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Use of Isomer Ratios to Characterize the Origins and Alteration State of the PCBs in 30 Species of Hudson River Fish Collected 1977-93.

By John F. Brown, Jr. and George M. Frame, II, General Electric Corporate Research and Development, Schenectady, NY 12301-0008.

ABSTRACT

The origin of the persistent PCB levels in Hudson River fish has remained controversial: primarily, we believe, for lack of chemical "fingerprinting" procedures that would permit distinguishing between alternative sources for the fishes' PCBs. Past attempts to provide such fingerprinting *via* descriptions of PCB congener distribution or principal components analysis have been generally unproductive; largely, it now appears, because of data confounding by variabilities in such processes as elutriation, bioaccumulation, and depuration. Since these processes impact much more heavily on inter-homolog ratios than on intra-homolog, or isomer, ratios, we have explored the use of isomer ratio data sets as informative indicators of the environmental alteration state, and hence environmental pathways, taken by the fishes' PCBs. Examination of over 300 such data sets, determined for the PCBs in Hudson River fish belonging to 30 species, 21 genera, and 11 families, collected over a 200-mile stretch of the river over a 16-year period, showed that the resident fishes' isomer ratio "fingerprints" have generally corresponded to those of the local surficial sediments in all sections of the river, except as altered by metabolic processes that were found characteristic of 9 of the 21 genera studied. Since 1977, the PCBs of the fish of the Thompson Island Pool (upper Hudson River Reach 8) have exhibited surficial sediment Pattern A, indicative of recently deposited Aroclor 1242. Those of fish

taken a hundred miles downstream in the mid-estuary have instead exhibited subsurficial sediment dechlorination Pattern H', indicative of PCB compositions, such as hydraulic fluids, that had long been present in the sediments. In between, there has been a smooth transition in pattern, indicating a decrease in the extent of fish PCB dechlorination with decreasing distance from the known source of undechlorinated Aroclor 1242 input at Hudson Falls.

INTRODUCTION

The Hudson River is the major waterway draining eastern New York State (Figure 1). Its fish have been known to be carrying elevated levels of PCBs (polychlorinated biphenyls) since 1970 (1). Although all industrial uses of PCBs ceased in the 1970's, the levels of PCBs in Hudson River fish have declined only slowly since 1982, especially in the upper Hudson (2,3). This has resulted in continuing controversies, revolving around such questions as: whether the PCBs in upper Hudson fish are coming from old local high level ("hot spot") sediment deposits or from ongoing drainage from rock fractures under a heavily contaminated plant site; whether the PCBs in lower Hudson resident fish are coming from old deposits in the local sediments or from ongoing inputs from the upper Hudson; and whether the PCBs in lower Hudson migratory fish are coming from either of these sources, or from the sediments and sewers of the New York metropolitan area.

The formerly commercial PCB products (e.g. Aroclors) that were released into the environment were complex mixtures of isomers (PCBs of the same Cl-number) and homologs (PCBs of different Cl-number), which are generically

referred to as congeners. The original distributions of such congeners can be altered by biological processes in each of the environmental compartments through which a PCB release may pass, e.g., by aerobic microbial biodegradation near the sediment surface (4,5,6); by anaerobic microbial dechlorination in subsurficial sediments (7,8,9,10); by limited microsomal metabolism in some fish species (11); and by more extensive microsomal metabolism in crustaceans, piscivores, and man (11, 12). Since each of these processes alters the PCB congener distribution in a different way, it should, in principle, be possible to identify the set of niches through which any environmental PCB has passed *via* observable alterations in congener distribution.

In practice, this has generally proved difficult, primarily because K_{ow}-dependent phenomena such as evaporation, elutriation, bioaccumulation, and depuration, as well as variations in Aroclor proportions in the original release, can produce variations in homolog distributions large enough to obscure the effects on congener distribution produced by niche-specific biological activities. It occurred to us, however, that this problem could be minimized by simply using isomer ratios rather than congener levels as indices of chemical composition. Accordingly, we undertook to determine enough PCB isomer ratios on enough types of fish samples to determine whether an isomer ratio data set could indeed provide a robust indicator of PCB source and alteration history.

MATERIALS AND METHODS

Site Description. - The lower 156 mi. (251 km) of the Hudson River, running from New York City to Troy, is a tidal estuary herein referred to as the lower

Hudson (Fig. 1). The next *ca.* 80 mi. (*ca.* 125 km), i.e., the lower part of the upper Hudson, consists of a series of dammed stillwaters called "reaches," numbered in order starting from the Federal Dam at Troy. Distances along the Hudson are measured as "river miles" (RM) starting from the Battery at the southern end of Manhattan Island (New York City). Several descriptions of the contamination of the Hudson River by PCBs have been published (13, 14, 15, 16, 17).

Fish Data Used. - The fish samples or analytical data used in this study came from collections made by seven other investigators: 1. From R.J. Sloan of the New York State Dept. of Environmental Conservation (DEC) we obtained about 800 archived analytical extracts of fish from his 1977-82 collections (2) that had been returned by his analyst after low resolution packed column analysis. We selected 75 specimens that reflected a variety of fish species, PCB levels, collection sites, and "Aroclor" ratios and submitted them to Northeast Analytical Services of Schenectady, NY (NEA) for DB-1 capillary gas chromatographic (GC) analysis by described procedures (18). These analyses revealed that a few of the extracts, notably those of the goldfish and eels, had been allowed to dry out and lose lower congeners, but that most still exhibited homolog distributions in accord with the original "Aroclor" determinations. 2. From P.A. Jones, also of DEC, we obtained splits of the fathead minnow samples resultant from his 1985 study (19) of Hudson River PCB uptake by caged minnows, which were analyzed here (18). 3. From J.M. O'Connor, then of New York University, we obtained the original packed column GCs of the *gammarus* collected in 1980 as a part of the NYU

