Assessing Surface Sediment Contamination by PBDE in a Recharge Point of Guarani Aquifer in Ribeirão Preto, Brazil

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Abstract: Polybrominated diphenyl ethers (PBDEs) are used as flame retardants in several products, although they can act as neurotoxic, hepatotoxic and endocrine disruptors in organisms. In Brazil, their levels in aquatic sediments are poorly known; thus, concerns about the degree of exposure of the Brazilian population to PBDEs have grown. This study aimed to quantify the presence of PBDEs in sediment samples from an important groundwater water supply in Ribeirão Preto, Brazil, and to contribute to studies related to the presence of PBDEs in Brazilian environments. Gas chromatography coupled with Electron Capture Detection (GC-ECD) was used for quantification after submitting the samples to ultrasound-assisted extraction and clean-up steps. Results showed the presence of six PBDE, BDE-47 being the most prevalent in the samples, indicating a major contamination of the penta-PBDE commercial mixture. The concentration of $\Sigma$PBDEs (including BDE-28, -47, -66, -85, -99, -100, -138, -153, -154 and -209) varied between nd (not detected) to 5.4 ± 0.2 ng g$^{-1}$. Although preliminary, our data show the anthropic contamination of a direct recharge area of the Aquifer Guarani by persistent and banned substances.

Keywords: PBDE; sediment; Guarani aquifer; persistent organic pollutants; flame retardants

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of pollutants that has gained notoriety in recent decades due to their increased level in biotic and abiotic samples, not to mention several “in vitro” and “in vivo” assays that have evidenced their potential to cause damage [1–7]. PBDEs belong to the group of brominated flame retardants (BFRs) that were introduced in the 1970s as an alternative to other banned flame retardants such as polychlorinated biphenyls (PCB) and polybrominated biphenyls (PBBs) [8,9].

PBDEs are applied as a security system to retard, suppress, or inhibit the combustion process, thereby reducing risks of fires [9–11]. They are used in electronic devices like televisions and computers, circuit boards, cables, automotive components, and construction materials; they are also employed in the textile industry [12,13]. The chemical structure of PBDEs comprises of two phenyl rings linked by an ether bond, which enables up to 10 substitutions with bromine and leads to up 209 congeners with...
distinct physicochemical characteristics, depending on the order of chemical bromine substitution [2,14]. These compounds are also considered harmful persistent organic pollutants because they are little soluble in water, have high octanol-water partition coefficient ($K_{ow}$), can persist in the environment, can accumulate in living organisms [15], and have shown toxicity to several organisms.

Dispersion of these compounds in the environment is aggravated by their weak chemical interaction with the surface of polymers, which facilitates their removal from manufactured products as well as their volatilization and dust formation during the use of treated products [8]. Their lipophilicity and persistence contribute to their accumulation in biota, soil, air particles, sewage, aquatic particles, sediments, and food [12,16]. PBDEs have been detected even in polar regions due to transport mechanisms in different trophic systems [17–19].

Once released into the environment, PBDEs can accumulate in house dust and food, and they can be biomagnified along the food chain [20–24]. Therefore, humans may be exposed to PBDEs when they inhale dust [22,25] and/or ingest contaminated food. The absorption of PBDEs is worrisome because these compounds are endocrine disrupting chemicals [26,27] and can thus lead to several diseases of the endocrine system [28,29]. There have also been evidences of their neurotoxicity [30–32] and hepatotoxicity [5–7]. The toxic effects of PBDEs to humans and other organisms are related to the original substances and also to their metabolites, such as OH-PBDEs, that are formed by their metabolization by cytochrome P450s enzymes [33–35].

Levels of PBDEs ranging from 0.04 ng g$^{-1}$ to 527,000 ng g$^{-1}$ have been found in sediment and dust [36–40]. Such levels depend on factors that include local anthropogenic activities, presence of degrading microorganisms, and environmental photodegradation [41–43].

