Patterns of Bioaccumulation of Polybrominated Diphenyl Ether and Polychlorinated Biphenyl Congeners in Marine Mussels

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Evidence for the bioaccumulative potential of PBDEs comes from a range of sources. Similarities in structure and physicochemical properties between PBDEs and PCBs suggest that environmental fate may be governed by similar processes. However, the ether linkage of the PBDEs in place of the biphenyl linkage of the PCBs and differences in the properties of bromine and chlorine as substituents distinguish PBDEs from PCBs in several key ways relevant to bioaccumulation. Importantly, PBDEs exhibit a wider range of molecular size and hydrophobicity than that of PCBs, with reports of measured and calculated octanol–water partition coefficients ($K_{OW}$) extending to $10^{10}$ or greater (3, 4). In addition, PBDEs appear to undergo debromination more readily than PCBs undergo dechlorination (5, 6). These characteristics would be expected to result in reduced bioaccumulation of the higher-substituted PBDE congeners relative to PCBs, but they may be expected to enhance the apparent bioaccumulative potential of intermediate-substituted congeners because of internal production from metabolic debromination of the higher congeners (7).

Empirical estimates of PBDE bioaccumulation are available for a range of taxa, including invertebrates (8, 9), fish (9–12), mammals (12–16) and birds (13). Biomagnification factors reported in these studies are typically on the order of 5–20 for BDE 47, indicating a bioaccumulative potential of some PBDEs comparable to that of the most bioaccumulative PCBs. Gustafsson et al. (8) found that bioaccumulation factors for BDE 47 and BDE 99 in blue mussels were several-fold higher than for PCBs of similar hydrophobicity. In contrast, Kelly et al. (17) reported no biomagnification of seven PBDE congeners and a trophic magnification factor for BDE 47 of only 1.6, substantially lower than most PCBs. A limitation of the previously reported data is that even studies that sampled many taxa generally report only a few key PBDE congeners. This restricts our ability to develop and validate general models of bioaccumulation for PBDEs (7, 18). Here, we report biota–sediment accumulation factors (BSAFs) for 27 detected congeners or coeluting pairs of congeners ranging in estimated $K_{OW}$ from $10^{4.5}$ to $10^{13.1}$. We compare these data to the patterns of bioaccumulation observed for 135 PCB congeners or coeluting sets of congeners measured in the same study organisms. Our objective is to describe the pattern of bioaccumulation among PBDE congeners relative to the well-known benchmark of the bioaccumulative PCBs to provide insight into the extent that a relatively good theoretical understanding of PCB bioaccumulation (e.g., ref 18) can be applied to modeling PBDEs.

**Experimental Section**

**Sampling.** Field sampling was conducted in September 2006 off the coast of Vancouver Island, British Columbia, Canada in the vicinity of the Capital Regional District’s Clover Point municipal wastewater outfall (48°23′67″N, 123°20′68″W) adjacent to the city of Victoria. Preliminary treated (screened) wastewater has been discharged from this outfall since 1981, resulting in localized effects on sediment chemistry and biology (19, 20). A total of 17 stations were sampled, including one adjacent to the diffuser (1.5 km from shore), 13 arranged in a radial design at 100, 200, 400, and 800 m from the diffuser (Figure S1 of the Supporting Information), and three in a reference area approximately 5.5 km southeast of the outfall. At each station, three grabs with a 0.1 m$^2$ Van Veen dredge were used to obtain a sample of surface sediment (top 2 cm) and 15 horse mussels (*Modiolus modiolus*), randomly selected from individuals >50 mm length (i.e., large enough that sufficient tissue mass would be available for all planned
analyses). Field duplicates of mussel samples were collected at the outfall terminus station. Shell length, shell width, total weight, tissue weight, age, and sex were determined for each mussel prior to compositing and homogenizing all mussels from each station for chemical analysis. Mussels were aged by counting annuli in the inner nacreous layer of an acetate peel preparation of a cross section cut through the umbole. Wastewater samples were obtained from a wet well at the treatment plant quarterly in 2006 as 24 h composites; field triplicate composites were taken in April 2006.

