

TRENDS IN POLYCHLORINATED BIPHENYL CONCENTRATIONS IN HUDSON RIVER
WATER FIVE YEARS AFTER ELIMINATION OF POINT SOURCES

By Roy A. Schroeder and Charles R. Barnes

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 83-4206

Prepared in cooperation with the

NEW YORK STATE DEPARTMENT OF
ENVIRONMENTAL CONSERVATION



Albany, New York

1983

UNITED STATES DEPARTMENT OF THE INTERIOR

WILLIAM P. CLARK, Secretary

GEOLOGICAL SURVEY

Dallas L. Peck, Director

For additional information write to:

U.S. Geological Survey
P.O. Box 1350
Albany, New York 12201
(518) 472-3107

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CONVERSION FACTORS AND ABBREVIATIONS

The following factors may be used to convert International System units of measurement to the inch-pound system of measurement.

<u>Multiply SI unit</u>	<u>by</u>	<u>To obtain inch-pound unit</u>
millimeter (mm)	0.03937	inch (in)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
cubic meter (m ³)	35.31	cubic foot (ft ³)
kilogram (kg)	2.205	pound (lb)
degree Celsius (°C)	$(1.8 \times ^\circ\text{C}) + 32$	degree Fahrenheit (°F)

Other abbreviations used in this report include:

g, gram	m ³ /s, cubic meter per second
μm, micrometer	μg/g, microgram per gram
mg/L, milligram per liter	kg/d, kilogram per day
μg/L, microgram per liter	cm/yr, centimeter per year

Trends in Polychlorinated Biphenyl Concentrations in Hudson River Water Five Years After Elimination of Point Sources

By Roy A. Schroeder and Charles R. Barnes

ABSTRACT

Discharge of polychlorinated biphenyls (PCB's) to the Hudson River during 1950-77 at two industrial outfalls approximately 1 kilometer apart in Hudson Falls and Fort Edward, N.Y., has resulted in serious degradation of river water in the 50-kilometer reach of the upper river and the 250-kilometer reach of the estuary. Although industrial discharges from both outfalls were stopped in 1977, contaminated river-bottom sediments continue to contribute PCB's to the river water. PCB concentrations in the sediments range from several hundred micrograms per gram near the outfalls to less than 10 micrograms per gram in the lower estuary. This level of contamination is 2 to 3 orders of magnitude higher than in other major rivers. The absence of large changes in isomeric composition of PCB's in Hudson River water with distance below the source, with river discharge, and through time is consistent with the concept of a single source and limited degradation of the contaminant since industrial discharge was halted.

PCB's are supplied by river-bottom sediment to the overlying river water by two mechanisms--(1) desorption and diffusion, and (2) resuspension. Because desorption and diffusion is a relatively constant process, dilution through increased water discharge causes concentrations of dissolved PCB's to decrease. During high flows, however, when scouring and resuspension of contaminated sediment occurs, concentrations of suspended PCB's in the river water increase.

Transport rates of waterborne PCB's in selected reaches indicate that virtually all PCB's enter the water from the most contaminated sediments, which are within 20 kilometers of the outfalls. Transport of PCB's from the upper river to the estuary (except during extremely high flows) decreased from 10 kilograms per day in 1976 to 5 kilograms per day in the late 1970's and to 1 kilogram per day in 1981. Because PCB's are highly resistant to chemical and biological degradation, this decrease through time probably results from some physical cause, such as the burial of highly contaminated sediments by cleaner sediments originating upstream.

INTRODUCTION

In the late 1960's, nearly four decades after the introduction of polychlorinated biphenyls (PCB's) into commercial use, scientists became aware of widespread PCB dispersion in the environment and the possible resultant hazard to public health. PCB's had a wide variety of uses, the major one of which was in electrical capacitors and transformers (Nisbet and Sarofim, 1972), where their resistance to degradation at high temperatures made them particularly suitable as insulators and coolants.

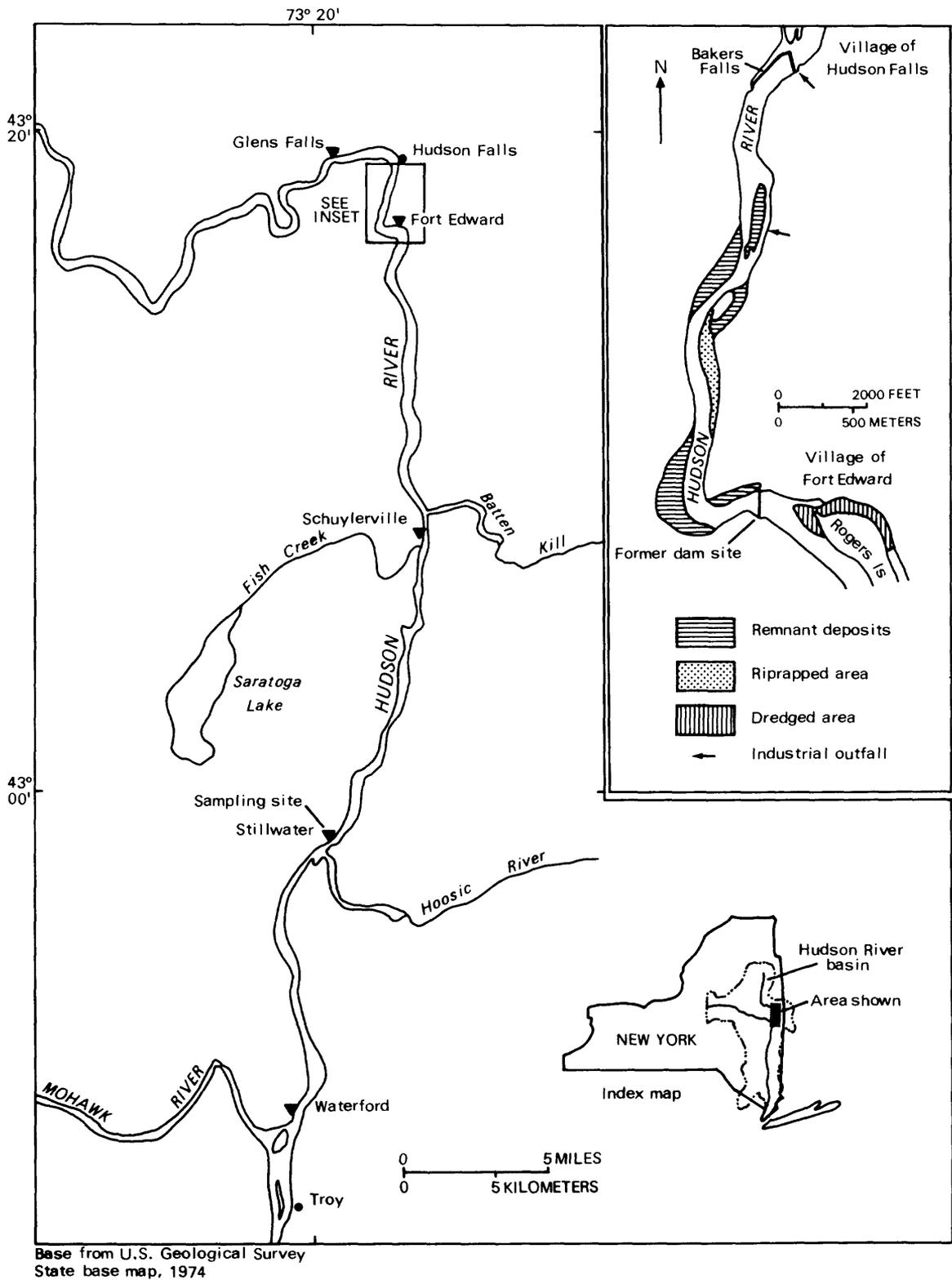


Figure 1.--Location of PCB-sampling sites in upper Hudson River and areas of PCB discharge. (Inset from Hetling and others, 1978.)

