Parameters affecting the occurrence and removal of polybrominated diphenyl ethers in twenty Canadian wastewater treatment plants

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A R T I C L E   I N F O
Article history:
Received 23 May 2012
Received in revised form 14 December 2012
Accepted 20 January 2013
Available online 6 February 2013

Keywords:
Polybrominated diphenyl ethers
Sewage
Wastewater treatment
Lagoon
Secondary treatment
Operational conditions

A B S T R A C T
This study determined PBDE levels in influent, primary effluent, and final effluent collected from diverse treatment processes including four aerated lagoons, two facultative lagoons, four primary treatments, eight secondary biological treatments and two advanced treatments. Parameters examined for correlation included seasonal temperature, community sizes, industrial inputs, and operational conditions. PBDE levels in influent were 21 –1000 ng/L (median 190 ng/L). Higher concentrations in influent samples were found during summer, and in WWTPs which treated leachate and higher proportions of industrial wastewater vs. residential wastewater. Final effluent levels ranged between 3 and 270 ng/L (median 12 ng/L). Among all congeners, the sum of BDE-209, -47 and -99 accounted for 79 and 71% of total PBDEs in influent and final effluent, respectively, with BDE-209 having the highest proportion. Median removal efficiencies for all process types exceeded 90% except primary treatment at 70%. PBDE levels and removals were correlated to the levels and removals of conventional parameters that represent wastewater strength, such as chemical oxygen demand and total suspended solids. The role of the primary clarifier was significant (w82% removal) and removal was associated with hydraulic retention time (HRT) and surface loading rate. Best removal of PBDEs was achieved at greater than 2000 mg/L mixed liquor suspended solids (MLSS), longer than 10 h of HRT, and 9 days of solids retention time.

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1. Introduction

Municipal wastewater treatment plants (WWTPs) collect and treat wastewater streams containing a variety of pollutants generated from industrial discharges, domestic/commercial wastes, leachate from landfills, and precipitation (Petrovic et al., 2003). They can efficiently remove large proportions of contaminants, including nutrients and biodegradable organics (Metcalf and Eddy, 2003). However, some persistent organic pollutants (POPs) have low removal efficiencies because WWTPs were not originally designed to remove them. Therefore, via effluents and biosolids disposal, WWTPs are a potential point source of POP discharge to the environment (Vogelsang et al., 2006; Clarke and Smith, 2011).

One group of POPs widely detected in the environment is polybrominated diphenyl ethers (PBDEs) (Clarke and Smith, 2011). They are used as additive flame retardants in consumer products such as plastics, textiles, and polyurethane...
foam, because they suppress the spread of fire; and were commercially formulated in three different mixtures: Penta-, Octa- and Deca-BDEs (Alaee et al., 2003). However, they are not bonded to the products, therefore, will be released to the environment during the time that the product is in use. This may be harmful because PBDEs were identified as persistent, bioaccumulative, and toxic, resulting in the development of worldwide regulations. In North America, Octa- and Penta-BDEs mixtures ceased production and use in 2005, while Deca-BDEs will be phased out by 2013 (Environment Canada, 2010b). These regulations will protect the environment from further contamination. However, PBDEs cannot be fully eliminated from the environment because they will continue to be released from in-use products.

The major route of PBDEs’ introduction to the environment is via WWTP effluents. WWTPs receive PBDEs through discharge from manufacturing sites, leachates, and industrial and residential wastewater (Environment Canada, 2010b). However, due to the implementation of regulations, the PBDEs burden from manufacturing sites should be minimal. Furthermore, historically, PBDEs were never manufactured in Canada. Thus, domestic wastewater and leachate are the primary sources of PBDEs to WWTPs. Vaporization from, and wear-out of day to day products containing PBDEs can allow PBDEs to be emitted into the air (Hazrati and Harrad, 2006; Webster et al., 2009). Once released, PBDEs’ high octanol–water coefficients and strong affinity to organic particles assist PBDE attachment to indoor particles such as dust (USEPA, 2010a; Richardson and Ternes, 2011). Then PBDEs are discharged to the sewer system through wash water from contaminated indoor dust, furniture and textiles (Environment Canada, 2010b).

