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Environmental Toxicology and Chemistry, Vol. 9, 1990

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Environmental Chemistry

PCB MOVEMENT, DECHLORINATION, AND DETOXICATION IN THE ACUSHNET ESTUARY

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(*Received* 8 *August* 1989; *Accepted* 22 *December* 1989)

Abstract – Congener-specific analyses of the PCBs in Acushnet Estuary (New Bedford, MA) sediments and waters were undertaken to identify the PCB alteration and transport processes occurring in coastal marine sediments. These analyses indicated that (a) the PCBs deposited at the sediment sites sampled had originally consisted of Aroclors 1242 and 1254, in widely varying proportions; (b) these PCBs had undergone vertical movement within the sediments, rather than remaining stratified, but not horizontal translocation between sites; (c) they had also undergone extraction into the water, albeit at declining rates, with some consequent changes in composition but (d) the major compositional change was caused by a previously unreported type of reductive dechlorination process, designated Process H. This presumably anaerobic microbial process, subsequently identified at several other locations as well, had selectively removed non-*ortho* chlorines from most of the higher PCB congeners, especially those associated with acute toxic effects. It appeared to have begun near the upper end of the estuary and not yet reached its lower portions, thus providing a marker for tracing the origin of the PCBs in estuarine water samples.

Keywords – Polychlorinated biphenyl PCB Dechlorination Detoxication New Bedford

INTRODUCTION

The polychlorinated biphenyls (PCBs) are a group of relatively persistent environmental contaminants with a unique combination of chemical characteristics. The commercial PCB products (e.g., Aroclors) that were originally released each consisted of a complex mixture of isomers and homologs (generically referred to as "congeners") that were produced in fixed and virtually invariant relative proportions by the manufacturing process used [1]. However, these individual PCB congeners differ greatly in their patterns of relative susceptibility to the various physicochemical and biological alteration processes that may occur in specific environmental compartments. This means that the congener distribution in an environmentally altered PCB specimen will present a record of all of the different alteration processes to which that particular specimen of PCB had been subjected since its release, or, alternatively, of all the different PCB-altering environmental niches through which it had passed.

To be able to interpret such records it is helpful, though not essential, to know which of the commercial Aroclors were originally present. More important is the knowledge of how the various possible interphase transfer and biodegradative processes affect congener distribution. This can be obtained through laboratory studies of Aroclor alteration by known physical, chemical or biological agents, and field studies aimed at finding out which alteration processes, whether previously known or unknown, are actually occurring in the environment.

In the recent past, laboratory studies have revealed distinctive patterns of PCB congener removal for more than two dozen strains of aerobic, terrestrial, PCB-degrading bacteria [2] and for the two cytochrome P-450 isozymes commonly involved in PCB metabolism in higher animals [3,4]. Previous field studies have indicated the occurrence of at least seven distinguishable types of reductive dechlorination, presumably mediated by various strains of anaerobic bacteria in aquatic sediments [5–7]. One of these reductive dechlorination processes was recently reported to have been duplicated under anaerobic culturing conditions [8], and further experimental studies of this and other anaerobic dechlorination systems are now underway in several laboratories. None of the previous studies, however, have indicated what sorts of intercompartment transfer or intracompartment deg-

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non-*ortho* (i.e., *meta* and *para*) chlorine atoms present per biphenyl nucleus. The latter parameters were determined by adding up the products of mole fraction times the number of *ortho* (i.e., 2-, or 6-) or non-*ortho* (i.e., 3-, 4-, or 5-) chlorine atoms for each of the observed PCB peaks.

Calculation of original Aroclor ratios and solubilization losses

These calculations were carried out by an "indicator peak" procedure. This presumes that we can identify in the sample chromatograms at least two peaks, A and B, whose ratio can serve as an indicator of the ratio of the Aroclors originally present, and whose levels relative to all other PCBs as an indicator of evaporative and elutriative loss. The first presumption requires that peaks be identified which, after correction if appropriate, can be considered to be unaffected by any chemical transformations underway. The second requires that data be included on the response of the indicator peak levels to whatever combination of evaporative and elutriative weight loss processes obtain for the tideflat sediments. Fortunately, observations in our laboratory (data not given) and elsewhere [16] have shown that the changes in PCB congener distribution induced by extraction into water are almost identical to those induced by evaporation, so that it is not necessary to establish the relative contribution of these two processes to the total evaporative/elutriative weight loss, and the data from the evaporation experiments can be used to relate compositional change to weight loss.

