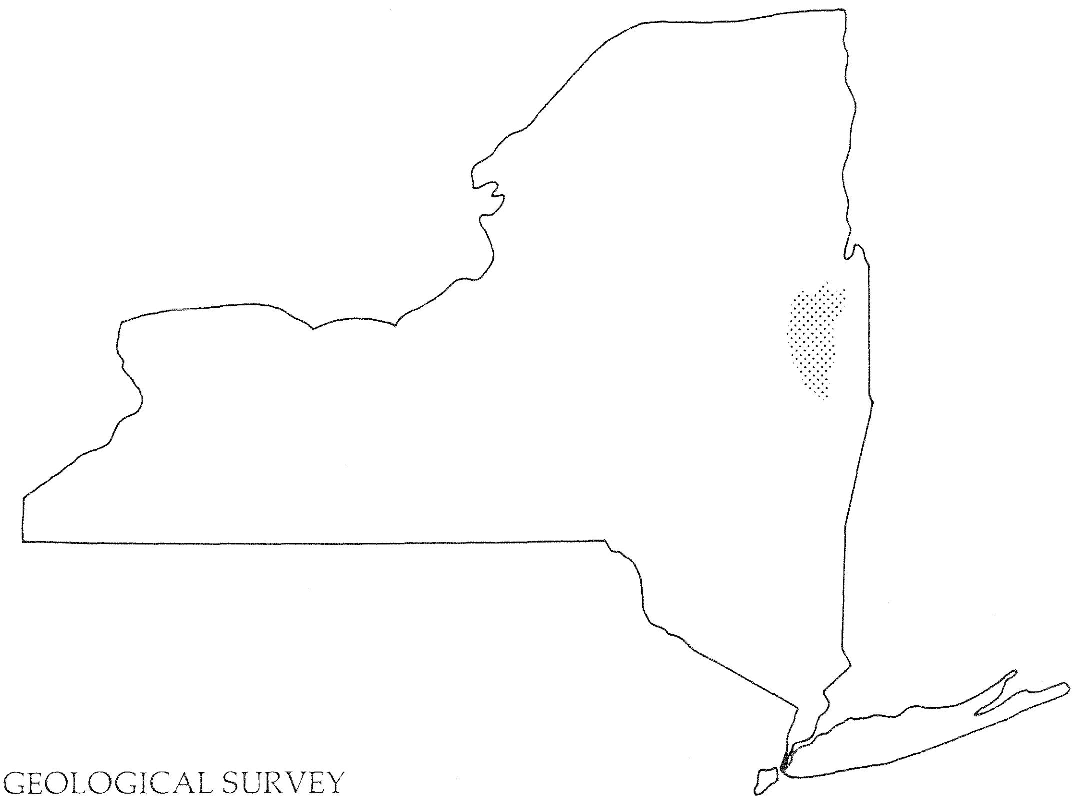
POLYCHLORINATED BIPHENYL TRANSPORT IN THE HUDSON RIVER, NEW YORK



U.S. GEOLOGICAL SURVEY
Water-Resources Investigations 81-9

Prepared in cooperation with

BOARD OF WATER COMMISSIONERS OF
THE TOWN OF WATERFORD, and

NEW YORK STATE DEPARTMENT OF
ENVIRONMENTAL CONSERVATION

50272-101

REPORT DOCUMENTATION PAGE	1. REPORT NO.	2.	3. Recipient's Accession No.

4. Title and Subtitle Polychlorinated biphenyl transport in the Hudson River, New York	5. Report Date March 1981 6.
7. Author(s) John T. Turk and David E. Troutman	8. Performing Organization Rept. No. USGS/WRI 81-9
9. Performing Organization Name and Address U.S. Geological Survey Water Resources Division 343 U.S. Post Office & Courthouse Albany, New York 12201	10. Project/Task/Work Unit No. 11. Contract(C) or Grant(G) No. (C) (G)
12. Sponsoring Organization Name and Address U.S. Geological Survey Water Resources Division 343 U.S. Post Office & Courthouse Albany, New York 12201	13. Type of Report & Period Covered Final, 1976-77 14.

15. Supplementary Notes

Prepared in cooperation with the
Board of Water Commissioners of the Town of Waterford, and the
New York State Department of Environmental Conservation

16. Abstract (Limit: 200 words)

Polychlorinated biphenyl (PCB) concentrations in the Hudson River at Waterford, New York are controlled by two processes. At discharges that are not extremely high--less than 600 cubic meters per second, a constant flux of PCB's from bottom deposits is the major source. At discharges greater than 600 cubic meters per second, resuspension of bottom materials containing PCB's is the principal mechanism. PCB concentrations resulting from either or both processes can be predicted from river discharge by equations developed and verified in this study. The transport rate of PCB's into the Hudson River estuary is approximately 1,700 kilograms per year, of which about 40 percent is transported at discharges greater than 600 cubic meters per second.

