 2 – Distribution of Kd values of PBDE congeners at different sampling locations (A) Kd_p (B) Kd_w (C) Kd_b (percentiles are shown: minimum, 25th, 75th, and maximum. The horizontal line inside the box represents the median).](image)

The effect of environmental and sewershed factors on PBDE concentrations in solids were examined for possible correlations. In general, population did not appear to influence PBDE levels in PS, WBS, and biosolids, showing low Spearman coefficients (−0.1 to 0.2). On the contrary, PBDEs concentration was higher in the plants receiving industrial input and leachate, which is similar to a previous study by Knoth et al. (2007). For instance, plant T had a small community with an industrial site (aviation). Median concentration of PS from plant T was 2500 ng/g (n = 6) higher than the 950 ng/g value at other plants (n = 101) (p = 0.02). In our companion study (Kim et al., 2013), influent concentrations was much higher in plant T than other plants, substantiating the fact that this plant was influenced by industrial input that used PBDEs (BSEF, 2012). Plant N receiving landfill leachate also showed high PBDEs concentration in biosolids (2700 ng/g) that was similar to some
plants with much larger community size (plants M, A, P), possibly indicating the influence of leachate input to the plant.

Temperature effect was pronounced; median PBDE levels in PS at temperatures below 16 °C (770 ng/g, n = 45) were significantly lower than PBDE levels above 16 °C (1460 ng/g, n = 36, p < 0.05). In addition, median PBDE concentrations in WBS below 16 °C were 1300 ng/g compared to 1800 ng/g above 16 °C (p < 0.05). In a companion paper the authors showed higher PBDE concentrations in influent and primary effluent during summer as well (Kim et al., 2013), where the higher PBDE concentrations were due to elevated suspended solids concentrations in influent wastewater during summer. Hence, seasonally higher concentration of suspended solids that carried PBDEs resulted in higher concentrations of PBDEs in PS at higher temperatures. Overall, higher PBDEs concentrations in solids were found in WWTPs with industrial and leachate input, and at temperatures higher than 16 °C.

Due to their high lipophlicity PBDEs are likely to partition to the solids stream (Environment Canada, 2006; USEPA, 2010a). To understand the distribution mechanism of PBDEs, solid—liquid distribution coefficients (Kd) were calculated by dividing PBDE concentrations in solids stream samples (ng/kg) by their respective concentration in liquid stream samples (ng/L). Kd values are often used to understand the fate of emerging compounds (Arvaniti et al., 2012). In the liquid stream, PBDEs ranged from 41,000 to 520,000 ng/L (median 160,000 ng/L) for primary effluent and from 2800 to 270,000 ng/L (median 14,000 ng/L) for final effluent. Detailed concentrations of congeners are summarized in Table S3. Using the large dataset of solid and liquid samples available in the current and previous study (Kim et al., 2013), the Kd (L/kg) values of eight frequently detected PBDE congeners and total PBDEs were calculated in the different stages of wastewater treatment where solids-liquid separation occurred: Kdp from PS and primary effluent, Kdw from WBS and final effluent and Kdb from biosolids and final effluent (Fig. 2). The eight congeners were divided into four lower brominated congeners (BDE-47,-99,-100,-153) and four higher brominated congeners (BDE-206,-207,-208,-209). Different results were obtained for Kdwp, Kdwp and Kdp.

In the case of log Kdwp, median values were statistically different (p < 0.00) for lower (3.7) and higher (4.1) brominated congeners. Comparing different clarification types, chemically-assisted primary treatment showed 0.7–0.8 higher log Kdp values than gravity clarification for both lower and higher brominated congeners (p < 0.00), indicating enhanced separation of PBDEs from the liquid stream in chemically-assisted primary treatment. Different Kdp pattern for lower and higher brominated congeners may be attributed to differences in molecular structure between the two groups of congeners; lower- and higher brominated congeners’ molecular weight ranged between 490 and 640 and 880 and 960 g/mol, respectively. Congeners with higher molecular weights tended to have higher octanol–water distribution coefficients (KOW) (Wania and Dugani, 2003). KOW represents hydrophobicity, which affects Kd values, and their strong correlation was shown in this study (Figure S2A). Examining the influence of molecular weight on Kdp also showed a strong positive correlation (R² = 0.94, p < 0.01) (Figure S2B), indicating that the molecular weight of congeners affects Kdp.

