Freely dissolved PBDEs in water and porewater of an urban estuary

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Polyethylene passive samplers (PE) were deployed in Narragansett Bay, RI, to examine freely dissolved concentrations of polybrominated diphenyl ethers (PBDEs) in surface, bottom, and sediment porewater. PBDE congeners in the water column and porewater were below 3 pg L⁻¹. In the surface water, only PBDE congeners containing up to 5 bromines were detected, while in the deeper water congeners 153 and 154 (6 bromines) were also detected. Activity ratios of surface-bottom water and porewater-bottom water suggested that lower brominated (di-tetra) congeners reached Narragansett Bay from surface waters and sediments. PBDEs in the surface water probably originated from a combination of air–water exchange, freshwater runoff, rivers, and wastewater treatment plants. It is suggested that deep water was the source of higher brominated PBDEs to the Bay implying that the more hydrophobic PBDEs reached depth on particles and/or that these congeners were degraded in sediments. On-going sources supply PBDEs to Narragansett Bay.

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) are persistent man-made chemicals designed to inhibit ignition and burning of consumer products such as furniture foams, electronics casings, and fabrics. Structurally, PBDEs closely resemble polychlorinated biphenyls (PCBs), a class of ubiquitous hydrophobic organic pollutants that were banned in the U.S. and by the United Nations Environment Programme (UNEP, 2001). Despite their ban, PCBs are still found in biota all over the world. Several PBDEs have recently been identified as persistent organic pollutants (POPs) like PCBs and were added to the Stockholm Convention on POPs in 2009 (UNEP, 2009).

Three technical formulations of PBDEs were produced and used by industry – pentaBDE, octaBDE, and decaBDE – named for the major homolog groups in the mixture. In toxicological studies PBDEs have been shown to cause impaired liver, thyroid, and neurobehavioral development in animals (Darnerud et al., 2001), and certain congeners have been shown to have endocrine disrupting qualities (Hamers et al., 2006; Darnerud, 2008). Production of the penta and octaBDE mixtures ceased in 2004 in the US, shortly after a ban of these chemicals in the European Union (EU) because of their ability to partition into biota and their high potential for bioaccumulation. These mixtures were further banned by UNEP worldwide in 2009 (UNEP, 2009). DecaBDE was banned in the EU in 2008, but it is still in production and use in the US. The deca molecule is deemed too large to be bioavailable and has been shown to exhibit the lowest toxicity (Darnerud, 2003). Other studies have shown it to be harmful because it can be debrominated into smaller congeners which can accumulate in biota (Watanabe and Tatsukawa, 1987; Kiørregaard et al., 1999; Hua et al., 2003; Eriksson et al., 2004; Soderstrom et al., 2004). This debromination of the deca molecule can occur by UV light or during metabolism once inside an organism.

Although penta and octa have been banned, the current load of penta, octa, and decaBDEs in buildings, cars, and homes ensures continued release of these chemicals into the environment. PBDEs have been detected in air (e.g. Zweidinger et al., 1979; Watanabe et al., 1992, 1995), sediments (e.g. Allchin et al., 1999; Oros et al., 2005; Wurl and Obbard, 2005), marine animals (e.g. Johnson and Olson, 2001; Booij et al., 2002; Hites et al., 2004; Oros et al., 2005; Hoenicke et al., 2007), households (e.g. Butt et al., 2004; Jones-Otazo et al., 2005; Stapleton et al., 2005), cars (Mandalakis et al., 2008), and human tissue and breast milk (e.g. Noren and Meironyte, 2000; She et al., 2002; Schecter et al., 2003; Johnston-Restrepo et al., 2005).

Major sources of PBDEs to the estuarine environment may include atmospheric transport (e.g. Strandberg et al., 2001), runoff, inflow from rivers and wastewater treatment plants, and releases during the manufacturing and use, as well as the recycling and disposal of commercial products. Hydrophobic persistent...
compounds such as PBDEs also sorb to particles and settle out of the water column into the sediments where they can be re-released to the water column (Morgan and Lohmann, 2010).