Since WWTPs were not designed to remove PBDEs, their presence can present a challenge for wastewater engineers and operators (Metcalfe and Eddy, 2003). Several studies showed that PBDEs were present in both effluents and sludge, although the levels in effluent were much lower (North, 2004), mainly due to PBDEs’ high partitioning to solids (Rayne and Ikonomou, 2005; Song et al., 2006). This indicates that PBDEs in the liquid stream of WWTPs are generally removed, but the overall fate of PBDEs during wastewater treatment requires more clarity. Previous studies have focused their attention only on PBDE concentrations in a limited number of influent and final effluent samples. However, WWTP performance is strongly affected by environmental and operational parameters such as season, treatment time, and process complexity (Metcalfe and Eddy, 2003). To date, those parameters have not been examined for PBDEs; therefore, the effect of operational conditions on the removal of these compounds is unknown.

In order to investigate the potential relationship between PBDEs removal and operational conditions during wastewater treatment a total of 377 liquid samples was collected from 20 Canadian WWTPs: 145 influent, 86 primary effluent, and 146 final effluent samples, encompassing lagoon, primary, secondary, and advanced treatment processes. Different seasons, configurations, sizes and operational conditions were also studied. To date, this is the first investigation addressing the parameters influencing PBDEs removal using the largest dataset published in the literature. This study offers a comprehensive understanding of the occurrence and removal of PBDEs in various types of WWTPs. A companion paper discusses PBDEs in the solid stream and mass balance during wastewater treatment (Kim et al., submitted for publication).

2. Materials and methods

2.1. WWTPs and sampling

A total of 20 WWTPs participated in this study, representing 15% of the Canadian population, different geographic regions, and widely-used typical wastewater treatment processes. Table 1 summarized the features of these WWTPs that included 4 aerated lagoons (AL), 2 facultative lagoons (FL), 4 primary treatments (PT), 8 secondary biological treatments (ST) and 2 advanced biological nutrient removal treatments (AT). ST processes included conventional activated sludge, trickling filter and biological aerated filter. The 20 plants varied widely in population served (1500–>1,000,000) and flow rate (0.8–>700,000 m³/day). Sampling from all plants was conducted seasonally (summer and winter), constituting three days per season to investigate seasonal differences. Samples from five WWTPs i.e. B, C, J, R, and L were collected during two consecutive project years to study annual variation.

Sampling points included influent wastewater and final effluent for lagoon and primary treatment processes. Primary clarifier effluent was also included for secondary and advanced treatment processes. Samples from final effluents were taken prior to chlorine disinfection in order to reduce potential chemical interferences in sample analysis (plants A, L, P, Q). However, where ultraviolet light (UV) was used for disinfection, effluent samples were collected after UV treatment (plants B, C, E, F, H, R, T, W). All samples were collected as 24 h equal volume composites (400 mL every 30 min) using Hach Sigma 900 refrigerated autosamplers (Hach Company, Loveland CO, USA), kept at 4 °C and transported to AXYS Analytical Services (Sidney, BC, Canada) on ice, by overnight courier, for analysis.

2.2. Sample and statistical analysis

All detailed sample analysis is described in the supporting information. PBDEs were analyzed according to USEPA (2010b) method 1614A. Analyzed data were statistically evaluated by non-parametric methods such as Mann–Whitney test and Spearman coefficients since the datasets were not normally distributed. All statistical analyses were performed using Minitab 16 Software (Minitab Inc., PA, USA).

3. Results and discussion

3.1. Variability in measurement of PBDEs

Because of the relatively small datasets reported to date, there is little information in the literature on the variability in measurement of PBDEs in wastewater treatment systems. Three samples were collected at each WWTP sampling point
Table 1 – Operational conditions of WWTPs.

