A mass budget of polybrominated diphenyl ethers in San Francisco Bay, CA

John J. Oram a,*, Lester J. McKee a, Christine E. Werme b, Michael S. Connor a, Daniel R. Oros a, Richard Grace c, Francois Rodari g

A mass budget of polybrominated diphenyl ethers (PBDEs) in San Francisco Bay is developed as a first step towards understanding the local sources and transport processes controlling PBDE fate in a highly urbanized estuary. Extensive monitoring of PBDEs in estuarine water and sediment, freshwater tributaries, air, and wastewater effluents and sludges were integrated with a mass budget model to provide a synthetic view of these emerging contaminants. The Bay inventories of BDE 47 and BDE 209 in 2006 were estimated to be 33 ± 3 kg and 153 ± 45 kg, respectively. Empirically derived estimates of annual inputs of BDE 47 and BDE 209 from all quantifiable external sources ranged from 11 to 28 kg/yr and 22 to 42 kg/yr, respectively. BDE 47 loads were dominated by wastewater while runoff from local tributaries represented the largest contributor to BDE 209 loads. Model results suggest the Bay PBDE inventory is highly sensitive to changes in external loads, with degradation and outflow being the major processes governing PBDE fate. The mass budget presented provides a framework for integrating future monitoring and modeling efforts.

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1. Introduction

Polybrominated diphenyl ethers (PBDEs), since their increase in use as flame retardants in plastics and textiles, are now observed in virtually every part of the biosphere and are rightly described as “ubiquitous environmental pollutants” (Jansson et al., 1987). Until recently they were unregulated and rarely included in environmental assessments. Beginning in the 1980s, reports of PBDEs in environmental samples emerged from North America (Stafford, 1983; Stanley et al., 1991), Scandinavia and Europe (Jansson et al., 1987; de Boer, 1990; Hagenmaier et al., 1992; Sellström et al., 1993), and Japan (Watanabe et al., 1987). Following on from this early work, a growing volume of recent studies have confirmed the ubiquitous nature of PBDEs which are now present in urban and rural soils (Harrad and Hunter, 2006), river and urban stormwater and bed sediment, lake and marine sediments, air, sewage sludge and wastewater, shellfish, fish, bird eggs and tissue, mammalian tissue and milk, and human blood, tissue and breast milk (see recent reviews: de Witt, 2002; Watanabe and Sakai, 2003; Hites, 2004; Law et al., 2006). European concentration as indicated by human breast milk have been increasing exponentially since the early 1970s (Meironyté et al., 1999) but there are indications of stabilization or even decline perhaps associated with the reduction in use of Penta-BDE mixture in Europe (see review by Law et al., 2006). In Japan, trends have been similar to those of Europe (rapid increases in the 1970s and 1980s with leveling off after bans of the tetra BDEs in 1990 (see review by Watanabe and Sakai, 2003). In contrast, the exponential increase appears to be more rapid in North America and is only in a few cases showing stabilization (de Wit, 2002; Hale et al., 2003; Hites, 2004; Jay Davis, personal communication). It is now becoming clear that the environment and people in North America are up to 10 or even 100 fold more contaminated with PBDEs as compared to Europe. These observations appear consistent with the facts that North America consumes about 51% of the world production (Rahman et al., 2001; Birnbaum and Staskal, 2004) and that controls on use and bans have only recently begun.

The pathways by which PBDEs get from a place of manufacture or use into the physical environment are not fully understood (Alcock et al., 2003), but conceptually release can occur during initial synthesis, during incorporation into commercial products, during wear or degradation of products, or during disposal and recycling (Hale et al., 2003). Since PBDEs are synthesized in just a few locations, direct release is not the likely cause of their ubiquitous nature (Hale et al., 2003). In contrast, there are many locations where commercial manufacture of PBDE-

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containing products occurs, and the impacts of some of these sites have been recognized (Allchin et al., 1999). There are few studies that describe the magnitude of release from in-use product (Palm et al., 2002; Alcock et al., 2003). Studies of concentrations in sewage sludge and, more recently, treated wastewater and its downstream effects are more numerous (Hagenmaier et al., 1992; de Boer et al., 2003; North, 2004; Gevao et al., 2006; Anderson and MacRae, 2006) but research on how PBDEs get from a location of use into the wastewater stream are still lacking. Research into PBDE release during disposal and recycling has been completed in a few locations; this work has considered incineration, end-of-life vehicles and furniture recycling, and landfill disposal (Alcock et al., 2003). There have been several efforts to evaluate PBDE sources and pathways through modeling. For example, Rayne and Ikonomou (2002) used an aquatic transport model in concert with semipermeable membrane devices to reconstruct source congener patterns. Atmospheric fate modeling was carried out by Gouin and Harner (2003) to better understand PBDE loading sources in remote regions. Although there are a number of papers that describe concentrations in sediments adjacent to urban areas (e.g. Lacorte et al., 2003), there has been only one paper on loads in river systems (Guan et al., 2007). Furthermore, there have been no attempts to estimate a PBDE mass balance for a receiving water body.

California, and in particular, San Francisco Bay, is a known global PBDE hot spot. Studies have found elevated concentrations of PBDEs in Bay Area wildlife and humans that are among the highest reported in the world. She et al. (2002) found concentrations of PBDEs in harbor seal blubber ranging from 88 to 8325 ng/g lipid weight. Especially alarming, the data suggested that concentrations of PBDEs in seal blubber had doubled every 1.8 years throughout the 1990s, with concentrations at the end of the decade among the highest ever reported. She et al. (2002) also reported high concentrations of PBDEs

![Fig. 1. Location map: Circles indicate RMP water stations; crosses indicate RMP sediment stations (2002–2006). The shaded area on the inset map represents the Sacramento River and San Joaquin River watersheds (collectively termed the Central Valley), which together comprise approximately 37% of California’s surface area.](image-url)

in human breast adipose tissue, with concentrations ranging from 17 to 462 ng/g lipid and averaging 86 ng/g lipid, the highest concentrations that had ever been reported in human tissues and at or near levels thought to be of concern for human health. PBDE concentrations in San Francisco Bay bivalves are among the highest reported worldwide (Oros et al., 2005) and concentrations in California coast fish (Brown et al., 2006) and San Francisco Bay fish (Holden et al., 2003; Brown et al., 2006) are one, or in some cases, two orders of magnitude greater than fish concentrations in Japan or Europe. Most recently, PBDE concentrations were studied in blood of pregnant women living in a California agricultural community and although lower than observed in other parts of the U.S., averages were well above European concentrations (Bradman et al., 2007). Clearly, understanding sources, release, fate, and toxicity of PBDEs in California and San Francisco Bay is of paramount importance. The decision to ban the use of Penta- and Octa-BDEs in California went into effect on June 1st 2006.

