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Comparisons of Patterns of Polychlorinated Biphenyl Congeners in Water, Sediment, and Indigenous Organisms from New Bedford Harbor, Massachusetts

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Abstract. Polychlorinated biphenyl patterns were compared in samples of water, surface sediment, and the indigenous organisms ribbed mussels *(Modiolus demissus)*, grass shrimp *(Paleomonetes pugio)*, mummichogs *(Fundulus heteroclitis)*, and eels *(Anguila rostrata)* collected from 1991 through 1993 at two stations in the highly contaminated New Bedford Harbor, Massachusetts. Principal component analysis of analytical data showed groups of points that corresponded to individual species, but little separation between stations for the same species was found. Linear correlations showed a high level of agreement between PCB patterns in samples of the exposure environment (water and sediments) and two species of organisms (ribbed mussels and mummichogs). However, due to two separate metabolic alterations of PCBs, the patterns in both shrimp and eels showed poor agreement with patterns in water and sediment. Selective enrichment factors (SEFs), the ratios of individual coplanar or mono-ortho substituted congeners to the total PCBs, were used to compare the relative abundance of congeners in samples. Due to metabolic differences, the SEFs were lower in eels and higher in shrimp than those found in Aroclor® standards.

The patterns of polychlorinated biphenyls found in organisms vary greatly depending on the type of PCB mixtures to which the organisms were exposed, the extent of environmental alterations of these mixtures, and the bioaccumulative and metabolic capabilities of the organisms. Changes in PCB patterns can be extensive enough to prohibit even the identification of the original Aroclor® mixture to which the organisms were exposed from the residues remaining in organisms (Schwartz *et al.* 1987). In the contaminated upper New Bedford Harbor (NBH), Massachusetts (Figure 1), the PCB inputs are known and the gas chromatographic patterns of the PCBs are well characterized (Weaver 1984; Brown and Wagner 1990; Lake *et al.* 1992). This harbor received large quantities of Aroclors® 1242 and 1254 from 1947 to 1970 and possibly Aroclor® 1016 from 1970 to 1978 from a capacitor manufacturing plant (Plant A) (Figure 1). The PCB concentrations in blue mussels *(Mytilus edulis)* deployed for intervals of 28 days at Station CB (Figure 1) during 1987, 1988, and 1989 ranged over only about a factor of two (Bergen personal communication, 1994). In addition, almost no change in gas chromatographic patterns of PCBs was found in filter feeding bivalves sampled at station HS and CB from 1991 to 1993 (Lake, unpublished data). These data suggest that the pattern of PCBs to which organisms were exposed was constant and allowed for differences in patterns of PCB congeners, including the mono-ortho and non-ortho congeners, to be ascribed to differences in bioaccumulation and metabolism.

Mono-ortho and coplanar congeners are of special interest because they cause a variety of deterimental health effects in mammals and appear to have the same mechanism of toxicity as Tetrachlorodibenzo-dioxin (Safe 1984, 1994). For lower level aquatic organisms, however, the toxicological effects of these congeners is unclear. High levels of coplanar congeners had effects on the reproductive process in mummichogs *(Fundulus heteroclitis)* (Black *et al.* 1993), and have been implicated in reproductive effects on salmon (Ankley *et al.* 1991). Conversely, studies of the toxicity of coplanar PCBs to the early life stage of trout suggest that these compounds may be less toxic to these organisms than to some higher level organisms, *e.g.*, mammals (Walker and Peterson 1991). Another study found that little acute toxicity resulted from exposure of two aquatic invertebrates to the coplanar congener BZ 77 (Dillon and Burton 1991). Nevertheless, coplanar congeners have higher lipophilicities (Kafafi *et al.* 1993) and lower depuration rate constants from bivalves (Sericano *et al.* 1992; Kannan *et al.* 1989) than other congeners with the same number of chlorines. These properties could potentially result in enrichments of co-

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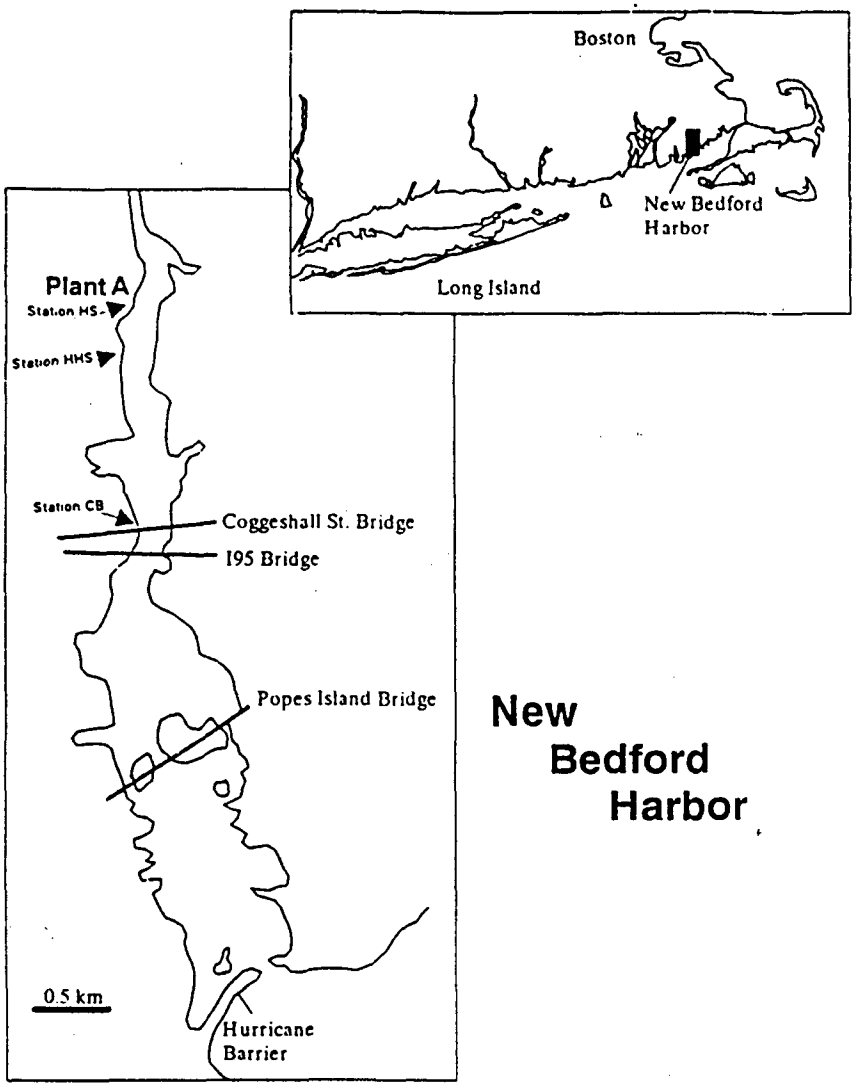

Fig. 1. Map of New Bedford showing sampling stations

planar congeners in lower trophic level organisms and in greater exposure levels for predators.

Since organisms vary greatly in their capacity to metabolize PCBs, we selected four species of organisms that encompassed a range of PCB degradative capabilities, but were exposed to similar concentrations and distributions of PCB congeners at two stations in the highly contaminated Upper New Bedford Harbor, Massachusetts. The species selected were a mollusk, the ribbed mussel *(Modiolus demissus)*, a crustacean, the grass shrimp *(Paleomonetes pugio)*, and two fish, the mummichog *(Fundulus heteroclitis)* and eel *(Anguila rostrata)*. This study identified differences in bioaccumulation and metabolic transformations between the species and determined the extent of enrichment of mono-ortho and coplanar congeners in these organisms.

Materials and Methods

Samples of water, sediment, and organisms were collected at the Hot Spot station (HS) and at the Coggeshall St. Bridge station (CB) on the dates shown (Table 1). Eels *(Anguila rostrata)* were only caught at Hot Spot South (HSS). Water samples were taken in jars. Intertidal surface sediments were collected during low tide by scraping the top 0.5 cm (approximately) of sediment into glass jars. Samples of mummichogs *(Fundulus heteroclitis)*, shrimp *(Paleomonetes pugio)*, and eels *(Anguila rostrata)* were collected in minnow traps baited with bread. Ribbed mussels *(Modiolus demissus)* were collected by hand from locations below the high tide mark. Water samples were extracted upon return to the laboratory. Sediment and organism samples were frozen (−20°C) until analyzed.