To make the necessary calculations, we may define the following parameters:

- a fraction Peak A in sample
- a_1 fraction Peak A in Aroclor 1242 standard
- a_2 fraction Peak A in Aroclor 1254 standard
- b fraction Peak B in sample
- b_1 fraction Peak B in Aroclor 1242 standard
- b_2 fraction Peak B in Aroclor 1254 standard
- c_1 relative effect of evaporative loss on A, that is, $\Delta a/a\Delta y$
- c_2 relative effect of evaporative loss on B, that is, $\Delta b/b\Delta y$
- c relative effect of evaporative loss on A/B ratio
- x original ratio of Aroclor 1242 to Aroclors 1242 + 1254
- y weight fraction of original PCB lost by evaporation or other processes (i.e., true solution) having a similar effect on PCB congener distribution

Simple material balances indicate that:

$$a = [(1 - c_1 y)/(1 - y)][a_1 x + a_2(1 - x)] \quad (1)$$

$$b = [(1 - c_2 y)/(1 - y)][b_1 x + b_2(1 - x)] \quad (2)$$

$$\frac{a}{b} = \frac{(1 - cy)[(a_1 - a_2)x + a_2]}{[(b_1 - b_2)x + b_2]} \quad (3)$$

Examination of the chromatograms (described below) indicated that congeners 26-34 and 236-34 were probably not being significantly formed or destroyed by the transformation processes at work in the sediments examined, and hence that Peak 39 (originally mainly 26-34 CB, with a little 236-4 and 234-2) and Peak 61 (originally mainly 236-34 CB, with a trace of 34-34) could be used as indicators for Aroclors 1242 and 1254, respectively. The only correction applied was that the 234-2 in Peak 39 was presumed to be originally present at the 10% level, but then to decline in proportion to any observed decline in Peak 50 (23-34 plus a little 234-4). For Peaks 39 as "A" and 61 as "B" we were able to evaluate the constants in Equations 1 through 3 from Aroclor 1242 and 1254 standards, and from the evaporative weight loss data as follows: a_1, 0.03160; a_2, 0.00789; b_1, 0.00743; b_2, 0.0895; c_1, 0.43; c_2, 0.1; c, 0.382.

Using these values, Equations 1 through 3 were solved for x and y by a process of successive approximations. Examination of the sensitivity of the solutions to variations in the observed parameters a and b indicated that for the average composition encountered ($x = 0.70$, $y = 0.18$) a conceivable $\pm 10\%$ error in the measurement of a/b (i.e., the corrected Peak 39/Peak 61 ratio) would result in only a ± 0.02 error in x; however, a $\pm 10\%$ error in a (i.e., the ratio of Peak 39 to total PCB) would produce a ± 0.12 error in y.

Calculation of indices of dechlorination

As indicators of dechlorinative loss affecting Aroclors 1242 and 1254, we selected the dechlorination-sensitive Peak 50 (23-34 plus a little 234-4 CB) and Peak 58 (234-25 plus traces of 2346-4 and 235-35 CB), respectively. Changes in these peaks were determined by reference to the same indicator peaks used above, and were expressed in terms of half-losses, thus:

Half-loss (P50)

$$= -\log_2 \frac{(\mathrm{P50}_{\mathrm{sample}})/(\mathrm{P39}_{\mathrm{sample}})}{(\mathrm{P50}_{\mathrm{standard}})/(\mathrm{P39}_{\mathrm{standard}})} \quad (4)$$

Half-loss (P58)

$$= -\log_2 \frac{(\mathrm{P58}_{\mathrm{sample}})/(\mathrm{P61}_{\mathrm{sample}})}{(\mathrm{P58}_{\mathrm{standard}})/(\mathrm{P61}_{\mathrm{standard}})} \quad (5)$$

Most of the half-loss calculations reported in Table 1 were derived from measurements on rela-

Table 2. Results of analyses of Acushnet Estuary water samples collected in December 1986

Estuary section[a]	Site no.[a]	PCB/water (μg/L) Total	On filter	Half-losses[b] P50,P58
Sediment study area:	1A	0.5	0.18	1.0
	1	1.7	0.16	2.0
	1 (rep)	1.5	0.15	2.0
	1B	1.1	0.10	2.0
	1C	0.7	0.8	1.5
	2	0.4	0.23	1.0
Between the bridges:	4	0.27	0.10	0.5
	4 (rep)	1.0	0.07	2.0
	5	0.36	0.07	0.5
	6	1.5	0.21	2.0
Inner harbor:	9	0.4	0.07	1.0
Outer harbor:	11	0.27	0.05	0.0
	12	0.4	0.06	2.0
	15	0.12	0.03	0.0

[a]Estuary sections and water-sampling sites as shown on Figure 1.
[b]Mean of $-\log_2$ fractional retention of Peak 50 (23-34 CB), as referenced to Peak 39 (26-34 CB), and of Peak 58 (234-25 CB) referenced to Peak 61 (236-34 CB), rounded to nearest half-log unit.

ative. At two of the sites, however, where the samples taken consisted of soft, black, organic muds, a positive, but unknown, rate of sedimentation could be presumed.