17. Document Analysis a. Descriptors

*Suspended solids, *Polychlorinated biphenyls, River flow, Equations, New York

b. Identifiers/Open-Ended Terms

Resuspension, Dilution

c. COSATI Field/Group

18. Availability Statement	19. Security Class (This Report)	21. No. of Pages
No restriction on distributon.	UNCLASSIFIED	15
	20. Security Class (This Page) UNCLASSIFIED	22. Price

(See ANSI–Z39.18) See Instructions on Reverse OPTIONAL FORM 272 (4–77)
(Formerly NTIS–35)
Department of Commerce

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Albany, New York

1981

UNITED STATES DEPARTMENT OF THE INTERIOR

JAMES G. WATT, Secretary

GEOLOGICAL SURVEY

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CONTENTS

ILLUSTRATIONS

TABLES

CONVERSION FACTORS AND ABBREVIATIONS

The following factors may be used to convert the International Systems (SI) units of measurement in this report to inch-pound units.

Multiply SI units	by	To obtain inch-pound units
gram (g)	.03527	ounce, avoirdupois (oz)
cubic meter (m^3)	35.31	cubic foot (ft^3)
liter (L)	0.2642	gallons (gal)

Abbreviations used in the text of this report include:

μg/s, micrograms per second

μg/g, micrograms per gram

μg/L, micrograms per liter

mg/L, milligrams per liter

kg/d, kilograms per day

m^3/s, cubic meters per second

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ABSTRACT

Polychlorinated biphenyl (PCB) concentrations in the Hudson River at Waterford, New York are controlled by two processes. At discharges that are not extremely high--less than 600 cubic meters per second--a constant flux of PCB's from bottom deposits is the major source. At discharges greater than 600 cubic meters per second, resuspension of bottom materials containing PCB's is the principal mechanism. PCB concentrations resulting from either or both processes can be predicted from river discharge by equations developed and verified in this study. The transport rate of PCB's into the Hudson River estuary is approximately 1,700 kilograms per year, of which about 40 percent is transported at discharges greater than 600 cubic meters per second.

INTRODUCTION

The discharge of polychlorinated biphenyls (PCB's) to the Hudson River between 1951 and 1976 has resulted in a potential health hazard to those using the river as a source of food and drinking water. All fishing has been banned from Fort Edward to Troy and to the first impassable fish barrier in the tributaries. The economic impact has been especially severe on the commercial fishery in the estuarine Hudson downstream (south) from Waterford, N.Y. The location of the study reach (Fort Edward to Troy) and principal geographic features of the upper Hudson basin are shown in figure 1.

Although the discharge of PCB's from the former point source, a manufacturing plant in Fort Edward, N.Y., has been discontinued, bottom materials, which include the organic as well as the mineral sediments from the Hudson River between Fort Edward and Waterford, are heavily contaminated with PCB's. PCB concentrations in these bottom materials range from 200 μg/g near Fort Edward to about 4 μg/g near Waterford. The total mass of PCB's in these bottom-material deposits has been estimated to be 225,000 kg (New York State Department of Environmental Conservation, 1976). Even in the absence of point discharges of PCB's, river-bottom deposits continue to supply PCB's to the river and its estuary.

Purpose and Scope

This report describes the interaction between river water and the river-bottom deposits above Troy and provides estimates of the yearly transport rate of PCB's from the study reach into the Hudson River estuary.

