A Model of PCB Fate in the Upper Hudson River

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A mechanistic model of PCB fate, transport, and bioaccumulation in the Upper Hudson River was developed to provide a quantitative tool to assess the effectiveness of natural recovery and active remediation in reducing PCB levels in water, sediment, and biota. The fate and transport modeling, which is the subject of this paper, builds on previous approaches by using a mechanistic sediment-transport model that describes erosion and deposition with sufficient accuracy to remove the requirement to adjust sediment transport as part of the contaminant calibration process. An additional significant aspect of the model is the calibration and validation for both the short time scale of erosion events and the decade-long time scale associated with trends in sediment contamination. The model demonstrates differences between PCB fate in cohesive and noncohesive sediments that are important to efforts to reduce perceived human health and ecological risks. Burial due to the deposition of solids with lower PCB concentrations is the principal mechanism responsible for the approximately 90% decline in surface sediment PCB concentrations since the late 1970s. The more moderate decline seen in noncohesive sediments is due principally to the movement of PCBs from these sediments to the water column. The PCB load passing from the Upper Hudson River to the tidal Lower Hudson River is attributable to a combination of an external source located near the General Electric facility upstream of the contaminated sediments and sediments throughout the river. Elimination of the upstream source will increase the rate at which PCB levels decline in the cohesive sediments because it will reduce the concentration of PCBs on depositing particles. It will also immediately reduce the PCB flux to the Lower Hudson River by as much as 20% and affect future reductions as surface sediment PCB levels decline.

Introduction

Over approximately 30 years, ending in 1977, the General Electric Company (GE) discharged wastewater containing polychlorinated biphenyls (PCBs) into the Hudson River from two capacitor manufacturing facilities in Hudson Falls and Fort Edward, New York (*1*). Between Fort Edward, NY and the Federal Dam in Troy, NY the Hudson River is a run-of-the-river reservoir system with a series of locks and dams that serve as navigational controls for the Champlain Canal system and divide the river into eight reaches, or pools (Figure

1). Much of the PCBs discharged by GE accumulated in sediments upstream of the former Fort Edward Dam (Figure 1) located approximately 2 miles downstream of the Hudson Falls capacitor plant (*2*). Removal of this dam in 1973 by its owner lowered the water level behind it and exposed PCB contaminated sediment and wood wastes that had accumulated upstream (referred to as the remnant deposits). Subsequent high flow events in the mid-1970s resulted in the movement of PCB-containing sediments downstream. A significant proportion of these sediments and associated PCBs settled within depositional zones of the river. These areas were extensively sampled and analyzed for PCBs by the New York State Department of Environmental Conservation (NYSDEC) between 1976 and 1978. From these data, 40 sediment PCB "hot spots" were identified between Fort Edward and Troy, half of which are in the Thompson Island Pool (TIP), which is the first backwater region downstream of the former Fort Edward dam location (*3*). In addition, in 1976 the State of New York banned fishing in the Upper Hudson River and commercial fishing of striped bass and several other species in the Lower Hudson River. The Upper Hudson was re-opened to catch and release fishing in 1995.

The site has been studied extensively since the late-1970s and was designated a Superfund site in 1983. The United States Environmental Protection Agency (USEPA) concluded its Superfund investigation in 1984 with decisions of no-action for the river sediments and in-place containment for the remnant deposits (*4*). In 1989, the USEPA began a reassessment of the no-action decision. Because of the complexity of the site and its scientific and political stature, the reassessment has gone on for 10 years and is currently scheduled to be completed in 2001.

We have developed a quantitative model of PCBs within the Upper Hudson River to address issues pertinent to the reassessment: (1) the rate of recovery in the absence of active remediation of sediments (i.e., natural recovery); and (2) the ability of additional control of external sources and sediment remediation to accelerate the recovery. This approach has been used at numerous sites, including the lower Fox River (*5*), Green Bay (*6*), the Pawtuxet River (*7*), the James River (*8*), and the Lower Hudson River (*9*). Past applications typically have used relatively simplistic representations of hydrodynamics and sediment transport. As a result, model calibration has involved the simultaneous adjustment of sediment dynamics (in the form of arbitrary settling and resuspension velocities) and PCB fate processes to best "fit" the data. The model described in this paper builds on the previous approaches by using a mechanistic sediment transport model that describes erosion and deposition with sufficient accuracy to remove the requirement to adjust sediment transport as part of the contaminant calibration process.

An additional significant aspect of the work described here is the calibration and validation of the model for both the short time scale of erosion events and the long time scale associated with trends in sediment contamination. A weakness in previous models has been an absence of calibration/validation at all the scales of importance. Typically, models have been developed using a short data record that does not examine the ability of the model to accurately describe long-term trends. Because a primary purpose of the models is to predict decadal trends in the future, the lack of sufficient validation was a significant weakness. The paper presents calibration/validation to a robust data set for a period of 21 years.

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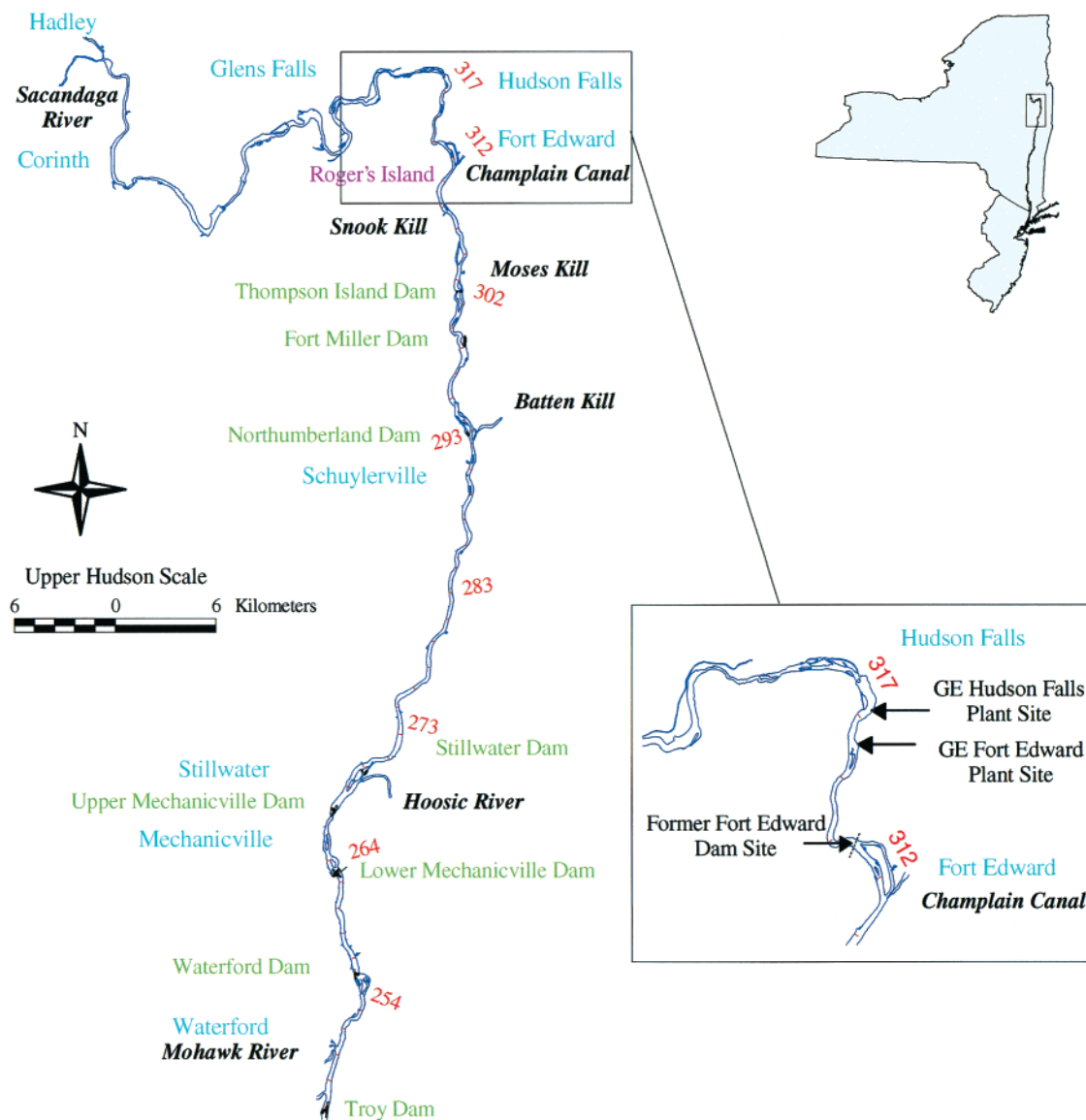
FIGURE 1. Upper Hudson River location map.