The objectives of this paper are to (1) document PBDE concentrations in an urbanized estuary; (2) quantify pathways including first-of-its-kind data on concentrations and loads in urban stormwater; (3) develop a mass balance for San Francisco Bay using empirical data collected locally in stormwater, wastewater, and atmospheric deposition; (4) estimate loss pathways and fate in the Bay at future times under a variety of plausible loading scenarios; and (5) provide a benchmark for future trend comparisons as bans are enforced. The focus is on BDE 47 and BDE 209, congeners selected because of their overlap in local monitoring efforts and because they are two of the most dominant congeners observed in San Francisco Bay (Oros et al., 2005). Further, BDE 47 is often elevated in biota (Hites, 2004) and BDE 209 concentrations are typically greatest in sediments (Hale et al., 2003).

2. Methods

2.1. Location and setting

San Francisco Bay (Fig. 1) receives runoff, sediments and pollutant loads from the Sacramento/San Joaquin watershed, commonly referred to as the Central Valley of California and from local Bay Area watersheds. The Central Valley, upstream from Mallard Island, has an area of 154,000 km² and covers 37% of the land area of California (411,000 km²). A further 6650 km² (4% of the total San Francisco Bay Area watershed) is associated with the urban and agricultural watersheds of the nine adjacent counties that directly fringe the Bay (Marin, Sonoma, Napa, Solano, Contra Costa, Alameda, Santa Clara, San Mateo, and San Francisco). The Bay has a volume of 5.5 km³ and an open water surface area of 1100 km² at mean sea level. In addition, a discontinuous fringe marsh with an area of 950 km² occupies the area between the conurbation and the open Bay. Tides in the Bay are semi-diurnal with a range of 1.78 m at the Golden Gate Bridge (mean lowest low water to mean highest high water) but vary in magnitude depending on location (e.g. Mallard Island: 1.25 m). Annual average water discharge for the period 1971–2000 from the Sacramento/San Joaquin watershed past Mallard Island was 24.9±10³ m³ (162 mm of runoff) (McKee et al., 2006). A further 1.05±10³ m³ (158 mm of runoff) or approximately 4% of the total freshwater input is provided by the local urban and agricultural drainages in the nine-county Bay Area. Suspended sediment loads entering the Bay past Mallard Island average 1 million metric t/y (McKee et al., 2006) or approximately 6.5 metric t/km². There is no recent estimate of suspended sediment loads entering the Bay from local tributaries; the best estimate remains 0.75 million metric t (Krone, 1979) or approximately 113 metric t/km² (43% of the Bay sediment budget). Based on the 2000 census, the population in the nine-county

| Table 1 | PBDE congeners, grouped by homologue, targeted in Bay water and sediment samples and water samples from Coyote Creek, Guadalupe River, and Mallard Island |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| BDE 007 | BDE 017/025 | BDE 047 | BDE 085 | BDE 128 |
| BDE 008/011 | BDE 028/033 | BDE 049 | BDE 099 | BDE 138/166 |
| BDE 010 | BDE 051 | BDE 100 | BDE 183 |
| BDE 012/013 | BDE 053 | BDE 066 | BDE 105 | BDE 190 |
| BDE 015 | BDE 055 | BDE 116 | BDE 154 |
| BDE 017 | BDE 075 | BDE 119/120 | BDE 155 |
| BDE 019 | BDE 077 | BDE 126 | BDE 209 |

1 Coeluting congeners.

Sampling was performed during normal dry weather operating conditions using ultra clean methods.

2.2.5. Laboratory analysis and quality assurance

Forty individual and co-eluting PBDE congeners were targeted for chemical analysis in all water and sediment samples (Table 1). Water samples were analyzed according to U.S. EPA Method 1614. Analysis was by high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) following methods outlined in Oros et al. (2005). For Bay water samples, both dissolved and particulate fractions were analyzed. Analysis of all other water samples (i.e., from tributaries, the Delta, and wastewater effluent) was performed on whole water. All sediment samples (from Bay and wastewater sludge) were analyzed by gas chromatography/mass spectrometry (GC/MS) following methods outlined in Oros et al. (2005). Determination of SSC in water samples collected at Mallard Island, Coyote Creek, and Guadalupe River was made using method 2540D (Standard Methods, 2005).

Quality assurance measures for PBDEs in the various environmental matrices are detailed in the RMP’s Quality Assurance Project Plan (SFEF, 1999) and in Oros et al. (2005). Briefly, for all matrices, cleaned sample extracts and blanks were spiked with surrogate recovery standards prior to solvent extraction to monitor methodological analyte losses. 13C-labeled PBDE surrogate standards were used for all water samples. A surrogate standard containing 2,2′,4,4′,6-pentachlorobiphenyl and 2,2′,3,3′,4,5,5′,6-octachlorobiphenyl was used for sediment samples. Recoveries between 50% and 120% were accepted. Concentrations in sediment were corrected for surrogate recoveries. Precision on replicate samples (RDP/RSD) and recoveries on matrix spike samples were evaluated to ensure accuracy were generally within targets (70–170%). Results in batches with these analyses outside of data quality objectives were censored and not reported.

2.3. Estimation of loads

2.3.1. Sacramento–San Joaquin River Delta

Sediment loads were determined for WWY 2005 and WWY 2006 following McKee et al. (2006). PBDE loads were calculated for WWY 2005 and WWY 2006 by multiplying flow weighted average concentrations (FWMC) for each water year by total annual Delta outflow. The use of a FWMC was necessary given that a significant relationship was not observed between PBDE concentrations and SSC at Mallard Island. Estimates of total annual Delta outflow for each water year were obtained from the California Department of Water Resources (DWR, 2007). PBDE loads were then corrected for dispersive effects using the method described by McKee et al. (2006) for suspended sediment.