Hudson River Survey (20). He also supplied us with a dozen lower Hudson striped bass, collected in 1985, that were analyzed here (18). 4. From B.K. Shephard, then of Harza Engineering Co., we obtained both NEA GCs and data for samples of sediments, Hester-Dendy (periphyton) plates, dialysis bags, invertebrates, and fish collected during his 1988-1998 survey of PCBs in the lower Hudson River, New York Harbor, and western Long Island Sound. 5. From J.G. Haggard of General Electric we obtained 90 frozen fish that had been collected from upper Hudson Reaches 1-11 by Law Environmental Services in 1990. These were submitted to NEA for the usual 118-peak DB-1 analysis (18), along with a separate analysis for congener 77, which is not well resolved from PCB 110 by DB-1. 6. From W.A. Ayling of O'Brien and Gere Engineers, Inc. of Syracuse, NY we obtained NEA chromatograms and data for fish, invertebrates, and sediment surface scrapings collected from the Thompson Island Pool in May, 1992, 8 months after the major PCB loading event of September, 1991 (21). 7. From L.J. Field of NOAA, Seattle WA, we received 145-congener dual column PCB data files for 115 fish samples that he had collected in collaboration with RJ Sloan (DEC) at 10 collection stations between RM 40 and 200 on the upper and lower Hudson in the autumn of 1993.

The sediment reference samples for A, B, C, H and H' alterations were taken from individual core sections that exhibited these patterns as previously described (7-9).

Data Processing. From each PCB congener data set we calculated, if not already provided, the total PCB level, the PCB/lipid ratio, the levels of the homolog groups, the ratios between successive homolog groups, and the ratios of about 40

of the stronger single congener peaks to those of a selected isomeric reference congener, as well as site and species averages. The selected reference congener(s) were, for the tri-CB (hereinafter CB(s) = chlorobiphenyl(s)), the sum of PCBs 28 + 31 (these are normally the highest and second highest level tri-CBs, respectively; but they elute so closely on a DB-1 column that we were dubious about the reliability of the peak splitting calculation); for most tetra-CBs, PCB 49 (which maintains a relatively constant level during the early stages of dechlorination); for the tetra-CB PCB 70, which is partially metabolized by a few fish species, the non-metabolized PCB 74 (which is also more similar in K_{ow} to PCB 70 than PCB 49); for most penta-CBs, the rather slowly dechlorinated PCB 110, with PCB 99 as a non-metabolizeable alternate; and for the hexa-CBs, PCB 153.

Adjustment for Reference Congener Depuration - We noted that the ratio between isomers 74 and 49, which differ somewhat in water solubility, became elevated in individual fish that were heavily depurated, as indicated by low levels of di- and tri-CB's. In such fish the elevation in log (PCB 74/PCB 49) averaged about 0.2 times that in log (tetra-CB/tri-CB). Accordingly, a possible depuration adjustment to the 74/49 ratio was calculated on that basis.

RESULTS

Table 1 lists the fish species examined, abbreviations used, and metabolic alteration patterns observed. Table 2 presents the mean values of the upper and lower Hudson River fish PCB homolog levels and selected PCB isomer ratios for the 1977-78, 1990, 1992, and 1993 fish collections, along with reference values for a 90:10 Aroclor 1242:1254 mix and Hudson River sediments exhibiting alteration

patterns A, B, C, H, and H'. The variability of all tetra-CB and some penta-CB homolog levels, and the upper Hudson PCB isomer ratios involving penta- and hexa-CBs was low (relative standard deviation, RSD, 5-20%). Tri- and hexa-CB homolog levels, and the other isomer ratios involving tetra-, penta-, or hexa-CBs displayed somewhat greater variability (RSD 20-40%). Generally, however, the RSDs were only about half as great for the isomer ratios as for the homolog levels. Much of this remaining variance in the Table 2 isomer ratio data, which arose from measurements of the PCBs in many different species of fish, taken over large geographical ranges, could be correlated with specific variables. These will be considered in turn.

Variations Arising from PCB Depuration. - Some of the individual fish collected from the upper Hudson in November, 1990 showed levels of tri-CBs that were reduced to as little as 10% of their usual values, and displayed even greater reductions in di-CBs. Such reductions in lower homolog levels occurred most frequently in walleye (WAL), largemouth bass (LMB), and smallmouth bass (SMB), and significantly influenced the average lower homolog levels reported for 1990, since SMB had been selected as the species to be measured in triplicate in every reach of the upper Hudson. The depurative losses could have resulted from either a late-season cessation of feeding, or from periods of feeding in uncontaminated tributary streams. These losses were much less prominent in the 1977-1978, 1992, and 1993 collections. However, the observation of the effects they might have on the PCB 74/49 isomer ratio prompted the inclusion of a possible 74/49 ratio adjustment for depuration in Table 2.

Variations Arising from Atypical Aroclor Inputs. Occasional fish in most collections exhibited congener profiles clearly divergent from the majority. Thus, most of the very lightly contaminated (<1ppm) fish taken from above Glens Falls showed only the broad PCB homolog distribution pattern and DDE content characteristic of atmospheric deposition, as did also the local sediments, those of the Mohawk River, and those of some mountaintop peat from the summit of Mt. Algonquin (elev. 5114') in the Adirondacks. However, two (out of 17) of the 1993 NOAA fish collected in that area exhibited patterns resembling Aroclor 1242, one showed the pattern of Aroclor 1268, and one 1990 fish showed Aroclor 1260; all probably reflecting exposure to local areas of low level contamination with these Aroclors. One of the 1990 Reach 8 LMB showed the low total PCB level and broad homolog distribution of the upstream region, indicating recent translocation. Both the 3 + 4 year age group of the 1982 Albany pumpkinseed (PKS) and the 1980 NYU *gammarus* collections from several lower Hudson stations showed substantial levels of Aroclor 1260, indicating the occurrence of a significant, but short-lived, 1260 contamination event around 1980.

