Estimation of Polychlorinated Biphenyl Removal Rates from the Upper Hudson River

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ABSTRACT

As part of the ongoing debate on managing the polychlorinated biphenyl (PCB) which has contaminated Hudson River sediments for 30 years, there is much interest in assessing the long-term fate of the PCB's in the river. An implicit Adams finite difference simulation model of the upper Hudson River can be used to predict upper Hudson River PCB concentrations in the benthic sediments.

Several combinations of parameter values for the anaerobic biodegradation rate, the contaminated sediment depth, and the resuspension rate yielded equally good fits to measured concentrations. The volatilization rate, the rate of aerobic degradation in the water column, and the suspended sediment settling rate were found to be insignificant in affecting the concentration of PCB in the benthic sediments. A probabilistic model working together with the mechanistic model developed here would be a useful way to differentiate between equally good combinations of parameter values.

Even the best predictions differed significantly from observed concentrations. This is attributed to the great spatial variability in the rate (and even the sign) of change between the initial concentrations measured in the upper Hudson River and concentrations measured in later years.

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INTRODUCTION

Polychlorinated biphenyl (PCB) contamination of the Hudson River dates from 1950 when General Electric began discharging PCBs from its electrical equipment manufacturing plants in Fort Edward and Hudson Falls, NY. (Schroeder and Barnes, 1983). Over 230,000 kilograms of PCBs were discharged into the Hudson River at these sites between 1950 and 1977 (Tofflemire et al., 1979). Due to the hydrophobicity of PCBs, most of the chemical sorbed to river sediments. Core samples taken since this time indicate that much of the PCB load is still in sediments (Schroeder and Barnes, 1983).

As part of the ongoing debate about how to manage the control of this contamination, there is interest in assessing the long-term fate of the PCBs in the river. One useful tool for making this assessment is a model which predicts PCB fate and transport by simulating the processes which act on PCBs in the river. One such model has already been developed by Thomann et al. (1989) for the lower Hudson River. However, efforts by Thomann et al. to calibrate the removal rates and to verify their model were largely thwarted by the minimal water column and sediment PCB concentration data available in the lower Hudson River. The upper Hudson River, on the other hand, has been intensely sampled and thus provides a better opportunity to calibrate and verify a simulation model.

The objective of this research is to create a simulation model to predict water column and benthic sediment PCB concentrations in the upper Hudson River, to test the sensitivity of the model to the removal rate parameters, and to evaluate parameter values by comparing predictions with measured PCB concentrations.

This work is part of a larger study which investigates a number of ways to predict PCB fate and transport. Whereas the model developed here is entirely deterministic, a stochastic approach to PCB concentrations may be taken as well. This leads to the development of a *likelihood function* which can be maximized to give the most likely

values of the parameters, given all the available concentration measurements. In applying the likelihood approach to prediction of PCB concentrations, the output of a simulation model such as the one developed in this work is essential.

In addition to the creation of a likelihood function, one can apply a probability density function to the parameter values. If this distribution represents the best guess of an expert investigator for the values of the model parameters, it is called a *prior distribution*. Water quality modelers applying *Bayesian statistics* can combine the prior distribution with the likelihood function to create a probability density function for the parameters. Using this probability density function, predictions of PCB concentrations can be made and the degree of uncertainty associated with them can be assessed. Thus, the ultimate use of the model created here is as input into a Bayesian analysis which will provide parameter estimates and predictions based on site-specific data and the expert judgement of the investigator.

Chemistry of PCBs

Polychlorinated biphenyls are a class of synthetic, non-polar hydrocarbons featuring 2 phenyl groups and the bonding of 1 to 10 chlorine atoms to associated carbon atoms. Two hundred and nine different chemicals, called congeners, can result from the 209 unique configurations of the chlorine atoms on the carbon rings. PCB congeners with the same number of chlorine atoms (but bonded to different carbons) are called homologues. Although each congener has a distinct set of chemical characteristics, patterns of chemical properties based on homologue group have been found. Nonetheless, the fact that PCBs are actually 209 different chemicals greatly complicates the prediction of their fate and transport.

PCBs were originally discharged to the upper Hudson River as "Aroclors", combinations of congeners marketed by Monsanto for use in industrial applications.

These compounds had a clear, oily appearance. Chlorine content by weight ranged from 20% to 60%, with the greatest concentration of chlorine occurring in Aroclors with the highest proportion of heavily chlorinated congeners.

The molecular weight of PCB molecules ranges from 189 to 499. All are extremely hydrophobic; Hawker and Connell (1988) provide estimates of the octanol-water partition coefficient ranging from $2.8*10^4$ to $1.5*10^8$, with hydrophobicity generally increasing as the number of chlorine increases. An important effect of this hydrophobicity is that a high proportion of PCBs in the Hudson River is found sorbed to the organic carbon in suspended or benthic sediments, rather than in the dissolved phase. Thus, in simulating fate and transport of PCBs in the Hudson, it is necessary to also simulate the movement of sediment.

The dimensionless Henry's Law constant for congeners found in Hudson River sediments was measured by Warren et al. (1987) and found to be between $1*10^{-3}$ and $8*10^{-2}$. Mackay et al. (1983) suggest that it increases as chlorine number increases. Solubility varies considerably among congeners, but is low for all; Mackay et al. (1983) cites literature values for the aqueous solubility of the solid phase from 0.9 g/m^3 for mono-chlorobiphenyls to 0.00002 g/m^3 for deca-chlorobiphenyls.

Fate of PCBs in the Upper Hudson River

PCBs in the upper Hudson River are subject to transport and degradation. These mechanisms are responsible for redistributing the PCB in the river, and for the loss of PCB from the river. The concentration predictions made by the simulation model are based on the initial state of the system (i.e., where the PCB is located and in what quantities) and on simulation of the processes which remove the PCB mass from the river, or redistribute it.