Polyethylene passive samplers (PE) are simple diffusive equilibrium sampling devices that are becoming popular because of their ability to sample only freely dissolved contaminants, used to evaluate bioavailability to aquatic organisms (Mayer et al., 2003). When dealing with highly hydrophobic trace contaminants, it has been difficult to measure only the dissolved fraction without the dissolved organic carbon (DOC) or colloidal bound fraction, but by the nature of their molecular uptake, PE can only sample the truly dissolved fraction. When PE is placed in the field, the plastic absorbs contaminants until equilibrium is reached. The freely dissolved concentrations of individual PBDEs ($C_w$) are then calculated using Eq. (1), where $C_{PE}$ is the concentration of PBDE found in the deployed sampler (ng g PE$^{-1}$ converted to ng mL$^{-1}$ using the density of PE), $K_{PEw}$ is the PE-water partitioning constant, and $f_{lost}$ is the fraction of performance reference compounds (PRCs) lost from the PE during deployment (Booij et al., 1998) which corrects $C_{PE}$ for disequilibrium (see Sacks and Lohmann, 2011).

$$C_w = \frac{C_{PE} f_{lost}}{K_{PEw}}$$

Freely dissolved concentrations of PBDEs in surface water, bottom water, and porewater are determined here using PE. Narragansett Bay is a small, urbanized estuary with a rich history of organic pollution. The Narragansett Bay watershed spans ~1700 square miles and supports a population of 2 million people (NBEP, 2010). The Blackstone, Taunton, and Pawtuxet Rivers in the north are the primary sources of freshwater to the bay while saltwater flushes in from the Block Island Sound at the mouth of the bay. Tidal flushing is the dominant circulation force of Narragansett Bay making it a well-mixed estuary with a high salinity range of 24 – 32 psu and small salinity gradients (Ely, 2002). Narragansett Bay sampling locations are included in Fig. 1.
We set out to study PBDEs in Narragansett Bay due to their recent inclusion in the global POPs treaty and concerns about their impacts on water quality (UNEPA, 2009). By deploying samplers in different locations and depths simultaneously, we were able to assess sources of contamination in Narragansett Bay by calculating activity ratios and quantifying gradients. More specifically, we could determine if sediments had already become a source of PBDEs to the water column, or if surface water was still the major exposure route. In summary, the goals of this research were to (i) determine \( K_{\text{PEw}} \) for a range of PBDEs; (ii) quantify the presence of PBDEs in Narragansett Bay water and porewater; and (iii) identify the sources of PBDEs to Narragansett Bay.

2. Methods

2.1. Reagents and chemicals

Analytical standards of PBDE congeners 28, 47, 49, 99, 100, 153, 183, and 209 (50 \( \mu \text{g} \cdot \text{mL}^{-1} \) in nonane), internal surrogate standards consisting of \( ^{13}\text{C} \)-labeled congeners 28, 47, 49, 153, 183, 209, and polychlorinated biphenyls (PCBs) used as PRCs (2,5 dibromobiphenyl, 2,2’,5,5’ tetra bromobiphenyl, and 2,2’,4,5,5’ pentabromo- biphenyl) were obtained from Cambridge Isotope Laboratories Inc. (Andover, MA, USA). PBDE congeners 2, 8, 15, and 30 (50 \( \mu \text{g} \cdot \text{mL}^{-1} \) ) were obtained from Accu- standard (New Haven, CT, USA).

2.2. Laboratory partitioning experiments

The method for partitioning experiments is detailed in (Sacks and Lohmann, 2011). In brief, low density PE was cut into 0.05 g pieces from 1 mil (25.4 \( \mu \text{m} \) thickness) plastic drop cloth (Covalence Plastics, Minneapolis, MN) and pre-cleaned twice by extraction in dichloromethane and hexane for 24 h. Each replicate was treated with milli-Q water, PRC-loaded, and spiked with 1000 ng of BDEs 2, 8, 15, 28, 30, 47, 49, 99, 100, 153, 183, and 209. Congener descriptions are included in SI Table 1. Triplicate samples and blanks in 250 mL round bottom flasks were placed in a climate controlled chamber (20 °C) and shaken on an orbital shaker table for 6 and 9 weeks.