History of Hudson River Contamination

Two electrical equipment manufacturing plants at Fort Edward and Hudson Falls, N.Y., used large quantities of PCB's that accounted for 15 percent of all domestic purchases of PCB's during 1966-74 (Tofflemire and Quinn, 1979). Discharge of PCB's into the Hudson River at each site, about 1 km apart, began about 1950. Records of amounts discharged were not available until the mid-1960's, which is about the time that usage in the United States peaked (Nisbet and Sarofim, 1972). Applications to permit discharges to the river state that during 1966-74, the quantity of PCB's discharged averaged 13.6 kg/d. By 1975, the quantity had been reduced to 2.2 kg/d, by 1976 to 0.23 kg/d, and by 1977 to less than 4 g/d (Tofflemire and Quinn, 1979).

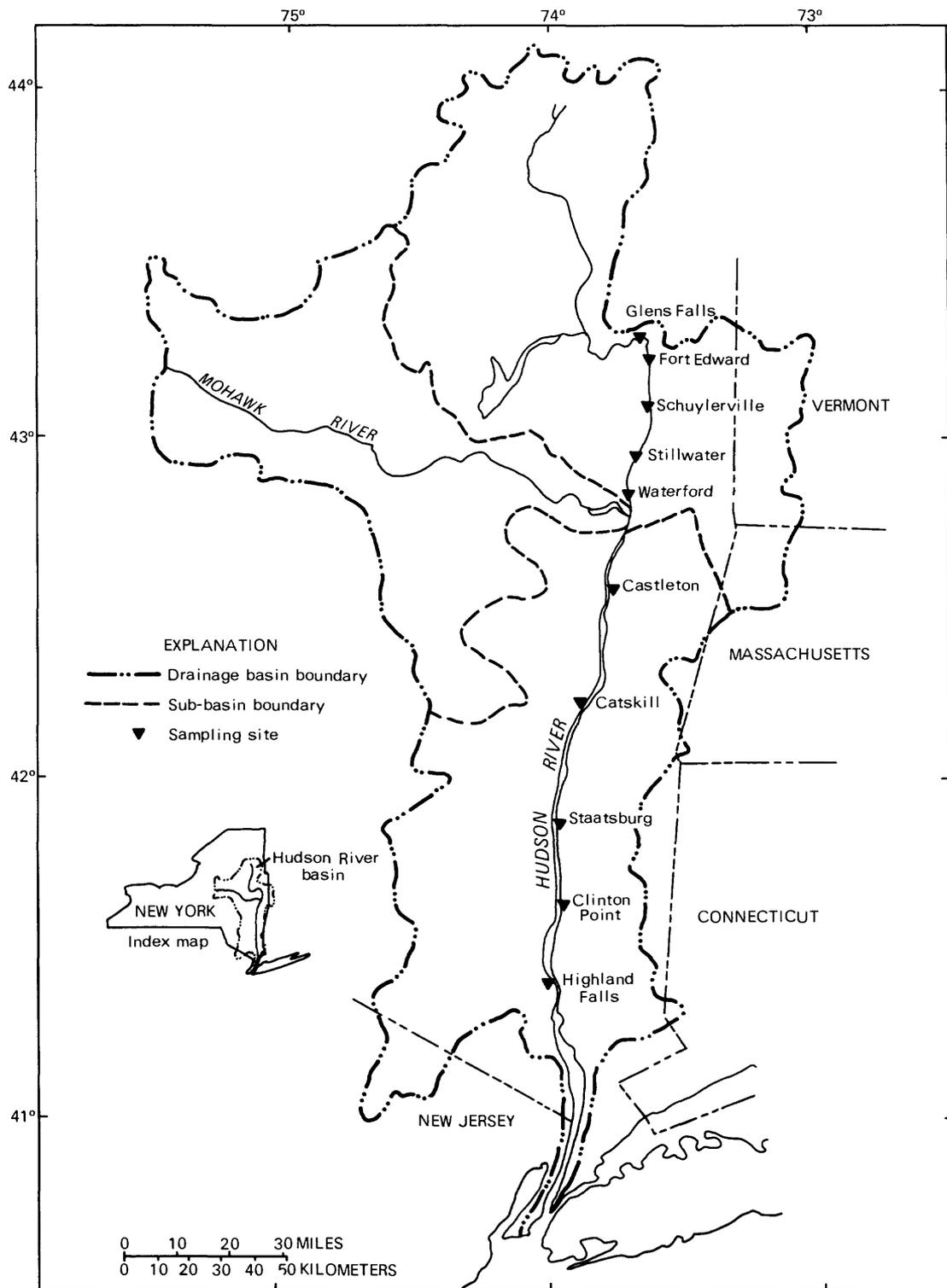
PCB's discharged to the river accumulated on river-bottom sediment in a river pool formed by the Fort Edward dam, a 150-year old, 15-ft stone and wood structure 3 km downstream from the upper outfall (fig. 1 inset). When the dam was removed in October 1973, massive quantities of PCB-contaminated sediment that had accumulated behind it were washed downstream. Concentration of PCB's in the sediment has been found to decrease with distance below the outfalls from several hundred $\mu\text{g/g}$ at Fort Edward to less than 10 $\mu\text{g/g}$ at the harbor in New York City 300 km downstream (Hetling and others, 1978; Tofflemire and Quinn, 1979). Because point discharges were eliminated in 1977, these sediments are probably the present source of PCB's in Hudson River water. This assertion is supported by evidence from sediment cores dated by cesium-137 and analyzed for PCB's (Tofflemire, Quinn, and Hague, 1979; Bopp and others, 1981). Highest PCB concentrations in cores from several sites along the river date to the mid-1960's, the time of greatest PCB discharges. Estimates based on sediment analyses are that 140,000 kg of PCB's now reside in riverbed sediments in the upper Hudson River, 90,000 kg reside in riverbed sediments in the Hudson estuary, and 300,000 kg are contained in dredge-spoil areas and dumps in the upper Hudson basin (Hetling and others, 1978).

The economic impact of contamination has been most pronounced in the 250-km tidal estuary below Troy (fig. 2), where commercial fishing for nearly all species has been banned and sport fishing substantially curtailed. All fishing has been banned in the contaminated reach from Troy north to the outfalls and to the first impassable fish barrier in all tributaries of that reach.

Purpose and Scope

Regular monitoring for PCB's in Hudson River water was begun by the U.S. Geological Survey in late 1975 at Waterford and was expanded to other contaminated upstream reaches in 1977 and to the estuary in the spring of 1978. The main purpose of this monitoring was to gather several years of data on PCB concentrations preparatory to removal of contaminated sediments by dredging, which was originally scheduled for the early 1980's. Plans for dredging and disposal of sediments are currently being reevaluated.

This report examines the contribution and transport of PCB's from various reaches of the Hudson River and the changes in PCB concentration since 1977, when industrial discharge was terminated.



Base from U.S. Geological Survey
State base map, 1974

Figure 2.--Location of PCB sampling sites in Hudson River estuary, which begins at Troy. (Locations of sampling sites in upper Hudson basin are shown in figure 1.)

This study of PCB concentrations and transport rates in the Hudson River by the U.S. Geological Survey is part of a larger investigation coordinated by the New York State Department of Environmental Conservation. Results of these studies have been summarized in a series of technical papers by the New York State Department of Environmental Conservation (1978, 1979; also Hetling and others, 1978; Tofflemire, 1979; Tofflemire and Quinn, 1979; Tofflemire, Hetling, and Quinn, 1979; Tofflemire, Quinn, and Hague, 1979; Shen and Tofflemire, 1979; Tofflemire, 1980; Tofflemire, Quinn, and Carcich, 1980; Brown, 1981; Tofflemire, Shen, and Buckley, 1982).

Acknowledgments

Data were collected and interpreted by the U.S. Geological Survey in cooperation with the New York State Department of Environmental Conservation.

METHODS

Data on water discharge, suspended-sediment concentration, and PCB concentration were collected by methods described in Buchanan and Somers (1968, 1969), Carter and Davidian (1968), Goerlitz and Brown (1972), Guy and Norman (1970), and U.S. Geological Survey (1977). Methods of sample collection in Hudson River PCB studies are described in Turk and Troutman (1981b) and are summarized briefly here. Most data are published annually by the U.S. Geological Survey (1977-82).

