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RESEARCH ARTICLE

Uptake and trophic changes in polybrominated diphenyl ethers in the benthic marine food chain in southwestern British Columbia, Canada

Brenda Burd[ab*], Chris Lowe[c], Carmen Morales-Caselles[b], Marie Noel[b], Peter Ross[b], and Tara Macdonald[d]

[a]Ecostat Research Ltd., North Saanich, Vancouver, BC V8L 5P6, Canada; [b]Vancouver Aquarium, Vancouver, BC V6G 3E2, Canada; [c]Capital Regional District, Victoria, BC V8W 2S6, Canada
[d]Biologica Environmental Services Ltd., Victoria, BC V8T 5H2, Canada

*burdb@dfo-mpo.gc.ca

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Abstract

We examined the physical and geochemical effects of sediment on the uptake of polybrominated diphenyl ethers (PBDEs) into marine sediment feeders and their transfer to higher trophic fauna. Sediment PBDEs increased with % total organic carbon (%TOC), organic carbon (OC) flux and grain size (%fines). Tissue PBDE variance was best explained ($R^2 = 0.70$) by sediment acid volatile sulfides (AVS), PBDEs, and organic lability and input, with the highest values near wastewater outfalls. Dry weight tissue/sediment PBDEs declined with increasing sediment PBDEs, resulting in tissue dilution (ratio <1) at >10 000 pg/g in harbours. Ratios also decreased with increasing %fines, resulting in regional differences. These patterns imply that high levels of fines and high sediment concentrations make PBDEs less bioavailable.

Dry weight PBDEs increased >100× between background deposit feeders and predators (polychaetes, crabs, bottom fish, seal), but lipid normalized PBDEs barely increased (<1.3%), suggesting remarkably high uptake in low-lipid sediment feeders, and that PBDEs don't accumulate at higher trophic levels, but lipid content does. Filter feeders had lower lipid-normalized PBDEs than deposit feeders, highlighting the importance of food resources in higher trophic fauna for bioaccumulation.

The most profound congener change occurred with sediment uptake, with nona/deca-BDEs declining and tetra-hexa-BDEs increasing. Harbour sediment feeders had more deca-BDEs than other samples, suggesting PBDEs mostly pass unmodifed through them. Deca-BDEs persist patchily in all tissues, reflecting variable dependence on sediment/pelagic food.

Key words: PBDEs, marine sediments, trophic transfer

Introduction

The uptake of persistent organic pollutants such as polybrominated diphenyl ethers (PBDEs) into marine food chains is not well understood. PBDEs are a globally dispersed group of compounds that can have serious health consequences to a wide variety of organisms. Although they have been found in Arctic and Antarctic food chains (Ross et al. 2009), they are most concentrated close to sources, which include industrial discharges, storm water, and municipal wastewater outfalls (Johannessen et al. 2008). In southern British Columbia (BC), Canada, these are also areas of critical habitat for a variety of fish and mammalian species protected under the Canadian Species at Risk Act (SARA).

Ross et al. (2009) reviewed the history of contamination and bioaccumulation studies of PBDEs in the marine environment, with an emphasis on southern BC. Since then, a number of papers have addressed food chain or food web transfer in a general sense (Hallanger et al. 2011; Alava et al. 2016). Because this class of contaminants is so strongly particle-active and hydrophobic, most of it ends up in sediments or in suspended particulates in the water column. Therefore, sediment inventories, tissue uptake, and composition of PBDEs in marine food chains cannot be understood outside the context of sediment geochemistry and physical structure, as well as source input. Conditions affecting source uptake are, in turn, critical for predicting contaminant accumulation at higher trophic levels.

Deca-BDE makes up about 80% of the total PBDEs in the marine sediments of southern BC (Ross et al. 2009), as found in other marine nearshore habitats (Boon et al. 2002). Understanding the fate of deca-BDEs in marine organisms has been particularly challenging for reasons discussed in Ross et al. (2009), who points out that there is a considerable reservoir in sediments that presents a risk to all trophic levels, particularly as the debromination products of deca-BDEs are toxic and persistent in the food chain.

Studies of marine sediment uptake of PBDEs into benthic infauna typically focus on specific organisms such as bivalves (Boon et al. 2002; Moon et al. 2007; deBruyn et al. 2009; Klosterhaus et al. 2011; La Guardia et al. 2012). Studies that examine uptake in whole sediment communities are rare (Dinn et al. 2012a; Burd et al. 2014). Burd et al. (2014) suggested that PBDE congener patterns in benthic infauna varied depending on feeding methods as well as the source and input dynamics of contaminants. However, the limited samples in that study did not cover key habitat conditions, making it challenging to clearly interpret PBDE uptake dynamics.

The purpose of this study was to improve the understanding of how habitat conditions affect the initial uptake of PBDEs into the food chain from sediments, and how concentrations and composition change at higher trophic levels. The uptake observations described by Burd et al. (2014) can now be expanded and improved by the addition of matched sediment/tissue samples of whole benthos over a broader range of sediment conditions in southern British Columbia (**Fig. 1**). In addition to whole benthos, matched tissue/sediment samples from specific taxa, including deposit feeders, filter feeders, and higher trophic level predators, have been examined to help understand trophic transfer patterns. Specifically, we compare congener patterns in sediments with those in taxa from different feeding types and trophic levels (i.e., deposit feeders, filter feeders, and predators) to examine:

a. geochemical and physical factors affecting sediment retention of PBDEs;

b. sediment factors affecting initial uptake of PBDEs into sediment deposit and filter feeders, and accumulation patterns at higher trophic levels; and

c. differences in proportional patterns of homologue groups between sediment, sediment feeders, and higher trophic level organisms.

Methods

Study area

All tissue and sediment samples were collected from southern British Columbia (**Fig. 1**). Most of the samples were from the inland Strait of Georgia, which is a glacial depression deeper than the continental shelf (maximum 400 m), with restricted water flow at the north and south ends. The oceanography (Thomson 2014) and high sedimentation flux (Johannessen et al. 2003) in the southern Strait of Georgia is driven by the massive freshwater discharge of the Fraser River. These conditions result in a relatively isolated topographic basin (low–moderate bottom currents except at the tidal channels)

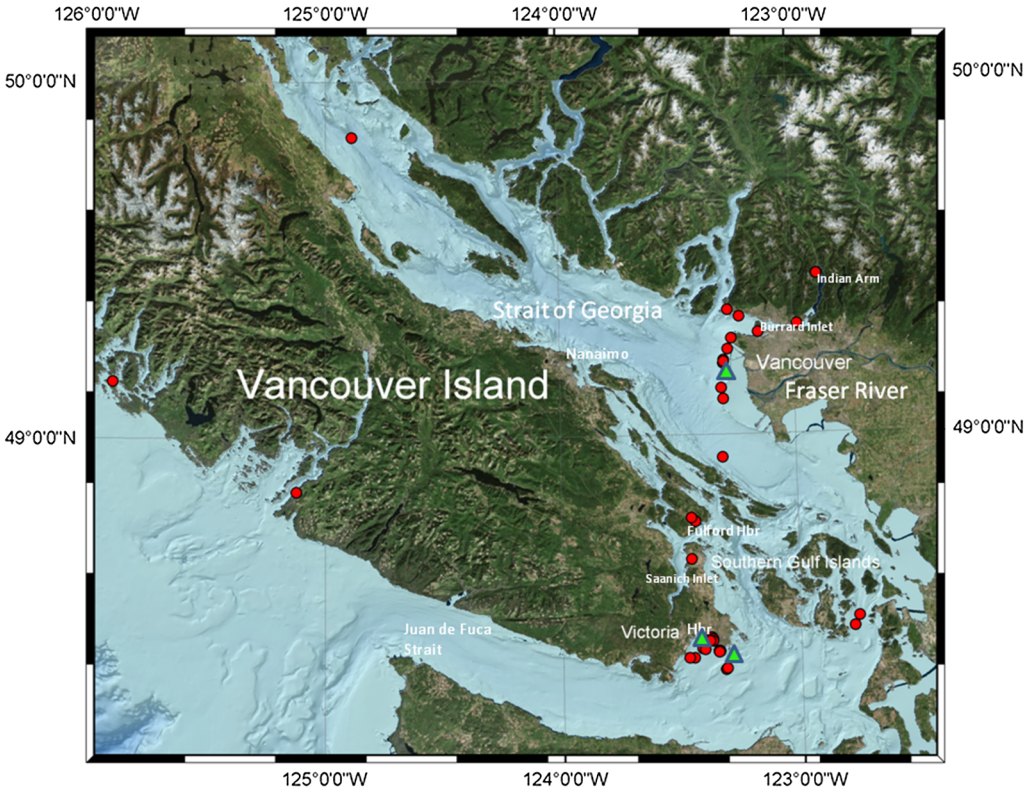

Fig. 1. Locations of matched tissue/sediment samples in southern BC shown as red dots (see **Table S1**). The three marine municipal wastewater outfalls are shown as green triangles (Macaulay and Clover Point off southern Victoria, and Iona off Vancouver). Map and attributes were generated using ArcGIS version 9 (ESRI Canada; esri.ca/en), using geo-referenced data provided by the Canadian Hydrographic Service.

with high sedimentation of fine-grained sediment and high water column and sediment productivity (Burd et al. 2008; Burd 2014). This is the typical habitat surrounding the primary treatment Iona wastewater outfall off Vancouver (**Fig. 1**), which is a concentrator for urban PBDE discharge (Johannessen et al. 2008). Vancouver Harbour (Burrard Inlet) also has relatively fine sediments, with more variable currents and reduced influence from the Fraser River (Burd 2014). Multiple industrial and urban discharges and shipping activities are present, including a primary treatment municipal wastewater outfall and various combined sewer overflows (CSOs) that discharge PBDEs (Johannessen et al. 2008). The north end of the Strait of Georgia is a shallower basin with minimal influence from Fraser River particulates (Johannessen et al. 2003). Sediments are less productive than in the southern basin (Burd 2014), with nutrient input dominated by reworked, fine marine detritus from the surface.

Samples collected in the Juan de Fuca Strait off the south end of Victoria and in the southern Gulf islands (**Fig. 1**), as well as on the west coast of Vancouver Island, are from sediments dominated by coarser sands, with typically high currents in exposed areas. This includes the sample locations surrounding the pre-treated (screened only) Macaulay and Clover Point municipal wastewater outfalls off Victoria, which tend to concentrate PBDEs (see deBruyn et al. 2009). These substrates are naturally productive (Burd 2014) because of a steady supply of suspended particulates from seasonal offshore upwelling and strong mixing around the southern Gulf islands (Thomson 2014). Victoria Harbour is a shallow and organically enriched sheltered bay, with various urban and industrial inputs and considerable bottom disturbance from shipping (UMA and Morrow 2007).

Samples

A description of all tissue types, including feeding method, typical taxa, and habitat usage is given in Table 1. Matched tissue/sediment samples were collected from (A) background areas over a range of depths throughout the Strait of Georgia, southern Gulf islands, Juan de Fuca Strait, and west coast Vancouver Island; (B) gradients (near- to far-field) away from three municipal wastewater outfalls; and (C) the two largest urban/industrial harbours in coastal BC. Most of the unmatched tissue samples (mostly higher trophic level tissues) were collected from background areas in southern BC, rather than near expected PBDE sources.

In total, 184 tissue samples were collected, with 56 matching sediment samples. A complete listing of all samples (matched and unmatched sediment and (or) tissue samples) and general locations is given

Table 1. Taxa descriptions and trophic types for biotic samples.

