Sorption–desorption behavior of polybrominated diphenyl ethers in soils

Yaniv Olshansky a, Tamara Polubesova a, Walter Vetter b, Benny Chefetz a, * 

a Department of Soil and Water Sciences, The Robert H. Smith Faculty of Agriculture, Food and Environment, The Hebrew University of Jerusalem, P.O. Box 12, Rehovot 76100, Israel 

b Institute of Food Chemistry (170b), University of Hohenheim, Garbenstr. 28, D-70599 Stuttgart, Germany

Abstract

Polybrominated diphenyl ethers (PBDEs) are flame retardants that are commonly found in commercial and household products. These compounds are considered persistent organic pollutants. In this study, we used 4,4’-dibromodiphenyl ether (BDE-15) as a model compound to elucidate the sorption and desorption behavior of PBDEs in soils. The organic carbon-normalized sorption coefficient (KOC) of BDE-15 was more than three times higher for humin than for bulk soils. However, pronounced desorption hysteresis was obtained mainly for bulk soils. For humin, increasing concentration of sorbed BDE-15 resulted in decreased desorption. Our data illustrate that BDE-15 and probably other PBDEs exhibit high sorption affinity to soils. Moreover, sorption is irreversible and thus PBDEs can potentially accumulate in the topsoil layer. We also suggest that although humin is probably a major sorbent for PBDEs in soils, other humic materials are also responsible for their sequestration.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are flame retardants that are commonly found in commercial and household products, such as polyurethane foam, plastics, textiles and electronics (Alaee et al., 2003). Electronic waste-dismantling sites and industrial parks have been suggested as point sources for PBDEs (Law et al., 2006). Because they are additive flame retardants (i.e. blended with polymers), they are likely to be released from the products to the environment (Ahn et al., 2005). Recently, PBDEs have been detected in the food chains, including marine biota (Ramu et al., 2007; Svendsen et al., 2007), terrestrial food webs (Voorspoels et al., 2006) and humans (Johnson-Restrepo et al., 2005). Due to their toxicity and increasing concentrations in the environment, PBDEs have been listed as persistent organic pollutants (Clarke and Smith, 2010), which may undergo transformation during degradation. Although PBDE occurrence and spatial distribution in soils and sediments have been estimated (Wania and Dugani, 2003; Law et al., 2006; Zou et al., 2007; Clarke and Smith, 2010), only two studies have reported data on their sorption (Liu et al., 2010; Wang et al., 2011). Moreover, to the best of our knowledge, the phenomenon of PBDEs sorption–desorption hysteresis in soils has never been reported. Thus, the aim of the current study was to investigate sorption and desorption behaviors of 4,4’-dibromodiphenyl ether (BDE-15) in soils. Understanding the interactions of BDE-15 with soils and with the major soil organo-mineral component, humin, will enable accurately predicting the fate of PBDEs in the environment.

2. Materials and methods

2.1. Chemicals

BDE-15 and 1,1’,2,2’-tetrachloroethane (TCE) were purchased from Alfa Aesar (Lancaster, UK). BDE-47 (2,2’,4,4’-tetrabromodiphenyl ether) was synthesized based on the method described by Vetter and Jun (2003). All solvents used in the present study were of analytical grade (Sigma–Aldrich, Rehovot, Israel). Stock solutions of BDE-15 and BDE-47 were prepared in acetonitrile and kept in the refrigerator. Aqueous solubility (μg L−1) and log octanol-water partition coefficient (Kow) are, respectively, 130 and 5.03 for BDE-15; 15 and 6.11 for BDE-47 (Wania and Dugani, 2003).

2.2. Sorbents: soils and humin

Soils (Grunisol, Rhodoxeralf and Loess) were sampled in Israel near the cities of Akko, Rehovot and Arad, respectively. The soils were collected from 5- to 30-cm depth, then air-dried, ground and sieved. Humin was isolated from Akko soil as described elsewhere (Drori et al., 2008). Briefly, Akko soil was treated with 0.1 M NaOH solution to remove humic and fulvic acids, and then the residue (i.e. humin) was washed with water to decrease the pH to 7 and remove excess salts. The bulk properties of the studied soils were measured by standard soil-testing methods (Sparks, 1996) and are summarized in Table 1.
2.3 Batch sorption–desorption experiments