An internal standard (BZ 198) was added to water, sediment, and organism samples. An additional internal standard, Octachloronaphthalene (OCN), was added to sediment and organism samples that were analyzed for coplanar congeners.

Water samples were extracted in a separatory funnel using methylene chloride (CH_2Cl_2). These extracts were volume reduced and the solvent was exchanged to heptane.

Sediment samples were thawed, thoroughly mixed with a spatula, and a small sample (~0.5 g) was removed. Another aliquot was removed and oven dried (110°C) to determine moisture content. Internal standards were added to the sample and it was extracted twice with acetone using a vortex mixer. After addition of water to the acetone extracts, the PCBs were partitioned into heptane.

Organism samples were thawed and shucked (if needed), chopped, and homogenized with a Polytron (Brinkman Instruments). An aliquot of the homogenate was oven dried (110°C) to determine moisture content. Internal standards were added (as above) and each sample was

Table 1. Total PCB concentration in samples collected from New Bedford Harbor (1)

Station	Type	Year	Concentration [month collected]**	Mean	RSD
	Water				
HS		1991	1520 [Nov] 1150 [Nov]		
HS		1992	3210 [Jun]	2330	49.8%
HS		1993	3430 [May]		
CB		1991	2410 [Nov] 1380 [Nov] 4240 [Nov] 530 [Nov]		
CB		1992	686 [Jun]	1870	73.2%
CB		1993	1970 [May]		
	Sediment				
HS		1991	881 [Oct] 354 [Nov] 139 [Nov]		
HS		1992	227 [Jun]	351	87.8%
HS		1993	154 [May] (48%)*@		
CB		1991	24.4 [Nov] 18.6 [Nov]		
CB		1992	26.4 [Jun]	20	35.1%
CB		1993	10.7 [May] (4.0%)*		
	Ribbed mussels				
HS		1991	not collected		
HS		1992	453 [Jun]	732	53.8%
HS		1993	1010 [May] (21%)*@		
CB		1991	154 [Nov] 82.1 [Dec]		
CB		1992	169 [Jun]	128	31.9%
CB		1993	106 [May] (34%)*		
	Shrimp				
HS		1991	25.7 [Nov] 88.9 [Nov]		
HS		1992	277 [Jun]	124	86.4%
HS		1993	106 [May] (1.3%)*@		
CB		1991	21.5 [Nov] 25.8 [Nov]	21.8	17.9%
CB		1992			
CB		1993	18.0 [Oct] (15%)*		
	Mummichogs				
HS		1991	1170 [Nov] 482 [Nov]		
HS		1992	1470 [Jun]	1370	56.3%
HS		1993	2340 [May] (4.5%)*		
CB		1991	1310 [Nov]		
CB		1992	198 [Jun]	655	89.0%
CB		1993	455 [May] (5.1%)*		
	Eels				
HSS		1991	266 [Nov] 565 [Nov]		
HSS		1992		380	42.3%
HSS		1993	311 [Oct] (1.6%)*@		
CB			not caught		

(1) concentrations in ng/l for water; ug/g(dry) for organisms
HS = Hot Spot
HSS = Hot Spot South
CB = Coggeshall St. Bridge
For analytical replicates, RSD% shown in parenthesis after mean
N = 3 for all analytical replicates
* = sample used for comparisons of patterns of SEFs (Figure 5)
@ = sample used for comparisons of relative uptake (Figure 4)
**½ detection limit was used for congener concentrations below detection

ground in 5 g Na_2SO_4 using a mortar and pestle. The sample-Na_2SO_4 mixture was transferred to a vial and extracted by the same procedure used for the sediments.

The heptane layer from all samples was reacted with concentrated H_2SO_4. Portions of the heptane extracts were used for analysis of total PCBs and for coplanar congeners. If necessary, sediment extracts were reacted with reduced copper powder to remove elemental sulfur.

Extracts were analyzed for total PCBs on a Hewlett-Packard 5890A gas chromatograph (GC) equipped with a splitless injection port, electron capture detector (ECD), and a 60-m fused silica column coated with DB-5 (J&W Scientific Inc.). The output of the detector was collected on a microvax computer.

PCB congeners were identified by individual congener standards and a secondary standard mixture of Aroclors® (Mullin 1987). Concentrations of PCBs were calculated by the internal standard (BZ 198) and were quantitated against the secondary standard mixture. The PCB congeners analyzed in this study and their structures are listed in Table 2. In this paper, congeners are referred to by the prefix BZ and its number using the congener numbering system adopted by Ballschmiter and Zell (1980). For the sediment and organism samples, the method detection limit for congeners was 25 ng/g (dry wt). For water samples, the method detection limit for congeners was 2 ng/L. Blanks were processed with sample sets and showed no contamination which interfered with the analysis of PCBs.

Table 2. Numbering and structures of PCB congeners* used in this study

Cogener BZ #	Structure	Cogener BZ #	Structure
004 + 010	2-2, 26-	087	234-25
007	24-	085	234-24
006	2-3	136	236-236
008 + 005	2-4, 23-	110 + 077	236-34, 34-34
019	26-2	151 + 082	2356-25, 234-23
018	25-2	135 + 144	235-236, 2346-25
017	24-2	149	236-245
027 + 024	26-3, 236-	118	245-34
016 + 032	23-2, 26-4	146	235-245
026	25-3	153	245-245
025	24-3	105	234-34
031	25-4	141	2345-25
028	24-4	176 + 137	2346-236, 2345-24
033	34-2	138 + 163	234-245, 2356-34
022	23-4	178 + 129 + 126	2356-235, 2345-23, 345-34
045	236-2	187 + 182	2356-245, 2345-246
046	23-26	183	2346-245
052	25-25	128	234-234
049	24-25	174	2345-236
047 + 048	24-24, 245-2	177	2356-234
044	23-25	156 + 171 + 202	2345-34, 2346-234, 2356-2356
042 + 037	23-24, 34-4	180	2345-245
064	236-4	170 + 190	2345-234, 23456-34
040	23-23	201	2345-2356
100	246-24	203 + 196	23456-245, 2345-2346
063	235-4	195 + 208	23456-234, 23456-2356
074	245-4	207	23456-2346
070 + 076	25-34, 345-2	194	2345-2345
095 + 066	236-25, 24-34	206	23456-2345
091	23-34, 234-4	209	23456-23456
056 + 060	23-34, 234-4	Coplanar PCBs	
101 + 092 + 084	245-25, 235-25, 236-23	077	34-34
099	245-24	126	345-34
097	245-23	169	345-345

*The position of chlorine atoms on biphenyl are noted by numbers, and a dash represents the separation of rings. For example, 2,2',4,4',5,5'-hexachlorobiphenyl (BZ 153) is shown as 245-245 in this paper. The major congener is listed first for peaks containing more than one congener

Nine mixtures of Aroclors® 1242 and 1254 (the predominant Aroclors® released in NBH) from 10% A-1242:90% A-1254 to 90% A-1242:10% A-1254 were analyzed. The mean percentage measured (measured total PCB concentration using secondary standard/actual total PCB concentration) was 98.7% (C.V. 2.2%).

Standards of PCB congeners were added to three samples of clean water and analyzed by the described procedures. Recoveries for the congeners, not including the coplanars BZ 77 and 126, averaged 69% and ranged from 51.0% to 81.7%. The mean relative standard deviation (RSD) for these congeners was 11%. Coplanar congeners were not analyzed in water samples.

Analysis of Standard Reference Materials (National Institute of Standards and Technology) #1941 Organics in Sediment, and #1974 PCBs in a Mussel Tissue Homogenate gave results that agreed within a factor of two of the published results for 25 of 27 congeners. Spike and recovery data for PCB congeners from clean sediment and clean scallop tissue showed average recoveries of 123% and 106%, respectively.