**Chemical Analysis.** Extraction, cleanup, and analysis of PBDEs and PCBs using high resolution gas chromatography–high resolution mass spectrometry (HRGC-HRMS) were conducted at AXYS Analytical Services Ltd. (Sidney, BC, Canada). Details of methods for PBDE and PCB determinations and quality assurance/quality control (QA/QC) procedures are provided in the USEPA Methods 1668A (21) and 1614 (22); modifications are described in the Supporting Information. Lipid content was determined gravimetrically. Organic carbon content was determined by USEPA Method 9060A (23) at the ALS Laboratory Group (Vancouver, BC, Canada). Data quality objectives were met for lipid (relative standard deviation of laboratory duplicates = 5%) and organic carbon [certified reference material recovery = 94 ± 1.1% (mean ± standard deviation, n = 5)]. Data quality objectives for PCBs and PBDEs were met for matrix spike recovery (50–150%) in all cases and for relative standard deviation of all duplicate analyses (<50%), with the exception of one or two congeners in some sediment duplicates that had relative standard deviations of 50–70%. Most congeners were below detection in laboratory blanks, and a few that were detected were generally at concentrations much less than the lowest sample value in the same batch (detailed QA/QC results are provided in the Supporting Information). Sediment PCB data from the eastern 800 m station were identified as suspect because this station had anomalously high PCB congener concentrations (up to 7-fold higher than the next highest of the 100–800 m stations) but only for congeners with K\textsubscript{OW} between 10\textsuperscript{5}–10\textsuperscript{6}; outside of this K\textsubscript{OW} range the suspect station was similar to the other stations. The analytical laboratory could offer no explanation for the anomalous data, but the resulting pattern of BSAFs (see below) suggested that this sample may have been compromised.

**Data Analysis.** Congener-specific BSAFs were calculated for PCBs and PBDEs at each location as the ratio of lipid-normalized concentration in mussel to organic carbon-normalized concentration in sediment. These BSAFs were then plotted as a function of the log K\textsubscript{OW} of each congener. Substances at thermodynamic equilibrium between mussel and sediment are expected to exhibit a BSAF of approximately 3, as this is the inverse of the mean organic carbon–octanol proportionality constant of 0.35 derived by Seth et al. (24). Many substances commonly exceed this benchmark due to processes that result in a magnification of chemical fugacity in biota relative to their diet or respiratory medium (25). For PCBs, the interplay of chemical property-dependent processes that determine the magnitude of bioaccumulation has been demonstrated to produce a parabolic relationship of the bioaccumulation factor (BAF) or BSAF as a function of log K\textsubscript{OW} (8, 11, 18, 26). Results for the few congeners reported by previous studies indicate that PBDEs may exhibit a similar relationship (8, 11, 27). Deviations of PBDE BSAFs from the parabolic relationship exhibited by PCBs would indicate possible differences in the processes underlying bioaccumulation for these two groups of chemicals.

Congener-specific estimates of K\textsubscript{OW} were obtained from the literature (28, 29). As we were most interested in exploring the pattern of bioaccumulation among congeners (i.e., it was the relative K\textsubscript{OW} of congeners that was important), we used K\textsubscript{OW} estimates generated by the same model for all congeners, rather than adopting (possibly more precise) measured values where available. Empirical data were plotted in comparison to the pattern of BSAFs predicted by a mechanistic bioaccumulation model (AQUAWEB (30)). The AQUAWEB model was parametrized for a benthic invertebrate consuming only sediment, ventilating 10% porewater, and with a first-order rate constant for metabolic transformation (k\textsubscript{M}) of either zero (i.e., no metabolism) or 0.01 d\textsuperscript{-1} (31) for all congeners. To explore the hypothesis of a “decoupling” of mussels from sediment chemical concentrations (discussed further below), we calculated predicted BSAFs assuming that the mussel diet had 1 times (i.e., similar to) and 10 times the measured sediment concentrations.