<table>
<thead>
<tr>
<th>Type</th>
<th>Process characteristics</th>
<th>PC&lt;sup&gt;a&lt;/sup&gt; Population (&lt;1000)</th>
<th>I&amp;C (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Sludge</th>
<th>Flow rate (1000 m&lt;sup&gt;3&lt;/sup&gt;/d)</th>
<th>HRT&lt;sup&gt;c&lt;/sup&gt; (Primary clarifier) (h)</th>
<th>SLR (m&lt;sup&gt;3&lt;/sup&gt;/m&lt;sup&gt;2&lt;/sup&gt;/d)&lt;sup&gt;d&lt;/sup&gt;</th>
<th>HRT (Bioreactor)&lt;sup&gt;e&lt;/sup&gt;</th>
<th>MLSS (mg/L)&lt;sup&gt;f&lt;/sup&gt;</th>
<th>HRT (Final clarifier)</th>
<th>SRT (days)&lt;sup&gt;g&lt;/sup&gt;</th>
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<tr>
<td>Lagoon</td>
<td>D</td>
<td>4.8</td>
<td>0</td>
<td>N/A</td>
<td>N/A</td>
<td>0.5 ± 0.0</td>
<td>0.5 ± 0.0</td>
<td>250 ± 24</td>
<td>220 ± 8</td>
<td>0.4 ± 0.1</td>
<td>0.7 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>LB</td>
<td>7.5</td>
<td>20</td>
<td>N/A</td>
<td>N/A</td>
<td>2.4 ± 0.0</td>
<td>1.7 ± 0.1</td>
<td>40 ± 1</td>
<td>57 ± 4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R</td>
<td>190</td>
<td>10</td>
<td>66</td>
<td>63</td>
<td>2.7 ± 0.1</td>
<td>2.6 ± 0.1</td>
<td>35 ± 1</td>
<td>37 ± 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>44</td>
<td>10</td>
<td>24</td>
<td>28</td>
<td>3.7 ± 0.4</td>
<td>2.7 ± 0.2</td>
<td>20 ± 2</td>
<td>20 ± 2</td>
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</tr>
<tr>
<td></td>
<td>F</td>
<td>75</td>
<td>10</td>
<td>28</td>
<td>40</td>
<td>4.3 ± 0.1</td>
<td>3.1 ± 0.1</td>
<td>17 ± 0.5</td>
<td>37 ± 2</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>500</td>
<td>67&lt;sup&gt;h&lt;/sup&gt;</td>
<td>320</td>
<td>280</td>
<td>5.7 ± 0.4</td>
<td>4.7 ± 0.2</td>
<td>19 ± 1</td>
<td>19 ± 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Q</td>
<td>400</td>
<td>10</td>
<td>28</td>
<td>40</td>
<td>6.8 ± 0.2</td>
<td>5.2 ± 0.1</td>
<td>15 ± 0.5</td>
<td>15 ± 0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>T</td>
<td>374</td>
<td>10</td>
<td>220</td>
<td>150</td>
<td>2.8 ± 0.2</td>
<td>3.1 ± 0.2</td>
<td>24 ± 1</td>
<td>24 ± 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>900</td>
<td>40</td>
<td>420</td>
<td>690</td>
<td>1.8 ± 0.3</td>
<td>0.1 ± 0.1</td>
<td>37 ± 0.7</td>
<td>60 ± 3.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>800</td>
<td>15</td>
<td>380</td>
<td>330</td>
<td>3.3 ± 0.6</td>
<td>2.3 ± 0.5</td>
<td>59 ± 2</td>
<td>59 ± 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>E</td>
<td>65</td>
<td>20</td>
<td>34</td>
<td>34</td>
<td>2.8 ± 0.2</td>
<td>2.9 ± 0.6</td>
<td>32 ± 1.7</td>
<td>33 ± 1.7</td>
<td>16 ± 2</td>
<td>16 ± 2</td>
</tr>
</tbody>
</table>

N/A = not available.