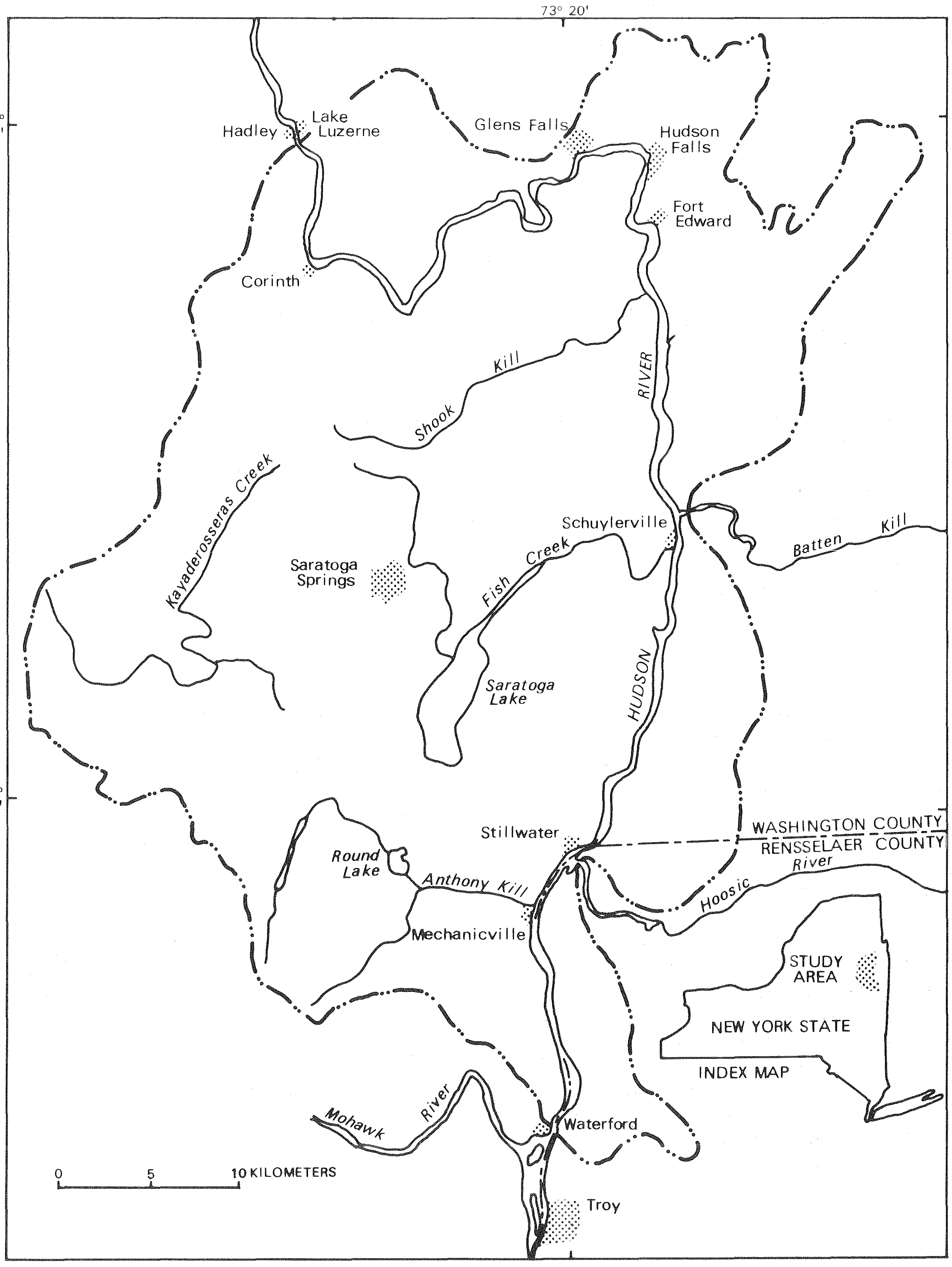

Figure 1.--Location and major geographic features of Hudson River basin from Fort Edward to Waterford, N.Y.

Acknowledgments

Data were collected and interpreted under projects funded cooperatively by the U.S. Geological Survey, the Board of Water Commissioners of the Town of Waterford, N.Y., and the New York State Department of Environmental Conservation. Additional funds were provided by the U.S. Environmental Protection Agency.

METHODS OF DATA COLLECTION

All data were collected during the 1977 water year (October 1976 through September 1977). Samples were taken with standard suspended-sediment sampling techniques as described by Guy and Norman (1970, p. 31). The depth-integrating samplers used for sample collection were modified for trace-contaminant sampling so that the sample would touch only Teflon[1] and stainless steel before entering the glass sample bottle. All surfaces to be touched by the sample were cleaned with laboratory-grade detergent and high-purity hexane or baked overnight at 500°C. Dissolved PCB samples were filtered immediately after collection with a stainless steel filtration apparatus and a 0.45-micrometer silver oxide membrane filter. Suspended PCB concentrations were determined from the remaining filtrate. Total PCB concentration are unfiltered, or whole, water samples and therefore include dissolved as well as the suspended fraction of PCB's in the water column. Laboratory analyses were done by the U.S. Geological Survey Central Laboratory in Atlanta, Ga.