Text signifier	Description	Trophic type	Typical taxa	Comments
Whole benthos	Subtidal, infaunal mixed assemblage	Mixed, primarily deposit feeders	Polychaetes, bivalves, some crustaceans, brittle stars	Proportions vary; crustaceans and echinoderms rare in contaminated sediments
Bivalves	Subtidal, infaunal burrowing	Deposit feeders	Mixed, mainly *Axinopsida, Macoma*	—
Butter clam	Intertidal, burrowing bivalve	Filter feeder	*Saxidomus gigantea*	sequester toxins in siphons for long periods
Mya	Intertidal, shallow subtidal burrowing bivalve	Filter feeder	*Mya arenaria (soft shell clam)*	—
Mytilus	Intertidal, epifaunal attached bivalves	Filter feeder	*Mytilus edulis*	—
Horse mussel	Subtidal, epifaunal attached bivalves	Filter feeder	*Modiolus modiolus*	—
Scallops	Subtidal epifaunal, mobile bivalves	Filter feeder	*Crassadoma gigantea*	—
Heteromastus[a]	Subtidal, infaunal polychaete	Redox boundary deposit feeder	*Heteromastus filobranchus*	Opportunistic species near Iona outfall (low O_2 sediment)
Polychaetes	Subtidal, infaunal	Deposit feeders and predators	Mixed taxa	—
Echinoderms	Subtidal, infaunal holothurians	Deposit feeders	*Brisaster, Molpadia*	—
Cerebratulus	Subtidal, infaunal nemertean	Nemertean predator	*Cerebratulus californiensis*	—
Midshipman	Subtidal, epifaunal fish	Predator	*Porichthys notatus*	—
Crab hepatopancreas	Subtidal, epifaunal, mobile crustacean	Predator	*Metacarcinus magister*	Hepatopancreas
Crab muscle	Subtidal, epifaunal, mobile crustacean	Predator	*Metacarcinus magister*	—
Salmon	Pelagic fish	Predator	*Oncorhynchus* spp.	—
Seal	Marine mammal	Predator	*Phoca vitulina*	—

[a]See Table 2 for sample types.

in Table S1, with a summary in Table 2. Overlap of some sediment samples with more than one tissue type increased the total matched tissue/sediment sample set to 90.

Twenty-five matching PBDE sample pairs for sediment and whole benthos were collected between March 2012 and January 2015. Sediment and tissue field sampling procedures and preservation methods for whole benthos are described in detail by Dinn et al. (2012a, 2012b) and Burd et al. (2014). Whole benthos samples were collected from three replicate 0.1 m^2 Van Veen grab samples and screened over 1 mm mesh stainless steel trays that were first cleaned with acetone (to remove organic material) and rinsed with distilled water. During screening, visible individual organisms were removed with clean forceps, placed in amber glass jars, weighed, and frozen. As many organisms as

Table 2. Summary of location type, feed type, and number of tissue and sediment samples.

Location type	Feed type	Taxon type	Tissue PBDE samples	Sediment PBDE samples
Background	Deposit	Bivalves	2	1
Outfall	Deposit	Bivalves	1	1
Background	Filter	Butter clam	9	—
Outfall	Predator	*Cerebratulus*	3	√
Background	Predator	Crab hepatopancreas	12	—
Background	Predator	Crab muscle	10	—
Background	Deposit	Echinoderm	5	√
Outfall	Deposit	*Heteromastus*	2	√
Background	Filter	Horse mussel	8	4
Outfall	Filter	Horse mussels	12	12
Background	Predator	Midshipman	1	√
Background	Filter	*Mya*	2	—
Background	Filter	*Mytilus*	8	8
Enriched Harbour	Filter	*Mytilus*	1	1
Harbour	Filter	*Mytilus*	6	5
Outfall	Filter	Polychaetes	1	√
Background	Filter	Polychaetes	1	√
Background	Predator	Salmon fillet	33	—
Background	Filter	Scallops	4	1
Background	Predator	Seal blubber	30	—
Background	Deposit	Whole benthos	9	7
Enriched Harbour	Deposit	Whole benthos	4	2
Harbour	Deposit	Whole benthos	4	3
Outfall	Deposit	Whole benthos	16	11
		Totals	**184**	**56**

Note: Check mark means that matching sediment samples were analyzed, but these have already been accounted for in other samples (to keep totals for each column accurate). PDBE, polybrominated diphenyl ether.

possible from a variety of available taxonomic groups and sizes were picked to meet the minimum analytical biomass threshold (10 g). During the screening and picking process, the composition of the community (identification of the dominant organisms to the lowest level possible without a microscope) was recorded by trained taxonomic experts from Biologica Environmental Services, Victoria, BC, Canada. Where there was adequate material, some subsamples of specific taxon types were separated out of the benthos for individual analyses (bivalves, polychaetes, echinoderms) in addition to whole benthos samples (**Table 2** and **Table S1**).

Nineteen sample sets of epibenthic filter feeders (swimming scallops *Chlamys hastata* and horse mussels *Modiolus modiolus*) matched with sediment samples were collected near the Clover Point municipal wastewater outfall and in background areas off Victoria. The sediment and horse mussel samples were collected and processed by the Capital Regional District (CRD) as part of their routine outfall monitoring program in 2012 and 2013 (crd.bc.ca/about/document-library/documents/annual-reports/environmental-protection/wastewater-marine-environment/macaulay-clover-points). Sample collection and processing methods for sediments and horse mussel tissue samples were described in detail by deBruyn et al. (2009). The scallop samples with matched sediments were collected and processed in January 2015 in the same manner as described for the horse mussels.

Ten sample pairs of intertidal blue mussels (*Mytilus edulis*) and nearby sediments collected as part of the coast-wide Pollution Tracker Program (Dr. Peter Ross, Vancouver Aquarium) in 2015 and 2016 were included in the data set. Older (2005) tissue samples from butter clams (*Saxidomus* sp.), softshell clams (*Mya* sp.), blue mussels (*Mytilus* sp.), crabs, salmon, and seal blubber collected from various parts of the BC coast have also been included for comparison of congener patterns. The crab samples were split into hepatopancreas and muscle tissues, the salmon samples were only muscle (fillet) and the seal blubber samples were subcutaneous fat tissues only. These larger organisms are difficult to process as full-body samples, and data were provided by the Department of Fisheries and Oceans Laboratories of Expertise in Aquatic Chemical Analysis (DFO LEACA) archive. Several of the LEACA *Mytilus* tissue samples had matching sediment data, but most did not (see **Table S1**).

All samples were subject to identical extraction, cleanup, and quantification procedures. High-resolution PBDE analyses of all tissue and sediment samples were conducted by SGS AXYS Analytical or LEACA at the Institute of Ocean Sciences (Fisheries and Oceans Canada, Sidney, BC, Canada). Both laboratories follow US EPA Method 1614 (epa.gov/sites/production/files/2015-08/documents/method_1614a_2010.pdf) to measure PBDEs by gas chromatography e mass spectrometry (GCeMS), and are certified by the Canadian Association for Laboratory Accreditation to analyze 47 PBDE congeners. Detailed methods for sample extraction, lipid determination, cleanup, and quantification are reported elsewhere (Ikonomou et al. 2001; Christensen et al. 2005; Frouin et al. 2013). Sample analysis batches included two procedural blanks, one standard reference material, and one duplicate sample. Recommended criteria for laboratory QA/QC for high-resolution PBDE analytical analyses are also described by Golder (2017).

All data are shown as blank-corrected dry weight pg/g unless otherwise stated. Although compatible in methodology, different analyses at different times have included co-elutriates of variable congener mixes. Therefore, it was necessary to ensure that the congeners were combined and matched in the same way for all sample batches. Any data anomalies were concurrently identified, and the original data and quality assurance/quality control (QA/QC) material checked. The final combined congener list for PBDEs is listed in **Table S2**. The steps for data QA/QC and processing have been standardized as part of the Vancouver Aquarium Pollution Tracker program (contact Dr. Peter Ross, director of the Ocean Pollution Research Program). For the calculation of total contaminant concentrations, all non-detects were replaced by the detection limit followed by blank-correction. The same approach was used for comparisons of congener homologue groups.

Associated sediment data (total organic carbon (%TOC), acid volatile sulfides (AVS), $\delta^{15}N$[1], %fines (grain size), and sedimentation (g/(cm^2·year)) and organic carbon flux (mg C/(cm^2·year)) rates were also compiled for most of the matched sediment/tissue samples. Most of the sediment factor data were collected concurrently with sediment PBDE samples using compatible methods. For methods see crd.bc.ca/about/document-library/documents/annual-reports/environmental-protection/wastewater-marine-environment/macaulay-clover-points; Burd et al. 2012a, 2014; USEPA Method 9060A (United States Environmental Protection Agency 2004); and Forestry Canada Method NOR-X319 (Kalra and Maynard 1991). Sedimentation and organic carbon flux rates were estimated from proximate Pb^{210} dated core samples based on the method of Johannessen and Macdonald (2012) (for regional data and patterns see Burd et al. 2012a, 2014; Johannessen and Macdonald 2012). Sediment AVS was used to infer geochemical conditions resulting from metabolism of organic material by microbes, as described by Burd et al. (2008).

Statistical evaluations of data relationships were performed using correlations, least squares regression, multiple regression (Wessa 2017) and principal component analysis (PCA) using software PRIMER 6 (Clarke and Gorley 2006). Data for multiple regressions and PCA were standardized (mean-centered) to reduce multicollinearity and meet normality requirements, as recommended for the statistical models.

Results

Matched sediment and tissue PBDE sample locations are shown in **Fig. 1** and **Table 3**. **Table 3** includes the georeferenced sediment factors measured for each paired tissue/sediment sample. Samples from background areas (removed from direct discharges likely to include PBDEs) are labelled "B" in **Table 3**. Samples considered to be located within organic enrichment gradients related to municipal wastewater outfalls are labelled "O". Samples labelled "H" were from industrial harbours (Victoria and Vancouver). Three of the four Victoria Harbour samples (VH1–VH3) were also considered to be organically enriched ("EH"), based on sediment AVS. All samples other than the "B" category were considered to have contaminated sediments, and tended to have elevated PBDEs.

Matched sediment/tissue samples

Whole benthos samples were dominated by small, infaunal polychaetes and bivalves (**Table 1**) in all locations, whereas small, infaunal echinoderms (mainly brittle stars) and crustaceans were rare in whole benthos samples from contaminated sites. Taxa that were analyzed separately (e.g., the polychaete *Heteromastus* and the nemertean *Cerebratulus*) were collected only in enriched sediments near municipal wastewater outfalls. Larger holothuroids were also analyzed separately but were found only in background sites. All remaining matched samples were collected from a range of outfall, harbour and enriched harbour sites (see below). These consisted mainly of mixed-species deposit-feeding bivalves from whole benthos samples, or specific filter-feeding bivalves as indicated in **Table 1** (*Mytilus, Modiolus,* and *Saxidomus*).

Total PBDEs

Total PBDEs for each congener group, including blank-corrected dry weights, wet weights, and lipid weights are listed for all samples in **Table S3**. Mean total PBDE concentrations in sediment and tissues for each faunal type are presented for background samples only (Location type B in **Table 3**) (**Fig. 2**), to provide a general comparison of differences in typical tissue levels for different faunal types. The number of samples and standard error (SE) of the mean for each taxon group was variable,

[1]Sediment $\delta^{15}N$ helps elucidate the source and quality of sediment organic material utilized by the sediment feeders, and thus feeding dynamics as they relate to contaminant uptake (as described by Burd et al. 2014).

Table 3. Locations, depths, and sediment factors for paired biotic/sediment samples (see also Table S1).

