POLYCHLORINATED BIPHENYL (PCB) ANAYLTICAL SURVEY OF BUZZARDS BAY, MASSACHUSETTS

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Introduction

The Buzzards Bay region of the southern Massachusetts coast has been at the focus of many marine pollution investigations over the past fourteen years. Spillages of fuel oil have inpacted areas of the Bay's coastline during this time as a result of at least three major spill events. However, of greatest concern at present and indeed over the past decade has been the input of PCB from the Acushnet River/New Bedford Harbor region (Figure 1). Farrington et al. (1983) estimate that at least 100 tons of PCB reside in the upper 50 cm of sediments in the estuarine-harbor region. That these PCB are transported out of the estuary is evident from elevated levels found in lobster, shellfish and finfish from the estuary region and in Buzzards Bay and from levels in suspended particulate matter from the area (Farrington et al. 1983).

The present study was undertaken to survey certain benthic macrobiotal species and to survey sediments specifically for their PCB levels and sources and to examine the detailed PCB composition of the samples. Of gretest interest in this study was an examination of the possibility of PCB impact related to the New Bedford problem further offshore in Buzzards Bay.

This study was an extension of previous work done by the Northeast Monitoring Program's chemistry team (Boehm, 1983a,b) on monitoring coastal and offshore sediments and biota for trends in pollutant exposure and transport.

An extensive amount of analytical chemical work has been done in the study region by Farrington and coworkers at WHOI (Woods Hole Oceanographic Institution) (Farrington et