On the other hand, different Kd values may be explained by the different sorption tendencies of the two groups of congeners. The lower Kd of lower brominated congeners indicated that they have a stronger tendency than higher brominated congeners to partition into dissolved and colloidal substances that escape through primary effluent during primary clarification. This observation could be supported by a recent study by McPhedran et al. (2013), reporting the higher partitioning tendency of fewer chlorinated benzene onto colloidal substances despite their lower log KOW. The authors speculated that this phenomenon may be affected by diverse molecular interactions, chemical properties, and characteristics of colloidal substances. In this case, solubility of lower brominated congeners in organic solvents is greater than higher brominated congeners. For instance, solubilities of a Penta- PBDE mixture consisting of lower brominated congeners is 1% in methanol and miscible in toluene while the solubility of Deca-PBDE mixture, consisting of higher brominated compounds, was 0.2% in toluene (ATSDR, 2004). Accordingly, higher solubility of lower brominated congeners may cause a stronger affinity to organic material, such as dissolved and colloidal organic substances; and higher molecular weight congeners have a higher tendency to bind to particulate matter. Therefore, it could be postulated that differences in molecular structure and sorption tendencies of lower- and higher brominated congeners can affect Kdp values.

Moving on, median log Kdwp values were close to 5.2 for all the congeners and median log Kdwp values were 0.1–0.2 higher than log Kdwp. These results indicated that partitioning to solids substantially increased as wastewater moved from primary clarifier to secondary clarifier. This observation was similar to a previous study (Song et al., 2006) where the authors suggested that a substantial amount of PBDEs may bind to dissolved organic solids in influent wastewater, then repartition to suspended solids when dissolved solids are reduced during treatment. The hydrophobic nature of biomass in the bioreactor may also enhance PBDEs partitioning to sludge; hence, PBDEs in the dissolved, colloidal, and particulate phases that escaped from primary clarification were captured by biomass and accumulated in WBS (Langford et al., 2005).

It was observed that Kd values varied widely for each congener (Fig. 2), which could be due to the influence of different operational conditions that affect solid separation from the liquid stream in WWTPs. Accordingly, the potential correlation between different parameters and Kd values were examined (Table S4). Selected parameters for Kdp obtained from gravity primary clarification in secondary/advanced treatment were temperature, hydraulic retention time (HRT), surface loading rate (SLR), total suspended solids (TSS) and chemical oxygen demand (COD) removal efficiency. Spearman coefficients showed that log Kdp for eight PBDE congeners in primary treatment was moderately correlated with HRT, SLR, TSS removal and COD removal (−0.5 or 0.4, p < 0.00) and less moderately correlated with temperature (0.2–0.4, p < 0.05). These findings indicated that longer HRT and lower SLR enhanced solids-liquid separations, resulting in transferring more solids and their attached PBDEs from the liquid stream to solid stream. The degree of solids separation during clarification is indeed a factor for distribution of PBDEs in liquid and solid streams. In the case of Kdp in chemically-assisted primary treatment, temperature, TSS
and COD removal efficiency were selected for comparison, and for COD removal good correlations were found for all eight congeners (0.6, p < 0.00) (Table S4).

With respect to log $K_{dw}$, Spearman coefficients indicated that total PBDEs correlated with HRT (bioreactor + clarifier), mixed liquor suspended solids (MLSS), SRT, TSS and COD removal, ranging from 0.4 to 0.5 ($p < 0.00$). At MLSS concentrations below 2 g/L, median $K_{dw}$ was 4.9 (n = 32) while at MLSS concentrations above 2 g/L it changed to 5.3 (n = 26) ($p < 0.00$). For SRT, the length of solids retention in the system, longer SRTs increase biomass diversity and concentration. SRTs were estimated as described in Kim et al. (2013). Median log $K_{dw}$ was 5.1 for SRT < 9 days (n = 25) and 5.3 for SRT > 9 days (n = 21) ($p < 0.00$) indicating the positive role of SRT on PBDE sorption. Thus, higher concentrations of MLSS and longer SRTs enhance partitioning to WBS, consistent with a previous investigation that studied PBDEs and nonylphenol polyethoxylates (Langford et al., 2005).

Among the parameters selected for log $K_{dw}$, HRT exerted different influences on the two groups of PBDEs. The lower brominated congeners showed a strong correlation (0.6, $p < 0.00$) while the higher brominated congeners had a weaker correlation with HRT (0.3, $p < 0.01$). This difference was not shown in correlations with other parameters. HRT also influenced organic solids removal: TSS and COD removal were lower at HRTs > 10 h compared with higher HRTs ($p < 0.00$). Higher removal of organic solids in the bioreactor and secondary clarifier at longer HRTs led PBDEs to accumulate more in WBS and discharge less through final effluent, resulting in elevation of log $K_{dw}$ values. However the reason for the lower PBDE congeners to be more sensitive to HRT was unclear. They could follow a trend similar to $K_d$ and show different partitioning tendencies over lower and higher brominated congeners. Better removal of lower brominated congeners may require longer HRTs in the bioreactor and secondary clarifier. Our complementary study (Kim et al., 2013) showed that 94% PBDE removal in the bioreactor was achieved at MLSS > 2 g/L, SRT > 9 days, and HRT > 10 h. Hence, MLSS, SRT, and HRT indeed govern PBDE removal by primarily enhancing PBDE sorption onto sludge.