One of processes which removes PCBs from the upper Hudson River is volatilization. The rate of this process is governed by a number of environmental factors, including temperature and river velocity. Whitman's two-film theory can be used to describe this process (Thomann and Mueller, 1987). It results in an equation of the form:

$$\frac{dC_d}{dt} = -\frac{k_l}{Z}\left(C_d - \frac{\rho_g}{H_e}\right) \qquad (1)$$

where:

C_d = *concentration of dissolved chemical*
k_l = *overall mass transfer coefficient*
ρ_g = *partial pressure of the vapor*
H_e = *Henry's Law constant*
Z = *depth of the water column*

k_l, the overall mass transfer coefficient, is defined with the equation:

$$\frac{1}{k_l} = \frac{1}{K_l} + \frac{1}{K_g * H_e} \qquad (2)$$

where:

K_l= *the liquid mass transfer rate*
K_g= *the gas mass transfer rate*
H_e= *Henry's Law constant*

Due to the high value of Henry's law constant relative to K_l, PCB is probably liquid-film controlled, and hence (1) can be reduced to:

$$\frac{dC_d}{dt} = -\frac{K_l}{Z} * C_d \qquad (3)$$

K_l can be modeled as a function of molecular weight, depth of the water column, river velocity, and temperature (Thomann and Mueller, 1987; Schnoor et al., 1987).

Biological degradation is also a removal process for PCBs in the Upper Hudson. Anaerobic degradation dechlorinates the PCB molecules, resulting in higher proportions of mono-, di-, and tri-chlorobiphenyls in the river PCB than originally appeared in the Aroclors. A number of investigators have shown that when PCB-contaminated sediment from the Hudson River is incubated with bacteria cultured from Hudson River sediment, the concentration of less chlorinated homologues increases, and the concentration of more chlorinated homologues decreases (e.g., Rhee et al., 1989; Quensen et al., 1990). Other evidence of dechlorination is the observed pattern of congeners in the sediment which does not match the proportions in the original Aroclors (Brown et al., 1987).

Aerobic biodegradation is also a sink for PCBs in the upper Hudson River. Experiments by Bedard et al. (1986; 1987) have shown that aerobic bacteria derived from Hudson River sediments are capable of degrading PCB congeners. They are especially effective on the less-chlorinated congeners. Aerobic biodegradation products are frequently benzoic acids.

The dual transport mechanisms of advection and dispersion also remove PCBs from the upper Hudson River. The immediate destination is the lower Hudson River. In the process of moving the PCBs downstream, advection and dispersion also redistribute it within the stream bed.

The Simulation Model

The simulation model is composed of three coupled equations describing the fate and transport of the PCBs.

$$\frac{dC}{dt} = -u\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2} - (k_{vol} + k_o)C_d - \frac{v_s}{Z}C_s + \frac{v_r}{Z}C_b \qquad (4)$$

$$\frac{dC_b}{dt} = \frac{v_s}{z_b}C_s - \frac{v_r}{z_b}C_b - k_a C_b \qquad (5)$$

$$\frac{C_d}{C_d + C_s} = \frac{1}{1 + C_{sed} f_{oc} K_{oc}} \qquad (6)$$

where:

C = *total PCB conc. in the water column (M/L^3)*
C^d = *dissolved PCB conc. in the water column (M/L^3)*
C_s = *sorbed PCB conc. in the water column (M/L^3)*
C_b = *conc. of PCB in the benthic sediments (M/L^3)*
u = *average river velocity (L/T)*
D = *dispersion (L^2/T)*
Z = *water column depth (L)*
v_s = *settling velocity (L/T)*
v_r = *resuspension rate (L/T)*
z_b = *thickness of the PCB-contaminated sediment layer (L)*
k_{vol} = *volatilization rate constant (1/T)*
k_a = *anaerobic biodegradation rate (1/T)*
k_o = *aerobic biodegradation rate (1/T)*
C_{sed} = *conc. of suspended sediment (M/L^3)*
f_{oc} = *fraction of organic carbon in sediment (M/M)*
K_{oc} = *organic carbon partition coefficient for PCB*

Equation 4 predicts the PCB concentration in the water column, while (5) predicts the PCB concentration in the benthic sediments. Equation 6 defines the distribution of the water column PCB between the sorbed and dissolved phases. PCB is moved

between the sediment layer and the water column via sedimentation of PCB-laden suspended sediments to the benthic sediments and resuspension of the contaminated benthic sediments to the water column.

The equations are solved with implicit Adams finite differences, using computer code which I wrote and developed. This solution method required the subdivision of the study area into 60 1000-meter subreaches, and the assignment of values for velocity, dispersion, resuspension, sedimentation, volatilization, aerobic biodegradation, anaerobic biodegradation, water column depth, and sediment depth. It was assumed that only advection, dispersion, and water column depth changed from subreach to subreach. Furthermore, it was assumed that only these three parameters changed their values over time.

Simulation Model Inputs

Hydraulics

Velocity is derived from the equation of continuity:

$$Q = uA = uWZ$$

where:

Q = *flow (L^3/T)*
u = *velocity (L/T)*
W = *channel width (L)*
Z = *water depth (L)*

Daily flow rates for flows at Fort Edward, Stillwater, and Waterford were taken from United States Geological Survey (USGS) records. River widths were measured from USGS maps. Depths vary from pool to pool, and are calculated as the sum of weir height and depth-of-flow over the weir (H). H is calculated using the weir

equation:

$$Q = CLH^{3/2}$$

where:
C = 3.2
L = length of the weir (feet)
H = height of the water over the weir (feet)

Weir lengths and the height of the weirs were obtained from the New York State Department of Environmental Conservation.

Dispersion was calculated using Fischer's equation (Fischer, 1979):

$$D = 0.011\frac{u^2W^2}{Z\sqrt{gZS}}$$

where:
g = acceleration of gravity (L/T^2)
S = slope of the water surface (L/L)

Biological Degradation

Rhee et al. (1992) present degradation data for PCBs degraded with bacteria cultured from Hudson River sediment. From these data, average biodegradation rates for the experiments can be calculated. These rates ranged from 0.0003/day to .0007/day. Experiments conducted by other investigators yielded biodegradation rates of 0.001/day to 0.003/day. The nature of laboratory tests makes it impossible to truly simulate river conditions - factors which could be different in the two environments and which are likely to affect biodegradation rates include bacterial type and population size, temperature, atmospheric gases, and composition of the PCB mixture. Because it is likely that the environment created in the laboratory is "ideal" in comparison to that in the field, a range of values for the anaerobic biodegradation

rate between 0.001/day and 0.00001/day was assigned.