a PC denoted plant code.
b I&C denoted industrial and commercial inputs.
c HRT denoted hydraulic retention time (mean of 3 days’ flow).
d SLR denoted surface loading rate calculated by flow rate divided by surface area of clarifier (m<sup>2</sup>/days).
e Plant A includes trickling filter and contact tank, plant L includes carbonaceous removal and nitrogen removal zone, plants B and E include all compartments (anaerobic, anoxic, and aerobic).
f MLSS denoted mixed liquor suspended solids concentration and the level in plant A was in contact tank.
g SRT denoted solids retention time, and plants E, Q, and T provided this information. For plants where the information was not given, SRT was estimated using known parameters (Metcalf and Eddy, 2003) i.e. influent and effluent organic strength, hydraulic retention time in bioreactor tank, mixed liquor volatile suspend solids (MLVSS) concentrations and published kinetic and stoichiometric coefficients. X = Y(S – S<sub>c</sub>/1 + b<sub>c</sub>θ/θ<sub>0</sub>) where: X = MLVSS (mg/L), Y – yield coefficient (0.45 mg VSS/mg COD), b – decay coefficient (0.05/d), S – effluent COD (mg/L), S<sub>c</sub> – influent COD (mg/L), θ<sub>0</sub> – SRT (days), θ – HRT (days). MLVSS concentrations accounted for 62-87% of MLSS concentrations, which were not shown in the table.
h Inflow and infiltration was included at 54% and there might be a significant dilution effect.
during each season for this study. Treating these samples as triplicates gives a strong indication of the variability in the system, including flow, concentrations, and analytical method. There was some overall variability in total PBDE levels, with a median relative standard deviation (RSD) of 18% across all samples at all WWTPs (n = 128 trios of results). There were 14 instances of RSD >50% (11% of the overall dataset). Based on these results the general variability in sampling and measurement of total PBDEs in wastewater is less than 50%.

3.2. Influent and effluent characteristics

All detailed information on PBDE concentrations and conventional parameters are summarized in Table S2. Among 46 congeners analyzed, 31 congeners frequently detected were taken into account to calculate total PBDEs. The remaining congeners showed 65–100% non-detection frequencies. Influent and final effluent levels of PBDEs are presented in Fig. 1a. The concentrations of PBDEs entering Canadian WWTPs have very wide ranges, with values from 21 to 1000 ng/L (median 190 ng/L), while PBDEs levels in effluents were much lower, ranging from 3 to 270 ng/L (median 12 ng/L). Influent levels were generally higher in summer than in winter (median 210 ng/L vs. 170 ng/L, p < 0.01) and may be related to influent total suspended solids (TSS) since PBDEs are likely to adsorb to organic compounds and TSS concentrations were also higher in summer (median 140 vs. 120 mg/L, p = 0.01). In addition, plant T’s influent consists of 80% wastewater from industrial sources, and it presented the highest concentration of PBDEs (median 440 ng/L), despite the small population. Plant N also showed a median influent level
similar to plant T, 430 ng/L in summer, probably due to its receipt of leachate from a municipal landfill. Annual variations in five plants were examined and no significant variations were observed \( (p > 0.05) \). Therefore, PBDEs occurrence was affected by season, industrial input and population.

A review of previous studies \( (\text{Table S3}) \) showed total PBDEs in influents and effluents ranging from 8 to 310 ng/L and from 0.07 to 36 ng/L, respectively. Median levels in this study were higher than levels in Sweden \( (\text{Ricklund et al., 2008}) \), Australia \( (\text{Clarke et al., 2010}) \) and Norway \( (\text{Vogelsang et al., 2006}) \) by one or two orders of magnitude. Similar concentrations were previously observed in WWTPs from USA \( (\text{North, 2004}) \) and Canada \( (\text{Rayne and Ikonomou, 2005; Song et al., 2006}) \).