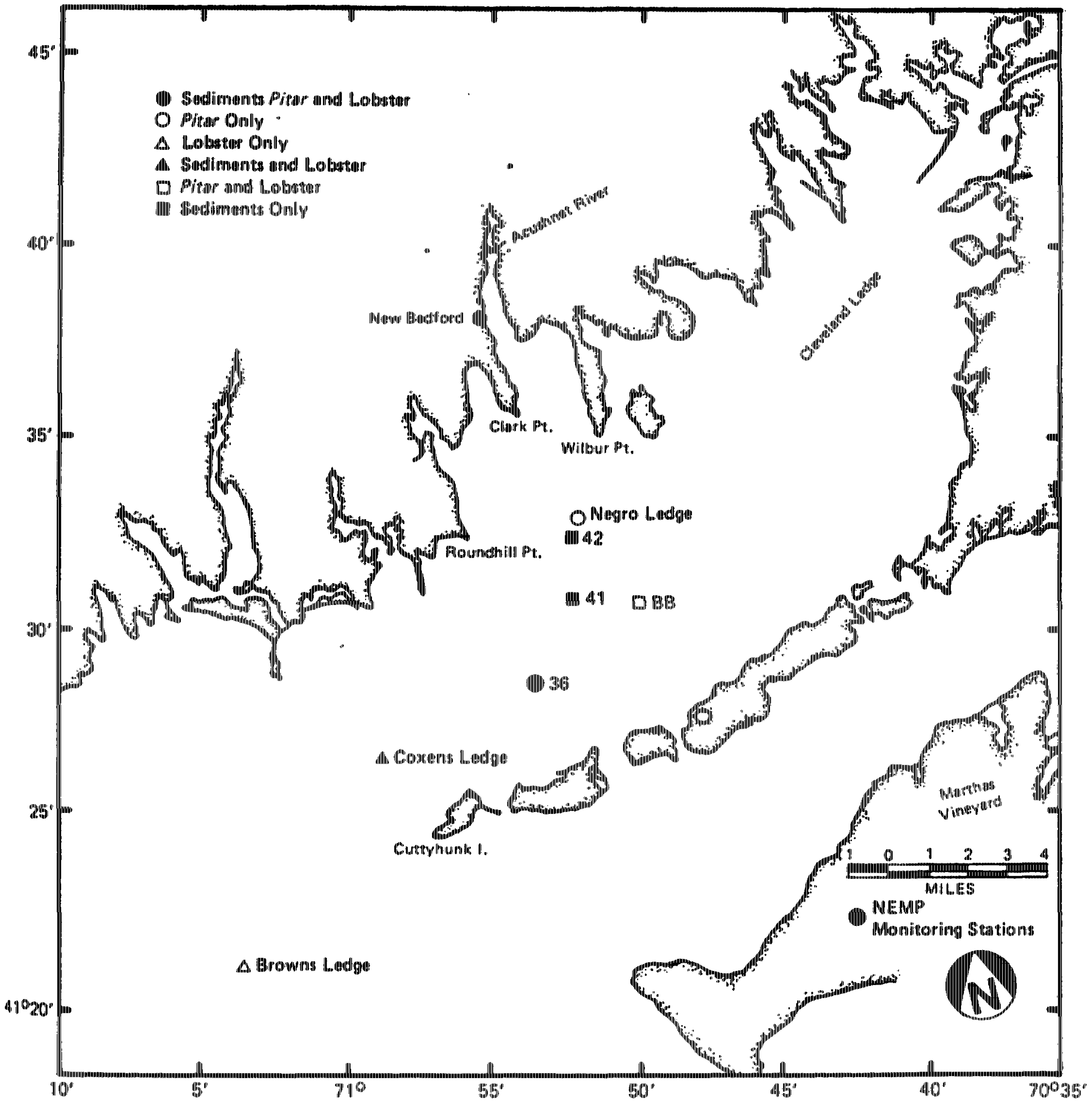

Figure 1. Location of sediment and benthic animal samplings in Buzzards Bay.

al., 1983) as well as by others in the region. Numerous tabulations of unpublished data on PCB levels in sediments, lobsters, and bivalve molluscs exist. These data were generated by Southeastern Massachusetts University, FDA, EPA, State of Massachusetts Laboratories as well as by Woods Hole. Levels of PCB in sediments range from a high of 190 mg/g in harbor sediments to <0.1 ug/g in Buzzards Bay sediments. A range of PCB concentrations in marine organisms has been found with levels exceeding the FDA recommended limit of 5 ppm (wet weight basis) in the viscera of lobster found at many locations throughout Buzzards Bay and in the edible flesh of lobster near New Bedford. Mussels transplanted to potentially impacted areas have demonstrated a marked uptake of PCB from the water column particulate matter. Farrington et al. (1983) have deomonstrated that the dichloro and trichlorobiphenyls which comprise a significant fractrion of Aroclor 1242 and 1016 mixtures are of higher concentration in sediments closer to the harbor entrance. The higher chlorinated compounds, the tetrachloro- through heptachloro isomers, are of greater environmental stability and apparently make up a greater proportion of the total PCB as one moves away from the source (i.e., the harbor, estuarine region).

Methods

Sampling

The sampling program consisted of obtaining sediment and benthic animals (Pitar morrhauna and Homarus americanus (lobster)) from several sites throughout Buzzards Bay out to Coxen's Ledge (Figure 1) and to Brown's Ledge. Five replicate sediment samples (0-3 cm) were obtained from five grab samples at each of three stations (36, 41, 42). Sediments from Coxen's Ledge were collected by divers. Lobsters were collected at Stations 36, BB, Coxen's Ledge and Brown's Ledge. Clams were collected at Stations 36, Negro Ledge and BB.

Analyses

Samples were analyzed according to protocols previously used on other NEMP projects (Boehm, 1983a,b). Analytical results were obtained from capillary GC/ECD and capillary GC/FID for PCB and coprostanol respectively. High resolution determinations allowed for the quantification of individual PCB compounds which were then summed into isomeric groups (dichloro, trichloro, . . . heptochlorobiphenyls) rather than the more classic Aroclor formulations (Ballschmitter and Zell 1980).

Sterols were quantified by high resolution GC with the five sterols 5β cholestanol (coprostanol), β-sitosterol, cholesterol, stigmasterol and 5 α cholestanol being quantified. Analyses proceeded according to the method of Hatcher et al. (1977) as modified for capillary GC determinations by Boehm (1983a).

Analyses of Pitar samples were performed on a pooling of five animals. The tail meat from two or three lobsters were pooled to yield one sample. One sediment sample consisted of 50g of wet sediment (0-3 cm). Five sediment samples were analyzed per station.

3. Results

3.1 Benthic Animals

The PCB results for the clams and lobsters are presented in Table 1. PCB values for the *Pitar* samples ranged from .021 to .045 ug/g wet weight (multiply by 8 to convert to dry weight basis). These levels are well below an "action level" of 5.0 μg/g wet tissue. Apparently, the pooled sample for Negro L dge, closest to New Bedford, contained higher PCB levels than those further in the Bay. However, the statistical validity of this conclusion cannot be tested.