The model consists of sub-models that describe hydro-dynamics, sediment transport, PCB fate, and PCB bioaccumulation. These sub-models are linked such that all the major processes affecting PCBs are described in a mechanistic fashion. Further, independent calibration and validation of the hydrodynamics and sediment transport were used to constrain the calibration process for PCB fate and, in turn, independent calibration and validation of PCB fate were used to constrain the calibration process for PCB bioaccumulation. This paper presents the development, calibration, and validation of the PCB fate sub-model and the insights regarding PCB fate that it provided. Descriptions of the hydrodynamic and sediment transport sub-models can be found in QEA (*10*) and Ziegler et al. (*11*). The bioaccumulation sub-model is presented in QEA (*10*) and Glaser et al. (*12*).

Model Structure. Temporal changes in Upper Hudson River PCBs reflect the net result of a variety of dynamic processes governing the transport, transfer, and transformation of PCBs within the river: transport of PCBs to the river from external sources, transport of PCBs with the flowing river water, influx of uncontaminated water and particulate matter from the surrounding watershed, partitioning of PCBs between dissolved and particulate phases in both the water column and the sediment, deposition and erosion of

particulate matter and associated PCBs at the sediment surface, diffusion of PCBs within the sediment and between the sediment and overlying water column, and loss of PCBs through volatilization and biologically mediated reactions.

These processes represent the basic elements of a mass balance for the system and are the framework of a conceptual model of PCB fate within the Upper Hudson River. The mass balance stems from the scientific principle of mass conservation and is the basis for the quantitative analysis of PCBs in the Hudson River.

Basic Equations. Using a one-dimensional representation of the river along its main axis, the basic mass balance equation for total PCB concentration (i.e., the sum of dissolved and sorbed phases) in the water column is

$$\frac{\partial c_T}{\partial t} = -\frac{\partial u c_T}{\partial x} - \frac{D_S}{h m_w}(f_p c_T) + S_D + S_R - S_V \qquad (1)$$

where t is time, x is distance along the main axis of the river, c_T is total PCB concentration (M/L^3), m_w is total suspended solids concentration (M/L^3), u is average cross-sectional river velocity (L/T), S represents the sources and sinks (M/(L^3 × T)) due to transfer from sediment pore water (S_D), resuspension of bed sediment (S_R) and volatilization (S_V), D_S is

depositional flux of solids calculated by the sediment transport model ($M/(L^2 \times T)$), and h is depth of the water column (L). Longitudinal dispersion beyond that inherent in the finite difference solution of the equations has been neglected, reflecting the dominance of advective mass transport under most circumstances in a riverine system like the Upper Hudson River. The relationships between total concentration and dissolved (c) and particulate (p) concentrations are

$$c = f_d c_T \quad (2)$$

$$p = f_p c_T \quad (3)$$

where f_d is fraction dissolved and f_p is fraction particulate.

The expressions for fraction dissolved and fraction particulate are derived using the conventional simplification of instantaneous equilibrium between sorbed and dissolved PCBs (13):

$$r = K_p c \quad (4)$$

where r is the sorbed PCB mass per unit mass of sorbant (M/M) and K_p is the adsorption partition coefficient (L^3/M). They are written as

$$f_d = \frac{\theta}{\theta + K_p m_w} \quad (5)$$

$$f_p = \frac{K_p m_w}{\theta + K_p m_w} \quad (6)$$

where θ is porosity (water volume/total volume).

Inclusion of a component sorbed to dissolved organic matter (DOM) alters eq 1 by changing the definitions of f_d and f_p and adding a third component equation for the fraction sorbed to DOM (f_{dom}). This component was not included because paired measurements of dissolved and sorbed PCBs in the water and sediment of the Hudson River indicate that DOM has an insignificant effect on the PCB phase distribution (14).

The transfer of PCBs between sediment pore water and the water column is expressed as a diffusive process:

$$S_D = \frac{k_f}{h}(c_s - c_w) \quad (7)$$

where k_f is the diffusive mass transfer coefficient (L/T), and the subscripts s and w refer to the sediment bed and water column, respectively. A diffusive model is reasonable because field studies indicate that vertical advection is not significant in the Upper Hudson River sediment bed (10).

The transport of particulate PCBs from the sediment surface to the water column via resuspension occurs at a rate that is proportional to the rate at which sediment particles are resuspended (R_S; $M/L^2 T$). The volumetric PCB flux is

$$S_R = \frac{R_S}{h m_s} f_{p_s} c_{T_s} \quad (8)$$

where m_s is the concentration of particulate matter in the surface sediment and f_{p_s} is the fraction particulate in the surface sediment.

The rate at which volatilization occurs is dependent on the mass transfer coefficient at the air−water interface and the concentration of PCBs in the water column. Only freely dissolved PCBs can be transported across the interface, and sorption to particulate or dissolved organic carbon reduces volatilization. The equation used to describe PCB flux due to volatilization is

$$S_v = \frac{k_L}{h}\left(c - \frac{c_{air}}{H}\right) \quad (9)$$

where k_L is the volatilization mass transfer coefficient (L/T), c_{air} is the vapor phase PCB concentration in air (M/L^3) and H is Henry's constant (dimensionless). The mass transfer coefficient is dependent on the rates of mass transfer through relatively thin layers of water and air at the interface, which are in turn dependent on the concentration gradients in the layers, and the temperature-dependent diffusivity of PCBs in the layers (15, 16):

$$k_L = \frac{k_g k_l}{k_g + \dfrac{k_l}{H}} \quad (10)$$

where k_g is the vapor phase mass transfer constant (L/T) and k_l is the water phase mass transfer constant (L/T).

Within the sediment bed, PCBs are subject to vertical migration due to the processes of mixing of particles by biological activity and water turbulence propagating into the bed, molecular diffusion within sediment pore water, and advection of water through the sediment.

In addition, the use of a fixed frame of reference causes net erosion or deposition of solids to be included as mechanisms of vertical migration. For example, net deposition imparts a velocity to the sediments by moving them below the fixed location of the sediment−water interface. The equation describing the vertical distribution of PCBs within the sediment bed is

$$\frac{\partial c_T}{\partial t} = \frac{\partial}{\partial z}\left(E_p \frac{\partial p}{\partial z}\right) + \frac{\partial}{\partial z}\left[E_d \frac{\partial c}{\partial z}\right] - \frac{\partial(u_z c)}{\partial z} - \frac{\partial(w_b c_T)}{\partial z} \quad (11)$$

where z is vertical distance in the sediment (L), E_p is a dispersion coefficient applied to sediment particles and particulate PCBs (L^2/T), E_d is a dispersion coefficient applied to pore water PCBs (L^2/T), u_z is the velocity at which pore water is advected through the sediments (L/T), and w_b is the velocity due to net deposition. The component concentrations in eq 11 are expressed as the product of the component fraction and the total chemical concentration (e.g., $c = f_d c_T$). The PCB fluxes at the sediment−water interface due to transfer between sediment pore water and the water column and to resuspension and deposition are boundary conditions for eq 11.