Sample	Location type	Latitude	Longitude	Depth (m)	OCflux (mg C/(cm^2·yr))	Sedflux (g/(cm^2·yr))	AVS	%TOC	δ^{15}N	%fines
AH10	B	48.3770	−123.4499	83	2.74	0.38	0.01	0.59	6.3	27.0
AH5	B	48.3778	−123.4699	74	2.74	0.38	0.30	0.72	7.4	27.0
AM10	B	49.8445	−124.8868	309	2.50	0.06	4.00	3.68	7.1	92.0
AM6	B	48.9367	−123.3133	186	37.80	2.70	1.30	1.30	5.8	85.0
C0	O	48.3943	−123.3459	65	1.90	0.38	0.62	0.50	7.6	10.0
C1E	O	48.3944	−123.3442	70	3.57	0.38	11.30	0.94	7.4	31.2
C1NE	O	48.3960	−123.3445	59	2.93	0.38	1.06	0.77	7.9	26.7
C1NW	O	48.3961	−123.3479	59	3.69	0.38	5.96	0.97	7.7	35.4
C1S	O	48.3930	−123.3458	75	2.74	0.38	3.61	0.72	7.9	17.5
C1SE	O	48.3935	−123.3445	75	2.13	0.38	9.89	0.56	8.2	14.8
C1SW	O	48.3935	−123.3474	69	3.42	0.38	2.89	0.90	8.1	13.9
C1W	O	48.3943	−123.3477	70	4.18	0.38	5.96	1.10	7.3	13.5
C1W	O	48.3943	−123.3477	70	4.18	0.38	5.96	1.10	7.3	13.5
C1W	O	48.3943	−123.3477	70	4.18	0.38	5.96	1.10	7.3	13.5
C2E	O	48.3943	−123.3431	68	2.74	0.38	11.90	0.72	7.6	20.4
C2S	O	48.3924	−123.3458	78	2.70	0.38	0.20	0.71	8.0	20.8
CB1	B	48.3440	−123.3180	67	2.74	0.38	0.55	0.70	8.7	22.8
CB2	B	48.3449	−123.3165	65	2.74	0.38	1.13	0.83	8.3	33.0
CB3	B	48.3433	−123.3197	63	2.74	0.38	1.79	0.89	8.6	24.6
CB4	B	48.3467	−123.3135	63	2.74	0.38	2.67	0.88	8.2	21.2
FC1	B	48.4574	−122.7733	70	2.60	0.39	1.41	0.69	7.8	30.9
FC2	B	48.4859	−122.7527	59	2.60	0.39	0.02	0.66	8.0	11.5
IO15	B	49.1304	−123.3114	80	40.00	6.00	1.00	0.95	3.7	77.5
IO200N	O	49.2388	−123.2820	80	15.00	1.20	8.00	1.00	1.9	70.0
IO200S	O	49.2692	−123.2641	80	9.80	0.81	6.00	1.30	2.3	68.0
IO400N	O	49.2075	−123.3000	80	18.00	1.10	10.00	1.13	1.9	75.0
IO400S	O	49.1992	−123.3012	80	9.70	0.76	3.36	0.77	2.5	74.0
IO8	O	49.2085	−123.3000	80	22.78	1.30	16.50	1.13	1.8	80.4
IONA ZERO	O	49.2038	−123.3006	80	13.00	1.30	7.4	0.76	2.0	63.2
LG12	H	49.3299	−123.2283	58	4.25	0.21	3.05	2.03	4.3	94.7
LG45	H	49.3488	−123.2782	52	3.78	0.21	0.20	1.82	4.3	71.6
M0	O	48.4026	−123.4104	60	36.90	0.84	26.00	4.40	4.1	30.0
MAC 200MSE	O	48.4017	−123.4083	60	21.80	0.84	12.60	2.60	4.2	28.0
MAC200NW	O	48.4035	−123.4126	60	10.92	0.84	2.00	0.96	5.1	36.0
MAC400MN	O	48.4027	−123.4158	60	7.50	0.79	1.50	0.75	5.5	36.0

(*continued*)

Table 3. (*concluded*)

Sample	Location type	Latitude	Longitude	Depth (m)	OCflux (mg C/(cm^2·yr))	Sedflux (g/(cm^2·yr))	AVS	%TOC	δ^{15}N	%fines
MAC400MS	O	48.4007	−123.4060	60	19.00	0.79	5.44	2.40	4.9	28.7
VH1	EH	48.4331	123.3767	8	37	0.80	7.20	4.64	7.1	98.4
VH2	H	48.4295	123.3724	8	35	0.80	2	4.41	6.5	49.0
VH3	H	48.4230	123.3721	7.6	40	0.80	4.2	5.04	7.0	97.6
VH4	H	48.4239	123.3832	8.3	24	0.80	3.07	3.08	6.5	71.7
1A1	B	49.4463	122.8922	16.8	N/A	N/A	N/A	2.61	1.0	49.0
Dix	B	48.8500	125.1232	20	N/A	N/A	1.46	1.51	7.1	35.2
FR1	B	49.1000	123.3034	10	N/A	N/A	1.30	0.19	4.9	11.1
GINP-1	B	48.7587	123.4345	15.6	N/A	N/A	0.24	1.30	7.7	8.2
GINP-2	B	48.7693	123.4512	13.3	N/A	N/A	0.21	0.67	6.0	18.9
Pat Bay	B	48.6536	123.4535	23	N/A	N/A	0.20	0.29	7.1	7.9
PMV3	H	49.3071	122.9816	12.2	N/A	N/A	0.20	0.34	3.7	7.9
PMV6	H	49.2852	123.1485	20.4	4.25	0.21	1.65	0.92	4.0	72.3
WCVI3	B	49.1593	125.9084	5	N/A	N/A	0.20	0.14	N/A	2.1

Note: Flux measurements were extrapolated from nearby core samples (see Burd et al. 2012a, 2014). Location types include: B, background; O, municipal wastewater outfall; background; H, harbour, and EH, organically enriched harbour sample. All O, H, and EH samples were considered to be from contaminated sediments. OCflux, organic carbon flux; Sedflux, sedimentation flux; AVS, acid volatile sulfides; TOC, total organic carbon; %fines, grain size.

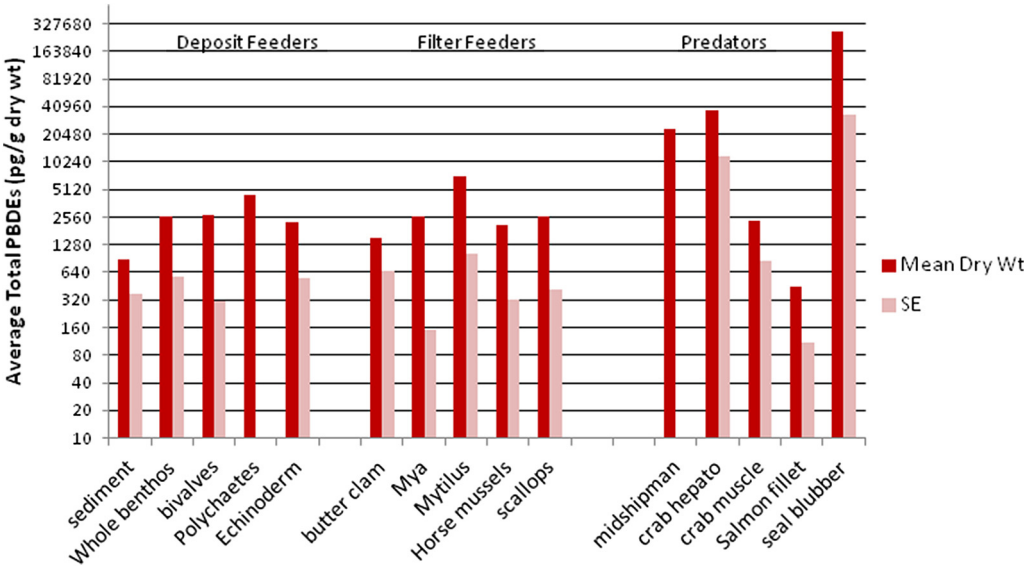

Fig. 2. Average (plus SE of mean) total dry weight polybrominated diphenyl ethers (PBDEs) in matched sediment and tissue samples of different taxa types from background areas only (excluding tissue samples near municipal wastewater outfalls, harbours or other known anthropogenic discharges—category B in Table 2).

so that only gross differences can be described. Dry-weight sediment total PBDE concentrations were lower, on average, than for any taxon group except salmon, which feeds primarily on pelagic fauna (including benthos larvae), but may have some benthic prey. Therefore, some dry weight accumulation occurred in all other taxon groups, with the highest concentrations in the predatory bottom fish (Midshipman), seals (as found in blubber), and crab (as found in muscle or hepatopancreas). Values for intertidal *Mytilus* were also relatively high. When PBDE concentrations were lipid-normalized for the same tissue samples (Fig. 3A), it can be seen that mean concentrations were similar for most deposit feeders and predators (see Table 1) including seal blubber, and considerably lower for the filter-feeding bivalves. For non-background samples only (categories O, H, and EH; Table 3; Fig. 3B), all particulate feeders except horse mussels had higher lipid-normalized total PBDEs than the crab, salmon, or seal blubber samples from background areas.

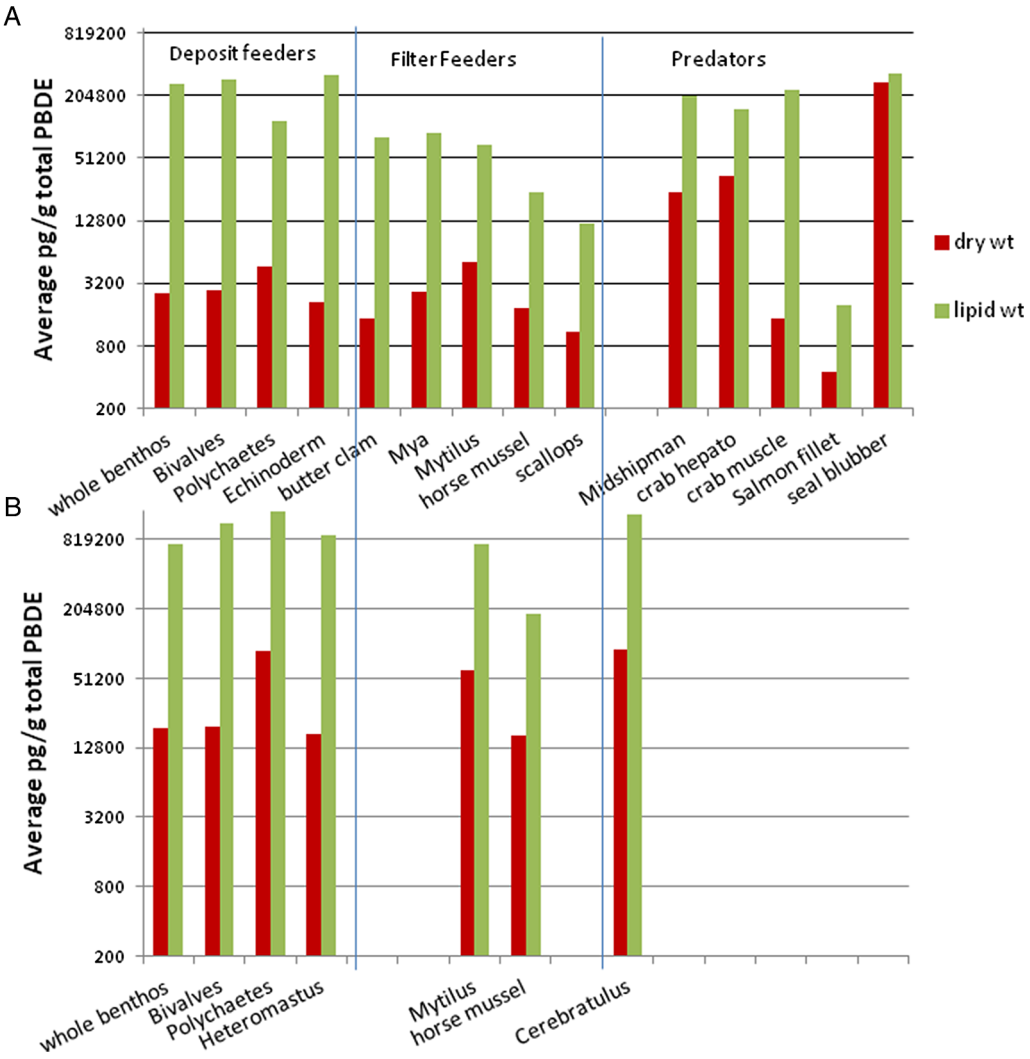

Fig. 3. A) Average total polybrominated diphenyl ether (PBDE) pg/g for dry weight pg/g and lipid-normalized pg/g for the same matched samples as shown in Fig. 2 (category B in Table 2; background samples only); and B) Total PBDE pg/g for dry weight and lipid weight—averages for each taxon for matched samples from contaminated sites near municipal wastewater outfalls or harbours (categories in Table 2).