Aqueous solutions of BDE-15 and BDE-47 were prepared by adding aliquots from acetonitrile stocks to a background solution containing 100 mg L\(^{-1}\) NaN\(_3\) to inhibit microbial activity. Acetonitrile concentration was maintained at less than 0.1% (v/v) to minimize co-solute effects. For single-solute sorption experiments, solutions (25 mL) of BDE-15 in a concentration range of 1–70 µg L\(^{-1}\) were added to the sorbents (pre-weighed in 30-mL glass centrifuge tubes with Teflon caps). To achieve 30–70% sorption, the following amounts of sorbents were used: 1, 0.25, 0.1 and 0.05 g for Rehovot, Arad and Akko soils and Akko humin, respectively. The tubes (three replicates for each initial concentration and the corresponding blanks) were agitated in the dark at 200 rpm (25 ± 1 °C) for 96 h. Then the tubes were centrifuged for 15 min at 7000 g, and 10-mL aliquots of the supernatant were removed for quantitative analysis of BDE-15. To perform desorption experiments, 10 mL of fresh background solution were added, and the tubes were further agitated under the same conditions for an additional 96 h. Three sequential desorption steps were performed. Preliminary experiments showed that BDE-15, in both single and bi-solute systems, reaches sorption and desorption equilibria within 96 h.

Bi-solute sorption experiments were conducted by adding BDE-47 solution at a constant concentration of 11 µg L\(^{-1}\) to background solutions containing elevated concentrations of BDE-15. Experimental conditions were similar to those of the single-solute batch method.

2.4 Analytical measurements

Extraction of BDE-15 from the supernatant solutions (obtained at the end of the sorption and desorption steps) was conducted based on a method modified from Li et al. (2008). Briefly, TCE (200 µL) was added to a conical-shape glass centrifuge tubes containing 10 mL of the supernatant. The tubes were sealed and vortexed for 30 s at the highest speed and then agitated in the dark at 350 rpm for 24 h. The tubes were then centrifuged for 5 min at 900 g and 100 mL of TCE phase containing BDE-15 was removed with a glass syringe for analysis. With this method, BDE-15 recovery was 97 ± 6% for a concentration range of 1–70 µg L\(^{-1}\).

BDE-15 concentration was determined using an Agilent 6890N GC equipped with electron-capture detector (Agilent G2397A). An HP-5 MS capillary column (30 m × 0.32 mm internal diameter, 0.25-µm film thickness) was used with helium as the carrier gas at a flow rate of 2 mL min\(^{-1}\). The detector temperature and detector temperatures were 270 and 300 °C, respectively. The oven was maintained at 120 °C for 1 min, and then the temperature was increased at a rate of 20 °C min\(^{-1}\)–300 °C.

2.5 Data analysis

Sorption isotherms were fitted to the Freundlich equation: 

\[ Q = K_f C^{1/n} \]

where \( Q \) is the amount sorbed per unit weight of sorbent (µg kg\(^{-1}\)), \( K_f \) (µg kg\(^{-1}\) × (µg L\(^{-1}\))\(^{-n}\)) is the Freundlich coefficient, and \( N \) (dimensionless) describes the isotherm curvature. Sorption coefficients (\( K_f \)) were calculated at an equilibrium concentration of 10 µg L\(^{-1}\). Organic carbon (OC)-normalized sorption coefficients (\( K_{OC} \)) were calculated for each sorbent by normalizing \( K_f \) to the OC contents. Hysteresis index (\( H \)) was calculated as the ratio of Freundlich coefficients (\( N_{OC}/N \)) derived from sorption and desorption data (Gunasekara and Xing, 2003).

3. Results and discussion

3.1 Sorption

BDE-15 is highly hydrophobic, and its overall fate in the environment is therefore expected to be governed by sorption and desorption interactions with soil organic matter. Isotherms of BDE-15 sorption and the calculated parameters are presented in Table 1.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Sand (%)</th>
<th>Silk (%)</th>
<th>Clay (%)</th>
<th>Texture</th>
<th>Organic carbon (%)</th>
<th>Humic and fulvic acids (%)</th>
<th>Humic (%)</th>
<th>Specfic surface area (m(^2) g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rehovot</td>
<td>93</td>
<td>1.25</td>
<td>5.57</td>
<td>Sand</td>
<td>0.009 ± 0.002</td>
<td>0.044 ± 0.002</td>
<td>0.046 ± 0.001</td>
<td>10.1 ± 0.7</td>
</tr>
<tr>
<td>Arad</td>
<td>50</td>
<td>17.5</td>
<td>32.5</td>
<td>Sandy</td>
<td>0.057 ± 0.019</td>
<td>0.23 ± 0.008</td>
<td>0.45 ± 0.01</td>
<td>118.8 ± 5</td>
</tr>
<tr>
<td>Akko</td>
<td>25</td>
<td>15</td>
<td>60</td>
<td>Clay</td>
<td>1.07 ± 0.017</td>
<td>0.57 ± 0.002</td>
<td>0.50 ± 0.02</td>
<td>410 ± 5</td>
</tr>
<tr>
<td>Humin</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.55 ± 0.004</td>
<td>0.57 ± 0.002</td>
<td>0.55 ± 0.004</td>
<td>97.8 ± 5</td>
</tr>
</tbody>
</table>

Equilibrium concentration µg L\(^{-1}\)

Fig. 1. Isotherms of BDE-15 sorption by bulk soils and humin (a) and sorption isotherms normalized to organic carbon content (b), (●, humin; soils: ○, Akko; ▽, Arad; △, Rehovot).