The use of PBDEs has been restricted and/or prohibited in parts of the world, such as Europe Union, United States of America, Japan and Australia and some congeners banished by the Stockholm Convention on persistent organic pollutants (POPs), a convention aiming to protect human health and the environment from POPs. However, there are no restrictions on the use of PBDEs in other locations, such as Brazil, even though the country has already ratified its signature to the convention, which has culminated to exposure to unknown concentrations of PBDEs in different regions [44]. Currently, knowledge of the levels of exposure to PBDEs in Brazil are limited because there are few reports about their presence in abiotic and biotic samples [2,11,45].

In Brazil, some sites are interesting targets to evaluate the level of environmental contamination with PBDEs. For example, the city of Ribeirao Preto in Brazil is located on a recharge area of the Guarani Aquifer, a groundwater reservoir that supplies all the drinking water to the city [46] However, this area is vulnerable to pollution due to the presence of strong agro-industrial activities in the region that are able to release many toxic substances into the environment, consequently affecting the quality of water and sediments [47–50]. In this context, the presence of PBDEs in sediments from the Saibro Lagoon, a recharge point of the Guarani Aquifer in the city of Ribeirao Preto, is a matter of concern and the object of the present investigation.

2. Experimental

2.1. Chemicals and Reagents

All the reagents were of analytical grade or higher purity. Acetone, n-pentane, and isoctane were pesticide grade, acquired from Tedia (Fairfield, CT, USA). Anhydrous sodium sulfate and silica gel 60 (0.05 to 0.2 mm) were purchased from Vetec (Rio de Janeiro, Brazil). The Lake Michigan Study standard (BDE-LMS) containing BDE-28, -47, -66, -85, -99, -100, -138, -153, and -154 was purchased from AccuStandard (New Haven, CT, USA). A 10 µg mL$^{-1}$ stock solution, prepared in isoctane was used to prepare working solutions (0.01, 0.1, 1.0, 5.0, 10.0, and 20.0 ng mL$^{-1}$) for the analytical curves. The 50 µg mL$^{-1}$ BDE-209 standard prepared in isoctane/toluene (9:1 v/v) was also obtained from AccuStandard and used to prepare appropriate working solutions. Quantification was carried out by
external calibration curves. Figure 1 shows the structure of the 10 PBDEs investigated in this work that are also among the main congeners investigated in environment and biological fluids.

![Structures of the 10 polybrominated diphenyl ethers (PBDEs) investigated in this work](image)

**Figure 1.** Structures of the 10 polybrominated diphenyl ethers (PBDEs) investigated in this work.

### 2.2. Study Site and Sampling

This work was carried out in the city of Ribeirao Preto, located in the northeastern portion of the State of Sao Paulo, Brazil. It is typically urban, and its activities are focused on trade, services, and sugarcane culture. Its climate is tropical humid, but the weather is dry in winter, when we collected the samples. Samples of surface sediment of Saibro Lagoon were collected in accessible points as can be seen in Figure 2.
Figure 2. Map of the sampling site. In the bottom left, the red circle indicates the location of sampling points in the Saibro Lagoon.

Samples were collected in June 2014 using a cylindrical corer. The obtained sediment pellet was packaged in clean amber glass bottles and stored in a refrigerator at a temperature below 4 °C until further preparation steps. Dry sediments were obtained by transferring portions of the samples to Petri dishes that were capped individually with aluminum foil to prevent cross contamination. Then, small holes were made in the cover foil to allow water to evaporate under room temperature (25 °C). Petri dishes were set in an exhaust hood and allowed to rest for 48 h.