PCB Constituents Modeled. The model simulated the dynamics of PCBs containing three or more chlorine atoms (PCB_{3+}). PCBs with fewer chlorine atoms were neglected because much of the data available for model calibration (i.e., most of the pre-1990 PCB data) was generated using analytical methods that did not measure a significant fraction of the mono- and di-chlorinated PCBs (10).

Hydrodynamics and Sediment Transport. A number of the terms in the basic equations were supplied by the hydrodynamic and sediment transport sub-models (10). The one-dimensional hydrodynamic sub-model provided water column velocities and depths. Suspended solids concentrations and deposition fluxes and resuspension fluxes were transferred to the PCB fate model via coupling procedures such that sediment transport model results (from a fine, two-dimensional grid) were temporally and spatially averaged to the coarse grid scale of the PCB fate sub-model. The sediment transport model uses mechanistic formulations to simulate cohesive and noncohesive resuspension and deposition processes. Site-specific data were extensively used to develop sediment transport model inputs and parameters, resulting in a highly constrained model that had only two parameters describing noncohesive resuspension and deposition that
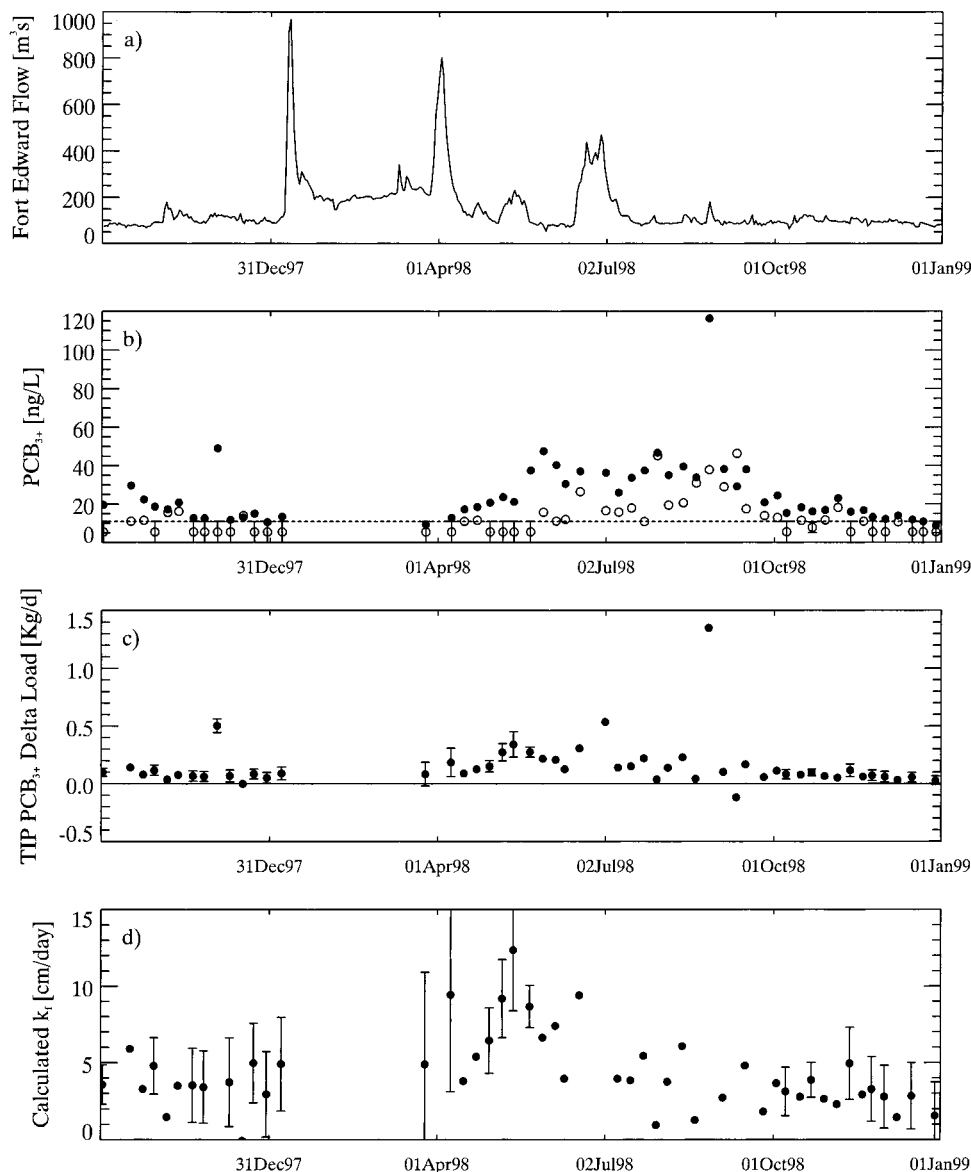
FIGURE 2. Temporal patterns in (a) Hudson River flow at Fort Edward, (b) water column PCB$_{3+}$ concentration, (c) PCB$_{3+}$ loading increase across TIP, and (d) calculated TIP sediment–water exchange coefficients.

were adjusted during model calibration. Rigorous calibration and validation of the model, for three flood events and a 22-year simulation, provided significant confidence in the predictive capabilities of the sediment transport model (10, 11).

Vertical Diffusion within the Bed. Diffusion within the pore water was assumed to be limited to molecular diffusion. The diffusion coefficient (E_d) was calculated by modifying the diffusivity by the tortuosity of the sediment. Experimental data have shown that the effect of tortuosity can be expressed by multiplying the molecular diffusion coefficient in solution by the bed porosity raised to an exponent of approximately 2 (17). Based on sediment porosity data (10) the diffusion coefficient at 20 °C was estimated to be 0.2 cm²/d for cohesive sediments and 0.1 cm²/d for noncohesive sediments.

PCB Exchange at the Sediment–Water Interface. The value of k_f in eq 7 was determined from synoptic sediment and water column PCB data collected in 1998 under low flow conditions when hydrodynamic resuspension would not contribute to the PCB flux at the sediment–water interface (10). The river flow at Fort Edward, water column PCB$_{3+}$ concentrations, the PCB$_{3+}$ load gain across the Thompson Island Pool, and the k_f needed to produce the PCB$_{3+}$ load

gain are shown in Figure 2. During the winter months (November to March), k_f is approximately 3 cm/day. It increases in early spring and peaks between 10 and 14 cm/d in late spring to early summer and declines through the summer into fall. The timing of the peak and subsequent decline suggests that k_f may be linked to biologically mediated mixing in the surface sediments. The calculated k_f values were used to visually define an annual k_f cycle that was applied in the model.

Particulate Mixing within the Bed. Based upon biological data and model calibration results, a partially mixed surficial sediment layer depth of 10 cm was chosen to represent conditions within Upper Hudson River cohesive sediments. The depth of particle-mixing was assumed to be lower in noncohesive sediment than in cohesive sediment because noncohesive sediment has a higher solids content and relatively low deposition of organic matter. On the basis of model calibration, a mixing depth of 3 cm was chosen for these sediments.

