POLYCHLORINATED BIPHENYLS

IN THE HUDSON RIVER

(HUDSON FALLS-FORT EDWARD, NEW YORK STATE)

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Polychlorinated biphenyls (PCB's), as recently as 1966, have been recognized as an environmental contaminant. PCB's are primarily used in industry and are even more persistent than DDT. These compounds are essentially nonalterable by microbial or physical-chemical activities and are incorporable into living protoplasm. The bonding between the chlorine atom and the biphenyl structure is resistant to shearing by natural degradation processes, therefore PCB's are not easily metabolized by enzyme systems presently found in nature (ALEXANDER 1975).

The atomic structure of PCB's gives them specific chemical characteristics very desirable for certain industrial uses, i.e. dielectric fluids in capacitors and transformers.

PCB's not only are incorporable into living biomass in natural ecosystems, but are transferable within food webs; the end result being a much higher concentration of these compounds occurring in specific tissues of summit carnivores (biomagnification).

It has been estimated that 4 to 5 x 10^3 tons/year of PCB's are lost into the Nation's fresh and coastal waters (NISBET & SAROFIM 1972). An indication of the widespread contamination of PCB's in today's society is illustrated in the Temporary Tolerance Limits (Table 1) set by the FDA in certain food products (KIMSBROUGH 1974).

TABLE 1

Temporary Tolerance Limits of PCB's

Substrate	Level (ppm)
Milk (fat basis)	2.5
Dairy Products (fat basis)	2.5
Poultry (fat basis)	5.0
Eggs	.5
Complete and finished animal feeds	.2
Animal feed components	2.0
Fish and shellfish (edible portion)	5.0
*Paper food-packaging material	10.0

*Does not apply to packaging material that is separated from the food by a barrier impermeable to PCB migration

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This paper describes the presence and extent of contamination of water, sediments, and biota of the Hudson River by industrial use and discharge of PCB's in the vicinity of Hudson Falls-Fort Edward, New York State.

MATERIALS & METHODS

Description of Sampling Area - Hudson River (Figure 1)

Station 0 is located near the town of Hudson Falls, New York in a hydroelectric impoundment area. This station is upstream and separated from the Ft. Edward discharge outfall by a hydroelectric dam (height - 15m). At sampling time (3:15 pm, August 12, 1974) the water was heavily laden with fibrous particulates being carried down from an upstream source. Several paper mills and fiber board manufacturers are located in Glens Falls, 3-5 miles upstream from Station 0. In the main channel area, the bottom is hard shale. In the shallows where water velocity is less, large deposits of sediments intermixed with bark, branches, lumber slabs, and cinders are found. A sediment sample was taken by coring into the sediments with a glass sampling jar and capping it underwater. A subsurface water sample was taken nearby.

A seine was used to collect fish near a patch of emergent vegetation on an opposite bank from the sediment deposits (east bank). The gastropod (snail) populations associated with the emergent vegetation were sampled simultaneously.

Station 1 is located at the junction of the Ft. Edward outfall and the Hudson River. There are smaller known discharges between Station 1 and Station 0. At Station 1 the Hudson River is a roaring, tumultuous river with a high velocity, high volume streamflow (4466 cfs)[1]. The river is heavily laden with heavy suspended loads of fibrous material. Water and sediment samples were taken at this point in the same manner as at Station 0 (9:15 am, August 13, 1974). The sediment sample was taken from a small submerged cinder-gravel spit at the outfall junction. An upstream gastropod population was sampled several meters above the junction. This station is only accessible by boat because the river banks are precipitous shale rock faces, 15m in height.

Station 2 is located about 0.25 miles downstream from the outfall junction where water and sediment samples were collected (10:00 am, August 13, 1974). River flow conditions are the same as at Station 1. No macroinvertebrate or piscine populations were observed at this station. The water is laden with the same fibrous suspended materials as evidenced at Station 0. The river bottom is mainly a shale ledge. A sediment sample was collected

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[1]Calculated from N.Y. State Water Resources Data Book, 1971.