The concentrations of major PBDE congeners in influent and final effluent were summarized in Fig. 1b. Among the 46 congeners, BDE-209, -47 and -99 were the most prevalent, accounting for 79% and 71% of total PBDEs in influent and final effluent respectively, with BDE-209 being the highest at 39% and 26%, respectively. The congeners BDE-100, -207, -206, -208, -153 and -154 accounted for 15–16% of total PBDEs at both sampling points. The proportion of BDE-209 in influent was close to 37% similar to the results reported in a previous study in Canada by \( \text{Rayne and Ikonomou (2005), however, substantially lower than 81% reported in a study in China where BDE-209 production was dominant (Peng et al., 2009).} \)

The congener profile in influent reflected the extensive use of products containing Deca-BDE in Canadian residences where BDE-209 is the predominant congener \( (98\%) \). Similarly, BDE-99 and -47 accounted for up to 87% in the Penta-BDE formulation which was phased out in Canada in 2006 \( (\text{Environment Canada, 2010b}) \). In contrast, the principal congeners of the banned Octa-BDE, namely BDE-183 and -203 accounted for less than 1% of PBDEs in influent implying that Octa-BDE was not used at high amounts. According to \( \text{BSEF (2003)} \) the market demand of Deca-, Penta-, and Octa-BDE formulations in North America in 2001 was 24,500, 7100, and 1500 MT, respectively. Hence, the different market demand and regulatory impacts of the three formulations were reflected in the different proportion of congeners in wastewater.

Seasonally, BDE-209 in influent was higher in summer than in winter at 44% vs. 36% median levels respectively \( (p < 0.05\), data not shown), possibly due to high log octanol–water partition coefficient \( (K_{ow}, \text{reportedly up to } 13) \) \( (\text{Environment Canada, 2010a}) \) and higher TSS levels during the summer. The distribution of congeners in effluent was similar to influent: however, among these three major congeners, BDE-209 proportion decreased in effluent \( (p < 0.05) \) while there was a noticeable increase in BDE-47 \( (p < 0.05) \) and a slight change in BDE-99. This could be due to the degradation of BDE-209 and/or shifts in partitioning of the congeners. On the other hand, PBDEs are known to be slowly degradable chemicals \( (\text{Gerecke et al., 2006}) \), thus a 7% (median level) drop might not be due to the breakdown of BDE-209. Rather, it could be associated with its higher tendency of partitioning to particles than other congeners due to its aforementioned physicochemical properties. The proportion of BDE-47 in effluent was slightly higher than BDE-99 even though their distribution in influent was similar. It may also be related to a slightly higher log \( K_{ow} \) value in BDE-99 than BDE-47 \(-7.7\) vs. 6.8 \( (\text{Palm et al., 2002}) \).
In some cases, ice formation reduced oxygen supply by wind and sunlight access, causing proliferation of algae (Web-1, 2012). In this study, the two plants were covered by ice and snow during winter samplings. In plant LB, the effluent was greenish with a noticeable odor and TSS and COD removal were also lower than in summer samples by 10 and 26% on a median level, respectively, possibly resulting in lower PBDE removal.

In plant S no excessive algae growth was observed; however, TSS levels in effluent were four-fold higher in winter than in summer, and PBDE levels were also three times higher. The temperature of the final effluent was extremely low for microorganism activity at $-3^\circ C$, and COD level in the effluent was 1.5 times higher than the level in summer, indicating that biological degradation was likely minimal. Therefore, the organic substances holding PBDEs remained in the effluent.

Contrary to the other lagoon WWTPs, plant D did not show good PBDE removal in summer. This plant was not well maintained: several mat aerators were not functioning, and there was excessive plant growth around the lagoon cells. In general, the results of this study indicated that lagoon processes were effective at removing PBDEs from municipal wastewater; however, it was not appropriate to compare among plants because they have different operational conditions. Plants N and U have conventional primary treatment with chemical coagulation and plants M and H employ lamella settling while plant H uses a high rate removal process featuring enhanced particle settling. Plants operating at significantly different HRTs between two sampling campaigns showed 13–54% higher PBDE removal and 11–41% higher TSS removal at longer HRTs. Plant M achieved the highest removal efficiencies at 93%. The main feature of this plant was the use of lamella settlers. This technology increases surface loading rates and reduces turbulence which reduces resuspension of settled particles (Droste, 1997). Thus, lamella settlers appeared to enhance PBDE removal efficiencies with TSS removal.