On average, total dry-weight PBDEs increased by a factor of ~107× from background infaunal benthos to seal blubber, but lipid-normalized accumulation was much lower (<1.3×), indicating an increase in lipid rather than PBDE concentrations up the food chain.

Figure 4 shows the relationship between total tissue PBDEs and sediment PBDEs for all matched samples (Table S1). Log-log transformed data have been plotted separately for (1) whole benthos from near municipal wastewater outfalls (category O; Table 3); (2) whole benthos collected from background areas (category B; Table 3) and harbours (categories H and EH; Table 3); and (3) horse mussels, scallops and intertidal *Mytilus* samples from all areas. The increase in tissue concentrations with increasing sediment PBDE concentrations appears to be similar for all plots, and exponential in character. For that reason, regression coefficients (R^2) were calculated from the best-fit (least squares) log-log transformed data (Fig. 4). There was a clear separation between the relationships for near-outfall and for background/ harbour whole benthos community samples. Over a similar sediment contaminant range, the near-outfall samples showed considerably higher tissue concentrations overall than the background/harbour samples. Horse mussels near the Clover Point municipal wastewater outfall and *Mytilus* from all locations had a similar sediment/tissue relationship to that of infaunal communities near municipal wastewater outfalls. The filter feeders (*Modiolus, Mytilus*, and *Chlamys*) appear to show similar sediment/tissue trends regardless of species, location (subtidal/intertidal), or substrate (sediment versus rock) separation.

Pearson correlations between the sediment factors in Table 3 and total PBDE concentrations in matching sediment feeders are shown in Table 4. Only samples for which all sediment factors were available have been included ($N = 60$). Sediment PBDEs were notably positively correlated with a number of sediment factors, primarily %TOC, %fines, and organic carbon (OC) flux. In contrast,

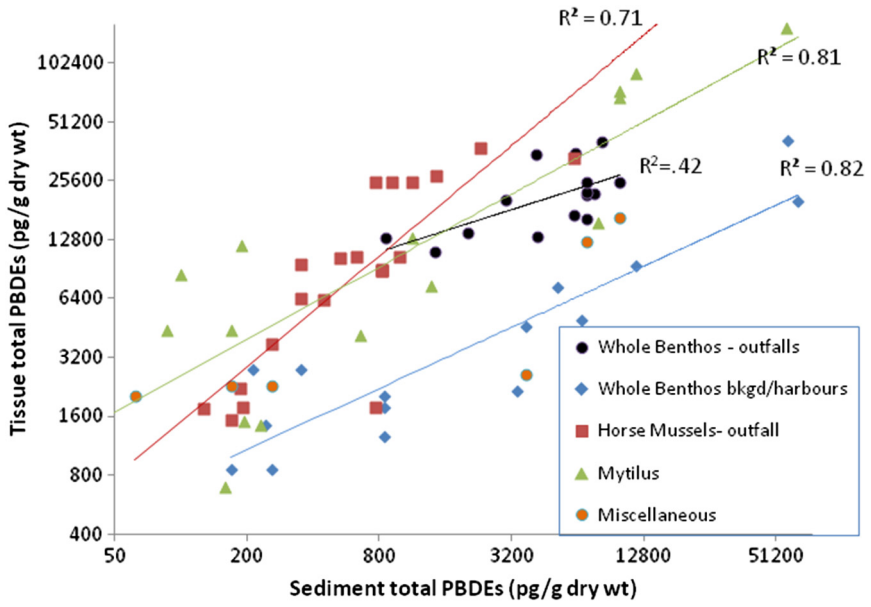

Fig. 4. Log/log total dry wt matched tissue and sediment total polybrominated diphenyl ethers (PBDEs) for whole infaunal benthos near municipal wastewater outfalls (Category O—Table 2), whole benthos in background areas and harbours (Categories B, H, and EH), and bottom filter feeders (horse mussels and scallops) from the area near the Clover Point municipal wastewater outfall. Note that the two highest sediment values for benthos from harbours (blue diamonds) were from organically enriched sites in Victoria Harbour (Category EH) and tended to also be in line with the outfall whole benthos samples.

Table 4. Pearson correlations (r) for matched tissue/sediment samples for sediment dwellers only ($N = 60$).

	Sediment PBDE	OCflux	Sedflux	OCflux/δ^{15}N	AVS	%TOC	δ^{15}N	%fines
OCflux	0.48	1.00	—	—	—	—	—	—
Sedflux	0.04	0.71	1.00	—	—	—	—	—
OCflux/δN	0.29	0.76	0.62	1.00	—	—	—	—
AVS	0.15	0.36	−0.04	0.50	1.00	—	—	—
%TOC	0.68	0.57	−0.02	0.21	0.42	1.00	—	—
δ^{15}N	−0.14	−0.47	−0.40	−0.86	−0.43	−0.05	1.00	—
%fines	0.51	0.64	0.46	0.65	0.07	0.41	−0.62	1.00
Fauna PBDE	0.40	0.27	−0.06	0.37	0.74	0.37	−0.41	0.13

Note: *Mytilus* were not included because sedimentation flux, δN and sometimes %OC and AVS data were missing for all but 2 samples, and the mussels are not in direct contact with sediments. All r values >0.32 had a $p < 0.05$. PDBE, polybrominated diphenyl ether; OCflux, organic carbon flux; Sedflux, sedimentation flux; δ^{15}N, ratio stable isotope of nitrogen; AVS, acid volatile sulfides; TOC, total organic carbon; %fines, grain size.

Table 5. Regression statistics for a multiple linear model, including the 5 sediment variables determined in combination to explain the most variability in total tissue PBDEs (Table 3).

	b	B	B × r_{xy}
Sediment PBDE	0.5817	0.5316	0.2122
AVS	1708.9118	0.8327	0.6135
%TOC	−2786.3535	−0.2458	−0.0918
δ^{15}N	−2294.5633	−0.4629	0.1884
OCflux/δN	−1631.3808	−0.5452	−0.2002

Note: Multiple $\boldsymbol{R^2} = 0.7221$, Adjusted Multiple $\boldsymbol{R^2} = 0.6963$. Results show that a relatively high amount of variance (multiple adjusted $R^2 \sim 0.7$) in tissue PBDEs can be explained by these five habitat variables. PDBE, polybrominated diphenyl ether; AVS, acid volatile sulfides; TOC, total organic carbon; OCflux, organic carbon flux.

tissue PBDEs had the strongest correlation with sediment AVS, followed by δ^{15}N, sediment PBDEs, % TOC, and OC flux/δ^{15}N (a hybrid measure of organic carbon flux modified by source and quality of material—see Burd et al. 2012a). Sediment %fines were not correlated with tissue contaminant concentrations.

A multiple linear regression (based on the results of the correlation model above) between the sediment factors from Table 3 and tissue PBDEs for sediment feeders (shown in Fig. 4) was performed to examine the combined variance in tissue PBDEs (and predictive ability) that could be explained by the habitat variables examined in the correlations above (Table 5). The regression model had the equation $Y = a + b_1X_1 + b_2X_2 + \cdots + b_kX_k$, where a is a starting-point constant analogous to the intercept in a simple two-variable regression, and b_1, b_2, etc., are the unstandardized regression weights for X_1, X_2, etc., each analogous to the slope in a multivariable regression. In the present analysis, $a = 0.68$ and the values of b are as indicated in Table 5. The values listed as B are the standardized regression weights. Trial and error results show that the best combination of sediment factors (highest R^2) to

explain tissue PBDE variance for matched tissue/sediment samples includes, in decreasing order, AVS, sediment PBDEs, OCflux/δ^{15}N, δ^{15}N, and %TOC. The adjusted multiple regression (which accounts for bias related to multiple variables) coefficient $R^2 \sim 0.7$, suggested that the model variables accounted for a high proportion of variability in tissue PBDEs for sediment feeders. The predictor variables were mean-centered (standardized) to reduce the potential effects of multicollinearity.

The total PBDE accumulation ratio (tissue/sediment PBDEs) for the matched samples (whole infaunal community, horse mussels, *Mytilus*, "other" = remaining sediment feeders such as scallops, infaunal bivalves, and echinoderms) in Fig. 5A shows variable but high positive uptake (accumulation ratio) at moderate sediment PBDE concentrations, with a generally negative uptake trend as sediment PBDE concentrations increased. This trend was present, but less clear, for *Mytilus* compared with the other taxa. This may be explained by the fact that *Mytilus* samples were often spatially disconnected from sediment samples because of their attachment to nearby intertidal hard substrates. The two Victoria harbour whole benthos tissue samples collected at sediment concentrations of about 10 000 pg/g dry wt showed a PBDE accumulation ratio of <1. Total PBDE accumulation also decreased progressively with increasing %fines (Fig. 5B), resulting in distinct regional differences in the PBDE uptake ratio from sediments between Juan de Fuca Strait (low %fines) and the Strait of Georgia (higher %fines). This relationship was not evident for %TOC, AVS, or OCflux. The uptake ratio in one background horse mussel sample was anomalous because sediment PBDE levels

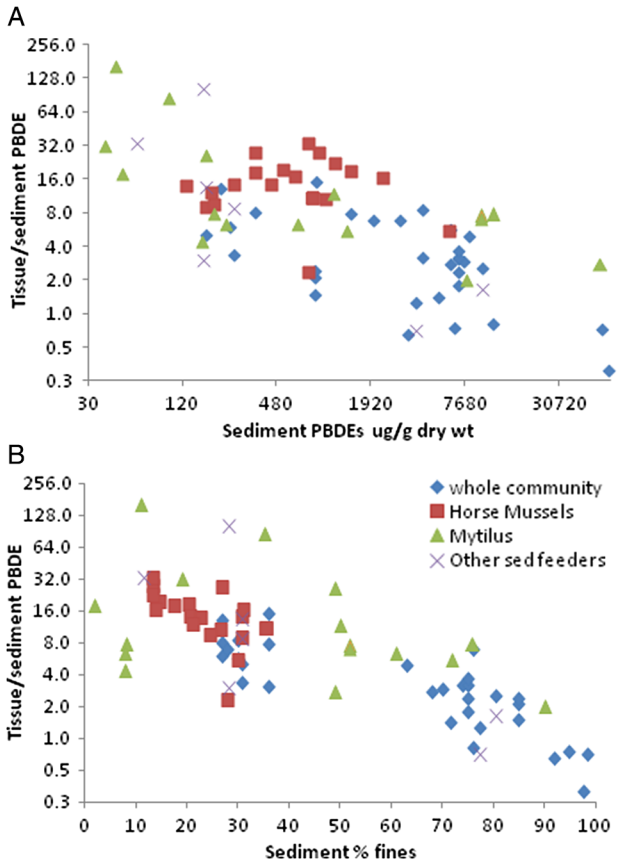

Fig. 5. Tissue accumulation (Tissue/sediment) of dry weight polybrominated diphenyl ethers (PBDEs) relative to A) sediment PBDE and B) sediment grain size (%fines) for the same samples as shown in Fig. 4.

were unusually high compared with other nearby background sites, whereas whole benthos PBDE tissue concentrations and sediment %fines were very similar to the other background sites. Reasons for this sediment outlier are not clear from the present study.