Results of sediment and water analyses

Figure 2 indicates GCs for Aroclor 1016, 1242 and 1254 standards, for an evaporated Aroclor 1242 specimen, and for two sediment samples that both showed progressive diminution of the peaks to the right of Peak 61 ("high-end drop-off") and extensive, though not quite identical, alterations of the relative intensities of the peaks between Peaks 21 and 58, inclusive, and of Peak 7. These two altered patterns were designated H and H′. One of these samples (19B) also indicated a progressive diminution of the peaks to the left of Peak 21 ("low-end drop-off"). All of the other sediment and water samples examined gave patterns that could be regarded as combinations of those for Aroclors 1242 and 1254, modified to varying extents by whatever processes were responsible for the "high-end" and "low-end" drop-off patterns shown in Figure 2.

The "low-end drop-off" in GC pattern was obviously similar to that shown by the evaporated Aroclor 1242 specimen of Figure 2, or described in more quantitative form in Figure 3. Had this drop-off arisen from aerobic microbial biodegradation [2] we would have expected to see relative persistence for Peaks 10, 16, 17 and 39, which are given by PCB congeners (26-2, 26-3, 26-4 and 26-34 CB) that are relatively resistant to microbial 2,3-dioxygenase attack. Had it arisen from aerobic eucaryotic metabolism, we would have expected to see relative persistence for Peaks 24, 46 and possibly 34, which are given by PCB congeners (24-4, 245-4 and 24-24 CB) that are relatively resistant to cytochrome P-450 monooxygenase attack. Evidently, this low-end drop-off arose from a simple interphase transfer process, such as evaporation of volatiles or extraction of soluble components into the water column [16]; both processes indicate similar patterns of congener depletion.

The "high-end drop-off" pattern alterations of types H and H′ involved complex sets of congener depletions and congener augmentations that are portrayed by the GC-MS pattern of Figure 4, and more fully described in Table 3. Patterns H and H′ (Fig. 2) differed only in the degree of their effects on Peaks 37, 38, 42, 45 and possibly 27.

The results of the various upper Acushnet Estuary sediment analyses are summarized in Table 1. This shows that the samples analyzed consisted of sands, gravel and biogenic muds in various proportions, as already indicated, but with no obvious connection between sediment texture and PCB level. Most samples contained high levels of total extractable "oil and grease," (average for all sites, 13,000 ppm) of which the PCBs constituted 7.8%, on the average. The PCBs present consisted mostly of tri-, tetra- and pentachlorobiphenyls, with only 1 to 3% of hepta- and higher CBs (data not shown) and highly variable levels of dichlorobiphenyls.

Table 3 continued.

DB-1 peak no.	Cl's per BP	PCB congeners in peak[a]	Relative change observed[b]	Suggested dechlorination process[c]
64	6	2356-25	±	
65	6	235-236	±	
66	5	345-25	−−	345-25 → 25-35
66	6	2346-25	>−−	2346-25 → 246-25[d]
67	5	235-34	−	235-34 → 235-3[d]
67	6	2356-24	>++	2356-234 → 2356-24[d]
68	5	345-24	>−	345-24 → 24-35[d]
69	5	245-34	−	245-34 →→ 25-3[d]
69	6	236-245	±	
71	6	2356-23	±	
71	5	2345-4	>−−	2345-4 → 235-4 → 25-4
72	6	235-235, 2346-23	±	
73	6	235-245	±	
74	5	234-34	−−−−	234-34 →→ 24-3[d]
74	6	234-236	−−−	234-236 → 236-24[d]
75	6	245-245	±	
77	6	2345-25	−−−	2345-25 → 235-25
78	7	2356-236	±	
79	6	234-235	−−−	234-235 → 235-24
80	6	2345-24	−−−	2345-24 → 235-24
81	7	2346-236	−−	2346-236 → 246-236
82	6	234-245, 2356-34, 236-345	−−	234-245 → 245-24[d]
83	6	2346-34	−−	2346-34 → 246-34[d]
84	6	2345-23	−−	2345-23 → 235-23
88	7	2356-245, 2345-246	±	
89	6	234-234	−−−	234-234 →→ 24-24[d]
90	7	2346-245	−−−	2346-245 → 245-246[d]
91	6	245-345	−	245-345 → 245-35
92	7	23456-25	−−	23456-25 → 2356-25
93	7	2345-236	−−	2345-236 → 235-236
94	7	2356-234	−−	2356-234 → 2356-24[d]
95	6	2345-34	−−	2345-34 →→ 235-3[d]
95	7	2346-234	−−−	2346-234 →→ 246-24[d]
97	6	234-345	>−−	234-345 →→ 24-35[d]
102	7	2345-245	−−	2345-245 → 235-245
106	7	2345-234	−−	2345-234 →→ 235-24
107	7	23456-34	−−	23456-34 → 2356-34