2.3.2. Local watersheds

PBDE loads from Coyote Creek and Guadalupe River were estimated on 15-min intervals by relating measured concentrations of PBDEs to measurements of stream discharge and SSC provided by the USGS. The SSC data were generated using the USGS using a regression estimator and USGS standard protocol to account for cross-sectional variation in SSC. Two linear regressions were established between contaminant concentrations and corresponding SSC: one regression for ‘rising’ stage samples when water was derived from urban runoff and another for ‘falling’ stage samples when water was derived mainly from the upper, undeveloped, watershed. The regressions were used to construct a series of estimated contaminant concentrations on 15-min intervals over the duration of the study (WWY 2005 for Coyote Creek and WWY 2005 and WWY 2006 for Guadalupe River). Contaminant concentrations were multiplied by 15-min discharge to calculate 15-min contaminant loads which could then be summed to any desired interval (days, months or annual).

2.4. Mass budget model

A one-box mass budget model of PBDEs in water and sediment was developed to enhance understanding of the fate of PBDEs in San Francisco Bay. The model was initially developed by Davis (2004) to predict the long-term fate of PCBs in San Francisco Bay and has proven useful in developing mass budgets for other organic contaminants (e.g., PAHS: Greenfield and Davis, 2005; organochlorine pesticides: Leatherbarrow et al., 2006). The one-box model of the Bay treats the ecosystem as a single well-mixed volume with two compartments representing the water column and surface sediments. Conceptually, the model assumes that exchange between these two compartments is more important than exchange between the geographic sub-regions of the Bay. The model includes parameters for describing the major physical processes governing transport and fate of organic contaminants in aquatic systems: external loads entering the water column, settling and resuspension of sediment particles, sediment-water diffusive exchange, atmospheric deposition, volitization, degradation in water and sediment, tidal flushing, and outflow. Burial was excluded from the model, as the Bay is believed to be net erosional (Davis, 2004; Schoenherr et al., 2005).

Bay-specific model parameters were identical to those used by Davis (2004) in predicting the long-term fate of PCBs in the Bay. The major difference between the one-box model used here and that used by Davis (2004) is the inclusion of tidal flushing.

Tidal flushing was added to the one-box model in response to comments on Davis (2004). These comments, including the equations governing tidal exchange, are found in Connolly et al. (2005). The response of Davis (2004) to these comments is in Davis and Oram (2005).

Chemical-specific model parameters include BDE-specific rate constants and coefficients (Table 2). The degradation rates listed in Table 2 are those estimated by Wania and Dugan (2003). Lacking any empirical quantitative information on the degradation rates of PBDEs, Wania and Dugan (2003) used an EPA software package (EPI Suite) to estimate the degradation rates of PBDEs in air, water, soil, and sediment. These values served as preliminary estimates for development of the one-box model used here. Further analysis and refinement of degradation rates is presented in the Results and discussions section.

Given the lack of reliable information regarding the diffusion of PBDEs between water and sediment, this process was ignored in this study. Sensitivity analysis conducted by Davis (2004) revealed the PCB one-box model results were insensitive to the water-to-sediment diffusion coefficient. Similar analyses performed in this study, using the range of values presented in Davis (2004), confirmed these findings and provided justification for omitting this process.

The model was run in both hindcast and forecast modes. For the hindcast scenario, the model was initialized with no PBDE mass in Bay water and sediment. The model was run for 30 years under continuous loading conditions until a steady-state PBDE mass was achieved. The hindcast scenario aimed in establishing a plausible range of loads of BDE 47 and BDE 209 to the Bay from all external sources. Moreover, the hindcast model allowed for calibration of BDE-specific degradation rates and served as an independent test of the PBDE loads estimated from monitoring results. In forecast mode, the model was initialized with the best estimate of the current PBDE mass in the Bay and run under various continuous loading scenarios. Forecast scenarios allowed for a preliminary but informative assessment of the future trajectory of the Bay under a range of scenarios. BDE 47 and BDE 209 were selected for modeling because they are the two most dominant congeners observed in San Francisco Bay (Oros et al., 2005). BDE 47 is often elevated in biota (Hites, 2004) and BDE 209 concentrations are typically greatest in sediments (Hale et al., 2003). These two congeners were modeled independently of each other. No attempt was made to account for the potential transformation of high molecular weight congeners to lower weight congeners. Laboratory studies have shown that BDE 209 can be reductively debranched via photoysis (e.g., Sellstrom et al., 1998) and microbial processes (e.g., He et al., 2006), however the extent of occurrence of these processes in the environment has not been established (de Wit, 2002).

3. Results and discussion

3.1. Concentrations and loads

3.1.1. Bay water and surface sediment

Concentrations of BDE 47 in whole water samples collected from 2002 to 2006 ranged from 15.5 to 337 p.p.l. (Table 3) with a spatially unbiased mean estimate of 54.9 ± 4.6 p.p.l. (mean ± t-stat. error). Concentrations of BDE 209 in whole water samples collected from 2002 to 2006 ranged from 12.3 to 533 p.p.l. with a spatially unbiased mean estimate of 32.8 ± 5.1 p.p.l. BDE 47 is fairly ubiquitous throughout the Bay, with slightly elevated concentrations in the northern reaches. BDE 209 concentrations are generally higher in the southern reaches of the Bay.

Concentrations of BDE 47 in surface sediment (top 5 cm) samples collected from 2004 to 2006 ranged from 0.04 to 3.84 ng/g with a spatially unbiased mean estimate of 0.41 ± 0.02 ng/g. Concentrations of BDE 209 in surface sediment samples collected from 2004 to 2006 ranged from 0.02 to 13.7 ng/g with a spatially unbiased mean estimate of 1.9 ± 0.3 ng/g. Both BDE 47 and BDE 209 are ubiquitous in Bay sediments, showing no clear regional patterns. Concentrations of BDE 47 in Bay surface sediments are similar to those reported in coastal and river sediments in Portugal, Spain, Sweden, and the United Kingdom (UK) (Table 4). The high concentration of BDE 47 in UK sediments

Table 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>BDE 47</th>
<th>BDE 209</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degradation rate in water (1/d)</td>
<td>0.0046</td>
<td>0.0046</td>
<td>Wania and Dugan, 2003</td>
</tr>
<tr>
<td>Degradation rate in sediment (1/d)</td>
<td>0.0012</td>
<td>0.0012</td>
<td>Wania and Dugan, 2003</td>
</tr>
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<td>Water-side evaporation coefficient (m/d)</td>
<td>0.67</td>
<td>0.59</td>
<td>Cetin and Otabasi, 2005</td>
</tr>
<tr>
<td>Air-side evaporation coefficient (m/d)</td>
<td>251</td>
<td>216</td>
<td>Cetin and Otabasi, 2005</td>
</tr>
<tr>
<td>Water-to-sediment diffusion coefficient (m/d)</td>
<td>0</td>
<td>0</td>
<td>Process ignored; See text for rational.</td>
</tr>
<tr>
<td>Octanol–water partitioning coefficient (Log Kow)</td>
<td>6.81</td>
<td>9.97</td>
<td>Mackay et al. (2006)</td>
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<tr>
<td>Henry’s law constant (Pa-m3/mol; ΔT = 15°C)</td>
<td>0.56</td>
<td>0.02</td>
<td>Cetin and Otabasi, 2005</td>
</tr>
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</table>

1Initial values used for model development. See text for discussion of sensitivity analysis and refinement of these parameters.