The four plants were operated at broad ranges of SLR (Fig. S1). This figure indicates better PBDE removal in plants H and M, which have a high rate SLR process and lamella settlers compared with plants that do not (plants U and N). Plant H effectively removed 60–90% of influent PBDEs at short HRTs of 20–47 min and wide ranges of SLR from 620 to 1500 m$^3$/m$^2$/d. This was similar to plant U’s performance at HRT of 2.5–2.8 h and SLR of 34–39 m$^3$/m$^2$/d. Therefore, PBDE removal in primary treatment can be optimized by the use of lamellar settlers.

### 3.4.3. Effect factors for PBDE removal in secondary and advanced treatment

#### 3.4.3.1. Primary clarifier (HRT, SLR)

PBDEs removal in ten secondary/advanced biological treatment processes was 93% on a median basis. These types of plants have more complexity in configurations than lagoon and primary treatment plants, i.e. primary clarification followed by a bioreactor and final clarifier. The removal contribution of the primary...
clarifier ranged widely from ~250 to 82% with a median value of 34%, indicating that primary clarification can contribute a significant degree to total PBDE removal. However, in some cases PBDE levels increased in primary effluent. This may be due to inadequate solids separation since TSS removal efficiencies in primary clarifiers also showed removals ranging from ~110% to 83% (median 45%). Inadequate clarification can be caused by short circuiting, temperature differences, wind effects and short retention time at elevated flow rates (Metcalfe and Eddy, 2003). The influence of HRT and SLR on PBDE removal was presented in Fig. S2. The obtained removal efficiencies were compared with the respective HRTs, which ranged from 1.1 to 7 h. At HRTs below 3.5 h, respective median values were 27% for PBDEs removal, and 41% for TSS removal. For HRTs above 3.5 h, these values were 48% for PBDEs, and 55% for TSS removal; this indicates that longer HRTs can enhance both TSS and PBDE removal. SLR ranged between 9.3 and 74 m³/m²/d; at SLRs below 25 m³/m²/d, the median value of PBDEs removal was 48% in comparison to 22% at SLRs greater than 25 m³/m²/d. TSS removal also decreased at higher SLRs. Therefore, a lower SLR was associated with higher removal of TSS and PBDEs in the primary clarifier. The relationship between PBDEs and HRT, SLR, and TSS was also confirmed by Spearman coefficients of 0.52, −0.58, and 0.60 respectively (p < 0.01). Our results demonstrated that optimized operation of the primary clarifier would be a first step in optimizing removal of PBDEs in secondary and advanced treatment.

3.4.3.2. Bioreactor and secondary clarifier (MLSS, HRT, SRT, system type). PBDEs removal efficiencies between primary and final effluent were calculated to study the factors affecting this process after primary clarification (Table 2). Temperature, solids retention time (SRT), HRTs of bioreactor and final clarifier, TSS removal, and MLSS in bioreactor were chosen as potential factors affecting PBDEs removal. Spearman correlation coefficients showed stronger relationship for MLSS (0.68), TSS removal (0.56), HRTs of bioreactor and final clarifier (0.5), SRT (0.39) and temperature (0.32) (p < 0.01). These correlation values indicated that MLSS was the most significant factor influencing PBDE removal. At MLSS concentrations below 2000 mg/L, PBDE removal efficiency was 77 ± 18% while at MLSS concentrations above 2000 mg/L, the removal increased to 95 ± 3%. However, in cases of MLSS less than 2000 mg/L, a co-effect of HRT on PBDE removal was observed. HRTs ranged from 4.6 to 25 h (2–17 h in the bioreactor alone) and when HRT was longer than 10 h the median PBDE removal was 13% higher. In contrast, at MLSS of 2000 mg/L and higher, HRT effect was insignificant. This is the first report on MLSS and HRT’s effect on PBDE removals in a full scale field study of WWTPs.

