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

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1 **Abstract**

2 Polychlorinated biphenyls (PCBs) are relict contaminants, while polybrominated
3 diphenyl ethers (PBDEs) are in increasing use. Using sediment cores collected in the
4 Strait of Georgia, we demonstrate that the surface sediment concentration of PCBs is
5 largely determined by environmental processes, such as sediment accumulation and
6 mixing rates, while that of PBDEs is strongly influenced by proximity to source. The
7 Iona Island wastewater outfall appears to be a primary pathway for PBDEs. As well,
8 Vancouver Harbour is highly contaminated with both classes of chemical. BDE-209, the
9 main component of deca-BDE, is the dominant PBDE congener. Environmental
10 debromination is not evident. Currently, the ranges of the surface concentration of PCBs
11 and PBDEs are similar to one another, but that will change in the future, as the
12 concentration of PBDEs continues to rise. The experience with PCBs suggests that if
13 PBDEs were banned today, it would take decades for inorganic sediment to bury them.
14
15
16
17 PCB, PBDE, contamination history, sediment, cores, Strait of Georgia

18 **1. Introduction**

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

30
31 PBDEs are more recent arrivals, used primarily as flame retardants on household goods,
32 including furniture and electronics. Their production was estimated at 40 kt/yr in 1990
33 and had grown to about 70 kt/yr by the late 1990s (Wania and Dugani, 2003). PBDEs
34 appeared in the marine environment in the late 1970s and have been increasing in
35 concentration ever since. They have been measured in sediment, water, and marine
36 organisms (for example de Boer et al., 1998; Elliott et al., 2005; Ikonomidou et al., 2006;
37 Ross, 2006), where they pose a threat as disruptors of the thyroid hormone system, which
38 controls the development of the central nervous system (Martin et al., 2004). PBDEs
39 have been used in three market formulations: penta, octa and deca. The penta
40 formulation, which contains the lightest congeners, was voluntarily phased out of use in

41 Canada in the early 2000s, and has recently been banned in Canada, the United States and
42 parts of Europe. The octa formulation has not been used locally. However, the heaviest
43 industrial formulation, deca-BDE, remains on the market. PCBs and PBDEs are particle-
44 reactive, especially the heavier PBDE congeners (de Boer et al., 2003), so marine
45 sediments serve as an archive of the fate of these chemicals and as a proxy for their
46 historical discharge to the marine environment.

47
48 The Strait of Georgia (Fig. 2), a large inland sea on the west coast of British Columbia,
49 Canada, has a rapidly growing population of ~4 million, almost half of whom live in
50 Greater Vancouver, at the mouth of the Fraser River. The Strait has long been valued for
51 fishing, transportation and recreation, but, like most coastal seas, it has also been used
52 directly and indirectly for discharge of industrial waste, including pulp mill, mining and
53 municipal wastewater effluents. Sediments in the Strait of Georgia record the entry of a
54 wide variety of anthropogenic contaminants, including lead (Macdonald et al., 1991),
55 mercury (Johannessen et al., 2005), chlorinated dioxins and furans (PCDD/Fs) and PCB-
56 77 (Macdonald et al., 1992), polynuclear aromatic hydrocarbons (PAHs, Yunker and
57 Macdonald, 2003) and industrial detergents (Shang et al., 1999).

58
59 Here we examine dated sediment cores collected from the Strait of Georgia which have
60 been analyzed for PCB and PBDE congeners. We use these sedimentary records in
61 comparison with other records, including sediment traps and effluent analyses, to infer
62 the controls on the distributions of PCBs and PBDEs in the sediments, to seek evidence
63 for debromination of deca-BDE to lighter, more toxic congeners, and to assess the present

64 role of the Iona Island wastewater outfall, which discharges directly into the Strait, in the
65 delivery of these chemicals to the Strait of Georgia.

66

67 **2. Methods**

68 *2.1 Sediment core collection and dating*

69 Seven sediment cores were collected in 2003 and 2004 from the central and northern
70 Strait of Georgia (Fig. 2), using a Pouliot box corer (20 cm × 30 cm cross section). The
71 cores were all approximately 50 cm long and composed mainly of silty mud.
72 Immediately on recovery, the cores were sectioned for analysis into 1 cm intervals for the
73 top 10 cm, 2 cm intervals for the next 10 cm and 5 cm intervals for the remainder of the
74 core. A subsample from each depth interval was analyzed by Flett Research Ltd.,
75 Winnipeg, Canada, for ^{210}Pb and ^{226}Ra to be used for radio-dating. ^{210}Pb was measured
76 in all sections of each core (~22 samples / core), following the procedure of Eakins and
77 Morrison (1978), in which the activity of ^{210}Pb is inferred from that of ^{210}Po (counting
78 errors < 3%). The activity of supported ^{210}Pb was determined as the average of the ^{226}Ra
79 activity measured at three depths (top, middle, bottom) in each core, from the ingrowth of
80 ^{222}Rn over at least 4 days.

81

82 Since the bottom waters of the Strait of Georgia are oxygenated, there is an active benthic
83 community, and the surface sediments are bioturbated. The depth of the surface mixed
84 layer in each core was determined by eye as the inflection point in the depth profile of the
85 natural log of ^{210}Pb (Fig. 3). The sedimentation and mixing rates were determined

86 assuming a constant supply of ^{210}Pb and a constant sedimentation rate (Robbins, 1978),
87 with mixing described by advective-diffusive equations (Lavelle et al., 1986).

88

89 *2.2 Sediment traps*

90 Moorings with two sediment traps each (attached 20 and 50 m off the bottom) were set
91 out at stations GVRD-A1 and GVRD-B1 (Fig. 2) in October 2003 and retrieved in April
92 2004. Each trap collected 10 sequential samples that represented 21 days each. For each
93 trap, we took a subsample from each of the 10 sequential vials, homogenized the
94 subsamples and sent them for analysis of PCBs and PBDES, as described in section 2.4.
95 The data from the traps were used for comparison of the congener patterns with those
96 measured in the sediment cores.

97

98 *2.3 Carbon and nitrogen analysis*

99 Carbon and nitrogen were analysed in the sediment core samples at the University of
100 British Columbia, using the method of Calvert et al. (1995), in which the concentration of
101 organic carbon is calculated as the difference between the concentrations of total and
102 carbonate carbon. Total carbon is measured by combustion and gas chromatography in a
103 CHS analyzer and carbonate carbon by coulometry (precision $\pm 1.6\%$, 1 standard
104 deviation).

105

106 *2.4 Analysis of PCBs and PBDEs*

107 A full suite of 209 PCB congeners, with some co-elutions, and 40 PBDE congeners were
108 measured by AXYS Analytical Services Ltd, in Sidney, B.C.. Both the PCBs and the

109 PBDEs were measured by high resolution gas chromatography / high resolution mass
110 spectroscopy (general precision $\pm 30\%$; precision of duplicates in a batch $\pm 20\%$ of the
111 mean). The PCB analysis was conducted according to the United States Environmental
112 Protection Agency method EPA 1668A (EPA, 2003a), the PBDE analysis, according to
113 method EPA 1614 (EPA, 2003b).

114

115 *2.5 Calculation of 10-year inventories of PCBs and PBDEs in sediment cores*

116 We calculated inventories of PCBs and PBDEs in the sediment cores for comparison with
117 the surface concentration values. Unfortunately, the sedimentation rates at four of the
118 stations (GVRD-3, -4, -5 and -6) were so high that the 50-cm core records were not long
119 enough to capture the entire PCB record, which commenced in ~1930. Accordingly, we
120 could not calculate a complete inventory for every core and have, instead, compared the
121 inventories over a shorter period. Benthic mixing makes it inappropriate to assign a
122 discrete date to any particular depth in these cores (See Guinasso and Schink, 1975 for
123 explanation of the age-smearing effect of benthic mixing). We estimated a 10-year
124 inventory for each core using a core depth that was scaled according to the sedimentation
125 rate (sedimentation velocity at each site (cm/yr) multiplied by 10 years). In general, this
126 method overestimates the inventory of the last 10 years of PCB deposition, since the
127 concentration of that contaminant is decreasing, and the benthic organisms mix older,
128 more highly contaminated material into the surface layer. Conversely, it underestimates
129 the PBDE inventory because of the mixing of older, cleaner sediment into the surface
130 layer. However, it provides a reasonable basis for comparison among the cores, since the
131 biases are in the same direction for all cores.