Table 3

<table>
<thead>
<tr>
<th>Location</th>
<th>Congener</th>
<th>Min</th>
<th>Max</th>
<th>FWMC¹</th>
<th>Slope (ng/mg)</th>
<th>Intercept (ng/L)</th>
<th>R²</th>
<th>Region of hydrograph</th>
<th>Water Year</th>
</tr>
</thead>
<tbody>
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<td>SF Bay</td>
<td>BDE 47</td>
<td>0.02</td>
<td>0.34</td>
<td>0.062</td>
<td>–</td>
<td>–</td>
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<td>2002–2006</td>
</tr>
<tr>
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<td>BDE 209</td>
<td>0.01</td>
<td>0.53</td>
<td>0.032</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2002–2006</td>
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<td>BDE 47</td>
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<td>26.6</td>
<td>14.8</td>
<td>0.1</td>
<td>1.5</td>
<td>0.7</td>
<td>Rising</td>
<td>2005</td>
</tr>
<tr>
<td>Guadalupe</td>
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<td>115.0</td>
<td>94.7</td>
<td>0.2</td>
<td>49.0</td>
<td>0.7</td>
<td>Rising</td>
<td>2005</td>
</tr>
<tr>
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<td>20.1</td>
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<td>0.7</td>
<td>0.7</td>
<td>Falling</td>
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<td>0.1</td>
<td>8.8</td>
<td>0.6</td>
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<td>2005</td>
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<tr>
<td>Guadalupe</td>
<td>BDE 47</td>
<td>1.7</td>
<td>26.5</td>
<td>8.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.9</td>
<td>Rising</td>
<td>2005</td>
</tr>
<tr>
<td>Guadalupe</td>
<td>BDE 209</td>
<td>8.5</td>
<td>115.0</td>
<td>43.3</td>
<td>0.1</td>
<td>8.0</td>
<td>0.7</td>
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<td>2005</td>
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<td>3.5</td>
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<td>0.0</td>
<td>0.7</td>
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<td>2005</td>
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<tr>
<td>Coyote Creek</td>
<td>BDE 209</td>
<td>3.4</td>
<td>5.9</td>
<td>4.6</td>
<td>0.0</td>
<td>0.0</td>
<td>0.7</td>
<td>Rising</td>
<td>2005</td>
</tr>
<tr>
<td>Coyote Creek</td>
<td>BDE 47</td>
<td>0.9</td>
<td>1.7</td>
<td>1.4</td>
<td>0.0</td>
<td>0.0</td>
<td>0.7</td>
<td>Rising</td>
<td>2005</td>
</tr>
<tr>
<td>Coyote Creek</td>
<td>BDE 209</td>
<td>1.7</td>
<td>119.0</td>
<td>32.3</td>
<td>0.1</td>
<td>0.0</td>
<td>0.9</td>
<td>All</td>
<td>2005</td>
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<tr>
<td>Mallard</td>
<td>BDE 47</td>
<td>0.1</td>
<td>0.4</td>
<td>0.1</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2006</td>
</tr>
<tr>
<td>Mallard</td>
<td>BDE 209</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2006</td>
</tr>
</tbody>
</table>

¹FWMC = Flow-Weighted Mean Concentration; calculated on a per sample basis.
²Spatially unbiased mean estimate.

(368 ng/L) reported by Allichin et al. (1999) was downstream of a potential source of PBBE. Concentrations of BDE 209 in surface sediment in San Francisco Bay fall towards the low end of concentrations reported elsewhere.

Assuming a total Bay water volume of 5.5 × 10⁶ m³ (Davis, 2004), current mass inventories of BDE 47 and BDE 209 in Bay water were estimated to be 0.30 kg (95% CI = 0.25–0.35) and 0.16 kg (95% CI = 0.10–0.22), respectively. Mass inventories in sediment were estimated assuming a sediment volume of 1.6 × 10⁷ m³ (top 15 cm) and a concentration of sediments in solid of 0.5 kg/L (Davis, 2004). Current mass inventories of BDE 47 and BDE 209 in Bay sediment were estimated to be 33 kg (95% CI = 30–36) and 153 kg (95% CI = 107–158), respectively.

3.1.2. Sacramento–San Joaquin River Delta

BDE 47 concentrations during flood flow at Mallard Island during WYs 2005 and 2006 ranged from 0.1 to 0.45 ng/L with a flow weighted mean concentration of 0.24 ng/L.

Table 4

<table>
<thead>
<tr>
<th>Location</th>
<th>BDE 47</th>
<th>BDE 209</th>
</tr>
</thead>
<tbody>
<tr>
<td>China (Pearl River Delta)</td>
<td>0.4–7340</td>
<td>–</td>
</tr>
<tr>
<td>China (Yangtze River Delta)²</td>
<td>0.16–946</td>
<td>–</td>
</tr>
<tr>
<td>Denmark³</td>
<td>3.67–215</td>
<td>–</td>
</tr>
<tr>
<td>Japan²</td>
<td>–25–1600</td>
<td>–</td>
</tr>
<tr>
<td>Netherlands⁵</td>
<td>4–510</td>
<td>–</td>
</tr>
<tr>
<td>Portugal⁴</td>
<td>0.03–9.91</td>
<td>–</td>
</tr>
<tr>
<td>Spain⁴</td>
<td>0.1–0.2</td>
<td>2.1–113²</td>
</tr>
<tr>
<td>Sweden⁴</td>
<td>–2.4</td>
<td>2.1–112³</td>
</tr>
<tr>
<td>UK</td>
<td>0.3–36²</td>
<td>0.6–319³</td>
</tr>
<tr>
<td>USA</td>
<td>0.5–52³</td>
<td>29–1548³</td>
</tr>
</tbody>
</table>

This study

- Coyote Creek, CA¹⁰         | 4.6–319 | 171–202.9 |
- Guadalupe River, CA¹⁰      | 7.4–219.9| 23.3–1997.6|
- Mallard Island, CA¹⁰       | 2.4–3.4 | 2.2–6.5   |
- SF Bay, CA¹¹               | 0.04–3.84| 0.02–19.3 |

ND = Non-detect.