2.3. PBDE Extraction and Quantification

The sediment was analyzed according to a method described and validated by Annunciação et al. [51]. Briefly, 3000 g of dried sediments and 10 mL of the extraction solvent mixture (acetone/n-pentane, 1:1 v/v) were transferred to glass tubes. Tubes were sealed, agitated for 30 s and suspensions were sonicated in a Cole-Parmer 8893 bath (Vernon Hills, IL, USA) operating at 40 kHz for 5 min at 25 °C and centrifuged (Kindly, KC5, São Paulo, Brazil) for 5 min at 1000× g. Then, the supernatant was transferred to a 250 mL flat-bottomed flask. The remaining solid fraction was
submitted to ultrasonic extraction four more times, to produce a final composite extract. Isooctane was added as solvent keeper (1.0 mL), and the extract volume was reduced to approximately 2 mL in a rotary evaporator (Fisatom 801, São Paulo, Brazil). Interferences were minimized by eluting the extract with 50 mL of n-pentane through a 30-cm column filled with acid, basic, and neutral silica gel (3 g, 2 g, and 3 g, respectively) as well as with anhydrous sodium sulfate between the silica gel phases. Details on the preparation of the silicas are available elsewhere [51]. After re-concentration to 1.0 mL of the keeper, the extracts were treated with copper strips to avoid interference of sulfur species during the quantification of the analytes. Finally, in order to improve detectability, extracts volume was reduced to 0.25 mL in a gently flow of N₂.

The content of PBDEs in the final extracts was assessed by gas chromatography with an electron capture detector (Shimadzu GC 2010 Plus, Kyoto, Japan). The PBDEs were separated with a Zebron ZB-XLB-HT (15 m × 0.25 mm × 0.25 µm, Agilent Technologies, Santa Clara, USA) chromatographic column for BDE-209 and with a SLM TM-5ms column (30 m × 0.25 mm × 0.25 µm, Supelco, Bellefonte, PA, USA) column for the less brominated congeners. The PBDEs were quantified by external calibration in triplicate. Limits of detection (LOD) were calculated by the signal-to-noise approach where ratios of three corresponded to LOD. Table 1 summarizes selected analytical parameters of the method.

<table>
<thead>
<tr>
<th>Congeners</th>
<th>Retention time/min</th>
<th>LOD/(ng g⁻¹) b</th>
<th>LOQ/(ng g⁻¹) c</th>
<th>Recovery%/ d</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDE-28</td>
<td>28.1</td>
<td>0.14</td>
<td>0.48</td>
<td>98.5 ± 2.5</td>
</tr>
<tr>
<td>BDE-47</td>
<td>33.1</td>
<td>0.15</td>
<td>0.52</td>
<td>98.2 ± 4.3</td>
</tr>
<tr>
<td>BDE-66</td>
<td>34.1</td>
<td>0.17</td>
<td>0.57</td>
<td>97.8 ± 4.7</td>
</tr>
<tr>
<td>BDE-85</td>
<td>40.4</td>
<td>0.17</td>
<td>0.58</td>
<td>92.9 ± 6.0</td>
</tr>
<tr>
<td>BDE-99</td>
<td>38.0</td>
<td>0.2</td>
<td>0.67</td>
<td>97.9 ± 6.0</td>
</tr>
<tr>
<td>BDE-100</td>
<td>36.9</td>
<td>0.17</td>
<td>0.57</td>
<td>97.6 ± 6.5</td>
</tr>
<tr>
<td>BDE-138</td>
<td>45.6</td>
<td>0.24</td>
<td>0.80</td>
<td>89.8 ± 2.8</td>
</tr>
<tr>
<td>BDE-153</td>
<td>43.0</td>
<td>0.21</td>
<td>0.72</td>
<td>90.5 ± 4.5</td>
</tr>
<tr>
<td>BDE-154</td>
<td>41.4</td>
<td>0.17</td>
<td>0.57</td>
<td>92.4 ± 7.1</td>
</tr>
<tr>
<td>BDE-209</td>
<td>23.5 a</td>
<td>0.14</td>
<td>0.48</td>
<td>94.2 ± 5.3</td>
</tr>
</tbody>
</table>

a In a single component analysis using a 15 m chromatographic column, b method limit of detection, c method limit of quantification, d for a fortified (5.0 ng g⁻¹) blank sediment (n = 7).