[a]Underline indicates predominant component of mixed congener peak.
[b]Each + (or −) indicates ~2× increase (or decrease) in indicated peak (adjusted for evaporative/elutriative losses) for tideflat sediment specimens showing ~3 half-losses of Peaks 50 and 58 (Table 1).
[c]Underline indicates process making sizeable change in a major peak.
[d]Indicated transformation supported by both increase in product and decrease in reactant peaks; in other cases co-elution or background problems preclude confirmatory observation.
[e]Extent of transformation larger in samples exhibiting Pattern H′.

The calculated extents of evaporative/elutriative loss and original 1242:1254 ratio also varied widely from site-to-site. Pattern H or H′ development, as indicated by the number of half-losses of Peaks 50 and 58, occurred to a somewhat variable extent. The net effects of both evaporative/elutriative and dechlorinative losses upon the overall levels of *ortho* and non-*ortho* chlorines in the residual PCBs are shown in Figure 5.

Because of the magnification of any experimental error that would occur in the calculation of evaporative/elutriative loss (i.e., the y in Eq. 1–3), the calculated y values were checked against the observed levels of dichlorobiphenyls. The average y value for all sites (18%) was in reasonably good agreement with the average dichlorobiphenyl level (predicted for 60% (Fig. 3) retention of the 13.2% dichlorobiphenyls expected to be formed by 50% Pattern H conversion of the reactive tri- and tetrachlorobiphenyls in a 61:39 1242:1254 mixture to