The magnitude of the particle-mixing coefficient (E_p) is uncertain. Values have been estimated at numerous sites by fitting a bed diffusion model to the measured vertical profiles of natural or introduced tracers. Thoms et al. (18) presented
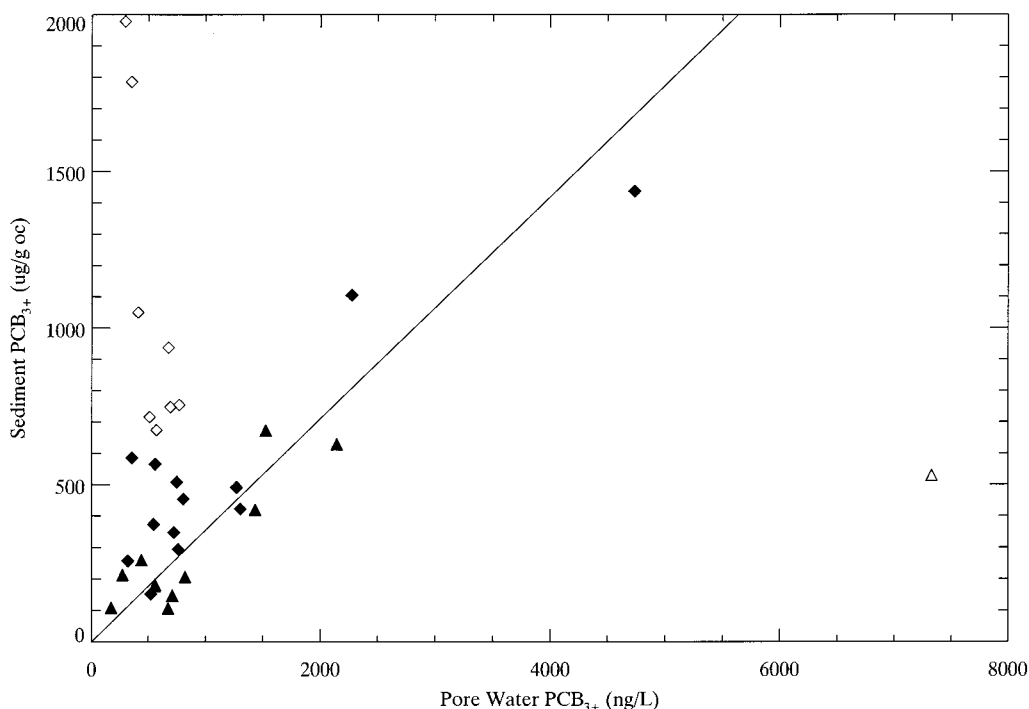
FIGURE 3. Relationship between sediment and porewater PCB_{3+} concentrations. Line conforms to regression of filled symbols ($K_{oc} = 10^{5.55}$).

a compilation of the available data that indicate that the mixing process varies seasonally and from site-to-site. Values of the particle diffusion coefficient range from about 10^{-9} to 10^{-6} cm^2/s. Olsen et al. (*19*) calculated surface values of about 10^{-8} cm^2/s in the Lower Hudson River. ^{7}Be (a radionuclide tracer) data from Upper Hudson River sediment cores (*20*) suggest a high particle mixing intensity because mean levels in the 2–4 cm layer were typically within a factor of 2 to 3 of levels in the 0–2 cm layer (*10*). On the basis of model calibration, a value of 10^{-7} cm^2/s was used for both cohesive and noncohesive sediments in this study.

Sorption Partition Coefficients. The organic carbon normalized partition coefficient (K_{oc}) of PCB_{3+} was estimated from regressions of paired measurements of particulate and filtrate PCBs in Upper Hudson River water samples (*20*). For samples taken at Fort Edward, which exhibited consistently higher partition coefficients than samples collected downstream of this location, regressions of data segregated by temperature yielded K_{oc} values in units of L/kg that increase from $10^{6.26}$ at 20 °C to $10^{6.75}$ at 1 °C. Similar regressions of data collected between Thompson Island Dam (TID) and Waterford yield K_{oc} values that range from $10^{5.62}$ to $10^{5.93}$. Values of K_{oc} at 20° C were specified as (1) $10^{6.3}$ at Fort Edward; (2) $10^{5.6}$ between TID and Waterford; and (3) linearly decreasing from $10^{6.3}$ to $10^{5.6}$ between Fort Edward and TID. The temperature dependency of K_{oc} was modeled using an Arrhenius equation whose coefficient was determined by regression (*10*):

$$\ln\left(\frac{K_{OC_T}}{K_{OC293}}\right) = 1375\left(0.0034 - \frac{1}{T}\right) \tag{12}$$

where T is temperature (°K).

The sorption of PCBs within the sediments was examined using measurements of Upper Hudson River sediment and pore water PCBs conducted in summer 1991 (*21*). An isotherm plot of these data suggests two groupings (Figure 3). One portion of the data (indicated by filled symbols) falls about a line that represents a K_{oc} of about $10^{5.6}$. The remainder of the data (represented by open symbols) forms an almost vertical line, indicating that a partition coefficient is not

applicable. These points correspond to samples from highly dechlorinated sediments. It is possible that dechlorination has eliminated much of the reversibly sorbed PCB_{3+} and the remaining PCB_{3+} is resistantly sorbed. The partition coefficient estimated without considering the data indicated by the open symbols in Figure 3 is the same as the 20 °C value generated from the TID through Waterford water column data, suggesting equality between water column and sediment K_{oc} with no evident influence of dissolved organic matter. Because of this equality and the tendency for surface sediments to be the least dechlorinated (*10*), the two-phase partition coefficients developed from the water column data for stations between TID and Waterford were applied to sediments throughout the model domain.

Volatilization Mass Transfer Coefficients. Henry's constant for PCB_{3+} was estimated from congener-specific Henry's constants (*22*) and measurements of PCB composition in Upper Hudson River water (*10*). The result was a dimensionless value of 0.0078 (19.8 Pa × m^3/mol) at 20 °C and a variation with temperature described by (*23*)

$$\ln(H_T) = 22.57 - \frac{5800}{T} \tag{13}$$

where H_T is Henry's constant (Pa × m^3/mol) at temperature T (°K). The water phase mass transfer coefficient was calculated from the O'Connor-Dobbins equation (*24*):

$$k_l = \sqrt{\frac{D_w u}{h}} \tag{14}$$

where D_w is the molecular diffusivity of the PCBs in water (L^2/T). The vapor phase mass transfer constant was assigned a constant value of 100 m/d, which is a reasonable approximation because of the limited impact of air motion (winds) on transfer in streams and rivers (*15*).

