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Joined by geochemistry, divided by history: PCBs and PBDEs in Strait of Georgia sediments

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ABSTRACT

Polychlorinated biphenyls (PCBs) are relict contaminants, while polybrominated diphenyl ethers (PBDEs) are in increasing use. Using sediment cores collected in the Strait of Georgia, we demonstrate that the surface sediment concentration of PCBs is largely determined by environmental processes, such as sediment accumulation and mixing rates, while that of PBDEs is strongly influenced by proximity to source. The Iona Island wastewater outfall appears to be a primary pathway for PBDEs. As well, Vancouver Harbour is highly contaminated with both classes of chemical. BDE-209, the main component of deca-BDE, is the dominant PBDE congener. Environmental debromination is not evident. Currently, the ranges of the surface concentration of PCBs and PBDEs are similar to one another, but that will change in the future, as the concentration of PBDEs continues to rise. The experience with PCBs suggests that if PBDEs were banned today, it would take decades for inorganic sediment to bury them.

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1. Introduction

Polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) are persistent, toxic, bioaccumulative, manufactured chemicals that are widely distributed in the environment, but their histories of use are different (Alaee, 2006; De Wit, 2002; Rapaport and Eisenreich, 1988). Introduced in the 1930s as lubricants and liquid insulators and later used for a wide variety of industrial and household uses, PCBs (estimated total global usage of 1.2 Mt, Macdonald et al., 2000) were banned in stages in the late 1970s and early 1980s as a result of concerns over their effects on the environment and on human health (Fig. 1). Despite their having been banned about 30 years ago, PCBs continue to cycle in marine and terrestrial ecosystems, where they still present health threats, especially to high trophic level, long-lived animals like killer whales (Hickie et al., 2007; Ross et al., 2000).

PBDEs are more recent arrivals, used primarily as flame retardants on household goods, including furniture and electronics. Their production was estimated at 40 kt/yr in 1990 and had grown to about 70 kt/yr by the late 1990s (Wania and Dugani, 2003). PBDEs appeared in the marine environment in the late 1970s and have been increasing in concentration ever since. They have been measured in sediment, water, and marine organisms (for example de Boer et al., 1998; Elliott et al., 2005; Ikonomou et al., 2006; Ross, 2006), where they pose a threat as disrupters of the thyroid hormone system, which controls the development of the central nervous system (Martin et al., 2004). PBDEs have been used in three market formulations: penta, octa and deca. The penta formulation, which contains the lightest congeners, was voluntarily phased out of use in Canada in the early 2000s, and has recently been banned in Canada, the United States and parts of Europe. The octa formulation has not been used locally. However, the heaviest industrial formulation, deca-BDE, remains on the market. PCBs and PBDEs are particle-reactive, especially the heavier PBDE congeners (de Boer et al., 2003), so marine sediments serve as an archive of the fate of these chemicals and as a proxy for their historical discharge to the marine environment.

The Strait of Georgia (Fig. 2), a large inland sea on the west coast of British Columbia, Canada, has a rapidly growing population of ~4 million, almost half of whom live in Greater Vancouver, at the mouth of the Fraser River. The Strait has long been valued for fishing, transportation and recreation, but, like most coastal seas, it has also been used directly and indirectly for discharge of industrial waste, including pulp mill, mining and municipal wastewater effluents. Sediments in the Strait of Georgia record the entry of a wide variety of anthropogenic contaminants, including lead (Macdonald et al., 1991), mercury (Johannessen et al., 2005), chlorinated

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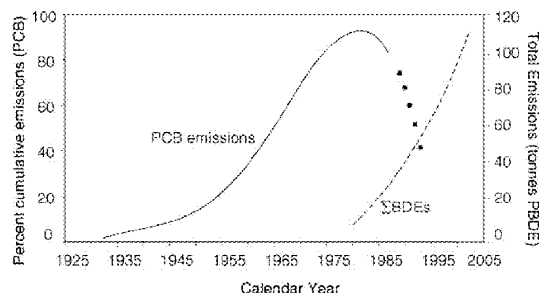E-mail address: johannessen@pac.dfo-mpo.gc.ca (S.C. Johannessen).

Fig. 1. Emission histories of PCBs and PBDEs, modified from Li et al. (2006) (North American PBDE emission trend) and Rapaport and Eisenreich (1988) (% of cumulative emissions of PCBs to Eastern North America). The last five years of the PCB trend (dotted) represent an extrapolation of Rapaport's polynomial fit beyond the date of its publication.

dioxins and furans (PCDD/Fs) and PCB-77 (Macdonald et al., 1992), polynuclear aromatic hydrocarbons (PAHs, Yunker and Macdonald, 2003) and industrial detergents (Shang et al., 1999).

Here, we examine dated sediment cores collected from the Strait of Georgia which have been analyzed for PCB and PBDE congeners. We use these sedimentary records in comparison with other records, including sediment traps and effluent analyses, to infer the controls on the distributions of PCBs and PBDEs in the sediments, to seek evidence for debromination of deca-BDE to lighter, more toxic congeners, and to assess the present role of the Iona Island wastewater outfall, which discharges directly into the Strait, in the delivery of these chemicals to the Strait of Georgia.

