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Polychlorinated Biphenyls in the Fish and Sediment of the Lower Fox River, Wisconsin

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The widespread contamination of the Great Lakes and associated watersheds by PCBs is well documented (DELFINO 1979, VEITH et al. 1981). A major concern is the potential serious human health effects in those individuals eating Great Lakes' fish (SONZOGNI & SWAIN 1980). Of the five Great Lakes, Lake Michigan may have the most severe PCB problem (DELFINO 1979). Recent data, however, indicate a downward trend in PCB concentrations in Lake Michigan fish (SHEFFY et al. in press).

The purpose of this paper is to examine the PCB concentrations in sediments and fish of the Lower Fox River. This river is the major tributary to Green Bay, one of the most biologically productive and important ecosystems of Lake Michigan (BERTRAND et al. 1976, GREAT LAKES FISHERY COMMISSION 1979) (Figure 1).

The PCB problem that exists in the Lower Fox River originated several years ago. The 64-km river is highly industrialized, and the paper industry dominates the industrial sector (SULLIVAN & DELFINO 1982). The largest source of PCBs to the river has apparently been the secondary fiber paper industry. These companies recycle waste paper to produce new paper products.

In the past, and still to some extent recently, the deinking of wastepapers released PCBs into the aquatic environment. Until 1971, PCBs were incorporated into carbonless copy paper (DELFINO & EASTY 1979, WALTER & ZAMBRANO 1981). When this type of paper was recycled and deinked, the PCBs were released to the aquatic environment through effluent discharge. Since PCBs have been discontinued for this use, the problem will eventually be alleviated, but extensive contamination has already occurred.

MATERIALS AND METHODS

Description of the Sampling Areas and Sample Handling:

Sediment. Samples were collected with a ponar dredge at the locations indicated on Figure 1. Sample No. 11 served as a background sample for the system. This sample was relatively free

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of industrial influence. The remaining samples were collected at appropriate locations along the river. Two grab samples at each location were homogenized, and a subsample was transferred to a one-quart solvent-cleaned Mason jar with foil-lined caps. The samples were initially placed on ice and then stored at 4°C until analysis.

Fish. Samples were collected at three locations. This approach was used to compare PCB burdens in fish along different stretches of the river since the river is impounded and discrete fish populations apparently exist in each stretch of the river. Fish were captured near sampling locations 8, 4 and 3 (Figure 1), by fyke netting or electro-shocking and shipped frozen to the laboratory. Both whole fish and fillet samples were prepared for analysis. A whole fish sample is defined as the entire fish, while a fillet sample is a skin-on portion taken from the dorsal area of the fish. Samples were initially coarsely ground and then frozen for storage.