132

133 *2.6 Modelling historical deposition of PCBs and PBDEs*

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

146

147

148 **3. Results and discussion**

149 The concentration profiles in the sediments clearly reflect the known histories of PCB
150 and PBDE discharge (Figs. 4 and 5). PCBs appeared in ~ 1930, increased rapidly until
151 the late 1960s, and then decreased. PBDEs first entered the local sediments in ~1978 and
152 have been increasing rapidly ever since. Because of the relatively high sedimentation
153 rates at stations GVRD-3, -4, -5 and -6, the deepest levels in those cores do not predate
154 the entry of PCB into the environment (1930), but the recent PCB decline is reflected in

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

164

165 The range of Total PCB concentration values in surface sediments (0 - 1 cm depth, or 1 -
166 2 cm in core GVRD-4) is similar to that of Total PBDEs (Table 2), but the two classes of
167 chemical do not have the same spatial distribution at the surface (Fig. 6a). The
168 concentration of PCBs is highest in the northern Strait (core GVRD-1), where there is no
169 obvious local source, and near the mouth of Vancouver Harbour (GVRD- 2). It is low in
170 the central Strait, near the mouth of the Fraser River. In contrast, the concentration of
171 PBDEs near the Iona Island wastewater outfall (GVRD-3, ~12,700 pg/g) dwarfs that
172 measured anywhere else in the Strait (range 270-1800 pg/g). Clearly, the distributions of
173 the two contaminants are determined by different factors.

174

175 The 10-year inventory at each site shows a different pattern than does surface
176 concentration (c.f. Figs. 6a and 6b), offering a clue to the cause of the distribution
177 observed in the surface concentration plot. Although the northern Strait (core GVRD-1)

178 has the highest surface concentration of PCBs, for example, the 10-year inventory of
179 PCBs at that station is relatively low (Table 2, Fig. 6). The highest inventories of PCBs
180 are found at stations GVRD-6 and GVRD-3 in the southern Strait, which have the highest
181 sediment accumulation rates of the set. Station GVRD-4, near the mouth of the Fraser
182 River, probably has the very highest inventory, but we were unable to calculate it,
183 because, as mentioned above, the sediment accumulation rate at that site was too high.
184 The spatial pattern in the 10-year inventory of PBDEs is similar to that of the PCBs (Fig.
185 6), except that the inventory of PBDEs is very high at station GVRD-3, near the
186 wastewater outfall. Excluding PBDEs at that station, the inventories of both classes of
187 contaminants are strongly positively related to the sediment accumulation rate (Fig. 7).
188 However, the surface concentration is not. There is no significant correlation between
189 surface concentration of PCBs or PBDEs and sediment accumulation rate (data not
190 shown).

191

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

200

201 Benthic mixing compounds the effect of sedimentation rate on the observed surface
202 concentration of PCBs. In the more recent (shallow) sections of the cores, the PCB
203 concentration decreases toward the sediment surface because the discharge and flux to
204 sediments was at its highest during the 1960s and 70s. When organisms mix the surface
205 sediments, they tend to move the more contaminated, older sediment up into the less
206 contaminated, post-1970 deposits. In an area like the northern Strait, which has a low
207 sediment accumulation rate, the sediment that is mixed to the surface dates more closely
208 to the PCB maximum and is, therefore, more contaminated than that mixed to the surface
209 in an area with a higher sedimentation rate.

210

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

223

224 A study of the concentrations of PCBs and PBDEs in fish from remote European
225 mountain lakes (Gallego et al., 2007) similarly illustrated the importance of both history
226 of emissions and environmental distribution processes. Gallego et al. (2007) showed that
227 the concentration gradients of PCBs and PBDEs were directly related to temperature and
228 to one another in the Pyrenees mountains, near long-standing sources of PBDEs, while, in
229 the Tatra mountains, near newer sources of PBDEs, PCBs were still related to
230 temperature, but PBDEs were not. They inferred from these observations that PCBs had
231 had much longer to be redistributed by environmental processes like seasonal temperature
232 cycling. Similarly, Spanish coastal sediments (Eljarrat et al., 2005) show correlations
233 between PCBs and dioxin-like compounds but not PBDEs, except near the mouth of the
234 river, which is likely a current pathway of PBDEs into that environment.

235

236 In the Strait of Georgia, the concentrations of PBDEs are highest near the wastewater
237 outfall (GVRD-3, Table 2, Fig. 2). Work in other environments has similarly shown that
238 the highest concentrations of PBDEs in sediment occur near industrial (particularly textile
239 industries) and domestic wastewater discharges (e.g. Gevaio et al., 2006; Law et al., 2006;
240 Samara et al., 2006). The concentration of total PBDE measured in the effluent from the
241 Iona Island wastewater treatment plant in 2002-2005 was 61 - 432 ng/L (Metro
242 Vancouver. Municipal Wastewater Effluent Characterization. Metro Vancouver,
243 Burnaby, B. C., in prep.), which is higher than that in local river or sea water (lower
244 Fraser River 0.2 – 1.8 ng/L in 2004-2006, Environment Canada, 2007, unpublished data,
245 southern Strait of Georgia seawater 0.01 – 0.02 ng/L Dangerfield et al., 2007). PBDEs
246 have been measured in high concentration in house dust in Canada and other countries

247 (e.g. Jones-Otazo et al., 2005; Wilford et al., 2005), and their high concentration in
248 wastewater likely reflects the ubiquitous use of flame retardants on household furniture,
249 electronics and toys.

250

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

266

267 The core collected at the entrance to Vancouver Harbour (GVRD-2) also shows
268 significant contamination by PCBs and PBDEs (Fig. 6, Table 2). The concentration of
269 PCBs is higher there than at the outfall station (GVRD-3), while that of PBDEs is lower.

270 There probably is a source of PBDEs bordering the harbour. This sediment core study
271 did not extend into the harbour, but independent measurements show a surface sediment
272 PBDE concentration there similar to that measured near the outfall (Peter Ross,
273 unpublished data, 2007.) Since the sediment accumulation rate is much lower inside the
274 harbour ($0.19 \text{ g cm}^{-2} \text{ yr}^{-1}$, Johannessen et al., 2003) than near the Iona Island outfall (1.3
275 $\text{g cm}^{-2} \text{ yr}^{-1}$), the flux of PBDEs must be lower there too.

276
277 Regardless of the actual fluxes to the sediments, benthic organisms are exposed to
278 contaminants, including PCBs, in proportion to concentration (e.g. Reynoldson, 1987).
279 Consequently, some of the areas of the Strait with the lowest contaminant fluxes may
280 actually be the major points of contaminant entry into the food chain from the sediments.
281 This would be particularly true of PCBs, which are in high concentration where the flux
282 is low, for example in the northern Strait. The highest flux and concentration of PBDEs
283 currently occur together, although that likely will change in the future, after PBDE use is
284 curtailed, and environmental cycling begins to dominate the transport processes as has
285 occurred with PCBs. Even the highest concentration of PCBs measured in these
286 sediments is well below that given as the Interim Sediment Quality Guideline (maximum
287 2910 pg/g outside Vancouver Harbour vs. guideline $21,500 \text{ pg/g}$, CCME, 2001), and the
288 PCB concentration will continue to decrease, in the absence of a new source. There are
289 no sediment quality guidelines for PBDEs, but, for comparison, the concentration of
290 PBDEs in sediment near the Iona Island outfall ($12,800 \text{ pg/g}$) is already more than half
291 the PCB guideline level and increasing rapidly.

292

293 So far we have only discussed Total PCBs and Total PBDEs, but each class of chemical
294 is made up of 209 possible congeners. PCBs and PBDEs can be considered in
295 homologue groups, that is, groups of congeners with the same number of chlorine or
296 bromine atoms. The PCB homologues are distributed with a peak in the mid-weight
297 range (Fig. 9a), reflecting the proportions in which the various congeners were used and
298 the number of congeners in each homologue group. This pattern is similar to the
299 distribution found in other environments and organisms (e.g. Ross et al., 2000). The
300 PBDEs, however, while theoretically comprising the same number of congeners per
301 homologue as the PCBs, are dominated by deca-BDE (Fig. 9b). This formulation,
302 composed principally of BDE-209, is the only form still on the market in North America.
303 It has an extremely strong affinity for particles (e.g. Law et al., 2006). The next most
304 highly concentrated congeners measured in this study are BDE-47, 99 and 100. These
305 four congeners are predominant in sediments almost everywhere that PBDEs have been
306 measured (De Wit, 2002; Eljarrat et al., 2005). BDE-47, 99 and 100, (but not BDE-209,
307 probably because it is less easily bioaccumulated) also predominate in the biota (De Wit,
308 2002). These congeners are usually interpreted to represent a mixture of the deca- and
309 penta- formulations. However, one exception is in the coastal sediments off Kuwait,
310 where high atmospheric temperatures (annual range 10-50°C over land) cause most of the
311 lighter congeners to remain gaseous, and the sediment pattern is dominated by BDE-183,
312 an indicator of the octa formulation that is in use in that country (Gevao et al., 2006.)
313
314 There has been increasing interest in the debromination of deca-BDE (mainly BDE-209)
315 to lighter, more toxic forms, in the environment. As de Boer et al. (2003) point out,

316 debromination of even a very small proportion of deca-BDE in the marine environment
317 would result in significant contamination by the more toxic congeners, because of the
318 high flux of deca-BDE. In laboratory experiments, deca-BDE has been shown to
319 debrominate on exposure to ultraviolet radiation (Eriksson et al., 2004) or zerovalent iron
320 (Keum and Li, 2005). Debromination is stepwise, one Br substitution at a time, and
321 products include all homologue groups from nona-BDE to mono-BDE. In laboratory
322 conditions the debromination occurs on the time scale of minutes to weeks, depending on
323 the product measured and on the medium in which the deca-BDE is dissolved (Eriksson
324 et al., 2004; Keum and Li, 2005). Environmental rates of debromination and the
325 distribution of products is unknown, so we did not know which homologues to expect to
326 find in this environment as the end products of debromination. Consequently, we
327 considered changes in the ratios of deca-BDE to all homologue groups as possible
328 indicators of debromination.