It is important to point out that the analytical method was previously validated [51] using fortified blank sediments and a certified reference sediment (RTC-SQC072) supplied by RTC (Laramie, WY, USA) containing PCBs. In this case, intraday recoveries (n = 7) varied from 89.8 ± 2.8% (BDE-138) to 98.5 ± 2.5% (BDE-28), as shown in Table 1, and inter-day recoveries (n = 9) varied between 87.7 ± 6.6% (BDE-138) and 98.7 ± 1.4% (BDE-28).

3. Results and Discussion

Figure 3 shows the chromatograms obtained during the determination of the less brominated congeners in the sediment samples.
In Figure 3 it is possible to observe that PBDE were detected only in the samples collected in Points 2 and 3. The sample collected at Point 1 did not present detectable concentrations of PBDEs probably due to the texture of the collected material, which consisted mostly of sand with naturally low specific surface area. Also, during the clean-up step, it was possible to notice that this sample presented small quantities of organic carbon, which may contribute to the fixation of PBDE in the sediment matrix. Furthermore, it was already shown that both the size of the grains and the content of organic matter can influence the absorption and accumulation of PBDEs in the sediments [52].

Chromatograms for the sediment samples from Points 2 and 3 revealed distinct analytical signals for the investigated PBDEs. However, in both cases, it is possible to notice that peaks height were near the chromatographic noise, revealing that low levels of PBDE were detected in the samples. Chromatograms did not reveal the presence of BDE-209 during the single component analysis. Table 2 lists the concentration of the investigated PBDEs in the sediment samples.
Table 2. Concentrations (ng g$^{-1}$ dry weight) of the investigated congeners in the sediment samples collected at the Saibro Lagoon.

<table>
<thead>
<tr>
<th>Congeners</th>
<th>Point 1</th>
<th>Point 2</th>
<th>Point 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDE-28</td>
<td>nd</td>
<td>0.68 ± 0.04</td>
<td>0.58 ± 0.03</td>
</tr>
<tr>
<td>BDE-47</td>
<td>nd</td>
<td>2.10 ± 0.06</td>
<td>2.7 ± 0.1</td>
</tr>
<tr>
<td>BDE-66</td>
<td>nd</td>
<td>0.76 ± 0.03</td>
<td>nd</td>
</tr>
<tr>
<td>BDE-85</td>
<td>nd</td>
<td>0.24 ± 0.02</td>
<td>0.80 ± 0.05</td>
</tr>
<tr>
<td>BDE-99</td>
<td>nd</td>
<td>0.25 ± 0.02</td>
<td>0.94 ± 0.08</td>
</tr>
<tr>
<td>BDE-100</td>
<td>nd</td>
<td>Nd</td>
<td>0.35 ± 0.02</td>
</tr>
<tr>
<td>BDE-138</td>
<td>nd</td>
<td>Nd</td>
<td>nd</td>
</tr>
<tr>
<td>BDE-153</td>
<td>nd</td>
<td>Nd</td>
<td>nd</td>
</tr>
<tr>
<td>BDE-154</td>
<td>nd</td>
<td>Nd</td>
<td>nd</td>
</tr>
<tr>
<td>BDE-209</td>
<td>nd</td>
<td>Nd</td>
<td>nd</td>
</tr>
<tr>
<td>$\Sigma_{10}$PBDE</td>
<td>-</td>
<td>4.03 ± 0.09</td>
<td>5.4 ± 0.2</td>
</tr>
</tbody>
</table>

nd—not detected.

Six of the 10 investigated congeners were detected in the sediment samples, i.e., BDE-28, -47, -66, -85, -99, and -100. The concentration of PBDEs in the Point 2 sample varied between 0.24 ± 0.02 (BDE-85) and 2.10 ± 0.06 ng g$^{-1}$ (BDE-47). For the sample collected at Point 3, the concentrations of PBDEs ranged from 0.35 ± 0.02 (BDE-100) to 2.7 ± 0.1 ng g$^{-1}$ (BDE-47). In both samples, BDE-47 was the most prevalent congener indicating a major contamination of the penta-PBDE commercial mixture [53,54]. This same conclusion was made by Annunciaç\ão et al. [51] investigating samples from the Paran\óa Lake in the Brazilian Federal District. Both results reveal an important contribution of the penta-BDE mixture in the consumer goods used in Brazil.