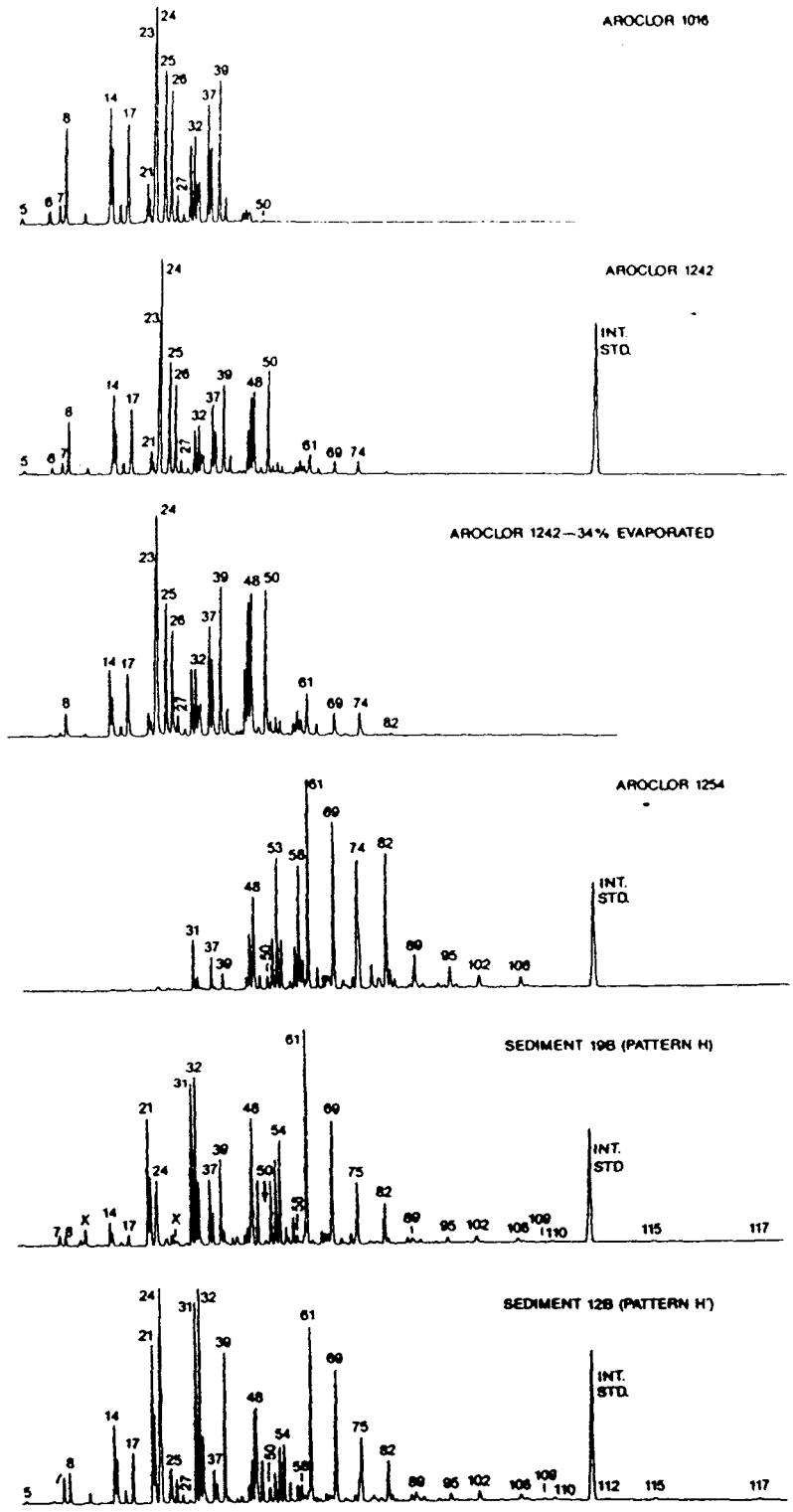

Fig. 2. DB-1 capillary gas chromatograms of Aroclor reference standards and Acushnet sediment samples exhibiting alteration Patterns H and H′.