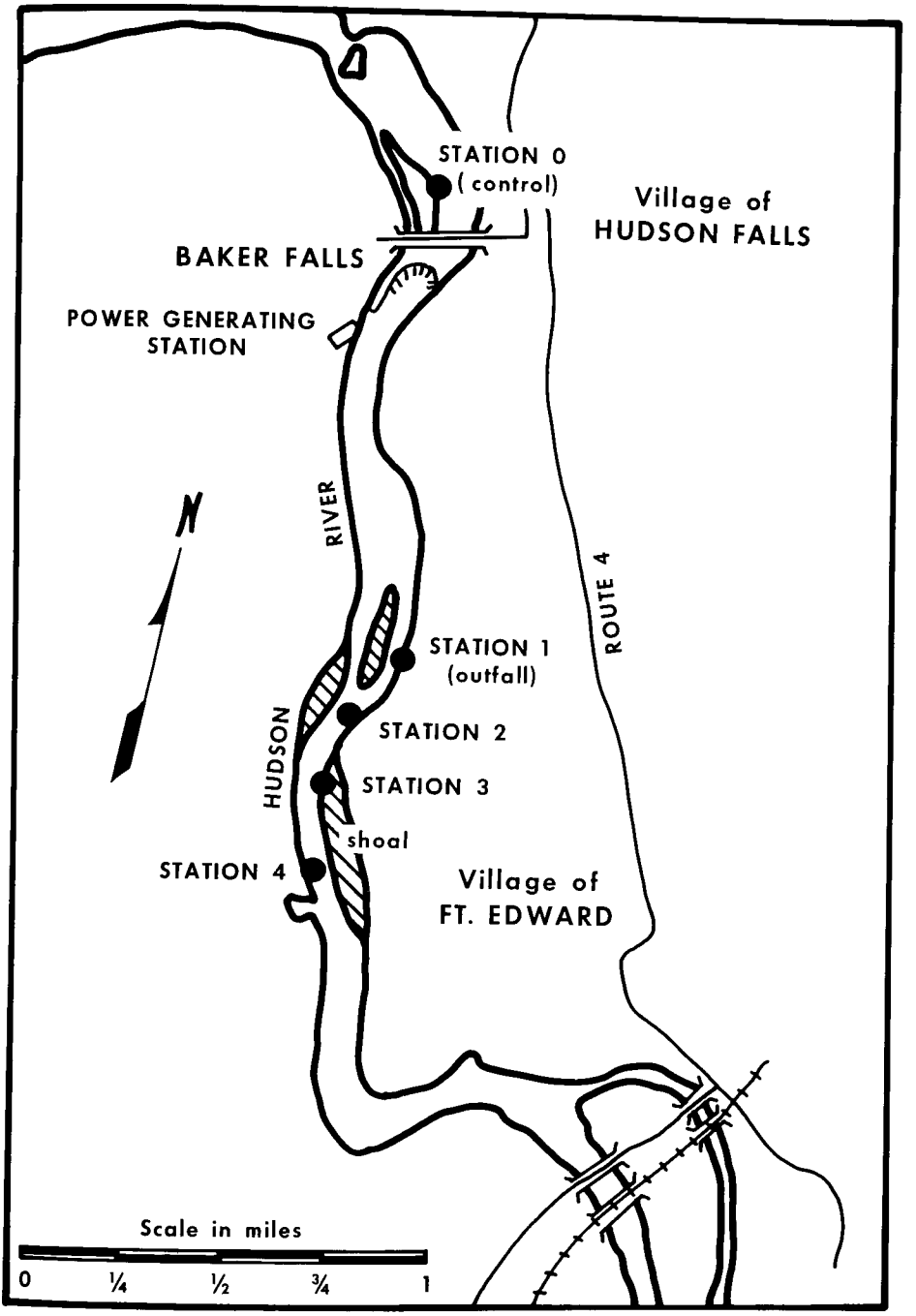

FIGURE 1 - Location of Sampling Sites in Hudson River in Hudson Falls-Fort Edward Area

from a remnant shale flake, cinder deposit bank above the high water mark. All the collecting sites downstream from Baker Falls were submerged until September 1973. When an abandoned hydroelectric dam at Fort Edward was removed, the water level was drastically lowered 5-15 meters.