In general, BDE-47, -99, -100, -153, -154, and -183 were the most commonly identified congeners because they are the major compounds in the penta-BDE commercial mixture [55]. The congener BDE-47 is most often employed in the furniture and upholstery industry [56]. The mixture penta-BDE, which includes BDE-47, -99, -100, -153, and -154, is typically applied in furniture, whereas the octa- and deca-BDEs mixtures are used in the manufacture of many types of polymers, especially those used in televisions, computers, and cables [8,56].

The total concentration of PBDEs (expressed as $\Sigma_{10}$PBDE) was higher in the sample obtained at Point 3 (5.4 ± 0.2 ng g$^{-1}$) as compared to the value calculated for Point 2 (4.03 ± 0.09 ng g$^{-1}$). In both cases, BDE-47 accounted for more than 50% of the total concentration of PBDEs, which showed that it was the most prevalent congener in the samples, followed by BDE-66 and BDE-99 in the samples extracted at Points 2 and Point 3, respectively.

According to the literature, BDE-47 and -99 are the PBDE congeners that are most frequently detected in environmental samples and biological fluids [57–60]. These congeners have also been identified in Brazilian biological samples reported by Dorneles and co-workers [61], who verified methoxylated metabolites of BDE-47 and BDE-68 in cetaceans of the Brazilian marine coast. BDE-47 and BDE-85 have also been detected in dolphins in the Paraiba do Sul River in Brazil [62], and the presence of PBDE commercial mixtures in whitemouth croakers from southeastern Brazil [45]. These data show main accumulation of BDE-47 in environmental samples [63,64].

The presence of PBDEs in the investigated region is explained by the habits of the surrounding population regarding the disposal of household waste. Weeks after the sampling takes place, the municipal government of Ribeir\ão Preto reported that they removed half a ton of garbage, mostly furniture and electronics, from the lake [65]. Although contamination of the environment may have occurred by the disposal of municipal waste, it is important to consider other important routes of urban water contamination by PBDE. In this context, much evidence indicates that PBDEs reach aquatic environments by dumping sewage, whether raw or treated [66–68]. In this case, as described by Annunciaç\ão et al. [11], the presence of PBDE in urban wastewater can be influenced by a sequence of processes that begin with the cleaning of surfaces in domestic, commercial or industrial environments.
Thus, dust particles are transferred to the washing waters and disposed either through drains, reaching storm water or sewage systems, or through sewers, reaching rainwater drainage networks. Furthermore, PBDEs can remain in the atmosphere in the form of particles that can precipitate with the rain, being further deposited in sediments, where they accumulate [69,70].

Our data represent one of the first involving the contamination of Brazilian aquatic sediments by PBDE. Annunciação et al. [51] investigated the presence of nine congeners in samples from Paranoá Lake, Brazil, collected in the proximity of two sewage treatment plants and evidenced the prevalence of BDE-47 and -66. Other Brazilian research groups have also evidenced environmental contamination of PBDE as they were able to quantify different congeners in samples from fish and marine mammals on the coast of the state of Rio de Janeiro, Brazil, as pointed out earlier [61,71].

In order to better visualize the results obtained in the present work, we compared the concentrations of PBDEs found herein with the concentrations reported worldwide, as depicted in Table 3.

### Table 3. Concentrations (ng g\(^{-1}\) dry weight) of PBDEs measured in this study in comparison with those reported form aquatic sediments collected around the world.