Of more general significance, the homolog distributions in Table 2 showed that there were higher levels of penta-, hexa-, and hepta-CBs in the lower Hudson than in the upper section, and also higher ratios of hexa- and hepta- to penta-CBs, which would not have been effected by elutriative, evaporative, or depurative losses of lower congeners. Evidently, the original source of the lower Hudson

River fish PCBs had been an Aroclor mix containing higher proportions of more heavily chlorinated Aroclors than that contaminating the upper Hudson.

Variations Correlatable with Fish Species or Genus. The PCBs in certain of the fish species showed consistent depletions of particular groups of congeners, thus defining an alteration pattern (AP), presumably arising from a species-specific PCB-metabolizing activity (Table 1). The commonest, Pattern AP-ICT (for *Ictalurus*, the first genus in which noted) was previously designed "P450-1A-like" (11); however, that term now seems better restricted to the somewhat different pattern seen in higher animals (12). AP-ICT shows a marked reduction in PCB 70 (and hence in the 70/74 ratio) and lesser reductions in PCBs 16, 17, 18, 22, 27, 33, 40, 49, 56, 91, 97, and possibly 101, 110, and 174; all of them congeners with adjacent unsubstituted 3+4-positions. By contrast, AP-PET (for *Petromyzon*) showed reduced levels of the 4,4'-substituted PCBs 28, 74, 118, 105, 128, 167, and 156, and also of PCBs 49, 52, and 174, leaving the peak given by the coeluting pair, PCBs 64 + 71, as the strongest in the G-C. Pattern AP-ESX (for *Esox*, where it appeared occasionally) showed clear reductions in every resolved congener carrying a 2, 3-dichlorophenyl group, i.e., PCBs 22, 40, 42, 44, 56, 82, 84, 97, and 129. Pattern AP-LEP (for *Lepomis*) showed clear reductions in just two of the above, namely, PCBs 40 and 44. Finally in AP-CAT (for Catostomus) the only clear reduction was in congener 52. Thus, the only observed fish alteration patterns that would affect a PCB 74/49 isomer ratio were AP-ICT and AP-PET.

A very different set of variations was observed in the anadromous (migratory) fish of the lower Hudson River. The striped bass (STB) and American shad (AMS) all showed substantial levels of DDE, sometimes accompanied by DDD or DDT; *trans*-nonachlor, sometimes accompanied by α- and γ-chlordane; and other pesticides as well, generally producing enough interfering peaks in the tri- through hexa-CB range to make calculation of isomer ratios from GC-ECD data problematical. The observed pesticide/PCB ratios generally corresponded to those seen in the sediments of the New York metropolitan area, including western Long Island Sound, which is where these species overwinter. Conversely, the two Atlantic tomcod (ATT) examined, both collected at RM 41 in January, 1978, showed only low levels of Aroclor 1242-like PCB contamination, without any pesticides, not even the low level of DDE present in the lower Hudson.

Variations Due to Biodegradation/Dechlorination State. Congener distributions in Hudson River subsurface PCB dechlorination Patterns B and C (7,8,10) and H and H' (9,10) have been previously described. Generally speaking, Pattern C dechlorination, which gives the most extensive conversion to mono- and di-CBs, is seen in the most heavily contaminated sediments of the upper Hudson; Patterns B and B' are seen in somewhat less heavily contaminated sediments as far downstream as Albany; and the rather selective Patterns H and H' are uncommon in the upper Hudson, but dominant in most of the more lightly contaminated lower Hudson (9). Bedard has argued that these patterns may all result from the dechlorination activities of just three microbial strains, all separable

in anaerobic laboratory cultures, designated M, Q, and H or H' (10), with most dechlorination of the higher congeners coming from the H/H' activity. This could explain why the patterns of higher congener loss are essentially identical for the observed alteration patterns B, C, H, and H', even though the distributions of the more lightly chlorinated PCB congeners formed are quite different.

The columns on the left side of Table 2 present the homolog distributions and selected PCB isomer ratios for some representative specimens of subsurface sediment PCBs exhibiting those patterns, along with comparable data for a 90:10 Aroclor 1242:1254 mix, selected as a representative example of an unaltered Aroclor release. The marked compositional changes effected by anaerobic dechlorination are evident.

Geographical Variations in Dechlorination State. Surficial PCB alteration Pattern A was noted as far back as 1984 (7), but was not seen free from admixed Pattern B until recently. It has now been observed in the 0-1 cm. sediment layers and "fluff" layers collected in the Thompson Island Pool at the same time as the 1992 fish sampling, and repeatedly reproduced in the upper (0-5mm.), presumably microaerobic, sediment layers in laboratory microcosms where upper Hudson sediments were spiked with fresh Aroclor 1242 (22). The Pattern A alteration appeared in the microcosms within six weeks. Its microbiological basis is uncertain; one speculation is that it arises from a combination of an oxygen-tolerant, *meta*-selective dechlorination process followed by an aerobic biodegradation of some of the dechlorination products. In sediments, it appears to

effect limited removal of PCBs 17, 18, 33, 97, 99, 101, 153, and 167 without attacking 40, 44, 56, 60, 66, 70, 74, 87, 105, 114, or 128, and to result in increases in 47, but not in 19 or 27. Its most sensitive indicator is a depression in the ratio 33/28+31, or if separately measurable, just 33/28. Such depressions, usually paralleled by increases in the 47/49 ratio, are almost universally observed in PCBs recovered from aquatic environments.