¹Adapted from Mai et al., 2005.
²Chen et al., 2006.
³From Mai et al., 2005.
⁴Lacorte et al., 2003.
⁵Ejlarret et al., 2004.
⁶Sellsborn et al., 1998.
⁷Allichin et al., 1999.
⁸Hale et al., 2001; sum of tetra- to hexa-BDEs: approx. 55% BDE 47.
⁹Raff and Hites, 2004; Conc. on suspended sediments; Sum of 15 congeners with approx. 96% BDE 209.
¹⁰Total concentration in water normalized to instantaneous SSC.
¹¹2004-2006 RMP Data; www.sfei.org/rmp.

Due to blanket contamination BDE 209 was only quantified in WY 2005 samples. BDE 209 concentrations during WY 2005 flood flow ranged from 0.1 to 0.3 ng/L with a flow weighted mean concentration of 0.14 ng/L (Table 3). WW 2006 was a wetter year that exhibited peak flow about 4 times greater than WW 2005. BDE concentrations have rarely been measured in flooding river water. However, the BDE 47 concentrations measured at Mallard Island appear to about four times greater than the average measured in eight rivers discharging to the Pearl River Delta (China), polluted with manufacturing and e-waste sources. In contrast, the Mallard Island BDE 209 concentrations appear to be an order of magnitude lower than measured in the Chinese example (Guan et al., 2007). The main sources of PBBEs in the Sacramento/San Joaquin watershed are likely the urban areas of Sacramento (Year 2000 census: 1.2 million people) and a number of smaller cities and towns (e.g. the greater Stockton area: 0.4 million people). During wetter years, the loads from urban areas in the watershed are likely diluted by water that is relatively low in PBBE concentrations derived from runoff from agricultural areas of the Central Valley floor and foothills and runoff and snow melt from the Sierra Nevada mountain range. Our observations for these two water years (Table 3) support a preliminary hypothesis that higher concentrations should be observed during lower flow years when proportional runoff from urban areas is greater. Significant relationships were not observed between PBBE concentrations and SSC for either water year (Table 3; Fig. 2). A FWMC was calculated for each year and used to estimate annual loads of PBBEs at Mallard Island. Annual loads of BDE 47 and BDE 209 were quantified for WW 2005. Only BDE 47 was quantified in WW 2006 (Table 5). BDE concentrations normalized to SSC appear to differ in their congeners profile to sediment concentrations measured in other parts of the world. Although concentrations were within the range reported in Portugal, Spain, Sweden, and the UK, the average ratio of BDE 47 to BDE 209 in Mallard Island samples (12) is much greater than for other locations where this can be estimated (Table 4). These ratios also differ to the only other river loading study to date (Guan et al., 2007) who reported BDE 209 dominating over BDE 47 by between 93:1 and 391:1 for eight rivers discharging to Pearl River Delta. Such a ratio suggests either a unique source of PBBEs to the Sacramento and San Joaquin River watersheds or a unique transport phenomenon.

Given the large size of the combined watersheds (approximately 37% of California’s surface area) and the land-use patterns of the region (25% urban, 31% agricultural, and 67% forest and open space) it is likely that atmospheric deposition of PBBEs onto watershed soils is a major driver for distributing PBBEs throughout the non-urban portions of the watershed. BDE 47 is more volatile than BDE 209 and is thus more susceptible to long-range atmospheric transport (Hale et al., 2001) and subsequent deposition. Unfortunately, information regarding PBBE congeners patterns in soils of the Sacramento-San Joaquin watershed is lacking, which precludes testing of this hypothesis.

Concentrations in air have been studied (see recent reviews: de Witt, 2002; Watanabe and Sakai, 2003; Hites, 2004; Law et al., 2006). These studies show a slow variation in the ratios of BDE 47:BDE 209 but in general show that BDE 209 can significantly dominate the ΣPBBE concentrations in atmospheric samples. However, due to differing use patterns between the U.S. and other countries and phase out of Perfluorodecane and BDE 47 and 49 (EU) and tetra-BDEs (Japan), atmospheric data collected in Europe and Japan are likely rendered inapplicable to the San Francisco Bay analysis presented here. Atmospheric concentrations in Great Lakes air may be more applicable and appear to indicate a dominance of BDE 209 relative to BDE 209 (Strandberg et al., 2001). Air concentrations have been studied in California and San Francisco by the California Air Resources Board. At their control site at University of California at Davis (25 km from the City of Sacramento), the ratio of BDE 47 to BDE 209
was 3.2:1 on average (Charles et al., 2005). Thus, the hypothesis for a dominance of atmospheric sources in water sampled at Mallard Island is not rejected but cannot be confirmed without further research.

Additionally, it is plausible that solubility is controlling the relative loads of BDE 47 and BDE 209 at Mallard Island. If the dissolved fraction of total loads at Mallard Island is significant, a likely scenario given the relatively low SSC, the greater solubility of BDE 47 combined with the long hydraulic residence time of the River-Delta system (weeks to months during non-flood conditions; Mięczka et al., 2006), could explain the high BDE 47 to BDE 209 ratio. A higher dissolved fraction would also help explain a lack of significant correlation between PBDEs and SSC at Mallard Island (Fig. 2). To date, only whole-water samples have been collected at Mallard Island and analyzed for PBDEs, which precludes testing of the solubility hypothesis. Presently it is uncertain which hypothesis provides the most plausible explanation (or perhaps a combination of both), but the ratio of BDE 47 to BDE 209 is unique when compared with other studies in the world and other tributaries in the Bay Area.

3.1.1. Local watersheds

BDE 47 concentrations in Guadalupe River water samples collected during WYs 2005 and 2006 varied from 0.6 to 26.5 ng/L (Table 3). BDE 209 concentrations ranged from 1.7 to 119 ng/L. When the data are stratified for rising stage (dominantly urban runoff) and falling stage (dominantly rural runoff), greater concentrations are observed in urban runoff water. Coyote Creek BDE concentrations varied in a similar manner but were generally lower (Table 3) probably due to sampling small floods with lower SSC concentrations and perhaps land use differences (Coyote Creek has proportionally less urban land use than Guadalupe River). Concentrations in both Coyote Creek and Guadalupe River were greater than those observed at Mallard Island on the Sacramento-San Joaquin River Delta, presumably due to proximity to sources and proportionally greater urban area in the small watersheds of Guadalupe (84%) and Coyote (34%) relative to the Sacramento-San Joaquin (2%). The BDE 47 and BDE 209 concentrations in Guadalupe River are about two orders and one order of magnitude greater than measured in the only other river loading study to-date in the Pearl River Delta, China (Guan et al., 2007). Concentrations of PBDEs in Coyote Creek and Guadalupe River samples normalized to SSC were compared to concentrations measured in coastal and river sediments throughout the world (Table 4). The ratios of BDE 47 to BDE 209 in both Coyote Creek and Guadalupe River samples (approximately 0.2) were within the range observed in sediments elsewhere.