Similar considerations apply to choosing a reasonable range for the aerobic biodegradation rate. While laboratory experiments have shown rates in the range of 0.26/day to 1.21/day (Bedard et al., 1986; 1987), I chose a range of rates between 0.1/day and 1.0/day, believing that the rate is likely slower in the river than in the laboratory.

Volatilization

The range for the volatilization rate was chosen after calculating reasonable values for the temperature, water depth, and river velocity. The resulting range is 0.1/day to 0.01/day.

Sediments

The gross resuspension rate is parameterized as the thickness of sediment which is resuspended from the benthic sediments per unit time. This is extremely difficult to assess. It is clearly a heterogenous phenomenon, as well as one that depends on flow rate. Sediment modeling work has suggested that no sediment is resuspended until a flow rate of 11,000 cfs at Fort Edward or 16,000 cfs at Waterford is reached (TAMS Consultants and Gradient Corporation, 1991). Here, the range assigned to this variable was 0 to 3 meters per year, recognizing that this variable represents the aggregated effect of resuspension throughout the study area.

The heterogeneity of sediment depth is similar to that for the resuspension rate. It may be considered a representative sediment depth - one useful for making predictions, rather than an actual depth of contaminated sediment. It was assigned a range of one to five meters.

The settling velocity range of 0.1 m/day to 10 m/day encompasses that given

in the EPA WASP4 manual (Schoor et al., 1987) for typical Stokes settling velocities for particles.

PCB Measurements

The model requires that initial concentration of PCB in the river bed be known. The 1976-1977 sediment survey was used to define initial conditions. Core sample concentrations measured in this survey (in ppm) are plotted in Figure 1. Average concentrations were computed for 1000-meter reaches of the upper Hudson River, converted to mg/l assuming a sediment density of 1.6 kg/l, and used to define initial concentrations for each reach. These are plotted in Figure 2.

Figure 2 also shows averaged concentrations from cores taken in 1984, 1985, and 1990, primarily from the pool above the Thompson Island dam. These are the concentrations assigned to the 1000-meter reaches and are the concentrations against which the model predictions are compared in the Results section.

The simulation model also requires PCB concentrations at the upstream end of the study area (Fort Edward) and at the downstream end (Waterford). These are needed as boundary conditions for the solution of the simulation model. Since measurements of PCB in the water column are not taken daily, there were many missing values. Regressions of PCB concentration versus daily average flow and year were carried out to estimate the daily PCB concentrations at these locations. The regression equations fit to the data are:

Fort Edward:

$$\text{Log(PCB conc)} = 16.98 + 0.000045\ \text{FLOW} - 0.241\ \text{YEAR}$$
$$n=294 \quad R^2=0.51$$

Waterford:

$$\text{Log(PCB conc)} = 20.14 + 0.0000087\ \text{FLOW} - 0.280\ \text{YEAR}$$
$$n=455 \quad R^2=0.53$$