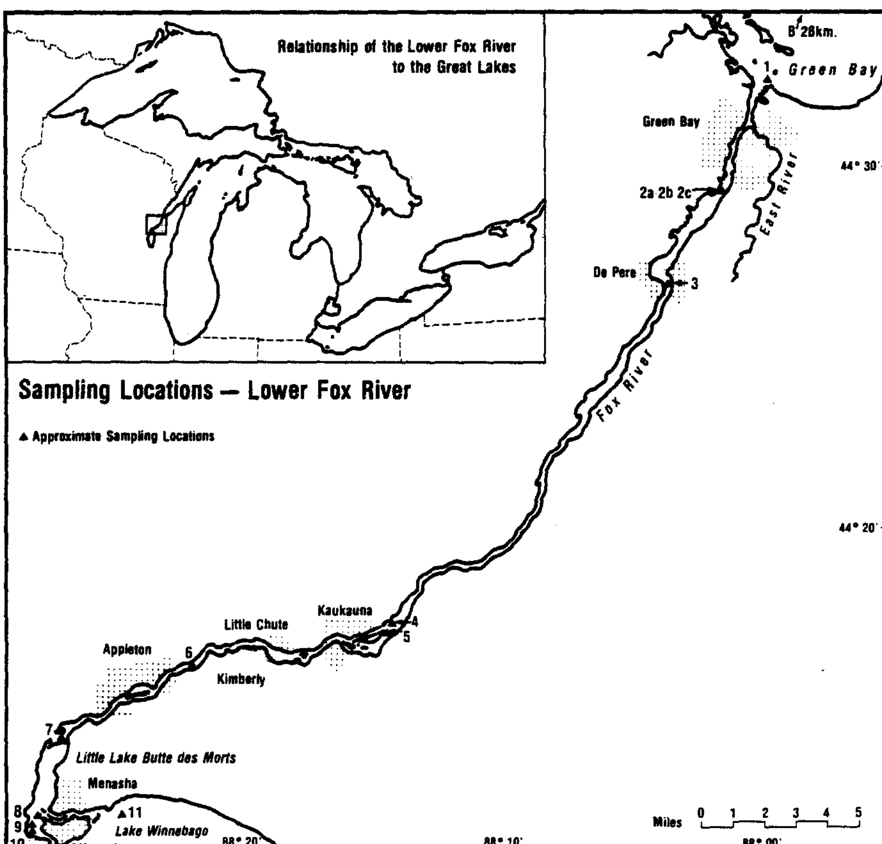

Figure 1. Study location and sampling sites - Lower Fox River, Wisconsin.

Analytical Methods:

Sediment. Prior to analysis, the entire sediment sample was homogenized in a high-speed blender. A 20 to 50 g subsample of wet sediment was decanted and acidified to pH 2 to 3 with concentrated HCl. The sediment was acidified to enhance acidic organic compound extraction (GROOSE 1982). The samples were then Soxhlet-extracted sequentially with acetone for 8 to 20 h and then with acetone/mixed hexanes (1:1) for an additional 8 to 20 h. The acetone and acetone/hexane extracts were filtered through Soxhlet-extracted glass wool and combined. The resulting extract was added to 200 mL of organic-free water at pH 11 to 12 for back extraction. The back extractions were performed sequentially with mixed hexanes using 100, 50, and 50 mL, respectively. Then the extracts were drained through anhydrous Na_2SO_4 to remove water. Next, the samples were concentrated to 5 mL by rotary evaporation and subjected to Florisil column chromatography. Cleanup was accomplished by elution with 200 mL of mixed hexanes/diethyl ether (9:1) at a flow rate of 3 to 5 mL/min. The eluates were concentrated by rotary evaporation and fractionated by silica gel chromatography. The silica gel was activated at 560°C for 4 h and partially deactivated (3% by weight) with distilled water before use. The samples were eluted at a flow rate of 2 to 4 mL/min with warm (30 to 40°C) mixed hexanes. The first 60 mL fraction was retained for PCB analysis. Finally, the samples were concentrated by rotary evaporation and then subjected to gas chromatographic analysis. Recovery of PCBs added to the sediments consistently exceeded 90%.

Fish. Prior to analysis the entire fish sample was ground to a powdered consistency with dry ice in a high-speed blender. After sublimation of the dry ice, a 10 g subsample of fish powder was combined with 60 g of anhydrous Na_2SO_4. The samples were column extracted with 230 mL of 20% diethyl ether in mixed hexanes with an elution rate of 5 mL/min. The eluants were concentrated to 10 mL under a gentle stream of filtered air. A 2-mL aliquot was taken for fat determination. The remaining 8-mL sample was subjected to a Florisil cleanup. Elution from the column was accomplished using 200 mL of 6% diethyl ether in mixed hexanes. Next, the samples were fractionated by silica gel chromatography as before. Three fractions were collected: the first 50-mL fraction contained the PCBs. Finally, the samples were concentrated under a gentle stream of filtered air and analyzed as before. Recovery of PCBs added to the fish tissue ranged from 85 to 97%.