Table 2 shows that in general the isomer ratios observed in upper Hudson fish fell between the values for fresh Aroclor and Pattern A altered PCB, with no obvious contribution from the subsurface Pattern B and C PCBs, with their high levels of dechlorination product PCBs 19 and 27, and low levels of readily dechlorinated PCBs 74, 87, 97, and 105. By contrast, the Table 2 data for isomer ratios in lower Hudson River fish generally fell between the values for dechlorination patterns H and H', indicating as much dechlorination as in the local sediments. Between the upper and lower river sampling stations there was a smooth progression in PCB isomer ratios. Figure 2 illustrates this for the PCB 74/49 ratio in the 1990, 1992, and 1993 fish; the 1995 caged minnows; and the 1989-90 *gammarus*, periphyton, dialysis bags, and surficial sediment grab samples.

The 1993 NOAA fish analyses by a dual column procedure permitted resolution of a number of congeners that were less readily quantified by the NEA single column analyses. Table 3 presents mean isomer ratios, calculated from the NOAA data, for 17 PCB congeners known (9) to be sensitive to Pattern H/H'

dechlorination, at various stations between the Thompson Island Pool (RM ~192) and Iona (RM 40). The levels of all of the dechlorination-sensitive congeners were found to decrease with distance downstream: most rapidly in the case of the toxic coplanar PCB 77; quite slowly for congeners 118 or 138; and with the major mono-*ortho* tetra-CBs 56, 60, 66, 74, and penta-CB 105 in between.

The 1993 EPA water and sediment analyses by the same procedure, as presented graphically in Figs. 3-73 to 3-80 of a recent report (17) were noted to show the same changes for congeners 56, 60, 66, 70, and 74. Their levels in upper Hudson water at RM 177.8 were similar to those in undechlorinated Aroclor 1242, while those in lower Hudson Pattern H/H' - dechlorinated sediments at RM 143.5, 88.5 or 43.2 were only half as great. For the surficial (0-2 cm., deposited 1991-1992) sediments at these four sites the observed (unadjusted for PCB 49 elution) PCB 74/49 ratios were 0.90, 0.53, 0.46 and 0.37 respectively, thus closely paralleling the declines seen in the 1993 NOAA fish (Table 2). In summary, throughout the river, the PCB isomer ratio patterns seen in the water and biota were found to have been tracking those of the local surficial sediments.

DISCUSSION

Utility of Isomer Ratio Analysis. The above results show that PCB isomer ratio analysis can be used to identify and quantify the niche-specific biological alteration processes to which an environmental PCB release may be subjected. These processes include the ubiquitous but enigmatic, possibly microaerophilic, microbial alteration process A at the sediment surface; the well-characterized

subsurficial anaerobic microbial dechlorination processes leading to alteration patterns B, C, H or H'; the genus-dependent fish PCB alteration processes leading to the patterns AP-ICT, AP-PET, AP-CAT, AP-ESX, and AP-LEP described above, and the microsomal P4502B-like alteration process exhibited by many crustaceans (which are frequently prey of the fish examined here) as well as by higher vertebrates (12). Characterization of such processes can be useful in defining the set of environmental niches through which a PCB composition has passed on its way from point of release to accumulation in a fish.

One complication of isomer ratio analysis is interference between the effects of different processes, especially as they affect the reference congeners used. For example, reference tri-CB 31, reference tetra-CB 49, and possibly penta-CB 110 are all potentially subject to metabolism by the AP-ICT system, and the first two of these also to losses under conditions of heavy depuration. We have presented here a procedure for correcting the 74/49 ratio for such losses of PCB 49 as a possible adjustment. An alternative would be to simply avoid the use of heavily depurated individuals, or of lampreys, eels, icterids or goldfish, in making quantitative determinations of local PCB alteration state *via* isomer ratio changes.

Previously, the most popular approach to handling environmental PCB congener distribution data has been by principal components analysis. This defines PCB composition in terms of two or three enigmatic "principal components". These may permit the grouping of samples into related sets, but do little to explain the chemical nature of the differences. It is now evident why this

happens: there are simply many more significant alteration processes affecting PCB composition than there are mathematically resolvable "components", so that the resolved "components" inevitably represent combinations of the effects of multiple alteration processes in various proportions.

Sources of the PCBs in Hudson River Fish. The PCB (and pesticide) "fingerprinting" provided by isomer ratio analysis, along with data from other environmental studies, show that the PCBs in Hudson River fish have been coming from four readily distinguished sources.

The first, and least important, of these is atmospheric deposition. This source is characterized by PCB homolog and pesticide distributions that are very different from those of the other sources, and is responsible for the low level PCB (and DDE) contamination seen in the fish and sediments of the upper reaches of the Hudson, the Mohawk River, and presumably other tributaries as well. The second identifiable source consists of the sewers and sediments of the New York Metropolitan area, which is where two important anadromous fish of the lower Hudson, the striped bass (STB) and the American shad (AMS) spend the winter before migrating upriver to spawn. These sediments are known to contain substantial levels of DDT-derived, chlordane-derived, and other pesticide residues (13), as well as PCB mixtures reflecting heavy contributions from Aroclors 1254 and 1260, which were particularly extensively used in railroad and substation transformers in that area. The 1978, 1982, and 1985 STB and AMS in our collection generally showed PCB homolog distributions and pesticide/PCB ratios

comparable to those of the sediments of New York Harbor and western Long Island Sound, indicating the significance of those sources.