PBDE congener homologue composition in tissue and sediments

A compilation of the mono-deca congener homologue group proportions is shown separately for the horse mussels near Clover Point municipal wastewater outfall, whole benthos community samples from near municipal wastewater outfalls, background and in harbours, and matched sediments as applicable (Fig. 6). Tissue PBDE congener composition changed dramatically with initial uptake from sediments for all sediment feeders. Sediments from all locations were dominated by deca-BDEs (60%–70%), with lesser proportions of tetra-, penta- and nona-BDEs (2%–13%). The tissue samples showed considerably different homologue mixtures than the sediments. The horse mussels and whole benthos near outfalls and in background areas were dominated by tetra-BDEs (30%–50%), followed by penta-BDEs (30%–50%), with <10% each of the hexa-, nona-, and deca-BDEs. However, the whole benthos samples from harbours showed a configuration more similar to that of the sediments (dominated by deca-BDE, followed by tetra- and penta-BDEs). Although the proportion of deca-BDEs was low in all sediment feeders relative to sediments (Fig. 6), the total concentrations were similar

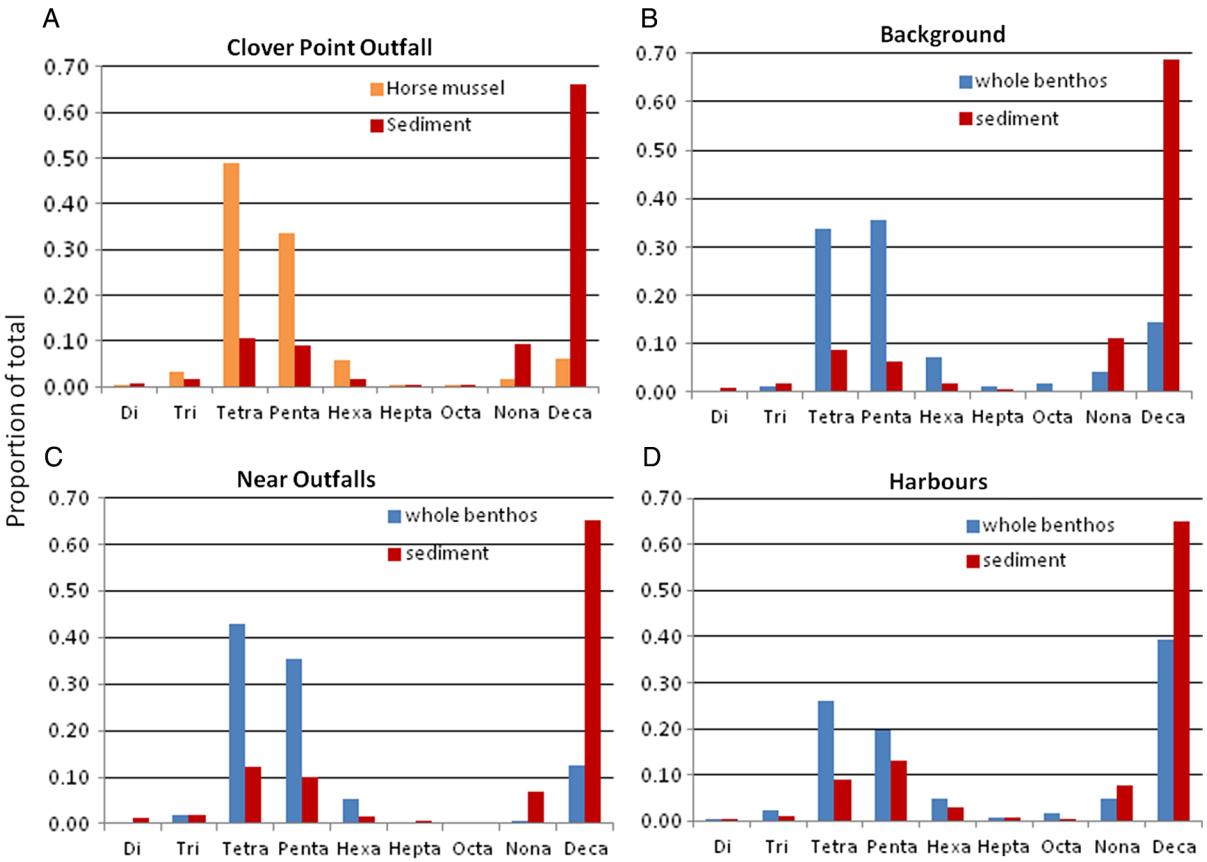

Fig. 6. Proportion of total polybrominated diphenyl ethers (PBDEs) in each congener group (di-deca) for A) horse mussels and matched sediments around the Clover Point municipal wastewater outfall; B) whole benthos and matched sediments from Vancouver and Victoria Harbours (categories H and EH—Table 2); C) whole benthos and matched sediments near Iona and Macaulay Point municipal wastewater outfalls (Category O—Table 2); and D) whole benthos and matched sediments from background areas away from all municipal wastewater outfalls and harbours (Category B—Table 2).

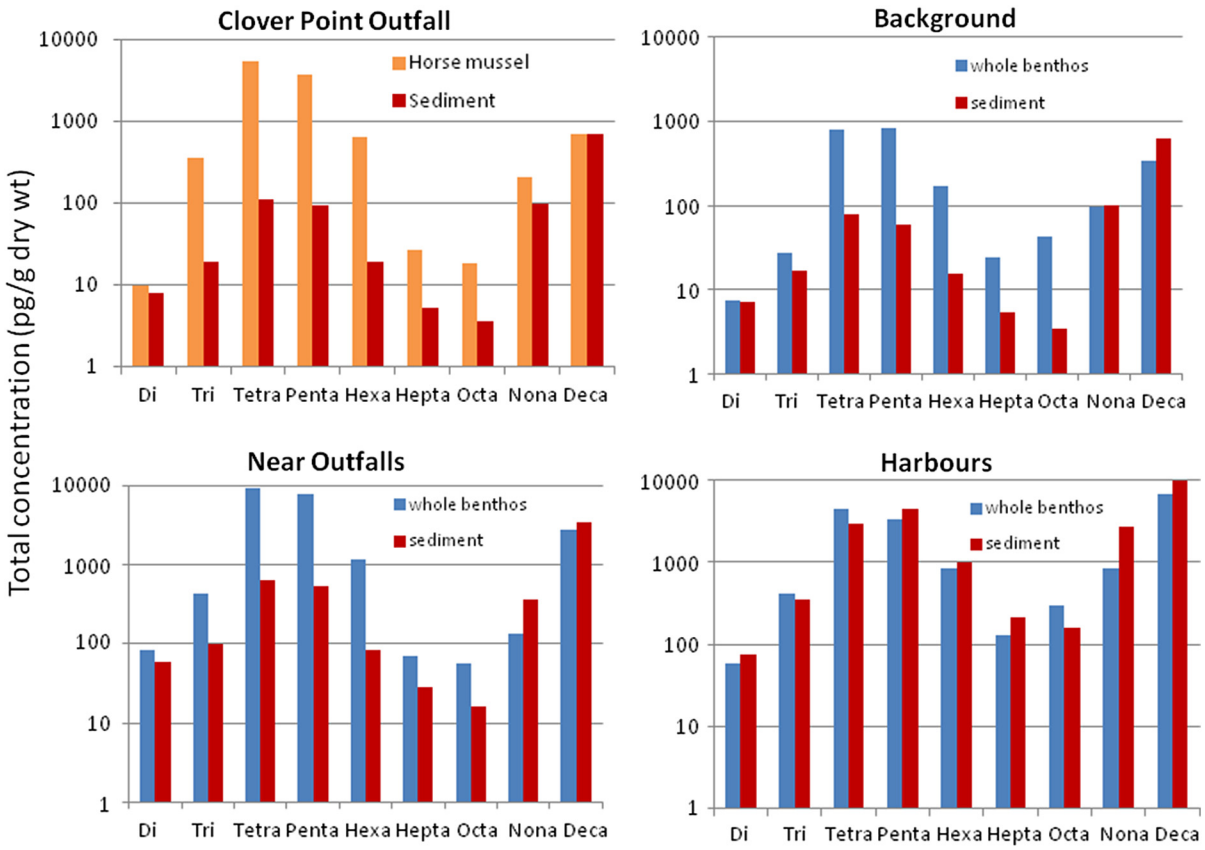

Fig. 7. Total polybrominated diphenyl ethers (PBDEs) (pg/g dry weight) in each congener group (di-deca) for tissue and matched sediments for the same sample groupings as Fig. 6.

between tissues and sediments (Fig. 7). Nona-BDEs showed a similar trend. This clearly suggests that most of the tissue accumulation from sediments occurred in the tetra–penta homologue groups.

Figure 8A shows the average congener homologue composition of all sediment and faunal types examined in this study, regardless of location. On average, deca-BDEs, although much reduced from sediment levels in all fauna, were still evident in higher trophic levels (salmon, crab, and seal). In contrast, tetra-BDEs, followed by tenta- and hexa-BDEs were, on average, considerably higher in proportion in all tissues than in the sediments. Variability within and between taxon groups is shown in the PCA analysis of proportional congener homologue composition for all sediment and tissue samples (Fig. 8B). PCA factors 1 and 2 accounted for 98% of the variance in the results, and were overwhelmingly dominated by deca-BDE (PC1), and tetra- and penta-BDEs (PC2). The proportion of deca-BDE varied considerably among sediment samples. The proportion of deca-BDEs in all individual tissue samples declined considerably relative to sediment proportions[2], with a concurrent increase in dominance in the tetra- and penta-BDEs (PC2). The penta-BDE dominance was most extreme in sediment feeders (whole benthos, filter-feeding *Mytilus,* horse mussels, scallops, subtidal bivalves, polychaetes

[2]Exceptions to this are several historical intertidal butter clam samples with tissue PBDE proportions very similar to sediment proportions (green triangles in Fig. 8B to far right of PC1). This taxon is unusual in its ability to sequester algal toxins in siphons for long periods of time (Kvitek et al. 2008), making the animals likely to also store other particulate organic contaminants such as PBDEs in the same way.