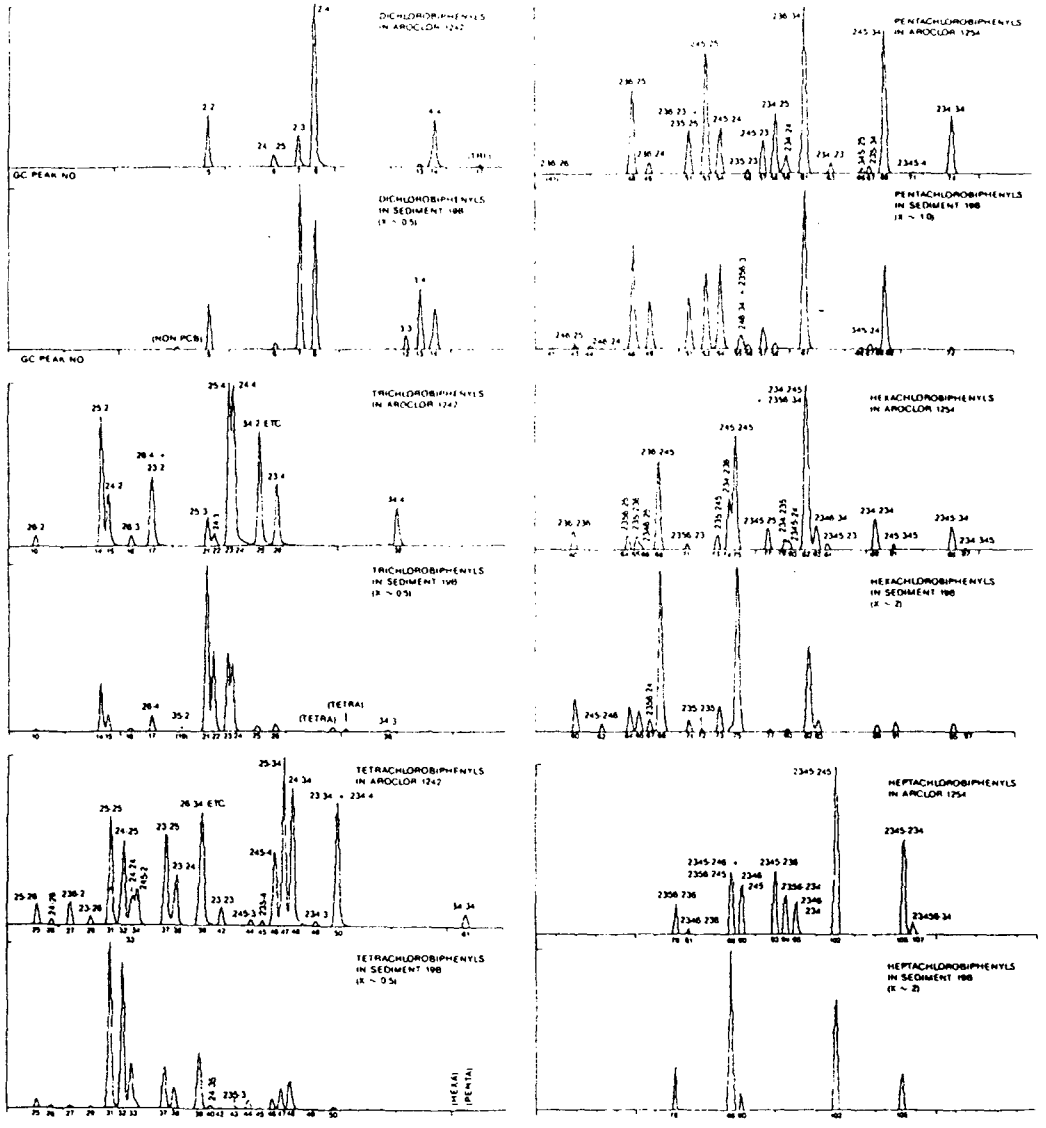

Fig. 4. Gas chromatographic–mass spectrometric ion chromatograms, showing summed parent ion isotope peaks for di- through heptachlorobiphenyls in Aroclor standards and Acushnet sediment sample 19B. Peak numbering along horizontal axis corresponds to that of Figure 2 and Table 3. Vertical scale on each chromatogram adjusted to give full-scale response for highest peak present.

it was replaced by Aroclor 1016. By the time of Aroclor 1016 introduction, however, there was already growing concern over PCB accumulations in the environment, and strenuous efforts were being made to control PCB releases. Accordingly, both local history and the analytical data indicate that the only significant PCB releases to the Acushnet sediments consisted of Aroclors 1242 and 1254.

Characterization of PCB alteration processes H and H′

Figure 5 shows that despite a considerable amount of evaporation and elutriative losses, which would increase the content of *meta* and *para* chlorine atoms in the residue, a net loss of such chlorine atoms occurred at all sites, indicating the

trichlorobiphenyls 25-3 and 24-3 CB, the di-*ortho* tetrachlorobiphenyls 25-25, 24-25 and 24-24 CB, and some 2,3′-dichlorobiphenyl. Gas chromatograms exhibiting Patterns H or H′ may be recognized as such by the increased levels of the above congeners, increases also in the levels of the 2,3,4-chlorophenyl group-derived congeners 236-24 CB (Peak 49), 245-24 CB (Peak 54) and 2356-24 CB (Peak 67) and the particularly decreased levels of congeners carrying 3,4-, 2,3,4- or 2,3,4,5-chlorophenyl groups. System F, by contrast, gives many of the same terminal dechlorination products but after an almost indiscriminate attack on the higher PCB congeners, whereas the B-like systems of the upper Hudson River, Waukegan Harbor and the Sheboygan River (e.g., systems B, B′, C and W) give largely mono- and dichlorobiphenyls, along with 26-2 and 26-3 CB [5–7].

Geographical range of pattern H/H′ dechlorination

Having delineated the recognition features of Process H/H′ dechlorination, a review of available chromatograms from the New Bedford area and elsewhere was undertaken to determine where else it might be occurring.

The 231 SE-30 packed-column GC tracings produced by the 1982 to 1983 Versar analyses of New Bedford area sediments lacked the resolution to reveal the DB-1 capillary Peak 50, and all contained DDE (added as an internal standard), which obscured Peak 58. However, they were fully adequate for showing the "high-end drop-off" feature of the Pattern H/H′ GCs. Accordingly, we scored the entire set for this feature and then obtained the key linking sample numbers to collection sites. This

Table 5. Comparison of PCB dechlorination systems F, H and B in terms of apparent relative reactivities to dechlorinating agent (R) and relative tendencies to appear in final dechlorination product (p) for the individual chlorophenyl groupings[a]

	Response to dechlorination system					
	F		H		B	
Chlorination pattern	Reactivity	Product	Reactivity	Product	Reactivity	Product
23456	RRR	–	RR	–	?	–
2345	RRR	–	RRR	–	RR	–
345	RRR	–	RR	–	RR	–
235	RR	–	R	p	–	p
2346	RRR	–	RRR	–	RR	–
2356	RRR	–	–	–	–	?
245	RR	–	R[b]	–	RR	–
234	RR	–	RRR	–	RR	–
34	RR	–	RR[b]	–	RRR	–
35	?	p	–	p	–	p
236	R?	p?	–	–	R	?
25	–	ppp	–	ppp	RR	?
23	?	pp	R[b]	?	RRR	–
246	–	p	–	p	?	–
24	–	ppp	–	ppp	R[b]	–
4	–	p	–	?	–[c]	pp
2	–	?	–	p	–	ppp
26	–	p	–	–	–	pp
3	–	ppp	–	ppp	–[c]	pp

[a]For systems H (Acushnet River) and B (upper Hudson River) relative reactivities based on disappearance rates of congeners having indicated substitution pattern on one ring and 24- or 25-substitution on the other. For both, reactivity is greater if opposite ring only mono-substituted, and lower if tri-substituted. Chlorophenyl groups are listed in order of increasing electrochemical reduction potential.
[b]Group apparently not dechlorinated when opposite ring carries chlorines in both 2 and 6 positions.
[c]Reactivity seen in the closely related system C, but questionable or negative in system B.