Analysis of both sediment and fish samples for PCBs was performed by using gas chromatographs equipped with a ^{63}Ni electron-capture detectors. A 1.8 m x 4 mm i.d. glass column packed with 4% SE-30 and 6% OV-210 liquid phase was used. The column was kept isothermal at 215°C for fish extracts and 205°C for sediment extracts. A detector temperature of 300°C was used. The carrier gas was 90% argon-10% methane at a flow rate of 40 mL/min. Quantitation was done by using the peak height method by summing as many peaks from the sample extract chromatogram as matched corresponding peaks in the appropriate Aroclor PCB-standard chromatogram.

RESULTS AND DISCUSSION

Sediments. PCB concentrations ranged from 0.1 to 100 μg/g (Table 1).

Table 1. PCB Concentration in Sediments (BUELOW 1982).

Location	PCB Concentration (μg/g)
B	1.3
1	3.3
2a	68
2b	8.3
2c	0.2
3	1.8
4	1.2
5	1.7
6	10
7	6.7
8	0.7
9	56
10	100
11	<0.1

All sediments were quantitated as Aroclor 1242. The two highest PCB residues measured, 100 and 68 μg/g, were in samples taken from depositional zones downstream from major recycling paper mills. A three sample transect at locations 2a, 2b, and 2c (Figure 1) showed the wide variability of sediment PCB concentrations that can exist from one side of the river to the other. Sample No. 1 collected at the mouth of the river and sample B collected from 17 mi (28 km) into lower Green Bay indicated that the lower Green Bay sediments have also been partially contaminated. PCBs in the background sample for the system, collected at location No. 11 (Figure 1), were <0.1 μg/g, the lowest PCB concentration observed in this study. Most other sediment PCB concentrations measured were well above this level, confirming extensive contamination from industrial discharges.

Fish. Since 1976, over 200 fish samples from this system, representing 15 different species, have been analyzed for PCBs. Concentrations ranged from <0.2 to 90 μg/g. Samples were collected and analyzed to support the Wisconsin Department of Natural Resources (WDNR) fish monitoring program. The WDNR monitoring program has two main objectives. The first objective is designed to screen large geographic areas and is accomplished by utilizing carp (whole fish) as an indicator species. Carp were selected due to their high fat content (up to 20%), their abundance, longevity, wide distribution in Wisconsin waters, ease of collection, and the fact that they are seldom sought by sport fishermen (SHEFFY 1980). The second objective is to assess the need for issuing a fish consumption warning to the public. If any carp from the monitoring program contained 5 or more μg/g PCB, a site specific investigation was initiated. This involved the testing of a wide range of species (fillet portion).

The Lower Fox River has been under a fish consumption warning since 1976. This was issued soon after the establishment of the FDA tolerance level of 5 µg/g. Undoubtedly, PCB concentrations in fish were high long before the initial consumption warning was issued and probably occurred concurrent with the initiation of the recycling of carbonless copy paper that contained PCBs. Although a fish consumption warning still remains for the Lower Fox River, the fish PCB concentrations have declined consistently over the past several years. This decrease has coincided with a substantial reduction of PCB input to the system (Figure 2). By 1977 the major recycling paper mill adjacent to Little Lake Butte des Morts had installed and was effectively operating a secondary (biological) treatment system.

In Lake Michigan proper, direct uptake of PCBs by lake trout accounts for a very small portion (2 to 3%) of the total PCB accumulation (WEININGER 1978). For fish in the Lower Fox River,