Sampling Sites

Sites sampled for PCB's are, in downstream order, Glens Falls, Rogers Island at Fort Edward, Schuylerville, Stillwater, and Waterford (fig. 1). Glens Falls serves as a background-data site because it is upstream from both outfalls. PCB's were detected in fewer than 5 percent of all samples collected at Glens Falls since 1977. At Rogers Island (fig. 1 inset), the Hudson River divides into a main stem and canal channel, both of which have been sampled regularly since 1978. Flow in the main stem is slightly greater than in the canal except during high flows, when an increasing proportion of total flow is through the main channel. The Schuylerville site is below the mouth of the Batten Kill, the Stillwater site is above the Hoosic River, and the Waterford site is above the Mohawk River (fig. 1). The Mohawk is by far the largest tributary; its flow is often nearly as large as that of the Hudson River at Waterford.

Locations of regular monitoring sites in the tidal (estuarine) Hudson River below Troy are shown in figure 2. In downstream order they are at Castleton, Catskill, Staatsburg, Clinton Point, and Highland Falls. Data were collected in the estuary during 1978-81, usually from late spring to early fall. An average of five samples was collected at each estuarine station during each year.

Field Methods

Depth-integrating samplers were used to collect river-water samples for analysis. Samples from the upper Hudson were taken from bridges; those from

the estuary were taken from a boat. The sampler held a wide-mouth glass bottle and was lowered and raised through the water column. Because several vertical passes were generally necessary to obtain a sufficient quantity of water (about 1 liter) for PCB analysis, water from each pass was transferred to a 1-liter narrow-mouth glass bottle with Teflon¹-lined screw cap. For collection of duplicate samples, water from each vertical pass was divided equally into two bottles.

Equipment coming in contact with the sample was cleaned with hexane and rinsed thoroughly with river water before use. Glass sample bottles were not rinsed with river water but were previously rinsed with hexane, then baked overnight at 300°C (Turk and Troutman, 1981b). All samples were shipped chilled on ice to the U.S. Geological Survey's National Water-Quality Laboratory in Doraville, Ga., where all PCB analyses were done.

Analysis for total recoverable PCB concentration was performed on unfiltered samples; results therefore include the dissolved as well as the suspended fraction. Dissolved PCB concentrations were determined on samples filtered through a 0.45- μ m silver oxide filter. Filtration was by nitrogen-pressurization of the sample contained in a stainless-steel holding vessel. Dissolved concentrations were determined on fewer than 5 percent of all samples. Dissolved-PCB data were used only to provide supporting evidence for the mechanism of transport; all other interpretations, such as calculation of loading rates, are based on total recoverable concentrations.

Analytical Methods

Hexane was added directly to the 1-liter glass sample bottles as soon as they arrived in the laboratory. The bottles were then stored in a refrigerator for a few days to a few weeks, depending on work load, to await further preparation for analysis. Elapsed time from sample collection to laboratory analysis was usually 2 to 6 weeks. Analysis of split samples retained in Albany for up to 7 months indicate that storage time had no discernible effect on concentration.

Allowing several days' contact time between solvent and water directly in the sample bottle is desirable because of the PCB's affinity for particulates (Haque and others, 1974; Halter and Johnson, 1977; Steen and others, 1978; Hiraizumi and others, 1979; Simmons and others, 1980), dissolved organic macromolecules (Hassett and Anderson, 1979), and even glass surfaces (Pepe and Byrne, 1980).

The hexane extracts, after alumina-column cleanup and evaporative concentration, were analyzed on a Tracor 560 dual-column gas chromatograph (GC). (Instrument operating conditions are summarized in table 1.) Although GC analysis can be quantitative, the nature of PCB's renders their analysis only semiquantitative for reasons discussed below.

¹ Use of corporation and brand names is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.

Table 1.--Operating conditions of gas chromatograph used
in analysis of polychlorinated biphenyls.

Column length: 6 ft (1.83 m)

diameter: 2 mm
material: glass

Support phase: Supelcoport 100-200 mesh

Liquid phase: column 1: 3 percent SP-2100
column 2: 1.95 percent SP-2401; 1.5 percent SP-2250

Carrier gas: nitrogen

Detector: nickel-63 (electron-capture)

Detector temperature: 350°C

Injector temperature: 210°C

Oven temperature: 210°C (isothermal)

The molecular structure of PCB's is illustrated in figure 3. Replacement of 1 to 10 chlorine atoms in any of the 10 positions on the biphenyl moiety yields 209 possible isomers, listed in table 2. PCB's were manufactured by catalytic chlorination of biphenyl at elevated temperatures. Chemical composition of the final product varied with degree of chlorination and blending process. The product was made and marketed in the United States by Monsanto Corporation under the trade name Aroclor. Each Aroclor consisted of a mixture of about 20 congeners (Westcott and others, 1981). Table 3 shows the approximate composition of various Aroclors.

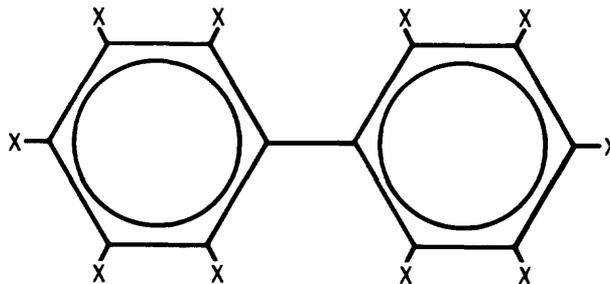


Figure 3.--Chemical structure of polychlorinated biphenyls.
X represents substitution of a hydrogen or chlorine
atom in each of the 10 positions. (From National
Research Council, 1979.)

Table 2.--Weight percent chlorine and number of isomers of polychlorinated biphenyls.

[Data from National Research Council, 1979]

Stoichiometric formula	Weight percent chlorine	Number of isomers
C ₁₂ H ₉ Cl ₁	18	3
C ₁₂ H ₈ Cl ₂	31	12
C ₁₂ H ₇ Cl ₃	41	24
C ₁₂ H ₆ Cl ₄	48	42
C ₁₂ H ₅ Cl ₅	54	46
C ₁₂ H ₄ Cl ₆	58	42
C ₁₂ H ₃ Cl ₇	62	24
C ₁₂ H ₂ Cl ₈	65	12
C ₁₂ HCl ₉	68	3
C ₁₂ Cl ₁₀	79	1

Table 3.--Approximate percentage composition of Arochlors.

[Data from National Research Council, 1979]

Stoichiometric formula	Aroclor type						
	1221	1232	1016	1242	1248	1254	1260
C ₁₂ H ₁₀	11	6	<0.1	<0.1	--	<0.1	--
C ₁₂ H ₉ Cl ₁	51	26	1	1	--	<0.1	--
C ₁₂ H ₈ Cl ₂	32	29	20	16	2	0.5	--
C ₁₂ H ₇ Cl ₃	4	24	57	49	18	1	--
C ₁₂ H ₆ Cl ₄	2	15	21	25	40	21	--
C ₁₂ H ₅ Cl ₅	0.5	0.5	1	8	36	48	12
C ₁₂ H ₄ Cl ₆	--	--	<0.1	1	4	23	38
C ₁₂ H ₃ Cl ₇	--	--	--	<0.1	--	6	41
C ₁₂ H ₂ Cl ₈	--	--	--	--	--	--	8
C ₁₂ HCl ₉	--	--	--	--	--	--	1
C ₁₂ Cl ₁₀	--	--	--	--	--	--	--

It was found in this study that Aroclors from the Hudson River were almost always in the composition range from 1232 to 1248¹, which consist mostly of biphenyls having from 1 to 5 chlorine atoms and probably representing a total of several tens of congeners (National Research Council, 1979).

Given the differences in chemical properties of each congener, fractionation processes in nature are likely to alter the mixture so that environmental samples will no longer precisely match the commercial Aroclors that are used as standards in the laboratory. In summary, then, the semiquantitative, as opposed to quantitative, nature of PCB analyses results from the facts that (1) commercial mixtures contain many congeners (not all of which are separated by a 6-ft chromatographic column), and (2) environmental samples rarely match precisely the commercial standards used to determine concentration.