2. Methods

2.1. Sediment core collection and dating

Seven sediment cores were collected in 2003 and 2004 from the central and northern Strait of Georgia (Fig. 2), using a Pouliot box corer (20 cm × 30 cm cross section). The cores were all approximately 50 cm long and composed mainly of silty mud. Immediately on recovery, the cores were sectioned for analysis into 1 cm intervals for the top 10 cm, 2 cm intervals for the next 10 cm and 5 cm intervals for the remainder of the core. A sub-sample from each depth interval was analyzed by Flett Research Ltd., Winnipeg, Canada, for ^{210}Pb and ^{226}Ra to be used for radio-dating. ^{210}Pb was measured in all sections of each core (~22 samples/core), following the procedure of Eakins and Morrison (1978), in which the activity of ^{210}Pb is inferred from that of ^{210}Po (counting errors <3%). The activity of supported ^{210}Pb was determined as the average of the ^{226}Ra activity measured at three depths (top, middle, bottom) in each core, from the ingrowths of ^{222}Rn over at least 4 days.

Since the bottom waters of the Strait of Georgia are oxygenated, there is an active benthic community, and the surface sediments are bioturbated. The depth of the surface mixed layer in each core was determined by eye as the inflection point in the depth profile of the natural log of ^{210}Pb (Fig. 3). The sedimentation and mixing rates were determined assuming a constant supply of ^{210}Pb and a constant sedimentation rate (Robbins, 1978), with mixing described by advective–diffusive equations (Lavelle et al., 1986).

2.2. Sediment traps

Moorings with two sediment traps each (attached 20 and 50 m off the bottom) were set out at stations GVRD-A1 and GVRD-B1 (Fig. 2) in October 2003 and retrieved in April 2004. Each trap
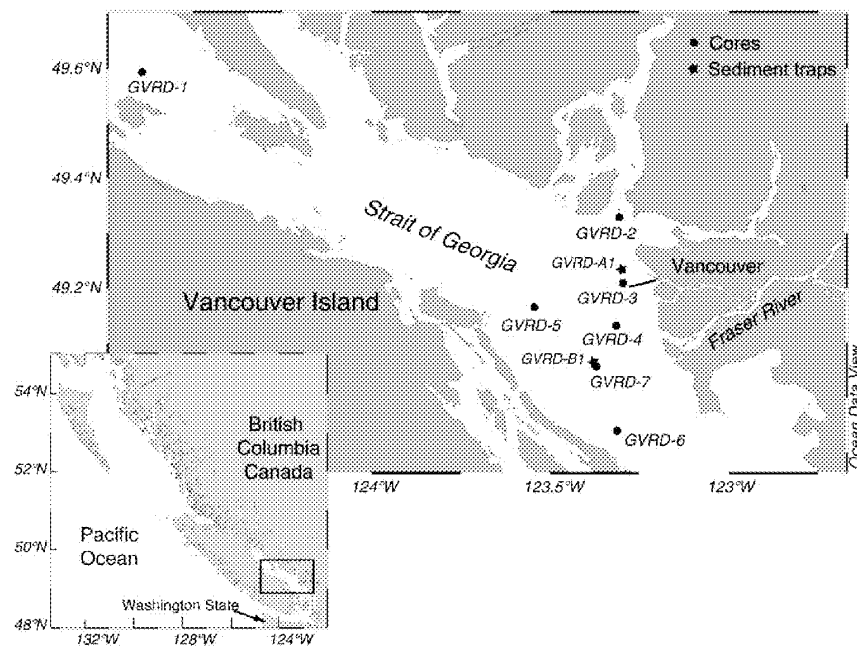

Fig. 2. Sediment core sampling locations (GVRD-1 to GVRD-7) and locations of sediment trap moorings (GVRD-A1, GVRD-B1) in the Strait of Georgia. The black line immediately to the east of station GVRD-3 represents the location of the Iona Island outfall pipe.
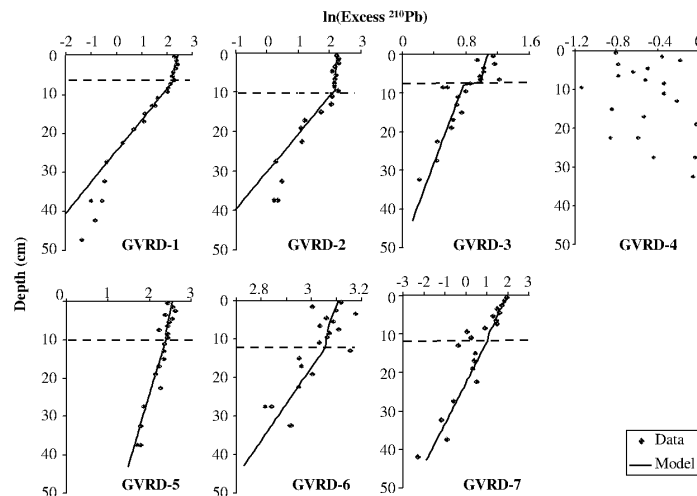
Fig. 3. Profiles of the natural log of the activity of excess ^{210}Pb in the sediment cores. Dots represent data, solid lines, the accumulation and mixing model, and dotted, horizontal lines, the bottom of the surface mixed layer for each core.

collected 10 sequential samples that represented 21 days each. For each trap, we took a sub-sample from each of the 10 sequential vials, homogenized the sub-samples and sent them for analysis of PCBs and PBDES, as described in Section 2.4. The data from the traps were used for comparison of the congener patterns with those measured in the sediment cores.

2.3. Carbon and nitrogen analysis

Carbon and nitrogen were analyzed in the sediment core samples at the University of British Columbia, using the method of Calvert and Pedersen (1995), in which the concentration of organic carbon is calculated as the difference between the concentrations of total and carbonate carbon. Total carbon is measured by combustion and gas chromatography in a CHS analyzer and carbonate carbon by coulometry (precision ±1.6%, 1 standard deviation).