329

330 To compare congener ratios down-core in all the cores, with their different sedimentation
331 rates, we calculated a time scale for each core as the depth of each measurement divided
332 by that core's sedimentation rate. This quotient does not represent exact years before
333 present because of the extensive benthic mixing of the surface sediment, but it does allow
334 a comparison among cores over approximately equivalent time scales. On this common
335 time scale we plotted the ratio of the sum of the five most abundant congeners (BDE-209,
336 -47, -49, -99, -100) to BDE-209 for each sediment core (Fig. 10a). If debromination were
337 occurring in the sediment, we would expect to see an increase in the BDE ratio downcore,
338 as the lighter congeners were formed from the heavy ones. Confounding this prediction,

339 we would expect the same trend as a result of the pattern of use over time, as the
340 commercial deca formulation has become more dominant. However, Fig. 10 does not
341 show that pattern. An average of the two profiles that extend the furthest back in time
342 shows at best a flat profile. If all the cores were included, the trend would be opposite to
343 that expected for both debromination and changes in usage.

344

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

361 reducing agents in the water column. However, it is not clear whether the increase is
362 environmentally significant.

363

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

376

377

378 **4. Conclusion**

379 PCBs and PBDEs both are persistent, have or have had local and long-range
380 anthropogenic sources, and have entered a geochemically identical sedimentary regime in
381 the Strait of Georgia. Nevertheless, their distribution in the sediments of the Strait of
382 Georgia differs due to the differing stages in their emission histories. From 1930 until the
383 early 1980s, PCBs were loaded into environmental reservoirs where they have been

384 sorted and redistributed by secondary environmental processes, including volatilization
385 and organic carbon cycling. The amounts cycling are gradually reducing as burial,
386 metabolism and degradation occur, but their cycle is presently controlled by exchanges in
387 which loss from one environmental compartment is accompanied by gain in another. The
388 current distribution of PCBs in Strait of Georgia sediments is largely controlled by
389 sediment flux, bio-mixing and organic/inorganic geochemistry. PCB concentration is
390 high where the flux of diluting, inorganic sediment is low; where the depth of benthic
391 mixing is high, bringing older, more highly contaminated sediment to the surface; and
392 where the concentration of organic carbon, for which PCBs have an affinity, is high.

393

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

401

402 The PBDEs are dominated by BDE-209, and environmental debromination in sediments
403 is not evident. There may be a slight increase in the proportion of nona- to deca-BDE
404 between the effluent and the sediment cores, but more data are required to demonstrate
405 that trend conclusively.

406

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

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418 Flett Research Ltd., in Winnipeg, Canada measured radioisotopes in the sediment cores,
419 which allowed us to calculate the sedimentation and mixing rates. AXYS Analytical Ltd.
420 in Sidney, Canada measured PCBs and PBDEs in the core and trap samples. Dr. Susan
421 Roe of Environment Canada sent and explained the Sediment Quality Guidelines for
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425 Basin Action Plan, and by Fisheries and Oceans Canada.

426 **References**

- 427 Alaei, M. (2006). Recent progress in understanding of the levels, trends, fate and effects
428 of BFRs in the environment. *Chemosphere*, 64,
- 429 Calvert, S.E. and Pedersen, T.F. (1995). On the organic carbon maximum on the
430 continental slope of the eastern Arabian Sea. *Journal of Marine Research*, 53, 269-
431 296.
- 432 CCME (2001). Canadian sediment quality guidelines for the protection of aquatic life:
433 Polychlorinated biphenyls (PCBs). Updated. In *Canadian Environmental Quality*
434 *Guidelines*, 1999, Canadian Council of Ministers of the Environment, Winnipeg.
- 435 Dangerfield, N., Macdonald, R.W., Crewe, N., Shaw, P. and Ross, P.S., 2007. PCBs and
436 PBDEs in the Georgia Basin water column, Georgia Basin Puget Sound Research
437 Conference, Vancouver, Canada, March 26 - 29, 2007.
- 438 de Boer, J., Wester, P.G., Klamer, H.J.C., Lewis, W.E. and Boon, J.P. (1998). Do flame
439 retardants threaten ocean life? *Nature*, 394, 28-29.
- 440 de Boer, J., Wester, P.G., van der Horst, A. and Leonards, P.E.G. (2003). Polybrominated
441 diphenyl ethers in influents, suspended particulate matter, sediments, sewage
442 treatment plant and effluents and biota from the Netherlands. *Environmental*
443 *Pollution*, 122, 63-74.
- 444 De Wit, C.A. (2002). An overview of brominated flame retardants in the environment.
445 *Chemosphere*, 46, 583-624.
- 446 Eakins, J.D. and Morrison, R.T. (1978). A new procedure for the determination of lead-
447 210 in lake and marine sediments. *International Journal of Applied Radiation and*
448 *Isotopes*, 29, 531-536.

- 449 Eljarrat, E., de la Cal, A., Larrazabal, D., Fabrellas, B., Fernandez-Alba, A.R., Borrull,
450 F., Marce, R.M. and Barcelo, D. (2005). Occurrence of polybrominated
451 diphenylethers, polychlorinated dibenzo-p-dioxins, dibenzofurans and biphenyls
452 in coastal sediments from Spain. *Environmental Pollution*, 136, 493-501.
- 453 Elliott, J.E., Wilson, L.K. and Wakeford, B. (2005). Polybrominated diphenyl ether
454 trends in eggs of marine and freshwater birds from British Columbia, Canada,
455 1979-2002. *Environmental Science and Technology*, 39, 5584-5591.
- 456 EPA (2003a). EPA Method 1668, Revision A - Chlorinated biphenyl congeners in water,
457 soil, sediment, biosolids, and tissue by HRGC/HRMS, with changes and
458 corrections through to August 20, 2003.
- 459 EPA (2003b). EPA Method 1614. Brominated diphenyl ethers in water, soil, sediment,
460 and tissue by HRGC/HRMS. Draft August, 2003.
- 461 Eriksson, J., Green, N., Marsh, G. and Bergman, Å. (2004). Photochemical
462 decomposition of 15 polybrominated diphenyl ether congeners in methanol /
463 water. *Environmental Science and Technology*, 38, 3119-3125.
- 464 Gallego, E., Grimalt, J.O., Bartrons, M., Lopez, J.F., Camarero, L., Catalan, J., Stuchlik,
465 E. and Battarbee, R. (2007). Altitudinal gradients of PBDEs and PCBs in fish
466 from European high mountain lakes. *Environmental Science and Technology*, 41,
467 2196-2202.
- 468 Gevao, B., Beg, M.U., Al-Ghadban, A.N., Al-Omair, A., Helaleh, M. and Zafar, J.
469 (2006). Spatial distribution of polybrominated diphenyl ethers in coastal marine
470 sediments receiving industrial and municipal effluents in Kuwait. *Chemosphere*,
471 62, 1078-1086.