Concentrations were calculated by dividing the area of a sample's identified PCB peaks by the area of all peaks for an Aroclor standard, then multiplying this ratio by the concentration of the Aroclor standard. Requirements for a calculation were that at least 60 percent² of the peaks in a standard be present in a sample, and both relative peak ratios and column detention time must match. In a few samples, chromatographic peaks resembled a mixture of two Aroclors. In such cases, calculations were based on a standard containing the two Aroclors.

As indicated in table 1, two columns having different physico-chemical characteristics were used. Concentrations were calculated individually for each column to the nearest hundredth of a $\mu\text{g/L}$. The lower of the two values was chosen as the correct one on the assumption that the higher value could include the contribution of "hidden" peaks from compounds other than PCB's.

Concentrations were rounded to the nearest tenth of a $\mu\text{g/L}$. Values are reported to that level of significance by the U.S. Geological Survey (1977-82); however, calculations in this report are based on the values provided before rounding.

Precision, expressed as standard deviation for field duplicates (splits), was 15 to 20 percent during the study. This figure includes combined variability due to both laboratory procedures and field sampling.

Concentrations as reported are uncorrected for incomplete extraction. Extraction efficiency probably exceeds 80 percent in nearly all samples but can be expected to vary somewhat with changes in the sample matrix. Extraction efficiency is high for Hudson River water because the water is relatively low in suspended sediment and dissolved organic carbon concentrations.

¹ Higher numbers in the 1200 series are assigned to the more highly chlorinated Aroclors. The last two digits are derived from the approximate weight percent chlorine content of the Aroclor.

² Generally, the match is about 80 percent for Hudson River water. Identifications were confirmed by mass spectrometry whenever total PCB concentration exceeded 2 $\mu\text{g/L}$.

PCB-TRANSPORT MECHANISMS AND TRENDS

Mechanism of Transport

Interpretation of data collected during the 1977 water year¹ revealed two distinct mechanisms of PCB transport in the upper Hudson River-- resuspension of PCB-laden bottom sediments during high discharge, and a steady movement of PCB's from bottom sediments into the overlying water the rest of the time (Turk, 1980; Turk and Troutman, 1981a,b). Results obtained in subsequent years support this interpretation.

Resuspension of bottom material by scour becomes negligible at flows less than 600 m³/s at Waterford and proportionately lower flows upstream. If resuspension were the sole mechanism for the entry of PCB's to the water, PCB concentration would decrease to below the detection limit at low flows. However, because PCB's also diffuse continuously from bottom sediments into the overlying water at a more or less steady rate, their concentration increases as flow decreases. The net result is that PCB concentrations are elevated at both high and low flows and are lowest at intermediate flows. This dual relationship between PCB concentration and river discharge was indicated by data from Schuylerville, Stillwater, and Waterford during the 1977 water year (Turk, 1980) and was confirmed in subsequent years. Data obtained from water years 1977-81 at Schuylerville are plotted in figure 4. The relationship between concentration and discharge is somewhat less obvious in figure 4 than in plots for a single year because of decreases in the diffusive loading rate with time and because of the event-specific nature of transport during periods of high flows, as discussed in section "Transport During High Flow."

Additional evidence supporting the two proposed mechanisms of PCB transport is the physical phase in which PCB's occur in the river. During high flow, when PCB's are associated with suspended material, the dissolved concentration is near zero, as shown in table 4. During lower (nonscouring) flows, however, the dissolved (filtered) concentration averages 80 percent of the total (unfiltered) concentration, as indicated by the data in figure 5. Suspended-sediment concentrations are typically only a few mg/L during base flow but may reach about 100 mg/L during high discharges. This pattern suggests that during nonscour periods, some mechanism other than turbulent resuspension of sediment is the dominant process adding PCB's to the water column.

Laboratory simulation experiments (Sodergren and Larsson, 1982) with sediment plus water "ecosystems" under sterile, anaerobic, and aerobic conditions indicate that simple molecular diffusion does not transport PCB's across the sediment-water interface, but that gas bubbles generated by microorganisms in anaerobic sediments, and bioturbation caused by macroorganisms in aerobic sediments, do transport PCB's across the interface. Both gas-bubble formation and bioturbation are likely to occur in the Hudson River. Although observed PCB concentrations of only a few tenths µg/L in the Hudson River are far less than measured PCB solubilities in pure water (National Research Council, 1979), they are comparable to dissolved concentrations reported in laboratory equilibrations with contaminated hydrosols (Halter and Johnson, 1977).

¹ The U.S. Geological Survey's water year begins October 1 of the previous calendar year and ends September 30.

Table 4.--Comparison of total recoverable and dissolved PCB concentrations during high flows at Waterford, 1977 and 1979.

[Discharge in cubic meters per second; concentrations in microgram per liter]

Date	Water discharge	Total PCB concentration	Dissolved PCB concentration
March 14, 1977	1,850	0.90	0.00
March 15, 1977	2,000	1.4	.00
March 6, 1979	900	.82	.04
March 7, 1979	1,340	.27	.16
November 27, 1979	610	.10	.00
November 28, 1979	790	.44	.00

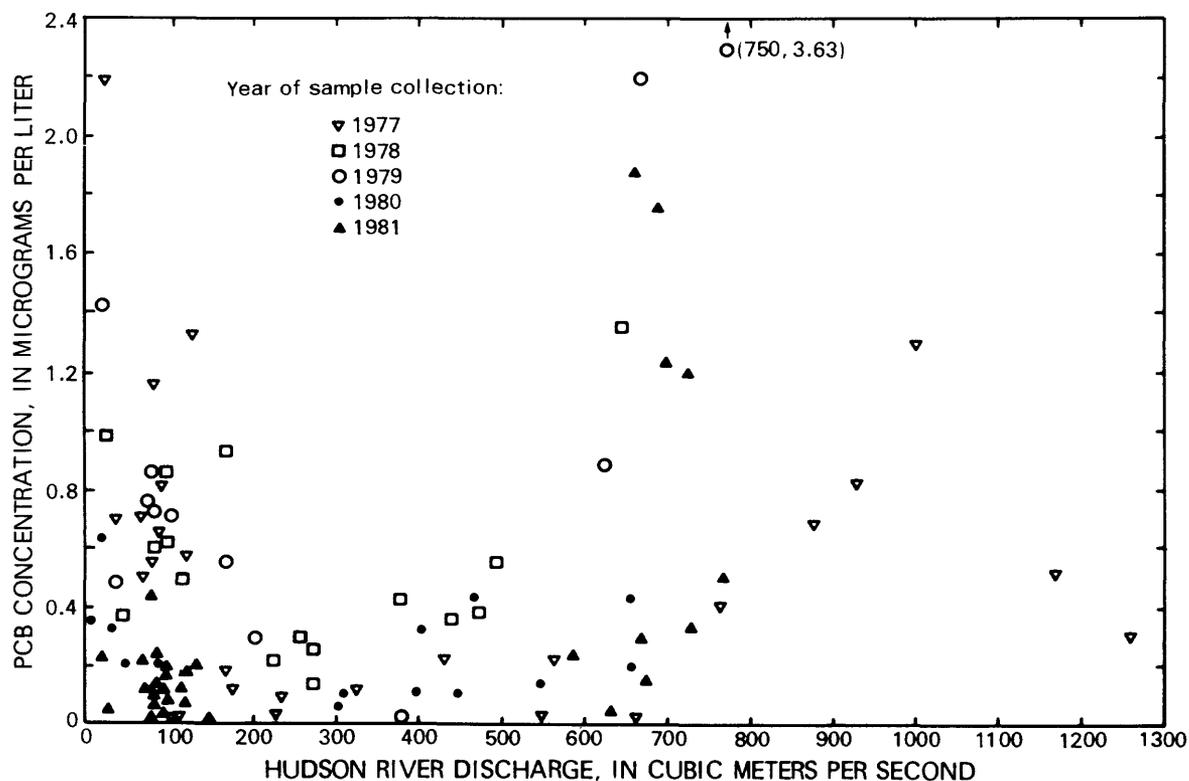


Figure 4.--Relationship between total recoverable PCB concentration and water discharge in Hudson River at Schuylerville. (Location is shown in figure 1.)