Fig. 1 and Table 2, respectively. The \( K_d \) values calculated for BDE-15 in the studied soils varied over a wide range (30–760 L kg\(^{-1}\)). In most cases, isotherms were linear (\( N \) values were >0.95); the lowest linearity was obtained with Arad soil (\( N = 0.88 \)). Since organic matter is the dominate sorbent of hydrophobic organic compounds in soils (Schwarzenbach et al., 2003; Chefetz and Xing, 2009), we expected the OC-normalized isotherms to coincide. However, this isotherm showed higher BDE-15 sorption affinity to humin than to soils (Fig. 1b). Hence, we concluded that in addition to the amount also the structure and properties of the soil organic matter (SOM) are affecting sorption of BDE-15 to soils. A similar conclusion was recently drawn by Wang et al. (2011) from an investigation of the sorptive behavior of other PBDEs. The calculated values of log \( K_{OC} \) (Table 2) were in the range of 4.53–4.61 for the soils. Although the studied soils differed in their properties.

Table 2

<table>
<thead>
<tr>
<th>Soil</th>
<th>Rehovot</th>
<th>Arad</th>
<th>Akko</th>
<th>Humin</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_d ) (µg kg(^{-1}) × (µg L(^{-1}))(^{-n}))</td>
<td>33.4 ± 2.5</td>
<td>352 ± 49</td>
<td>334 ± 63</td>
<td>864 ± 136</td>
</tr>
<tr>
<td>( N )</td>
<td>0.943 ± 0.03</td>
<td>0.875 ± 0.05</td>
<td>1.073 ± 0.06</td>
<td>0.950 ± 0.05</td>
</tr>
<tr>
<td>( r^2 )</td>
<td>0.993</td>
<td>0.977</td>
<td>0.980</td>
<td>0.971</td>
</tr>
<tr>
<td>Log ( K_d )</td>
<td>1.48 ± 0.01</td>
<td>2.44 ± 0.02</td>
<td>2.61 ± 0.02</td>
<td>2.88 ± 0.02</td>
</tr>
<tr>
<td>Log ( K_{OC} )</td>
<td>4.53 ± 0.01</td>
<td>4.61 ± 0.02</td>
<td>4.58 ± 0.02</td>
<td>5.14 ± 0.02</td>
</tr>
</tbody>
</table>

Y. Olshansky et al. / Environmental Pollution 159 (2011) 2375–2379
phenols in soils, they suggested that dichlorophenol served as a sorbate in the sorption process. Smejkalova and Piccolo (2008) studied the sorption of dichlorophenol and its degradation products in natural soils. They found that dichlorophenol was sorbed irreversibly, but the degradation products were sorbed reversibly. This suggests that dichlorophenol can be considered a major sorption domain for PBDEs in soils.

The $K_{OC}$ values for the sorption of BDE-28 to natural soils were calculated from data reported by Liu et al. (2010). Based on their study, the $Q_{OC}$ values ranged from 4.5 to 5.5 for equilibrium concentrations within the range of $3-20 \mu g \text{ L}^{-1}$. Weibull et al. (1998) reported $Q_{OC}$ values ranging from 4.95 to 6.1 (measured for four sediments spiked with $0.5-2 \mu g \text{ g}^{-1}$ BDE-28). The $Q_{OC}$ values calculated for BDE-15 in the current study were lower than those reported for BDE-28. This is in accordance with the trend of increasing $Q_{OC}$ with the increase in $Q_{OW}$ of PBDEs (Wang et al., 2011).

Higher $K_{OC}$ values for humin than for soils have been reported in several studies (Salloum et al., 2001; Kang and Xing, 2005; Simpson and Johnson, 2006). Humin consists of resistant non-polar moieties derived from plant materials which are associated with the soil’s mineral components (Hayes et al., 2010). Removal of humic and fulvic fractions during isolation of humin exposes non-polar polyethylene domains, enhancing humin’s sorptive efficiency for hydrophobic organic compounds (Simpson and Johnson, 2006; Drori et al., 2008). Therefore, it is not surprising that the sorptive data for humin in our study are higher than for the corresponding soil.