- 472 Guinasso, N.L. and Schink, D.R. (1975). Quantitative estimates of biological mixing
473 rates in abyssal sediments. *Journal of Geophysical Research*, 80, 3032-3043.
- 474 Hickie, B.E., Ross, P.S., Macdonald, R.W. and Ford, J.K.B. (2007). Killer whales
475 (*Orcinus orca*) face protracted health risks associated with lifetime exposure to
476 PCBs. *Environmental Science and Technology*, in press,
- 477 Ikonomou, M.G., Fernandez, M.P. and Hickman, Z.L. (2006). Spatio-temporal and
478 species-specific variation in PBDE levels / patterns in British Columbia's coastal
479 waters. *Environmental Pollution*, 140, 355-363.
- 480 Johannessen, S.C., Macdonald, R.W. and Eek, M.K. (2005). Historical trends in mercury
481 sedimentation and mixing in the Strait of Georgia, Canada. *Environmental*
482 *Science and Technology*, 39, 4361-4368.
- 483 Johannessen, S.C., Macdonald, R.W. and Paton, D.W. (2003). A sediment and organic
484 carbon budget for the greater Strait of Georgia. *Estuarine, Coastal and Shelf*
485 *Science*, 56, 845-860.
- 486 Jones-Otazo, H.A., Clarke, J.P., Diamond, M.L., Archbold, J.A., Ferguson, G., Harner,
487 T., Richardson, G.M., Ryan, J.J. and Wilford, B.H. (2005). Is house dust the
488 missing exposure pathway for PBDEs? An analysis of the urban fate and Human
489 Exposure to PBDEs. *Environmental Science and Technology*, 39, 5121-5130.
- 490 Keum, Y.-S. and Li, Q.X. (2005). Reductive debromination of polybrominated diphenyl
491 ethers by zerovalent iron. *Environmental Science and Technology*, 39, 2280-2286.
- 492 Lavelle, J.W., Massoth, G.J. and Crecelius, E.A. (1986). Accumulation rates of recent
493 sediments in Puget Sound, Washington. *Marine Geology*, 72, 59-70.

- 494 Law, R.J., Allchin, C.R., de Boer, J., Covaci, A., Herzke, D., Lepom, P., Morris, S.,
495 Tronczynski, J. and de Wit, C.A. (2006). Levels and trends of brominated flame
496 retardants in the European environment. *Chemosphere*, 64, 187-208.
- 497 Li, A., Rockne, K.J., Sturchio, N., Song, W., Ford, J.C., Buckley, D.R. and Mills, W.J.
498 (2006). Polybrominated diphenyl ethers in the sediments of the Great Lakes. 4.
499 Influencing factors, trends, and implications. *Environmental Science and*
500 *Technology*, 40, 7528-7534.
- 501 Luternauer, J.L., Clague, J.J. and Pharo, C.H. (1983). Substrates of the Strait of Georgia,
502 British Columbia. *Canadian Journal of Fisheries and Aquatic Sciences*, 40, 1026-
503 1032.
- 504 Macdonald, R.W., Barrie, L.A., Bidleman, T.F., Diamond, M.L., Gregor, D.J., Semkin,
505 R.G., Strachan, W.M.J., Li, Y.F., Wania, F., Alae, M., Alexeeva, L.B., Backus,
506 S.M., Bailey, R., Bowers, J.M., Gobeil, C., Halsall, C.J., Harner, T., Hoff, J.T.,
507 Jantunen, L.M.M., Lockhart, W.L., Mackay, D., Muir, D.C.G., Pudykiewicz, J.,
508 Reimer, K.J., Smith, J.N., Stern, G.A., Schroeder, W.H., Wagemann, R. and
509 Yunker, M.B. (2000). Contaminants in the Canadian Arctic: 5 years of progress
510 in understanding sources occurrence and pathways. *The Science of the Total*
511 *Environment*, 254, 93-234.
- 512 Macdonald, R.W., Cretney, W.J., Crewe, N. and Paton, D. (1992). A history of
513 octachlordibenzo-p-dioxin, 2,3,7,8-tetrachlorodibenzofuran, and 3,3',4,4'-
514 tetrachlorobiphenyl contamination in Howe Sound, British Columbia.
515 *Environmental Science and Technology*, 26, 1544-550.

- 516 Macdonald, R.W., Macdonald, D.M., O'Brien, M.O. and Gobeil, C. (1991).
517 Accumulation of heavy metals (Pb, Zn, Cu, Cd), carbon and nitrogen in sediments
518 from Strait of Georgia, B.C., Canada. *Marine Chemistry*, 34, 109-135.
- 519 Martin, M., Lam, P.K.S. and Richardson, B.J. (2004). An Asian quandary: where have all
520 of the PBDEs gone? *Marine Pollution Bulletin*, 49, 375-382.
- 521 Rapaport, R.A. and Eisenreich, S.J. (1988). Historical atmospheric inputs of high
522 molecular weight chlorinated hydrocarbons to eastern North America.
523 *Environmental Science and Technology*, 22, 931-941.
- 524 Reynoldson, T.B. (1987). Interactions between sediment contaminants and benthic
525 organisms. *Hydrobiologia*, 149, 53-66.
- 526 Robbins, J.A. (1978). Geochemical and geophysical applications of radioactive lead.
527 Nriagu (Eds.). *The Biogeochemistry of Lead in the Environment*. Elsevier /
528 North-Holland Biomedical Press, 285-393 pp.
- 529 Ross, P.S. (2006). Fireproof killer whales (*Orcinus orca*): flame-retardant chemicals and
530 the conservation imperative in the charismatic icon of British Columbia, Canada.
531 *Canadian Journal of Fisheries and Aquatic Science*, 63, 224-234.
- 532 Ross, P.S., Ellis, G.M., Ikonomou, M.G., Barrett-Lennard, L.G. and Addison, R.F.
533 (2000). High PCB concentrations in free-ranging Pacific killer whales, *Orcinus*
534 *orca*: Effects of age, sex and dietary preference. *Marine Pollution Bulletin*, 40,
535 505-515.
- 536 Samara, F., Tsai, C.W. and Aga, D.S. (2006). Determination of potential sources of PCBs
537 and PBDEs in sediments of the Niagara River. *Environmental Pollution*, 139,
538 489-497.

- 539 Shang, D.Y., Macdonald, R.W. and Ikonomou, M.G. (1999). Persistence of nonylphenol
540 ethoxylate surfactants and their primary degradation products in sediments from
541 near a municipal outfall in the Strait of Georgia, British Columbia, Canada.
542 Environmental Science and Technology, 33, 1366-1372.
- 543 Wania, F. and Dugani, C.B. (2003). Assessing the long-range transport potential of
544 polybrominated diphenyl ethers: A comparison of four multimedia models.
545 Environmental Toxicology and Chemistry, 22, 1252-1261.
- 546 Wilford, B.H., Shoeib, M., Harner, T., Zhu, J. and Jones, K.C. (2005). Polybrominated
547 diphenyl ethers in indoor dust in Ottawa, Canada: implications for sources and
548 exposure. Environmental Science and Technology, 39, 7027-7035.
- 549 Yunker, M.B. and Macdonald, R.W. (2003). Alkane and PAH depositional history,
550 sources and fluxes in sediments from the Fraser River Basin and Strait of Georgia.
551 Environmental Toxicology and Chemistry, 34, 1429-1454.

552

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

553

554 **Table 1.** Sedimentation parameters in sediment cores determined using Pb-210 and an
555 advective-diffusive mixing model. See Fig. 1 for core collection locations. The sediment
556 accumulation rate in core GVRD-3 appears to have increased significantly about 15 years
557 ago. The sedimentation and mixing rates for core GVRD-4 could not be determined from
558 the Pb-210 data, but the sedimentation rate in that core is clearly higher than in any of the
559 others.

560

561

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	11200	4700
GVRD-3	1210	12647	18450	109600
GVRD-4	484	1105	unknown	unknown
GVRD-5	1120	539	8560	5500
GVRD-6	668	728	70260	18400
GVRD-7	507	271	1330	840

562

563

564 **Table 2.** Concentrations of selected components of surface sediments and 10-year
565 inventories of total PCBs and total PBDEs. The inventory does not represent exactly 10
566 years, because benthic organisms mix the surface sediments. The inventory for each core
567 was calculated by multiplying the sedimentation rate by 10 years and summing the
568 contaminants over the resulting depth. It was not possible to calculate the inventory for
569 station 4, because the sedimentation rate is unknown, and we did not analyze all the depth
570 sections for contaminants.

571 **List of Figures**

572

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

577

578 Fig. 2. Sediment core sampling locations (GVRD-1 to GVRD-7) and locations of
579 sediment trap moorings (GVRD-A1, GVRD-B1) in the Strait of Georgia. The black line
580 immediately to the east of station GVRD-3 represents the location of the Iona Island
581 outfall pipe.

582

583 Fig. 3. Profiles of the natural log of the activity of excess ^{210}Pb in the sediment cores.
584 Dots represent data, solid lines, the accumulation and mixing model, and dotted,
585 horizontal lines, the bottom of the surface mixed layer for each core.