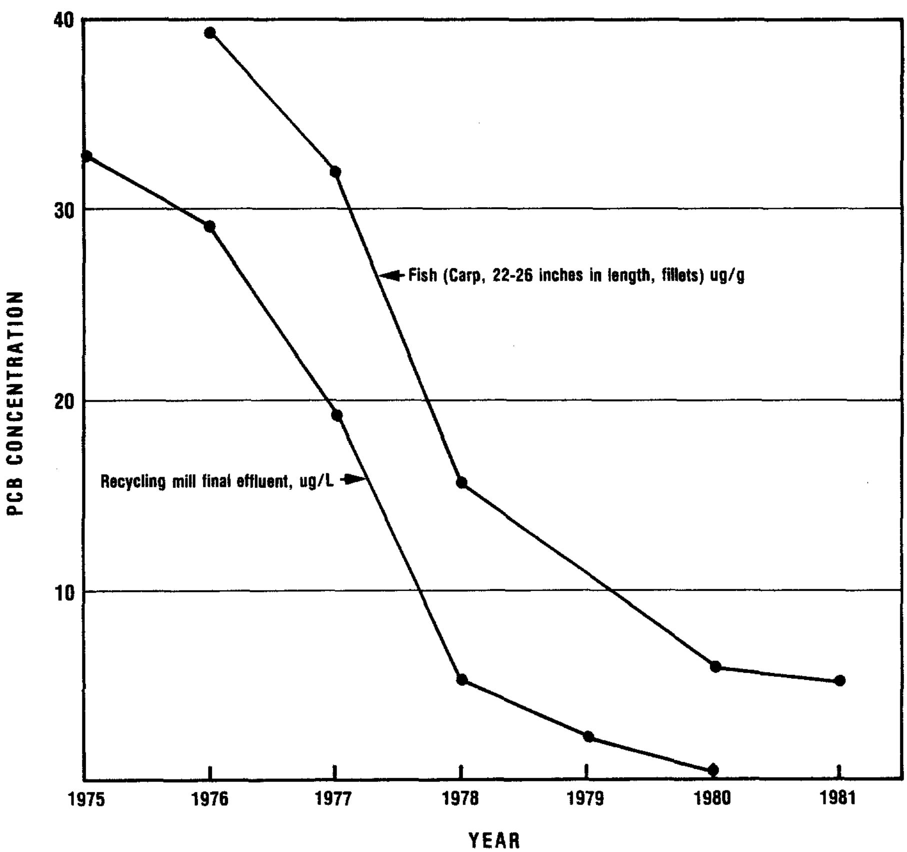

Figure 2. PCB concentrations in a recycling paper mill final effluent and in carp (1975-1981 average concentrations) in Little Lake Butte des Morts.

it appears that direct uptake of PCBs through the gills accounts for a greater portion of the total PCBs accumulated. This may be due to the differences in water column PCB concentrations that exist in the two water systems. Concentrations in Lake Michigan are very low (1 to 5 ng/L) (RICE et al. 1982) while the concentrations in the Lower Fox River have been reported to be much higher (50 to 850 ng/L) (PETERMAN et al. 1980).

Elevated PCB concentrations in Lower Fox River fish do not directly reflect the elevated PCB concentrations in sediments. For example, in 1978, carp (fillet samples) collected from near Kaukauna had PCB concentrations equal to or greater than carp of the same size in Little Lake Butte des Morts. In comparison, sediments collected near Kaukauna (locations 4 and 5, Figure 1) seldom contained PCB concentrations greater than 2 µg/g while sediments in Little Lake Butte des Morts contained PCB concentrations up to 100 µg/g. We offer this explanation. In Lake Michigan up to 20% of the PCB burden in adult lake trout is expected to have been cycled through sediment (WEININGER & ARMSTRONG 1980). In the Lower Fox River this percentage is probably substantially lower since benthic invertebrates are not present in large numbers, and therefore are not available as a food source (ZANELLA 1980). Also, the benthic invertebrates that are present do not appear to be a highly desirable food source for most fish species.

Since benthic invertebrates are not an important food source, the food chain that exists in the Lower Fox River is largely a water column or pelagic food chain. This would help to explain the decline in PCB concentrations in fish despite the high PCB concentrations that remain in the sediments. It can be expected that PCBs in the sediments will serve as a reservoir and that resuspension and transport of PCBs from this reservoir will serve as the major downstream source of PCBs for some time.

Conclusions. Pollution abatement technologies instituted by recycling paper mills have resulted in a decrease in PCBs in final effluents discharged to the Lower Fox River. Concurrent declines in fish PCB body burdens have also been noted. It is not certain, however, whether the resultant decrease in PCB final effluent concentrations is sufficient to protect aquatic life from bioaccumulation of PCBs above an acceptable level. Furthermore, sediment PCB concentrations remain high in previously impacted areas.

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