Lobsters from Station 36 contained .088 ± .017 g/g PCB wet weight which was higher than levels observed at Station BB (.035 μg/g), Coxen's Ledge (.050 μg/g) or Brown's Ledge (.024 g/g).

PCB values for *Pitar* are in good agreement with the results (Farrington, unpublished) from another bivalve (*Mytilus edulis*) from mid-Buzzards Bay (0.1-0.7 μg/g dry weight = .02-.12 μg/g wet weight). PCB levels in lobster flesh from mid-Bay have been reported in the <0.1 to 0.3 μg/g wet weight range which are generally higher, by a factor of 2-5, than the values reported here. Whether or not this represents any trend is not known. Both laboratories involved have participated successfully in an EPA-coordinated PCB "mussel-watch" intercalibration exercise (Lake, EPA; personal communication) which lends credence to the inter-comparability of results.

PCB compositions of *Pitar* and lobsters (Figures 2 and 3) are quite different though from one another. *Pitar* (Figure 3A) contains a slightly varying PCB assemblage, with important

Table 1. PCB concentratins in benthic animals from Buzzards Bay

Sample Type	Location	PCB Concentrations (ug/g Wet Tissue[a])					
		Total	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7
Pitar	36	.029	.006	.003	.009	.011	.0004
Pitar	Negro Ledge	.045	.003	.013	.013	.018	.0004
Pitar	BB Buoy	.021	.003	.003	.006	.011	nd
Lobster	Coxens Ledge	.050	.0004	.001	.010	.038	.0008
Lobster	Browns Ledge	.024	.001	nd	.003	.016	.0005
Lobster	BB Buoy	.035	<.001	.003	.006	.030	.001
Lobster (QC)	36	.068	<.001	.005	.014	.048	.001
Lobster (QC)	36	.094	<.001	.006	.019	.065	.004
Lobster (QC)	36	.101	<.001	.008	.018	.071	.004
Blank		.0001	nd	.0001	nd	nd	nd

[a]To convert to dry weight basis multiply concentration by factor of eight.

