Heightened Biological Uptake of Polybrominated Diphenyl Ethers Relative to Polychlorinated Biphenyls Near-Source Revealed by Sediment and Plankton Profiles along a Coastal Transect in British Columbia

Jean-Pierre W. Desforges,† Neil Dangerfield,‡ Patrick D. Shaw,§ and Peter S. Ross*,†

†Ocean Pollution Research Program, Vancouver Aquarium, P.O. Box 3232, Vancouver BC V6B 3X8, Canada
‡Institute of Ocean Sciences, Fisheries and Oceans Canada, P.O. Box 6000, Sidney BC V8L 4B2, Canada
§Environment Canada, 201-401 Burrard Street, Vancouver, BC V6C 3S5, Canada

ABSTRACT: Polychlorinated biphenyl (PCB) and polybrominated diphenyl ether (PBDE) concentrations and profiles in paired sediment—plankton samples were determined along a 500 km transect in coastal British Columbia, Canada. PCB and PBDE levels in sediment were both greater in the industrialized Strait of Georgia than in remote northern sites and exhibited parallel spatial trends. In plankton, recent-use PBDE levels were higher near-source, while levels of legacy PCBs were uniform across sites. Principal component analysis of 95 PCB congeners illustrated the influence of proximity to source (i.e., latitude) on congener patterns for both matrices (sediment, \( r^2 = 0.52, p = 0.012 \); plankton, \( r^2 = 0.59, p = 0.016 \)). The PCB pattern in plankton grew lighter with latitude, but the opposite pattern in sediments suggested that temperature-related fractionation, sediment processes, and basin-wide oceanography had divergent effects on each matrix. Biota-sediment accumulation factors (BSAFs) were greater for PBDEs than PCBs, but spatial profiles were similar; PCBs and PBDEs were near equilibrium in remote atmospherically driven sites (BSAF = 1.7 and 1.3) but accumulated preferentially in sediments at source-driven sites (BSAF = 0.2 and 0.4). The influences of particle-binding and hydrophobicity on the aquatic fate of PCBs and PBDEs was evident by the strong influence of log \( K_{OW} \) on congener-specific BSAFs (PCBs, \( r^2 = 0.18 p < 0.001 \); PBDEs, \( r^2 = 0.61 p < 0.001 \)). While biotic uptake of PCBs has become spatially uniform in coastal BC because of dilution over time, biomagnification of PBDEs remains higher in industrialized waters.

INTRODUCTION

Chemicals released into the environment cycle through various media, with pathways and ultimate fate dependent upon the interaction of chemical properties and environmental conditions. The global distribution of persistent organic pollutants (POPs) has been largely attributed to long-range atmospheric transport (LRAT), a temperature-driven process of volatilization and deposition which influences chemical fractionation. Despite the importance of LRAT, POP fate in the marine environment may be ultimately driven by biogeochemical processes. Air–water exchange, uptake by phytoplankton, and sedimentation of particles are among the most important processes affecting the fate of POPs in aquatic environments. As POPs sorb preferentially to organic matter, sequestration by sinking particles and burial in deep ocean sediment is a major sink for these lipophilic contaminants.

The calculation of a biota-sediment accumulation factor (BSAF) provides insight into the propensity of a contaminant to biomagnify in food webs. A BSAF between 1 and 2 typically reflects thermodynamic equilibrium between the organic carbon fraction in sediment and the lipid fraction in biota. Given that sediment and biota may not be tightly coupled and that equilibrium conditions are rarely observed in the field, the BSAF approach may be more useful as a tool to evaluate deviation from equilibrium (i.e., BSAF ~1 to 2) in order to garner insight into chemical behavior and fate. In this manner, the "equilibrium status" may be used to shed light on spatial patterns and help identify potential source and sink regions.