RATES AND MECHANISMS OF PCB TRANSPORT

To calculate the transport rate of PCB's from the study reach into the estuary, the concentration of total PCB's in unfiltered water samples must be correlated with the discharge rate at the time of collection. Figure 2 is a plot of total PCB concentration in relation to river discharge. Although the data may at first seem widely scattered, inspection reveals that the data points fall into three major groups. At discharges less than 400 m^3/s, PCB concentrations range widely--from less than the detection limit of 0.1 μg/L to 0.9 μg/L--and average 0.3 μg/L, with a standard deviation of 0.3 μg/L. At discharges greater than 800 m^3/s, the range is similar--from less than the detection limit to 1.4 μg/L--with an average of 0.6 μg/L and a standard deviation of 0.4 μg/L. Within the 400- to 800-m^3/s discharge range, however, PCB concentrations range from less than detection limit to only 0.2 μg/L and average 0.1 μg/L, with a standard deviation of 0.1 μg/L.

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

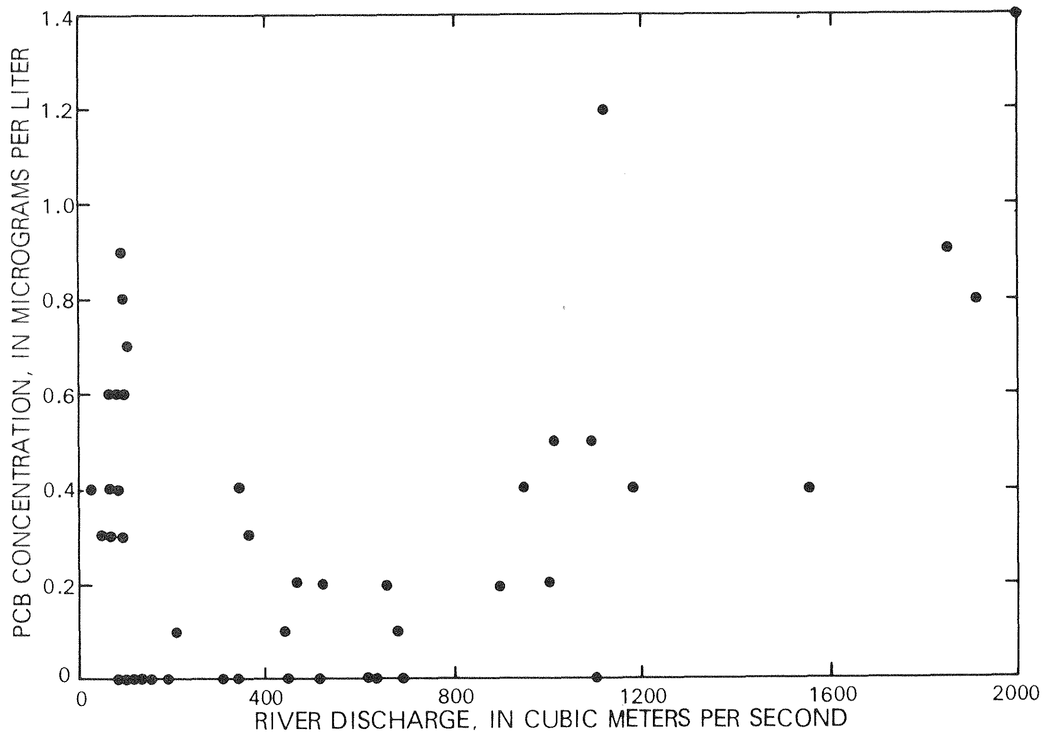

Figure 2.--Relation of total PCB concentration to river discharge, Hudson River at Waterford, 1976-77.

It will be shown that PCB concentrations in the reach studied are controlled by two separate mechanisms--resuspension of PCB-laden bottom materials during high discharges and a steady supply of PCB's derived from bottom-material sediments the rest of the time. Resuspension of bottom material becomes minimal at discharges less than about 600 m^3/s, and, if this were the only source of PCB's, their concentration would be below the detection limit at discharges below 600 m^3/s. However, because PCB's also enter the river water from the bottom sediments at a steady rate, their concentration increases at lower discharges as dilution is reduced. In the intermediate range of discharges (400 to 800 m^3/s), PCB's are contributed by both processes at similar rates, but because these rates are at minimum levels, their combined effect on PCB concentrations is less than during high or low discharges.