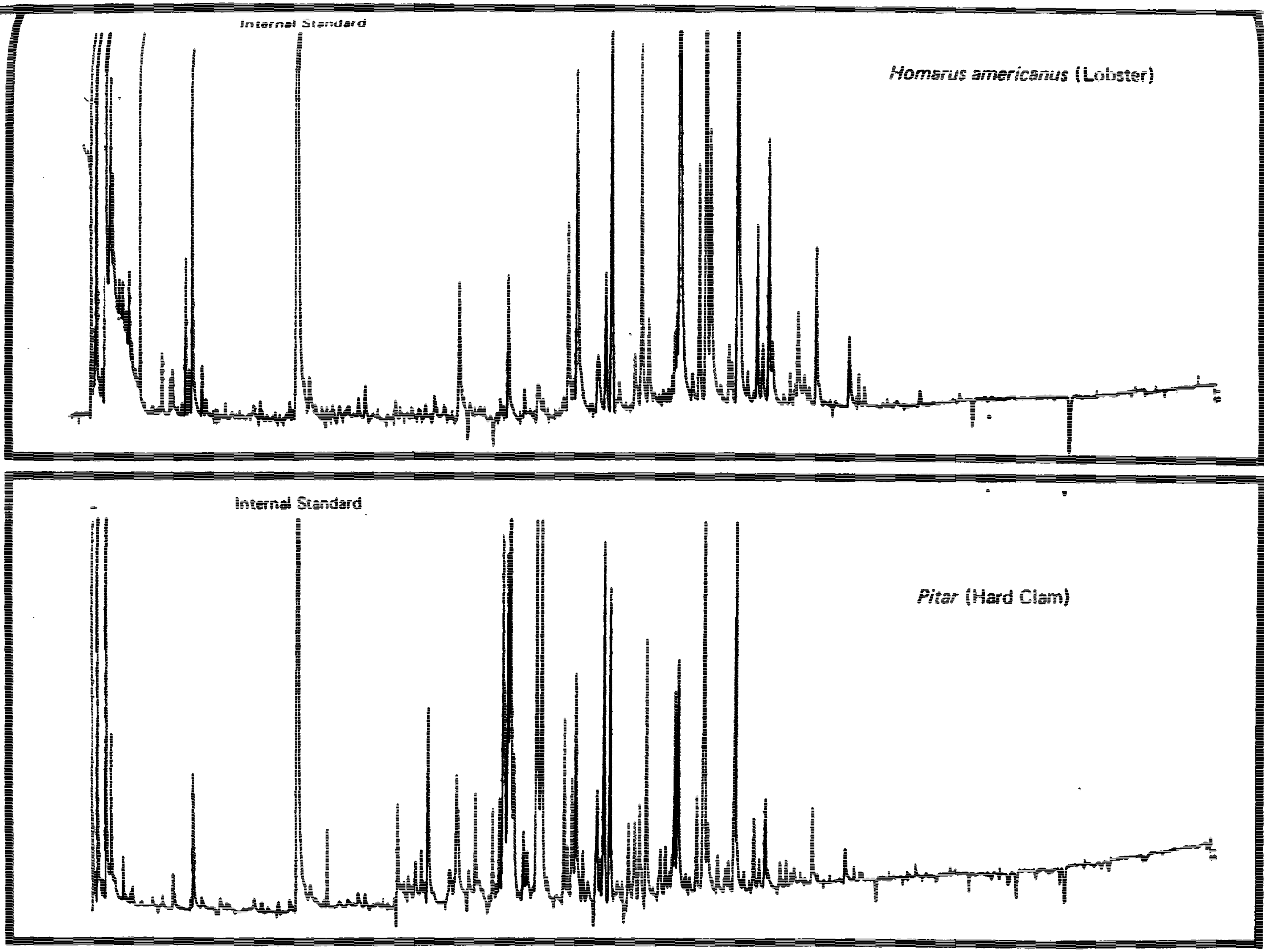

Figure 2. Capillary GC/ECD traces of PCB composition of benthic animal tissue.