In addition to HRT and MLSS, there was also an effect of SRT on PBDE removal in the bioreactor (data not shown). SRT is the mean residence time of microorganisms in the bioreactor controlled by the sludge wastage rate, determining the type and enrichment of microorganisms retained in the bioreactor. SRT was estimated using measured organic strength and reported kinetic values (Metcalfe and Eddy, 2003) as shown in Table 1, SRTs ranged from 3 to 18 days. Higher and more consistent PBDEs removals were observed at SRTs of 9+ days, compared to shorter SRTs (p = 0.06). Hence, based on our observation the optimum operational conditions to achieve best PBDE removal in bioreactors and secondary clarifiers is to start from 2000 mg/L of MLSS, 10 h of HRT and 9 days of SRT. These conditions also showed optimum COD and TSS removal.

Regarding the fate of PBDEs in bioreactors, most compounds likely partitioned to MLSS whereas volatilization and degradation of PBDEs was probably minimal due to their low Henry’s Law constant (<10⁻⁴ atm m³/mol) and persistence to biodegradation (USEPA, 2010a). Our data showed that PBDEs removal (mg/L) in bioreactor and final clarifier was correlated with TSS removal (mg/L), (R² = 0.4, p < 0.00) (Fig. S3a), supporting the concomitant removal of PBDEs and particulate solids. In addition, PBDEs mass removal (g/d) in the bioreactor and final clarifier was linearly correlated with PBDE load (g/d) to the bioreactor (R² = 0.99, p < 0.00) (Fig. S3b). The strong correlation in the linear zone over the ranges of low and high loading supported the PBDE removal through sorption rather than biodegradation.

To further understand the sorption to MLSS during treatment, the relationship between MLSS level (mg/L) (x) and the mass of PBDE removed per unit mass of MLSS and per unit HRT (ng/mg h) (y) was examined. The regression equation was LN(y) = −1.3 × LN(x) + 12 showing that PBDE levels decreased with the increase in MLSS (R² = 0.63, p < 0.01). Most likely, this pattern occurred because the sorption capacity of MLSS might be enhanced with MLSS level increase, providing excess capacity to sorb available PBDEs. Longer SRT also promotes the growth of different kinds of microorganisms than shorter SRT. Similar to this study, Langford et al. (2005) observed that better PBDE partitioning occurred at higher MLSS and longer HRT in a batch test at different levels of MLSS (2.6–22 g/L) and two different retention times of 10 min and

| Table 2 – The effect of MLSS concentrations and HRT in bioreactors and secondary clarifiers on PBDE removal. |
|---------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| PBDE removal (%)a               | MLSS (<2000 mg/L) | MLSS (2000–7000 mg/L) |
| HRTs b                         | Count | Median (%) | Average (%) | Stdev (%) | Count | Median (%) | Average (%) | Stdev (%) |
| ~25 h                          | 34    | 83b        | 77           | 18        | 28    | 95d        | 95           | 3         |
| ~10 h                          | 13    | 70a        | 70           | 14        | 4     | 93e        | 93           | 2         |
| 10–25 h                        | 21    | 88f        | 82           | 19        | 24    | 95h        | 95           | 3         |

Statistical differences between c and d and between e and f were significant (p < 0.05) but between g and h were insignificant (p > 0.05).  

a. PBDE removal efficiencies were calculated based on the level of primary effluent and final effluent.  
b. HRTs were summation of retention time in bioreactor and final clarifier.
7 h. The authors also suggested that longer SRT could enhance PBDE partitioning since MLSS levels increased and the sludge surface became more hydrophobic, conducive to more adsorption of PBDEs. Agreement between these lab and field studies supports the relationship among MLSS, HRT, SRT, and PBDE removal. Overall, the predominant mechanism of PBDEs removal in bioreactor was most likely partitioning to the biomass floc. In a follow-up paper (Kim et al., submitted for publication), detailed mass distribution of PBDE in liquid and solids stream will examine the removal of PBDEs in the liquid treatment train.