Analyses of Mono-ortho and Coplanar Congeners

The mono-ortho congenes BZ 105 and 118 were resolved from other congeners by the 60 m capillary column and were quantitated from the total PCB analytical runs. The coplanar congeners BZ 77, 126, and 169 were separated from other congeners on a 15 cm × 0.4 cm column containing 1.30 of 4.7% carbon (Super A activated carbon AX-21, Anderson Development Co, USA) in fully activated Biosil A silicic acid (100-200 mesh). An aliquot of extract containing the OCN internal standard was charged onto the column and separated into the following fractions and rinses: F1) 20 ml 7.5% CH_2Cl_2 in hexane, contained PCB congeners with 2, 3, and 4 ortho-chlorines; F2) 20 ml CH_2Cl_2, contained congeners with one ortho-chlorine; Rinse 1) 10 ml CH_2Cl_2; Rinse 2) 10 ml CH_2Cl_2; and F3) 10 ml toluene (reverse elution), contained internal standard OCN and congeners with no ortho-chlorines (coplanar congeners). For the present study, only Rinse 2 and the F3 fractions were collected and analyzed. Rinse 2 was collected and analyzed to ensure that mono-ortho PCB congeners that eluted inF2 were separated from the coplanar PCBs in the F3.

Coplanar congeners were identified in the F3 fractions by comparisons of gas chromatographic retention times with those of known standards. Concentrations of coplanar compounds were calculated using the internal standard (OCN) and were quantitated against the mixture containing the coplanar compounds.

Spikes of coplanar congeners and of the internal standard were added to triplicate samples of uncontaminated sediment and taken through the described procedures. These analyses showed the following percentage returns: BZ 77 (92.2, RSD = 15.5%); BZ 126 (84.1, RSD = 6.0%); BZ 169 (86.3, RSD = 6.8%); OCN (87.8, RSD =

Table 3. Comparisons of concentrations of BZ 118, 105, 77, and 126 in Aroclors® 1242 and 1254

Aroclor® 1242 This Study			Reported in Literature
CB#	weight %	rsd % (n = 3)	weight % (reference)
118	0.45	2.6	1.62 (1)
105	0.32	3.8	0.86 (1), 0.31 (2)
77	0.28	1.4	0.52 (3), 0.24 (4), 0.35 (2)
126	0.0037	10.1	0.0017 (3)
Aroclor® 1254			
CB #	weight %	rsd % (n =3)	weight %
118	6.08	1.4	6.39 (1)
105	3.18	2.9	3.83 (1), 2.71 (2)
77	0.1	58.6	0.06 (3), 0.02 (4), 0.11 (2)
126	0.0088	24.1	0.0046 (3)

(1) Schulz *et al.* 1989
(2) Mullin 1985
(3) Kannan *et al.* 1988
(4) Huckins *et al.* 1980

7.2%). Similarly, analysis of samples consisting of spikes of coplanar congeners added to an uncontaminated tissue matrix (abalone tissue) gave the following percentage returns: BZ 77 (53.0, RSD = 13.4%); BZ 126 (53.2, RSD = 15.2%); BZ 169 (54.0, RSD = 15.2%); OCN (55.0, RSD = 20.8%).

Due to documented difficulties in the following separations, BZ 110 from BZ 77, BZ 126 from BZ 129 and 178 (Kannan *et al.* 1991), a rinse of the carbon column was taken prior to inverting the column for the reverse elution with toluene. This rinse was analyzed by ECD to ensure that the ortho-substituted congeners BZ 110, 129, and 178 had been eluted from the column and would not be important interferences in the F3 fraction. In spite of these precautions, analysis by gas chromatography/mass spectrometry (GC/MS) in selected ion mode showed that BZ 110 was presnt in the F3 fraction and could interfere with quantitation of coplanar BZ 77. However, BZ 129 and 178 were not important interferences in the quantitation of BZ 126. Based on extracted ion current profiles and total ion current profiles from GC-MS analysis, the mummichog had the highest level (22%) of BZ 110 coeluting in the F3 fraction with BZ 77. Interference with quantitation of BZ 126 was <1%.

The content of the mono-ortho substituted BZ 118 and 105 and the coplanars BZ 77 and 126 in Aroclor® 1242 (A-1242) and Aroclor® 1254 (A-1254) were analyzed by the above procedures. For A-1242, the weight percentage for BZ 118 was a factor of four less than the published values, but the other congeners agreed within a factor of two of the published values (Table 3). For the four congeners in A-1254, the results of the present study agreed within a factor of two of published values, except for one analysis of BZ 77. The lack of agreement for BZ 118 in A-1242 and BZ 77 in A-1254 may indicate the variability present in PCB mixtures (Albro *et al.* 1981).

Coplanar compounds were measured on triplicate analytical replicates of 1993 samples of sediment, mussels, shrimp, and mummichogs from the HS and CB stations, and on eels from the HSS station (Table 1). Mean selective enrichment factors (SEFs), the decimal fraction of coplanars BZ 77, 126, and the mono-ortho substituted BZ 118 and 105 were calculated and compared. Coplanar BZ 169 was below detection in all samples. In this study, the total PCB concentration included all PCBs. However, total PCB calculations from other studies sometimes included just the major congeners or were done using the concentrations of selected PCB congeners and extrapolations to total Aroclor® equivalents or total PCB concentrations. As a consequence, some variability in SEFs between studies is expected. The methods for calculating total PCBs in the SEF calculations are listed (Table 4).

Numerical Analysis

Prior to pattern analysis of the data, for each sample the individual congener data were expressed as a fraction of the total PCB concentration. These data (for all individual samples) were compared using principal component analysis (Lavine 1992). Graphical comparisons (Figure 3) and linear regressions (Table 5) were made at each station using mean data from all years.

Results and Discussion

Congener Accumulation

In surface sediments, the mean total PCB concentration for all years was a fctor of 17 higher at the HS station than at the CB station. Mean total PCB concentrations in ribbed mussels, shrimp, and mummichogs were factors of six, six, and two higher at the HS station than at the CB station, respectively. For water samples, mean concentrations were about equal (Table 1). Due to high variability, no significant differences in mean concentrations of total PCBs over all years were found between the HS and CB stations for the same sample types ($p \leq .05$).

Principal component analysis (PCA) showed principal components PC1, PC2, and PC3 accounted for 48%, 12%, and 10% of the variance in the data set. A plot of PC1 vs PC3 shows a separation of organism samples by sample type, but little separation between stations for the same sample type was found (Figure 2). In general, PC1 loads negatively for congeners containing less than six chlorines and positively for congeners with six or greater chlorines. Thererfore, on the PC1 axis, water, mussel, and some sediment samples which contain higher relative amounts of congeners with less than six chlorines have lower PC1 values than found for the other samples (Figure 2). PC3 loads positively for congeners containing three or fewer chlorines and for congeners with seven or more chlorines. Since biota do not accumulate low and high PCB congeners as effectively as mid range congeners (Lake *et al.* 1987), the biota samples are lower and separate from the samples of the water and sediment on the PC3 axis.

Graphical analysis showed similar patterns in the same species at both stations (Figure 3). To make direct comparisons of patterns in organisms with those in the water and sediments, linear correlations of decimal fraction data of the congeners were calculated. A high degree of correlation was found for the mussels and mummichogs vs water and sediment at both stations (Table 5). The shrimp at the CB station, and the shrimp and eel samples at the HS station, showed far lower correlation coefficients with the water and sediments. The differences between patterns in organisms and those in the water and sediment samples may be attributed to interspecific differences in bioaccumulation and metabolism.

While mussels do not appear to metabolize PCBs (Brown 1992), the patterns in mussels are not an exact match of the patterns in the water and sediments because lower mw PCBs (<4 Cl atoms per molecule) and higher mw PCBs (those with >6 Cl atoms per molecule) which were present in the water and sediments were not as highly bioaccumulated by the mussels as the midrange congeners (those with 4, 5, and 6 Cl atoms per molecule) (Figure 3). The pattern in mussels is similar to those found in other studies with bivalve mollusks (Lake *et al.* 1987).