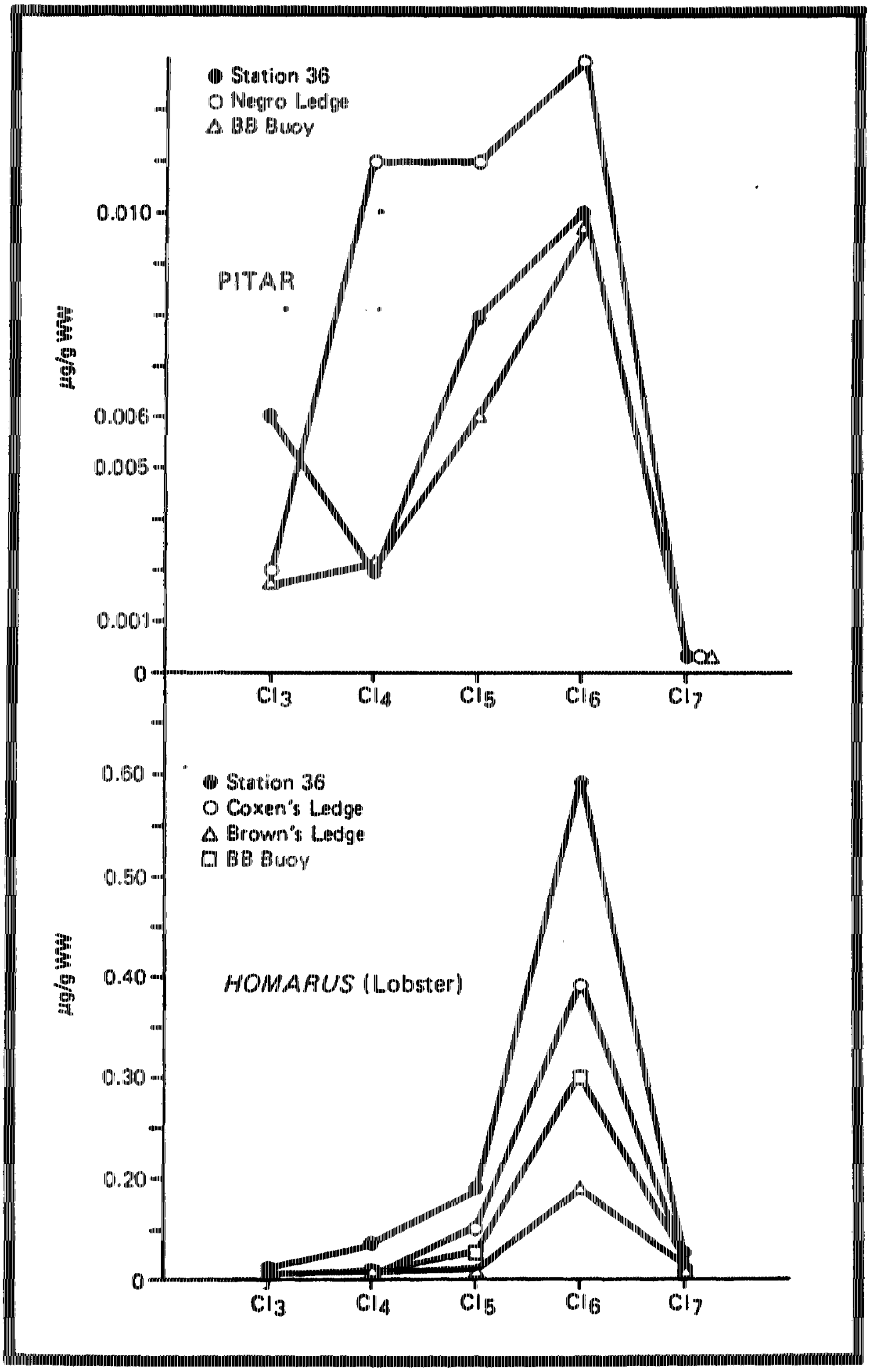

Figure 3. PCB isomeric distributions for *Pitar* (clams) and *Homarus* (lobsters).

relative inputs of the lesser chlorinated isomeric (i.e., trichlorobiphenyls, Cl_3, and tetrachlorbiphenyls, Cl_4). Lobsters (Figure 3A) on the other hand contain a uniform PCB composition with most of the total PCB value comprised of the hexachlorobiphenyls. Such an assemblage would have been identified in low resolution GC studies as an Aroclor 1254 distribution which according to the plots in Figure 4 it clearly is not. Thus, it is important to analyze the specific PCB composition not just report a "closest match" to known Aroclor formulations in order to establish the exact nature of chemical contaminants in marine animals.

3.2 Sediments

PCB levels in sediments (Table 2) are highest (.08 ± .013 μg PCB/g dry sediment) at Station 42, closest to the harbor, with levels decreasing offshore to a low of .003 μg/g at Coxens Ledge. PCB clearly associate with fine-grained sediments as exist at Stations 36, 41 and 42. The sediment type at Coxens Ledge is sandy and one would expect low deposition of silt/clay, total organic carbon and hence PCB. Further offshore on the adjacent shelf, Boehm (1983a) has determined that PCB levels in depositional areas are .003-.005 μg/g.

The PCB compositions in the silt/clay sediments is not unlike that in *Pitar* animals. In Figure 5 we see a typical high resolution sediment PCB trace with the isomeric compositional plot below. Levels of the trichlorobiphenyls, pentachlorobiphenyls and hexachlorobiphenyls are roughly the same indicating multiple source for the PCB found here (e.g., Aroclor 1242 and 1254). PCB compositions are similar (Table 2) at Stations 41 and 42. At Coxens Ledge, the

