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The Biogeochemistry of Polychlorinated Biphenyls in the Acushnet River Estuary, Massachusetts

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Analyses of PCBs in sediment, water and organisms by high resolution gas chromatographic quantitative determination of individual chlorobiphenyls revealed marked compositional differences in segments of the Acushnet River estuary ecosystem. Dramatic differences in chlorobiphenyl compositions in tissues of lobster, crab and fish compared to compositions in industrial PCB mixtures released to the environment suggest that public health criteria based on PCB industrial mixture determinations should be revised. Predictions of bioconcentration based on K_{ow} of chlorobiphenyls are of limited accuracy for several chlorobiphenyls for which metabolism or membrane transfer selectivity are apparently the major determinants in some organisms. The importance of understanding the biogeochemistry of individual chlorobiphenyls as toxic compounds and as model compounds for studies of biogeochemistry of organic matter in aquatic ecosystems is discussed briefly.

An understanding of the biogeochemistry of organic matter in the contemporary marine environment is important in order to facilitate a greater understanding of: i) the C, N, S and P cycle; ii) interactions between organic compounds and biota, e.g. chemotaxis; iii) interpretations of molecular paleontology in ancient sediments and petroleum formation; iv) the inputs, fates and effects of pollutants as has been set forth in several reviews (1-6).

Our study reported herein primarily addresses this latter issue although we think that xenobiotic compounds can be used as valuable tracers of processes influencing most naturally occurring organic compounds. This is analogous to the use of anthropogenic releases of radioactive elements in the studies of the biogeochemistry of metals (7, 8). Polychlorinated biphenyls are useful compounds in this regard because of the wide range of solubilities and reactivities among individual chlorobiphenyls (9-12). In addition, there are continuing concerns about the adverse impacts of environmental burdens of PCBs with respect to human health and the viability of

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valuable living natural resources even though releases to the environment have been markedly reduced (12-14). This is the result, in part, of the preferential accumulation of PCBs in parts of contemporary environments such as landfills, toxic waste disposal areas, and aquatic sediments near prior effluent discharges, and the probability of release of PCBs back to other components of contiguous ecosystems long after the initial input to the environment (12, 15). For example, in estuaries there is a close dynamic coupling between the atmosphere/water/sediment/biota at relatively short time scales.

Most of the previous research on the biogeochemistry of PCBs has focused on the measurement of types of industrial mixtures (e.g. Aroclor 1016, 1242, 1254) by packed column gas chromatography, although it was recognized that several of the individial chlorobiphenyls had different types and intensities of biological effects (12, 14). Recent advances in analytical methodology, particularly glass capillary gas chromatography with electron capture detection (16, 17), and the more general availability of standards of individual chlorobiphenyls via impressive synthesis and verification analyses (e.g. 18) have made it feasible to undertake in-depth studies of the biogeochemistry of individual chlorobiphenyls (10, 17-20).

We report here on the distributions of several chlorobiphenyls in samples of water, sediment and biota of the Acushnet River Estuary - New Bedford Harbor, Buzzards Bay, Massachusetts, U.S.A. Our general objective is to gain information of generic utility in addition to providing specific data and interpretations of assistance to remedial action at this Superfund site. Our specific objectives in this paper are to: i) document the composition of individual chlorobiphenyls in biota normally harvested by commercial and recreational fishermen and discuss factors which could lead to the observed distributions and potential implications for public health standards for PCBs in fish; and ii) to investigate, in a preliminary manner, the adherence of bioconcentration of PCBs to predictions based on equilibrium assumptions and octanol/water (K_{ow}) partition coefficients (21, 22).

The study site is shown in Figure 1 which also presents a generalized composite of PCB concentrations in surface sediments based on analyses of hundreds of surface sediment samples by several different laboratories (23). Concentrations range from over 1 part per thousand (10^{-3} g/g dry weight) in segments of the inner harbor sediments to generally less than 1×10^{-6} g/g dry weight (ppm) in segments of the outer harbor area (Figure 1). The commercial harvesting of lobsters in the harbor area and of certain fish and bivalves in segments of the harbor is banned by the Massachusetts Department of Public Health because of PCB concentrations in excess of the 5 ppm wet weight edible tissue guidelines (24). Warnings have been posted to inform recreational and subsistence fishermen about the PCB pollution in these same areas. Descriptions of the history and severity of PCB contamination in the area leading to designation as a U.S. EPA Superfund site are available (24, 25).

Sampling and Methods

The dates and types of samples are given in Table I and locations of stations in Figure 1. Water samples were obtained using glass sampling devices (26, 30). Sediment samples were obtained by coring using a box core and careful sectioning (10). Biota were obtained by hand collection techniques or by net hauls, and precautions were taken to avoid contamination during sampling and dissection (27).

Water samples were stored in precleaned glass carboys and returned to the laboratory where they were filtered and extracted within 18 hours of sampling. Filters were Soxhlet extracted with hexane/acetone (1:1) for 24 hours and again with fresh hexane/acetone for an additional 24 hours. Water and pore water samples were extracted three times with CH_2Cl_2 in a separatory funnel. Extracts were dried over Na_2SO_4, concentrated to near dryness, and hexane was added with further concentration by rotary evaporation under vacuum until hexane replaced the CH_2Cl_2.

Sediments were Soxhlet extracted with acetone/hexane and the extract was concentrated (10). Biota samples were extracted by aqueous KOH digestion followed by extraction of non-saponifiable lipids into ethyl ether (28).