To understand the implication of $K_{db}$ values, log $K_{db}$ was plotted against the proportion of PBDE in biosolids mass loading to total PBDE mass loading in biosolids and final effluent i.e. (biosolids, g/d) × 100/(biosolids, g/d + final effluent, g/d) as presented in Figure S3. This proportion was strongly correlated with log $K_{db}$ values; an $R^2$ value of 0.92 was obtained confirming that higher $K_{db}$ values indicate greater accumulation of PBDEs in biosolids and less PBDEs discharged through final effluent. This strong correlation also indicates that without information on final effluent flowrate and biosolid production rate, estimation of PBDE mass fraction in biosolids and final effluent is possible by using $K_d$ values generated from PBDE concentrations in biosolids and final effluent. Overall, various $K_d$ values and effect factors herein indicate that solids-liquid distribution is dependent on operational conditions of the liquid stream and the degree of organic solids removal.

### 3.3 Effect of sludge treatment on PBDE levels

PS and WBS were combined and treated in order to produce biosolids. In this study, the treatment employed for biosolids production included dewatering, digestion and alkaline stabilization. Biosolids from five plants without digestion showed significantly lower PBDE levels than digested biosolids from ten plants: 1700 ± 1200 ng/g and 2300 ± 990 ng/g respectively ($p < 0.05$). In order to examine the effect of digestion, PBDE levels before and after digestion were compared on a congener basis (Figure S4). “Feed” was a mixture of PS and WBS at an assumed 50:50 mixing ratio, or PS alone entering digestion at plants with a co-thickening stream. “Product” referred to the digested biosolids. The slope of the regression line indicated that PBDEs concentration in biosolids was 1.5 times higher compared to the levels in the feed ($p < 0.05$), suggesting that PBDEs were concentrated during digestion. This observation is similar to Knoth et al. (2007) showing higher PBDE levels in digested biosolids than in PS and/or WBS. This phenomenon could be explained by the substantial reduction of volatile solids (VS) during digestion; PBDE increase (%) was linearly correlated with VS reduction (%) in several plants ($R^2 = 0.9$ and $p < 0.00$) (Figure S5). Therefore, the basis of measurement (ng PBDE per gram dry solids) changed. In our dataset, the median ratios of VS/TS were 0.74–0.77 for PS and WBS, and this ratio decreased to 0.62 after digestion. Thus, PBDEs may be desorbed then repartitioned into the reduced mass of solids. In the literature, PBDE showed a half-life of 700 days in digestion (Gerecke et al., 2006), much longer than the 20 days estimated for 60% VS destruction (Metcalfe and Eddy, 2003). Accordingly, the degradation of volatile solids resulted in the accumulation of PBDEs.

To further examine the fate of PBDEs in digestion, a mass balance was conducted using data from plant C where flow-rate data of sludge feeding to digestion was provided. Mass changes before and after digestion were tracked according to the equation: PBDE mass loading in biosolids (g/d) = PBDE mass loading before digestion (g/d). The mass balance closed at 120 ± 24% ($n = 12$), indicating insignificant mass change during digestion.

Overall, digestion considerably affected the fate of PBDEs on a concentration basis but insignificantly on a mass basis.

Contrary to digestion, PBDE levels in biosolids decreased after alkaline stabilization treatment (Figure S4). Plants F and H1 added lime or alkaline admixture to sludge (typically at 6–43% of dry solids) for pathogen control at a pH of 12 and temperature of 50–60 °C (Metcalfe and Eddy, 2003), which dilutes PBDE concentrations during treatment. Total PBDE concentrations significantly decreased from 2000 ± 630 ng/g to 1100 ± 29 ng/g for plant F and from 1100 ± 170 to 470 ± 99 ng/g in plant H1. The slope of the regression line in Figure S4 indicated that the level of PBDE congeners decreased by 40% after treatment. There was no change in the profile of congeners ($p > 0.05$). In the literature, Clarke et al. (2008) reported that 10% lower PBDEs in biosolids (300 ng/g) than average concentrations in the feed (PS and WBS, 340 ng/g) were reported. Thus, alkaline stabilization appeared to decrease some PBDE levels via dilution. However, it is uncertain whether PBDE decrease occurred through a loss in addition to dilution, and a detailed mass balance to examine this hypothesis was unavailable in this study.