Sediment Resuspension as a Source of PCB's

During high discharges, resuspension of bottom materials is the principal mechanism by which PCB's enter the water column. Figure 3 is a plot of suspended-sediment concentration in relation to discharge for the samples represented in figure 2. In the 400- to 800-m^3/s discharge range, the

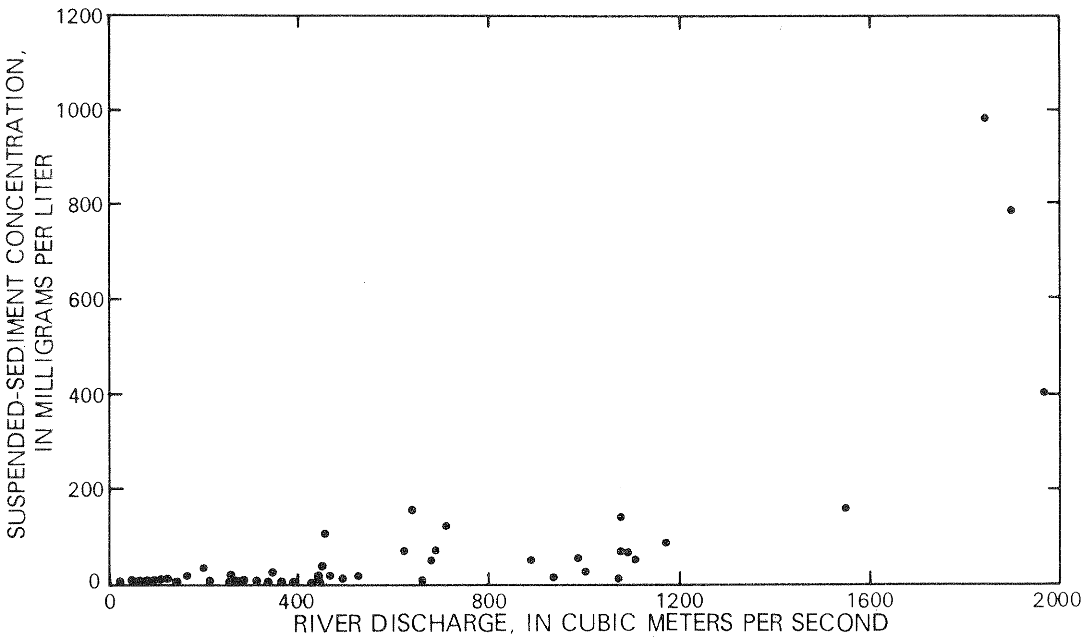

Figure 3.--Relation of suspended-sediment concentration to river discharge, Hudson River at Waterford, 1976-77.

suspended-sediment concentrations are higher and far more variable than at lesser discharges, which indicates increased sediment-transport rates. Further, the hypothesis that resuspension is the principal source of PCB's at discharges greater than about 600 m^3/s is supported by data on the dissolved versus the suspended fraction of PCB's from three samples collected during March 14-23, 1977, a period of high discharge (table 1).

Table 1 indicates that, in samples taken during discharges greater than 600 m^3/s, PCB's are carried in the suspended load. However, other data show that the relationship between suspended-sediment concentration and PCB concentration is not consistent. The data in figures 4A and 4B represent samples

Table 1.--Concentration of dissolved and suspended PCB's at selected river discharges, Hudson River at Waterford, N.Y., 1977.

[Concentrations are in micrograms per liter]

Date	River discharge (m^3/s)	Dissolved PCB's	Suspended PCB's
March 14	1,850	0.0	0.9
March 15	2,000	0.0	1.4
March 23	460	0.2	0.0