Column chromatography of the lipid or non-saponifiable lipid extracts on alumina over silica gel columns, or silica gel columns, to partially isolate polychlorinated biphenyls from other classes of compounds used procedures described previously (10, 28, 29).

Chlorobiphenyls were quantified by high resolution capillary chromatography using response curves generated for a standard of each chlorobiphenyl. A 0.32 mm i.d. x 30 M SE-52 column (J & W Scientific Company) installed in a Carlo Erba Model 2150 GC equipped with a split/splitless injector and Ni-63 electron capture detector, interfaced with a Columbia Scientific Instruments Supergrator 3 electronic integrator and a 30 m DB5 fused silica column (J & W Scientific Company) installed in a Hewlett-Packard Model 5840 GC equipped with Ni-63 electron capture detector and splitless injector were used for analyses. A Finnigan 4510 quadrupole mass spectrometer interfaced with a Carlo Erba 4160 gas chromatograph (0.32 mm i.d. x 25 M DB-5 bonded fused silica column - J & W Scientific), and interfaced with a Finnigan INCOS 2300 data system and standard EI/CI ion source and PPNICI accessory, was employed for GC-MS analyses to confirm that the compounds under study were chlorobiphenyls.

Duplicate analyses of homogenate samples agree within $\pm$ 20% based on replicate analyses of tissue homogenates of Mytilus edulis. All data are corrected for recovery of internal standards (chlorobiphenyls number 29 and 143), added at the time of extraction. Average recoveries were 80-95% for the different types of samples.

Results and Discussion

Figure 2 presents representative glass capillary gas chromatograms for two industrial Aroclor mixtures used in the area. Aroclor 1242 is very similar to Aroclor 1016 (not shown) which was the predominant mixture used, but for which we had no standard. Figures 3 and

Table I. Sampling Data (see Figure 1 for station locations).

Station	Date (year, month, day)	Sample Type*
67	830901	Ast. 67- 0.25 m^2 Sandia Hessler MKIII Box Core.
	790709	Pseudopleuronectes americanus (black back, winter flounder) 15-49 cm length, 3 each, fillets edible tissue homogenized; Lephopsetta maculata (sand flounder) 20-28 cm length, 3 each, fillets of edible tissue homogenized; Homarus americanus (lobsters) 2 each, tail and claw muscle tissue, and viscera analyzed for each individual; Neopanope taxons (green crab) 16 each, whole crabs homogenized.
233 approx. 1 mile south of Station 92 - not shown	800617	Homarus americanus (one each), tail and claw muscle tissue and viscera analyzed.
74	820922	Ast. 65 - 14-17 L composite of 2 L samples each hour during ebb and flood tides sampled with glass stoppered 2 L glass flask (29).
92	810724	Ast. 49 - 20 L sample obtained with glass Bodman type sampler (25).
48	780311	Clarks Point - Mercenaria mercenaria (hard shell clam, quahog) - pooled tissue samples, 2-10 individuals.
Fort Phoenix (intertidal area near hurricane barrier)	810504	Mytilus edulis (blue mussel) - homogenized pooled tissue, from 20-30 individuals.
Cleveland Ledge Light (eastern Buzzards Bay Station 227-not shown)	780320	Aequipectan irradians (scallops) homogenized pooled tissue from 10-15 individuals.

*Ast. means R/V Asterias Cruise No.

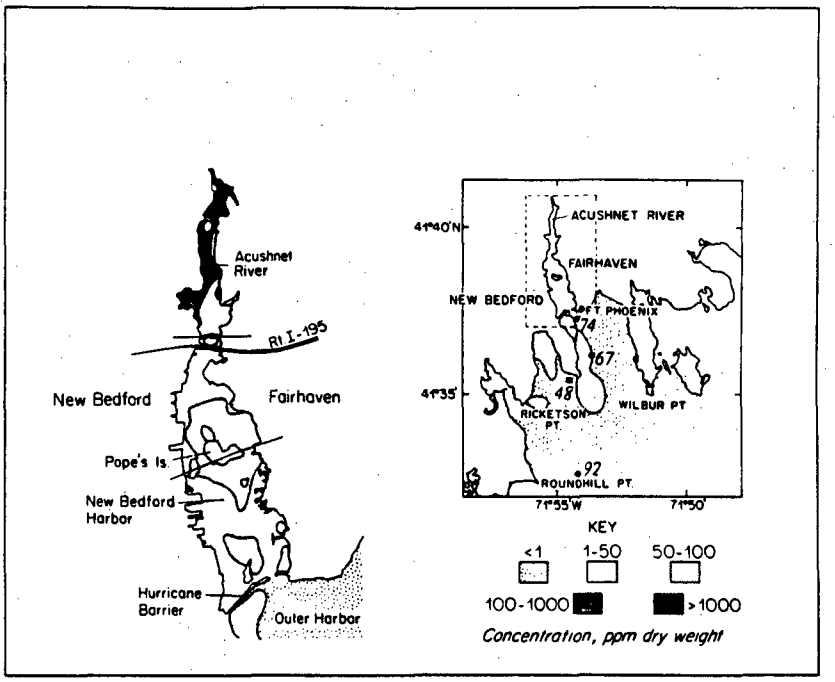

Figure 1. Study site location, station locations and contours of PCB concentrations in surface sediments.