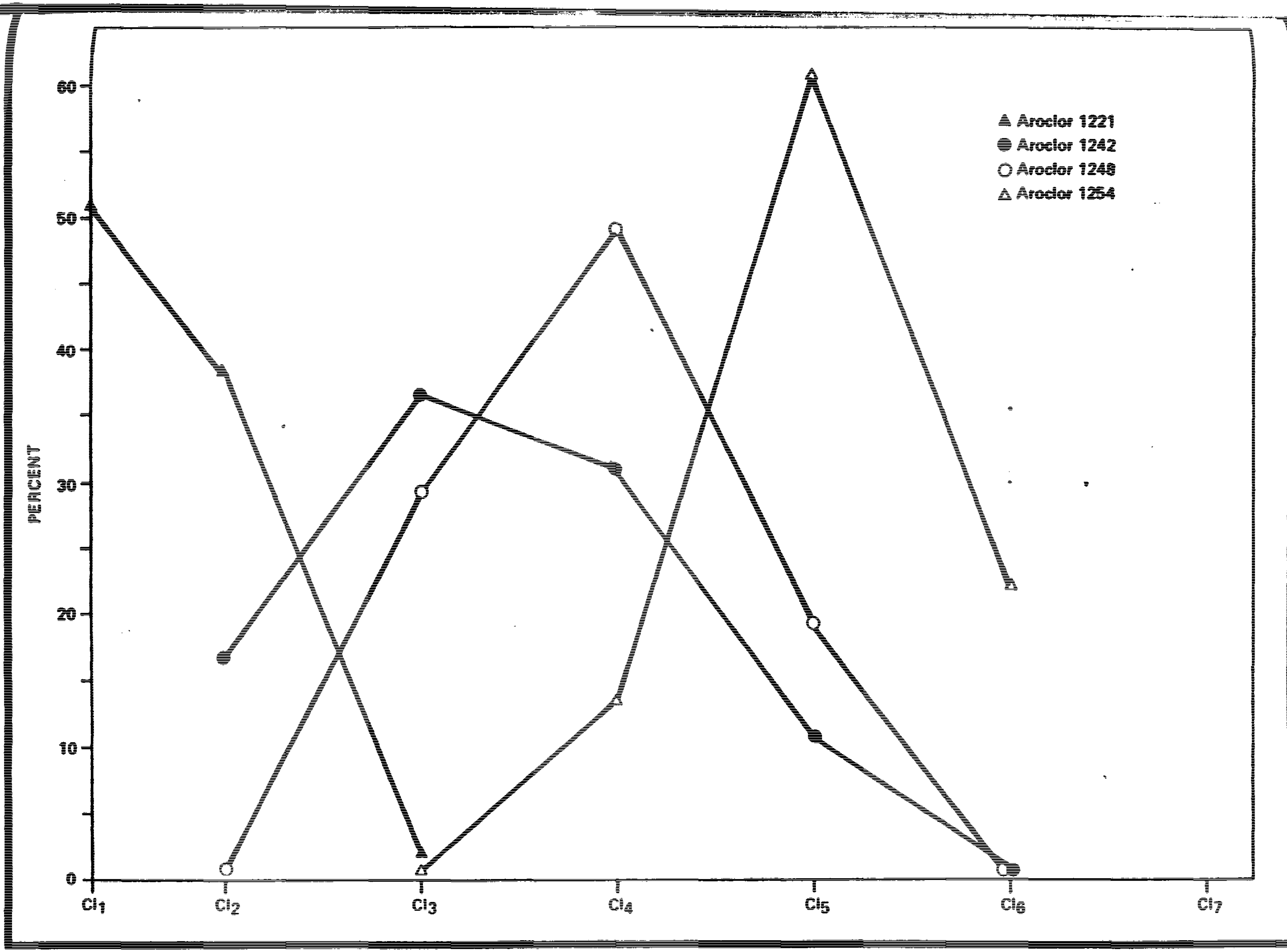

Figure 4. PCB compositional plots of some common Aroclor formulations.