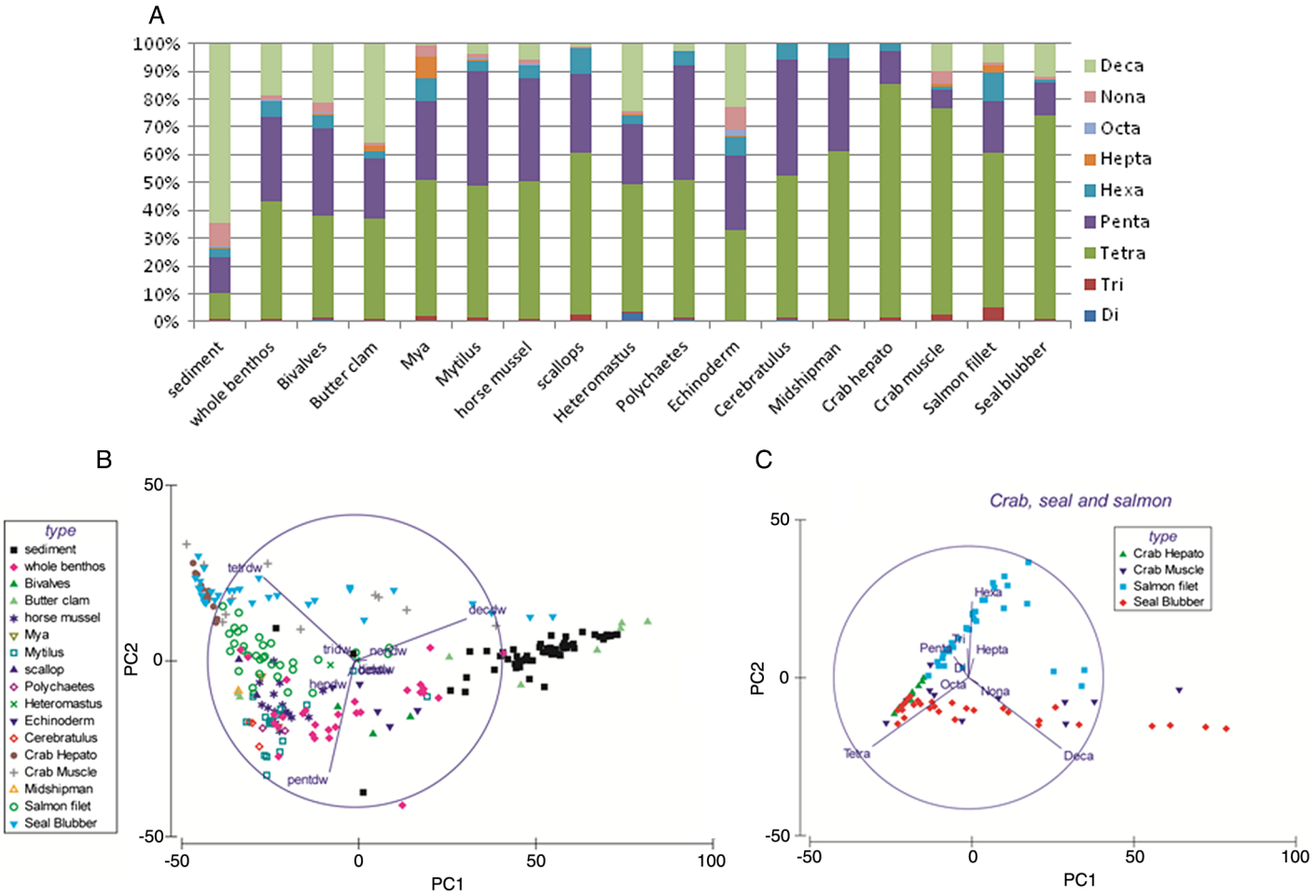

Fig. 8. A) Congener group (di-deca brominated diphenyl ethers (BDEs)) average proportional composition for sediments and all faunal types regardless of location; B) principal component analysis (PCA) of congener proportional composition for all samples to illustrate variability within faunal types; and C) PCA of proportional composition of di- to deca BDEs in all salmon, seal, and crab samples only.

and echinoderms), whereas tetra-BDEs dominated in salmon, crab hepatopancreas, and most seal blubber samples.

Because of the high variability in the results, PBDE congener homologue group proportions for crab, salmon, and seal blubber were examined in a separate PCA analysis (Fig. 8C). The first two orthogonal factors explain 95% of the variation in samples. PC1 is dominated by tetra- and deca-BDE congeners, which varied mainly in crab and seal blubber samples, with PC2 dominated by these plus hexa-BDE congeners, variable mainly in salmon fillet samples. Penta-BDEs were relatively consistent over all samples. There was a general similarity in PBDE congener composition between crab muscle and seal blubber cores, whereas crab hepatopancreas samples had a much more homogeneous (mostly tetra-BDE) composition than the other samples. As all crab, salmon and seal samples were taken within a short sampling period (about 1 week), these patterns were unlikely to reflect seasonal differences. Most salmon tested (26 of 33 samples) had no detectable deca-BDE; however, the remainder had an average of 27% deca-BDE. Crab muscle tissue tended to have almost 40% deca-BDE, although crab hepatopancreas samples had almost none. When deca-BDEs were proportionally high, tetra-BDEs were reduced by a similar proportion.

PBDE accumulation (uptake) ratios of homologue groups

Figure 9 shows the average PBDE accumulation ratio (ratio of tissue to matching sediment concentrations in pg/g dry wt) of homologue groups for each faunal group studied. Because salmon, seal, and crab data were not collected with concurrent sediment data (which is not feasible for these mobile animals), an average background sediment composition was used for the accumulation ratio. Because of the distinct dichotomy between samples with and without deca-BDEs, crab muscle, salmon, and seal blubber samples were grouped into (a) no detectable deca-BDE (pattern 1) and (b) detectable deca-BDE (pattern 2).

Tissue accumulation on a dry weight basis can be assumed to occur at tissue/sediment ratios >1, whereas dilution occurs at ratios <1. A ratio close to 1 was found in the intertidal infaunal clams (butter clam, *Mya*), as well as salmon muscle (Figure 9). The highest overall accumulation (ratio of most congeners >>1) occurred in the benthic predators (*Cerebratulus*, Midshipman) and lipid-rich higher trophic samples (seal blubber and crab hepatopancreas). The bottom half of the figure shows the mean proportion of total PBDE accumulation ratio contributed by each congener group for all taxa types. The tetra-BDEs showed the greatest accumulation, followed by penta-, hexa-, and sometimes hepta-BDEs. Even in taxa with an uptake ratio >1 for nona- and deca-BDEs, the overall proportion of these groups to total accumulation were minor. Results were variable for the other congener groups, with echinoderms showing the most unusual (high octa-BDE) accumulation. The dry weight

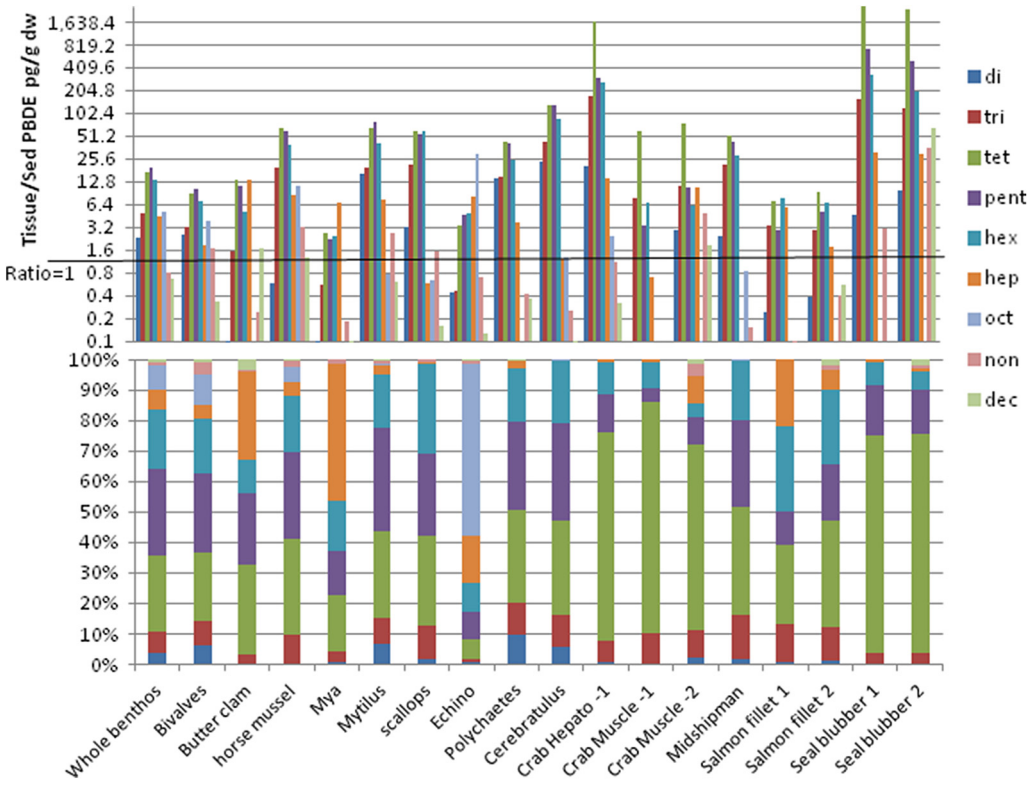

Fig. 9. Ratio of tissue/sediment dry weight polybrominated diphenyl ethers (PBDEs) for each congener group averaged for each faunal type. Lower half of figure is proportional makeup of this ratio. Where the ratio = 1 is considered the "zero" accumulation point. Note the appended -1 or -2 for crab, salmon and seal samples refers to "pattern 1" (no detectable deca-BDE) and "pattern 2" (detectable deca-BDE).

accumulation of tetra-BDE in crab hepatopancreas and seal blubber samples was several orders of magnitude higher than for any other tissue type.

Pearson linear correlations (**Table 6**) of homologue composition in uptake ratios were relatively high (values >0.75 highlighted) between taxa. All bottom feeders except crab showed high intercorrelations (between taxa) in PBDE uptake patterns, along with the high deca-BDE salmon (i.e., group 2). This suggests that the group 2 salmon are more closely linked with a benthic food web than the group 1 salmon (i.e., those with no detectable deca-BDE). Both seal blubber groups (no detectable and detectable deca-BDE) showed moderate ($r = 0.6–0.75$) correlations with some bottom taxa, which may also reflect feeding habits. The group 1 (no detectable deca-BDE) salmon showed low correlations with all other taxa, which may reflect a non-benthic food chain (see Frouin et al. 2013). There were very strong correlations between all crab tissue types, high deca-BDE salmon, and seal blubber. The overall uptake pattern was highly correlated between seal blubber groups 1 and 2.

Discussion

In this study, we focused on the influence of sediment physical and geochemical factors on initial uptake of PBDEs into a variety of sediment feeders in southern British Columbia marine waters. We then examined how total and congener homologue group PBDEs changed in higher trophic levels which may be connected to benthic food sources. Understanding the initial uptake of these contaminants into the marine food chain will help to determine how they affect higher trophic levels.

Differences in total PBDE concentrations in sediments near municipal wastewater outfalls, in harbours, and from background locations illustrate the tight depositional gradient of PBDEs relative to distance from source (Johannessen et al. 2008). This also appears to be true for water column dissolved and particulate fractions (Desforges et al. 2014) in southern British Columbia.

Gouin and Harner (2003) modelled the environmental fate of PBDEs and suggested that they are largely partitioned to organic matter in sediments. Li et al. (2010) found that sediment PBDE content off the coast of southeastern China was not related to the organic content of sediments, but rather to particle size, although Zhao et al. (2010) and Zhu et al. (2014) found that grain size and organic content were both important factors in tropical mangrove swamps. In all three aforementioned studies, sediment % fines was a stronger correlate of sediment PBDE levels than organic content. In the present study, sediment PBDEs increased with sediment organic carbon flux, content, and %fines (in decreasing order). We conclude from this that sediment geochemistry and physical structure are critical for determining PBDE storage in sediments, and fine, organic particles tend to bind these contaminants most efficiently. As a result, the coarser, less organic sediments of the Juan de Fuca Strait tend to have a lower inventory of PBDEs than the organically richer and finer sediments of the southern Strait of Georgia.

PBDEs in sediment feeders

Sediment consumers are the main entry point into the food chain of PBDEs from the marine habitat, as these contaminants are typically particle-bound. Most sediment feeders live for 1–4 years (Robertson 1979). PBDE uptake from sediments and subsequent incorporation into the food chain is limited by sediment feeder lifespan and habitat conditions, but has been shown to be higher in situ than in short-term uptake experiments (Klosterhaus et al. 2011). This finding suggests that tissue uptake may be cumulative over the life span of the animals.

Johannessen et al. (2008) noted that regardless of the actual rate of input to the sediments, benthic organisms are exposed to contaminants in proportion to sediment concentrations (e.g., Reynoldson 1987). In the present study, sediment feeders clearly took up contaminants in proportion to sediment concentrations, but this relationship is not simple or linear, and other factors modify uptake.