The third distinguishable source consists of the moderately Pattern H/H'-dechlorinated PCBs of the sediments of the lower Hudson, which exhibit an isomer ratio "fingerprint" closely matching that of the lower Hudson resident fish. These PCBs have been there a long time. Radionuclide dating has shown that most were deposited in the 1950's and 1960's (14) and elevated levels in fish were seen in 1970 and 1973 (1), all before the removal of the Ft. Edward dam and sediment scouring/redeposition events of 1974-76 caused the heavy PCB contamination of the upper Hudson (16). In contrast to the stratification seen in the upper Hudson stillwater deposits, the PCBs in the cores collected at RM 143.5, 88.5, and 43.2 showed dechlorination-sensitive isomer levels in the surficial (i.e., deposited 1991-1992) strata that were little different from those in the subsurface (deposited 1982-90) strata (17). This is believed to have occurred because stratification in lower (tidal) Hudson sediments is disturbed by bioturbation and tidal scouring/redeposition in most areas (14, 23). These lower Hudson processes continue to make the PCBs from old deposits available at the sediment surface and thus accumulable by the biota. One original source of the old deposits is the formerly extensive industrial usage of PCB-based hydraulic systems in many of the riverside communities. Available Monsanto sales records for 1957-1977 document purchases by such users of over 3×10^6 lbs. of PCB products, especially the hydraulic fluid Pydraul A-200, an Aroclor 1242-1248

blend. Releases of such compositions into the river would result in the moderate elevations in higher homolog levels exhibited by lower Hudson sediments and fish (Table 2). A less plausible source would be inputs of dissolved PCBs eluted from upstream deposits, since these are depleted, rather than enriched, in the higher homologs (17), and these are substantially undechlorinated.

The fourth distinguishable source of the 1977-1993 Hudson River fish PCBs consists of Aroclor 1242-like compositions that have been on the surface of the sediments of the Thompson Island pool only long enough to have undergone a limited Pattern A alteration, thus indicating a continuing deposition. A recently identified source of this PCB input is an accumulation of old PCB spillage in the fractured bedrock under the former capacitor manufacturing plant at Hudson Falls. Seepage from this reservoir is now known to have been entering river as dense, water-insoluble, oily droplets of undechlorinated Aroclor 1242 that accumulate on the sediments of the Thompson Island Pool, the first downstream stillwater. There, the PCBs soon undergo Pattern A alteration and partial extraction into the water column and its biota, leading to the appearance of undechlorinated Pattern A PCBs in the fish. Eventually, of course, ongoing sedimentation covers each increment of PCB and allows anaerobic microbial dechlorination to the Pattern B- or C-dechlorinated PCBs of the local subsurface accumulations. However, because of the preservation of stratification in the upper Hudson stillwaters (17) the subsurface (and "hot spot") PCBs are no longer accessible to the resident biota. Therefore, the concentration of the Pattern A-altered PCBs in the surficial sediments, and hence the PCB level in the local fish, must be determined by the

ratio of the rate of fresh Aroclor 1242 deposition to the rate of fresh sediment input; and the near-stability of those levels over the 1980-1996 period must reflect the near-stability of that ratio. This implies that these steady state levels of PCB contamination should be unaffected by removal of the subsurface "hot spots". Instead, control of upper Hudson fish PCB levels will depend upon the success of ongoing efforts to control the Hudson Falls Aroclor 1242 influx.

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Figure Captions

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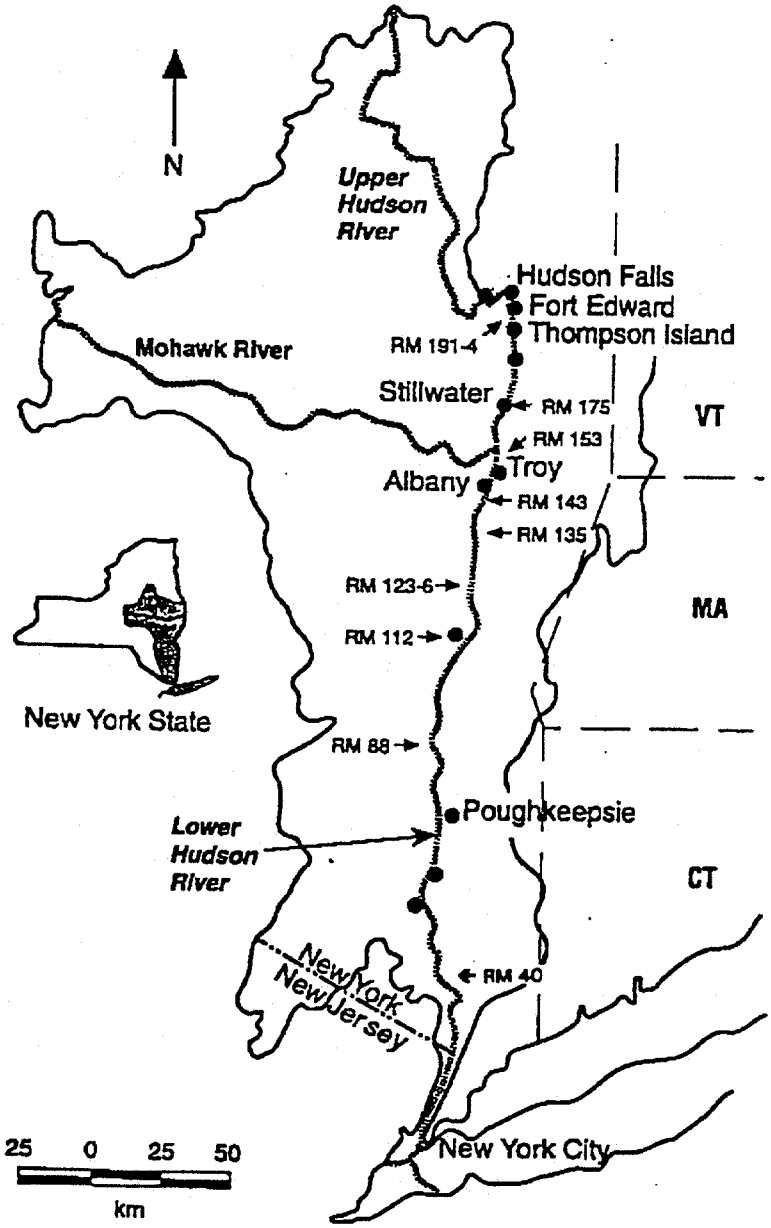
Figure 1 The Hudson River drainage basin.