Uptake of POPs by phytoplankton is governed by equilibrium partitioning between tissue and water. Uptake in phytoplankton is particularly important as their settling to sediment drives regional and global POP fate and because plankton represent the entry point of POPs to marine foodwebs.
The accumulation of POPs in plankton with subsequent food web biomagnification leads to high concentrations in higher trophic levels, such as the heavily PCB contaminated killer whales (*Orcinus orca*) in the NE Pacific Ocean. Consequently, sediment and plankton POP concentrations can be used to predict uptake by higher trophic level organisms such as killer whales and provide guidance on different sediment management or ocean disposal scenarios. 

Polychlorinated biphenyls and polybrominated diphenyl ethers (PBDEs) are two contaminants of particular concern since both are persistent, bioaccumulative, and toxic. PCBs are legacy pollutants (banned in 1970s in Canada and the USA), whereas PBDEs have only recently faced regulatory scrutiny. The contrasting history of these pollutants has implications for their current environmental distribution: PCBs largely reflect cycling of legacy reservoirs while PBDEs continue to reflect point-source releases. In addition, PBDEs have a wider range of molecular size and $K_{OW}$ and are more influenced by environmental transformation than PCBs, resulting in differences in their behavior and fate.

While studies have been conducted along transects for contaminants in air, water, soil, vegetation, and biota, few such studies compare different contaminants in biota and sediment in the marine environment. Here we present the first large spatial transect study of PCB and PBDE profiles in paired sediment—plankton samples. We investigated congenerspecific concentrations and patterns along a 500 km transect of coastal British Columbia from Hecate Strait to the southern Strait of Georgia (SoG). The SoG is urbanized (~4 million people) and receives industrial and wastewater discharges from multiple sources (e.g., urban Victoria and Vancouver, and Seattle in the adjacent Puget Sound), while the northern part of the transect is remote and has no major point-sources of contaminants. The SoG is semiclosed and subject to high sedimentation rates and elevated inputs of organic carbon through net primary production, the Fraser River and anthropogenic sources (i.e., wastewater discharge and pulp mills). In contrast, Hecate Strait/Queen Charlotte Sound is characterized by open ocean conditions with moderate to high exposure and low sedimentation rates and organic carbon. Our aim was to examine the geographical pattern and bioaccumulation of PCBs and PBDEs along a marine transect in order to garner insight into the uptake of these two priority pollutants in marine food webs.

### METHODS

**Sample Collection.** Sediment samples were taken from nine sites and plankton samples from 11 equidistant sites along a transect from Hecate Strait, Queen Charlotte Sound (QCS), Johnstone Strait through to the southern Strait of Georgia (BC, Canada) in September 2006 aboard the CCGS *Vector* (Figure 1). Surface sediments were collected using a Smith-McIntyre grab sampler (~15 cm depth), and the top few centimeters were transferred to solvent-rinsed amber glass jars after

---

**Figure 1.** Total concentration of PCBs and PBDEs in sediment (ng/g TOC) and plankton (ng/g lw) samples along a coastal transect in the northeast Pacific Ocean from Hecate Strait to the Strait of Georgia, British Columbia, Canada. Sediment PBDEs include BDE-209 (displayed in stacked gray bar) while plankton do not (see Methods). Sediment samples from sites 3 and 6 were not collected (nc) due to the rocky nature of the seabottom.
Table 1. Concentrations of total PCBs and total PBDEs in Sediments and Plankton (ng/g wet weight)\textsuperscript{a}