3.4.3.3. Comparison of different secondary and advanced treatment processes. Types of secondary treatment processes in our study included conventional activated sludge, trickling filter, and biological aerated filter. Plant L operated a nitrifying biological aerated filter at shorter HRT than six activated sludge processes (plants C, F, P, T, W, Q) i.e. 2.3 vs. 8.0 h on average (bioreactor only). Average total PBDE removal efficiency of plant L was 90% with 0.55 of removal fraction in primary clarifier, indicating that this played a large role in PBDE removal. The trickling filter/solids contact process at plant A ran at relatively short bioreactor HRTs of 4 and 2.5 h summer and winter, respectively and MLSS concentrations in the contact tank of 1300 ± 100 mg/L for both seasons. Total PBDE removal was different at 89 and 69% for summer and winter, respectively. The deterioration in winter operations was associated with failure in primary clarification showing −110% to 8% removal efficiencies, possibly due to the decrease in clarifier HRT (from 1.8 to 1.1 h on average) and temperature (from 21 to 9 °C on average) causing poor settling. These results indicated that biological aerated filter and trickling filter processes can achieve good overall PBDE removal with good operation of the primary clarifier. Since it is operated by MLSS and SRT, the activated sludge process has been analyzed above.

Advanced treatment processes (biological nutrient removal plants B and E) outperformed other processes. These processes had 3–4 compartments, each with different microbial conditions (anaerobic–anaerobic–aerobic bioreactor for plant B and anoxic–anaerobic–anoxic–aerobic bioreactor for plant E) that are suited for the growth of diverse microorganisms at longer HRT and SRT than secondary treatment processes. These two plants achieved excellent overall removal efficiencies averaging 96%. The HRTs of both plants were similar at 21 h in the bioreactor and final clarifier, while average MLSS level of all compartments were different at 5600 mg/L for plant B and 2000 mg/L for plant E. Therefore, longer total HRT and/or higher MLSS, and the biological diversity may contribute to higher removal of PBDEs in advanced treatment.

This study analyzed the correlations between PBDE removal and environmental/operational parameters. For statistical analysis, PBDE removal efficiency was used to normalize different removal performances obtained from various operational conditions, facilitating statistical comparisons between the removal and parameters. The good correlation between PBDE removal efficiencies and the examined parameters is useful information for wastewater engineers and facilities to estimate the removal of this compound based on patterns of organic solids and operational conditions. We also examined correlations between mass removal rate of PBDE and operational parameters as listed in Table S4; however, little significant relationships were exhibited, possibly requiring a further designed study for the information.

4. Conclusions

This study investigated environmental and operational parameters affecting the occurrence and removal of PBDEs in various WWTPs. PBDEs predominantly consisting of BDE-209, -47, -99 in influent were higher in summer due to higher organic solids content in wastewater during this season. Considerable detection of two phased-out congeners i.e. BDE-47 and -99 in influent wastewater indicated the continual emission of the compounds from their applied products to the environment. The profile of PBDE congeners in the influent provides a reference point for future PBDE monitoring in wastewater to evaluate the effectiveness of prohibition risk management measures over time. PBDE levels correlated well with TSS and COD levels, indicating that the fate of PBDEs were associated with the organic and solids removal. To optimize PBDE removal, lagoons require more attention for winter operation and primary treatment plants require operation at sufficient retention time and/or surface loading rate for enhancing solids removal and consequent PBDE removal. To maximize PBDE removal in secondary/advanced treatment plants, optimized hydraulic retention time and solids loading rate of the primary clarifier would be a first step for achieving high removal. Significant reduction can be achieved under these operational conditions in bioreactors; MLSS >2000 mg/L, HRTs >10 h and SRTs >9 days. The highest removal in all plants was obtained at longer retention time and higher MLSS in advanced treatment process. The primary removal mechanism is sorption to solids, as opposed to biodegradation or volatilization; therefore optimization of removal from the liquid train will maximize PBDE concentrations in the solids streams. Kim et al. (submitted for publication) examines the solids treatment aspect of this study.

Acknowledgments

The authors would like to thank the WWTPs that granted access for this study, Timothy Ng, Laura Kinsman, Sam Dith, and Scott Dunlop for extensive assistance with field sampling, AXYS Analytical Services Ltd for PBDE analysis and Environment Canada’s Chemicals Management Plan. Mingu Kim & Paula Guerra thank NSERC for post-doctoral funding.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2013.01.031.


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