The vapor phase concentration of PCBs in air (c_{air}) was neglected in volatilization calculations on the basis of measured atmospheric PCB concentrations (*25–27*) that are sufficiently low as to be insignificant in comparison to water column dissolved PCB concentrations. Volatilization at each
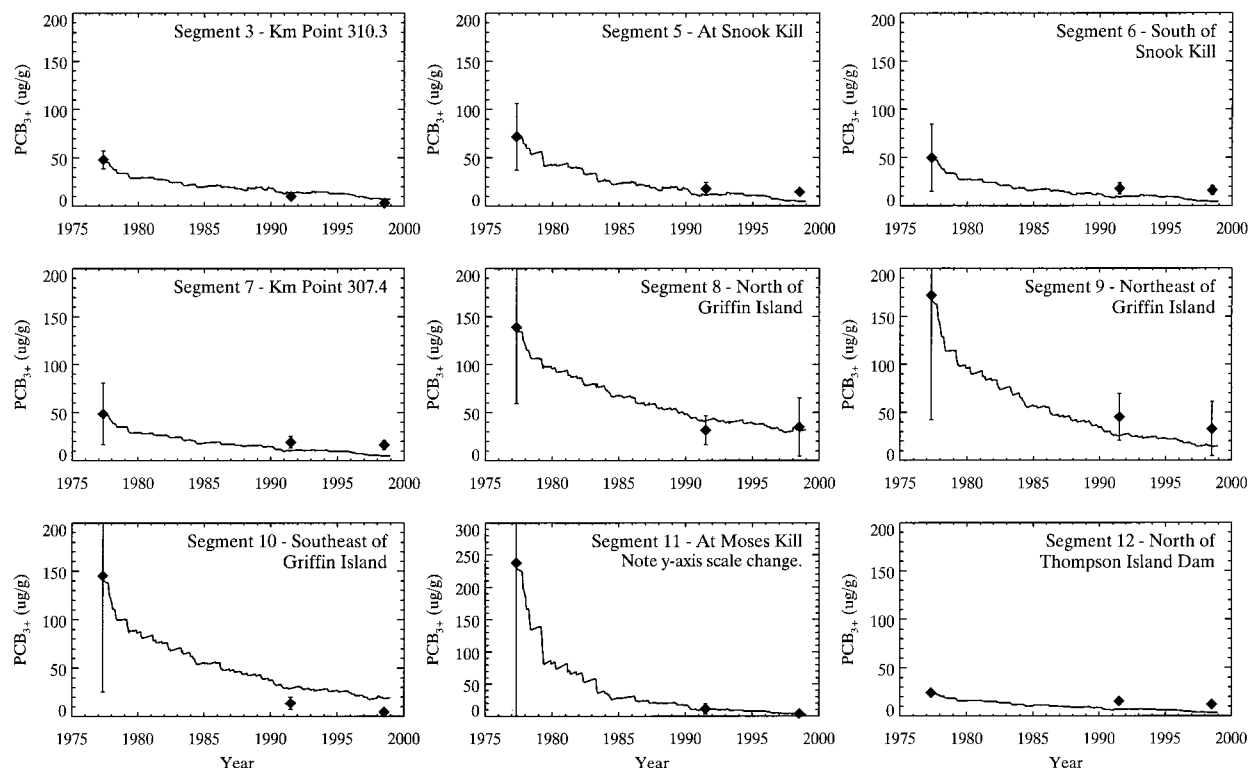
FIGURE 4. Data to model comparison of 0−5 cm cohesive surface PCB$_{3+}$ sediment concentrations at nine select model segments in the TIP.

of the eight dams along the Upper Hudson was estimated to result in less than 3% loss of PCBs (*10*) and was excluded from the model.

Segmentation of the River. The water column of the Upper Hudson River is sufficiently well-mixed over the cross-section that a one-dimensional representation of the water column is a valid approximation. The greatest longitudinal change in PCBs occurs across the TIP. For this reason, the water column was segmented more finely within the TIP than in reaches downstream of the TIP. The TIP was represented by twelve grid cells; with each grid cell approximately 0.8 km long. The region from the TID to Troy was divided into fourteen grid cells that vary in length from about 3 to 5 km. Field data were used to specify the cross-sectional geometry, and the annual temperature and suspended solids organic carbon content cycles for each segment (*10*).

Segmentation of the Sediment. The sediment transport model separated the sediment bed into areas of three bed types: cohesive (fine), noncohesive (coarse) and hard bottom (rocky). The PCB fate model used the same differentiation, but with a coarser segmentation. The cohesive and noncohesive sediments associated with each water column grid cell were vertically segmented at 25 and 5 one-centimeter intervals, respectively. A shallower bed depth was specified for the noncohesive sediment areas because data for these coarse sediments generally are limited to surface sediment grab samples. Field data were used to specify surface area, dry bulk density, particle density, and solids organic matter content for each sediment segment (*10*).

Results and Discussion

Calibration and Validation. Calibration and validation of the PCB fate model was accomplished by comparing predicted and observed PCB$_{3+}$ concentrations in the water column and sediment of the river over the period from 1977, the time of the first comprehensive survey of sediment PCB levels, to 1998. The depth and extent of particle mixing in the

surface sediments were the primary calibration parameters. The sediment bed PCB data collected by NYSDEC between 1976 and 1978 were used to determine the initial PCB$_{3+}$ concentrations for each sediment segment of the model. These concentrations were established by grouping the available data within cohesive and noncohesive areas of the Upper Hudson River (from Fort Edward to Troy) and averaging the data by depth in each group (*10*). Daily average PCB$_{3+}$ flux across the upstream boundary of the model at Fort Edward was estimated using data from the Rogers Island monitoring station. The 1977 to March 1991 loads were developed from United States Geological Survey (USGS) data and the April 1991 to December 1998 loads were estimated using GE data.

The model was calibrated using multiple data sets for model-data comparisons. Water column PCB data consisted of two data sets: (1) approximately 2000 measurements from water samples collected by the USGS at Schuylerville, Stillwater, and Waterford from 1975 to 1995; and, (2) approximately 3000 samples collected by GE from 1991 to present at TID. GE sampled additional stations during portions of this time period, including Schuylerville (1991−1992, 1997 − present), Stillwater (1991−1992), and Waterford (1991−1992). Sediment bed PCB data used for model calibration consisted of four data sets: (1) 1984−85 NYSDEC survey of the TIP; (2) 1991 GE survey from Fort Edward to Waterford; (3) 1992 and 1994 USEPA surveys from Fort Edward to Waterford; and (4) 1998 GE survey of the TIP.