Table 4. Comparisons of selective enrichment factors in fish, bivalves, and crustaceans

	BZ 77 (×1000)	BZ 126 (×10000)
Walleye (1987) Lake Kernaala (e)*	0.066 (2)	0.037
Pike (1987) Lake Kernaala, South Finland (e)*	0.045 (1)	0.080
Pike (1987) Lake Kernaala, South Finland (e)*	0.31 (6)	0.23
Eel—Hot Spot (b)***#	0.26 (5)	bd
Perna viridis (green-lipped mussels) (1985) Hang Hau, Hong Kong (f)***#	1.4 (15)	0.80
Ribbed mussel—Hot Spot (b)***#	3.2 (24)	0.81
Salmo salar (salmon) Baltic Sea (g)*###	1.1 (13)	0.99
Mummichog—Hot Spot (b)***#	2.5 (21)	1.2
Ribbed mussel—Coggeshall Bridge (b)***#	3.2 (24)	1.2
Salmon (1987) Gulf of Finland (e)*	0.56 (9)	1.5
Salmon (1986) Gulf of Bothnia (e)*	0.48 (7)	1.5
Clupea harengus (herring) Baltic Sea (g)###	1.5 (16)	1.5
Cadus mordhua (cod) Baltic Sea (g)****###	0.82 (11)	1.6
Mummichog—Coggeshall Bridge (b)***#	2.2 (20)	1.6
Salmon (1986) Baltic Sea (e)*	0.72 (10)	1.7
Perna viridis (green-lipped mussels) (1985) Hang Hau, Hong Kong (f)***#	2.1 (19)	1.8
Cod (1987) Arctic Coast, Norway (e)**	0.11 (3)	1.9
Salmon (1987) Gulf of Finland (e)*	0.49 (8)	2.1
Salmon (1987) Gulf of Finland (e)*	0.86 (12)	2.2
Shrimp—Hot Spot (b)***#	4.4 (30)	2.3
Salmo salar (salmon) Baltic Sea (g)*###	3.4 (26)	3.1
Salmo salar (salmon) Arctic Sea (g)*###	4.6 (31)	3.1
Salmo salar (salmon) Baltic Sea (g)*###	3.1 (23)	3.3
Salmo salar (salmon) Baltic Sea (g)*###	3.5 (27)	4.1
Cod (1988) Arctic Coast, Norway (e)****	0.14 (4)	4.3
Shrimp—Coggeshall Bridge (b)***#	7.7 (33)	4.6
Cadus mordhua (cod) Arctic Sea (g)****###	2.5 (21)	5.4
Crassostrea virginia (oyster)—Tampa Bay (d)***	2.6 (22)	5.7
Coregonus (white fish) (1986) Lapland (a)*##	4.3 (29)	8.3
Crassostrea virginia (oyster)—Galveston Bay (d)***	1.6 (17)	10.0
Clupea harengus (herring) (1986) Bothnian Sea (a)*##	8.5 (34)	10.8
Crassostrea virginia (oyster)—Galveston Bay (d)***	1.3 (14)	10.9
Winter flounder (1988) New Bedford, Mass. (c)****#	9.2 (35)	11.4
Crassostrea virginia (oyster)—Tampa Bay (d)***	2.2 (20)	11.7
Crassostrea virginia (oyster)—Galveston Bay (d)***	1.3 (14)	12.2
Winter flounder (1988)—Gaspee Pt, RI (c)****#	3.2 (24)	12.7
Clupea harengus (herring) (1987) Baltic Sea (a)*##	11 (36)	12.9
Crassostrea virginia (oyster)—Tampa Bay (d)***	1.1 (13)	13.3
Salvelinus alpina (arctic char) (1987) Lake Vattern, Sweden (a)*##	5.0 (32)	19.2
Crassostrea virginia (oyster)—Galveston Bay (d)***	1.8 (18)	20.0
Pleuronectes americanus (Winter flounder) (1988)—Fox Island, RI (c)****#	3.3 (25)	20.1
Crassostrea virginia (oyster)—Galveston Bay (d)***	1.8 (18)	22.0
Crassostrea virginia (oyster)—Galveston Bay (d)***	3.1 (23)	25.0
Crassostrea virginia (oyster)—Tampa Bay (d)***	3.1 (23)	58.2
Crassostrea virginia (oyster)—Tampa Bay (d)***	4.1 (28)	59.2

sum of detected PCB congeners
total PCB calculated by summing several selected congeners
total PCB determined as mixture Clophen A-60
* muscle tissue
** fat
*** whole organism
**** liver
(a) Jansson *et al.* 1993
(b) This study
(c) Elskus *et al.* 1994
(d) Sericano *et al.* 1992
(e) Koistinen *et al.* 1989
(f) Kannan *et al.* 1989
(g) Paasivirta and Rantio 1991
bd = below detection
( )Rank in increasing order of SEF factors for BZ 77

Table 5. Comparison of correlation coefficients of decimal fraction data for PCB congeners between sample types

Station		Water	Sediment
HS			
	Mussels	0.93	0.89
	Mummichog	0.86	0.86
	Shrimp	0.27	0.33
	Eel	0.31	0.42
CB	Mussels	0.85	0.89
	Mummichog	0.81	0.82
	Shrimp	0.26	0.33

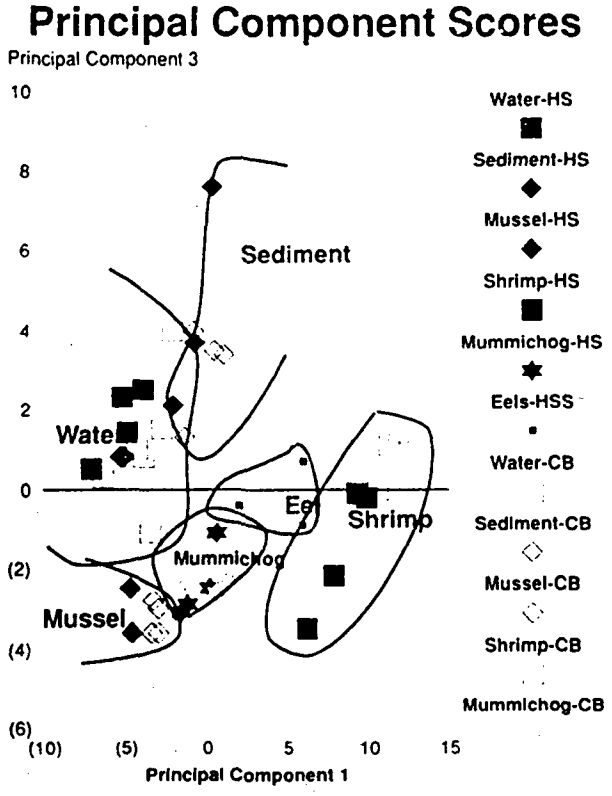

Fig. 2. Graph of principal components one vs. three for decimal fraction data for congeners—HS, HSS, and CB stations

Relative to the pattern in all other sample types, the shrimp showed a decreased abundance of PCB congeners that contained vicinal hydrogens in the meta and para positions (*e.g.*, BZ 52, 49, 44, 101, 97, 110, 151, and 149) (Figure 3(c)). These decreases likely resulted from the metabolic activities of this crustacean. This pattern of congeners has been found in other organisms, including some crustaceans, and is designated P4502B-like (Brown 1992).

In mummichogs, only minor pattern alterations that were consistent with P4502B-like metabolic processes were found. This result is in contrast to other studies that indicated mummichogs exhibited P4501A-like metabolism, which is characterized by losses of lower non-ortho-substituted congeners and mono-ortho-substituted congeners without para, para'-chlorines (Brown 1992). Mummichogs prey heavily on shrimp, and possibly the P4502B-like patterns found in these fish reflect uptake from food as well as other sources of bioaccumulation at these contaminated stations.