**Results and Discussion**

Of the 47 PBDE congeners and 209 PCB congeners analyzed, 34 PBDE and 153 PCB congeners or coeluting groups of congeners were detected in one or more matrices. Total PBDE concentrations (sum of all detected congeners) ranged from 5.59 to 96.1 ng/g dry weight (dw) in mussels, from 0.32 to 6.20 ng/g dw in sediment, and from 96.5 to 255 ng/L in wastewater. Total PCB concentrations (sum of all detected congeners) ranged from 5.38 to 11.7 ng/g dw in mussels, from 0.37 to 2.23 ng/g dw in sediment, and from 5.72 to 9.40 ng/L in wastewater. The predominant PBDE congeners were BDEs 47, 99, 100, and 209, accounting for 80–90% of total PBDEs in all matrices (Figure 1); the predominance of these congeners is consistent with the findings of recent studies in the region (32). BDE 209 was the predominant congener in sediment, exhibiting a gradient of decreasing predominance with proximity to the outfall, from ∼40% at reference locations to ∼10% at the outfall station and in wastewater. BDEs 47, 99, and 100 increased in predominance with proximity to the outfall, reflecting a higher abundance of these congeners in wastewater relative to other PBDE sources (Figure 1). BDEs 47 and 99 predominated in mussel tissue, which is also consistent with the findings of recent studies in the region (33). Concentrations were above the limits of quantification in mussels and sediment for at least one station (i.e., sufficient to calculate a BSAF) for 27 PBDE and 135 PCB congeners or coeluting groups of congeners (Table S1 of the Supporting Information). If a congener was not detected in both matrices at a station, no BSAF was calculated. Consistent with previous observations (8, 11, 18, 26), PCBs exhibited a parabolic relationship of bioaccumulation with log K\textsubscript{OW} at all sampling stations (Figure 2). Below K\textsubscript{OW} 10\textsuperscript{5}, BSAFs ranged between 1 and 3, reflecting approximate
equilibrium between mussels and sediment for these relatively water-soluble congeners. Above K_{OW} 10^3–5, BSAFs increased to maximum values of approximately 30 for congeners with K_{OW} ∼10^4 and then declined at higher K_{OW} to a value of approximately 5 for PCB 209. These values are consistent with the distribution of BSAFs previously reported for PCB congeners in benthic biota (26), although some congeners were up to 3-fold higher than predicted by AQUAWEB for a generic sediment-feeding invertebrate. The elevation of the parabola (i.e., the magnitude of BSAFs) was similar for the three reference stations and the 11 stations between 100 and 400 m from the outfall. At the station directly adjacent to the outfall, BSAFs for PCBs were 2- to 3-fold lower than at other stations (Figure 2). At the western 800 m station, BSAFs for PCBs were approximately an order of magnitude higher than at any other station (Figure S2 of the Supporting Information). As noted above, the sediment PCB data for the eastern 800 m station were considered suspect but are also shown in Figure S2 of the Supporting Information for comparison.

The PBDEs exhibited a parabolic relationship similar to that of the PCBs but shifted to higher maximum BSAF values across the entire range of K_{OW} (Figure 2). At the reference stations, BSAFs for most PBDEs were 2- to 3-fold higher than for PCBs of similar log K_{OW}, or approximately 3- to 10-fold higher than predicted by AQUAWEB. Similar patterns were observed at the 100–400 m stations and the eastern 800 m station, although the magnitude of the shift between PCBs and PBDEs was slightly greater. As for PCBs, BSAFs for PBDEs were approximately an order of magnitude higher at the western 800 m station than at any other station (Figure S2 of the Supporting Information) and appeared to be depressed at the outfall station relative to the remaining stations (Figure 2). BSAFs of the highly brominated PBDEs were lower than those of the highly chlorinated PCBs, which is consistent with expectations based on the very high estimated K_{OW} of these PBDEs (18, 25, 30).

Spatial variation in the elevation and form of the parabolic relationship between BSAF and log K_{OW} suggests that either bioaccumulation truly varies with distance from the outfall or there is a measurement artifact related to the outfall that is confounding the observed BSAF values. Lipid content of mussels and organic content of sediment varied little among stations (Table 1). Enhanced growth at the outfall station may have contributed to the depression of BSAFs of PCBs and PBDEs at this location (Table 1). However, the spatial pattern of growth data suggests a general gradient of slower growth at the reference stations (Table 1), which is not consistent with the finding that BSAFs were similar (PCBs) or higher (PBDEs) at the 100–400 m stations relative to the reference stations. Therefore, variation in growth cannot explain all of the observed spatial patterns.