Table 2. Buzzards Bay surface sediment PCB and coprostanol results

Station (Rep)	PCB (ug/gdw) Total	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7	Coprostanol ug/gdw	Coprostanol / Total Steroids	Coprostanol / PCB
36 (1)[a]	.050			NA				.143	.021	2.9
(2)[a]	.070			NA				.124	.018	1.8
(3)[a]	.062			NA				.125	.017	2.0
(4)[a]	.056			NA				.138	.023	2.4
(5)[a]	.065			NA				.156	.018	2.4
	$\bar{x}$=.061±.008							$\bar{x}$=.137±.013	$\bar{x}$=.019±.003	$\bar{x}$=2.3±.40
41 (1)	.065	-	.016	.005	.017	.019	.0008	.262	.027	4.0
(2)	.054	-	.013	.006	.015	.018	.002	.325	.031	5.9
(3)	.040	-	.008	.004	.013	.014	.001	.215	.022	5.7
(4)	.072	-	.013	.008	.022	.028	.001	.291	.032	4.0
(5)	.047	-	.012	.005	.013	.015	.002	.276	.026	5.9
	$\bar{x}$=.056±.013							$\bar{x}$=.274±.040	$\bar{x}$=.028±.004	$\bar{x}$=5.1±1.0
42 (1)	.074	-	.020	.011	.023	.019	.001	.377	.037	5.1
(2)	.105	-	.023	.015	.033	.032	.002	.382	.038	3.6
(3)	.080	-	.019	.012	.025	.023	.001	.186	.045	2.3
(4)	.085	-	.021	.012	.025	.025	.002	.405	.040	4.8
(5)	.073	-	.017	.010	.024	.021	.001	.354	.037	4.8
	$\bar{x}$=.083±.013							$\bar{x}$=.341±.088	$\bar{x}$=.040±.003	$\bar{x}$=4.1±1.2
Coxens Ledge										
(1)	.0003	-	-	-	<.0001	.0002	<.001	.021	.011	70
(2)	.0004	-	-	-	-	.0004	<.001	.049	.010	120
(3)	<.0001	-	-	-	-	<.0001	-	.022	.003	220
(4)	.0002	-	-	-	-	.0002	-	.020	.010	100
	$\bar{x}$=.0003							$\bar{x}$=.028±.014	$\bar{x}$=.009±.004	$\bar{x}$=130±65

NA = not analyzed.

[a]From Boehm, 1983a.