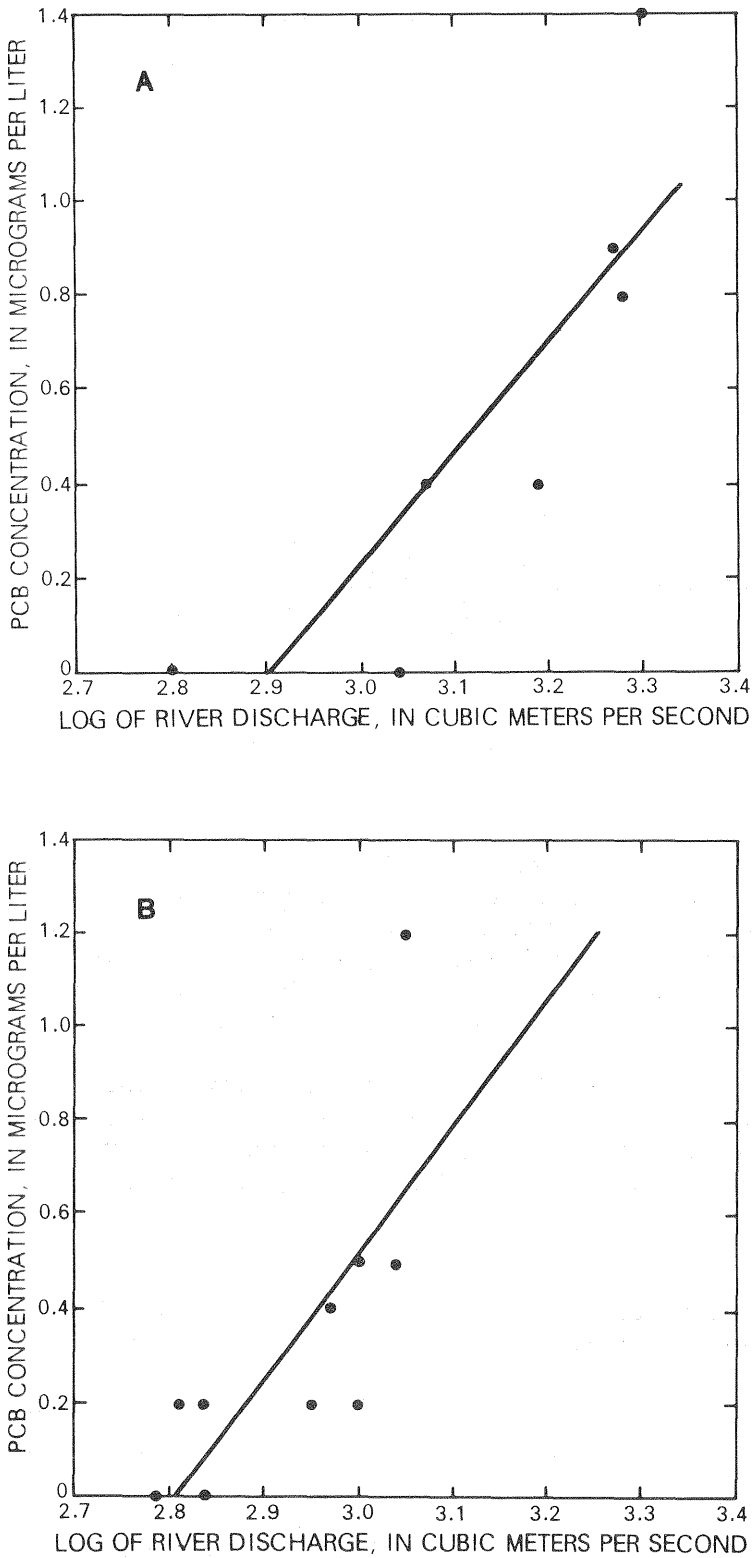

Figure 4.--PCB concentration as function of logarithm (base 10) of river discharge during high discharge: A, March 13-17, 1977; B, March 30 - April 28, 1977.

collected during high discharges on March 13-17 and March 30-April 28, respectively. Although the range of total PCB concentrations during the two time periods differs by only approximately 15 percent, the range in suspended-sediment concentrations was 70 to 987 mg/L during March 13-17 and 8 to 75 mg/L during March 30-April 28. This inconsistency may be attributed to the fact that suspended sediment is derived not only from the resuspension of bottom materials but also from land surface and tributaries in amounts that vary seasonally and according to geographic distribution of severe storms and snowmelt. Despite the dissimilarity in range of sediment concentrations in figures 4A and 4B, both support the hypothesis that resuspension of bottom materials is the major source of PCB's during periods of high discharge.

Calculation of Resuspended-PCB Concentrations

Because resuspension of bottom materials is dependent primarily upon the shear force exerted by the moving water, and because this force is related to discharge, empirical equations may be developed to relate the concentration of substances derived through resuspension to the cause of resuspension--namely increased discharge. Such equations were derived by linear least-squares fits of the data from figures 4A and 4B and are presented here as equations 1 and 2, respectively.

$$PCB = 2.37 \ Log_{10}Q - 2.13 \qquad (1)$$

$$PCB = 2.75 \ Log_{10}Q - 2.23 \qquad (2)$$

where: PCB is concentration of resuspended PCB's, in μg/L, and

Q is river discharge, in units of 100 m^3/s.

The correlation coefficients for equations 1 and 2 are 0.84 and 0.76, respectively. The probability that correlation coefficients as large or larger would be observed in random data pairs from unrelated variables is less than 0.02.

The ability of equations 1 and 2 to estimate PCB concentrations in the river for times other than those actually measured can be evaluated as follows. Equation 1 can be used as a calibrated empirical model of PCB concentrations as a function of discharge and can be verified by the data given in figure 4B. The results of this comparison are shown in table 2.