Figure 2 Unadjusted Ratio of PCB Congener 74 to Congener 49 in Hudson River Biota, Sediments, and Water, 1985-1993, RM 40-203.

FIGURE 1
Hudson River Drainage Basin



RM indicates Fish Collection Site River Mile

Figure 2

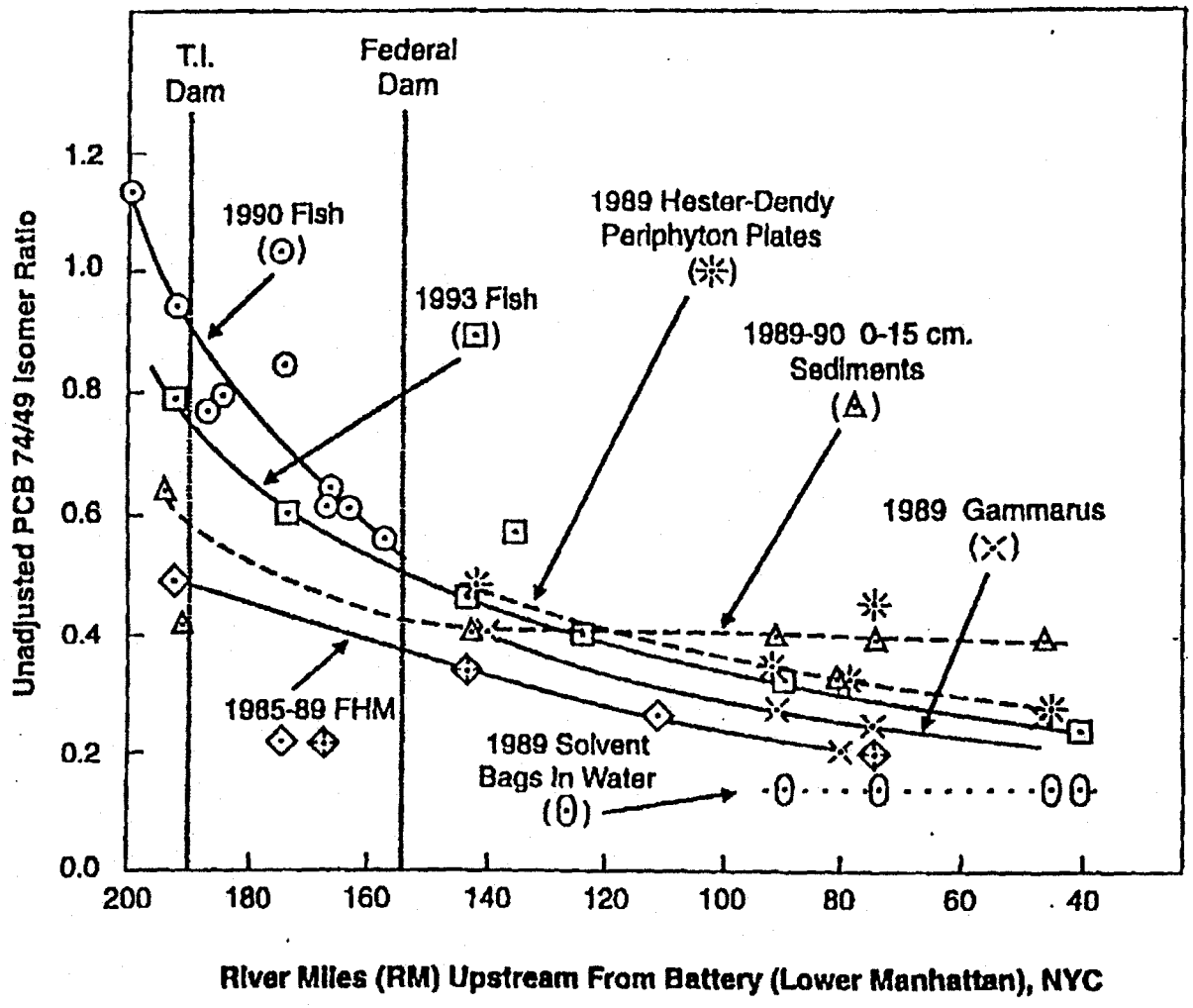


Table 1. Species-Characteristic PCB Alteration Patterns Observed in Hudson River Fish