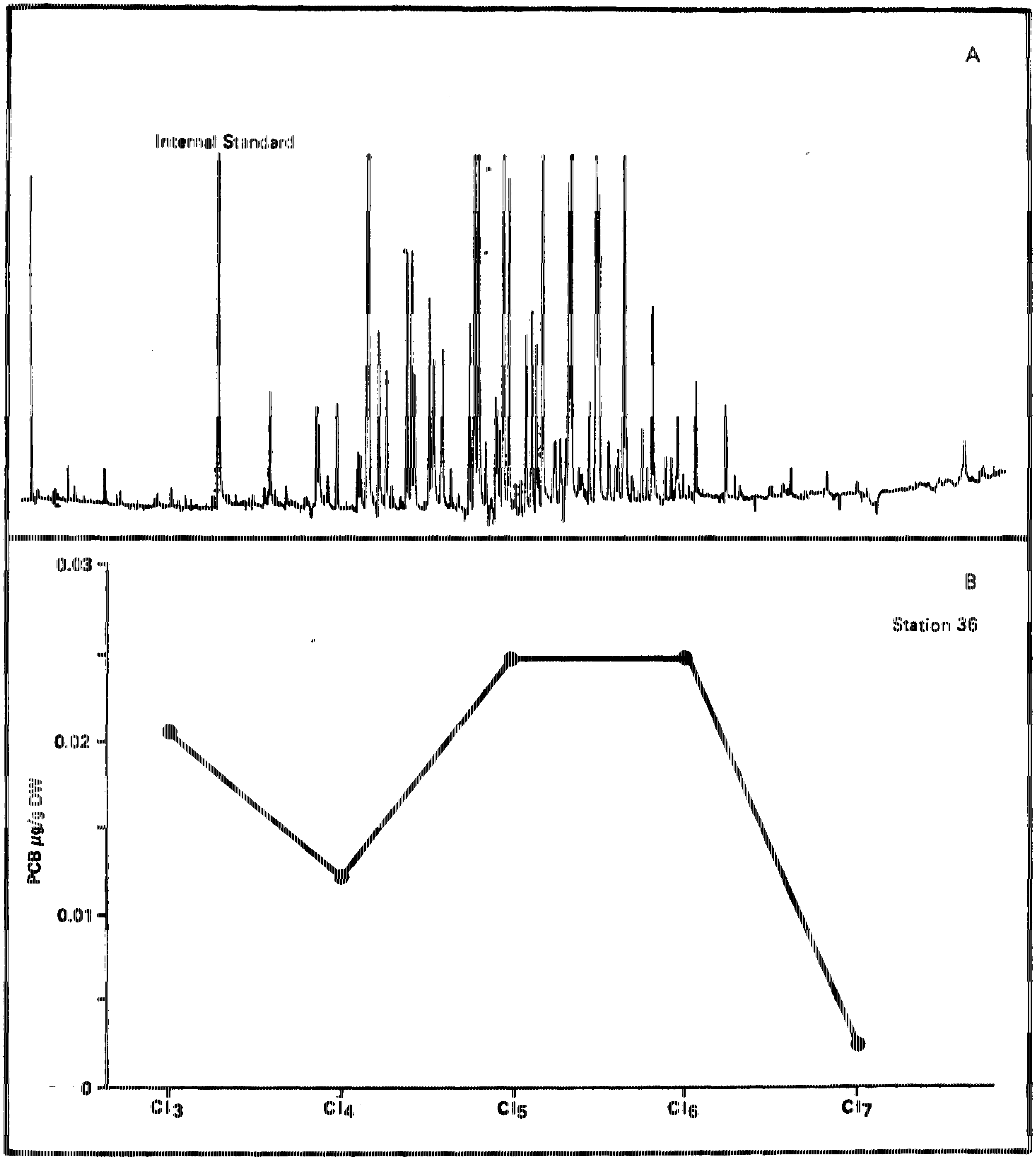

Figure 5. Capillary GC/ECD trace (A) and isomeric composition (B) of typical Buzzards Bay sediment sample.

levels are low and the composition is different. Here the only detectable PCB compounds are the hexachlorobiphenyls.

Coprostanol concentrations in the sediments clearly decrease with distance offshore. Observed levels range from 0.34 ppm to 0.03 ppm. These levels indicate a significant sewage input to the sediment. By comparison coprostanol levels in sediments near the sewage sludge dumpsite in New York Bight (e.g., Station NYB 10, Boehm, 1983a) are 0.3-0.4 ppm. Levels in the dumpsite itself were approximately 20 ppm. The sewage discharges northeast of Station 42 are most certainly the source of the coprostanol found in the sediments. The coprostanol to PCB ratio (Table 2) is approximately equal at Stations 41 and 42 (4-5) is low (2.3) at Station 36 in the middle of Buzzards Bay and is very high at the sandy Coxen's Ledge. Differential transport of PCB and coprostanol is indicated here. The influence of sewage as indicated by the coprostanol to total steriod ratio (Table 2) decreases with distance off-shore.

4. Discussion

The sediment geochemical data suggests that PCB are more strongly associated with fine grained sediment than is coprostanol. With increasing distance from a sewage source coprostanol concentrations decrease while PCB do not. Thus, the coprostanol/PCB ratio decreases. These results suggest that PCB and coprostanol are decoupled and for the most part have different sources. Significant concentrations of coprostanol found in the sandy sediment of Coxens Ledge without associated PCB values (and thus a very high coprostanol/PCB ratio) suggests that PCBs are more strongly associated with the silt/clay particles and coprostanol with coarser particles). PCB are most likely transported on suspended particles (Farrington et al., 1983) and deposited preferentially in depositional regions. This accounts for the PCB values in mid-shelf depositional areas being higher than at areas like Coxens Ledge. That there is offshore transport of PCB originating in New Bedford can be inferred from the suspended particulate measurements in Buzzards Bay and from PCB measurements in offshore sediments. Of course, other longer range contributions from the New York Bight and Long Island Sound as well as aeolian transport cannot be ruled out, but are less likely.

That the PCB compositions of the benthic animals varies between species is significant and is a result of a combination of feeding behavior and metabolic transformations. Pitar as sentinels of water-borne PCB or resuspended PCB contain a range of PCB compounds not unlike the surface sediments with the presence of trichlorobiphenyls and tetrachlorobiphenyls. Lobster on the other hand contain primarily the hexachlorobiphenyls. Therefore, we suggest that "action limits" and toxicological evaluations of the impact of the New Bedford PCB situation as well as from other environmental exposures (i.e., ocean dumping events) be based on the chemical reality of the nature of the individual PCB compounds in the animals, as the assemblage clearly changes from species to species. It is also recommended that high resolution PCB analyses be conducted as part of NEMP and other research grade programs in the future and that potential sources (e.g. sewage discharges) be analyzed for (1) their PCB composition, and (2) the ratio of individual PCB isomers to coprostanol. In doing so, one would approach biogeochemical and environmental problems with much more refined interpretative tools for looking at sources and fates of pollutants in the nearshore and offshore environments.

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