### 3.4 Mass balances in liquid and solids stream

In this study, various examinations in the liquid and solid streams of WWTPs were performed, showing that PBDEs...
significantly partition to solids. In order to address the final fate of PBDEs, mass balances were conducted on different WWTPs operating at various operational conditions. Mass flow was calculated by multiplying total PBDE concentrations with volumetric flow rates for the liquid stream and production rate for biosolids. Analysis of PBDEs mass flow in influent, final effluent and biosolids from thirteen WWTPs are presented in Table S5; PS and WBS were not included due to the absence of flow information. Mass rate significantly decreased when wastewater moved from influent to final effluent, thus in final effluent, mass fraction accounted for 1–45% (median 10%) of influent mass loadings. Lower fractions were seen in secondary/advanced treatment plants compared with primary treatments, indicating greater reduction in the former treatment type. Contrarily, higher PBDE mass flow was found in the solids stream i.e. biosolids vs. final effluent, showing mass fractions of 30–180% (median 110%). To assess detailed changes of mass flow entering and leaving WWTPs, mass balance was calculated using the equation mass balance (%) = (Final effluent, g/d + Biosolids, g/d) / 100/(Influent, g/d). Closure of the mass balance ranged widely from 53 to 190% (median 130%). Median values were close to 100%; this strongly indicated that PBDE loss via degradation or evaporation was insignificant and sorption was the predominant mechanism of PBDE removal. This was in agreement with previous studies (North, 2004; Song et al., 2006). On the other hand, three WWTPs showed less than 60% and greater than 140% removal; this wide variability indicates limitations in the mass balance approach due to different retention times of the liquid and solid streams; PBDEs concentrations in samples taken from the liquid stream were an average of the variability of PBDEs concentration over a day while PBDEs concentration in biosolids, particularly digested biosolids, represented average concentration occurring over three to four weeks.

Our study also conducted more detailed mass balances using PS and WBS from two plants (C and Q) where PS and WBS flow rates were available. Plants C and Q were both secondary activated sludge treatment plants; however, the capacity of plant Q was 15 fold larger than plant C. Mass loading in PS and WBS were computed by multiplying total PBDE levels in PS or WBS by the flow rates of the respective sludge (Figure S6). Mass fractions in primary effluent were around 60% of influent mass loadings, indicating that around 40% of incoming PBDEs were removed during primary clarification. To investigate the possible loss of PBDEs through biodegradation in the bioreactor, mass flow reduction from primary effluent to final effluent was compared to mass flow of WBS using the following equation: (WBS, g/d) × 100/(Primary effluent, g/d – Final effluent, g/d). Results were 87 and 130% for plants C and Q respectively (median 110% of 18 cases) and reflected the inherent variability from sampling and analysis. These results confirmed that the loss of this highly persistent compound through biodegradation was negligible in the bioreactor.

3.5. PBDE burden in land amended biosolids

The mass balances calculated above confirmed that PBDEs substantially contaminated biosolids, which increases the concern for their use in land application. In this study, biosolids from six plants (B, C, T, W, Q, N) were used for land application. Their median total PBDE levels ranged from 1300 ng/g to 2700 ng/g. In the province of Ontario (Canada), the maximum biosolids application rate for grain corn is approximately 12 tonnes/hectare once in five years (Nutrient Management Act, 2002). Thus, PBDE levels in biosolids added to agricultural land in Ontario at the maximum application rate, could be in the range of 16–32 kg/ha, resulting in different exposure concentrations to soil organisms. PBDE levels in biosolids amended soil and earthworms were positively correlated (Sellström et al., 2005). Therefore, PBDEs could potentially accumulate at a higher rate in earthworms living in heavier PBDE burdened land.

4. Conclusions

This study examined factors affecting the variability of PBDE levels in 288 sludge and biosolids samples from 15 WWTPs. Since low variability in PBDE measurement was found for biosolids collected for three consecutive days, future sampling strategies might consider using fewer samples because it does not impact results but may decrease costs. PBDEs levels in sludges primarily consisted of BDE-209, 47 and –99, and were influenced by industrial and leachate input and temperature. Investigation of the fate of PBDEs indicated that debromination was minimal during liquid and solids treatment. Analysis of factors affecting solids-liquid separation as quantified by solid–liquid distribution coefficients indicated that PBDEs partitioning to solids can be optimized through operational conditions i.e. HRT, SLR, MLSS, and SKRT. Particularly, to enhance the sorption of lower brominated congeners, a longer retention time is required. In addition, the fate of PBDEs during digestion and alkaline treatment needs to be considered when biosolids are destined for agricultural land application because this study showed higher and lower PBDE levels during digestion and alkaline treatment, respectively. Through mass balances, sorption was confirmed to be a predominant removal mechanism of PBDEs in different WWTPs. Our findings indicate that PBDE concentrations in biosolids differ amongst various wastewater treatment types, which could result in different environmental loads of PBDEs when biosolids are applied to agricultural land.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2013.08.022.
References