Significant relationships were observed between PBDE concentrations and SSC at both Guadalupe River (Fig. 2; Table 3) and Coyote Creek (Table 3). During WY 2005 stronger relationships were observed when the data were stratified by rising and falling stage in both Guadalupe River and Coyote Creek (Table 3). The differences between rising and falling stage PBDE concentrations were attributed to land use and fit with our conceptual understanding of the association of PBDEs with urban land use more than agricultural or open space land use. During the rising stage, water is derived mainly from the lower areas of these watersheds, which are almost completely urbanized. Water from the rural upper watershed dominates the falling stage. Concentrations of PBDEs are known to be elevated in urban areas relative to rural areas (Butt et al., 2004), which supports the rising/falling dichotomy seen in Guadalupe River and Coyote Creek WY 2005 data. Stratifying the data relative to source water was not justified in WY 2006 partly because the sampling strategy that year focused on capturing more samples in the “falling stage” water associated more with the upper watershed where there are mercury sources (mercury data will be reported in a future paper). The watershed received many low intensity rainstorms in WY 2006. Although the total annual discharge was much higher, under low rainfall intensity conditions, most of the runoff was generated from impervious surfaces in the urban areas and proportionally less was derived from rural areas. Thus, the falling stages tended to have mixed urban and rural water disallowing stratification of the PBDE data. Regressions were applied to the appropriate regions of the hydrograph to determine the annual loads of BDE 47 and BDE 209 (Table 5). Because most base flow is generated from the upper watershed, loads during base flow conditions were generated using flow and 15-min estimates of

![Fig. 2. Scatter plots of BDE 47 and BDE 209 versus instantaneous SSC at Guadalupe River and Mallard Island during WY 2005 and WY 2006.](image)

concentrations based on the “falling stage” regressions. In any case, because SSC is <50 mg/L during base flow, applying either regression equation made little difference to the estimates of annual load.

Loads determined for Coyote Creek and Guadalupe River were used to derive a preliminary estimate of combined loads from all local small tributaries to the Bay Area conurbation. This estimate was based on the assumption that Coyote Creek and Guadalupe River was representative of all the local watersheds both in terms of land use and runoff characteristics (although neither assumption is strictly valid; these issues are discussed further below in relation to BDE 209 loading estimates). Runoff in Guadalupe River during WY 2005 was near average but Coyote Creek had below average runoff. Better methods for extrapolation of these limited data sets, including watershed models, are being developed. Here, using the assumption of representative land use and climate, loads were extrapolated based on watershed area excluding area upstream from reservoirs (Coyote Creek = 336 km², Guadalupe River = 236 km²), Bay watersheds = 5,050 km²) and BDE data for WY 2005 (the only water year with data from both Coyote Creek and Guadalupe River). The total loads from all local small tributaries were estimated to be 2.9 kg/y and 17.3 kg/y for BDE 47 and BDE 209 respectively (Table 6).

Table 6
Summary of estimated annual PBDE loads (kg) to San Francisco Bay

<table>
<thead>
<tr>
<th>Source</th>
<th>BDE 47</th>
<th>BDE 209</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sacramento-San Joaquin Delta 1</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Local tributaries *</td>
<td>3</td>
<td>17</td>
</tr>
<tr>
<td>Municipal wastewater</td>
<td>4-21</td>
<td>1-3</td>
</tr>
<tr>
<td>Atmospheric deposition</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>Total</td>
<td>11-28</td>
<td>22-24</td>
</tr>
</tbody>
</table>

* Determined using only data from WY 2005. Assumes WY 2005 representative of average water year.

3.1.4. Municipal wastewater

Concentrations of ΣPBDEs in treated effluents ranged from 14 to 66 ng/L. Percent contribution from BDE 209 ranged from 6% to 28%. A previous study of a municipal wastewater treatment plant which discharges effluent into the southern reach of San Francisco Bay reported effluent ΣPBDEs ranging from 0.004 to 29 ng/L, with BDEs 47 and 209 accounting for 36% and 6%, respectively (North, 2004). Mean concentrations in municipal sludge ranged from 1400 to 4900 ng/g ΣPBDEs. Municipal sludges in the region are incinerated, used as soil amendments, or are applied as alternative daily cover at municipal landfills and do not directly enter the Bay. It is estimated that 96% of the PBDEs entering municipal treatment plants are removed in sludges (North, 2004).

North (2004) reported ΣPBDE loads in effluent from a single wastewater treatment plant to be 0.9 kg/y. Using the range of measured concentrations in municipal effluent reported above and extrapolating to all municipal dischargers in the Bay (total discharge of approximately 230,000 Mg/y (equivalent to 8.71×10⁶ m³/y); Oros et al., 2005) results in an estimated annual load range of 12.2 to 57.5 kg ΣPBDEs. Oros et al. (2005) estimated an annual load of 23 kg from all municipal discharges, within the range estimated here. Using more accurate data and methods reported by North (2004), annual loads of BDE 47 and BDE 209 were estimated to be 4.4 to 20.7 kg and 0.7 to 3.4 kg, respectively.

3.1.5. Atmospheric deposition

In 2003 and 2004 the California Air Resources Board measured PBDE concentrations of ambient air at six urban areas, three of which are in the San Francisco Bay Area. Site average ΣPBDE concentrations ranged from 35 to 420 pg/m³ (CARB, 2004). The 420 pg/m³ site average concentration was anomalously high and has not been explained. Using 35 pg/m³ as the representative concentration in air, a deposition rate of 0.2 cm/s (the rate for 0.5 μm particles), the surface area of the Bay (approximately 1100 km²), and assuming PBDEs are half gaseous and half particulate (a reasonable assumption given findings by Harner and Shoich, 2002), an estimated 1 to 2 kg of ΣPBDEs enter the Bay through atmospheric deposition annually.