The accuracy of equation 1 in calculating suspended PCB concentrations (table 2), and the high correlation coefficients associated with both equations 1 and 2, suggest that either of these equations may be used to calculate PCB concentrations during large discharges. Combining the two data sets (figs. 4 and 5) from which equations 1 and 2 were derived gives equation 3, which is generally more applicable than either equation 1 or 2.

$$PCB = 1.77 \ Log_{10}Q - 1.36 \qquad (3)$$

The correlation coefficient for equation 3 is 0.76, which has a probability of less than 0.001 of being equaled or exceeded for random data pairs from unrelated variables. Equation 3 will be used in a later section to predict other PCB concentrations and loads during the study period.

Table 2.--Comparison of predicted and observed PCB concentrations, Hudson River at Waterford, N.Y., 1977.

[Discharges are in units of 100 cubic meters per second; concentrations are in micrograms per liter]

River discharge	Observed PCB concentrations	Predicted PCB concentrations	Percent error
6.23	0.0	<0.0	undefined
6.91	0.0	<0.0	undefined
9.97	0.2	0.2	0
8.95	0.2	0.1	50
6.60	0.2	<0.0	100
6.85	0.1	<0.0	100
10.9	0.5	0.3	40
11.2	1.2	0.4	67
10.1	0.5	0.3	40
9.43	0.4	0.2	50
			Average 56

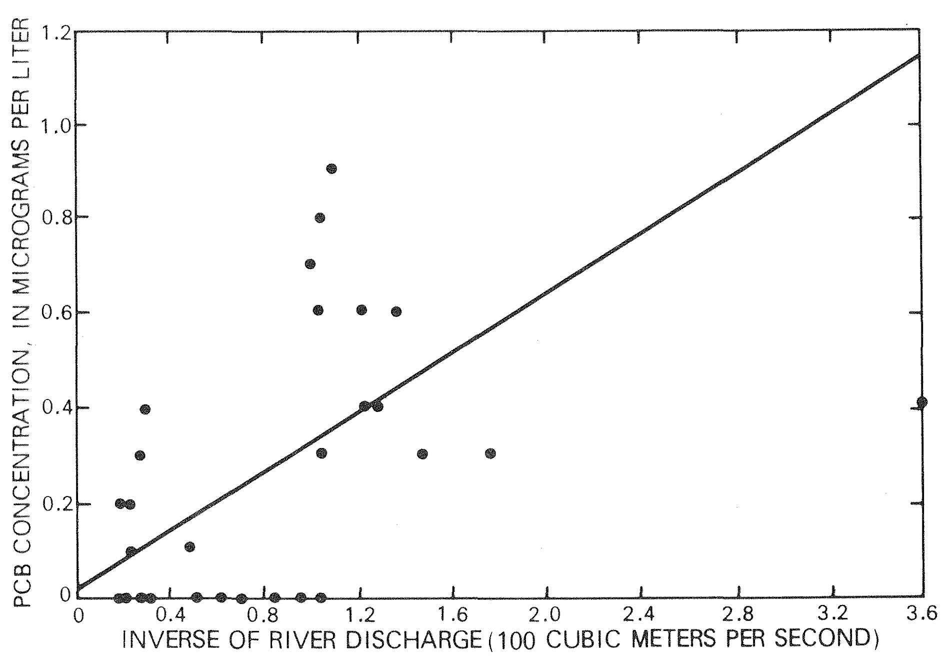

Figure 5.--PCB concentration as an inverse function of discharge, Hudson River at Waterford, 1976-77.

Constant Loading as a Source of PCB's

The observed tendency of PCB concentrations to increase with decreasing discharge at discharges less than 400 m^3/s indicates an additional source of PCB's, and the distribution of PCB concentrations at discharges less than 600 m^3/s (fig. 2) suggests that PCB's are added at a constant rate independent of variations in discharge.

It was beyond the scope of this study to investigate mechanisms of constant PCB transfer to the water column. Inflow of PCB's from external sources does not seem to be significant because the one known point source has been discontinued, and PCB concentrations at a control station above the former point source have never been above the detection limit. Other mechanisms that could promote this transfer include upward seepage of ground water through the river bed, molecular diffusion, circulation of water by burrowing invertebrates, and methane release from decomposing paper-pulp detritus. Although no estimate of the relative contributions of these mechanisms can be made at present, the quantity of PCB's already contained in sediment deposits between Fort Edward and Waterford is sufficient to account for the measured load if 0.5 percent of it is transported to the water column each year.