The PCB pattern in the eel showed that only relatively small amounts of the lower mw congeners were accumulated (Figure 3(c)). In the mid-range of PCBs, the relative accumulation increased, and some accumulation of higher mw congeners was found. The major PCB pattern in the eel was the P4501A-like pattern (shown by, for example, losses of BZ 31 and 70 and the coplanars BZ 77 and 126), but the alterations found in the eel were more extensive than those normally found in aquatic fauna. These alterations included a large relative loss of BZ 28 and a lower abundance of BZ 74 relative to the residues in other oragnisms (Figure 3). The eel also showed minor alterations of PCBs consistent with the P4502B pattern (*e.g.*, loss of BZ 52 and 101). Similar patterns have been found in other (n = 9) eel samples collected from the HSS station. Eel samples from the lower Hudson River were found to have the P4502B-like pattern (no P4501A-like pattern was reported) (Brown 1992). Possibly the high concentrations of PCBs in the eel in the present study (380 ppm dry wt) were sufficient to induce P4501A-like metabolism in these organisms.

A comparison was made of our data with those of another study which examined the accumulation of PCBs by organisms in a freshwater lake with a low level of PCB contamination (van der Oost *et al.* 1988). We normalized the concentrations of selected individual congeners to BZ 153 in samples from the HS station (see Table 1 for samples) to allow comparisons of the patterns. Sediment from the New Bedford HS station showed a greater relative abundance of lower molecular weight congeners compared to that in the sediment from the freshwater lake (Figure 4). In general, the PCB distributions in mollusks at both locations reflected the distributions in the sediments. For crustaceans, the relative distributions of congeners between the two studies were different (Figure 4). Crustaceans in the lake study showed a higher relative accumulation of BZ 52 and 101 than was found in the crustaceans in our study. These differences appear to result from metabolic variations between the crustacean species in the two studies. The PCB pattern reported in *Gammarus* (the freshwater crustacean), and presumably the two other freshwater species (*Asellus aquaticus* and *Orchestia carimana*) that were also sampled in the lake study, showed no alteration of PCBs (Brown 1992). In contrast, the crustaceans in our study metabolized BZ 52 and 101. The relative PCB pattern in eels was similar between the two studies. The relative increases in higher mw PCB congeners in the eel in the lake study were attributed to the fact that eels, in contrast to the other species, live long enough to accumulate the higher mw PCBs, which are slowly accumulated and slowly depurated. In the present study, however, the relative accumulation of high mw PCB congeners in the eel is no more extensive than in the shrimp that they consume.

Selective Enrichment Factors—Coplanar and Mono-ortho Congeners

To compare the relative accumulation of coplanars BZ 77 and 126 and the mono-orthos BZ 118 and 105, these compounds

Figure 3(a) WATER

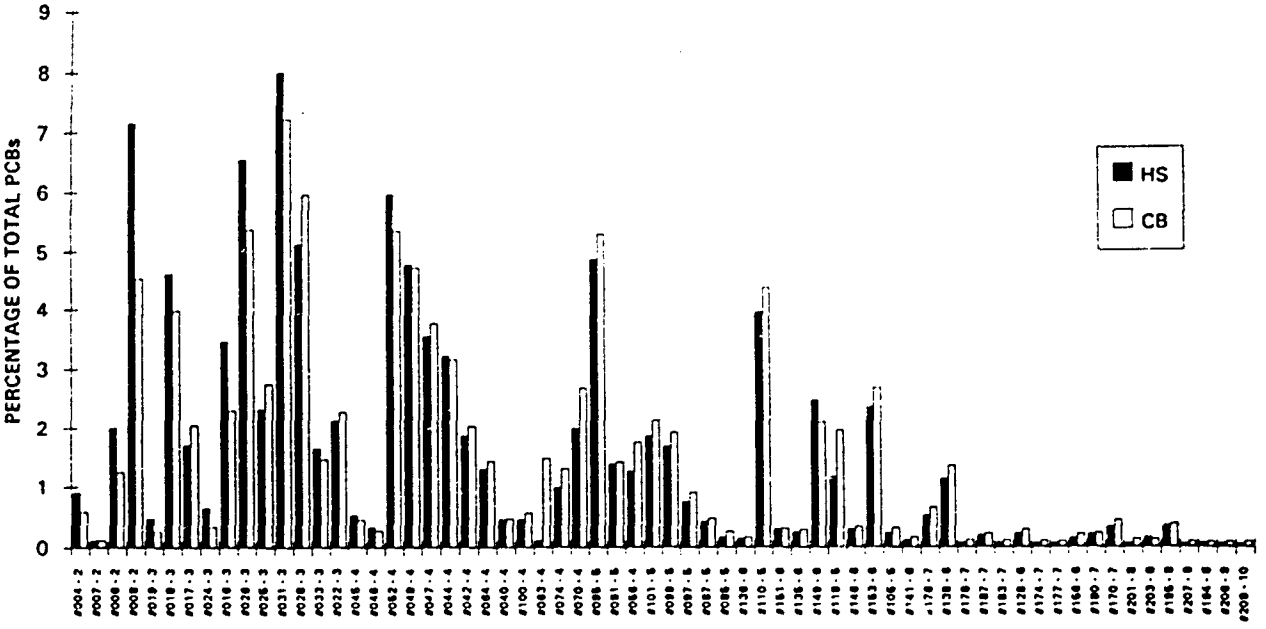

Figure 3(a) SEDIMENT

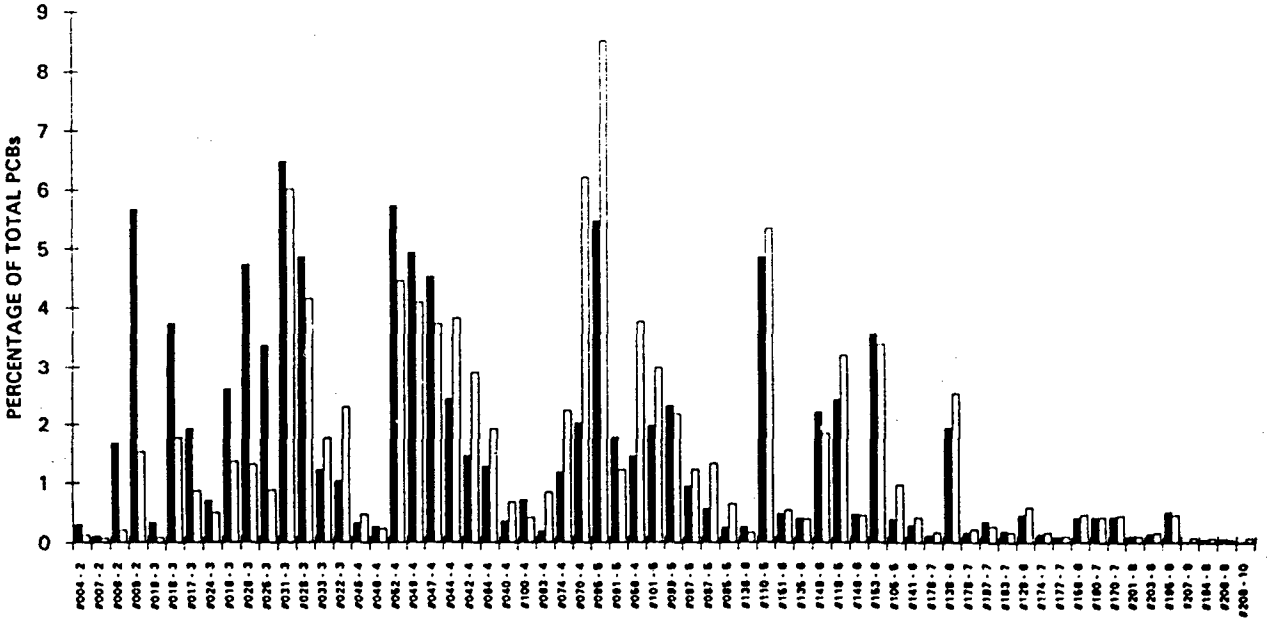

Fig. 3(a). Bar graph of mean percentage of total PCBs for congeners in water and sediment at HS and CB stations