[23,24]. Demonstrations that these particular components of the Aroclor mixtures (e.g., congeners such as 34-34, 234-34 and 345-34) are the ones responsible for the observable toxic effects have now been presented for hepatomegaly [23], body weight loss [24] and thymic involution [23,24] in rats, and for embryonic mortality and birth defects in Forster's tern [25,26].

Note that although the H/H′ dechlorination process attacks a somewhat narrower range of PCB congeners than do those of Silver Lake or the upper Hudson (Table 5), it is particularly effective at attacking precisely those *non-ortho* and *mono-ortho* substituted congeners that are of toxicological concern (Tables 3, 4). Because these species are thus indicated to be at least as responsive to Process H/H′ attack as are the indicator Peaks 50 and 58, it would appear that the extent of dechlorination, as measured by the declines in Peaks 50 or 58, can also be used as a measure of the detoxication that has occurred.

DISCUSSION

PCB transport processes of the Acushnet Estuary

The detailed analyses of PCB levels and congener distributions now available present two unexpected features regarding PCB transport processes in an estuarine environment.

The first such feature concerns vertical mixing within the sediments. Previous investigations of PCBs in freshwater sediments, for example, those of Lake Superior [27], Lake Michigan [28] and the upper Hudson [5–7] have shown good preservation of stratification, indicating very little vertical mobility for the PCBs. In sharp contrast, our 12 pairs of tideflat samples showed no large compositional differences between the 5 to 7.5 cm and 15 to 17.5 cm levels for any of the nine parameters listed in Table 1, including the ratios of Aroclor 1242 to Aroclor 1254, which may have been released five to 30 years apart. Furthermore, substantial levels of PCBs have been seen even below 40 cm at some sites [10,15], and sediment surface PCB levels have been found to be equal or nearly equal to those in the subsurface [10,13,15], despite the ongoing losses of PCBs to the water column. All these observations indicate the occurrence of an active vertical transport (mixing) process within the upper estuary sediments.

There are two possible mechanisms by which vertical transport might occur. First, Brownawell and Farrington [15] have shown that the pore water in these sediments contains detergent-like agents that solubilize the PCBs. These would permit the movement of the otherwise highly water-insoluble PCBs from particle to particle in the sediments. Alternatively, bioturbation processes, which are much more evident in the tidal flats of the Acushnet Estuary than in freshwater sediments, could be effecting the observed mixing.

Whatever the cause, this vertical diffusivity of the PCBs has some significant consequences. One is that all of the PCBs now in the sediments may be able to reach those anaerobic layers where dechlorination is proceeding. Another is that they may also be able to reach the surface, and then elute out into the water. A third is that the lower boundary of the PCB-containing zone should continue to move downward, thus reducing the levels of PCBs at all depths within the zone, including the surface, with a consequent reduction in the rate of elution into the water.

The second unexpected feature concerns horizontal movement between sediment sites. Both we (Table 1) and others [10] observed extraordinarily spotty distributions of the PCBs in the upper estuary sediments, with many instances of 1,000-fold concentration differences between nearby sites. Our data (Table 1) show that there are also significant differences in chemical composition between such sites, indicating that the spottiness in the distribution pattern cannot be attributed to hydrodynamic factors leading to local areas of scouring or redeposition. Even more striking, there appear to be virtually no dechlorinated PCBs in the sediments of the outer harbor, at least as of 1982, despite their presence at high levels in the upper estuary sediments, and in at least one of the lower estuary water samples. All of these observations indicate that no significant horizontal movement of PCBs from one patch of sediment to another has been occurring.

There are two obvious mechanisms by which such movement might have occurred. One would be by scouring and redeposition of sediment particles carrying bound PCBs. The other would involve dissolution into and readsorption from the water column. A priori, both mechanisms would appear eminently plausible and both have been frequently invoked in the past to rationalize or model the movement of PCBs or other xenobiotics in aquatic environments. The fact that interchange of PCBs between sediment sites is not occurring in the Acushnet means that neither mechanism is operative there.