| LD. | site              | depth (m) | TOC (%) | lipid (%) | sediment |  | plankton |  |
|-----|-------------------|-----------|---------|-----------|----------|  |          |   |
|     |                   |           |         |           | PCB      | PBDE | PCB       | PBDE |
| 1   | Queen’s Sound     | 167       | 6.2     | 1.9       | 1.4      | 0.5 | 0.5       | 0.2  |
| 2   | W. Calvert Island | 126       | 0.5     | 1.8       | 0.2      | 0.1 | 0.7       | 0.2  |
| 3   | S. Calvert Island | 151       |         | 3.8       |          |     | 0.6       | 0.2  |
| 4   | N. Malcolm Island | 175       | 3.8     | 1.6       | 1.2      | 0.4 | 0.4       | 0.2  |
| 5   | Hannah Channel    | 367       | 4.7     | 3.9       | 0.3      | 0.2 | 0.8       | 0.4  |
| 6   | S. Hardwicke Island | 200       |         | 0.4       |          |     | 0.2       | 0.3  |
|     | North (x)         | 198 (±0.87) | 3.8 (±2.4) | 2.2 (±1.4) | 0.8 (±0.6) | 0.3 (±0.2) | 0.6 (±0.2) | 0.2 (±0.1) |
| 7   | E. of Oyster River | 288       | 1.5     | 2.6       | 2.9      | 0.7 | 1.2       | 0.7  |
| 8   | N. Hornby Island  | 180       | 3.5     | 1.3       | 5.1      | 0.7 | 0.6       | 0.4  |
| 9   | E. Gabriola Island | 380       | 1.8     | 2.6       | 2.6      | 1.6 | 0.8       | 0.6  |
| 10  | Active Pass       | 154       | 0.5     | 1.6       | 1.2      | 0.5 | 0.5       | 0.5  |
| 11  | Patricia Bay      | 185       | 2.9     | 3.2       | 14.9     | 1.5 | 0.6       | 0.2  |
|     | South (x)         | 237 (±0.95) | 2.0 (±1.2) | 2.3 (±0.8) | 5.3 (±5.5) | 1.0 (±0.5) | 0.7 (±0.3) | 0.5 (±0.2) |
|     | p-value (North vs South) | 0.49       | 0.19     | 0.98      | 0.021    | 0.035 | 0.27      | 0.015 |

\textsuperscript{a}Samples were collected along a transect in the northeast Pacific Ocean from Hecate Strait to the Strait of Georgia, British Columbia, Canada. Sites are divided geographically into north and south groupings via delineation by the oceanographically constrained Discovery Passage, with mean ± standard deviation for each region presented in italics.
nine stations, and concentrations ranged over several orders of magnitude across sites (Figure 1, Table 1). Cluster analysis (HCA) of PCBs and PBDEs separated sites in the north from the south on the basis of total concentrations, with the delineation occurring at the hydrographically constrained Discovery Passage (Figure 1). Sediment PCB concentrations were 7 and 11 times greater in the south compared to the north for raw and TOC-corrected data respectively, while PBDE concentrations were three and five times greater (Figure 1, Table 1). This was not unexpected, as these trends follow known emissions histories in the NE Pacific. The SoG and adjacent water bodies (Juan de Fuca and Puget Sound) are home to large urban centers, including Vancouver, Victoria, and Seattle, and receive industrial discharges from sewage treatment facilities and pulp and paper mills. In comparison, Hecate Strait and QCS are remote, relatively unpopulated, and have no major documented point sources of contaminants.

Cluster analysis of PBDE concentrations in plankton separated northern from southern sites, excluding site 6 which fell separately as an outlier (low lipid content and % carbon). Plankton from southern sites had higher PBDE levels than those in the north (ww t test p = 0.015; lw t test, p = 0.019). In contrast, PCB concentrations did not differ between northern and southern regions (ww t test, p = 0.27; lw t test, p = 0.77). The increasing PBDE–PCB ratio with proximity to wastewater discharge sources in the SoG reflects the contrasting usage history of the two contaminants (Supporting Information, Figure S1). In the SoG, PBDE tissue levels in plankton were found to rapidly respond to ongoing PBDE inputs to the water column via wastewater effluent, whereas PCBs appeared to be less available due to high particle scavenging of already low background concentrations. Our results are consistent with this model in the SoG and further show that PCB levels in plankton are relatively uniform over larger spatial scales due to biogeochemical cycling and environmental dilution over time, while spatial PBDE trends reflect those of a more recent-use contaminant.