3.1.6. Summary of loads

Based on local data reported here, PBDE sources to San Francisco Bay are dominated by municipal wastewater and local tributary loads (Table 6). The Sacramento/San Joaquin watershed was a smaller contributor despite its large size and dominance in the water budget of the Bay. BDE 209 dominated the loads in the local urbanized tributaries of the nine-county Bay Area conurbation, whereas BDE 47 dominated loads at Mallard Island on the Sacramento/San Joaquin River system. Wastewater, in contrast, was dominated by BDE 47 largely because the treatment process more efficiently removed BDE 209 in sludge (North, 2004). Total external loads of BDE 47 and BDE 209 to San Francisco Bay are estimated to be 20 kg/y and 23 kg/y (Table 6). Due to the balance between municipal wastewater and urban storm water from local tributaries, the ratio of BDE 47 to BDE 209 in combined loads is 0.87:1.

Fig. 3. Hindcast model results for BDE 047 and BDE 209. The dashed lines indicate the best current estimates of mass inventory in Bay water and sediment. The shaded regions indicate the 95% confidence intervals around the best estimates. Blank contamination of a large number of samples is the cause of the wide confidence interval for BDE 209. Slow degr. = slow degradation in water (13 y half-life) and sediment (50 y half-life).

3.2. Mass budget model

3.2.1. Hindcast–estimation/verification of current loads and degradation rates

The model was used in hindcast mode to estimate a plausible range of PBDE loads to the Bay from all external sources (Fig. 3). The shaded regions indicate best estimates of the current inventory of BDE 47 and BDE 209 in Bay water and sediment. For BDE 47, results indicate that under a continuous external loading scenario of 20 kg/y there would be slightly less than 30 kg BDE 47 in the Bay after 30 years. Running the model with an annual external loading scenario of 30 kg/y yields an estimate of approximately 40 kg BDE 47 in the Bay after 30 years. The mass of BDE 47 in the Bay estimated using these two loading scenarios bound the independent estimates of mass inventory determined from monitoring data, providing further evidence that our empirical measurements of annual BDE 47 loads from external sources are likely well quantified and between 20 and 30 kg/y.

Sensitivity of model results to changes in degradation rates was evaluated to evaluate confidence in model predictions of BDE 47. The default degradation rates for BDE 47 in water and sediment (Table 2) were altered to simulate slow degradation. Results indicate that considerable degradation is needed to keep model results in agreement with empirical inventory and loading estimates for BDE 47 (Fig. 3). These findings suggest that the degradation estimates of Wania and Dugani (2003) are sufficient for the first-order mass budget of BDE 47 presented here.

For BDE 209, model results indicate that under a continuous external loading scenario of 80 kg/y there would be slightly more than 100 kg BDE 209 in the Bay after 30 years. Running the model with a continuous loading scenario of 140 kg/y estimates there would be approximately 200 kg BDE 209 in the Bay after 30 years. The estimates of BDE 209 mass in the Bay given by these two loading scenarios closely approximate the 95% confidence intervals around the mean estimate determined from empirical data. These loads are considerably higher than the range estimated from empirical data (22–24 kg/y; Table 6), indicating that either the rates governing the key BDE 209 loss pathways in the model (e.g., degradation) are incorrect or that the actual BDE 209 load from all external sources is in the range of 80 to 140 kg/y.

There are arguments to support both hypotheses. First, the agreement between model results and empirical inventory estimates of BDE 209 is indeed improved when the model is run with substantially slower degradation rates (half-lives of 13 y for water and 50 y for sediment) (Fig. 3). This suggests that the degradation rates estimated by Wania and Dugani (2003) for BDE 209 (Table 2) are not appropriate for San Francisco Bay. It is interesting to note that degradation rates estimated by Wania and Dugani (2003) were the same for BDE 47 and BDE 209. Indeed, there is no reason to expect that 47 and 209 would exhibit the same degradation rates. As for PCBs, one might expect higher degrees of halogenation to decrease the rate of degradation (e.g., Sinkkonen and Paasivirta, 2000). In fact, a recent study suggests such a trend for PBDEs (e.g., Robrock et al., 2008). The one-box model results presented here support such a relationship between halogenation and degradability of BDEs. Alternatively, the hypothesis of underestimated BDE 209 loads from empirical data is supported by the facts that only one, below average, water-year was used to construct the loads and that the Guadalupe River and Coyote Creek watersheds may not be representative of land uses found in the rest of the San Francisco Bay area. It is difficult to determine which of these two hypotheses explains the discrepancy between modeled and empirical loading estimates of BDE 209. In actuality it may be a combination of both. Continued monitoring efforts and model refinements will help resolve this discrepancy and yield a more accurate mass budget of BDE 209.

While using the model to estimate current PBDE loads to the Bay it must be acknowledged that currently no information exists regarding historic loads. While such information would be useful in refining the mass budget presented here the lack of information likely has only a small effect on model results. Davis (2004) found the long-term steady-state mass (of PCBs) estimated by the model to be independent of the initial mass. Further, the PBDE model achieves quasi-steady-state within 10 years, thereby minimizing the effects of unknown loading histories. Finally, one must acknowledge that the model parameters for BDE 47 and BDE 209 are uncertain. The model results presented here could indicate that the uncertainty of the BDE 209 parameters is greater than that of the BDE 47 parameters.

3.2.2. Forecast—estimation of recovery under various management scenarios

Forecast modeling was used to estimate the trajectory of the Bay under plausible future scenarios. Bay water and sediment were initialized with best estimates of current PBDE concentrations (Table 7). A quarter of the Bay-wide mean PBDE concentration was used to represent the PBDE concentration in ocean water near the Golden Gate (Fig. 1; Table 7). This estimate remains a key information gap for the forecast model. However, model results were only moderately sensitive to this parameter (not shown). For BDE 47, the degradation rates used in the forecast were identical to those used in the hindcast (Table 2). For BDE 209, however, forecasts scenarios were run using the degradation rates in Table 2 as well as those that produced the best agreement between model and data (Fig. 3).

Running the model using a scenario of BDE 47 loads continuing at the upper end of estimates of today’s annual loading (approximately 30 kg/y), a nearly 40% increase in the total BDE 47 inventory is likely (Fig. 4). However, using a scenario at the lower end of current load estimates (approximately 10 kg/y), a 50% decrease in the total inventory of BDE 47 in 40 years was predicted. Actually, the model suggests most of the 55% decrease will be realized in 10 years. Important loss pathways of BDE 47 from the Bay were degradation in sediment and outflow (Table 8).