Sediment Bed Temporal Trends. The PCB$_{3+}$ bed concentrations computed for each model segment in the TIP were compared with average PCB$_{3+}$ bed data collected in 1991 and 1998 (Figure 4). The model reproduced the trends in most segments, including substantial differences in trends among the segments. For example, measured PCB$_{3+}$ concentrations decreased in Segment 8 (north of Griffin Island) from 140 ppm in 1977 to 35 ppm in 1998, whereas PCB$_{3+}$ concentrations in Segment 13 (at Moses Kill) declined from 240 ppm in 1977 to 5 ppm in 1998. The model simulated
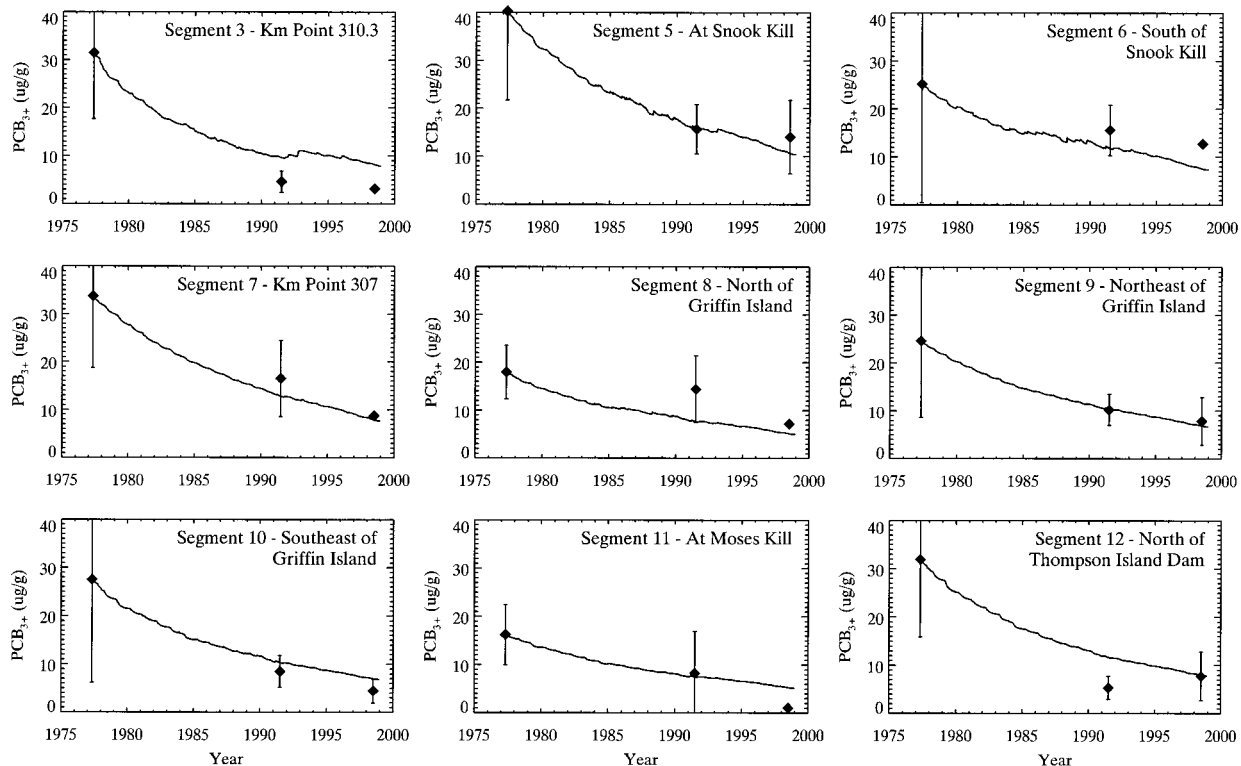
FIGURE 5. Data to model comparison of 0–5 cm noncohesive surface PCB$_{3+}$ sediment concentrations at nine select model segments in the TIP.
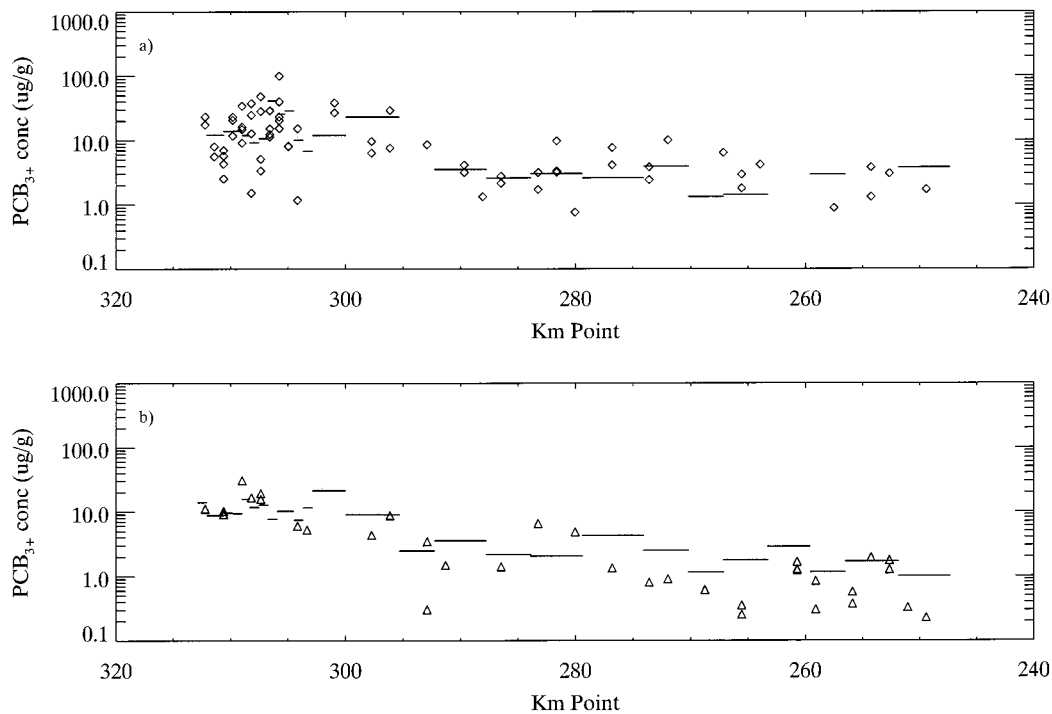

FIGURE 6. Spatial pattern of 0–5 cm (a) cohesive and (b) noncohesive sediment PCB$_{3+}$ concentrations calculated by the model (solid lines, predicted average) and measured (symbols, composite core average) in 1991. Shaded areas indicate model range.

these spatial variations in temporal trends almost exactly. In other segments, the model sometimes over-predicted or under-predicted the trend, but the deviations were not large. In some cases, the 1998 data point represents a single sample (indicated by symbols without error bars) and the deviations between model and data may reflect uncertainty in the actual average sediment concentrations.

The results for noncohesive sediments were similar to those for cohesive sediments (Figure 5). For example, PCB$_{3+}$ concentrations in Segment 5 (at Snook Kill) declined from 40 ppm in 1977 to 14 ppm in 1998, whereas in Segment 8 (north of Griffin Island) a smaller decline, from 17 to 8 ppm, occurred during this period. The model predicted this difference as well as most of the other differences among the locations. The only segments in which the predicted 1998 concentrations did not fall within the 95% confidence limits of the data mean are those in which the data is from a single sample.
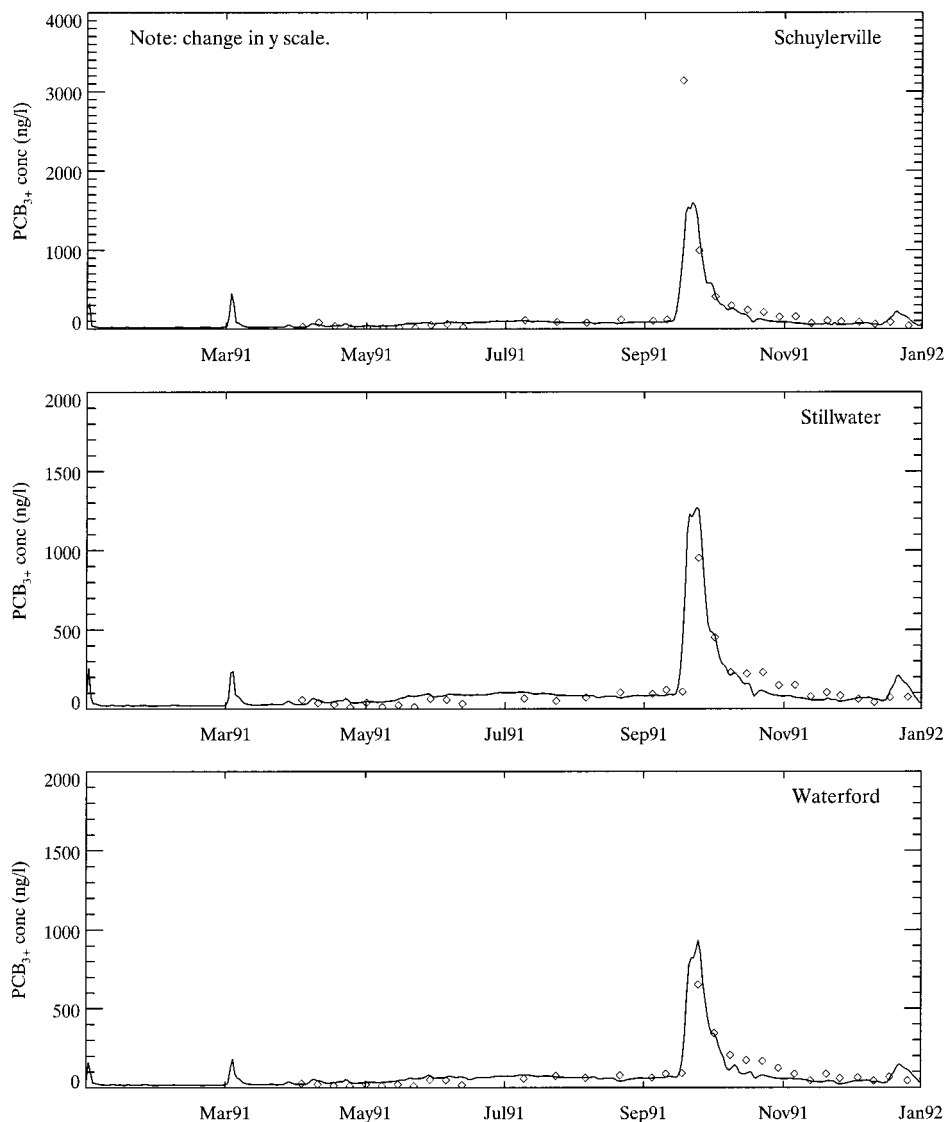
FIGURE 7. Comparison of predicted (lines) and measured (symbols) water column PCB_{3+} at Schuylerville, Stillwater, and Waterford.