Station 3 is located about 0.5 miles downstream from Station 1, water and sediment samples were collected (11:00 am, August 13, 1974). In this area an extensive sludge bank exists as a remnant of past industrial activity. The bank sediments consist of gravel, cinders, lumber slabs, and bark from logging activities that ceased 40 years ago. The sediment sample was collected from a submerged deposit near the same area where several fish were collected by seining. In the shallow area, the fibrous material, suspended at the upstream stations has flocculated onto the river bottom, coating the bottom with a "paper wrapping".

Station 4 is located 0.75 miles downstream from Station 1. The river is slightly wider at this point with decreased velocity. Fish populations are abundant in the shallow shoreline areas. These populations were sampled by seining. Water and sediment samples were collected in the river, three (3) meters upstream from the junction of a small stream that flows in on the west shore (1:15 pm, August 13, 1974).

Chemical Analysis

A measured volume of water sample was extracted with hexane. The extract was dehydrated, concentrated, and analyzed by computerized gas chromatography/mass spectrometry (GC/MS).[1]

The sediment sample was partially dried and extracted by column elution with a mixture of 1:1 acetone/hexane. The extract was washed with water to remove the acetone and then the polychlorinated biphenyls were extracted from the water with 15 percent CH_2Cl_2 in hexane. This extract was then dehydrated, concentrated to a suitable volume, and analyzed by computerized GC/MS.[2]

The biota samples were blended with anhydrous sodium sulfate (prewashed with redistilled acetone) and the homogenate was extracted with a mixture of hexane and ethyl ether (3:1 v/v). The extracts were placed on a 20 gm florisil column, eluted with 25 ml

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[1] A modification of methods published in METHODS FOR ORGANIC RESIDUES IN WATER AND WASTEWATER, 1971. Environmental Protection Agency, National Environmental Research Center, Cincinnati, Ohio.

[2] A modification of methods published in ANALYSIS OF PESTICIDE RESIDUES IN HUMAN AND ENVIRONMENTAL SAMPLES, 1961. Perrine Research Laboratories, Environmental Protection Agency.

of hexane, and the volume of the eluate was adjusted so the final concentration of PCB's was within the linear range of the gas chromatograph. The sample of rock bass from the discharge required a 50 fold dilution before analysis.

The presence of PCB's in all samples was confirmed by prechlorinating the samples with $SbCl_5$ for four hours at 170° C to form $C_{12}Cl_{10}$. The $C_{12}Cl_{10}$ was subsequently analyzed by gas chromatography using a three-foot column of 3 percent Dexsil-300 at 200° C.

Subsequently, a GC/MS analysis of the rock bass extract was performed along with analysis on Aroclor 1016 and 1242 standards.

Analysis Results

Detection of PCB's in water and sediments was accomplished by comparing computerized GC/MS Spectra of various Aroclor mixtures including 1016 supplied by the discharger and EPA with environmental sample extracts.

PCB's identified as Aroclor 1016 were found in the water samples at detectable concentrations at all sampling locations except Station 0 (control) and Station 4 (furthest downstream) (Table 2).

TABLE 2

Analysis of Water and Sediment Samples for Aroclor 1016 from the Hudson River in the Area of Fort Edward, New York

	Contamination Levels	
Location	Water ug/l (ppb)	Sediment mg/kg (ppm)
Station 0	1.0	6.9
Station 1	2800.0	6700.0
Station 2	2.2	540.0
Station 3	(3.0)* (3.1)	2980.0
Station 4	1.0	6.6

*Results of replicate analysis - a quality assurance procedure.