586

587 Fig. 4. Profiles of the concentration of (a) total PCB and (b) total PBDE in all sediment
588 cores.

589

590 Fig. 5. Profiles of the concentration of (a) total PCB and (b) total PBDE in sediment core
591 GVRD-1. This core was chosen, because its low sediment accumulation rate means that
592 the entire history of PCB contamination is visible in the 50 cm core. All the cores show
593 the same trends, although they do not all represent the same amount of time. (See Table
594 1 for sediment accumulation rates.) Error bars are $\pm 20\%$, the measurement uncertainty
595 reported by the analytical laboratory.

596

597 Fig. 6. Distribution of total PCBs and total PBDEs in Strait of Georgia sediments: (a)
598 surface concentration, (b) 10-year inventory, as described in text.

599

600 Fig. 7. Relationship between the 10-year inventories of (a) total PCB and (b) total PBDE
601 vs. sediment accumulation rate. In panel b, the value for station GVRD-3, near the Iona
602 Island wastewater outfall, is not included in the regression.

603

604 Fig. 8. Profile of the concentration of Total PCB in sediment core GVRD-3, collected
605 near the Iona Island outfall, with the model fit shown as the solid line. The model only
606 fits the data with a sudden decrease in the PCB concentration of the incident particles in
607 1989. Error bars are $\pm 20\%$, the measurement uncertainty reported by the analytical
608 laboratory.

609

610 Fig. 9. Homologue distribution in surface sediments averaged over all 7 stations.
611 Because the range of concentrations was so wide, each station's values were mean-
612 weighted over all homologues, to preserve the shape of the distribution while giving
613 equal weight to all stations.

614

615 Fig. 10. (a) Ratio of the sum of the five most abundant congeners (BDE-209, 47, 49, 99,
616 100) to BDE-209 in sediment cores. The horizontal axis represents a time scale

617 calculated as the measurement depth divided by the sedimentation velocity. This does
618 not represent actual years before present, because of benthic mixing, but it is an
619 approximately common time scale for all stations. The heavy black line represents the
620 average of the BDE ratios measured in the two cores that represent the longest time
621 (GVRD-1 and GVRD-2). On this plot, debromination would appear as an increase in the
622 BDE ratio with increasing depth. It is not evident in these data.

623 (b) Homologue ratios in wastewater treatment plant effluent, sediment trap particulates
624 and sediment cores.

625

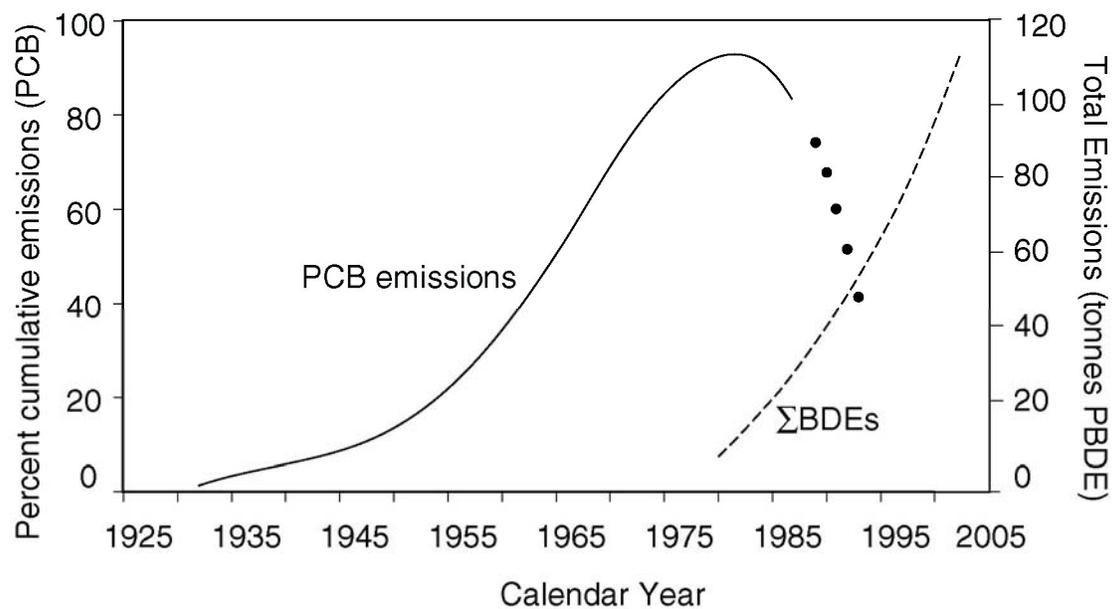
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Figure