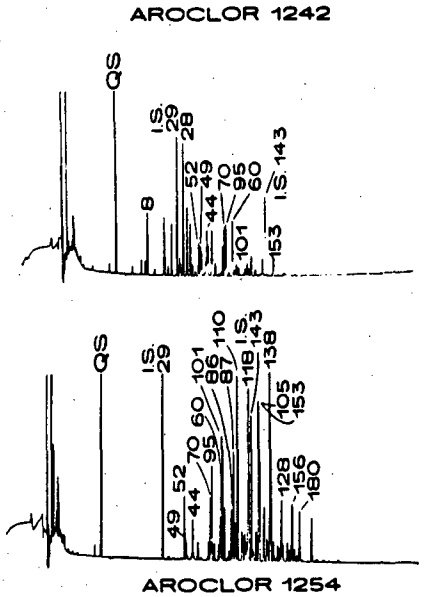

Figure 2. High resolution gas chromatograms of Aroclor 1242 and Aroclor 1254. QS refers to quantitation standard, IS refers to internal standard, and numbers are IUPAC numbers for chlorobiphenyls.

4 present glass capillary gas chromatograms of PCBs in lobster (Homarus americanus), a small crab (Neopanope taxons), surface sediments and tissue of Mytilus edulis (the common blue mussel). Table II gives the IUPAC numbers for chlorobiphenyls and corresponding chlorine substitution patterns as a key to the peaks identified in the gas chromatograms with IUPAC numbers. Figure 5 gives examples of packed column gas chromatograms of some of the same samples shown in Figures 2-4. The increased information content about PCBs in glass capillary gas chromagography is illustrated by comparison of Figure 5 with Figures 2-4.

The composition of the chlorobiphenyl mixtures present in the surface sediment, particulate matter in the water column, filtrate from water column samples, and mussels reflect a combination of Aroclor 1242 and 1254 mixtures of chlorobiphenyls although there are distinct differences in each sample type. The chlorobiphenyl composition of water column samples (gas chromatograms not shown) resembles that of the mussels and surface sediments, although further measurements of a larger set of samples may reveal small but significant differences in composition.

Examination of the gas chromatograms of PCBs in the samples of lobster and crab reveals the marked contrast in composition of PCBs in these types of biota samples and the composition of PCBs in water, sediment, bivalves and Aroclor mixtures. For example, the chlorobiphenyl composition of the lobsters are dominated by IUPAC chlorobiphenyl (CB) numbers 118, 153 and 138 while numbers 118 and 153 dominate the composition in the crab (Figure 2). Several more chlorobiphenyls, e.g. 28, 52, 44, 70, 95, 101, 110, are present in the mussel and sediment samples in addition to 118, 153 and 138 (Figure 2). PCBs in flesh of flounder species (L. maculata and P. americanus) were intermediate in composition between the lobsters and the mussels based upon examination of the gas chromatograms (not shown), i.e. 118, 153 and 138 predominate but not as much as in the lobsters. The possible reasons for these differences will be discussed below.

Table III contains data for concentrations of several individual chlorobiphenyls dissolved in the water or associated with particulate matter in the water column, and in surface sediments and pore waters. Concentrations of total PCBs estimated from these data are quite high for water, sediments and biota (2, 24). There are few quantitative data for individual chlorobiphenyls in water samples and this prevents extensive comparisons with other data of this type. The concentrations we report are within a factor of two to four of individual chlorobiphenyl data for a few water samples from the upper Hudson River (31). We have discussed water column and sediment data in more detail in two other papers (10, 30).

Concentrations of individual chlorobiphenyls in selected biota samples are presented in Table IV. The data for viscera and combined tail and claw muscle tissue from two different lobsters collected at the same location and one lobster collected at a second location provides an example of the variation in concentrations to be found for biota samples when comparing individuals. Concentrations in the viscera are expected to be higher than in muscle tissue because of the lipid rich nature of the viscera and the lipophilicity of the chlorobiphenyls.

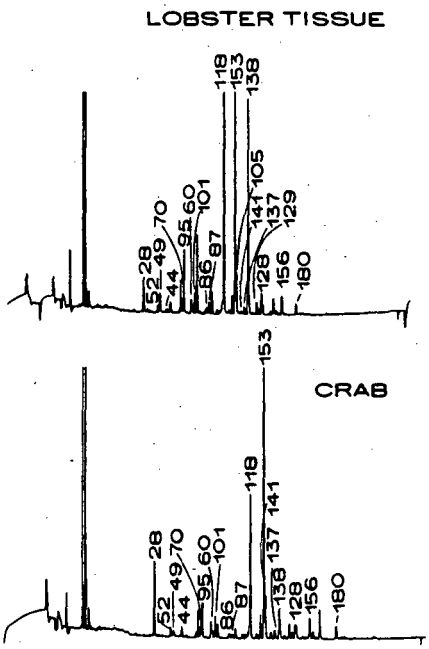

Figure 3. High resolution gas chromatograms of PCBs in lobster tail and claw mussel tissue and whole green crab (N. taxons). Also see legend Figure 2.