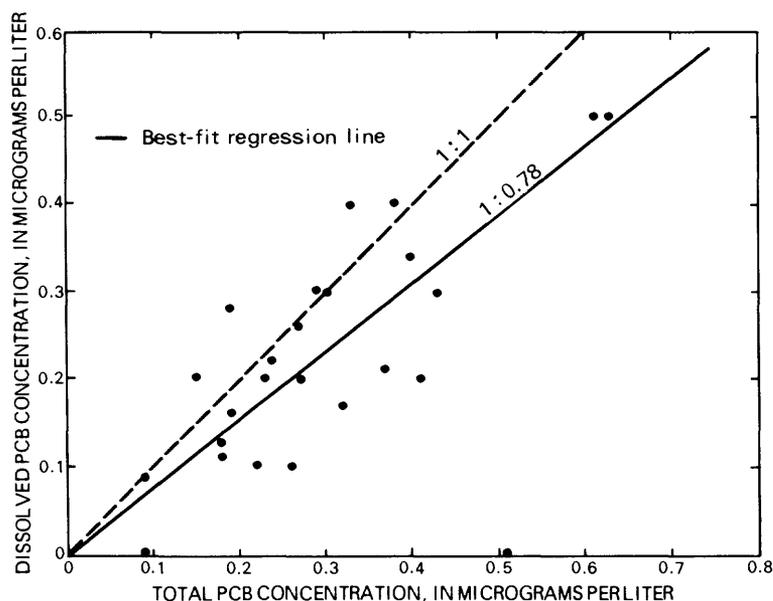


Figure 5.

Comparison of total recoverable and dissolved PCB concentrations in Hudson River at Waterford during nonscouring discharges. Slope of the line represents average ratio of dissolved PCB's to total PCB's.

Transport Rates During Nonscouring Periods

If the release of PCB's from bottom sediments by diffusion at nonscouring discharges is assumed to be constant, concentration is inversely proportional to water discharge, and the slope of the regression line between concentration and inverse discharge will equal the average PCB load transported. Average daily transport rates at Schuylerville, Stillwater, and Waterford during water year 1977 were calculated from regression equations (Turk, 1980). Transport rates were about 4 kg/d with a standard error of estimate slightly less than 1 kg/d (about 20 percent).

The relationship between PCB concentration and inverse discharge at Waterford was plotted by Turk and Troutman (1981b). The regression equation they derived had an intercept (PCB concentration at zero inverse discharge) of 0.02 $\mu\text{g/L}$. In theory, dilution at infinite discharge should result in an intercept of zero. Because the value for all stations in all years of this study was close to zero, all results reported herein were calculated from regressions through the origin.

Samples from Waterford in the 1977 water year included one at very low discharge (the point at 30 m^3/s in fig. 6), during which PCB concentration fell far below the calculated regression line. Turk and Troutman (1981b), noting the anomalous nature of this data point, state that the sample was collected just after the Labor Day weekend, during which upstream reservoir releases were restricted, causing a temporary low discharge in the river.

Evidence from the following year provides a basis for excluding all data obtained during extreme low flows from calculations of the average loading rate. The summer of 1978 was a period of sustained low base flow, which permitted collection of numerous low-flow samples for several weeks. Figure 6 clearly illustrates the failure of PCB concentration at Waterford to continue increasing as discharge decreases below about 60 m^3/s . For this reason, constant-load regression equations were calculated from data obtained only within the following discharge ranges: 36.6 to 366 m^3/s at Rogers Island;

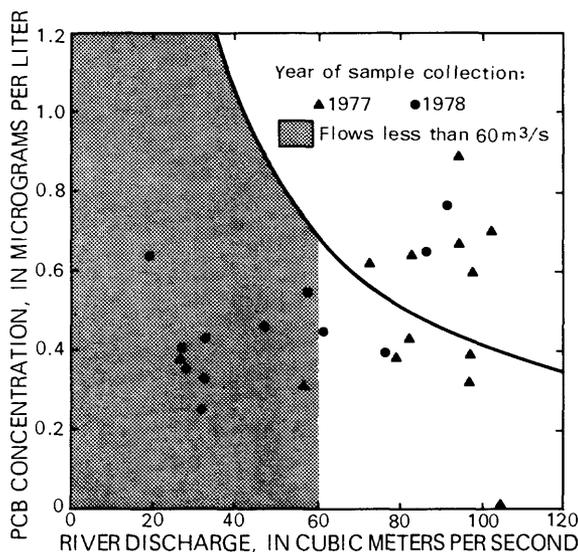


Figure 6.

Relationship between PCB concentration and water discharge during low flow in Hudson River at Waterford. Regression relationship between concentration and discharge is based on discharges between 60 and 600 m³/s.

44.7 to 447 m³/s at Schuylerville; 49 to 490 m³/s at Stillwater, and 60 to 600 m³/s at Waterford. The lower limit was chosen to equal one-tenth the upper limit, and the upper limit upstream from Waterford was reduced in proportion to the drainage areas above each respective site. Although the basis for these limits is reasonable, the values remain somewhat arbitrary.

The reason for the decrease in PCB concentration at very low discharge is unknown. One possibility is that PCB loss by volatilization may become significant in midsummer, when water temperature is high. However, it would seem likely that the physical and (or) biological processes that cause PCB's to diffuse from bottom sediments to the overlying water column should operate more rapidly at higher temperatures, thereby possibly offsetting any loss by volatilization. Furthermore, loading rates calculated from regressions on seasonally grouped data do not show evidence of a temperature-related effect.

Alternatively, the decrease in PCB concentration at very low flows may result from morphologic features of the river. The reach between Fort Edward and the estuary at Troy contains eight dams, so that the river at very low flow resembles a series of "pools" rather than an actively flowing stream. Although the preceding section states that PCB's at low flow are in the dissolved phase, filtration to obtain dissolved concentration does not exclude the possibility that the PCB's may be associated with colloidal material, which may pass through the filter but is capable of settling to the bottom of the river within these pools. Techniques such as ultrafiltration (dialysis) or high-speed centrifugation could establish the nature of association of PCB's.

Addition of salt¹ to river water has been shown to induce flocculation of macromolecular organic matter and its associated heavy metals (Sholkovitz, 1976) and might be used to adduce whether PCB's are similarly associated in Hudson water.

¹ Although PCB solubility decreases with increased salinity, solubility still far exceeds concentrations found in Hudson waters (Wiese and Griffin, 1978).

PCB transport rates at each station, calculated by regression for each water year, are given in figure 7A. The squares of the correlation coefficients range from 0.50 to 0.98 and average 0.76. The regression relationships are significant at the $P = 0.01$ level in 18 of 19 calculations ($P = 0.03$ for Schuylerville in 1980). The standard error of estimate, depicted by the line at the top of each bar, averages 15 percent.

Transport rates were also calculated by a second method--multiplying PCB concentration by instantaneous water discharge to obtain an instantaneous rate of transport, then averaging values obtained from all samples taken during nonscouring periods each water year. Results obtained by this method are given in figure 7B. In most years, 15 to 20 samples were collected at each station, and results of the two load-calculation methods are in close agreement. This, despite differences in statistical assumptions on which the methods are based, supports the apparent decrease in PCB concentrations with time, as explained below.

The histograms in figure 7 indicate (1) a substantially lower PCB-transport rate at Rogers Island than at the three downstream stations, (2) nearly equal rates at the three downstream stations, and (3) a decrease with time at all four stations. Results imply that most of the PCB's transported from the upper river to the estuary have their origin in sediments between Rogers Island and Schuylerville--a conclusion supported by analyses of bed material showing that the most highly contaminated sediments reside upstream from Schuylerville (Tofflemire and Quinn, 1979).