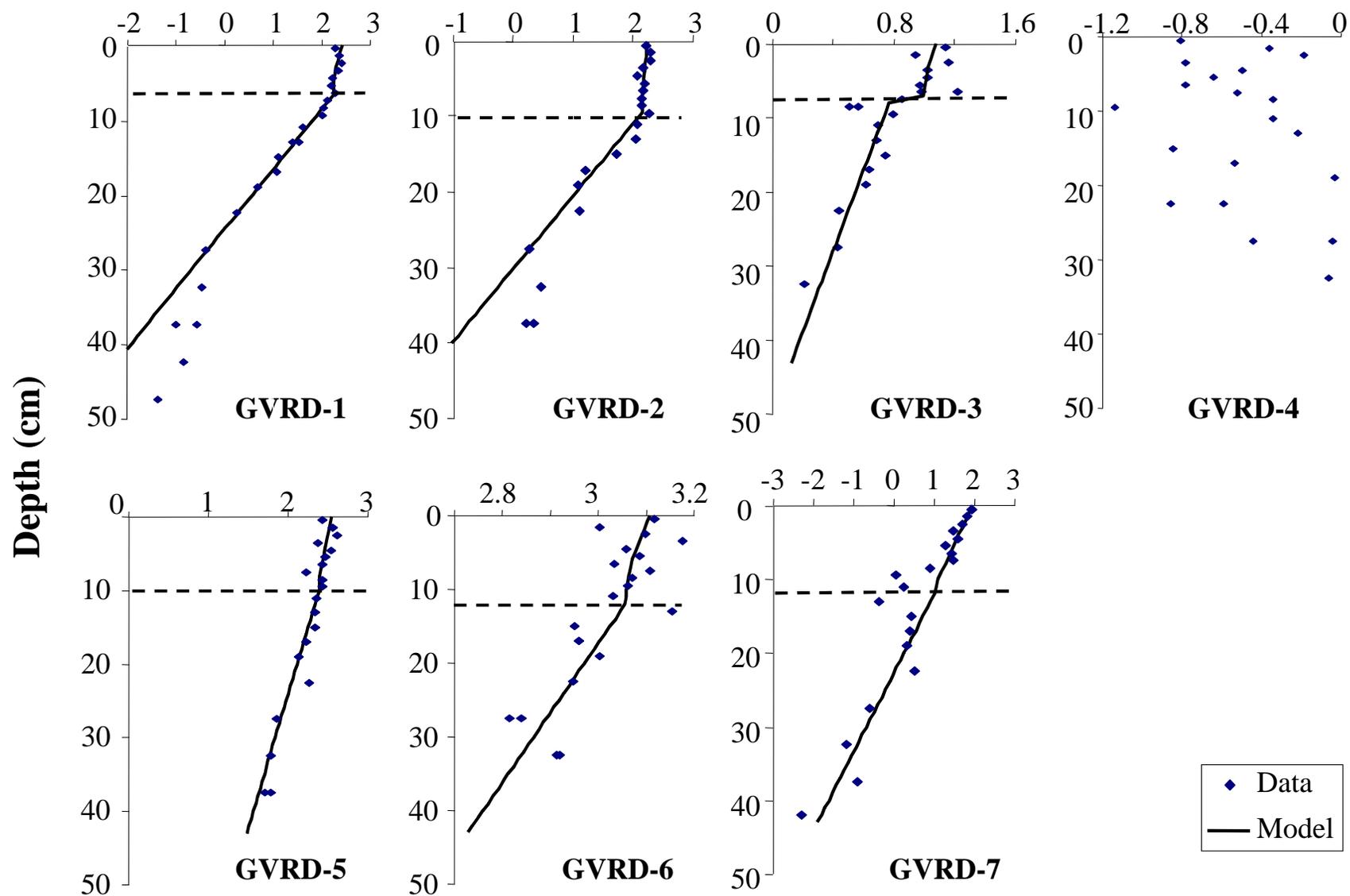


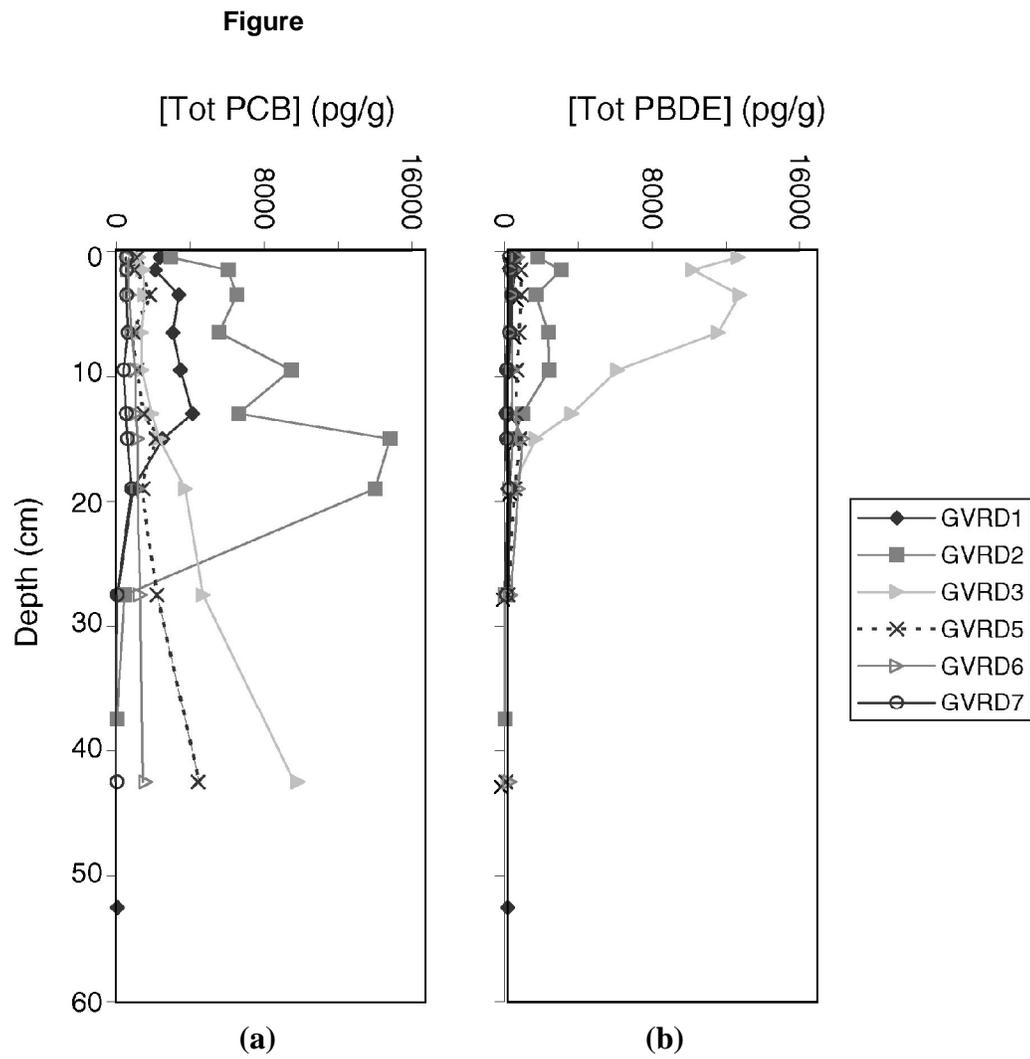
Figure



Figure

$\ln(\text{Excess } ^{210}\text{Pb})$