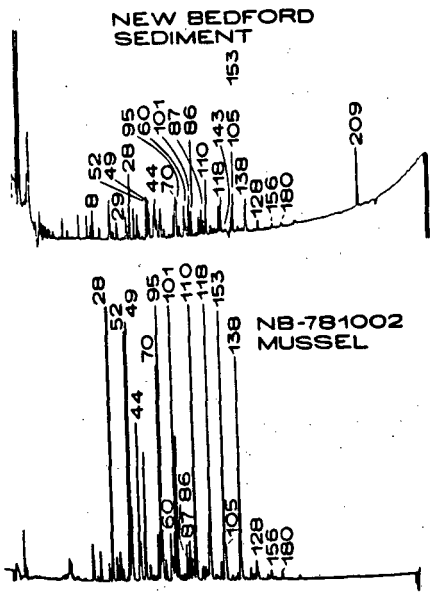

Figure 4. High resolution gas chromatograms of PCBs in surface sediment and mussel (M. edulis) tissue. Also see legend Figure 2.

Table II. Individual Chlorobiphenyls

IUPAC No.	Chlorine Substitution
28	2,4,4'
29	2,4,5
44	2,2',3,5'
49	2,2',4,5'
52	2,2',5,5'
60	2,3,4,4'
70	2,3',4',5
86	2,2',3,4,5
87	2,2',3,4,5'
95	2,2',3,5',6
101	2,2',4,5,5'
105	2,3,3',4,4'
110	2,3,3',4',6
118	2,3',4,4',5
128	2,2',3,3',4,4'
129	2,2',3,3',4,5
137	2,2',3,4,4'5
138	2,2',3,4,4',5'
143	2,2',3,4,5,6'
153	2,2',4,4',5,5'
156	2,3,3',4,4',5
180	2,2',3,4,4',5,5'

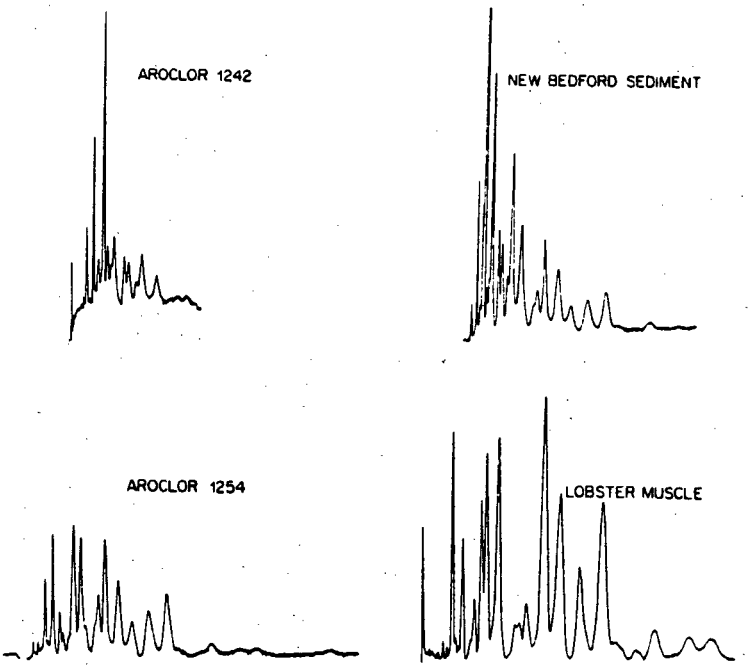

Figure 5. Packed column gas chromatograms of PCBs in representative samples from the study site.

Table IIIb. Concentrations of Chlorobiphenyls of Water and Particulates (x 10^{-12} g/g) and Sediment (x 10^{-9} g/g)

Sample	Station No.	IUPAC No. 60	153	141	138	128	156	180	194
Ast. 67 3-5 cm Sediment	67	300	540	58	610	130	90	75	0
Ast. 67 3-5 cm Pore Water	67	54	210	21	250	41	32	35	0
Ast. 65 Surface Water	74	.94	.46	.02	.47	.08	.02	.02	.02
Ast. 65 Bottom Water	74	.76	.37	.02	.50	.07	.04	.04	.02
Ast. 65 Surface Particulates	74	.67	1.3	.14	1.8	.30	.18	.19	.05
Ast. 65 Bottom Particulates	74	.42	.99	.13	1.9	.36	.24	.20	.05
Ast. 49 Surface Water	92	.06	.16	.02	.14	.04	.02	.02	.02
Ast. 49 Bottom Water	92	1.8	.68	.11	.76	.16	.13	.13	.02

Table IIIa. Concentrations of Chlorobiphenyls of Water and Particulates ($\times 10^{-12}$ g/g) and Sediment ($\times 10^{-9}$ g/g)

Sample	Station No.	IUPAC No. 28	52	49	44	70	95	101	87
Ast. 67 3-5 cm Sediment	67	1200	360	400	390	590	1700	650	270
Ast. 67 3-5 cm Pore Water	67	160	94	100	89	120	450	210	69
Ast. 65 Surface Water	74	9.5	2.1	2.4	2.1	1.8	5.7	1.4	.43
Ast. 65 Bottom Water	74	7.1	1.7	1.9	1.5	1.3	4.6	1.3	.35
Ast. 65 Surface Particulates	74	3.0	1.1	1.4	1.0	1.3	3.7	1.9	.58
Ast. 65 Bottom Particulates	74	1.8	0.75	.87	.71	.98	2.5	1.3	.44
Ast. 49 Surface Water	92	.18	.14	.14	.19	.12	.44	.29	.07
Ast. 49 Bottom Water	92	12	3.8	3.4	3.7	3.2	8.7	2.1	.66

Table IIIb. Concentrations of Chlorobiphenyls of Water and Particulates ($\times 10^{-12}$ g/g) and Sediment ($\times 10^{-9}$ g/g)