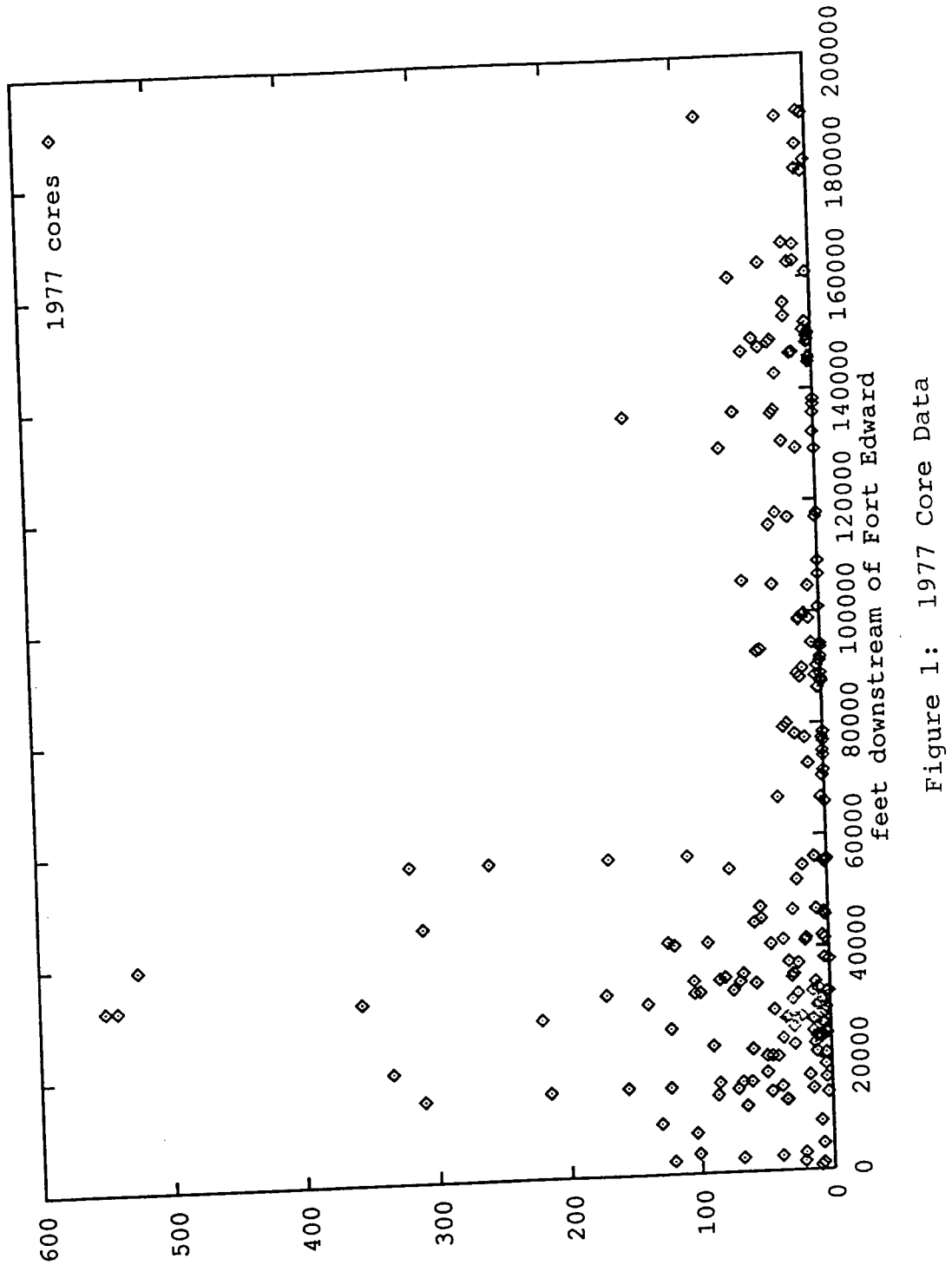


Figure 1: 1977 Core Data

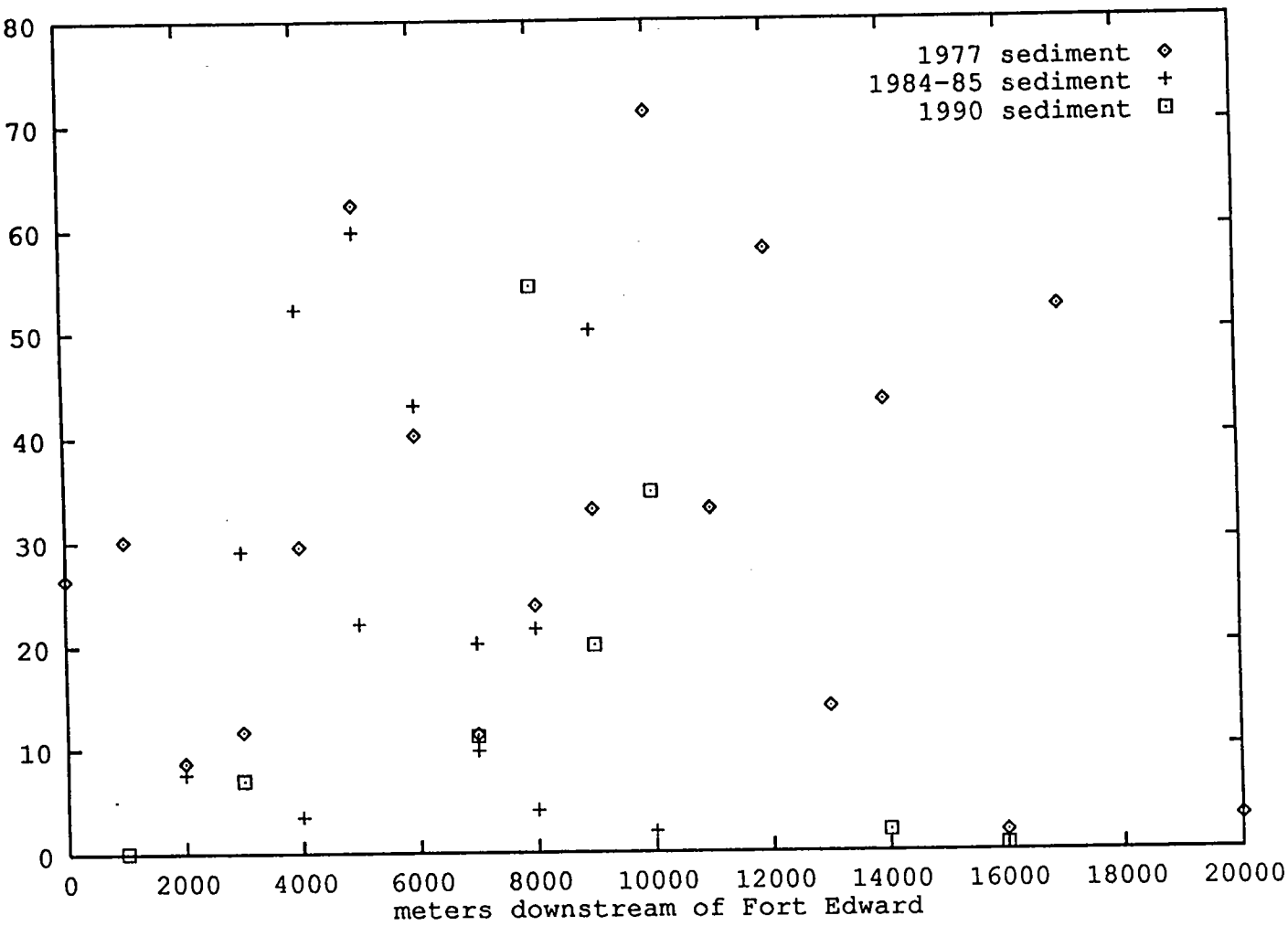


Figure 2a: Reach Concentration of PCB as Calculated from Field Data

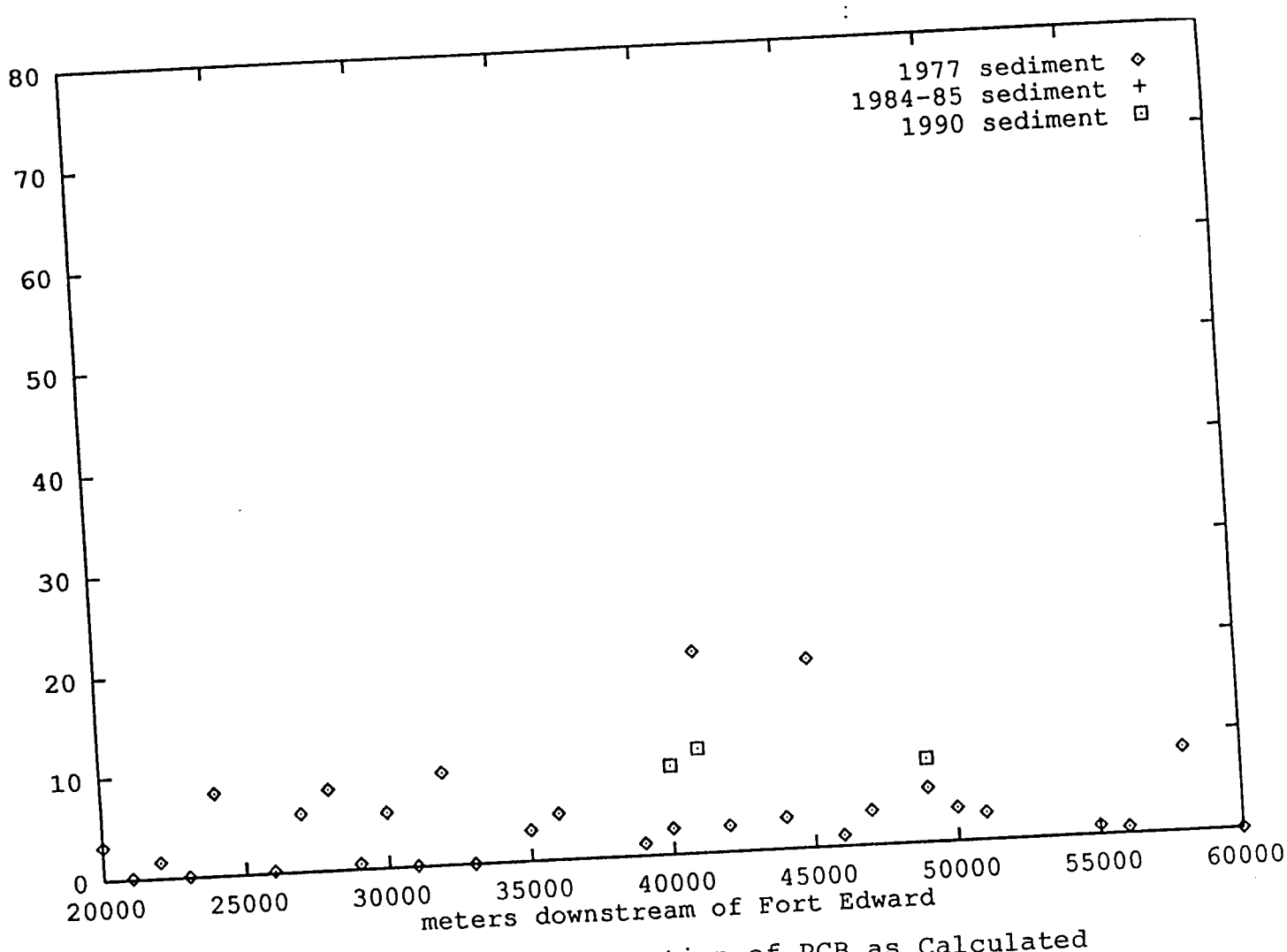


Figure 2b: Reach Concentration of PCB as Calculated from Field Data

where:

PCB conc = conc at the sampling location (micrograms/l)
FLOW = daily average flow (cfs)
YEAR = year - 1900

Suspended Sediment Concentrations

Suspended sediment concentrations are used in (6) to separate the water column PCB into sorbed and dissolved phases. The assumption of instantaneous equilibrium is implicit in this equation. Since suspended sediment concentrations are not taken daily, regressions were performed to estimate daily suspended sediment concentrations at Waterford, Stillwater, and Fort Edward.

Waterford:

Missing values for suspended sediment at Waterford were estimated using a regression of suspended solids at Waterford (SSCONCWA) (mg/l) versus suspended solids at Stillwater (SSCONCST) (mg/l). For days on which no suspended solids were measured at either Waterford or Stillwater, missing values were supplied using a regression equation for log (SSCONCWA) versus average daily flow (cfs) at Waterford. These regression are given below.

$$SSCONCWA = 0.454 + 1.34\ SSCONCST \qquad R^2=0.59 \quad n=3186$$

$$\log(SSCONCWA) = 1.32 + 0.0000808\ FLOW \qquad R^2=0.38 \quad n=3919$$

Stillwater:

Missing values for Stillwater were estimated from either a regression of suspended sediment at Stillwater versus suspended sediment at Waterford (for days when suspended sediment measurements were available at Waterford but not at Stillwater) or from a linear regression of log(suspended sediment concentration at Stillwater) versus flow at Stillwater. The resulting equations are:

$$SSCONCST = 3.65 + 0.44\ SSCONCWA \qquad R^2=0.59 \quad n=3186$$

$$\log(SSCONST) = 1.13 + 0.0000914\ FLOW \qquad R^2=0.30 \quad n=3296$$

Fort Edward:

Missing values for Fort Edward proved more difficult to estimate that those of Waterford or Stillwater. Regressions between suspended solids concentrations at Fort Edward (SSCONCFT) and at Waterford, Stillwater, or Schylerville showed very little relationship between the sites. The best regression that could be obtained was to regress the log of the suspended solids concentration at Fort Edward against the flow at Fort Edward. The resulting regression equation is:

$$\log(SSCONCFT) = 1.36 + 0.0000433\ FLOW \qquad R^2=0.07 \quad n=477$$

Although this is clearly a very poor relationship in terms of explanatory power, the property of regressing towards the mean results in most predictions being very close to the mean of log(SSCONCFT). In the absence of more information, this is a reasonable method for estimating suspended solids at Fort Edward.

Intermediate points:

In the simulation model, the suspended sediment concentration at any point between Fort Edward and Stillwater is calculated as the average of the concentrations at these two locations. Similarly, the suspended sediment concentration at any point between Stillwater and Waterford is calculated as the average of the concentrations at Stillwater and Waterford.

f_{oc} and K_{oc}

f_{oc} and K_{oc} are used in the calculation of the distribution of sorbed and dissolved PCB in the water column. For the purposes of this model, the estimate of f_{oc} was taken as the median of the f_{oc} reported with the sediment PCB concentration data. K_{oc} is congener-specific, but it was estimated in the model as the weighted average of the K_{oc} values of all the homologues in Aroclor 1242 and Aroclor 1016. These are the Aroclors thought to be most dominant in the original PCB mixture discharged into the Hudson River (Bopp, 1979). The weighting was done by relative frequency of each homologue in the 1242/1016 mixture. The resulting estimates of f_{oc} and K_{oc} are 0.63 mg/mg and $10^{5.36}$, respectively.