Figure

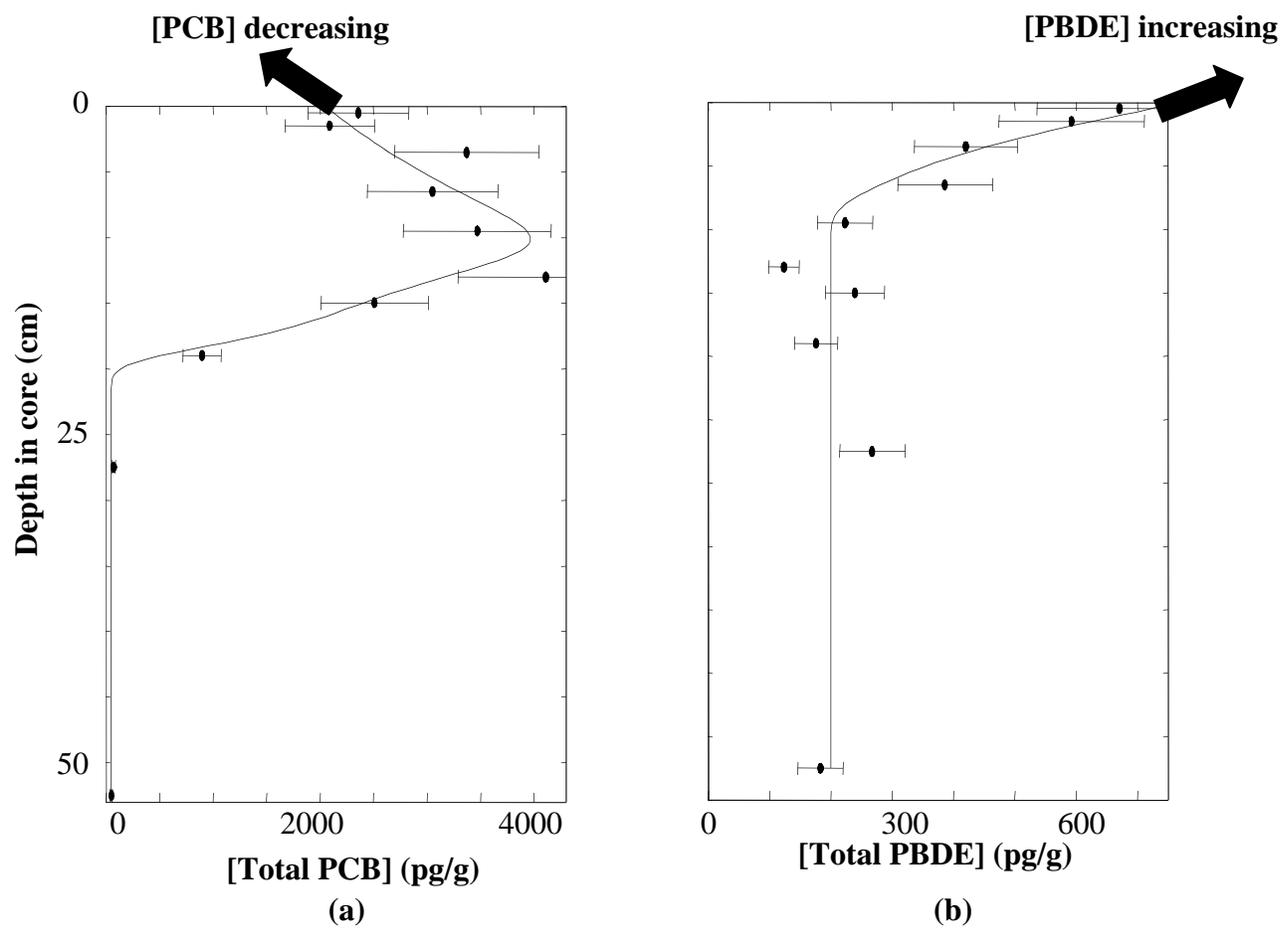
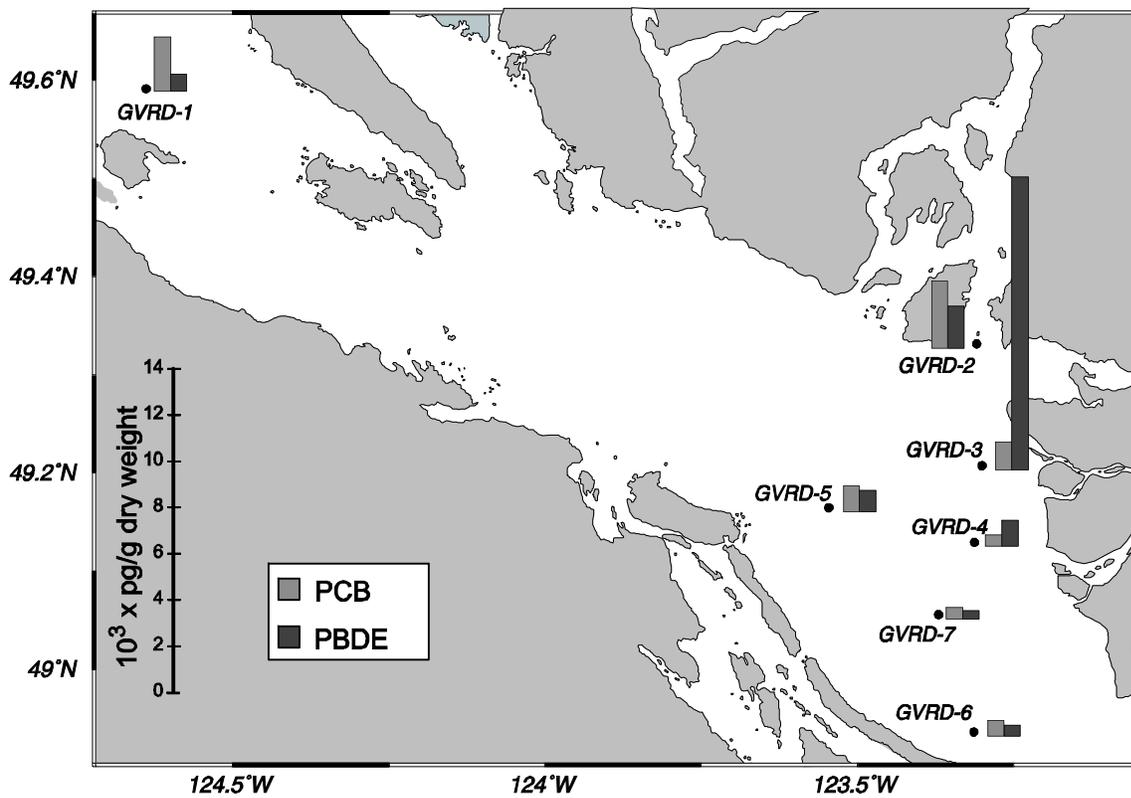
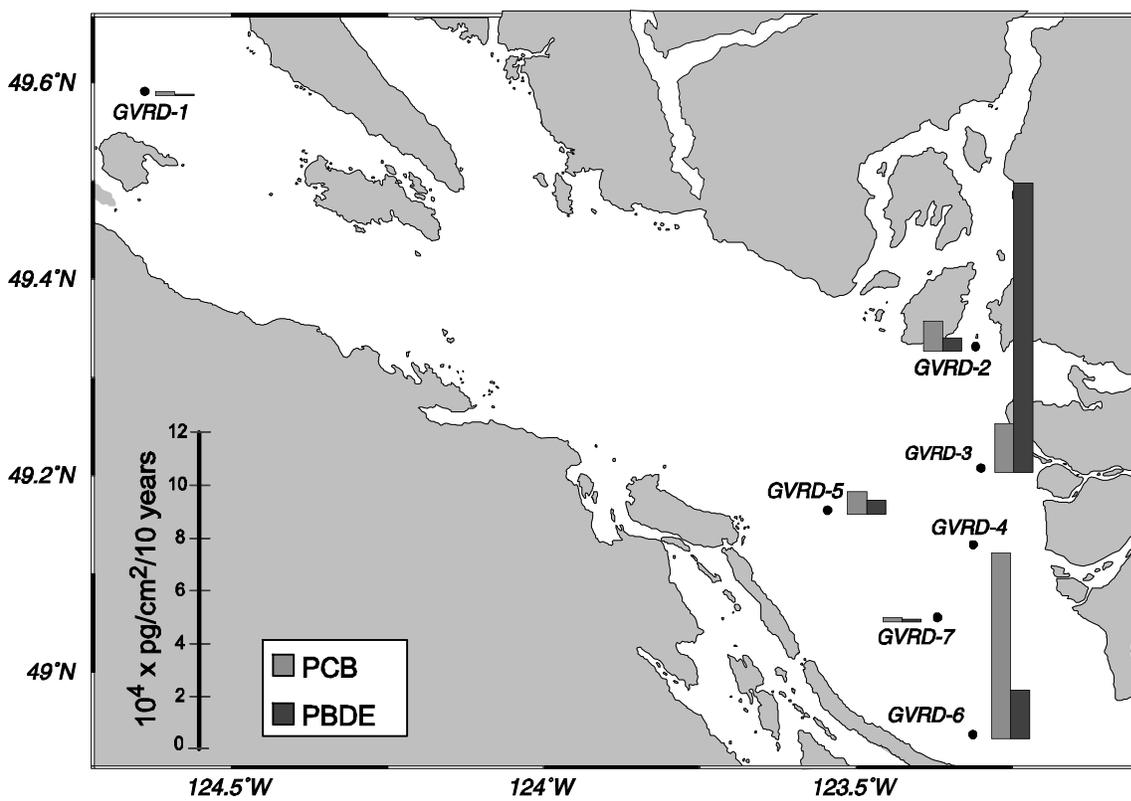