Sample	Station No.	IUPAC No. 60	153	141	138	128	156	180	194
Ast. 67 3-5 cm Sediment	67	300	540	58	610	130	90	75	0
Ast. 67 3-5 cm Pore Water	67	54	210	21	250	41	32	35	0
Ast. 65 Surface Water	74	.94	.46	.02	.47	.08	.02	.02	.02
Ast. 65 Bottom Water	74	.76	.37	.02	.50	.07	.04	.04	.02
Ast. 65 Surface Particulates	74	.67	1.3	.14	1.8	.30	.18	.19	.05
Ast. 65 Bottom Particulates	74	.42	.99	.13	1.9	.36	.24	.20	.05
Ast. 49 Surface Water	92	.06	.16	.02	.14	.04	.02	.02	.02
Ast. 49 Bottom Water	92	1.8	.68	.11	.76	.16	.13	.13	.02

Table IVa. Concentrations of Chlorobiphenyls of Selected Organisms ($\times 10^{-9}$ g/g wet wt.)

Sample	Station Location or No.	IUPAC No. 28	52	49	44	70	95	101	87
Bivalves									
M. edulis (mussel)	Ft. Phoenix	52	56	70	64	130	340	180	57
M. mercenaria (clam)	48	22	13	15	15	15	36	22	8.6
A. irradians (scallop)	Cleve. Ledge	2.7	1.1	12	9.3	1.5	5.7	4.9	0.3

Table IVb. Concentrations of Chlorobiphenyls of Selected Organisms ($\times 10^{-9}$ g/g wet wt.)

Sample	Station Location or No.	IUPAC No. 60	153	141	138	128	156	180	194	Percent Water
Bivalves										
M. edulis (mussel)	Ft. Phoenix	52	140	4.1	130	21	14	5.6	0.0	86
M. mercenaria (clam)	48	7.3	21	3.0	26	4.0	3.6	3.6	0.4	88
A. irradians (scallop)	Cleve. Ledge	0.7	5.2	0.4	5.8	0.7	0.2	0.4	0.0	84

Table IVc. Concentrations of Chlorobiphenyls of Selected Organisms
(x 10^{-9} g/g wet wt.)

Sample	Station No.	IUPAC No. 28	52	49	44	70	95	101	87
Crustacea									
N. texons (crab)	67	63	9.5	4.2	3.0	13	99	36	9.9
H. americanus									
Lob A Musc.	67	130	19	18	13	29	320	72	16
Lob A Visc.	67	2200	590	520	260	780	11000	2800	580
Lob B Musc.	67	71	6.3	3.2	2.7	9	160	18	5.8
Lob B Visc.	67	840	150	74	58	220	3600	760	160
Lob C Musc.	67	0.8	0	0	0	0	10	2.4	1.0
Lob C Visc.	67	360	36	36	41	58	1600	220	52
Ground Fish									
L. maculata (flounder)	67	180	290	270	240	300	1100	640	250
P. americanus (flounder)	67	21	10	21	11	83	200	150	84

Table IVd. Concentrations of Chlorobiphenyls of Selected Organisms
($\times 10^{-9}$ g/g wet wt.)

Sample	Station No.	IUPAC No. 60	153	141	138	128	156	180	194	Percent Water
Crustacea										
N. texons (crab)	67	22	220	6.0	54	15	25	25	1.5	N.C.*
H. americanus										
Lob A Musc.	67	50	260	6.2	250	48	44	31	2.5	82
Lob A Visc.	67	1300	13000	270	11000	2000	1800	1500	110	N.C.
Lob B Musc.	67	18	110	1.4	91	21	17	11	0.9	N.C.
Lob B Visc.	67	480	5500	65	4800	1000	890	800	59	N.C.
Lob C Musc.	67	1.0	29	0.3	26	3.9	3.7	3.7	0.4	N.C.
Lob C Visc.	67	150	2300	22	2200	440	310	290	34	N.C.
Ground Fish										
L. maculata (flounder)	67	150	770	72	750	120	100	84	0	82
P. americanus (flounder)	67	29	370	34	330	77	63	62	0	78

*N.C. = not calculated or measured.

The visual inspection of gas chromatograms (Figures 2-4) provides only a qualitative impression of the relative differences in composition of PCBs in the biota and their habitat. Therefore, we have calculated a parameter to provide a more quantitative means for evaluating the differences in composition. We have chosen a chlorobiphenyl, IUPAC No. 153, which is present in appreciable quantities in the industrial mixture of Aroclor 1254 and was identified as one of the major components in the samples of biota from the study area, and calculated the following ratio:

$$\frac{\left[\frac{\text{chlorobiphenyl i}}{\text{IUPAC No. 153}}\right]_{\text{sample}}}{\left[\frac{\text{chlorobiphenyl i}}{\text{IUPAC No. 153}}\right]_{\text{PCB standard Aroclor 1254}}} \qquad (1)$$

where i = any specific chlorobiphenyl.

Calculated ratios for several chlorobiphenyls are given in Tables V and VI. Values greater than 1.0 indicate that the chlorobiphenyl is enriched in that segment of the ecosystem being sampled, relative to No. 153. Values less than 1 indicate the opposite and values close to 1 indicate that the chlorobiphenyl has a biogeochemical behavior close to that of No. 153. There are groupings of chlorobiphenyls in all three categories (> 1, ≈ 1, < 1), (Tables V and VI).