PCB-transport rates shown in figure 7 have decreased nearly 80 percent since 1978. A similar decrease in PCB concentration has been observed in Hudson River fish (Armstrong and Sloan, 1982; Sloan and Armstrong, 1982), caddisfly larvae (Simpson, 1982), and multiplate residues (Simpson, 1982). Although cause of the decrease is not known, some of the proposed explanations can be eliminated and a tentative one offered. Although in some microorganisms (Yagi and Sudo, 1980) and animals (Hinz and Matsumura, 1977) are capable of degrading PCB's (National Research Council, 1979), the quantitative effect of microorganisms in natural environments is unknown (Sayler and others, 1978). However, the long-term persistence of PCB's in other contaminated estuaries (Wilson and Forester, 1978), plus a lack of evidence for biodegradation in laboratory simulation studies (Sodergeren and Larsson, 1982), suggests that biological degradation is minimal. Thus, some natural physical cause for the decrease since the elimination of point discharges after 1977 would seem more plausible.

Monitoring at Waterford during 1976 included the period of continued PCB discharges from the outfalls, which is why the average low-flow transport rate of about 10 kg/d (not shown in fig. 7) during that water year exceeded the rate noted after elimination of the point discharges. The continued decrease in PCB loading rates could be a result of subsequent covering of contaminated sediments with a thin layer of newly weathered or relatively clean sediments from upstream. Sedimentation rates of 1 to 2 mm/yr have been noted from cores at selected locations in the upper river (Tofflemire and others, 1979) and in the estuary (Bopp and others, 1981). Olsen and others (1978) divided the Hudson estuary into sedimentation regimes ranging from zero accumulation to rates of 100 to 200 mm/yr. Because most of the riverbed undergoes little or

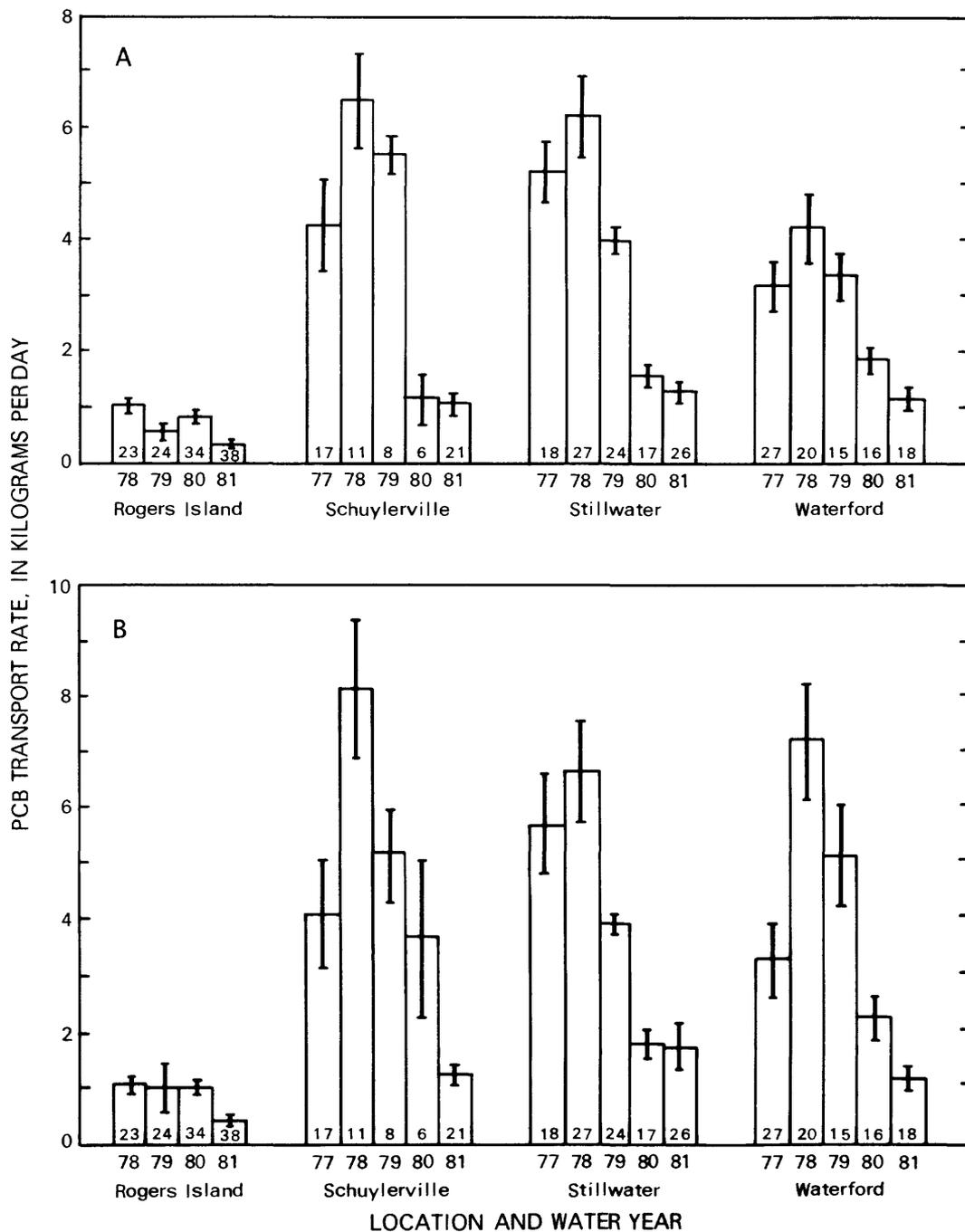


Figure 7.--Transport rates of PCB's in upper Hudson River during nonscouring discharges. A, Calculated from slope of the regression relationship between PCB concentration and inverse discharge, and B, calculated by multiplying PCB concentration by river discharge. (Number of samples is shown within bar for each water year. Standard error for each transport rate indicated at top of bar.)

no sediment deposition, the accumulation rates indicated by the above-mentioned cores are probably greater than average. However, it is in just such areas of greater-than-average sedimentation where contaminated sediments would likely settle and, in turn, soon be covered by newer, uncontaminated sediments from upstream. A layer of relatively uncontaminated sediment a few centimeters thick might then provide a barrier to transfer of PCB's from sediment to the water column by processes such as bioturbation or microbial generation of gas bubbles, though it would not necessarily be effective against active processes such as resuspension during high flows.

Transport During High Flow

High flow or scour periods are defined herein as river discharges exceeding 600 m³/s at Waterford and proportionately less at upstream locations. This flow rate was exceeded at Waterford on a mean daily basis during 28 days in water year 1977, 13 days in 1978, 28 days in 1979, 6 days in 1980, and 7 days in 1981. Turk and Troutman (1981b) estimated that about 40 percent of the total PCB load at Waterford during 1977 was transported by flood-induced scour and resuspension but attributed an uncertainty of 50 percent to that estimate.

The major impediment to quantifying PCB transport during high flow is the individual nature of each event. Figure 4 illustrates the considerable variation in high-flow PCB concentrations from year to year. As a result, the relationship between PCB concentration and water discharge during a specific high-flow event is of limited usefulness in prediction for a subsequent event. Factors such as duration of the event and time of sampling (position on either rising or falling limb of the hydrograph) are important, but the major cause of PCB variation among high flows is probably source of the water--that is, the subbasin in which most of the water originated. The influence of water source on several water-quality characteristics, including PCB concentration and sediment yield, was shown by Turk and Troutman (1981a) in a comparison of data from a March 1977 flood, which originated mostly in lower parts of the upper Hudson basin, with data from an April 1977 event, which originated in upper parts of the basin. In that study, the ratio of PCB concentration to suspended-sediment concentration during the April event at Waterford was seven times greater than that during the March event because a greater proportion of the water in the April event passed over the contaminated reaches upstream from Schuylerville. Despite the uncertainties in high-flow PCB concentrations, the lack of large runoff events in 1980 and 1981 seems to be significant in the reduction of observed PCB concentrations. Likewise, in 1977 and 1979 the source of high flows was different from that in 1978. Therefore, discharge is a major factor in the trends observed in PCB concentrations.