PE was extracted twice in n-hexane for 24 h per extraction and concentrated to 50 \( \mu \text{L} \) using a Turbovap (Turbovap II, Caliper Sciences, Inc.; 38 L using a Turbovap and a gentle stream of nitrogen gas. Gas chromatography tandem mass spectrometry analysis was conducted on an Agilent 6890N GC coupled to a Waters’ (R) Quattro Micro MS/MS under electron-impact ionization (EI, 70 eV) in multiple reaction monitoring mode (MRM) using a DB-5MS column (Agilent J&W GC Columns, 122—5353, length 30 m, ID 0.25 mm, film 0.25 \( \mu \text{m} \) ) and splitless injection (200 °C). The temperature program began at 40 °C, ramped at 10 °C min^{-1} to 180 °C, 13.5 °C min^{-1} to 280 °C and held for 21 min. Ions used for quantification were adapted from a Waters’ (R) method (SI Table 3) (Worrall et al., 2004). A calibration standard curve was created for each congener such that the internal standard concentration remained constant at 2 ng \( \mu \text{L}^{-1} \) and analytes, PRCs, and injection standard varied from 1 to 500 pg \( \mu \text{L}^{-1} \). This curve was used to derive response factors of analytes relative to the appropriate isotope-labeled internal standards.

2.7. Quality control

For quality assurance and recovery monitoring of extractions, internal standards of \( ^{13}\text{C} \)-labeled surrogate compounds were added prior to extraction (50 ng). In addition, p-terphenyl-\( \text{d}_{4} \) was added to final extracts as injection standard to monitor analytical and instrumental variability (50 ng). Recoveries of internal standards ranged from 63% to 96%. Instrumental detection limit ranged from 6.2 pg \( \mu \text{L}^{-1} \) to 0.3 fg \( \mu \text{L}^{-1} \) (low K \text{LOW} — high K \text{LOW} PBDEs).

3. Results and discussion

3.1. Partitioning constants — \( K_{\text{PEw}} \)

PE-water partitioning constants (\( K_{\text{PEw}} \)) for PBDEs were derived from an updated relationship between \( K_{\text{PEw}} \) and \( K_{\text{b}} \) from Lohmann and Muir (2010) (Eq. (2)), based on measured values for a range of HOCs from different laboratories:

\[
\log K_{\text{PEw}} = 1.08 \log K_{\text{b}} - 0.67
\]

(2)

Laboratory experiments were conducted to verify that PBDEs partition as predicted from the general relationship between \( K_{\text{PEw}} \) and \( K_{\text{b}} \) (Lohmann and Muir, 2010). For PBDEs 2 (mono) and 15 (di), the predicted and the measured \( \log K_{\text{PEw}} \) agreed within 60% or less (SI Fig. 1). We thus predicted \( K_{\text{PEw}} \) for all PBDE congeners of interest based on the predicted relationship. More details are given in the SI.

3.2. Freely dissolved concentrations of PBDEs in Narragansett Bay

Three PRCs were used in this study — a di, tetra, and penta PBB. At the end of the one month deployment, on average 100% of the di congener, 76% of the tetra, and 43% of the penta congener had been dissipated. Smaller congeners equilibrate faster due to higher diffusivities (Schwarzenbach et al., 2003). A correlation between the degree of bromination of PBBs (size) and \( f_{\text{act}} \) was established \( f_{\text{act}} = -0.19 \times (\# \text{ of Br}) + 1.4 \) to extrapolate \( f_{\text{act}} \) for other PBB homologs. We assumed that a penta PBB and a penta PBDE reach equilibrium at approximately the same time due to their similar molecular structure and size. The correlation between degree of bromination and \( f_{\text{act}} \) was used for PBDE homologs up to the hexa (31% lost). Higher congeners were not detected. BDE 209 (deca) was not able to be quantified because it had equilibrated less than 1%. In order to study a molecule as large as BDE 209 with PE, it is clear that a much longer deployment time is necessary. Freely dissolved concentrations of individual PBDEs were calculated with Eq. (1).

Samples were deployed from mid-September to mid-October, 2009 at an average water temperature of 18.1 °C. Lohmann & Muir \( \log K_{\text{PEw}} \) values calculated at 25 °C agreed with our 20 °C experiments (near to field conditions) so the derived \( K_{\text{PEw}} \) were not corrected for any possible temperature effects. \( K_{\text{PEw}} \) was salt
corrected using the Setschenow equation, a value of 0.3 for $K_s$ (modified from Schwarzenbach et al., 2003), and an average molar salt concentration of 0.4 for field conditions (Sacks and Lohmann, 2011). Table 1 shows dissolved concentrations of all PBDE congeners studied in Narragansett Bay. PBDE congeners 8, 28, 47, 49, 99, and 100 (di, tri, tetra, and penta) were detected in surface water and congeners 47, 49, 99, 100, 153, and 154 (tetra, penta, and hexa) were detected in bottom water at all locations sampled (<2.3 pg L$^{-1}$). BDE 15 (di) was only detected in samples (surface and bottom) from Bullock’s Reach (BR), and BDE 8 was detected in bottom water only at BR. BDEs 2 (mono), 30 (tri), and 183 (hepta) were not detected. BDE 47 was the most abundant congener detected.