<table>
<thead>
<tr>
<th>Country</th>
<th>Aquatic System</th>
<th>n (^a)</th>
<th>(\sum) PBDEs (^b)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brazil</td>
<td>Saibro Lagoon</td>
<td>10</td>
<td>nd (^c) -5.4</td>
<td>This Study</td>
</tr>
<tr>
<td>Brazil</td>
<td>Paranoá Lake</td>
<td>9</td>
<td>2.5–8.1</td>
<td>[51]</td>
</tr>
<tr>
<td>Chile</td>
<td>Concepción Bay</td>
<td>10</td>
<td>0.02–21</td>
<td>[72]</td>
</tr>
<tr>
<td>China</td>
<td>Baiyangdian Lake</td>
<td>8</td>
<td>0.05–5.03</td>
<td>[73]</td>
</tr>
<tr>
<td>China</td>
<td>Fuhe River</td>
<td>8</td>
<td>0.13–6.39</td>
<td>[73]</td>
</tr>
<tr>
<td>China</td>
<td>Shanghai rivers</td>
<td>16</td>
<td>0.44–12.0</td>
<td>[74]</td>
</tr>
<tr>
<td>China</td>
<td>Jiaoning River</td>
<td>10</td>
<td>8.93–45.0</td>
<td>[74]</td>
</tr>
<tr>
<td>South Korea</td>
<td>Shihwa Lake</td>
<td>23</td>
<td>1.13–18700</td>
<td>[39]</td>
</tr>
<tr>
<td>Canada</td>
<td>Nigara River</td>
<td>9</td>
<td>1.10–148</td>
<td>[75]</td>
</tr>
<tr>
<td>USA</td>
<td>White Lake</td>
<td>23</td>
<td>0.39–2.4</td>
<td>[76]</td>
</tr>
<tr>
<td>USA</td>
<td>Muskegon Lake</td>
<td>23</td>
<td>0.98–3.9</td>
<td>[76]</td>
</tr>
<tr>
<td>Italy</td>
<td>Maggiore Lake</td>
<td>8</td>
<td>0.02–27.1</td>
<td>[70]</td>
</tr>
<tr>
<td>Russia</td>
<td>Olkhon Island</td>
<td>40</td>
<td>0.164–0.670</td>
<td>[69]</td>
</tr>
</tbody>
</table>

\(^a\) Number of PBDEs congeners analyzed in sample. \(^b\) Sum of all target PBDE congeners except for BDE 209. \(^c\) Not detected.

Compared to some regions in the Fuhe River, the Baiyangdian Lake, and the Chaohu Lake, all of them in China, and on the Olkhon Island, in Russia, the mean concentrations of \(\sum\) PBDEs without BDE-209 detected in this study were higher. Cheng-Yu, an economic region in China, presented much lower mean values of PBDEs as compared to the Saibro Lagoon investigated herein. Compared to some regions in Korea (four major rivers) or even in China (Jiaojian River), our values were much lower, which means that this lagoon in Ribeirão Preto was moderately contaminated with PBDEs.

The toxicity of PBDEs to living beings will also depend on the rate of absorption and on the metabolic system of the exposed species. Nevertheless, we must keep in mind that exposure to these pollutants or biomagnification through the food chain cause PBDEs to accumulate in lipids. For example, Hites [63] has shown that the concentration of PBDEs in Canadian Arctic seals has increased throughout the years, even though the Canadian Arctic is a remote region without direct release of these compounds into the environment. The increased presence of this compound can be related to its efficient atmospheric transport and bioaccumulation [77].

### 4. Conclusions

PBDE congeners were found in samples collected from the Saibro Lagoon (Ribeirão Preto, Brazil), in a recharge point of Guarani Aquifer. The highest \(\sum_{10}\) PBDE concentration, i.e., \(5.4 \pm 0.2\) ng g\(^{-1}\), agreed with the lowest levels determined in sediments collected around the world. BDE-47 was the most prevalent congener, accounting for more than 50% of the PBDE concentration in the samples evidencing the major use of the penta-PBDE commercial mixture widely used as flame retardant in
furniture. Contamination of the aquifer recharge area probably occurs via inappropriate disposal of municipal solid wastes. Our results have shown that this important recharge area is already contaminated with PBDEs, which may affect local population due to their potential to bioaccumulate and to induce damage in all exposed organisms. This contamination can still increase in the coming years considering that the use of PBDE is not controlled in Brazil. As the preservation of this site is vital, this work will help the scientific community to clarify the degree of exposure to PBDEs in Brazil.

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