The model also accurately reproduced the overall average decline in sediment PCB_{3+} concentrations in the TIP. PCB_{3+} levels in the top 5 cm of cohesive sediments declined from 105 ppm in 1977 to 20 ppm in 1991 and to 14 ppm in 1998, declines of about 80% and 87%, respectively. The model predicted 18 ppm in 1991 and 10 ppm in 1998, declines of about 83% and 90%, respectively. The average noncohesive sediment PCB_{3+} level declined from 40 ppm in 1977 to 12 ppm in 1991 and 7 ppm in 1998, declines of about 70% and 83%, respectively. The model computed concentrations of 11 ppm in 1991 and 8 ppm in 1998.

The ability of the model to reproduce the average temporal trend in TIP sediments, and the major features of the spatial variation of that trend within the TIP, provides strong evidence of its predictive capabilities. We are unaware of any other model of a contaminated sediment site that has demonstrated this degree of accuracy.

Sediment Bed Spatial Trends. The capability of the model to capture PCB trends throughout the Upper Hudson River was evaluated using the 1991 data. The model reproduced the large-scale spatial trend evident in the cohesive surface sediment (0−5 cm) data (Figure 6a) and subsurface sediment data (results not shown). The model over-predicted PCB_{3+} concentration in the most-downstream segment between km points 248 and 254. The single composite core in this region yielded a concentration of about 2 ppm, whereas the

model computed a concentration of about 4 ppm. This difference may be due to uncertainty in the initial condition because 1977 data were not available for this region of the river and the initial value from the closest upstream segment was used. It may also reflect an under-prediction of burial in this region. The model under-predicted PCB_{3+} concentrations in the two segments between km points 264 and 271. The data in this region range from about 1.8 to 6 ppm, whereas the model computed concentrations of about 1.5 ppm. This difference appears to be due to an over-estimation of burial in this region. The inaccuracies in burial rate in the lower reaches of the river are the result of limited knowledge of sediment bed conditions and bathymetry, and the relatively coarse resolution of the model in that region.

The model also reproduces the general features of the spatial trend in noncohesive sediments (Figure 6b). However, it tends to over-predict concentrations downstream of km point 279. The model computes concentrations of 1 to 3 ppm, whereas the data indicate concentrations in the range of 0.2 to 2 ppm. The bias could be due to over-estimation of the 1977 initial condition or over-estimation of the depth of contamination in the coarse sediments in this area of the river. From a practical standpoint, the over-estimation is not significant to the overall modeling because of the relatively low PCB concentrations in this area of the river.
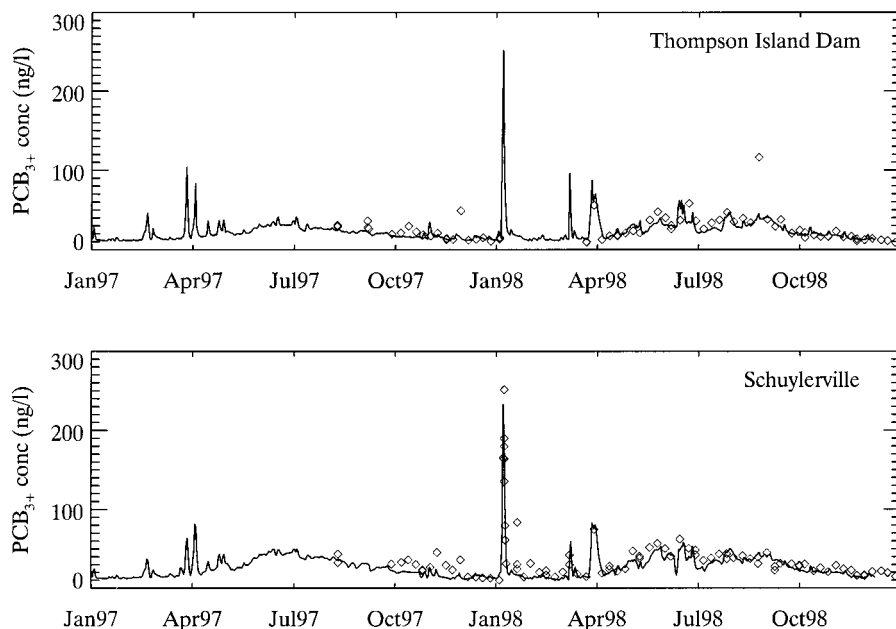
FIGURE 8. Comparison of predicted (line) and measured (symbols) water column PCB$_{3+}$ concentrations at Schuylerville and the Thompson Island Dam.

Water Column Trends. Comparisons of predicted and measured water column PCB$_{3+}$ concentrations at Schuylerville, Stillwater, and Waterford in 1991 are presented in Figure 7. From April to September 1991, the model predicted concentrations that closely match the measured values at each of the stations. The large PCB$_{3+}$ concentration increase in September is associated with increased PCB contribution to the river in the vicinity of GE's facility at Hudson Falls that resulted from the flooding of an abandoned mill that contained PCB oil and contaminated sediment. Following this event, the model under-predicted water column concentrations for a period of about 1 month. Apparently the event had a residual effect that the model did not capture. However, the bias disappears after a month and the predicted PCB$_{3+}$ concentrations are similar to the measured values.

Comparisons of predicted and measured water column PCB$_{3+}$ concentrations at the TID and Schuylerville in 1997 and 1998 are presented in Figure 8. A seasonal cycle in PCB$_{3+}$ concentration, interrupted by occasional spikes associated with high flow events or inputs upstream of Fort Edward, is evident at both stations. Concentrations are minimum in winter and maximum in early summer; the result of a seasonal variation in PCB flux from sediments that has been observed at other sites (*28, 29*). The model generally reproduced the seasonal trend and the absolute PCB$_{3+}$ concentrations at both stations. The large PCB$_{3+}$ concentration spike in January 1998, which the model accurately predicted, is associated with a high flow event that had a peak flow of about 34 000 cfs at Fort Edward, which corresponds to approximately a 10-year flood. The ability of the model to reproduce the PCB$_{3+}$ concentration increase during this flood is evidence that it has accurately represented the resuspension processes occurring during such a rare event.

Mass Balance Analyses. A model-generated mass balance over the period from 1977 to 1998 for PCB$_{3+}$ in the Upper Hudson River from Rogers Island to the Troy Dam is shown in Figure 9. Between 1978 and 1998, 7700 kg of PCB$_{3+}$ entered the Upper Hudson River from upstream. An additional 4400 kg entered from the sediments, in annual fluxes that ranged from about 630 kg in 1979 to about 110 kg in 1997. The bioavailable surface sediments also experienced a loss of 7100 kg as a result of burial in subsurface sediments. Of the 12 100 kg that entered the water over the 21-year period
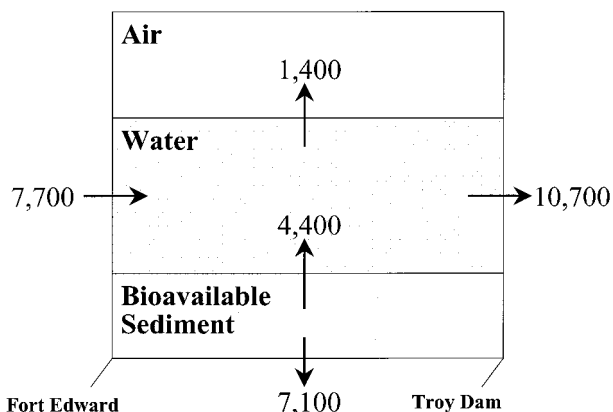

FIGURE 9. Estimated mass balance for PCB$_{3+}$ in the water and surface sediments of the Upper Hudson River between Rogers Island and the Troy Dam for the period from 1978 to 1998. Numbers are in units of kilograms.

examined, 10 700 kg were transported to the Lower Hudson River and 1400 kg were lost to the atmosphere via volatilization.