Calculation of PCB Concentrations

The general distribution of PCB concentrations at discharges less than 600 m^3/s can be expressed as a simple relationship such as equation 4:

$$PCB = L/Q \qquad (4)$$

where: L is the constant load of PCB's supplied to the river from the sediments, in units of 10^5 μg/s, and

Q is the river discharge, in units of 100 m^3/s.

If equation 4 correctly describes the process, a plot of PCB concentration against the inverse of the discharge must be linear. Figure 5 presents PCB concentrations at discharges less than 600 m^3/s. The correlation coefficient of 0.40 has a probability of less than 0.05 of being equaled or exceeded for randomly selected data pairs from unrelated variables.

If the data point at L/Q equals 3.6 were deleted from the data set, the correlation coefficient would be 0.51, which has a probability of only 0.01 for unrelated variables. (The probable reason for the outlying data point is regulation of discharge. The sample was collected just after the Labor Day weekend, when reservoir releases were minimal, which resulted in a temporary low discharge.) Although the linear regression is statistically significant with or without this anomalous data point, its effect on the slope of the regression line is significant. The slope, which represents the magnitude of the PCB loading, is 1.3 kg/d (kilograms per day) with the data point and 2.7 kg/d without it. An alternative method of calculating the average load would be to multiply the PCB concentration by the discharge for each data pair and to determine the mean of the individual loads; this gives a PCB loading of 3.2 kg/d if the questionable data point is included and 3.3 kg/d if not. Thus, the flux of PCB's from the sediments is likely to be about 3 kg/d.

An indirect verification of equation 4 was necessary because discharges below 600 m^3/s did not occur at evenly spaced time intervals during the study. A regression analysis of data subsets, separated at some arbitrary date, would represent differing ranges of discharge and would, therefore, make the subsets subject to erroneous correlation. However, equation 4 can be verified by comparing the average PCB loads for two such periods--(a) November 15, 1976, to June 9, 1977, and (b) June 10, 1977, to September 27, 1977. The average PCB load during the first period was 2.8 kg/d, with a standard deviation of 4.1 kg/d, and the average PCB load during second period was 3.1 kg/d, with a standard deviation of 2.4 kg/d. Thus, the average PCB load (L in equation 4) calculated from the first data set is not significantly different from that of the verification set.

Calculation of Yearly Transport Rates

Equations 3 and 4 have been shown to provide statistically valid estimates of PCB concentrations in river water. Equation 3 was verified by comparing results of equation 1 with the data set used to generate equation 2. The slope calculated for equation 4 was verified by comparing the average load of PCB's for two separate time periods. Multiplying the PCB concentration obtained from equations 3 and 4 by the average daily discharge gives an estimate of the PCB load for each day; these values can then be summed to give the yearly transport rate. When multiplied by the discharge, the value obtained through equation 4 will always yield a constant value of 3 kg/d over its range of validity, that is, at discharges less than 600 m^3/s. Thus, to estimate yearly transport rates of PCB's to the estuary, only the average daily discharges that exceed 600 m^3/s must be known.

During the 1-year study period, discharge exceeded 600 m^3/s on 28 days (U.S. Geological Survey, 1978, p. 66-72). Multiplying discharge (U.S. Geological Survey, 1978) by PCB concentration, as determined from equation 3, gives a total load of 700 kg during the 28 days of high discharge. An average PCB load of 3 kg/d during the remaining 337 days gives a total of 1,000 kg for all days of low discharge. Thus, the yearly load during the study period was about 1,700 kg of PCB's, about 40 percent of which was transported during discharges greater than 600 m^3/s. Therefore, the major mechanism of transport that accounts for the remaining 60 percent of the total annual load is not by resuspension of the PCB-laden bottom material.

SUMMARY AND CONCLUSIONS

Equations developed in this study can be applied to two questions that relate to PCB contamination of the Hudson River--(a) what river conditions will produce the highest PCB concentrations in the water and (b) how rapidly are PCB's in the upper Hudson River being transferred to the Hudson River estuary. Both high and low discharges promote high PCB concentrations; medium discharges do not. High concentrations are more likely to persist during extreme drought than during periods of high discharge because droughts tend to persist longer than floods. During periods of low discharge, PCB's are derived mainly from the bottom sediments, whereas during periods of high discharge they are supplied as the sediments become resuspended.

At the rates of transport indicated by this study, the PCB's now estimated to be in sediment deposits (225,000 kg) are sufficient to maintain the current level of water contamination for approximately a century. As PCB's are removed and new sediments are deposited, the transport rate would be expected to decrease. It was beyond the scope of this study to estimate the rate of decrease, however.

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