PCB and PBDE Patterns: Influence of Sources, Physicochemical Properties, and Receiving Environments. Dominant PCB congeners in sediment consisted of PCB congeners 138 > 153 > 118 > 101 > 110 > 149. The PCB concentration-weighted log $K_{OW}$ (herein referred as weighted $K_{OW}$) varied with latitude but did not differ between northern and southern sites (t test, p = 0.10; Supporting Information, Figure S2). Sediments in southern sites had higher contributions of tri- and tetrachlorinated homologue groups, while sediment from the north had higher contributions of hexa- and heptachlorinated congeners (Figure S3). The dominant PCB congeners in plankton consisted of PCB congeners 153 > 138 > 101 > 149 > 99 > 70/76. The geographical pattern in plankton diverged from that of sediment; northern sites were compositionally higher in di- and trichlorinated congeners whereas the southern sites had greater hexa- and heptachlorinated congeners (Figure S3). This resulted in a decrease of the concentration-weighted log $K_{OW}$ with latitude (Figure S2).

A PCA of 95 PCB congeners in sediments and plankton (Figure 2) clearly illustrates the influence of a number of key processes, including bioaccumulation of select congeners, latitudinal fractionation, and biogeochemical influences on environmental partitioning. The first principal component (p1) related to the BSAF ($r^2 = 0.68, p < 0.001$) and distinguished plankton samples (midweight congeners) from sediment (light and heavy congeners). The second component (p2) contrasted light (2−5 Cl) and heavy congeners (6−8 Cl), which associated
with latitudinal groupings of sediment and plankton samples (north vs south). Although p2 correlated with latitude for both sediment ($r^2 = 0.52, p = 0.012$) and plankton ($r^2 = 0.59, p = 0.016$), the direction of the relationship was inverted: sediments in the southern and northern groupings plotted with light and heavy congeners, respectively, while the opposite occurred for plankton (Figure 2). It is interesting to note that proximity to source (i.e., in this case, latitude) had little effect on PCB concentrations in plankton but did influence PCB patterns.

The lighter PCB pattern with latitude in plankton is likely the result of the combined effect of fractionation during atmospheric transport and biogeochemical processes, while biogeochemical processes alone appear to drive the pattern in sediment. This divergent latitudinal pattern in sediment and plankton likely reflects the difference in response time as well as the contrasting influence of sediment processes on each matrix. Plankton are more strongly associated with patterns in the atmosphere which respond quickly to changes in emissions, while sediments respond much more slowly and can retain legacy patterns.\(^6\) We propose that the heavier PCB pattern in plankton of the SoG is a response to continuous terrestrial inputs (i.e., Fraser River and anthropogenic sources) which act to replenish PCBs in the water column, whereas the lack of replenishment in Hecate Strait/QCS contributes to the depletion of mid- and heavy-weight congeners in plankton. Source history and biogeochemical processes have the opposite effect on patterns in sediment; new terrestrial inputs of PCBs are mixing with legacy deposits in the SoG (e.g., bioturbation) and dilute the historically heavier profile, while this legacy signal is retained in the north as a consequence of minimal new inputs and continued erosion of seafloor sediments. Overall, the importance of sediment—contaminant property interactions in governing the PCB fate is highlighted by the relationship between log $K_{OW}$ (i.e., hydrophobicity) and congener patterns in both matrices (log $K_{OW}$ vs p2: $r^2 = 0.33, p < 0.001$) (Figure 2).

A total of 49 PBDE congeners were detected in sediments, with BDE-209 contributing 66 ± 18% of $\sum$PBDE on average, BDE-47 (10.5 ± 6.6%), BDE-99 (7.0 ± 7.7), and BDE-100 (2.5 ± 2.2) were the next most dominant congeners. Forty congeners were detected in plankton, and the dominant congeners were BDE-47 (36.4 ± 9.9%), BDE-99 (27.9 ± 7.1%), and BDE-100 (7.4 ± 1.7%). The dominance of these congeners in sediment and biota correspond well with patterns observed in other studies and reflect the partitioning of congeners over a log $K_{OW}$ range of 4.5–7.5.\(^{10,13,26}\)