In most cases, di- and tri-brominated congeners (8 and 28) were detected only in surface water, and hexa-brominated congeners (153 and 154) were detected only in bottom water. Higher concentrations of PBDEs were observed at the head of Narragansett Bay (especially at Bullock’s Reach) and lower concentrations near the mouth. Bullock’s Reach is the northernmost sampling station, closest to a large city (Providence, RI), and receives the least amount of tidal flushing. We expect that Bullock’s reach would be our most contaminated station. A perspective view of the concentration distribution of BDEs 47 and 99 in Narragansett Bay is shown in Fig. 2.

3.3. Comparison with previously published data

A number of studies have measured dissolved PBDE concentrations in urban waters. Most of these studies filtered water through an XAD column. By measuring the water concentration in this way, the “dissolved” concentration consists of the dissolved phase as well as the colloidal phase and anything else that passes through the filter (Oros et al., 2005). The strong effect DOC/colloids can have on water concentrations was evident in our partitioning experiments when water was extracted directly. Similarly, in the environment, PBDEs are expected to bind to DOC/colloids. This effect is most pronounced for the higher brominated (more hydrophobic) PBDEs. PE only measures the truly dissolved fraction, thus comparison between PE-derived and XAD-derived dissolved concentrations is difficult. Here, we focus on BDEs 47 and 99 for comparison because these two congeners have been widely studied (Table 2).

Highest concentrations of BDEs 47 and 99 measured in Narragansett Bay, RI, in this study (PE-derived) were 2.3 and 0.8 pg L$^{-1}$.
respectively. In contrast, Oros et al. (2005) found concentrations of BDEs 47 and 99 in the range of 16–180 and 12–91 pg L$^{-1}$ respectively in San Francisco Bay (XAD-derived); Streets et al. (2006) determined concentrations of 10 and 6 pg L$^{-1}$ respectively in Lake Michigan waters (XAD-derived). These two studies used a filter and XAD for collection of PBDEs and, as expected, report much higher “dissolved” concentrations of BDE 47 and 99 than what we found using PE in Narragansett Bay. Zarnadze and Rodenburg, 2008 also measured PBDEs using XAD resin coupled with filters in Raritan Bay in the New York Metropolitan area. Recognizing the limitations of XAD and filters for measuring dissolved concentrations, they attempted to convert the “apparent” dissolved fraction to the “truly” dissolved fraction of PBDEs (Zarnadze and Rodenburg, 2008). In their paper, they determined that a substantial fraction of BDEs 47 and 99 should be sorbed to colloids in an estuarine environment based on the large $K_{ow}$ of most PBDEs. Taking these fractions into account, Zarnadze & Rodenburg estimated dissolved concentrations of 2.2–22 and 1.8–19 pg L$^{-1}$ for BDEs 47 and 99 respectively. Higher concentrations in Raritan Bay are expected as it is a much more urbanized/industrialized estuary.

Booj et al. (2002) used passive semipermeable membrane devices (SPMD) to measure dissolved concentrations along the Dutch coast. Highest concentrations of BDEs 47 and 99 measured were 1 and 0.5 pg L$^{-1}$, comparable to the (PE-derived) concentrations for Narragansett Bay reported in this study. The close agreement supports the concept that passive sampling devices (such as SPMDs or PEs) only measure the truly dissolved fraction.

3.4. Porewater concentrations

Six week sediment incubations with PE samplers were used to derive concentrations and activities of PBDE congeners in porewater. In previous work (Lambert et al., 2011) we show that 8–9 weeks were required for octachlorodibenzo-p-dioxin to reach equilibrium in PE-sediment slurries. We performed additional, 9-week-long equilibrations, which resulted in lower PE concentrations than in the 6 week samples indicating that PBDEs were not stable in sediments, even in the dark and in the presence of sodium azide to prevent microbial activity. Sediment aging (chemical-sediment interactions related to contact time) has been held responsible for an observed decrease in sediment concentrations over time in similar studies (Ciparis and Hale, 2005; Klosterhaus et al., 2011).