The processes which change the chlorobiphenyl composition of the Aroclor type mixtures once they are discharged to the estuary are: i) volatilization - the lesser chlorinated biphenyls, e.g. tri- and tetrachlorobiphenyls, would be partitioned to the atmosphere to a greater extent than the more chlorinated penta-, hexa-, and heptachlorobiphenyls (12); ii) sorption - the complicated partitioning interactions between particulate matter, colloids, water in the water column, and surface sediments, can have a marked influence on compositions of chlorobiphenyl mixtures (10, 30); iii) microbial degradation - evidence to date suggests that lesser chlorinated biphenyls would be more rapidly degraded than the more chlorinated biphenyls (12); iv) selective uptake and metabolism by marine biota - the influence of this on compositions of chlorobiphenyls in our biota samples is discussed in the next several paragraphs.

The hypothesis has been advanced that changes in relative concentrations of lipid type compounds, when comparing aquatic biota and their habitat, can be explained in large part by an estimate of their tendency to partition into tissues which has been related to octanol/water partition coefficients - K_{ow}s (21, 22). Table VII presents tabulated data for K_{ow} and water to biota bioaccumulation concentration factors calculated from data in Tables III and IV. Representative data from Table VII are plotted in Figure 6 in the manner of Mackay (21) and Chiou (22), who have reviewed data on bioaccumulation of neutral hydrophobic compounds in aquatic biota. The solid line is the expected distribution of data based on Chiou's review (22) of predictability for equilibrium situations. Our data is different in an absolute sense than the data used by Mackay and Chiou, because they used concentrations in biota

Table Va. Concentration of Chlorobiphenyls Relative to No. 153

Sample	IUPAC No. 52	49	44	70	95	101	87
Ast. 67 3-5 cm Sediment	1.5	6.2	2.5	2.7	2.2	1.2	.85
Ast. 67 3-5 cm Pore Water	1.0	4.0	1.5	1.4	1.5	1.0	.55
Ast. 65 Water Surface	7.0	25	9.3	7.1	6.2	2.2	1.2
Ast. 65 Water Bottom	7.1	25	8.5	6.4	6.4	2.6	1.2
Ast. 65 Part. Surface	1.4	5.5	1.6	1.9	1.5	1.1	.57
Ast. 65 Part. Bottom	1.2	4.3	1.5	1.8	1.3	.93	.55
Ast. 49 Water Surface	2.1	7.3	4.1	1.8	2.0	1.9	.81
Ast. 49 Water Bottom	12	41	19	12	9.1	3.1	1.6

Table Vb. Concentration of Chlorobiphenyls Relative to No. 153

Sample	IUPAC No. 60	141	138	128	156	180
Ast. 67 3-5 cm Sediment	8.9	.77	1.2	1.5	1.1	1.4
Ast. 67 3-5 cm Pore Water	4.1	.70	1.2	1.2	.95	1.7
Ast. 65 Water Surface	24	.33	.70	.70	.29	.48
Ast. 65 Water Bottom	24	.42	.92	.76	.48	.80
Ast. 65 Part. Surface	6.2	.58	.99	.97	.63	1.1
Ast. 65 Part. Bottom	5.0	.68	1.3	1.5	1.1	1.5
Ast. 49 Water Surface	5.7	1.1	.93	1.8	.56	.84
Ast. 49 Water Bottom	3.9	1.1	1.1	1.4	1.2	1.9

Table VIa. Concentration of Chlorobiphenyls Relative to No. 153

	IUPAC No.						
Sample	52	49	44	70	95	101	87
Bivalves							
M. edulis	0.93	4.2	1.6	2.2	1.8	1.3	.69
M. mercenaria	1.4	6.0	2.5	1.7	1.2	1.0	.69
A. irradians	.48	19	6.2	.71	.79	.94	.10

Table VIb. Concentration of Chlorobiphenyls Relative to No. 153

	IUPAC No.					
Sample	60	141	138	128	156	180
Bivalves						
M. edulis	6.1	.21	.97	.94	.63	.40
M. mercenaria	5.7	1.0	1.3	1.2	1.1	1.7
A. irradians	2.1	.57	1.1	.81	.25	.80

Table VIc. Concentration of Chlorobiphenyls Relative to No. 153

	IUPAC No.						
Sample	52	49	44	70	95	101	87
Crustacea							
N. texons	.09	.16	.05	.15	.33	.17	.08
H. americanus							
Lob A Musc.	.16	.58	.17	.27	.86	.28	.10
Lob A Visc.	.09	.33	.07	.15	.57	.21	.07
Lob B Musc.	.14	.24	.09	.20	1.1	.17	.08
Lob B Visc.	.07	.11	.04	.10	.47	.14	.04
Lob C Musc.	.05	0	0	.05	.24	.08	.04
Lob C Visc.	.05	.13	.06	.07	.51	.10	.03
Fish							
L. maculata	.86	2.9	1.1	.95	1.1	.84	.54
P. Americanus	.07	.47	.10	.56	.40	.40	.39