PBDE patterns in sediment did not follow a clear geographical trend (Supporting Information, Figures S2 & S3). This lack of a trend for PBDEs across coastal BC highlights a dichotomy with PCBs and underscores the influence of physicochemical properties on the fate of these two contaminants. PBDE fate is strongly linked to particle processes and organic carbon content,\(^{10,11,13,27}\) and indeed we found that patterns in sediment (weighted log $K_{OW}$) were strongly related to sediment TOC ($r^2 = 0.53, p = 0.025$). In plankton, the PBDE-weighted log $K_{OW}$ increased with latitude and was negatively correlated with water depth ($r^2 = 0.44, p = 0.036$) (Supporting Information, Figure S2). The relatively lighter congener patterns in southern plankton may result from the sedimentation and burial of heavier congeners in the SoG and/or the influence of particle composition and transport on the fate of hydrophobic PBDEs in the marine environment.

### Biota-Sediment Accumulation Factors (BSAF)

Given the persistence of PCBs and PBDEs in the environment, evaluating their biota-sediment equilibrium status (BSAF ≈ 1–2) can provide valuable context on accumulation history and enable the assessment of chemical fate in the ocean.\(^6\) For both PCBs and PBDEs, observed BSAFs were at, or above, the equilibrium reference value for northern sites (PCB, 1.7 ± 1.3; PBDE, 1.3 ± 1.0) and below equilibrium in southern sites (PCB, 0.2 ± 0.1; PBDE, 0.4 ± 0.4) (Figure 3). The difference between the northern and the southern portion of the transect clearly illustrates the effect of source-driven vs atmospherically driven systems. Continued terrestrial and point-source release of pollutants in the SoG has resulted in a source-driven system where sediments are a major sink of PCBs and PBDEs. This is compounded by intense particle scavenging which can reduce the bioavailability of contaminants in the water column.\(^{28}\) The dominant input of pollutants for northern sites is presumably via atmospheric deposition, and combined with low sedimentation rates and strong mixing of the water column,\(^{28}\) it appears as though both PCBs and PBDEs have reached some level of equilibrium between sediment and biota. In other words, the sediment compartment does not act as a strong contaminant source to plankton, and vice versa.

Deviation from equilibrium was not only a function of source-proximity but was also influenced by physicochemical properties (Figure 4). Congener-specific BSAFs were correlated with Log $K_{OW}$ with a parabolic fit best describing the relationship (PCB: $r^2=0.18, p < 0.001$; PBDE: $r^2=0.61, p < 0.001$). BSAFs peaked for congeners with log $K_{OW}$ ≈ 6–7. Unlike PCBs, there was no dramatic decline in BSAFs for the heaviest PBDEs (Figure 4); however, BDE-209 was excluded in

---

**Figure 3.** Biota–sediment accumulation factors (BSAFs) for PCBs and PBDEs at sites along a coastal transect in the northeast Pacific Ocean from Hecate Strait to the Strait of Georgia, British Columbia, Canada. The vertical dotted line separates northern from southern sites, which are delineated by the oceanographically constrained Discovery Passage. The horizontal dashed line represents theoretical equilibrium conditions between plankton and sediment (BSAF = 1). BSAFs were calculated using lipid- and TOC-corrected concentrations for plankton and sediment, respectively.

---

dx.doi.org/10.1021/es500218b}
plankton due to high detection limits (see Methods) but trends did reveal a decline in biotic uptake relative to octa- and nona-BDEs (not shown). High BSAFs for those congeners expected to not be bioavailable may be due to plankton stomach contents or cell adsorption rather than retained tissue burden. The parabolic log \(K_{OW}\) curve has been widely reported in studies of biota–water accumulation, maternal transfer to offspring, and biomagnification in food webs, making evident the universal influence of physicochemical properties on the fate of POPs.