2.4. Analysis of PCBs and PBDEs

A full suite of 209 PCB congeners, with some co-elutions, and 40 PBDE congeners were measured by AXYS Analytical Services Ltd., in Sidney, BC. Both the PCBs and the PBDEs were measured by high resolution gas chromatography/high resolution mass spectroscopy (general precision ±30%; precision of duplicates in a batch ±20% of the mean). The PCB analysis was conducted according to the United States Environmental Protection Agency method EPA 1668A (EPA, 2003a), the PBDE analysis, according to method EPA 1614 (EPA, 2003b).

2.5. Calculation of 10-yr inventories of PCBs and PBDEs in sediment cores

We calculated inventories of PCBs and PBDEs in the sediment cores for comparison with the surface concentration values. Unfortunately, the sedimentation rates at four of the stations (GVRD-3, −4, −5 and −6) were so high that the 50-cm core records were not long enough to capture the entire PCB record, which commenced in ∼1930. Accordingly, we could not calculate a complete inventory for every core and have, instead, compared the inventories over a shorter period. Benthic mixing makes it inappropriate to

assign a discrete date to any particular depth in these cores (see Guinasso and Schink, 1975 for explanation of the age-smearing effect of benthic mixing). We estimated a 10-yr inventory for each core using a core depth that was scaled according to the sedimentation rate (sedimentation velocity at each site (cm/yr) multiplied by 10 years). In general, this method overestimates the inventory of the last 10 years of PCB deposition, since the concentration of that contaminant is decreasing, and the benthic organisms mix older, more highly contaminated material into the surface layer. Conversely, it underestimates the PBDE inventory because of the mixing of older, cleaner sediment into the surface layer. However, it provides a reasonable basis for comparison among the cores, since the biases are in the same direction for all cores.

2.6. Modelling historical deposition of PCBs and PBDEs

Bioturbation of surface sediment modifies the profile shape of a transient contaminant as it passes through this mixed layer (e.g., Guinasso and Schink, 1975). We therefore modelled the historical deposition of PCBs in the cores, using a program developed in Matlab™ (Johannessen et al., 2005) that explicitly accounts for the sedimentation and mixing rates. The method is most robust where there is an abrupt change, however, and there are too many degrees of freedom in the model to describe uniquely a flux that varies gradually, as those of both PCBs and PBDEs have done in most of these cores. However, at station GVRD-3, there was an abrupt change in the PCB concentration flux (as discussed in Section 3), and the model illustrates the effect of the newly-constructed outfall on the concentration of PCBs in the incident surface sediment. We have also used the model fit to some profiles (in Section 3) for a graphic illustration of the main trends with time.

3. Results and discussion

The concentration profiles in the sediments clearly reflect the known histories of PCB and PBDE discharge (Figs. 4 and 5). PCBs appeared in ∼1930, increased rapidly until the late 1960s, and then decreased. PBDEs first entered the local sediments in ∼1978 and have been increasing rapidly ever since. Because of the relatively high sedimentation rates at stations GVRD-3, -4, -5 and -6, the
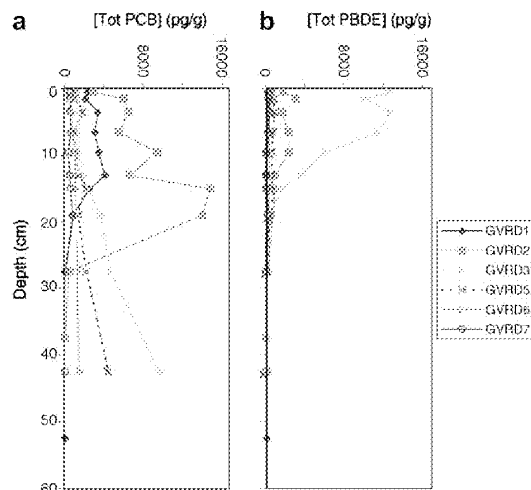
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Fig. 4. Profiles of the concentration of (a) total PCB and (b) total PBDE in all sediment cores.

Table 1
Sedimentation parameters in sediment cores determined using ^{210}Pb and an advective–diffusive mixing model

Core name	Sedimentation velocity (cm yr^{-1})	Sediment accumulation rate (g cm^{-2} yr^{-1})	Surface mixed layer depth (cm)	Mixing rate in upper layer (cm^2 yr^{-1})	Mixing rate in lower layer (cm^2 yr^{-1})
GVRD-1	0.25	0.078	7	3	0.01
GVRD-2	0.35	0.26	10	15	0.01
GVRD-3 (outfall)	1.2	1.3	7	20	0.01
GVRD-4	Unknown (>3)	Unknown (>3)	Unknown	Unknown	Unknown
GVRD-5	1.1	0.64	10	5	0.01
GVRD-6	2.9	2.7	12	30	0.01
GVRD-7	0.30	0.32	12	0.5	0.01

See Fig. 1 for core collection locations. The sediment accumulation rate in core GVRD-3 (outfall) appears to have increased significantly about 15 years ago. The sedimentation and mixing rates for core GVRD-4 could not be determined from the ^{210}Pb data, but the sedimentation rate in that core is clearly higher than in any of the others.

deepest levels in those cores do not predate the entry of PCB into the environment (1930), but the recent PCB decline is reflected in every core. (The sedimentation rate at station GVRD-4, near the mouth of the Fraser River, was so high that we could not determine it with ^{210}Pb in a 50-cm core. Since we were unable to determine the amount of time represented by the core, we only measured contaminants at a few depths. Consequently, core GVRD-4 only appears on plots showing surface concentrations and not depth profiles or fluxes.) In contrast, PBDE profiles imply a pervasive rapid increase toward the sediment surface. Already in some parts of the world, the flux of PBDEs has overtaken that of PCBs. For example, the atmospheric flux of PBDEs to the Baltic Sea is estimated at almost 40 times that of PCBs (Law et al., 2006).