We took average concentrations from the 0.2 g and 0.6 g samplers in the 6 week-long experiments to represent $C_{iPE}$. The uncertainty in this calculation ranged from 36% to 69% based on the difference between the concentrations in the two PE samplers. Uncertainty for congeners 28 and 99 was higher. These congeners were thus excluded from further discussion. Porewater concentrations were then calculated using Eq. (1). Of the congeners studied, BDEs $30$, $100$, $153$, $154$, and $183$ were not detected in porewater. Congeners $8$, $15$, $47$, and $49$ were detected at concentrations up to 0.5 ng g$^{-1}$ PE$^{-1}$, or concentrations up to 3 pg L$^{-1}$ in the porewater (BDE 8). At Quonset Point and Conimicut Point BDE 8 was detected at 0.2 and 3.0 pg L$^{-1}$. BDE 28 was detected at 0.04 and 0.09 pg L$^{-1}$. BDEs 47 and 49 were both detected at 0.03 and 0.07 pg L$^{-1}$, and BDEs 9 and 15 were detected only at Conimicut Point at concentrations of 2.7 and 0.01 pg L$^{-1}$ respectively.

A number of papers have reported EC$_{50}$ for PBDEs (effective concentrations determined to affect 50% of a population) in the pg L$^{-1}$ to mg L$^{-1}$ range (Wollenberger et al., 2005; Usenko et al., 2011). Concentrations observed in this study were in the fg L$^{-1}$ range thus not at concentrations high enough to be significantly detrimental to the environment on their own.

3.5. PBDE activity ratios

Characterizing source inputs in a mixed estuary is difficult because there are multiple factors contributing to PBDE concentrations and environmental partitioning. By deriving activity ratios in the field, we are able assess possible sources of PBDEs in Narragansett Bay. The ‘true’ activity is described as the ratio of $C_{iPE}$ to the solubility of PBDE at saturation in PE (Schwarzenbach et al., 2003; Morgan and Lohmann, 2008). Since $C_{iPE}$ was measured at a constant temperature in this case (and in other cases are corrected to a constant temperature), the solubility is a constant and $C_{iPE}$ is directly proportional to the PBDE’s activity. We can therefore use $C_{iPE}$ to represent the activity of PBDE.

Water column activity ratios (activity$_{wc}$, Eq. (3)) were calculated at all locations to determine gradients within the water column, and porewater-bottom water activity ratios (activity$_{pw-bw}$, Eq. (4)) were calculated at Quonset and Conimicut Points to determine concentration gradients between porewater and bottom water. A net gradient is reported when the ratio ± uncertainty was significantly different from one. In these equations, $C_{iPE}$, surf is the concentration in PE deployed in surface water (ng g$^{-1}$ PE$^{-1}$), $C_{iPE}$, bottom is the concentration in PE deployed in bottom water (ng g$^{-1}$ PE$^{-1}$), and $C_{iPE}$, pw is the concentration in PE obtained from porewater tumbling experiments (ng g$^{-1}$ PE$^{-1}$). A value of ½ detection limit was used for non-detects to calculate activity ratios and all concentrations have been corrected for equilibrium.

$$activity_{wc} = \frac{C_{iPE, \text{surf}}}{C_{iPE, \text{bottom}}} \quad (3)$$

$$activity_{pw-bw} = \frac{C_{iPE, \text{pw}}}{C_{iPE, \text{bottom}}} \quad (4)$$

3.6. Environmental gradients

Water column activity ratios (activity$_{wc}$) were calculated for PBDEs at all sites (SI Table 4). For locations in which surface and bottom samples were not both retrieved, a nearby sampling location was used as a surrogate. This was the case at Poppasquash Point, Quonset Point, and Conimicut Point (for locations, see Fig. 1). Due to high levels of uncertainty, activity$_{wc}$ were not derived for BDEs 15, 154, and 153. In addition, BDEs 30 and 183 were not

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Table 2

Comparison of dissolved concentrations of PBDE 47 and 99 (highest and range) from this (Narragansett Bay) and other studies.
detected in either surface or bottom samplers so an activity_{wc} could not be calculated.