Table 6. Pearson correlations (*r*) of dry weight tissue accumulation (tissue/sediment polybrominated diphenyl ethers (PBDEs)) homologue composition for all taxon groups as shown in **Fig. 9**.

r	Whole benthos	Bivalves	Butter clam	Horse mussel	*Mya*	*Mytilus*	Scallops	Echinoderm	Polychaete	*Cerebratulus*	Crab Hepato-1	Crab Muscle-1	Crab Muscle-2	Midshipman	Salmon-1	Salmon-2	Sea-2
Bivalves	**0.99**	1.00	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Butter clam	0.67	0.56	1.00	—	—	—	—	—	—	—	—	—	—	—	—	—	—
horse mussel	**0.98**	*0.96*	0.67	1.00	—	—	—	—	—	—	—	—	—	—	—	—	—
Mya	0.34	0.21	0.86	0.29	1.00	—	—	—	—	—	—	—	—	—	—	—	—
Mytilus	**0.96**	**0.96**	0.63	**0.96**	0.25	1.00	—	—	—	—	—	—	—	—	—	—	—
scallops	**0.94**	**0.92**	0.53	**0.94**	0.23	**0.92**	1.00	—	—	—	—	—	—	—	—	—	—
Echinoderms	0.02	0.05	−0.09	−0.06	0.00	−0.21	−0.19	1.00	—	—	—	—	—	—	—	—	—
Polychaete	**0.93**	**0.93**	0.61	**0.95**	0.22	**0.98**	**0.92**	−0.25	1.00	—	—	—	—	—	—	—	—
Cerebratulus	**0.96**	**0.96**	0.59	**0.97**	0.20	**0.99**	**0.96**	−0.21	**0.99**	1.00	—	—	—	—	—	—	—
Crab Hepato-1	0.64	0.62	0.57	**0.76**	0.20	0.65	0.66	−0.14	0.74	0.70	1.00	—	—	—	—	—	—
Crab Muscle-1	0.60	0.57	0.61	0.73	0.26	0.62	0.60	−0.16	0.71	0.66	**0.99**	1.00	—	—	—	—	—
Crab Muscle-2	0.49	0.46	0.57	0.63	0.24	0.51	0.50	−0.15	0.60	0.55	**0.98**	**0.99**	1.00	—	—	—	—
Midshipman	**0.93**	**0.92**	0.59	**0.98**	0.20	0.95	**0.95**	−0.20	**0.97**	**0.98**	**0.79**	**0.76**	0.66	1.00	—	—	—
Salmon-1	0.63	0.55	0.73	0.65	0.73	0.54	0.71	−0.14	0.58	0.58	0.56	0.56	0.50	0.63	1.00	—	—
Salmon-2	**0.88**	**0.85**	0.68	**0.95**	0.30	**0.89**	**0.91**	−0.22	**0.93**	**0.92**	**0.90**	**0.88**	**0.81**	**0.96**	0.70	1.00	—
Seal-1	0.64	0.62	0.60	**0.76**	0.21	0.66	0.64	−0.14	0.73	0.70	**0.99**	**0.99**	**0.98**	**0.78**	0.51	**0.90**	**1.00**
Seal-2	0.68	0.66	0.62	**0.79**	0.22	0.70	0.67	−0.13	**0.77**	0.73	**0.99**	**0.99**	**0.97**	**0.81**	0.53	**0.92**	1.00

Note: Notable correlations (arbitrarily >0.75) are in bold. All *r* values >0.576 were significant at $p < 0.05$. Hepato, hepatopancreas tissue.

Zhao et al. (2010) also noted that although marine sediment PBDE concentration are often correlated with both %TOC and %fines, benthos tissue concentrations are not. In the present study, tissue concentrations were correlated with sediment AVS, %TOC, $\delta^{15}N$, and organic carbon flux and quality. Unlike sediments, tissue PBDE concentrations in sediment feeders had a negligible correlation with %fines.

Although sediment PBDEs are often TOC-normalized for interpretation of biotic uptake (Dinn et al. 2012a), organic input and burn-down cannot always be interpreted from sediment %TOC. Low % TOC can occur where considerable, labile organic material is being input if the relative inorganic flux is high (Burd et al. 2012a, 2012b). In the present study, increasing organic content and input (%TOC, organic carbon flux), organic lability ($\delta^{15}N$) and bacterial metabolism (inferred from AVS[3]) enhanced tissue PBDE uptake. This pattern is illustrated by the considerably higher tissue PBDEs relative to sediment PBDEs near municipal wastewater outfalls (see also Burd et al. 2014). Elevated sediment AVS is an indicator of enhanced burn-down of this organic material, primarily by bacteria. The organic material from wastewater outfalls is fresh and labile, and it is expected that benthos would selectively feed on this material (Burd et al. 2014). Biomass turnover of benthos is, therefore, increased near municipal wastewater outfalls relative to background because of high bacterial metabolism, as well as dominance by smaller, rapid-turnover invertebrates (Burd et al. 2013), so that contaminant uptake rates are also expected to be higher than in background areas (Burd et al. 2014).

The accumulation or uptake ratio of PBDEs in sediment feeders is illustrated herein as the dry-weight ratio of tissue/sediment PBDEs. Tissue accumulation showed a general negative trend as sediment PBDEs increased, so that above sediment total PBDE concentrations of about 10 000 pg/g dry wt, a dilution effect (ratio <1) was evident. This dilution was most evident in the highly PBDE-contaminated urban harbour samples. Similarly, tissue PBDE accumulation decreased progressively with increasing %fines, resulting in a regional dichotomy in PBDE tissue accumulation rates between the Juan de Fuca Strait (typically sandy, low depositional rate, and low organic carbon flux) and the Strait of Georgia (more silty and a high depositional rate with higher organic carbon flux; Burd et al. 2012a). Therefore, despite the lower sediment inventory of PBDEs in the Juan de Fuca Strait, the rate of uptake into sediment feeders is higher than in the Strait of Georgia.

The above patterns imply that at very high sediment PBDE levels, only likely to be found in samples with high %fines, most of the PBDEs are not bioavailable, possibly because they are bound to inorganic particles. PBDEs bound to inorganic fine particles are unlikely to be incorporated into tissues due to selective feeding of benthos on organic particles.

It is also expected that there would be a difference in contaminant loads between suspended particles and deposited (sediment) particles, although this was not measured in the current study. In suspended particles, there is less dilution from coarse, inorganic sands (which sink faster), and suspension feeders may, therefore, be exposed to a more concentrated source of organically bound contaminants than deposit feeders. This is supported by the finding that total PBDEs in tissues (relative to sediment) of the suspension feeders *Mytilus* and *Modiolus* were similar to whole benthos near municipal wastewater outfalls, all of which were higher than whole benthos from background areas. Although some of the *Modiolus* were sampled near a municipal wastewater outfall, the *Mytilus* samples were not.

To summarize, selective feeding on fresh municipal wastewater outfall deposits versus older organic particulates and on organic versus inorganic particulates likely accounts for much of the variability

[3]Based on the assumption that burndown of organic carbon by bacteria increases AVS in sediments under suboxic conditions.

in the relationship between total tissue PBDEs and sediment PBDEs and explains why accumulation of PBDEs from sediments is not linear or predictable from sediment concentrations alone.

Trophic transfer

There has been considerable literature focusing on trophic transfer and bio-magnification of hydrophobic organic contaminants such as PBDEs in marine food chains (Natale 2007; Ross et al. 2009; Cullon et al. 2012). There are a number of factors that contribute to trophic transfer in secondary consumers. For example, the sex and age of animals clearly contribute significantly to tissue content in marine mammals (Wolkers et al. 2006; Mongillo et al. 2012; Shaw et al. 2012). In general, trophic transfer is dependent on the history of food consumption and individual mechanisms for contaminant loss. The higher total dry-weight PBDEs in benthic feeders (deposit or filter feeders) than in salmon fillets reflects the strongly particle active nature of these contaminants and, thus, their likelihood to accumulate most within organisms associated with sediments. Li et al. (2010) also found that lagoon fish offshore of Xiamen Island in southeastern China had lower BDE (particularly deca-BDEs) concentrations than clams and crabs.

Determining trophic transfer is complicated by the logistical difficulties in the calculation of whole-body burden in large crustaceans, fish, and marine mammals. The difference in matched crab hepatopancreas and muscle PBDE concentrations (higher in dry weight but lower in lipid weight for hepatopancreas) in the current study illustrates this problem. There is very limited information on the relative concentration of PBDEs in different tissue types for higher trophic level marine animals (Wolkers et al. 2009; Yordy et al. 2010; Shaw et al. 2012; Trumble et al. 2012).

The general consensus in the literature is that PBDE accumulation is primarily lipid-mediated (Raach et al. 2011). For that reason, trophic transfer studies typically focus on lipid-weight contaminant comparisons. Samples taken from living mammals are typically from the lipid-rich subcutaneous fat layer, as they were for seals in the current study. Yordy et al. (2010) measured persistent organic pollutant (POP) distributions in a range of tissue types in stranded bottlenose dolphin and showed that blubber, the primary site of metabolic lipid storage, is also the primary site for POP accumulation, contributing >90% to the whole-body burden. However, they note that as lipid mobilizes from blubber, contaminants may redistribute to other tissues. Shaw et al. (2012) showed no differences between hepatic and blubber tissue total PBDEs in stranded seals in the northwestern Atlantic, although BDE 209 was much more concentrated in liver than in blubber. Boon et al. (2002) found generally higher PBDE concentrations in liver than blubber in North Sea marine mammals, although BDE 209 was not included in the analysis. In contrast, Moon et al. (2010) found higher overall concentrations of PBDEs in blubber than in liver for Korean marine mammals. Based on the above examples from the literature, it is clear that PBDE distribution in different body tissues is not simply related to lipid distribution. Therefore, there is a lack of understanding of how PBDEs sequester into different tissue types in apex predators, particularly mammals.

The much higher accumulation of total PBDEs (107×) on a dry-weight basis from background infaunal benthos to seal blubber was not borne out by lipid-weight PBDE accumulation (~1.3×). It is probable that the PBDE lipid accumulation rate would be still lower for total body burden in seals. This suggests a lack of lipid-normalized accumulation of total PBDEs from primary sediment feeders to higher trophic levels, but that PBDE uptake is remarkably high in the low-lipid primary sediment feeders, particularly near organic enrichment sources. The assumption of PBDE storage primarily in lipids is therefore questionable for primary consumers. It seems unlikely that the contaminants would be so concentrated in the very limited lipid reserves of these direct sediment feeders.

The filter-feeding bivalves (rock scallops, horse, and blue mussels) showed a much lower lipid-weight PBDE concentration than direct sediment feeders. If these organisms are more important in the diet of seals than bottom fish or crabs, then lipid-weight accumulation (about 4×) of PBDEs in seal blubber was clearly evident. All other taxa showed biodilution of lipid-weight PBDEs relative to whole benthic infauna. This low or negative trophic accumulation of PBDEs has also been noted in food webs for the Canadian Arctic (Kelly et al. 2008). Biodilution of selected PBDE congeners has also been reported off the coast of China (Zhang et al. 2012) for marine fish, and in mesocosm studies of benthos and carp (Tian et al. 2010; Tian et al. 2012). Thus, a clear understanding of food resources for higher trophic fauna is required to understand bioaccumulation of persistent contaminants. The results of the current study suggest that biomagnification of total PBDEs may not be occurring in the organisms tested in this study, but rather, lipids become an increasingly prominent PBDE storage component at higher trophic levels.

PBDE congener homologue groups

The rate of debromination of PBDEs in sediments or water is positively correlated with level of bromination (Keum and Li 2005; see also Shaw et al. 2012), so that lower-brominated forms break down more slowly than higher ones. Although BDE 209 initially debrominates quickly with fresh deposits in sediments, this process slows down considerably (Keum and Li 2005) and stops after a period of time (Gerecke et al. 2005). Debromination in sediments seems to occur in a step-wise pattern culminating in the highly toxic tetra forms (Lee and He 2010), and can be enhanced by reducing agents such as iron-bearing minerals and sufides (Young et al. 2005), low redox (Keum and Li 2005), anaerobic bacteria (Gerecke et al. 2005; He et al. 2006; Lee and He 2010) and photolysis (Wei et al. 2013). Thus BDE 209 tends to be fairly stable in sediments under aerobic, subtidal conditions (as in background samples in the current study). In support of this supposed stability, the proportional composition of sediment PBDE homologue groups in the current study was very similar near municipal wastewater outfalls, in harbours, and in background areas. This does not suggest that significant debromination occurred with distance from source in southern BC (see also Johannessen et al. 2008; Grant et al. 2011).