Figure 3(b) MUSSELS

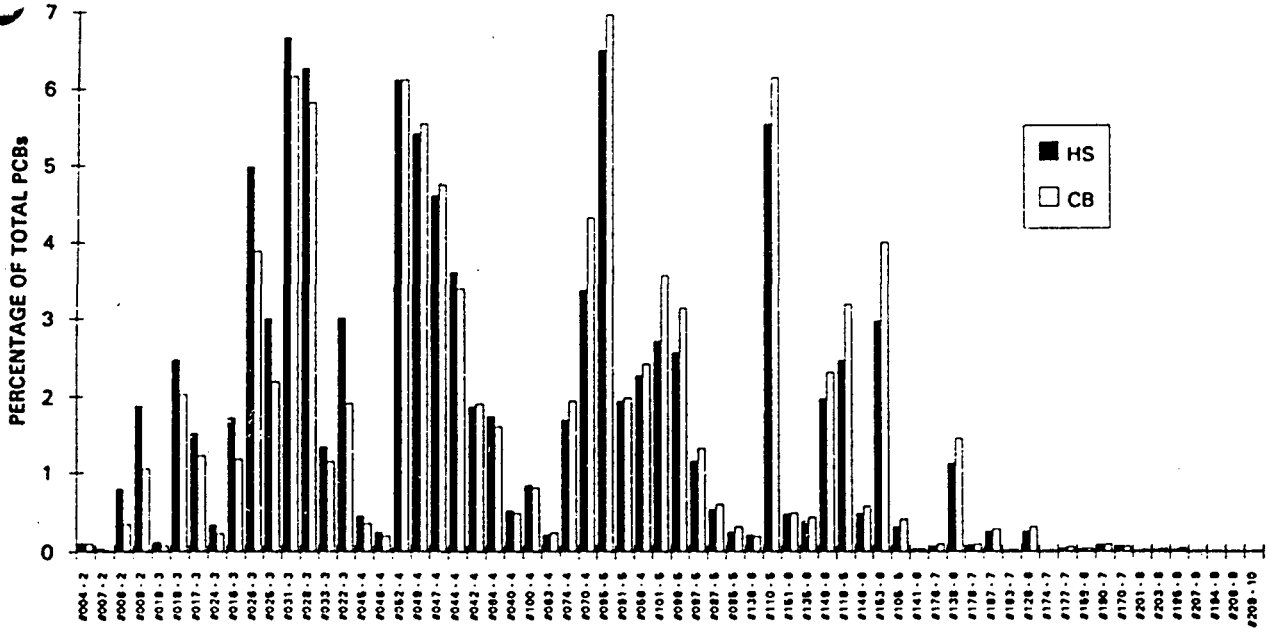

Figure 3(b) MUMMICHOGS

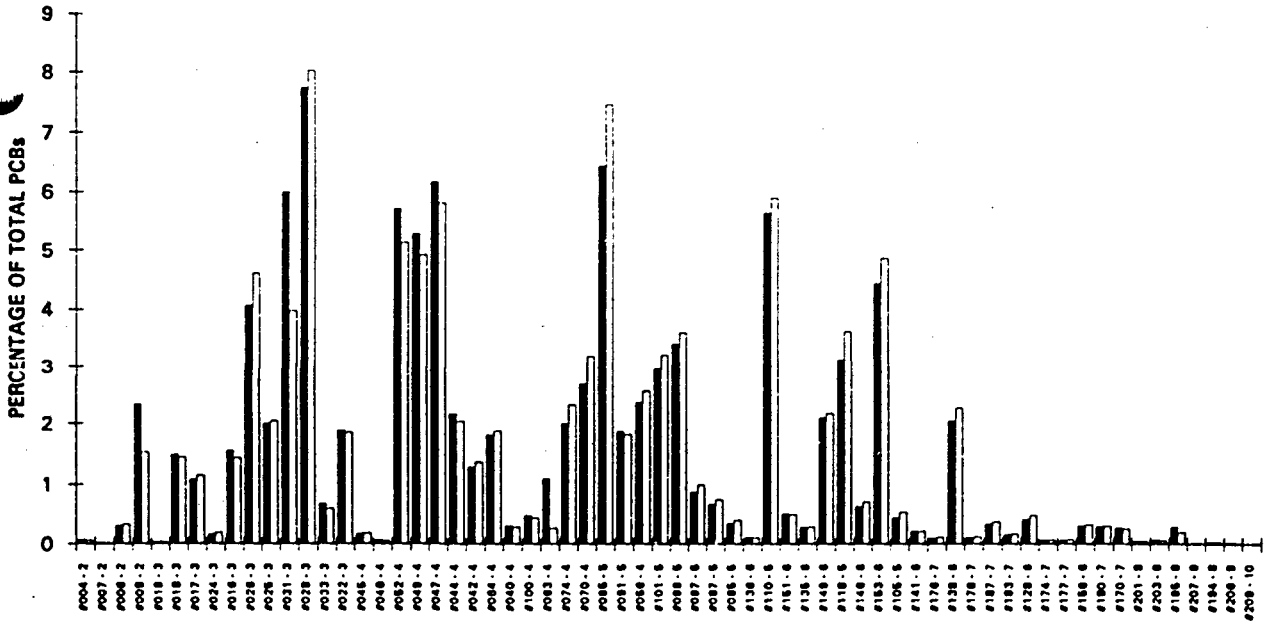

Fig. 3(b). Bar graph of mean percentage of total PCBs for congeners in mussels and mummichogs at HS and CB stations