Maximum PCB concentrations during snowmelt-induced high flows¹ at the upper basin sites (Rogers Island, Schuylerville, Stillwater, Waterford) are summarized in table 5. With the possible exception of Rogers Island, maximum concentrations have not been clearly decreasing with time. (See also fig. 4.) This contrasts with the distinct decrease in transport rates (and concentrations) at all stations during nonscouring flows.

¹ Most high flows resulted from melting snow in late winter and early spring. A few high flows occurred in the fall.

Table 5.--Highest PCB concentrations observed during annual snowmelt-induced floods in the upper Hudson River.

Discharge is in cubic meters per second; concentration is in micrograms per liter. Site locations are shown in figure 1]

Date	Rogers Island		Schuylerville		Stillwater		Waterford	
	Water Discharge	PCB Concentration Canal River	Water Discharge	PCB Concentration	Water Discharge	PCB Concentration	Water Discharge	PCB Concentration
March 14-15, 1977	680	-- 1.3	1,200	0.55	1,200	0.29	2,000	1.40
April 25-26, 1977	--	--	1,000	1.30	990	1.80	1,120	1.00
March 28, 1978	250	-- .00	440	.36	420	.54	670	.43
April 13-15, 1978	320	-- .11	380	.43	500	.42	650	.59
March 6-8, 1979	330	0.45	630	.89	750	.40	900	.82
March 26-27, 1979	570	2.62	750	3.63	870	5.11	1,080	1.41
April 28-29, 1979	910	1.86	--	--	1,110	1.92	1,130	2.58
March 22, 1980	410	.57	470	.44	530	.13	1,170	.12
April 10-11, 1980	620	.24	660	.43	770	.57	1,020	.45
February 21-22, 1981	640	.30	690	1.76	830	1.33	1,100	.57

-- No sample taken.

Some of the contaminated sediments were removed from the canal channel at Rogers Island in 1978, and other sediments were stabilized by riprapping along part of the riverbank above Rogers Island (fig. 1 inset). Although PCB concentrations at Rogers Island were still high in 1979,¹ they were markedly lower thereafter--especially in the canal.

The relationship between total recoverable PCB concentration and suspended-sediment concentration at Schuylerville during high flow is plotted in figure 8. Because PCB's during these events are associated almost entirely with the suspended-sediment fraction, the PCB-to-suspended sediment ratio indicated in figure 8 can be considered a close approximation of the contaminant concentration on the suspended sediment. Regression lines indicate that concentration decreased from a range of about 20 to 35 $\mu\text{g/g}$ in 1977-79 to a range of 4 to 8 $\mu\text{g/g}$ in 1980-82. An additional year or two of data are needed before this apparent decrease can be assessed, however.

The observed decrease with time in both the nonscour and scour-period data may have been accelerated by the lower than normal spring flows during 1980 and 1981. These lower flows cause less scour of older contaminated sediment and higher net annual deposition, thereby lowering the PCB-to-suspended sediment ratio. Greater deposition could in turn lead to lower rates of PCB transfer from the bottom sediments to the overlying water during summer low flow periods.

¹ A 1-year lag in flushing of contaminated sediments stirred by dredging may be indicated.

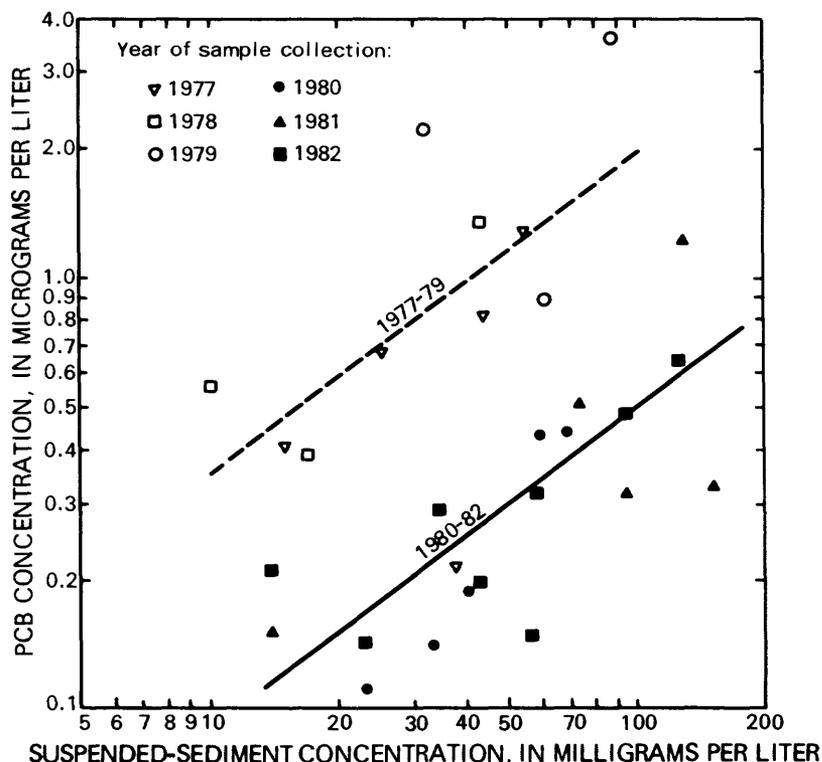


Figure 8.

Relationship between total recoverable PCB concentrations and suspended-sediment concentration in Hudson River at Schuylerville during high flows.

Concentration in Estuary

PCB concentrations at five sites in the Hudson River estuary below Troy (fig. 2) were determined during 1978-81. An average of five samples was taken annually at each site, mostly during summer. Although instantaneous discharge may exceed net downstream discharge by as much as 100 times (Giese and Barr, 1967), sampling over a tidal cycle at Castleton on August 15, 1979 showed that PCB concentration does not vary with the tide (U.S. Geological Survey, 1980).

PCB concentrations in samples collected in the estuary are given in table 6, which provides the following observations:

- Concentration is lower in the estuary than in the upper river,
- Concentration decreases downstream in the estuary, and
- Concentration has decreased with time.

The lower concentrations at the uppermost estuarine station (Castleton) relative to concentrations at the lowermost upper-river station (Waterford) can be attributed to dilution by relatively uncontaminated Mohawk River water, which enters the Hudson just below Waterford (figs. 1 and 2). During summer sampling periods, the Mohawk typically contributed from a third to half the total flow entering the upper estuary, whereas the upper Hudson contributed the remainder. Data in table 6 show that the PCB concentration at Castleton was about half that at Waterford, as expected from this comparison.

*Table 6.--Mean PCB concentration in samples
from five Hudson River estuary sites
and Hudson River at Waterford.*

[Concentrations in microgram per liter;
site locations are shown in figure 2]

Site	Mean PCB concentration			
	1978	1979	1980	1981
Waterford	0.45	0.36	0.25	0.14
Castleton	.23	.20	.11	.08
Catskill	.17	.17	.16	.05
Staatsburg	.14	.16	.19	.07
Poughkeepsie ¹	-- ²	--	--	.07
Clinton Point	.15	.12	.17	.08
Highland Falls	--	.17	.07	--

¹ From raw-water tap at Poughkeepsie water-treatment plant.

² Not sampled.

The continued decrease in PCB concentration with downstream distance in the estuary (table 6) is attributed to dilution by tributaries, whereas the decrease in concentration at each site with time simply reflects a similar trend in the upper river.

Limited significance should be attached to the individual values in table 6. They are subject to large uncertainty because of the small number of samples and the low concentrations, particularly since 1980, when many concentrations were close to the detection limit. Accurate measurement of the low concentrations now present in the estuary would require special analytical methods in which the water to be tested is concentrated, such as adsorption on synthetic substrates (Bedford, 1974) or bioconcentration by organisms.

Aroclor Distribution

PCB concentrations were calculated from Aroclor standards that most clearly matched Hudson River samples, as discussed in the section "Analytical Methods." Results of these matches are tabulated in this section to discern variations with location, river discharge, and time. If environmental pathways other than waterborne transport, such as biological degradation, volatilization, irreversible adsorption on bottom sediments, and so on, are large, their significance should be reflected in such variations.