Most tissue accumulation studies for PBDEs focus on the kinetic properties of various-sized molecules and their hydrophobicity to explain uptake dynamics of different PBDE congeners into various faunal types and tissues. Tissue accumulation of different molecular weight (degree of bromination) PBDEs has typically been related to octanol/water partitioning (K_{ow}) in many taxa and ecosystems (deBruyn et al. 2009; Tian et al. 2012; Frouin et al. 2013; Alava et al. 2016). Kelly et al. (2004, 2008) questioned the use of log K_{ow} for predicting uptake potential of hydrophobic organic compound groups in Arctic food chains, as error levels and variability in observations are often high, and other factors besides kinetic properties of the compounds are clearly important (see also Magnusson and Tiselius 2010; Klosterhaus et al. 2011). In a passive physical system, log K_{ow} clearly affects contaminant uptake from water into lipids (Macdonald et al. 2002). However, we still don't understand how these contaminants are processed in the guts of most marine organisms. For example, rapid debromination of higher brominated congeners to lower, more recalcitrant ones (likely in the gut) tends to give the mistaken impression that the larger compounds are less easy to assimilate than smaller ones (Munschy et al. 2011). In addition, age (size) appears to affect congener balance in Dungeness crabs in BC (Ikonomou et al. 2006), suggesting that further debromination may occur in tissues over time. Without a clear understanding of internal processes in all taxon groups, it is not possible to predict uptake rates of different congener groups from kinetic properties of molecules. We can only measure the ultimate balance of them in tissues and hope to empirically determine internal and external conditions in biota and tissues that mediate this balance.

In addition, studies that selectively examine only a few congeners are unlikely to determine the full bioaccumulation potential of PBDEs. Tissue PBDEs are a mixture of non-degradable congeners

(especially penta 99 and tetra 47—see He et al. 2006) which cannot be excreted, congeners that are more readily metabolized and excreted (low-brominated congeners—Shaw et al. 2009), and congeners that debrominate during trophic transfer. Metabolic degradation of PBDEs in living tissue is expected to be due to oxidation or ether-bond cleavage that does not seem to occur in sediment-bound PBDEs (Keum and Li 2005) and appears to be limited in marine taxa. Some tissue debromination has been found in freshwater and marine fish (Shaw et al. 2009; Munschy et al. 2011; Zeng et al. 2013) and in crabs (Ikonomou et al. 2006), and hepatic debromination of 6%–25% of BDE 209 has been found in marine mammals (McKinney et al. 2011). The absence of BDE 209 in crab hepatopancreas but not muscle in the current study is suggestive of greater or more rapid debromination within the hepatopancreas than the muscle, and highlights the aforementioned problem of comparing contaminant levels in different tissue types for large taxa.

In the current study, it appears that most of the debromination and (or) differential concentration of the highly brominated congener groups occurs with initial uptake of sediment PBDE in the guts of sediment feeders. This process is likely mediated by anaerobic microbes (Gerecke et al. 2005; He et al. 2006; Lee and He 2010). Debromination of BDE 209 in aquatic organisms to congeners not present in the habitat matrix has been demonstrated (La Guardia et al. 2007), and shown to be strongest in primary consumers (Bartrons et al. 2012). In the current study, concentrations of deca-BDE and nona-BDE were very similar between sediments and sediment feeder tissues regardless of the location; however, the relative proportion of these congener groups was markedly lower in sediment feeders than matched sediment samples, in conjunction with a 50- to >200-fold increase in proportion of other congener groups (tetra-, penta-, and hexa-BDEs).

The sediment feeders near municipal wastewater outfalls and in background locations tended to have the same general proportions of all congener groups. However, in the harbour sediment feeders, there were higher proportions of deca-BDE in tissues and an overall similar proportional configuration to sediments. This suggests that uptake of PBDEs may be much more rapid in the harbours than in other habitats because of very high sediment PBDE concentrations; thus, intake may overtake the rate of elimination and debromination. Considering the biodilution evident in the total PBDE uptake in the harbour sediment feeders, it appears that the PBDEs in intensely contaminated harbour sediments mostly pass through the guts of the sediment feeders. Laboratory studies of deca- and nona-BDE uptake and elimination in a marine oligochaete show that these congeners accumulate in tissues initially, then stop accumulating at a much lower concentration than in the sediments after a few weeks, and rapidly decline further during depuration (Tian and Zhu 2011).

The proportional loss of nona- and deca-BDEs relative to sediment occurs in all organisms. This pattern becomes more extreme, along with increasing tetra–hexa congener proportions in crab, some salmon, and seal blubber samples. This could be due to ongoing debromination in the gut at each trophic level, as well as excretion or metabolization of nona- and deca-BDEs.

Deca-BDE is assumed to be poorly absorbed in the gut of marine mammals, but this was not found during a specific food uptake study by Thomas et al. (2005). In addition, once it migrates to blubber it tends to be persistent (Thomas et al. 2005), as found in some seal blubber samples in the present study. Certainly, the seal blubber, crab muscle, and salmon samples had the broadest range of deca-BDE, as well as the most pronounced and variable accumulation of tetra- and penta-BDEs, whereas the crab hepatopancreas samples were consistently lacking in deca-BDE. The high deca-BDE in seal, crab, and salmon group 2 samples (**Fig. 9**) and strong between-species correlations for congener accumulation patterns (**Table 5**) suggests that these higher trophic organisms share common food sources, which are likely benthic. Shaw et al. (2009, 2012) also suggested that the measureable BDE 209 levels in Atlantic seals and fish reflect a strong benthic connection in the food web.

A comparison of sample locations does not suggest that deca-BDE accumulation in the crab, seal, or salmon samples was related to local discharge sources of PBDEs or lipid content of tissue samples. In other words, different samples of crab, salmon, or seal from the same location and sample batch had highly variable deca-BDE proportions. Other studies have shown that tissue BDE 209 concentrations in marine taxa can vary seasonally, with age, sex, and reproduction (Ikonomou et al. 2006; Wolkers et al. 2009; Mongillo et al. 2012), resulting in a broad range in the proportion of BDE 209 between and within faunal types, particularly in the longer-lived higher trophic level taxa (crab, salmon, and seal). In addition, further variability may arise because there is a high probability that BDE 209 preferentially migrates to certain tissue types (Munschy et al. 2011; Shaw et al. 2012), where it may debrominate faster. A kinetic model of combined debromination, methoxylation, ether-bond breakage, excretion and reproductive transfer remains to be formulated for any marine taxon groups.

The large increase of tri- to hexa-BDE proportions and concentrations in sediment feeders relative to sediments is unlikely due simply to lipid concentration over time, as most of these sediment feeders are short-lived (usually annual or biannual) and have very low lipid content (see **Table S3**). The dry weight tetra-BDEs accumulated in whole benthos at a far higher rate than all other congener groups (about 229×), which is about 3× higher than for total PBDEs. A simple summation suggests that potential debromination of all higher congeners can account for this gain in tetra-BDE. This tetra-BDE accumulation, closely followed by penta-BDE, has been described by many researchers for a wide variety of heterotrophs (e.g., Shaw et al. 2009; Hallanger et al. 2011; Bartrons et al. 2012; Frouin et al. 2013), including bacteria (Lee and He 2010).

The extreme proportional increase in tetra-BDEs and decline in penta-BDEs in crab and seal blubber samples relative to the sediment feeders may be related to selective debromination of the penta-BDEs (particularly BDE 99) and hexa-BDEs to tetra-BDE (particularly BDE-47) in the guts of these organisms (Guo et al. 2007; Ikonomou et al. 2011), and relative lack of debromination in tetra-BDEs in higher trophic level taxa. Shaw et al. (2009) indicated that penta-BDE 99 debrominates to tetra BDE 47 in the guts of some fish (Stapleton et al. 2004), or may be preferentially excreted (Isosaari et al. 2005). This tetra/penta debromination dynamic is described for an Arctic food chain by Kelly et al. (2008). These studies support the contention that the tetra-BDEs are a recalcitrant "dead-end" in the metabolic processing of PBDEs in marine organisms.

Conclusions

In this study we examined the influence of physical and geochemical habitat conditions on sediment inventory, tissue PBDE uptake into sediment consumers, and bioaccumulation in other levels of the food chain. Sediment PBDE inventory is dependent on input source, and increases with sediment organic carbon flux and content, and sediment %fines. This reflects the affinity of these contaminants for fine, organic particles in the environment. Whole benthos tissue PBDEs relative to sediment levels were elevated near municipal wastewater outfalls compared with background and harbour samples, suggesting more efficient contaminant uptake from on-going, fresh organic input from the outfalls.

The actual rate of tissue PBDE uptake tapered off with increasing sediment PBDEs and %fines for all sediment feeders, so that, in general, tissue uptake was lower in the finer sediments of the Strait of Georgia than in the Juan de Fuca Strait. Biodilution occurred at extreme sediment PBDE concentrations (>10 000 pg/g dry wt) in urban harbours, suggesting an "over-saturation" effect whereby ingested PBDEs may be passing right through the gut, possibly because they can't be assimilated as fast as consumed.

The dynamics of life-cycle uptake and release of PBDEs in direct sediment feeders remains to be studied. There is clearly a high initial rate of uptake of PBDEs from sediments in spite of low tissue lipid content. This belies the assumption that PBDE uptake is lipid-mediated, at least at the lower trophic

levels. High-lipid reproductive (gamete) output from benthic infauna provides an important, unstudied mechanism of transport from sediments to the water column and, thus, into zooplankton and higher trophic levels that feed in the water column (such as salmon).

Despite considerable accumulation of dry-weight PBDEs in the higher trophic level organisms, the lipid-normalized accumulation in these animals relative to direct sediment feeders was very low (ratio close to 1), suggesting no bioaccumulation. This suggests that PBDEs in predators accumulate as a result of increasing lipid content of these larger animals, rather than biomagnifying. However, more detailed knowledge of the diet of the predators and their relative dependence on a deposit feeder based food chain (bottom-feeding fish, crabs, or infauna) versus a filter-feeder-based food chain (mussels and scallops) could alter this conclusion, as the filter feeders have considerably lower lipid-weight PBDE concentrations than the direct sediment feeders and their predators. Added to this complexity, understanding the PBDE trophic accumulation patterns will continue to be confounded by the difficulty in determining whole-body burdens and the lack of research on temporal accumulation in larger, long-lived organisms.

The most profound change to congener composition occurs at the point of sediment uptake, a pattern also seen in primary consumer zooplankton (Frouin et al. 2013). The dominant nona- and deca-BDEs in sediments decline considerably in importance with initial consumption by sediment feeders, with a concurrent increase in the tetra–hexa congeners, for reasons attributed mainly to debromination in the guts of primary consumers, and secondarily to metabolization in hepatic tissues or selective excretion of the larger molecules. Unusually high rates of consumption relative to the debromination of PBDEs may explain why tissue composition in harbour whole benthos more closely resembled that of sediments than for all other sediment feeders.

Deca-BDEs persist patchily throughout the marine food chain, reflecting variable dependence on sediment versus pelagic food resources, along with long-term storage in certain tissues. Farther up the food chain, the debromination of penta-/hexa-BDEs to tetras continues over time, but obviously more slowly than the initial debromination of the deca- and nona-BDEs. Ultimately, the tetra-BDEs appear to be a metabolic "dead-end" in the breakdown process, showing by far the greatest accumulation throughout the food chain.

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Author contributions

BB and CL conceived and designed the study. BB, CM, MN, and TM performed the experiments/collected the data. BB, MN, and TM analyzed and interpreted the data. CL and PR contributed resources. BB drafted or revised the manuscript.

Competing interests

At the time when she was offered the opportunity to handle the paper the handling editor (Dr. S. Johannessen) acknowledged that she has previously worked and published with Dr. Brenda

Burd. Dr. Johannessen declared that she was nonetheless able to deliver an unbiased handling of the peer review of the paper to inform the eventual editorial decision.

Data availability statement

All relevant data are within the paper and in the Supplementary Material.

Supplementary Material

The following Supplementary Material is available with the article through the journal website at doi:10.1139/facets-2018-0021.

Supplementary Material 1

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