The range of total PCB concentration values in surface sediments (0–1 cm depth, or 1–2 cm in core GVRD-4) is similar to that of total PBDEs (Table 2), but the two classes of chemical do not have the same spatial distribution at the surface (Fig. 6a). The con-

centration of PCBs is highest in the northern Strait (core GVRD-1), where there is no obvious local source, and near the mouth of Vancouver Harbour (GVRD-2). It is low in the central Strait, near the mouth of the Fraser River. In contrast, the concentration of PBDEs near the Iona Island wastewater outfall (GVRD-3, ~12,700 pg/g) dwarfs that measured anywhere else in the Strait (range 270–1800 pg/g). Clearly, the distributions of the two contaminants are determined by different factors.

The 10-yr inventory at each site shows a different pattern than does surface concentration (c.f. Fig. 6a and b), offering a clue to the cause of the distribution observed in the surface concentration plot. Although the northern Strait (core GVRD-1) has the highest surface concentration of PCBs, for example, the 10-yr inventory of PCBs at that station is relatively low (Table 2, Fig. 6). The highest inventories of PCBs are found at stations GVRD-6 and GVRD-3 in the southern Strait, which have the highest sediment accumulation rates of the set. Station GVRD-4, near the mouth of the Fraser River, probably has the very highest inventory, but we were unable to calculate it, because, as mentioned above, the sediment accumulation rate at that site was too high. The spatial pattern in the 10-yr inventory of PBDEs is similar to that of the PCBs (Fig. 6), except that
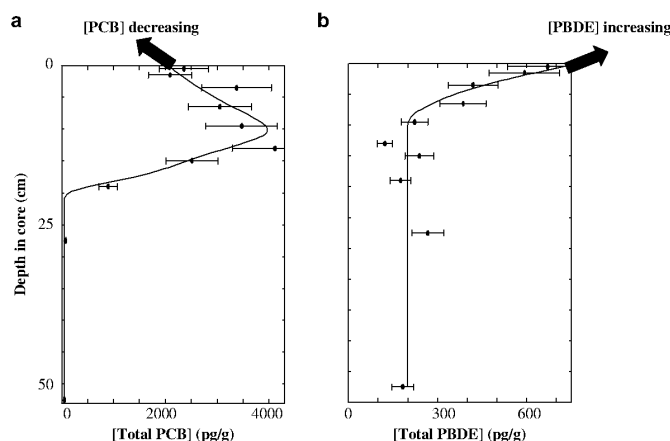

Fig. 5. Profiles of the concentration of (a) total PCB and (b) total PBDE in sediment core GVRD-1. This core was chosen, because its low sediment accumulation rate means that the entire history of PCB contamination is visible in the 50 cm core. All the cores show the same trends, although they do not all represent the same amount of time. (See Table 1 for sediment accumulation rates.) Error bars are ±20%, the measurement uncertainty reported by the analytical laboratory.

Table 2
Concentrations of selected components of surface sediments and 10-yr inventories of total PCBs and total PBDEs

Station	[Total PCB] at surface (pg/g)	[Total PBDE] at surface (pg/g)	10-yr inventory of PCB (pg/cm²)	10-yr Inventory of PBDE (pg/cm²)
GVRD-1	2360	671	1400	400
GVRD-2	2910	1793	11,200	4700
GVRD-3	1210	12,647	18,450	109,600
GVRD-4	484	1105	Unknown	Unknown
GVRD-5	1120	539	8560	5500
GVRD-6	668	728	70,260	18,400
GVRD-7	507	271	1330	840

The inventory does not represent exactly 10 years, because benthic organisms mix the surface sediments. The inventory for each core was calculated by multiplying the sedimentation rate by 10 years and summing the contaminants over the resulting depth. It was not possible to calculate the inventory for station 4, because the sedimentation rate is unknown, and we did not analyze all the depth sections for contaminants.

the inventory of PBDEs is very high at station GVRD-3, near the wastewater outfall. Excluding PBDEs at that station, the inventories of both classes of contaminants are strongly positively related to the sediment accumulation rate (Fig. 7). However, the surface concentration is not. There is no significant correlation between surface concentration of PCBs or PBDEs and sediment accumulation rate (data not shown).

The measured surface concentration of a contaminant is strongly influenced by the local sediment accumulation and mixing rates (e.g., Johannessen et al., 2005). The sediment accumulation rate is much lower in the northern Strait of Georgia than near the mouth of the Fraser River, which supplies about 80% of the sediment to the Strait (Luternauer et al., 1983). We infer that the concentration of PCBs in surface sediment is lower at the southern stations near the mouth of the Fraser River than in the northern Strait, because the inorganic particles discharged near these southern stations tend to dilute the sediment contaminant burden.