Vapor pressure decreases with increasing chlorine substitution (Westcott and Bidleman, 1981; Westcott and others, 1981); hence, volatilization should preferentially remove less chlorinated congeners from the river. Susceptibility to microbial degradation depends on the degree of chlorination and position of chlorine atoms on the molecule, but, in general, this process results in preferential degradation of the less chlorinated congeners (National Research Council, 1979). Adsorption on soils and sediments is greater for less soluble, more chlorinated congeners (Halter and Johnson, 1977). Because each of these processes causes fractionation in the same direction, it might be anticipated that Hudson River water would become enriched in the more highly chlorinated congeners with downstream distance and through time. As explained below, however, variations in Aroclor-congener ratios are small, which supports the conclusion that riverborne transport is the major mechanism of PCB dispersal in the Hudson River.

As stated previously, industrial Aroclors contain many congeners (Westcott and others, 1981), and environmental PCB's are unlikely to precisely match any Aroclor standard. Even though the potential value of analysis for individual isomers is recognized, tedious and expensive capillary-column chromatographic methods would be required. For purposes of this study, compilation of the closest Aroclor matches is sufficient to permit general conclusions.

Various Aroclors have likely been used by the industrial plants discharging to the Hudson. Purchase records show that Aroclor 1242 was used from 1966-71 and Aroclor 1016 was used thereafter. Both are nearly identical in chlorine content, as shown in table 3. These types were identified in about 20 percent of all samples taken from the Hudson River in this 5-year study. Aroclor 1232, which has a slightly lower chlorine content, was identified in

almost two-thirds of all samples. The difference in composition between Aroclors 1232 and 1242 is not great; Aroclor 1232 averages about one less chlorine atom per molecule.

Frequency of occurrence of identified Aroclors, tabulated from nonscour flow range data (table 7), shows that Aroclor distribution varies little, if at all, from site to site in the upper river. PCB's in the estuary (data from all five stations combined) seem to be somewhat more highly chlorinated, although the difference from those in the upper river is very slight. A slight decrease in the percentage of less chlorinated isomers and enrichment in the more highly chlorinated isomers with distance down the entire estuarine reach was reported by Bopp and others (1981). Absence of a downstream shift to higher Aroclor numbers is consistent with the concept of an upstream source of small areal extent and limited importance of processes such as readsorption to the riverbed or volatilization.

Data in table 8 indicate that Aroclor 1248 in samples collected during high flows has only a slightly greater frequency of occurrence than in samples collected during nonscour stages. Although differences are small, the shift is in the direction predicted by preferential adsorption of the more chlorinated isomers. The observation that river samples are very similar in composition despite two different mechanisms of loading (sediment resuspension and constant leaking) is again consistent with the concept of a single source of PCB's (contaminated riverbed sediments) at all discharges.

Aroclor data from 1978-81 (table 9) indicate no shift in Aroclor ratios since 1978. PCB's in samples before 1978 seem to be more highly chlorinated than those thereafter; however, this may reflect the greater proportion of samples collected during high flows in 1976 and 1977. The lack of change in PCB composition since point discharges to the river were stopped supports the concept of an original source of limited areal extent and relatively minor effects of environmental processes that would alter composition.

Table 7.--Percentage frequency of identified Aroclors in Hudson River during nonscour discharges from 1978-81.

[Site locations shown in figures. 2 and 3]

Location	Number of samples	Aroclors				
		1221	1232	1016 and 1242	1248	1254
Rogers Island ¹	109	5	76	18	1	0
Schuylerville	51	2	55	35	7	1
Stillwater	93	1	77	16	5	0
Waterford	96	1	68	29	2	0
Estuary ²	99	0	51	41	6	1

¹Includes canal and main river channels.

²Includes 5 locations shown in figure 2.

Table 8.--Percentage frequency of identified Arochlors in upper Hudson River during high-flow and nonscour periods, 1977-81.

River stage	Number of samples	Arochlors				
		1221	1232	1016 and 1242	1248	1254
High flow	118	0	53	18	25	4
Nonscour	424	2	70	22	5	0

Table 9.--Percentage frequency of identified Arochlors in upper Hudson River, 1976-81.

[Data include both flood and nonflood discharges.]

Water years	Number of samples	Arochlors				
		1221	1232	1016 and 1242	1248	1254
1976-77	101	0	50	18	32	0
1978-79	200	2	68	24	5	1
1980-81	266	1	70	21	7	1

Implications for Future Plans

Nearly three decades of PCB discharge to the Hudson River at Fort Edward has resulted in serious degradation of water quality downstream. PCB concentrations in bottom sediment from much of the Hudson exceed those of other major rivers by about two orders of magnitude (Bopp and others, 1981) and those of small remote streams by more than three orders of magnitude (Crump-Wiesner and others, 1973).

When regular monitoring of Hudson River water began in the late 1970's, PCB concentrations were expected to remain high for many decades. Also, measurements made in the late 1970's, after elimination of point sources, combined with estimates of total quantity stored in sediments, led several investigators (for example, Apicella and Zimmie, 1978; Turk, 1980; Schroeder, 1981) to conclude that a sufficient quantity of PCB's was contained in sediments of the upper river to maintain transport rates equal to those of the late 1970's for almost a century. Projections based on such mass balances, however, did not account for loss by other mechanisms.

Regular monitoring during 1976-81 demonstrates that PCB concentrations and transport rates are decreasing more rapidly than anticipated. Although this decrease has resulted in unexpected improvement of water quality, it may delay complete removal of PCB's by transport (if other pathways for depletion

are ignored) by more than 100 years. During the 1976-81 monitoring period, however, both flow and sediment-transport rates have both decreased, although not enough to directly account for the observed decrease in PCB transport rates.

Plans are in preparation to cleanse the Hudson River by dredging contaminated sediments from the reach between Rogers Island and Schuylerville. Sediment is to be removed from so-called "hot spots" in which PCB concentration of the sediment exceeds 50 $\mu\text{g/g}$. The recent decreasing trend in annual loading rate with time during nonscouring flows will make it difficult to evaluate the incremental improvement that results from dredging. A substantial decrease in concentrations of PCB's adsorbed on suspended sediment during high flows from year to year may be the strongest evidence of improvement in water quality. Monitoring in the upper river, both during and after dredging, would be continued to discern changes in river quality.

SUMMARY AND CONCLUSIONS

Polychlorinated biphenyls discharged to the Hudson River from point sources near Fort Edward during 1950-77 have contaminated sediments in the entire 300-km downstream channel. Although the point discharges have been eliminated, these sediments provide a steady source of PCB's to river water. Frequent measurements of PCB concentrations in Hudson River water have been made since 1976.

PCB concentrations are highest at both high and low discharges and are lowest at intermediate flows. This pattern is attributed to the transfer of PCB's to the overlying water by two mechanisms--(1) resuspension of bottom sediments through turbulence, and (2) steady diffusion from bottom sediments. PCB's (mostly in dissolved form) are desorbed from bottom sediments to the water at constant rate so that an increase in river discharge causes dissolved PCB concentrations to decrease as a result of dilution. When discharge increases beyond a certain limit, however, water velocity and turbulence become sufficient to scour and resuspend the contaminated bottom sediment, thereby causing total PCB concentrations in the water to increase. During high discharges, this mechanism predominates, although desorption presumably continues also.

During the first 5 years after elimination of industrial discharges, average daily transport of PCB's from the upper river to the estuary during nonscour periods decreased from about 5 kg/d to about 1 kg/d. This decrease may be a consequence of the burial of contaminated deposits by clean sediments from weathering and erosion upstream.

Transport rates within selected reaches indicate that virtually all PCB loading to the river is derived from sediments within about 20 km downstream from the original source. Therefore, removal of the most highly contaminated sediments (those from the 23-km reach between Fort Edward and Schuylerville) has been considered. The recent trend of decreasing PCB concentrations and transport rates will make the incremental improvement of Hudson River water quality from dredging difficult to discern. The most conspicuous criterion for improvement may be the concentrations and transport rates during high flows, which occur mainly by resuspension during the annual spring runoff period.

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