At all stations the sediments contained higher concentrations of Aroclor 1016 than the water column because PCB's preferentially adsorb onto suspended or already settled materials.

The high contamination level at Station 1 indicates the adsorptive capacity and constant exposure of the sediments nearest the outfall to the Aroclor 1016. These sediments were also heavily laden with noticeable oil and grease which serves as a solvent for PCB compounds.

At Station 3, high concentrations (2980 mg/kg) occur in the sediments, representing accumulated levels of PCB's, 10^3 fold greater than the outfall concentration. The high level is a product of historical plus present adsorption and deposition of PCB compounds. The PCB level at Station 2 represents historical deposition mainly. Although PCB's in the water column are below dectectable limits at Station 4, PCB's occur in significant quantities in the sediments.

Biological Tissue

Station 0

The samples collected above the discharge contained the later-eluting PCB's with retention times of 84, 98, 104, 112, 125, 146, and 174 relative to pp DDE. These are characteristic of Aroclor 1254, another PCB that was used extensively prior to Aroclor 1016. In addition, major PCB components were found at relative retention times of 37, 40, 47, 54, 58, 70, and 78. The relative concentration of the PCB components found in the control station samples and the absence of PCB components eluting earlier than 28 suggest that the PCB's in the biota can best be estimated as a mixture of Aroclor 1254 and Aroclor 1248. Using the later-eluting components of Aroclor 1254 and the earlier-eluting components of Aroclor 1248, the PCB concentrations in the biota samples were estimated and are presented in TABLE 3.

TABLE 3

PCB Concentrations in Biota Collected in the Hudson River

Location	Piscine Name	Total PCB ug/gm wet-wt.	Gastropod Name	Total PCB ug/gm wet-wt.
Station O	Notopis cornutus frontalis (Agassiz) (Northern Common Shiner)	7.0	Helisoma sp Physa sp	1.9
	Perca flavescens (Mitchell) (Yellow Perch)	17.0		
Station 1 (Above Outfall)	None		Helisoma sp Physa sp	[0.45]
Station 3	Ambloplites rupestris rupestris (Rainesque) (Northern Rock Bass)	350.0		
Station 4	Notropis cornutus frontalis (Agassiz) (Northern Common Shiner)	78.0	Helisoma sp Physa sp Limnacea sp	[27.0]

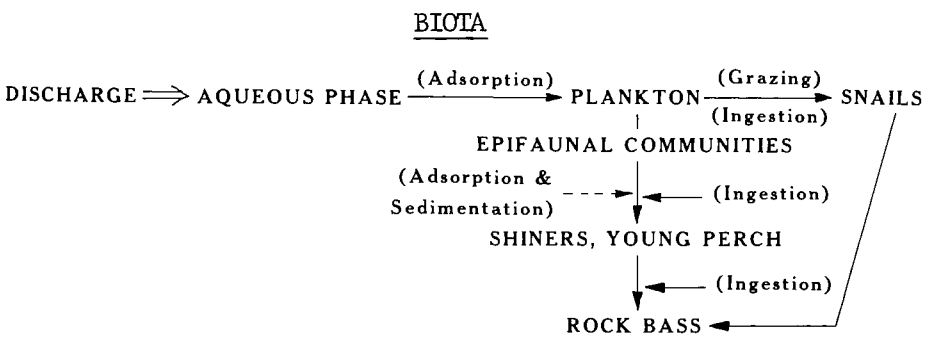
Distinctly different from the samples from the control area were the samples collected in the vicinity of or below the discharge. It is evident from a chromatogram of the sample of bass below the discharge that there are no major PCB components eluting after 78 relative to DDE. Moreover, the 21, 28, and 32 components are present in higher concentrations relative to the 37 component. This suggests that Aroclor 1242, Aroclor 1016, or a mixture of these two formulations are present in the Hudson River below the discharge.