Benthic mixing compounds the effect of sedimentation rate on the observed surface concentration of PCBs. In the more recent (shallow) sections of the cores, the PCB concentration decreases toward the sediment surface because the discharge and flux to sediments was at its highest during the 1960s and 1970s. When organisms mix the surface sediments, they tend to move the more contaminated, older sediment up into the less contaminated, post-1970 deposits. In an area like the northern Strait, which has a low sediment accumulation rate, the sediment that is mixed to the surface dates more closely to the PCB maximum and is, therefore, more contaminated than that mixed to the surface in an area with a higher sedimentation rate.

Because the PBDE concentration increases toward the surface, mixing has the opposite effect on its surface value than on that of PCBs. Older sediment mixed up to the surface has a lower concentration of PBDEs than the recent material, so the concentration of PBDEs measured at the surface of the sediments is lower than that in the particles currently accumulating. However, the surface concentration of PBDEs shows no relationship with sediment accumulation rate, even if it is normalized to the mixing rate (data not shown). Because of the recency of their arrival in this environment, PBDEs are still mainly concentrated near their sources. The linear relationship between sediment accumulation rate and the 10-yr inventory of PBDEs shown in Fig. 7 implies an average concentration of PBDEs on particles deposited over the last 10 years that is the same throughout the study area (~660 pg/g, from the slope of the regression line), except at the outfall station.

A study of the concentrations of PCBs and PBDEs in fish from remote European mountain lakes (Gallego et al., 2007) similarly illustrated the importance of both history of emissions and envi-

ronmental distribution processes. Gallego et al. (2007) showed that the concentration gradients of PCBs and PBDEs were directly related to temperature and to one another in the Pyrenees mountains, near long-standing sources of PBDEs, while, in the Tatras mountains, near newer sources of PBDEs, PCBs were still related to temperature, but PBDEs were not. They inferred from these observations that PCBs had had much longer to be redistributed by environmental processes like seasonal temperature cycling. Similarly, Spanish coastal sediments (Eljarrat et al., 2005) show correlations between PCBs and dioxin-like compounds but not PBDEs, except near the mouth of the river, which is likely a current pathway of PBDEs into that environment.

In the Strait of Georgia, the concentrations of PBDEs are highest near the wastewater outfall (GVRD-3, Table 2, Fig. 2). Work in other environments has similarly shown that the highest concentrations of PBDEs in sediment occur near industrial (particularly textile industries) and domestic wastewater discharges (e.g., Gevao et al., 2006; Law et al., 2006; Samara et al., 2006). The concentration of total PBDE measured in the effluent from the Iona Island wastewater treatment plant in 2002–2005 was 61–432 ng/L (Metro Vancouver, Municipal Wastewater Effluent Characterization, Metro Vancouver, Burnaby, BC, in preparation), which is higher than that in local river or sea water (lower Fraser River 0.2–1.8 ng/L in 2004–2006, Environment Canada, 2007, unpublished data; southern Strait of Georgia seawater 0.01–0.02 ng/L, Dangerfield et al., 2007). PBDEs have been measured in high concentration in house dust in Canada and other countries (e.g., Jones-Otazo et al., 2005; Wilford et al., 2005), and their high concentration in wastewater likely reflects the ubiquitous use of flame retardants on household furniture, electronics and toys.

In contrast to PBDEs, PCBs are not actively used in homes or industry in Canada any more, although there is still relict PCB-containing equipment left, such as some transformers (Environment Canada, 2007, http://www.ec.gc.ca/wmd-dgd/default.asp?lang=En&n=13426772-1), and they are still found pervasively in the environment. Accordingly, the sediments near the outfall record PBDEs and PCBs differently. Accounting for sediment accumulation and mixing, the best fit model of PCB deposition (see Section 2) requires a sudden decrease in the concentration of PCBs in the particles falling onto that site in 1989, the year after the deep water outfall was opened (Fig. 8). PCBs, which are ubiquitously associated with organic matter, are discharged with effluent from the outfall. Concentrations of PCBs in effluent are set by the present PCB background in material entering the treatment plant, and their concentration in the local effluent (9.3–17.4 ng/L, Metro Vancouver, in preparation) is lower than that of PBDEs. Accordingly, the increased load of particles from effluent discharged near GVRD-3 appears to have diluted the flux of PCBs while at the same time increasing the load of PBDEs.

The core collected at the entrance to Vancouver Harbour (GVRD-2) also shows significant contamination by PCBs and PBDEs (Fig. 6, Table 2). The concentration of PCBs is higher there than at the outfall station (GVRD-3), while that of PBDEs is lower. There probably is a source of PBDEs bordering the harbour. This sediment core study did not extend into the harbour, but independent measurements show a surface sediment PBDE concentration there similar to that measured near the outfall (Peter Ross, unpublished data, 2007) Since the sediment accumulation rate is much lower inside the harbour (0.19 g cm^{-2} yr^{-1}, Johannessen et al., 2003) than near the Iona Island outfall (1.3 g cm^{-2} yr^{-1}), the flux of PBDEs must be lower there too.