To study competitive sorption of flame retardants, we measured the sorption isotherms of BDE-15 for Rehovot and Arad soils in the presence of BDE-47 at $11 \mu g \text{ L}^{-1}$. Since some of the adsorption isotherms were non-linear, competitive behavior between the studied BDEs was expected. However, in our experimental setup BDE-47 did not affect sorption of BDE-15 in Rehovot and Rehovot soils (Fig. 2). It is important to note that the elevated concentration of BDE-15 in the bi-solute experiments did not affect the sorption of BDE-47. Sorption of BDE-47 was higher than BDE-15, in Arad soil about 95% of the added DBE-47 was adsorbed, with Rehovot soil about 90% of the added DBE-47 was adsorbed. The equilibrium concentrations of BDE-47 were $0.35 \pm 0.05$ and $1.15 \pm 0.2 \mu g \text{ L}^{-1}$ for the two soils, respectively. We assume that since the overall loading of BDE-15 was very low (less than 0.1% by weight), thus the competition for sorption sites was not pronounced. In addition, BDE-15 molecules are much smaller in size than BDE-47 molecules, which can restrict the ability of the latter to compete with BDE-15 for sorption sites. Moreover, the unchanged concentration of BDE-47 (competitor) in the bi-solute experiments suggests that complementary sorption did not occur in our system.

### 3.2. Desorption

Desorption data can provide further insight into the sorption mechanism. In our study, all desorption isotherms exhibited pronounced hysteresis (Fig. 3). It is important to note that BDE-15 was not desorbed from Arad soil (calculated HI was about zero), even after three sequential desorption steps. Desorption of BDE-15 from Rehovot and Akko soils were somewhat higher, but still sorption can be considered as irreversible. Desorption hysteresis might be induced by irreversible chemical binding, physical entrapment of molecules within the SOM matrix and/or by deformation of the sorbent matrix (Weber et al., 1998). Smejkalova and Piccolo (2008) studied the sorption of dichlorophenols in soils, they suggested that dichlorophenol served as an electron acceptor. Based on that, in our system, $\pi-\pi$ interactions between BDE-15 and SOM may occur when the molecules of BDE-15 act as electron acceptors and aromatic moieties of the SOM (e.g. aniline, polycondensed aromatic systems) are electron donors. Twisted configuration of the two ring moieties of BDE-15 provides a better access to SOM moieties as compared to polychlorinated and polybrominated biphenyls (Zhao et al., 2008). This can enhance the $\pi-\pi$ interactions and therefore impede desorption.

In contrast to the irreversible sorption of BDE-15 by the bulk soils, desorption hysteresis of BDE-15 from the humin was not pronounced. Moreover, unlike the desorption trend observed for the soils (concentration independent), the HI for humin decreased (from 1 to 0.3) with increasing sorbed concentration (i.e. BDE-15 was less readily desorbed from humin at higher sorbed concentrations). A decrease in HI with increasing concentrations of sorbed material has been reported in several studies (Chefetz et al., 2004; Chen and Xing, 2005; Oren and Chefetz, 2005). It has been suggested that a concentration gradient forces sorbed molecules to penetrate deeper into the sorbent micropores, resulting in deformation of the micropores and entrainment of the sorbate molecules into the newly formed pores. We suggest that this might be the mechanism of BDE-15 sorption in the case of humin.

The structure and properties of humin OM differ from the bulk SOM. In general, humin organic matter is less aromatic than SOM (Hayes et al., 2010), and thus we suggest that humin organic matter is less capable for $\pi-\pi$ interaction. Therefore, although humin can be considered a major sorption domain for PBDEs, their sequestration in soils is probably governed by other SOM constituents and not by the humin.
4. Conclusions

The sorption and desorption data reported in this study are important for understanding PBDEs behavior in soils. It appears that the structure and chemistry of SOM is a dominant factor in PBDEs’ sorption affinities and desorption hysteresis, which differed for soils and humin. Humin appears to be a major sorption domain for PBDEs. However, high desorption from humin implies that PBDEs accumulation in soils is regulated by other SOM fractions and their interactions with minerals. To evaluate environmental behavior and health risk of PBDEs, and to estimate their transport and bioavailability, desorption hysteresis of PBDEs in soils and sediments should be considered.

Acknowledgments

This research was supported by a research grant from the Environment and Health Fund, Jerusalem, Israel and by a joint program between the University of Hohenheim and the Hebrew University of Jerusalem.

References

Ahn, M.-Y., Filley, T.R., Jafvert, C.T., Nies, L., Hua, I., Bezares-Cruz, J., 2005. Photo...