The absence of PCB transport by scouring and redeposition of PCB-containing sediments is con-

weight of PCBs of the type analyzed in the upper 20 cm of the upper estuary sediments to be about 10^5 kg, indicating the total losses to the water column to have been about 50,000 kg. (This figure may be highly conservative; other estimates of the total quantity of PCBs in the upper Acushnet are considerably higher than ours (L.S. Sarapas, private communication).

Applied Science Associates [12] has estimated the current flux of PCBs from the sediments to the water by a two-dimensional vertically averaged finite element pollutant transport model as 189 kg/yr. Three calculations using a simple one-dimensional model gave fluxes averaging 99 kg/yr. Even the larger, and presumably more reliable, value represents a current annual flux of only 1/265 the conservatively estimated losses. The inescapable conclusion is that during and shortly after the period of active discharges the rate of PCB extraction into the water column must have been between 10- and 100-fold greater than at present, and that the elution rate has been dropping sharply since that time. An obvious explanation for this drop in elution rate is the vertical movement of the PCBs down into the sediment column.

PCB dechlorination/detoxication processes of the Acushnet Estuary

The results of this investigation showed that a previously unreported type of PCB dechlorination and detoxication process is occurring in the sediments of the upper and middle sections of the Acushnet Estuary. In sediment specimens examined to date, removals of up to 91% (3.5 half-clearances) have been seen for the "indicator" congeners 23-24 CB (Peak 50) and 234-34 CB (Peak 58) and for the major toxic congeners 34-34 CB (Peak 61-4, PCB No. 77) and 234-34 CB (Peak 74, PCB No. 105). The dechlorinative congener transformations were found to be occurring in two very similar patterns, designated H and H′ (Fig. 2). These patterns are clearly different from the previously reported Patterns B, B′, C and E of the upper Hudson River, the Pattern W of Waukegan Harbor or the Patterns F and G of Silver Lake [5-7]. They were similar, however, to unpublished dechlorination patterns seen at two other marine sites, that is, Escambia Bay (FL) and New York Harbor (NY) and at several freshwater sites, that is, Woods Pond, near Lenox, Massachusetts, and Hudson River/Estuary sites with elevated PCB levels near Mechanicville, Troy, Albany, Catskill, Kingston and Poughkeepsie, New York; as well as in laboratory cultures grown up from upper Hudson River inocula. Thus H-like PCB dechlorinations appear to be occurring in a variety of geographical settings. Whether or not they are all mediated by the same type of microbe is still unknown.

The distinction between Patterns H and H′ is a subtle one, and may not be significant. Pattern H′ appeared at only two (adjacent) sites on the upper Acushnet tideflats (Table 1), but was also seen in the Hudson Estuary. In the latter case, it almost certainly arose from the contribution of a different dechlorination system, M, which could also be cultured from the same Hudson River sediments in the laboratory. Other investigators of upper Acushnet Estuary PCBs (J.F. Quensen III, Anna Yoakum and J.L. Lake, private communications, and [29]) have found that some samples of mid-channel sediments exhibit dechlorination patterns other than the Pattern H of the tideflats, and that such dechlorinations may be reproduced in laboratory cultures. However, we still cannot be certain whether the Pattern H′ of tideflat Sites 9 and 12 arose from the incipient appearance of a second dechlorination system, a mutation of the local System H population, or simply a particular stage in the development of dechlorination Pattern H.

At most PCB spill sites it is easy enough to determine the extent of dechlorination (e.g., number of half-clearances) but difficult to determine the rate of dechlorination (e.g., the mean half-time for clearance) because of uncertainties as to just when the local population of PCB-dechlorinating anaerobes became established. At the Acushnet study site, however, we have data on the differences between the extents of clearance of the largely 1242-derived Peak 50 and the largely 1254-derived Peak 58, as shown by the P58-50 values given in the last column of Table 1. These indicate more extensive dechlorination of the Aroclor 1254 in the upper half of the study site and of the Aroclor 1242 in the lower. A plausible interpretation would be that dechlorination began in the northern end of the upper estuary in the 1950s, when the release was largely Aroclor 1254, reached the southern part of our sediment study area sometime after the 1960 to 1965 changeover to Aroclor 1242, and the southern part of the inner harbor by the time of the GCA/EPA/Versar sampling in early 1982. Thus, in the northern part of the study site dechlorination of Aroclor 1254 is further advanced because of the longer dechlorination time; in the southern part, less so, because the concentrated fresh deposits of Aroclor 1242 responded more rapidly to the arrival of the dechlorination system than did the underlying Aroclor 1254 deposits; and

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