Table VId. Concentration of Chlorobiphenyls Relative to No. 153

	IUPAC No.					
Sample	60	141	138	128	156	180
Crustacea						
N. texons	1.6	.21	.25	.44	.75	1.2
H. americanus						
Lob A Musc.	3.1	.14	.97	1.2	1.1	1.2
Lob A Visc.	1.6	.07	.86	.94	.88	1.1
Lob B Musc.	2.7	.07	.86	1.3	1.0	1.0
Lob B Visc.	1.5	.07	.89	1.2	1.0	1.4
Lob C Musc.	.48	.07	.91	.81	.81	1.3
Lob C Visc.	1.1	.07	.96	1.2	.81	1.3
Fish						
L. maculata	3.2	.64	.99	1.0	.81	1.1
P. americanus	1.3	.64	.91	1.3	1.1	1.7

Table VII. Octanol-Water Partition Coefficients and Bioaccumulation Concentration Factors on a Wet Wt. Basis of Selected Chlorobiphenyls

		Log BCF						
		(*M. edulis*)	(*M. mercenaria*)	(*H. americanus*)				(*P. americanus*)
IUPAC No.	Log K_{ow}*	Mussel	Clam	Lobster A		Lobster B		Flounder
				Muscle	Viscera	Muscle	Viscera	
28	5.69	3.74	3.66	4.14	5.37	3.87	4.95	3.35
52	6.09	4.42	4.06	3.95	5.44	3.47	4.86	3.67
49	6.22	4.47	4.08	3.88	5.35	3.13	4.50	3.95
44	5.81	4.48	4.11	3.80	5.09	3.11	4.44	3.72
70	6.23	4.84	4.17	4.20	5.63	3.69	5.07	4.66
95	6.55	4.78	4.07	4.75	6.28	4.44	5.81	4.56
101	7.07	5.10	4.41	4.70	6.28	4.10	5.72	5.01
87	6.37	5.12	4.54	4.57	6.13	4.13	5.56	5.29
60	5.84	4.74	4.16	4.72	6.15	4.28	5.71	4.49
153	7.75	5.48	4.83	5.75	7.46	5.37	7.08	5.90
138	6.96	5.42	4.81	5.78	7.39	5.42	7.12	5.85
128	6.96	5.42	4.81	5.78	7.39	5.42	7.12	5.33

*Brownawell and Farrington, 1985 (10) tabulated from several studies.

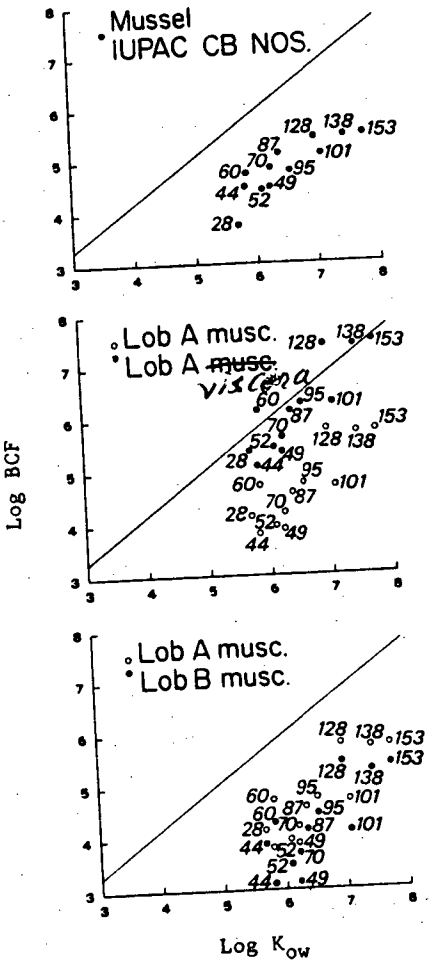

Figure 6. Plot of log K_{ow} vs. log BCF. Numbers are IUPAC numbers for chlorobiphenyls. Solid line is expected plot from Chiou (22) using his equation log (BCF) = 0.893 log K_{ow} + 0.607.

normalized to lipid concentrations. However, we have not done this for three reasons. First, we do not have lipid concentration data for these samples; unfortunately. Second, methods of lipid determination are operational in practice, and standardized or even common methodology for "total" lipid measurements are not commonly used. Third, incorporation of lipid values does not alter the expected linear correlation in a log-log plot and thus the lipid data are not essential to our interpretations and discussion which follow.

We have included examples for M. edulis and H. americanus muscle and viscera from an individual organism and H. americanus muscle from duplicate samples at the same station and sampling time to indicate the range of variability for these types of plots. The viscera data plot closer to the region of the theoretical line because of the lipid rich nature of viscera relative to muscle and whole mussel tissue. The data for the mussel are arranged in a more linear fashion or more tightly grouped around a linear plot than the lobster data. Our data agree with those reviewed by MacKay (21) and Chiou (22) in that K_{ow} provides an estimate of bioconcentration for neutral hydrophobic molecules.

There appear to be some significant departures from linearity in the log BCF-log K_{ow} plot, but we cannot be certain because of the limited set of data. Also, we must caution that our assessment is only preliminary in this regard because we have assumed for purposes of this paper that our data are representative of the field situation over a period of time sufficient for "equilibrium" to be approximated closely. There are very few water measurements of this type available and certainly more are needed to test these assumptions of equilibrium. The few measurements we have made over the last few years have indicated that fluctuations of a factor of 2 to 4 may occur in total PCBs in the water column in this area. Storm conditions may be an exception to this, but no data are available. Biota samples in this study were not obtained immediately after a storm. Repeated measurements of total PCBs in lobsters from this area by Massachusetts agency laboratories using packed column gas chromatography (23, 32), and less voluminous (unpublished) data from our laboratory by both packed column and glass capillary gas chromatography, suggest that concentrations of PCBs and more importantly relative amounts of chlorobiphenyls, do not fluctuate temporally by a factor of more than 4 in a given area, when averaging over a number of organisms. Data for the mussel M. edulis at a station near Ft. Phoenix (Figure 1) on the hurricane barrier, remained within a factor of 3 for the period 1978 to 1981 (25), encompassing the sampling period for most of the samples being considered.