RESULTS

Results of the simulation modelling are shown in Table 1. Column 8 is a summary description of the predictions produced. Column 9 is the sum of the squared differences between the predictions and the measured, averaged concentrations. The

Table 1: Simulation Results

Sim. #	k_{vol}	k_a	k_o	Sediment Depth (meters)	Settling Velocity (m/day)	v_r (m/yr)	Summary of Predicted Concentrations	Sum of Squared Errors
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
1	0.10	0.0001	1.0	1	10	0.00	high concentrations	42121
2	0.10	0.0001	0.0	1	10	0.00	high concentrations	42119
3	0.00	0.0001	0.0	1	10	0.00	high concentrations	42112
4	0.01	0.00001	0.1	5	10	0.00	high concentrations	44070
5	0.01	0.00001	1.0	5	10	0.00	high concentrations	44068
6	0.01	0.00001	0.0	5	10	3.00	0 - 1 mg/l	59866
7	0.01	0.00001	0.1	5	10	3.00	0 - 1 mg/l	59871
8	0.01	0.00001	1.0	5	10	0.30	high concentrations	43086
9	0.01	0.00001	0.1	5	10	0.30	high concentrations	43073
10	0.01	0.00001	0.0	1	10	0.00	high concentrations	44060
11	0.01	0.00001	0.0	5	10	0.30	high concentrations	43071
12	0.01	0.00001	0.0	1	10	0.30	0 - 9 mg/l	56173
13	0.01	0.00001	1.0	5	0.1	3.00	0 - 1 mg/l	59977
14	0.01	0.00001	0.0	1	10	3.00	all predictions are 0 mg/l	60341
15	0.10	0.00001	1.0	5	10	0.30	high concentrations	43095
16	0.10	0.001	1.0	5	10	0.30	0 - 4 mg/l	59014

Table 1: Simulation Results (cont'd)

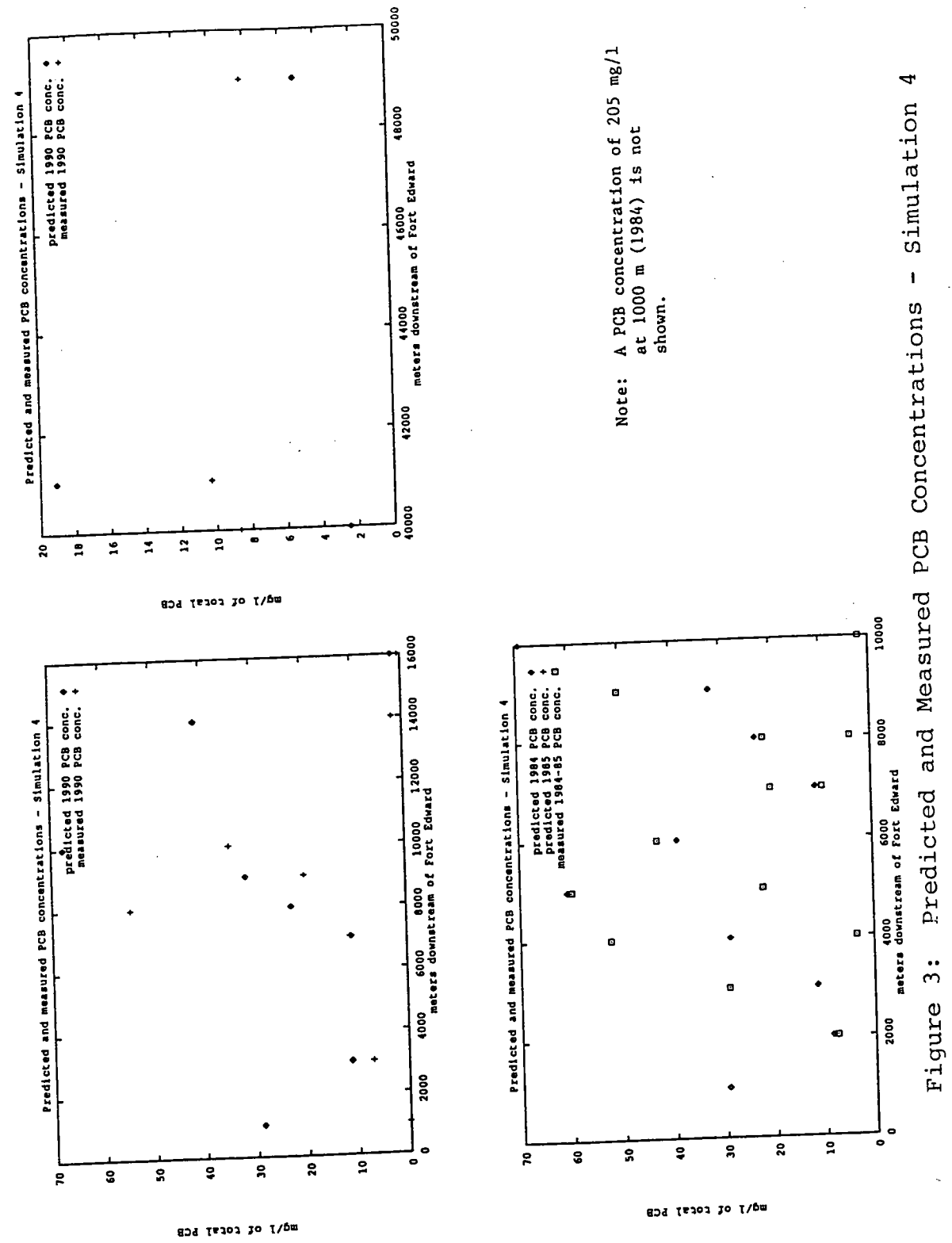
Sim. # (1)	k_{vol} (2)	k_s (3)	k_o (4)	Sediment Depth (meters) (5)	Settling Velocity (m/day) (6)	v_r (m/yr) (7)	Summary of Predicted Concentrations (8)	Sum of Squared Errors (9)
17	0.1	0.0001	1.0	5	10	0.30	high concentrations	45458
18	0.01	0.001	0.1	1	10	0.30	0 - 1 mg/l	60064
19	0.01	0.0001	0.1	1	10	0.30	0 - 5 mg/l	58225
20	0.01	0.00001	1.0	5	.1	0.03	high concentrations	43316
21	0.01	0.00001	1.0	5	10	0.03	high concentrations	43360
22	0.01	0.00001	0.0	5	10	0.30	high concentrations	43283
23	0.01	0.00001	0.0	5	0.1	0.30	high concentrations	43311
24	0.01	0.0001	0.1	5	10	0.00	high concentrations	42230
25	0.01	0.00001	1.0	1	10	0.03	high concentrations	42140
26	0.10	0.001	0.0	1	10	0.00	0 - 4 mg/l	58228