The considerable difference between the 30 kg/y and 10 kg/y scenarios highlights the sensitivity of the Bay to changes in BDE 47 loads. The trajectory of the Bay is uncertain if loads remain the same. However, if loads are reduced slightly from current levels it is predicted that the mass in the Bay will decline appreciably. The recovery would be more rapid and more complete if loads of BDE 47 were stopped altogether; a recovery of 90% in less than 10 years is possible. This rate of recovery is considerably smaller as the degradation rates used in the model are the same for both BDE 47 and BDE 209, and lower than those used in the hindcast model for BDE 209.

Table 7

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Magnitude</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average BDE 47 conc. in water (pg/L)</td>
<td>45.9</td>
<td>RMP data 2002–2006</td>
</tr>
<tr>
<td>Average BDE 47 conc. in water in Central Bay (pg/L)</td>
<td>46.8</td>
<td>RMP data 2002–2006</td>
</tr>
<tr>
<td>Average BDE 47 conc. in sediment (ng/g)</td>
<td>0.4</td>
<td>RMP data 2004–2006</td>
</tr>
<tr>
<td>Average BDE 47 conc. in Pacific Ocean water (pg/L)</td>
<td>13.7</td>
<td>0.25-yr average estimated estimate</td>
</tr>
<tr>
<td>Average BDE 209 conc. in water (pg/L)</td>
<td>29.2</td>
<td>RMP data 2002–2006</td>
</tr>
<tr>
<td>Average BDE 209 conc. in water in Central Bay (pg/L)</td>
<td>19.4</td>
<td>RMP data 2002–2006</td>
</tr>
<tr>
<td>Average BDE 209 conc. in sediment (ng/g)</td>
<td>1.9</td>
<td>RMP data 2004–2006</td>
</tr>
<tr>
<td>Average BDE 209 conc. in Pacific Ocean water (pg/L)</td>
<td>7.3</td>
<td>0.25-yr average estimated estimate</td>
</tr>
</tbody>
</table>

Fig. 4. Model estimated future trajectory of BDE 47 mass in Bay water and sediment.

Table 8
Cumulative mass (kg) in each loss pathway after 40 y forecast simulation

<table>
<thead>
<tr>
<th>Loss pathway</th>
<th>BDE 47</th>
<th>BDE 209</th>
<th>BDE 209–slow degr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Burial</td>
<td>0 (0%)</td>
<td>0 (0%)</td>
<td>0 (0%)</td>
</tr>
<tr>
<td>Degradation in sediment</td>
<td>537</td>
<td>681</td>
<td>107 (14%)</td>
</tr>
<tr>
<td>Degradation in water</td>
<td>26</td>
<td>28 (3%)</td>
<td>2 (0%)</td>
</tr>
<tr>
<td>Outflow</td>
<td>290</td>
<td>244 (26%)</td>
<td>672 (80%)</td>
</tr>
<tr>
<td>Volatilization</td>
<td>4</td>
<td>0 (0%)</td>
<td>0 (0%)</td>
</tr>
<tr>
<td>Total</td>
<td>856</td>
<td>952</td>
<td>781</td>
</tr>
</tbody>
</table>

Each simulation used a total external loading rate of 20 kg/y. Degradation rates in the BDE 47 scenario are listed in Table 2. For BDE 209, the first scenario used degradation rates from Table 2 while the second scenario (slow degr.) used the degradation rates that produced the best agreement between the hindcast model and empirical inventory and loading estimates (see Fig. 3).

Different than that estimated for PCBs by Davis (2004) (90% recovery in 70 years) owing to higher degradation rates of PBDEs relative to PCBs. Fortunately reductions in BDE 47 loads appear to be imminent. As of June 2006 the manufacture, distribution, and processing of products containing Penta-BDE and Octa-BDE commercial mixtures were prohibited in the State of California. BDE 47 is a significant congener in the Penta-BDE mixture. As use of these mixtures declines, loads to the Bay are expected to also gradually decline as the inventory in the watershed is depleted over time.

Similarly, model results suggest high sensitivity of the Bay to BDE 209 loads. Using the degradation rates in Table 2 and the estimates of current loads that produced the best agreement with empirical inventory estimates in the previous section (80–140 kg/y), the Bay appears to be at the point where inventories will either continue to increase or begin to decrease (Fig. 5, top panel). Under this scenario, a total reduction of BDE 209 loads (0 kg/y) resulted in a 90% decrease in Bay inventory in less than 10 years. Alternatively, when using the degradation rates that produced the best agreement between model and empirical data, a much slower recovery of the Bay is forecast. A total reduction of loads under this scenario resulted in a 50% reduction in Bay inventory in approximately 10 years (Fig. 5, bottom panel). Important loss pathways of BDE 209 from the Bay were outflow and degradation in sediment (Table 8). The relative importance of these two processes was dependent on which degradation rates were used in the model; slow degradation rates increased the importance of outflow as a loss pathway for BDE 209.

Given the uncertainty in determining true environmental degradation rates for BDE 209, it is difficult to discern which of the BDE 209 scenarios is most plausible. Results from the Zone 4 Line A study and continued monitoring at Guadalupe River and Coyote Creek will help gauge the accuracy of present load estimates. As the load estimates are refined, the hypothesis of slow degradation will also be tested. If load estimates prove to be correct, for example, slow degradation of BDE 209 will become the more plausible scenario. The implications of reduced BDE 209 loads on the recovery of San Francisco Bay are therefore uncertain, though the model estimates presented here suggest a quick response (relative to PCBs for example) in the total inventory of BDE 209 in the Bay is plausible. Additionally, there remains concern that DecaBDE can degrade to lower molecular weight congeners (de Wit, 2002) that will continue to affect the Bay ecosystem, a process not accounted for in this mass budget.

4. Conclusions

The simple mass budget of BDE 47 and BDE 209 presented represents a first step towards understanding the fate of PBDEs in San Francisco Bay. Considerable uncertainty surrounds the derivation of model parameters (especially degradation rates), current in-Bay inventories, and current loads from external sources. However, the field data presented represent a pioneering effort to monitor these contaminants of emerging concern in an urbanized estuary while the mass budget model provides a framework in which these data can be integrated and synthesized. The end result is a more complete understanding of the pathways.
transporting PBDEs to the Bay, the processes controlling their ultimate fate, and the potential for management actions. Additionally, this mass budget provides a framework into which future monitoring and modeling efforts can be incorporated.

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