Figure 6

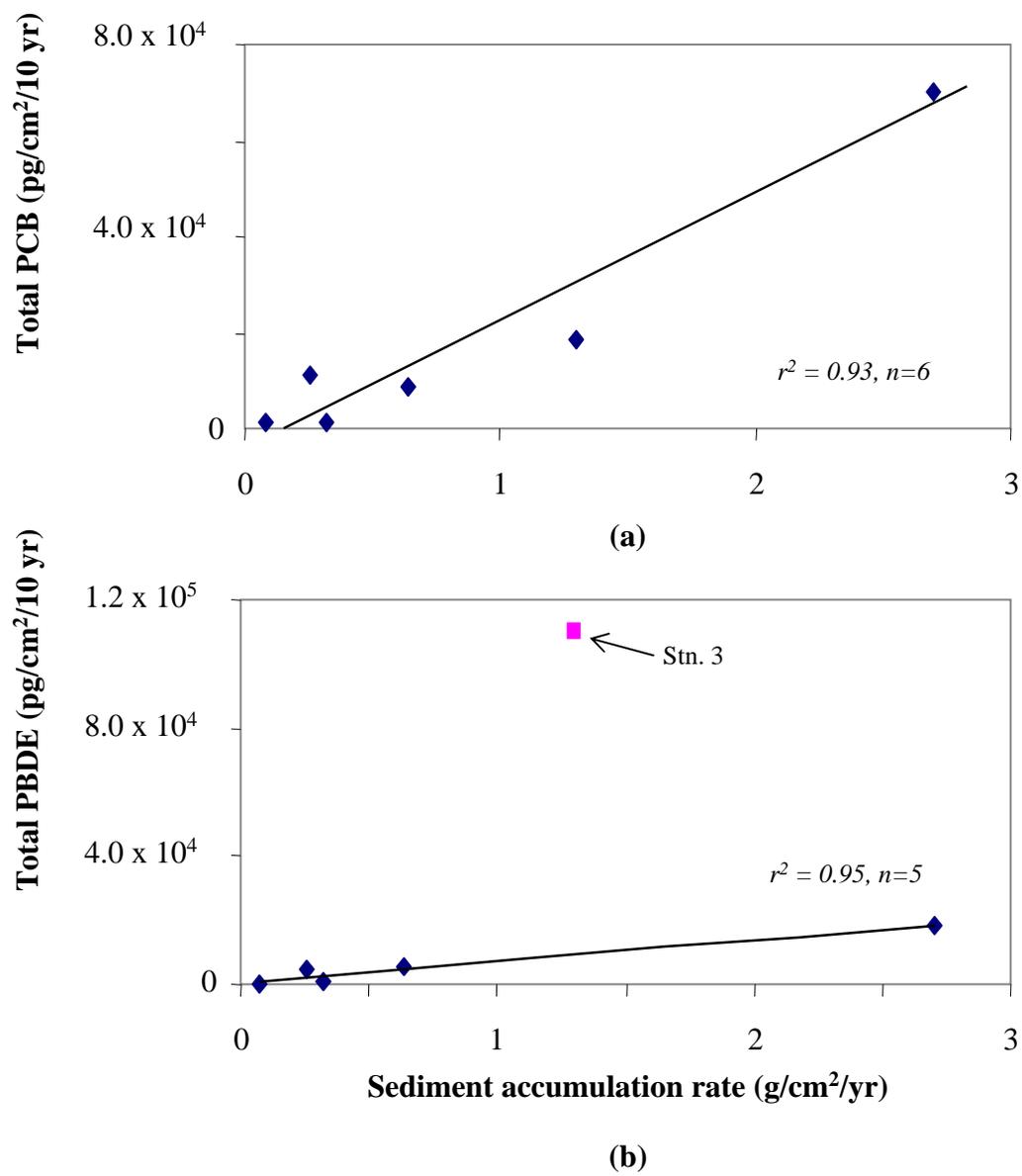


(a) Surface concentration

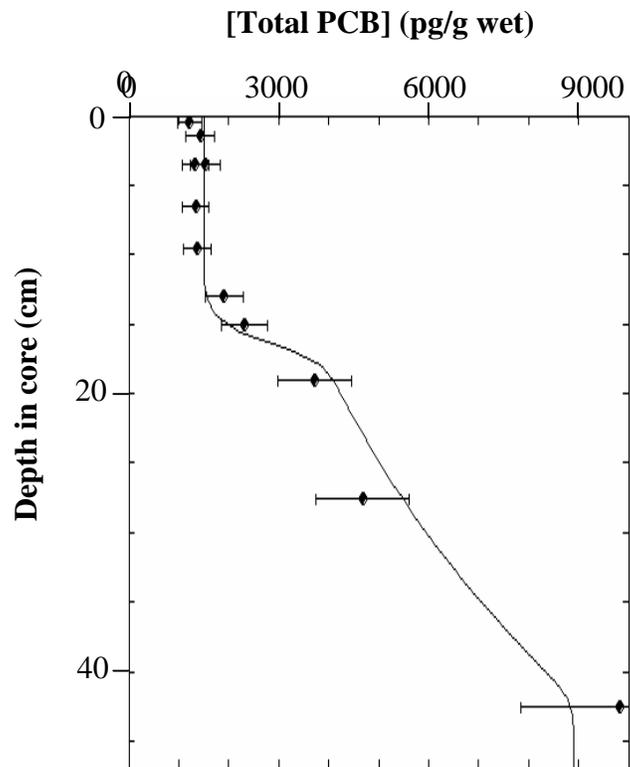


(a) 10-year inventory

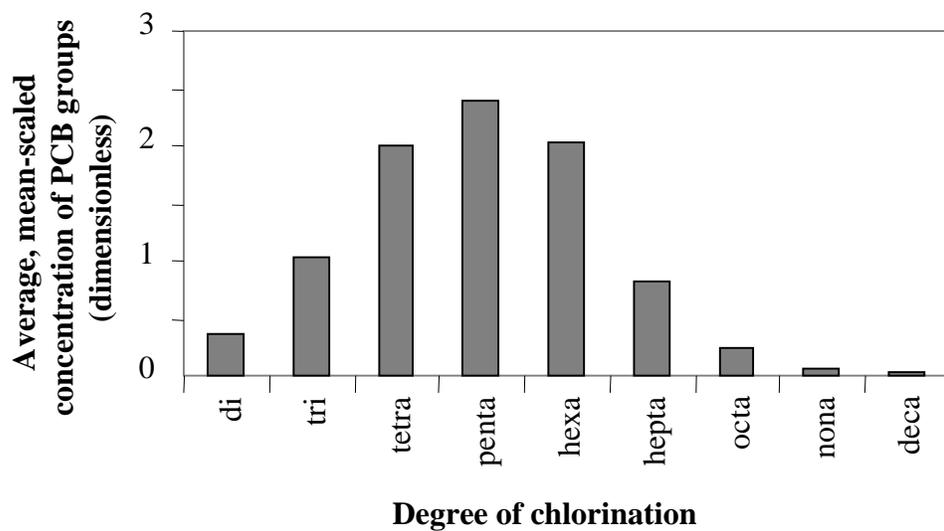
Figure



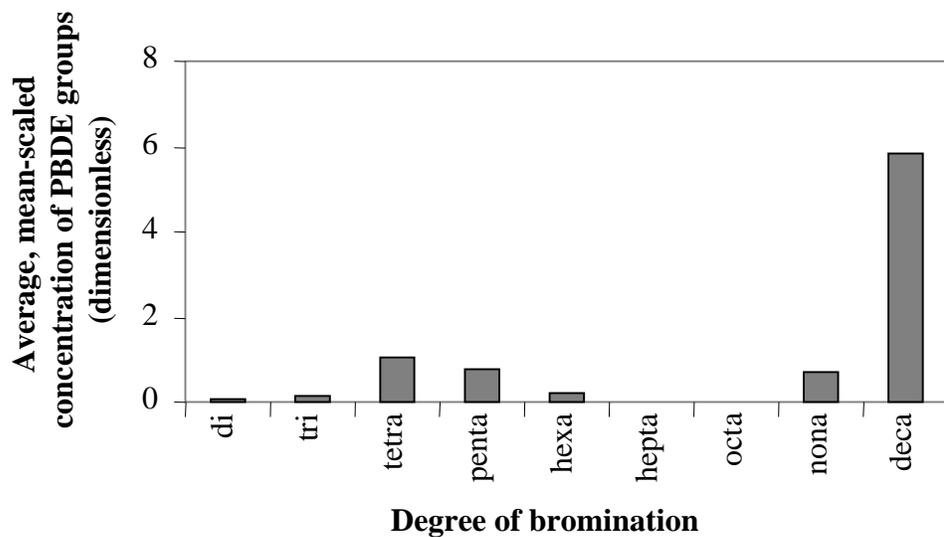
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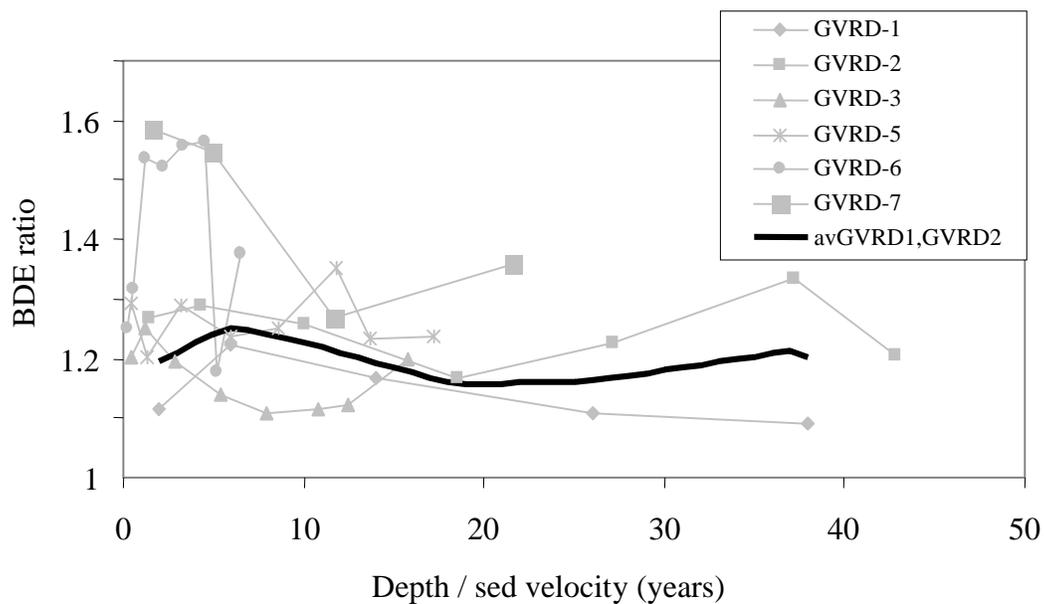


(a)

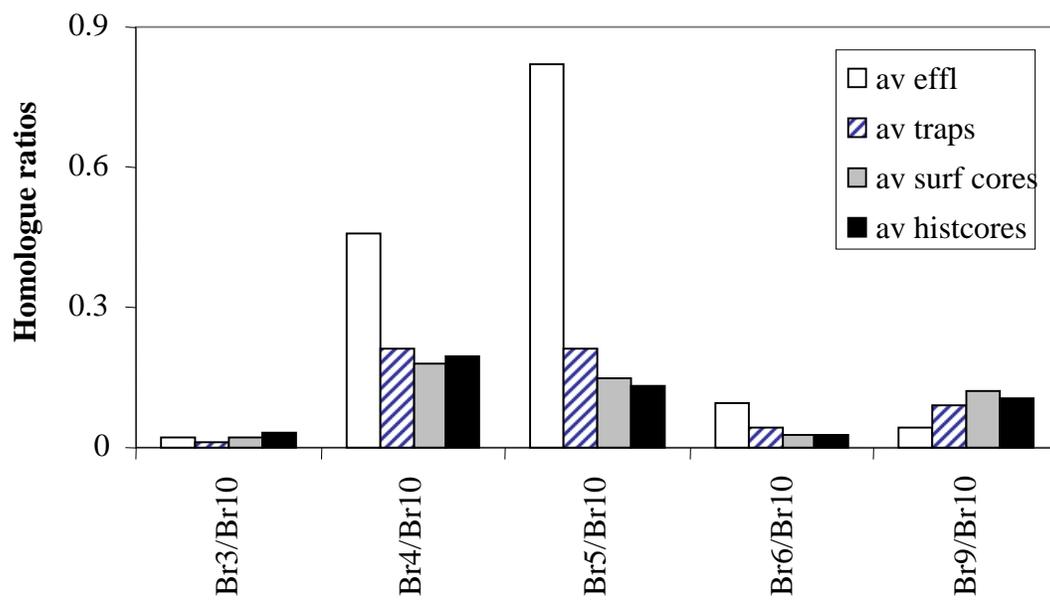


(b)

Figure



(a)



(b)