Note: Units of columns 2, 3, and 4 are 1/day

Table 2: Measured PCB Concentrations

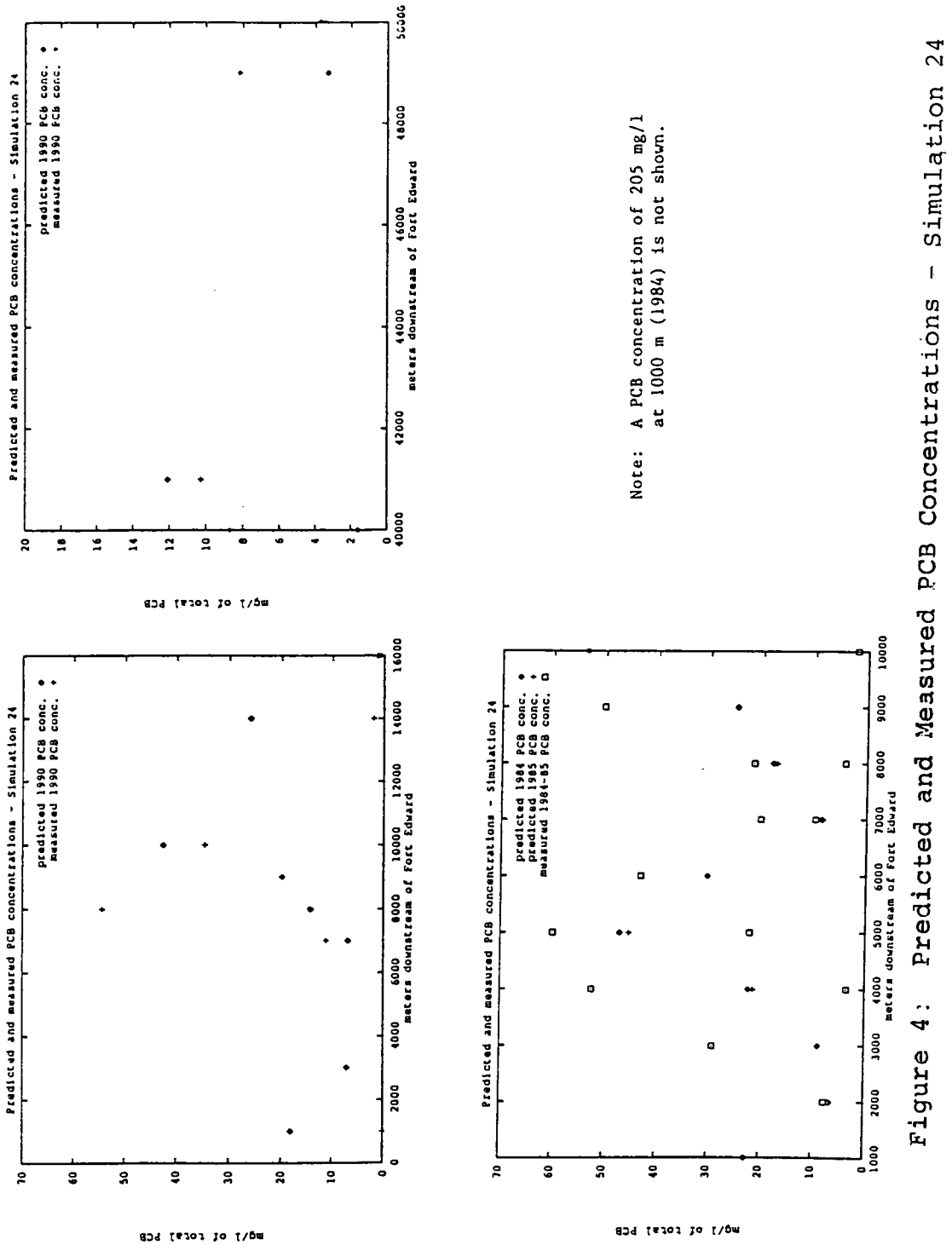
Meters downstream of Ft. Edward	PCB concentrations calculated from field data (ppm) 1977	1984	1985	1990
1000	30.1	205.6		
2000	8.6	7.6		
3000	11.7	29.1		
4000	29.5	52.3		
5000	62.3	59.8		
6000	40.1	43.0		
7000	11.4	20.2		
8000	23.8	21.6		
9000	33.0	50.2		
10000	71.1	2.0		
4000	29.5		3.5	
5000	62.3		22.1	
7000	11.4		9.8	
8000	23.8		4.1	
1000	30.1			0.1
3000	11.7			7.0
7000	11.4			11.2
8000	23.8			54.5
9000	33.0			20.0
10000	71.1			34.7
14000	43.2			2.0
16000	1.9			0.6
40000	2.5			8.7
41000	20.0			10.3
49000	5.3			8.2

Table 2: Measured PCB Concentrations				
Meters downstream of Ft. Edward	PCB concentrations calculated from field data (ppm)			
	1977	1984	1985	1990
1000	30.1	205.6		
2000	8.6	7.6		
3000	11.7	29.1		
4000	29.5	52.3		
5000	62.3	59.8		
6000	40.1	43.0		
7000	11.4	20.2		
8000	23.8	21.6		
9000	33.0	50.2		
10000	71.1	2.0		
4000	29.5		3.5	
5000	62.3		22.1	
7000	11.4		9.8	
8000	23.8		4.1	
1000	30.1			0.1
3000	11.7			7.0
7000	11.4			11.2
8000	23.8			54.5
9000	33.0			20.0
10000	71.1			34.7
14000	43.2			2.0
16000	1.9			0.6
40000	2.5			8.7
41000	20.0			10.3
49000	5.3			8.2



Note: A PCB concentration of 205 mg/l at 1000 m (1984) is not shown.

Figure 3: Predicted and Measured PCB Concentrations - Simulation 4



Note: A PCB concentration of 205 mg/l at 1000 m (1984) is not shown.