Figure 3(c) SHRIMP

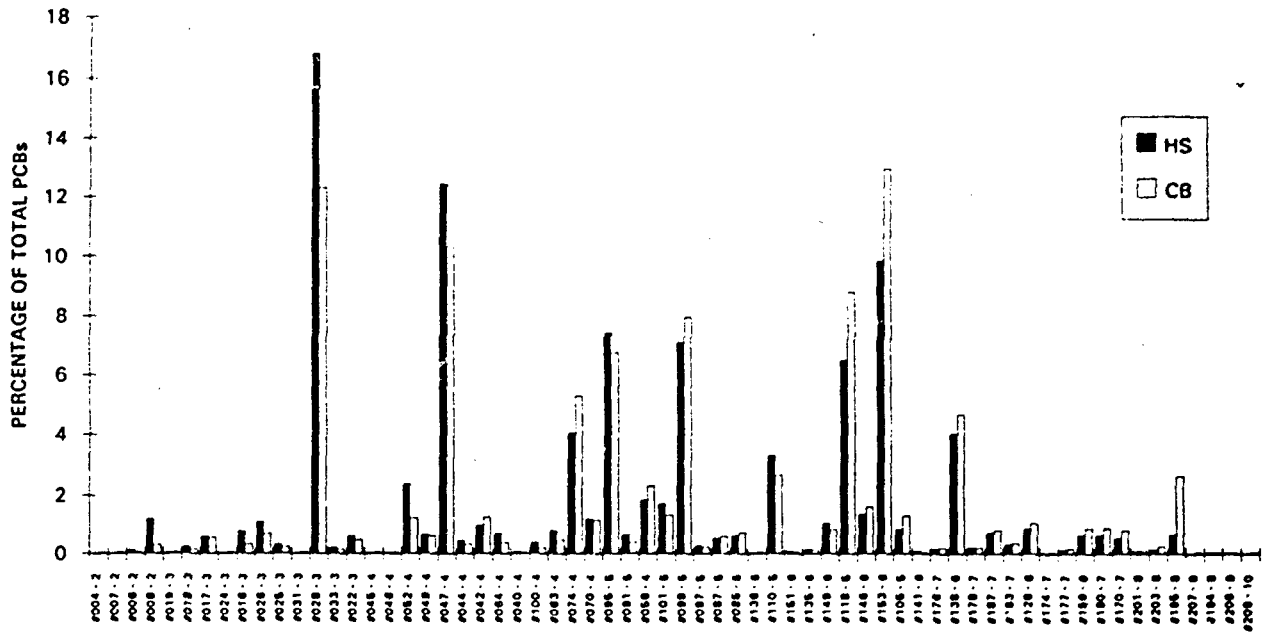

Figure 3(c) EEL

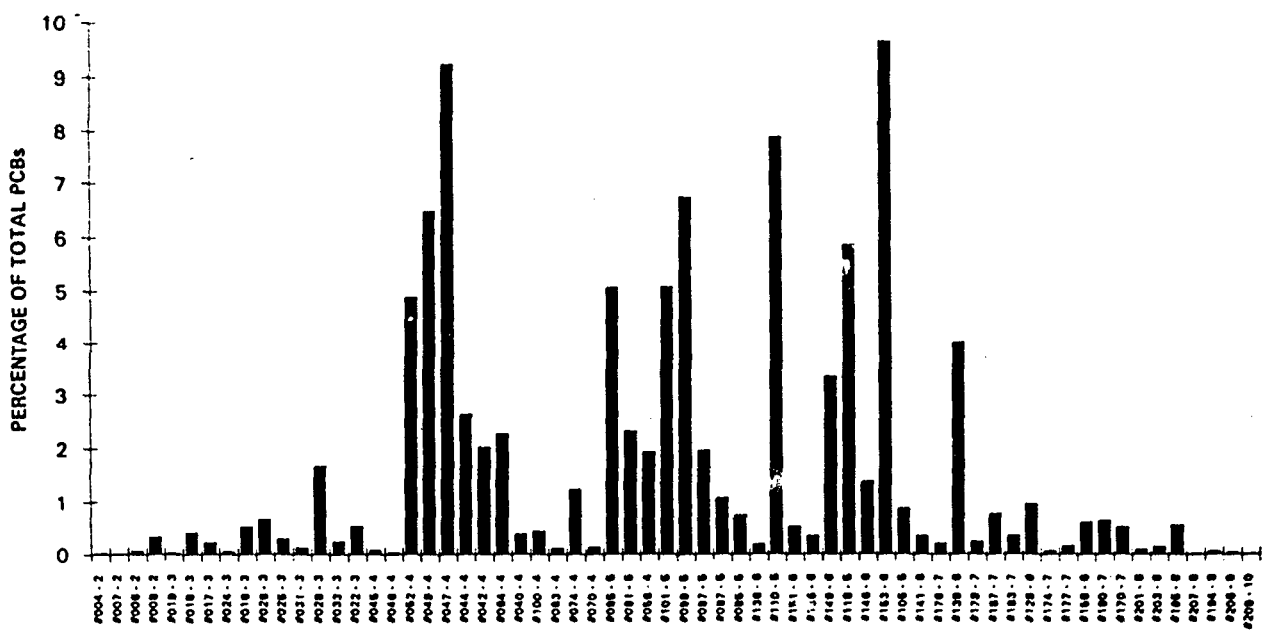

Fig. 3(c). Bar graph of mean percentage of total PCBs for congeners: in shrimp, at HS and CB stations, and in eels, at HSS station. *Integers* above BZ #'s on x axis refer to the number of chlorines in the dominant congener in peak

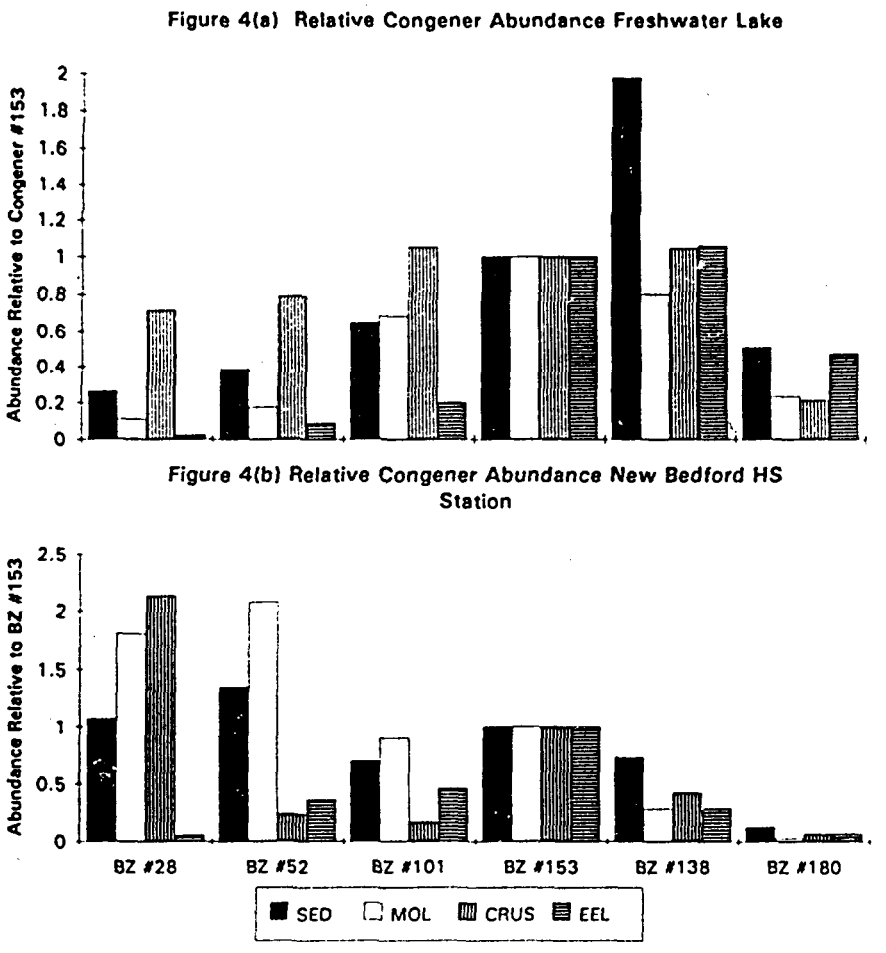

Fig. 4. (a) Abundance of selected congeners relative to BZ #153 in a freshwater lake (van der Oost *et al.* 1988). (b) Abundance of selected congeners relative to BZ #153 at New Bedford HS and HSS stations

were measured in three analytical replicates of 1993 samples of sediments, mussels, shrimp, and mummichogs from the HS and CB stations and in the eel from the HSS station (Table 1). The results of these analyses were compared using selective enrichment factors (SEFs) defined as the concentration of individual coplanar or mono-ortho congener divided by the total PCB concentration (see Methods). Comparisons of SEFs from samples and Aroclor® mixtures show the relative abundance of these toxic congeners. Sediment samples showed SEFs for mono-ortho substituted BZ 118 and 105 that were in the range of those found for the A-1242 and A-1254 standards (Figure 5). In contrast, graphs of SEFs for coplanar BZ 77 and 126 were higher in the HS sediment than in the Aroclor® standards.

Possible reasons for the higher SEFs for coplanar congeners in the HS sediment include: 1) the PCB mixture discharged by the plant that contaminated the surface sediments at the HS station contained a higher level of BZ 77 and 126 than found in Aroclors® analyzed in this study; 2) selective retention of these coplanar congeners occurred; or 3) a process or processes (*e.g.*, photodechlorination of higher chlorinated PCB congeners) resulted in the formation of coplanar congeners.

Selective enrichment factors in the mussel and mummichog were in the range of those found in the Aroclor® standards. SEFs were elevated for shrimp, probably because they metabolized congeners with vicinal hydrogens in the meta and para positions, but did not as effectively metabolize coplanar and mono-ortho substituted congeners (Figure 5). Due to the extensive P4501A-like metabolism of the eel, low SEFs for mono-ortho and coplanar congeners were expected. In eels, the SEFs for the coplanars BZ 77 and 126 were low, but unexpectedly, SEFs for BZ 118 and 105 were not below those found in A-42 or A-54 standards. Additional analysis of eels has confirmed these findings, but the reasons for it are unknown.