DISCUSSION

The results illustrate that PCB's are ubiquitous in distribution within the Hudson River within a variety of substrates. Nevertheless, higher-than-background concentration in the sediments and biota can be found in the immediate vicinity of the PCB discharge.

Although the pattern of accumulation and magnification of PCB's in the biota was similar to that reported in the literature, insufficient information exists on transfer rates of PCB's within environmental substrates. The PCB's being discharged are in sufficient quantities that contamination of all environmental substrates have occurred; water, sediment, and biota.

Although an exact accumulation and transfer model could not be determined for the sampling area, a hypothetical presentation is given below:



At all stations the biota had higher levels of PCB's than the background water concentration. At all stations, except Station 3, the biota contain higher levels of PCB's than the sediments.

At all stations the snail populations are important accumulators and concentrators of PCB's (TABLE 4). The species collected are primarily herbivorous grazers, living off the periphyton growing on rocks, lumber slabs, and benthic surfaces. The snails ingest sedimented materials containing adsorbed PCB's along with their natural food.

TABLE 4

Concentration Factors of PCB's in the Hudson River

Location	Substrate	Concentration Factor Tissue/Water	Concentration Factor Tissue/Sediment
Station 0	Snails	$>1.9 \times 10^3$	3.63
	Common Shiner	$>7.0 \times 10^3$	.98
	Yellow Perch	$>17.0 \times 10^3$	.41
Station 1 (Above Outfall)	Snails	45×10^3	6.52
Station 3	Rock Bass	117×10^3	.12
Station 4	Snails	$>27 \times 10^3$	11.82
	Common Shiner	$>78 \times 10^3$	4.09

The adsorbed PCB's remain biologically active within the food web since snails are normal dietary constituents of larger game fish. This is a possible pathway for biomagnification. Likewise, the PCB's are remaining environmentally active and are not taken out of circulation by the geologic sedimentation process.

An indication of the seriousness of the problem in the Hudson River is that the PCB level in the Perca flavescens (Yellow Perch) at Station 0 is 68 times greater than that found in the same species from Lake Erie (KELSO & FRANK 1974). The fish analyzed in the Lake Erie study were even older and larger than those collected in the Hudson River. The most probable route of contamination for fish is through the dietary pathway and direct diffusion across exposed gill, intestinal, and integument surfaces. If the perch collected at Station 0 were older and larger, their source of PCB's might be the snails, however, small perch are mainly plankton and epifauna consumers (THARRATT 1969).

It is significant that the shiners and snails both contained PCB's, especially since these species are important grazers upon periphyton communities and serve as food for large consumers, namely the game fish; i.e., pike, pickerel, bass, and larger yellow perch.

The PCB level in the rock bass is greater than the maximum level documented for fish taken from any industrial river of the U.S. (NISBET & SAROFIM 1972). This represents a new record for PCB contamination of fresh water fish.

Although the game fish species are not commercially utilized in this stretch of the Hudson, sport fishing is a common widespread recreational activity. Ingestion of these fish by the populace would certainly lead to contamination of specific tissues in their bodies. Occurrence of PCB's in human tissues has

documented in the literature, especially in people who are constantly exposed to PCB's through their occupation or life styles. Even though these compounds have a comparatively low acute toxicity for mammals, the long term effects may be much more insiduous and devastating. A number of investigators have shown that PCB's induce production of liver microsomal enzymes. Others have shown that PCB's can decrease Vitamin A content in the liver (CECIL, et al. 1973). Transplacental passage of PCB's has also been shown (GRANT, et al. 1971). PCB's have been detected in human adipose tissue in such widespread occurrence that 41-45 percent of the U.S. population contains 1 ppm or more (PRICE & WELCH 1972).

Little is known concerning the specific mode of entry of PCB's into the organisms of the contaminated ecosystem. Information on transfer rates and modes is necessary before a plan of action can be recommended for removing the contaminated substrates from the Hudson Falls-Fort Edward area.

ACKNOWLEDGMENTS

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