Regardless of the actual fluxes to the sediments, benthic organisms are exposed to contaminants, including PCBs, in proportion to concentration (e.g., Reynoldson, 1987). Consequently, some of the areas of the Strait with the lowest contaminant fluxes may actually

be the major points of contaminant entry into the food chain from the sediments. This would be particularly true of PCBs, which are in high concentration where the flux is low, for example in the northern Strait. The highest flux and concentration of PBDEs currently occur together, although that likely will change in the future, after PBDE use is curtailed, and environmental cycling begins to domi-

nate the transport processes as has occurred with PCBs. Even the highest concentration of PCBs measured in these sediments is well below that given as the Interim Sediment Quality Guideline (maximum 2910 pg/g outside Vancouver Harbour vs. guideline 21,500 pg/g, CCME, 2001), and the PCB concentration will continue to decrease, in the absence of a new source. There are no sediment
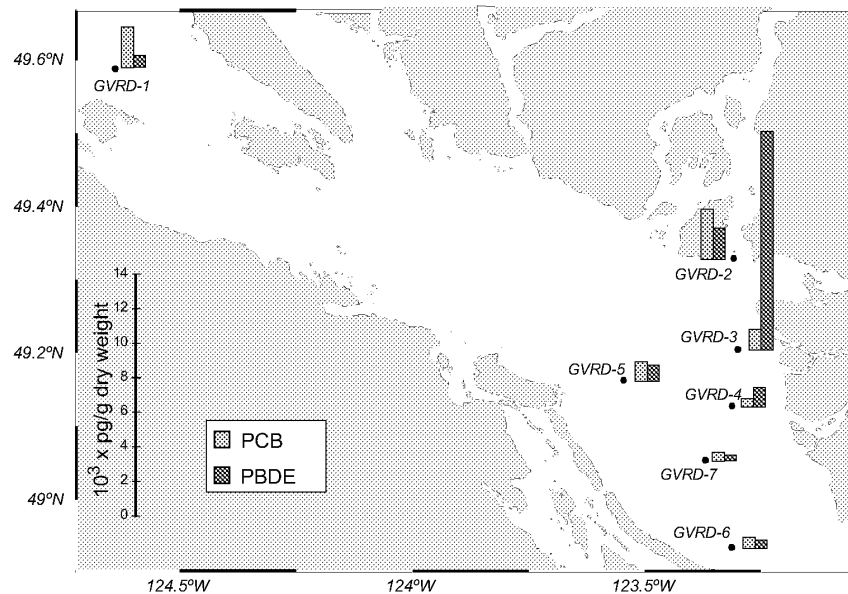
(a) Surface concentration
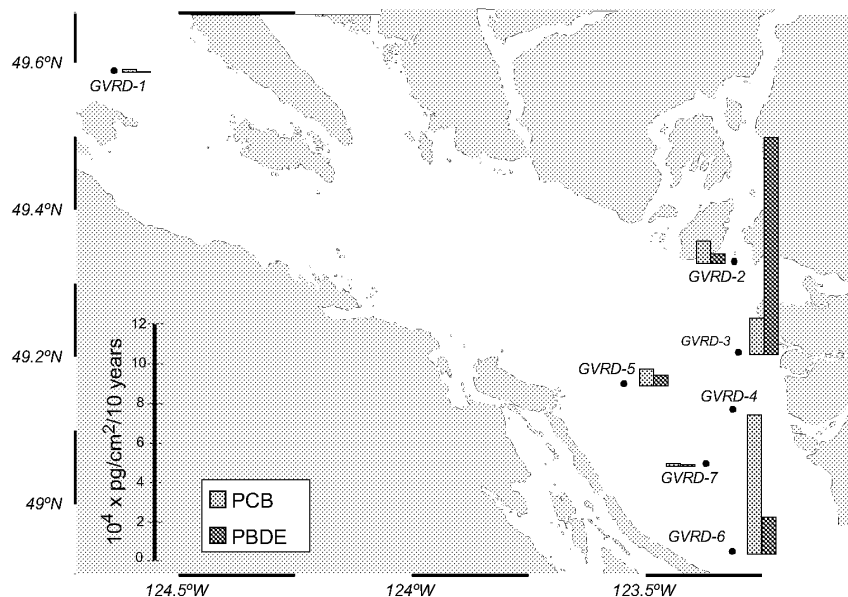
(a) 10-year inventory

Fig. 6. Distribution of total PCBs and total PBDEs in Strait of Georgia sediments: (a) surface concentration, (b) 10-yr inventory, as described in text.
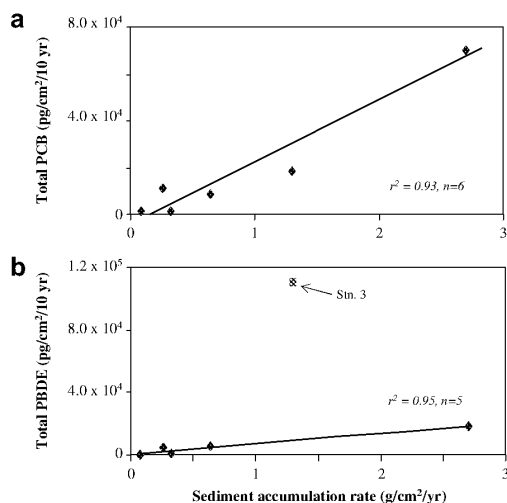
Fig. 7. Relationship between the 10-yr inventories of (a) total PCB and (b) total PBDE vs. sediment accumulation rate. In panel b, the value for station GVRD-3, near the Iona Island wastewater outfall, is not included in the regression.

Fig. 8. Profile of the concentration of total PCB in sediment core GVRD-3, collected near the Iona Island outfall, with the model fit shown as the solid line. The model only fits the data with a sudden decrease in the PCB concentration of the incident particles in 1989. Error bars are ±20%, the measurement uncertainty reported by the analytical laboratory.

quality guidelines for PBDEs, but, for comparison, the concentration of PBDEs in sediment near the Iona Island outfall (12,800 pg/g) is already more than half the PCB guideline level and increasing rapidly.