Family	Common Name	Abrv.	Species Name	Alteration Pattern
Lampreys (Petromyzontidae)				
	Sea Lamprey	SLP	*Petromyzon marinus*	AP - PET
Freshwater Eels (Anguillidae)				
	American Eel	AME	*Anguilla rostada*	AP - ICT
Herrings (Clupidae)				
	American Shad	AMS	*Alosa sapidissima*	None
Bullhead/Catfish (Ictaluridae)				
	Brown Bullhead	BRB	*Ictalurus nebulosus*	AP - ICT
	Yellow Bullhead	YBH	*Ictalurus natalus*	AP - ICT
	White Catfish	WCF	*Ictalurus catus*	AP - ICT
Suckers (Catostomidae)				
	Northern Hogsucker	NHS	*Hypentelium nigricans*	AP - CAT
	White Sucker	WSR	*Catostomas commersoni*	AP - CAT(a)
Minnows (Cyprinidae)				
	Carp	CAR	*Cyprinus carpio*	None
	Goldfish	GLF	*Carassius auratue*	AP - ICT
	Golden Shiner	GSH	*Notemigonis crysoleucas*	None
	"Minnows"	MMM	*Cyprinia spp.*	None
	Fathead Minnow	FHM	*Dimephales promelas*	None
Pikes (Esocidae)				
	Chain Pickerel	CHP	*Esox niger*	AP - ESX(a)
	Northern Pike	NOP	*Esox lucius*	None
Codfish (Gadidae)				
	Atlantic Tomcod	ATT	*Microgadus tomcod*	AP - ICT
Temperate Bass (Moronidae)				
	Striped Bass	STB	*Morone saxatilis*	None(b)
	White Perch	WPR	*Morone americana*	None(b)
Sunfishes (Centrarchidae)				
	Largemouth Bass	LMB	*Micropterus salmoides*	None(b)
	Smallmouth Bass	SMB	*Micropterus dolomieui*	None(b)
	Rock Bass	RKB	*Amblophites ropestris*	None
	Black Crappie	BLC	*Pomoxis nigromaculatus*	None
	White Crappie	WCR	*Pomoxis annularis*	None
	Bluegill	BLG	*Lepomis macrochirus*	AP - LEP
	Longear Sunfish	LSF	*Lepomis megalotis*	AP - LEP
	Pumpkinseed	PKS	*Lepomis gibbosus*	AP - LEP
	Redbreast Sunfish	RBS	*Lepomis auritus*	AP - LEP(b)
Perches (Perchidae)				
	Yellow Perch	YPR	*Percha flara*	None
	Walleye	WAL	*Stizostedion vitreum*	None
	Tesselated Darter	TES	*Etheostoma olmstedi*	None

(a) Distinctive alteration seen in some, but not all individuals
(b) Some individuals showed weak and variable AP - ICT - like depressions in PCB 70, and occasionally also P4502B-like depressions in PCB 110, presumably altered in prey species.

Table 2. Mean Values of PCB Homolog Levels and Isomer Ratios in Upper and Lower Hudson Resident Fish Collected 1977 - 1993

Parameter	Reference Distributions						Upper Hudson River Means								Lower H.R. Means			
	Aroclor	Dechlorination Patterns					1977-1978		1990		1982		1993		1977-1978		1993	
	50:10	A	B	C	H	H'	Mean	%	Mean	%	Mean	%	Mean	%	Mean	%	Mean	%
	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	RSD	Wt%	RSD	Wt%	RSD	Wt%	RSD	Wt%	RSD	Wt%	RSD
Footnotes —	1	2	2	2	2	2	3		4		5		6		7		8	
No. of Fish in Mean -							n=18		n=29		n=16		n=36		n=15		n=45	
Homolog Distribution																		
% 1 Cl	.40	8.51	7.20	20.94	.90	1.03	.20	**	.37	**	.21	**	.47	**	.04	**	.01	**
% 2 Cl	12.96	13.88	33.76	48.01	15.77	10.79	3.86	*	1.90	**	2.62	*	2.26	*	2.41	**	1.44	*
% 3 Cl	42.14	31.72	33.38	18.38	38.36	42.72	23.48		18.39		24.35		19.79		18.56		18.93	
% 4 Cl	30.85	32.11	16.02	5.85	23.66	28.76	46.44		46.18		46.28		46.80		43.79		36.84	
% 5 Cl	8.06	8.79	5.81	2.64	11.89	11.28	16.95		19.54		16.95		21.63		20.02		24.35	
% 6 Cl	3.88	3.83	3.03	2.01	6.60	3.64	6.42		10.26		7.89		7.04		11.25		13.86	
% 7 Cl	.61	.86	.56	.70	1.27	1.22	2.07		2.66	*	2.23	**	1.61		3.26		4.88	*
% 8 Cl	.01	.19	.15	.16	.24	.28	.40		.56	**	.60	**	.36	*	.48	*	1.33	*
% 9 Cl	.00	.06	.10	.16	.10	.31	.17	*	.12	**	.15	**	.06	**	.17	**	.23	*
Mean %RSD all 2Cl-9Cl								38		54		88		38		45		42
Isomer Ratios PCB/PCB	Mean	Mean	Mean	Mean	Mean	Mean	Mean	RSD	Mean	RSD	Mean	RSD	Mean	RSD	Mean	RSD	Mean	RSD
Trichlorobiphenyls																		
19/28+31	.06	.10	.49	1.76	.09	.04	.07	**	.06	**	.02	**	.09	*	.08	**	.10	
18/28+31	.68	.28	.43	.97	.83	.55	.15		.12	*	.13		.16		.27	*	.34	
17/28+31	.31	.23	.42	.27	.46	.33	.21		.13	*	.13		.12		.22	*	.26	
27/28+31	.06	.09	.28	1.18	.10	.06	.10		.06	**	.03	*	.09	*	.11	**	.12	
26/28+31	.09	.14	.32	.33	.21	.18	.18		.12		.10		.16		.18		.24	
33/28+31	.43	.35	.22	.38	.20	.12	.11		.25		.24		.21		.12		.20	
22/28+31	.19	.33	.07	.10	.15	.07	.11		.28		.27		.17		.11		.11	
Tetrachlorobiphenyls																		
49	1.40	1.36	1.32	1.80	1.24	1.00	.99		1.29		1.24		1.01		1.06		.97	
47/48	.38	.56	.74	1.12	.70	.78	1.06		.72		.64		.51		.85		.58	
44/48	1.26	1.37	.08	.27	.68	.28	.48		.78		.98		.51		.64		.44	
40/48	.36	.34	.04	.07	.25	.19	.13		.15		.16		.08	*	.11		.02	**
74/48	.61	.73	.04	.25	.33	.22	.70		.84		.83		.78		.50		.36	
Adjusted 74/48 (note 9.)	.61	.71	.06	.39	.38	.26	.52		.59		.62		.52		.34		.28	
77/49	.13								.12	*			.10				.03	*
70/74	2.21	2.76	1.66	1.16	1.52	1.64	.76		1.89		2.30		1.41		.72	*	1.17	
Pentachlorobiphenyls																		
101/99	1.69	1.93	3.07	3.04	1.80	1.86	1.31		1.68		1.76		1.50		1.40		1.42	
87/101	.87	1.03	.63	.35	.33	.22	.49		.80		.82		.48		.42		.61	*
101/110	.91	.53	.48	.66	.76	.96	1.16		.71		.69		.86		.99		1.06	
99/110	.54	.28	.17	.18	.42	.53	.88		.42		.41		.64		.67		.75	
97/110	.48	.28	.06	.06	.21	.19	.36		.31		.28		.36		.26		.28	
87/110	.81	.54	.26	.18	.26	.22	.55		.57		.55		.46		.41		.63	*
118/110	.98	.87	.63	.72	.89	1.13	1.69		1.26		1.16		1.18		1.22		1.26	
105/110	.59	.74	.17	.21	.25	.31	.68		.91		.83		.83		.39		.49	
Hexachlorobiphenyls																		
146/153	.14	.26	.60	.73	.16	.26	.22		.24		.27		.34		.21		.36	
141/153	.18	.41	.00	.00	.12	.07	.12		.26		.29		.16		.13		.10	
138+163/153	1.10	1.43	3.83	1.91	1.04	1.17	1.29		1.27		1.34		1.38		1.16		1.04	
128/153	.25	.25	.17	.09	.19	.16	.22		.22		.21		.26		.15		.15	
167/153	.11	.03	.00	.06	.09	.07	.09		.03		.03		.09		.07		.10	**
156+171/153	.17	.42	.16	.12	.14	.15	.23		.32		.39		.19		.14		.12	
Mean %RSD (29 Ratios)								17		30		28		22		29		38