For the organisms evaluated in this study, the SEFs for BZ 77 and 126 were generally within the range of values from other studies (Table 4). Another study reported high SEFs for BZ 126 in some oyster samples (Sericano *et al.* 1992). The average

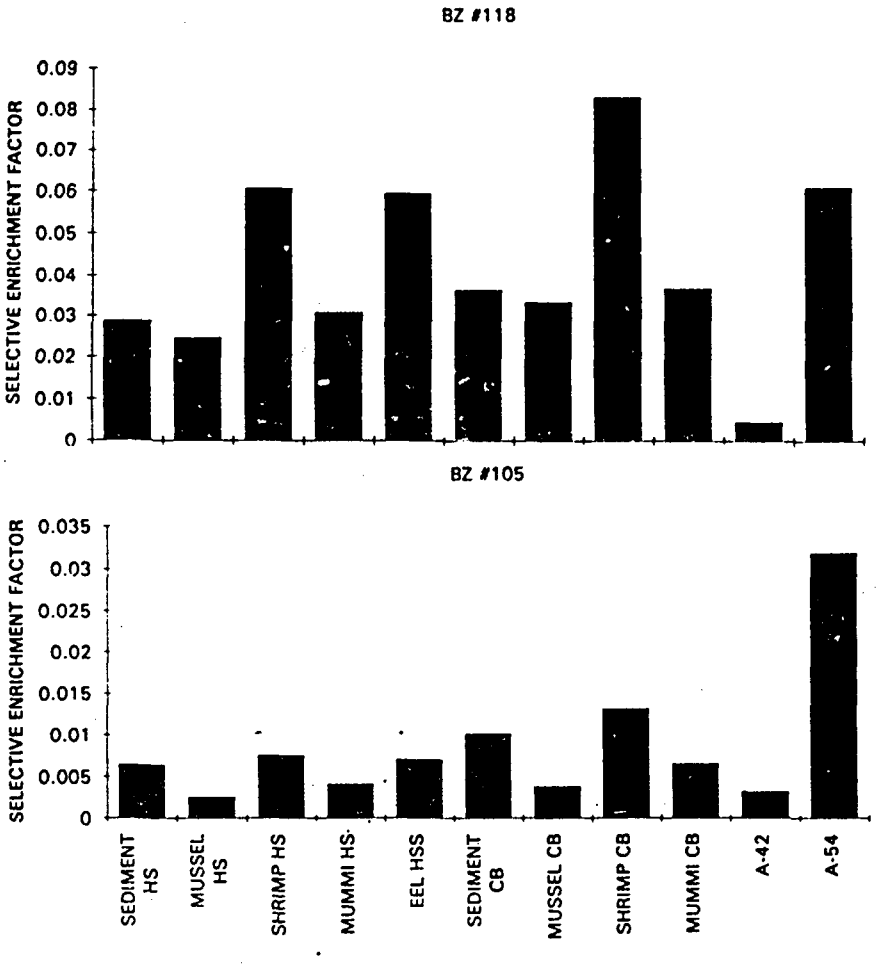

Fig. 5(a). Mean selective enrichment factors (SEFs) for mono-ortho congeners 118 and 105 for 1993 samples and Aroclor® standards.

SEFs for these oysters are about 25 times the SEFs calculated for ribbed mussels in the present study. However, the mean concentration of total PCBs present in the oysters was a factor of 1500 below those found in ribbed mussels in the present study. Possibly these large differences in exposure concentrations between these studies may have impacted bioaccumulation by changing the realtive exposure to dissolved and particulate bound PCBs. Alternatively, studies on the uptake and depuration of PCBs by filter feeding mollusks have shown that the coplanar congeners are more slowly depurated than the other congeners (i.e., those that contain ortho-chlorines) (Kannan *et al.* 1989; Sericano *et al.* 1992). Differences in depuration rates between coplanar and other PCBs may result in elevated SEFs if organisms were exposed to high levels of total PCBs for a time (i.e., after events like storms, which increase suspended particulate concentrations in the aqueous phase) followed by periods of lower exposure.

Comparisons of PCB congener patterns between organisms and surface sediment and water showed variations in organisms that could be attributed to differences in bioaccumulation and metabolism. The pattern in ribbed mussel, which does not metabolize PCBs, most closely matched the pattern in the sediment and water. PCB patterns in the mummichog were also similar to those in the water and sediment, but showed evidence of a small amount of P4502B-like metabolism. The pattern found in the shrimp was extensively altered due to the metabolism of congeners with vicinal hydrogens in the meta and para positions. This pattern is consistent with P4502B-like metabolism. The metabolic pattern in the eel showed extensive metabolism of lower molecular weight congeners with vicinal hydrogens in the ortho and meta positions, called a P4501A-like pattern. Eels also showed slight P4502B-like pattern alterations. SEFs for coplanar congeners indicated levels below those found in Aroclor® standards only for the eel. This finding is in agreement with expectations due to the P4501A-like metabolism found in this species. The SEFs for coplanar congeners in the shrimp were elevated due to their extensive metabolism of congeners with vicinal hydrogens in the meta and para positions and their lack of metabolism of the coplanar congeners. Overall, the SEFs for coplanar congeners in this study were in the mid-level of a range of SEFs from other studies.

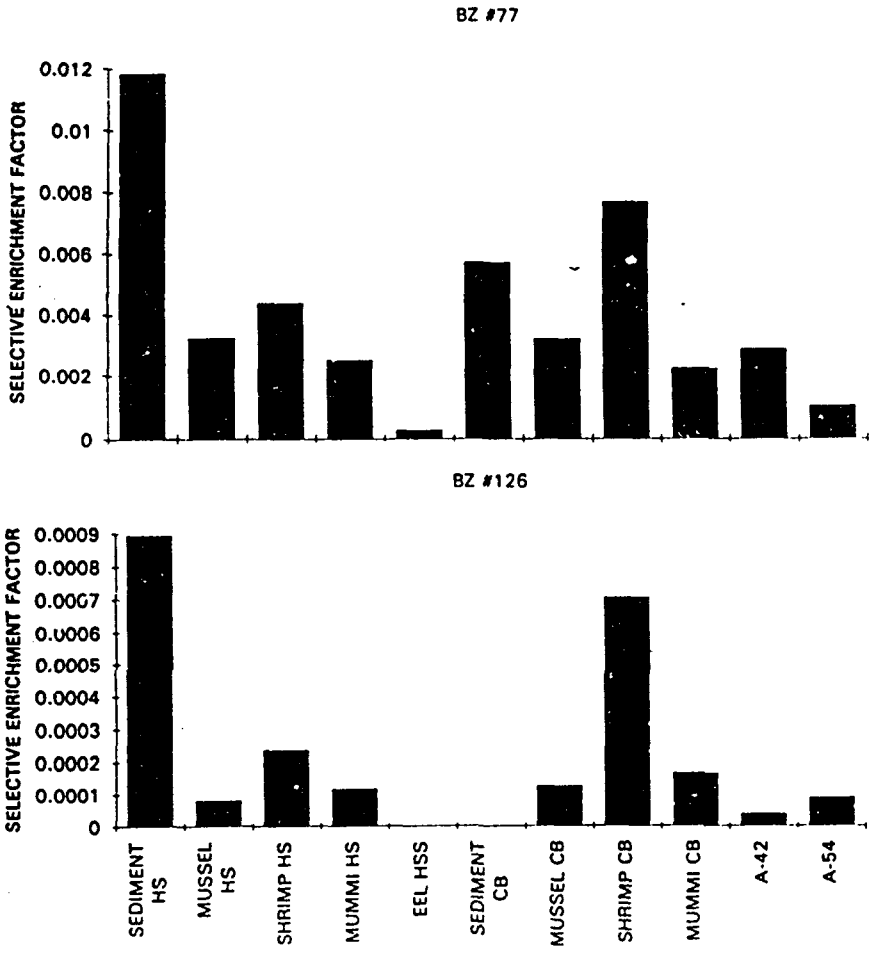

Fig. 5(b). Mean selective enrichment factors (SEFs) for coplanar congeners 77 and 126 for 1993 samples and Aroclor® standards

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