BDE 8 did not show either a significant surface or bottom source (not reliably < or > 1) except at Sally Rock where a bottom source was apparent (<1). Activity_{bw} of BDE 28 indicated a surface source at all locations (>1). Activity_{wt} of tetra BDEs (47 and 49) indicated equilibrium conditions or a surface source (>1) for most locations but 49 showed a bottom source (<1) at Conimicut Point and Mount View. Activity_{bw} of penta BDEs (99 and 100) showed a mixture of results with equilibrium conditions at many locations and bottom sources at Mount View and Sally Rock. Due to the low concentrations of the higher molecular weight (MW)/K_{mw} hexaBDEs (153 and 154), the uncertainty was very high, however these congeners were only detected in bottom water PE samples implying a bottom source to surface water.

In summary, lighter PBDEs displayed a higher activity in surface water while heavier PBDEs displayed a higher activity in bottom water. This suggests that lighter PBDEs may be deposited from the atmosphere via air–water exchange or are flushed into the Bay as runoff with rivers or from wastewater treatment plants, while heavier PBDEs are released to the water from below, possibly by desorbing from settling particles or being released from historically contaminated sediments.

For BDEs 8, 49, and 100, we were able to show a significant environmental gradient between porewater and bottom water (activity_{pw-bw}) at Conimicut point. Activity_{pw-bw} of BDE 8, a low MW PBDE detected, was >1 implying that porewater is a source of this congener to bottom water. Conversely, activity_{pw-bw} of BDEs 49 and 100 at Quonset and Conimicut points, indicated a water column source (<1). BDEs 15, 28, 47, and 99 could not be included in this analysis because of high uncertainties due to large differences between replicate samplers. In addition, the uncertainty in the high-MW congeners was also high due to their low water solubility. No statistical evidence can be provided, but hexa congeners were not detected in porewater or surface water implying that larger PBDEs may be debrominated into smaller congeners in the sediments.

By examining activity_{wc} and activity_{pw-bw} we can assess the flux directions of PBDEs in the entire water column. These net gradients are illustrated for various PBDEs at Quonset and Conimicut Points in Fig. 3. Statistically significant water column/porewater gradients could only be derived for BDEs 8, 49, and 100. BDE 8 (di) displayed a higher activity in porewater relative to bottom water, but was at/near equilibrium in the water column (Fig. 3). This implies that on-going deposition as well as previously deposited PBDE 8 (or larger PBDEs degrading in sediments) contribute to bottom water contamination.

BDEs 49 and 100 (tetra and penta) displayed a higher activity in bottom water relative to porewater at both sites. Within the water column, BDE 100 was at/near equilibrium, while BDE 49 activity ratios indicated that bottom water had a higher activity than surface water at Conimicut Point and Mount View (Fig. 3). It is important to note that Quonset bottom samplers were related to Mount View surface (nearby), and Conimicut bottom samplers were related to North Prudence.

HexaBDEs (153 and 154) were not detected in surface or porewater implying a higher activity in bottom water relative to both surface and porewater. This could be due to degradation/debromination of these PBDEs in the sediments coupled with on-going deposition from the water column on settling particles.

4. Conclusions

Dissolved PBDEs were detected in Narragansett Bay up to 3 pg L⁻¹ orders of magnitude smaller than effective concentrations measured for aquatic organisms. Concentrations derived in this study were comparable to studies that have measured water concentrations using other methods (SPMD, filter and XAD with correction factor), however it is important to note that comparison of these studies using different methods is prone to errors. By deploying PE in different water depths and sediments, we were able to deduce gradients of PBDEs in Narragansett Bay. Our gradients imply that the lower brominated PBDE 8 was likely deposited via air–water exchange and runoff to surface waters. Simultaneously, there seemed to be re-release of this congener from sediments back to the water column. For the higher brominated PBDEs, the deeper water appeared to be acting as a source, suggesting that the PBDEs reach depth on particles, and/or that these congeners are degraded in sediments, leading to net uptake. All data indicated that on-going sources continue to deliver PBDEs to Narragansett Bay and most likely will continue to do so for years to come.

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Appendix. Supplementary information


References


Fig. 3. Environmental gradients as determined using water column activity ratios and porewater-bottom water activity ratios.