Figure 4: Predicted and Measured PCB Concentrations - Simulation 24

higher the number in Column 9, the further the predicted points are from the averaged, measured concentrations (shown in Figure 2 and in Table 2) and the worse the model simulates PCB fate and transport in the upper Hudson River.

The model produces predictions at 1000 meter intervals (called "nodes") along the river. Only predictions at those nodes where initial concentration measurements were available (i.e., where the 1976-77 sediment survey measured concentrations) were used to compute values in column 8. In addition to requiring initial concentration measurements, column 9 values could only be evaluated for nodes where concentrations had been measured in 1984, 1985, or 1990. Table 2 shows the location of these nodes, the initial concentration assigned to the nodes, and the averaged, measured concentrations to which the model results are matched.

From Table 2, it is clear that the reason the sum of the squared differences in column 9 of Table 1 is so high is that an unusually high averaged concentration of 205 mg/l was measured at 1000 meters in 1984, but the earlier 1977-78 sediment survey report yielded only a measured, average concentration of about 30 mg/l (Figure 2). For example, if the simulation model predicts a concentration at 1000 meters which is close to 0, the sum of squared differences immediately becomes 40,000. Thus, a good deal of the error in the predictions can be traced to this one concentration measurement. Unfortunately, because of this large discrepancy between the 1977-78 data and the 1984 data, there is very little the model can do to match the 1984 data at this node.

DISCUSSION

Sensitivity Analysis

No attempt was made to calculate the sensitivity of the model to *all* combinations of the parameters (which are infinite, in any case), but extrapolations

based on model performance and theoretical considerations were made regarding the overall prediction sensitivity to each parameter.

Some variables had a much greater impact on simulation results than did others. For example, simulations 1, 2 and 3, and 4 and 5 (Table 1) indicated that the volatilization rate and aerobic biodegradation rates had little influence on sediment concentrations when the resuspension rate is assumed to be zero. This was expected, since without resuspension, very little PCB gets into the water column and thus very little PCB is available for volatilization and aerobic biodegradation. On the other hand, simulations 6 and 7 indicated that when resuspension rates were high, the effect of changing these rates was low also, because resuspension removes virtually all the PCB from the benthic sediment layer. Simulations 8 and 9 indicated that even when the resuspension rate was only one-tenth that of simulations 6 and 7, the volatilization rate and aerobic biodegradation rates had little effect on predictions of sediment concentrations. (It is expected, of course, that the reaction of the model to changes in these two parameters will be similar, since they work only on dissolved PCB in the water column.)

The effects of sediment depth and the resuspension rate were closely linked. When resuspension is low, changes in sediment depth did not impact the predicted concentrations because this parameter was only used to distribute the PCB mass lost due to resuspension throughout the depth of benthic sediments (see Eq. 5 and simulations 5 and 10). With resuspension, on the other hand, sediment depth did make a difference, as comparison of simulations 11 and 12 illustrates. At fast resuspension rates, however, sediment depth didn't matter - the rate was so fast that all the PCB was removed no matter how deep the sediment was or how slow anaerobic biodegradation was (simulations 13 and 14).

The predictions were very sensitive to the anaerobic biodegradation rate, as comparisons of simulations 15, 16, and 17, and 18, 19, and 12 illustrate. Anaerobic biodegradation rates at the high end of the range (0.001/day) degraded nearly all the

PCB by 1984, regardless of the values of the other parameters. The settling velocity, on the other hand, appeared to have little impact on the predictions (simulations 20 and 21, and 22 and 23) at low resuspension rates, nor could it counteract the high PCB removal rates associated with fast resuspension, as simulations 6 and 13 demonstrated.

Comparison of Predictions to Measured Concentrations

Figures 3 and 4 show measured versus predicted concentrations for anaerobic biodegradation rates of 0.00001/day (simulation 4) and 0.0001/day (simulation 24) at sediment depths of 5 meters with no resuspension (simulations 4 and 24). As discussed in the previous section, anaerobic biodegradation rates at the high end of the range reduced all concentrations to 0 to 4 mg/l.

Several combinations of values for the anaerobic biodegradation rate, the sediment depth, and the resuspension rate produced equally good matches between the predictions and the measured concentrations. One good combination has a biodegradation rate in the middle of the acceptable range (0.0001/day), sediment depth of one meter, and no resuspension (simulations 1, 2, and 3). An alternative is to use an anaerobic rate of only 0.00001/day, but balance the resulting slow PCB removal rate by allowing some resuspension (simulation 25). At sediment depths of five meters, the best predictions are made with resuspension rates of 0.3 m/day and anaerorobic biodegradation rates of 0.00001/day (simulations 15, 8, and 9), or with no resuspension at all and an anaerobic biodegradation rate of 0.0001/day (simulation 24).

CONCLUSIONS

This work has shown that volatilization, aerobic biodegradation in the water column, and the sediment settling velocity are not important in determining the PCB concentration in the sediment of the upper Hudson River. Of much greater importance is the rate of anaerobic biodegradation, the resuspension rate, and the depth of the contaminated sediment. Several combinations of these three parameters were shown to produce equally good matches with the data.

A more thorough investigation of simulation results, using many more parameter values for resuspension, anaerobic biodegradation, and sediment depths (within the ranges specified in Section 5) might reveal combinations of these parameters which would better fit the measured concentrations. However, Figure 2 illustrates the difficulty in matching these predictions precisely: there is great spatial variability in the amount of change (and even in the sign of the change) in PCB concentration from the initial, 1977 concentrations and the 1984, 1985, and 1990 measured concentrations. Thus, it is very difficult for a model with spatially constant parameter values to match these measured concentrations. On the other hand, at least one very important parameter i.e., the anaerobic biodegradation rate, is unlikely to change much from location to location. The values of other sensitive parameters which are likely to be site-specific, e.g. sediment depth and resuspension rate, are poorly resolved by the available data.

The difficulty the model has in differentiating between several equally good sets of parameter values permits the investigator to claim several values of the resuspension rate, sediment depth and anaerobic biodegradation are equally likely, given the data. An approach which produces probability estimates of the parameter values, given the data, would be more useful than the strictly mechanistic methodology used here. One form of this approach was outlined in the Introduction to this paper, and the author is presently pursuing its implementation.

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