There can be errors in estimation or measurement of K_{ow} values that could cause some departure from linearity in these plots by as much as factors of 2 to 4 (less than a log unit or factor of 10), which is much less than some of the departures from linearity for a few chlorobiphenyls. Chiou (22) has noted that non-steady state exposure concentrations, short exposure times, storage of compounds in non-lipid portions of tissues, and metabolism by organisms will lead to discrepancies between predicted and measured BCF-K_{ow} relationships.

We think that factors other than non-equilibrium conditions explain much of the departure from prediction of BCFs using K_{ow}'s. There is evidence to suggest selective metabolism of chlorobiphenyls in certain species (14) and it has been shown that some species of fish and crustacea contain mixed function oxidase activity that is probably capable of metabolizing certain biphenyls at different rates (33). Furthermore, the mixed function oxidase activity in selected species of fish and crustacea tested has been induced to higher levels of activity by exposure to xenobiotics while, thus far, only low levels of activity can be demonstrated in bivalves (33). This is interesting as it is consistent with our finding that the mixture of chlorobiphenyls in bivalves more closely approximates a mixture of Aroclors than does the mixture of chlorobiphenyls in lobster, crab and flounder.

Duinker and co-workers (20) noted results similar to ours for comparison of PCBs in Crangon sp. (a shrimp) and PCBs in its habitat. Ballschmitter and co-workers have published detailed analyses of chlorinated hydrocarbon pesticides and PCBs in various individual fish from different habitats, usually well removed from the immediate vicinity of point source inputs (34). The glass capillary gas chromatographic patterns they report are generally similar to those we have found for fish from our study site in that they depart significantly from an Aroclor 1254 or 1242 type mixture. There are some differences in detail among species in our study and in their studies, that are as yet unexplained, but could be related to specificity of uptake or metabolism by biota. For example, there is the marked difference of the presence of chlorobiphenyl No. 138 in the lobster and its absence in appreciable amounts in the small green crab (Figure 3), even though both are crustacea and inhabit the same benthic region.

This may be due to specificity of metabolism of certain chlorobiphenyls by species specific enzyme systems.

There are as yet no conclusions nor even a consensus hypothesis as to which types of chlorine substitution patterns govern ease of metabolism by enzymes. Some researchers favor the hypothesis that chlorine substitution at the 4,4' or combinations at the 3,5; 3'5' positions of the biphenyl molecule block ease of enzymatic epoxidation of easily accessible vicinal carbons (14, 35). Other researchers suggest that 2,2' or 6,6' substitutions or some combination reduce coplanarity of the biphenyl rings thereby causing a steric hinderance to enzymatic activity or transfer across membranes (14, 36). Our data on individual chlorobiphenyls in biota does not yet encompass a wide enough range of chlorobiphenyl structures to test these hypotheses which must be tested rigorously with isotopically labeled chlorobiphenyls in carefully controlled experiments in any event.

General Discussion

It should have been obvious from first principles and certainly reinforced by the advent of several sets of data by glass capillary gas chromatography, that packed column gas chromatographic analyses do not provide adequate information about marked compositional differences between species of biota and between species and their habitat. More detailed compositional information is

important for understanding factors controlling the biogeochemical cycle of PCBs in the environment; more specifically aquatic ecosystems including estuaries. Our data have demonstrated this for the case of a severely polluted coastal estuarine area, both for the data discussed herein and for pore water, sediment and water column data presented and discussed elsewhere (10, 30).

Parameters such as solubilities and K_{ow}'s provide a first order predictive capability concerning bioconcentration in biota, but departures from predicted distributions due to kinetic factors involved with uptake and release and metabolic transformations have a marked influence. While equilibrium considerations are a good starting point, it is necessary to move beyond these to dynamical considerations to provide better general knowledge for such questions as risk assessment in waste disposal to the ocean, and clean-up of severely polluted estuarine coastal areas. There has been some progress, but more research concerned with kinetic factors and dynamics in biogeochemical cycles of pollutant organics is needed.

The most important message contained in our glass capillary gas chromatographic analyses of PCBs, and those of others, is that public health standards are probably outdated. The edible portions of fish and lobsters in samples from our study area contain mixtures of PCBs markedly different in composition compared to industrial Aroclor mixtures used in most experiments assessing adverse effects on animals. The 2 to 5 ppm (wet weight) total PCBs guideline may be overprotecting or underprotecting public health. This dual edge sword problem could cut either way and needs evaluation in the public health research sector. Some attention has been focused on this issue in the European community (37). Since it has been established that individual chlorobiphenyls can have a range of potency in regard to biological activity (14), it is important to understand the biogeochemical cycles of individual chlorobiphenyls as well as the bulk mixture, for which there is a significant amount of information in regard to first order environmental behavior (12, 14).

Furthermore, as we emphasized in the introduction, PCBs can serve as model compounds for studying several aspects of processes active on a wide range of organic compounds. The full potential of this approach can be realized only via experiments and field programs involving determinations and interpretations of a range of types of individual chlorobiphenyls.

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