So far we have only discussed total PCBs and total PBDEs, but each class of chemical is made up of 209 possible congeners. PCBs and PBDEs can be considered in homologue groups, that is, groups of congeners with the same number of chlorine or bromine atoms. The PCB homologues are distributed with a peak in the mid-weight range (Fig. 9a), reflecting the proportions in which the various congeners were used and the number of congeners in each homologue group. This pattern is similar to the distribution found in other environments and organisms (e.g., Ross et al., 2000). The PBDEs, however, while theoretically comprising the same number of congeners per homologue as the PCBs, are dominated by deca-BDE (Fig. 9b). This formulation, composed principally of BDE-209, is the only form still on the market in North America. It has an extremely strong affinity for particles (e.g., Law et al., 2006). The next most highly concentrated congeners measured in this study are BDE-47, 99 and 100. These four congeners are predominant in sediments almost everywhere that PBDEs have been measured (De Wit, 2002; Eljarrat et al., 2005). BDE-47, 99 and 100, (but not BDE-209, probably because it is less easily bioaccumulated) also predominate in the biota (De Wit, 2002). These congeners are usually interpreted to represent a mixture of the deca- and penta- formulations. However, one exception is in the coastal sediments off Kuwait, where high atmospheric temperatures (annual range 10–50 °C over land) cause most of the lighter congeners to remain gaseous, and the sediment pattern is dominated by BDE-183, an indicator of the octa formulation that is in use in that country (Gevao et al., 2006).

There has been increasing interest in the debromination of deca-BDE (mainly BDE-209) to lighter, more toxic forms, in the environment. As de Boer et al. (2003) point out, debromination of even a very small proportion of deca-BDE in the marine environment would result in significant contamination by the more toxic congeners, because of the high flux of deca-BDE. In laboratory experiments, deca-BDE has been shown to debrominate on exposure to ultraviolet radiation (Eriksson et al., 2004) or zero-valent
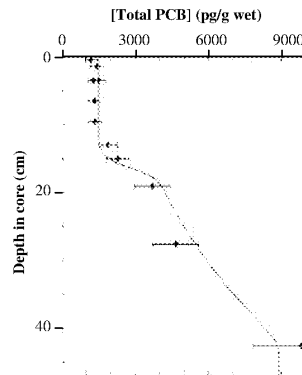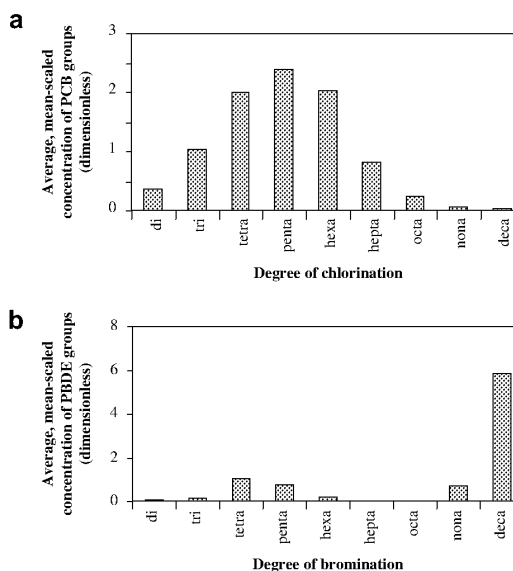

Fig. 9. Homologue distribution in surface sediments averaged over all seven stations. Because the range of concentrations was so wide, each station's values were mean-weighted over all homologues, to preserve the shape of the distribution while giving equal weight to all stations.

iron (Keum and Li, 2005). Debromination is stepwise, one Br substitution at a time, and products include all homologue groups from nona-BDE to mono-BDE. In laboratory conditions the debromination occurs on the time scale of minutes to weeks, depending on the product measured and on the medium in which the deca-BDE is dissolved (Eriksson et al., 2004; Keum and Li, 2005). Environmental rates of debromination and the distribution of products is unknown, so we did not know which homologues to expect to find in this environment as the end products of debromination. Consequently, we considered changes in the ratios of deca-BDE to all homologue groups as possible indicators of debromination.

To compare congener ratios down-core in all the cores, with their different sedimentation rates, we calculated a time scale for each core as the depth of each measurement divided by that core's sedimentation rate. This quotient does not represent exact years before present because of the extensive benthic mixing of the surface sediment, but it does allow a comparison among cores over approximately equivalent time scales. On this common time scale we plotted the ratio of the sum of the five most abundant congeners (BDE-209, -47, -49, -99, -100) to BDE-209 for each sediment core (Fig. 10a). If debromination were occurring in the sediment, we would expect to see an increase in the BDE ratio downcore, as the lighter congeners were formed from the heavy ones. Confounding this prediction, we would expect the same trend as a result of the pattern of use over time, as the commercial deca-formulation has become more dominant. However, Fig. 10 does not show that pattern. An average of the two profiles that extend the furthest back in time shows at best a flat profile. If all the cores were included, the trend would be opposite to that expected for both debromination and changes in usage.