We hypothesize that the observed spatial variation in BSAFs for PBDEs primarily reflects a decoupling of mussel tissue contaminant concentrations from those of the sediment. This hypothesis arises from our understanding of the fate of outfall-derived particulate organic matter and associated contaminants. Mussels filter outfall-derived particulate organic matter from the water column as is apparent from spatial patterns in mussel growth (Table 1) and in concentrations of outfall-related substances in mussel tissue (19, 20). However, deposition on the sediment is expected to be limited in the well-flushed environment surrounding the outfall. As a consequence, sediment samples may underestimate the exposure of mussels to dietary PBDEs. Even 2 cm surface sediment samples may be “diluted” by underlying material that has relatively low influence from the wastewater-derived particulate matter on which mussels are feeding. This effect would be expected to be greatest where sewage-derived particulates are abundant in the seston but deposition is low due to flushing and dilution, i.e., in the 100–800 m stations. Both sediment and tissue contaminant concentrations are greater near the outfall than at the 100–800 m stations (Table 1), but the effect of outfall proximity on sediment (i.e., via deposition) appears to be greater than that on mussel tissue (i.e., via dietary exposure). Therefore, decoupling would be lessened near the outfall by relatively high deposition of the mussels’ diet, resulting in BSAFs that more closely resemble a biomagnification factor. Conversely, the 800 m stations have relatively low sediment concentrations (indicating lower deposition) but similar mussel tissue concentrations (indicating a similar dietary exposure), resulting in elevated BSAFs. Mussels at the reference stations are exposed only to “background” PBDE levels in seston, but these would also be expected to be greater than in historically deposited material (32). The highest
observed PBDE BSAFs tended to fall an order of magnitude above the AQUAWEB predicted curve (Figure 2), suggesting that the measured sediment concentrations may be underestimating the concentrations in mussel diet by approximately the same amount. Station-specific deposition rates or sediment contamination profiles could help resolve this hypothesis, but such data are not available at this time.

Decoupling of mussel tissue contaminant concentrations from those of the sediment may also account for the observed differences in BSAFs between PBDEs and PCBs. Historical contamination of coastal sediments with PCBs has occurred over a relatively long time frame, and therefore the dilution effect of underlying sediment would likely be less important for PCBs. Johannessen et al. (32) showed that PCB concentrations in sediment cores collected in the region of our study (Strait of Georgia, British Columbia) showed a peak at depth and a decreasing trend toward the sediment surface, whereas PBDE concentrations increased sharply toward the sediment surface, consistent with the history of releases of these two chemical groups. Thus, concentrations in a 2 cm surface sediment sample would be expected to resemble (or possibly overestimate) current seston concentrations of PCBs, whereas they would likely underestimate current seston concentrations of PBDEs.

Alternatively, some PBDE congeners may be inherently more bioaccumulative than PCBs of similar $K_{ow}$ because they have higher dietary uptake rates, lower elimination rates, or uptake (or production) routes that PCBs do not have. While the first two of these possibilities cannot be ruled out, only the third has an apparent plausible mechanism. Reductive debromination has been demonstrated in mussels (31) and other species (3) and could represent an important internal source of some congeners and an important loss term for others. The relatively low magnitude of some BSAFs compared to the curve predicted by AQUAWEB may indicate that mussels have the capacity to metabolize these congeners. Consistent with a laboratory elimination study with mussels (31), we found relatively high bioaccumulation of BDEs 28, 47, 75, and 100 and relatively low bioaccumulation of BDE 183; BDE 190 (the other congener for which Drouillard et al. (31) found evidence of debromination) was not detected in any matrix. We also observed relatively low bioaccumulation of BDEs 8/11, 15, 17/25, 37, 49, 51, and 71. However, it is unknown whether these relatively low BSAFs indicate poor uptake, efficient elimination, or lower sediment–mussel decoupling (e.g., due to relatively high concentrations in deeper sediments) than for other PBDE congeners.

In summary, the calculated BSAFs for PBDE congeners, although apparently influenced at some locations by a decoupling of mussel tissue from sediment concentrations, indicate that PBDEs have a pattern of bioaccumulative potential in mussels similar to that of the PCBs. Furthermore, results for the reference stations (generally supported by observations from the outfall-influenced stations) indicate somewhat higher BSAFs for the most bioaccumulative PBDE congeners relative to those of PCBs of similar $K_{ow}$.

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**Supporting Information Available**

Map of sampling stations, plots of log BSAF versus log $K_{ow}$ for individual sampling stations, PCB and PBDE concentrations in sediment and mussels, calculated BSAFs for individual sampling stations, analytical methods, and details of analytical quality assurance/quality control. This information is available free of charge via the Internet at http://pubs.acs.org.

**Literature Cited**

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