1. Mixture of Aroclors 1242:1254 in ratio of 50:10
2. Means (n=) of sediment core values: A (5); B (3); C (1); H (3); H' (1)
3. 6 BRB, 12 LMB. 1977-78, Upper Hudson Mile 175
4. 1 AME, 3 BLC, 3 CAR, 2 CHP, 1 LMB, 1 NOP, 2 PKS, 3 RBS, 3 RKB, 3 SMB, 3 WAL, 1 WSR, 3 YPR. Autumn 1990, Upper Hudson Mile 191
5. 2 BRB, 2 CHP, 2 PKS, 2 RKB, 2 SMB, 2 WSR, 1 YPR. May 1982, Upper Hudson Miles 174, 188, 192
6. 6 LMB, 13 PKS, 6 RBS, 6 TES, 4 YPR. NOAA Autumn 1993, Upper Hudson Mile "192
7. 5 BRB, 3 LMB, 2 SMB, 2 WCF, 3 WPR. 1977-78, Lower Hudson Miles 112, 126, 153
8. 3 BRB, 3 LMB, 6 PKS, 6 RBS, 3 SMB, 3 WCF, 19 WPR. NOAA Autumn 1993, Lower Hudson Miles 143, 135, 123, 88, 40
9. ADJ = 74/48 ratio adjusted for greater elution of PCB 48, as estimated from trichlorobiphenyl/tetrachlorobiphenyl BSAF ratio

* Indicates RSD in range of 50% - 70%; ** Indicates RSD > 70%

Table 3. Downstream Declines in 1993 NOAA Fish PCB Isomer Ratios (a.) that are Reduced by Subsurface Dechlorination Processes

				Tetrachlorobiphenyls							Pentachlorobiphenyls				Hexachlorobiphenyls					
		Isomer Cl Level -		1	1	1	1	1	1	0	1	1	1	1	2	2	1	1	2	1
		No. of Ortho- Cls -																		
		BZ#/BZ#		56/49	60/49	63/49	66/49	67/49	74/49	77/49	105/110	114/110	118/110	123/110	128/153	138/153	156/153	157/153	158/153	167/153
NOAA Station	River Mile	Species	(no.)																	
1,3,4	192	Pumpkinseed	(13)	.37	.37	.11	1.13	.06	.69	.09	.40	.07	.82	.01	.26	1.43	.17	.03	.17	.08
		All Species	(36)	.42	.44	.12	1.25	.07	.78	.10	.47	.09	.90	.01	.26	1.38	.16	.03	.16	.09
8	176	Pumpkinseed	(5)	.28	.26	.08	.85	.04	.55	.05	.33	.04	.73		.21	1.35	.13	.02	.12	.07
		All Species	(11)	.29	.29	.09	.89	.04	.59	.05	.39	.06	.83		.20	1.31	.13	.02	.11	.06
10	143	Pumpkinseed	(4)	.21		.08	.64	.02	.44	.04	.31	.03	.76		.16	1.12	.10	.01	.09	.20
		All Species	(18)	.20	.19	.08	.85	.04	.46	.04	.32	.04	.81		.15	1.05	.09	.01	.09	.10
11	135	White Perch	(4)	.25	.18	.09	.74	.05	.56	.04	.29	.05	.69	.00	.16	1.11	.10	.02	.11	.06
12	123	White Perch	(5)	.18	.15	.08	.54	.02	.40	.03	.24	.04	.71		.14	.95	.08	.01	.09	.09
15	88	Pumpkinseed	(4)	.10		.06	.31	.00	.24	.01	.17	.00	.61		.12	.92	.07		.07	.04
		All Species	(19)	.09	.10	.08	.42	.02	.31	.01	.23	.02	.72		.17	1.08	.08	.02	.09	.11
17	40	White Perch	(5)	.12	.05	.05	.35	.02	.21	.02	.14	.01	.52		.13	.85	.06	.01	.07	.06

a.) Ratios of PCB isomer levels as reported by Aquatech; not translated into Northeast Analytical equivalents as in Table 2.