All but two PBDE congeners were above the equilibrium reference value (i.e., BSAF > 1) in the north and approximately half were above in the south. As with total BSAF, the BSAF vs log \(K_{OW}\) slopes were higher for PBDEs than PCBs for both regions (Figure 4). Annual atmospheric deposition in urban and remote regions of coastal BC delivers over twice as much PBDEs as PCBs. Therefore, despite shared physicochemical properties for PCBs and PBDEs, the greater input of PBDEs to the environment results in increased uptake at the base of the food web.

The BSAF can be used predictively in models to forward calculate contaminant concentrations in biota from the concentration in sediment (i.e., \(C_{Biota} = BSAF \times C_{Sed}\)) or can be used to back calculate sediment concentrations protective of biological thresholds (i.e., \(C_{Sed} = C_{Biota}/BSAF\)). However, the utility of predictive models using literature BSAF values will depend on the applicability of values from one site to another. Our findings using oceanic plankton indicate that total and congener-specific BSAF vary among sites as a function of source history, physicochemical properties, sedimentation rates, sediment composition, and water depth. Thus, incorporating local source history and characteristics of the receiving environment is essential for accurate modeling of contaminant fate in marine environments.

The definition of BSAF includes a biotic as well as a sediment term and resulting BSAFs are therefore sensitive to the features of both matrices. Plankton collected in this study were dominated by calanoid copepods and euphausiids, representing 70 and 8.2% of all organisms, respectively. While plankton composition in northern and southern sites were similar and overall lipid content did not differ between regions (t test; \(p = 0.98\)), species-specific differences in growth rates, lipid composition, feeding rate, feeding preferences, and uptake and elimination may have contributed to some of the variability in resulting contaminant patterns. Biotransformation of some PCB and PBDE congeners, through oxidation or debromination, has been observed in invertebrates and other bottom food web organisms. However, exposure from water and diet appear to more strongly drive chemical accumulation in plankton while biotransformation becomes more important in higher trophic level consumers. For sediment, although no general TOC pattern was evident along the transect (Table 1), site-specific differences in particle and organic carbon composition can influence BSAFs. For instance, high affinity carbonaceous geosorbents, such as black carbon, strongly bind to hydrophobic contaminants and considerably reduce their bioavailability. Models that include feeding parameters and sediment composition have been shown to accurately predict bioaccumulation of contaminants from sediment.

In a north–south transect spanning much of coastal BC, we show that highest BSAFs do not correspond with areas receiving the highest contaminant inputs. Nonetheless, higher trophic organisms accumulate pollutants in proportion to absolute concentrations. Despite higher BSAFs in remote waters, higher PBDEs but not PCBs in plankton near-source highlight the dichotomy between current-use and legacy pollutants. This trend is extended up the food web to harbor seals which have greater blubber levels of PBDEs but not PCBs. This trend is also true for much longer lived killer whales appear to retain the legacy PCB spatial profile. Evidence from plankton in this study has shown that while the bioavailability of PCBs has become spatially uniform in coastal BC, the risk of food web magnification of PBDEs is explicitly higher in the industrialized southern waters.

### ASSOCIATED CONTENT

#### Supporting Information

Additional information on spatial patterns of contaminant ratios, concentration weighted log \(K_{OW}\) and homologue groupings. This material is available free of charge via the Internet at http://pubs.acs.org.

#### AUTHOR INFORMATION

*Corresponding Author*

Phone: 604-659-3563, fax: 604-659-3562, e-mail: peter.ross@vanaqua.org.

*Notes*

The authors declare no competing financial interest.
ACKNOWLEDGMENTS

This study was supported by Fisheries and Oceans Canada (DFO) and the Georgia Basin Ecosystem Initiative of Environment Canada. Thanks to the crew of the CCGS Vector, the staff at the former Laboratory of Expertise for Aquatic Chemical Analysis (LEACA) in Sidney, BC (DFO) and to Axys Analytical Services in Sidney, BC. The authors gratefully acknowledge comments from Robie W. Macdonald, Sophia Johannessen, and Moira Galbraith.

REFERENCES

(32) Fisk, A. T.; Hobson, K. A.; Norstrom, R. J. Influence of Chemical and Biological Factors on Trophic Transfer of Persistent