Because we can interpret the sediment cores on a time scale of years to decades, while laboratory results suggest a much shorter half life for deca-BDE, it is possible that the debromination occurs in the environment before the BDEs reach the sediments. We compared the ratios of individual homologues to deca-BDE in effluent from the Iona Island wastewater treatment plant (2002–2005, Metro Vancouver, in preparation) with those in the sediment traps moored nearby (2003–2004; see Section 2) and those in the sediment cores (collected in 2003). (The mono-, hepta- and octa-BDE homologue groups were frequently undetectable in our samples and were excluded from this calculation.) If debromination had occurred between the effluent and the traps or between the traps (in the water column) and the bottom sediment, we would expect to see the homologue ratios increasing from effluent to traps to surface sediment to sediment averaged over the depth range for which BDE-209 was detectable. Such a pattern in not discernable (Fig. 10b), except possibly for the ratio of nona- to deca-BDE. The apparent increase in the nona- to deca-BDE ratio between the effluent and the sediments might indicate debromination that occurs more slowly in the environment than in the laboratory because of the low intensity of light where the wastewater is discharged (80 m water depth) and the absence of strong reducing agents in the water column. However, it is not clear whether the increase is environmentally significant.

The ratio of the sum of PBDEs to BDE 209 in surface sediments is lowest near the wastewater outfall (GVRD-3) and in the remote northern Strait (GVRD-1), showing greater dominance by BDE-209 at those sites. The higher proportion of BDE-209 near the outfall is not surprising, because that congener's affinity for particles makes it likely to drop out preferentially near the source. If all the other sites had proportionately less BDE-209, the distribution could even be evidence of environmental debromination during the movement through the Strait. However, the high proportion of BDE-209 in the northern Strait is puzzling. Possibly BDE-209 is transported on dust and does not sink until it gets packaged, whereas the lighter BDEs are partitioned into larger, organic-rich particles like zooplankton. This would imply that the dust-bound material could travel farther in water than the larger organic particles. A comparison of congener ratios among a larger number of cores might help to resolve this question.

4. Conclusion

PCBs and PBDEs both are persistent, have or have had local and long-range anthropogenic sources, and have entered a geochemically identical sedimentary regime in the Strait of Georgia. Nevertheless, their distribution in the sediments of the Strait of Georgia differs due to the differing stages in their emission histories. From 1930 until the early 1980s, PCBs were loaded into environmental reservoirs where they have been sorted and redistributed by secondary environmental processes, including volatilization and organic carbon cycling. The amounts cycling are gradually reducing as burial, metabolism and degradation occur, but their cycle is presently controlled by exchanges in which loss from one environmental compartment is accompanied by gain in another. The current distribution of PCBs in Strait of Georgia sediments is largely controlled by sediment flux, bio-mixing and organic/inorganic geochemistry. PCB concentration is high where the flux of diluting, inorganic sediment is low; where the depth of benthic mixing is high, bringing older, more highly contaminated sediment to the surface; and where the concentration of organic carbon, for which PCBs have an affinity, is high.

In contrast, PBDEs are relatively new to the system and growing in importance. Their distribution is strongly controlled by current sources and use patterns; in particular, the entry of these chemicals into domestic dust through the use of treated fabric supports the efficient transport of these compounds to the coastal ocean by municipal wastewater systems. At present the range of surface concentration is similar for the two contaminants, but with PCBs decreasing and PBDEs increasing we expect the latter to predominate in the next decade.

The PBDEs are dominated by BDE-209, and environmental debromination in sediments is not evident. There may be a slight increase in the proportion of nona- to deca-BDE between the
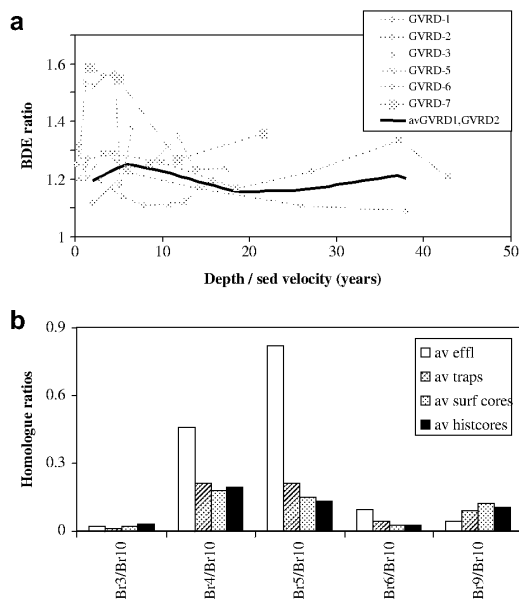
a

b

Fig. 10. (a) Ratio of the sum of the five most abundant congeners (BDE-209, 47, 49, 99, 100) to BDE-209 in sediment cores. The horizontal axis represents a time scale calculated as the measurement depth divided by the sedimentation velocity. This does not represent actual years before present, because of benthic mixing, but it is an approximately common time scale for all stations. The heavy black line represents the average of the BDE ratios measured in the two cores that represent the longest time (GVRD-1 and GVRD-2). On this plot, debromination would appear as an increase in the BDE ratio with increasing depth. It is not evident in these data. (b) Homologue ratios in wastewater treatment plant effluent, sediment trap particulates and sediment cores.

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effluent and the sediment cores, but more data are required to demonstrate that trend conclusively.

PBDE emissions are repeating the experience with PCBs, such that we are now at the same point reached for PCBs in the late 1960s. PBDE discharge continues to increase, and these compounds continue to load into all compartments of the environment. The experience with PCBs suggests that once the discharge of PBDEs stops, there will be a period of readjustment in the sediments that will change the pattern of surface concentration and exposure of the benthos. Eventually, inorganic sediment will bury the PBDEs, but that will take decades after the end of the discharge.

Acknowledgements

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