The 4400 kg of PCB$_{3+}$ that were predicted to enter the water from the sediment bed came mostly from the noncohesive sediments via continuous flux from sediment pore water (Table 1). The deposition and erosion fluxes have been closely balanced, yielding a net flux from the water column to cohesive sediments of 560 kg and a net flux from noncohesive sediments to the water column of 160 kg. The continuous flux from sediment pore water contributed 710 kg from cohesive sediments and 4110 kg from noncohesive sediments.

The surface sediments of the TIP were an important component of the total input of PCB$_{3+}$ to the water column, but the majority of the sediment input came from sediments downstream of the TID. The TIP sediments contributed 1450 kg of PCB$_{3+}$ to the water; about 33% of the total input from the sediment bed. Most of that input came from noncohesive surface sediments largely due to the greater surface area represented by these sediments (Table 1). Noncohesive sediments accounted for 1040 kg, which was the net of 2790 kg entering the water via continuous flux from sediment pore water and erosion and 1750 kg leaving the water and entering

TABLE 1. Model-Derived 1978−1998 PCB Mass Balance around the Bioavailable Surface Sediments (± = Source/Sink)

| | PCB$_{3+}$ mass flux (kg) | | | |
| | cohesive sediments | | non-cohesive sediments | |
process	Upper Hudson River	TIP	Upper Hudson River	TIP
diffusion within pore water	+20	+10	+190	+20
diffusion between pore water & water column	−710	−270	−4,110	−1,160
resuspension	−3,920	−1,600	−5,660	−1,630
deposition	+4,480	+1,460	+5,500	+1,750
burial	−7,610	−2,550	+320	+40
net flux	−7,740	−2,950	−3,760	−980

the sediments via settling. The cohesive sediments contributed 410 kg to the water; the net result of 1870 kg moving to the water from the sediment and 1460 kg moving to the sediment from the water.

As the net result of burial and diffusion within pore water, about 7100 kg of PCB$_{3+}$ were transported below the surficial sediment layer (10 cm in cohesive sediments; 3 cm in noncohesive sediments) between 1978 and 1998. This loss occurred entirely in the cohesive sediments. The Upper Hudson River model predicted that 7610 kg were buried in the cohesive sediments and 320 kg were brought into the surface layer from buried sediments in the noncohesive sediments (Table 1). About one-third of burial was predicted to have occurred within the TIP, where 2550 kg were buried in cohesive sediments and 40 kg were brought in to the surface layer in noncohesive sediments (Table 1).

The mass balance analysis further indicated that burial was primarily responsible for the decline in PCB$_{3+}$ observed in the cohesive sediments. Over the entire study area, the 7610 kg that were buried dwarf the net flux of 150 kg at the sediment surface to the water column due to settling, resuspension, and nonerosion exchange. Within the TIP, the conclusion is the same, although the comparison is not quite as dramatic, with 2550 kg being buried, whereas 410 kg were transferred to the water column. In contrast to the cohesive sediments, the mass balance indicated that the declines observed in noncohesive sediments were principally due to PCB$_{3+}$ flux to the water column. Within the surface layer, minimal burial occurred in noncohesive sediments over the study area or within the TIP.

The mass balance analyses indicated that the TIP sediments have been a minor contributor to the PCB$_{3+}$ flux from the Upper Hudson River to the Lower Hudson River, as indicated by the PCB$_{3+}$ flux passing Waterford (Figure 10). These sediments accounted for 13 to 26% of the flux, depending on the year examined. The upstream source (PCBs entering with water passing Fort Edward) contributed amounts about equal to the TIP sediments, except during the period of high upstream releases from the plant site area when the upstream source dominated (e.g., 1992). Thus, the major contribution to the PCB$_{3+}$ flux passing Waterford came from sediments between the TID and Waterford. The model predicted that PCBs originating from TIP sediments (or the upstream source) are lost due to settling and, to a lesser extent, volatilization as water moves downstream. These PCBs are replaced by PCBs fluxing to the water column from downstream sediments. Overall, the contribution of PCB within sediments in any specific region of the Upper Hudson River to the flux to the Lower Hudson River is a function of the sediment PCB concentration and the distance between the region and the Federal Dam in Troy (the upstream boundary of the Lower Hudson River).

Implications for Remediation. The model provides numerous insights pertinent to the issues of natural recovery and the effectiveness of active remediation. The natural recovery evident in the decline of sediment PCB levels is attributable mainly to sediment deposition in cohesive
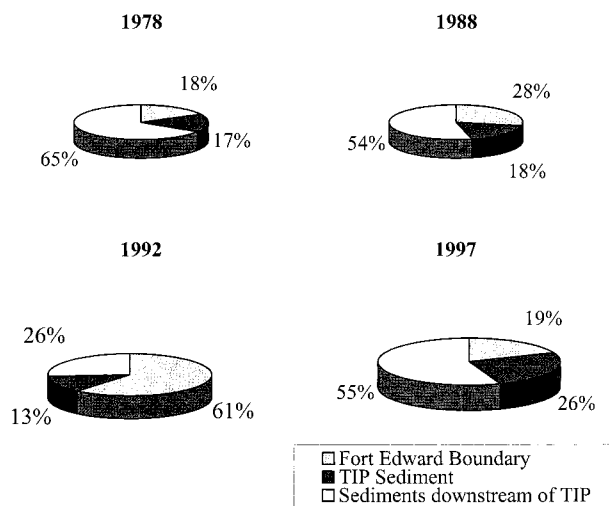

FIGURE 10. Estimated relative contribution of upstream sources, TIP sediments, and Reaches 1 through 7 sediments to the PCB$_{3+}$ flux passing over Troy Dam.

sediments and PCB flux to the water column from noncohesive sediment pore water. These processes will continue to reduce sediment PCB levels into the future until the system reaches some steady-state with the ongoing external PCB source (the upstream source). The continuation of sediment deposition for at least the next several decades is predicted by the sediment transport model, even if the river experiences extreme events such as the 100-year flood (10).

Elimination of the upstream source will increase the rate at which PCB levels decline in the cohesive sediments because it will reduce the concentration of PCBs on depositing particles. It will also immediately reduce the PCB flux to the Lower Hudson River by as much as 20% and affect future reductions as surface sediment PCB levels decline. Because the majority of the sediment PCB flux is attributed to the noncohesive sediments, sediment remediation would be most effective in reducing water column PCB levels if directed at these sediments. Sediment remediation in the TIP would be less effective at reducing PCB flux to the Lower Hudson River in the short term than would remediation of sediments downstream of the TIP.

The effectiveness of natural recovery and active remediation can be quantitatively estimated by using the model to project future conditions for conceived scenarios. In this way the model acts as a tool for evaluation of remedial scenarios. We are using the Upper Hudson River model in such a manner and have conducted initial projections (10). This work will continue as part of an overall evaluation of PCBs in the river.

Acknowledgments

Notation

c	concentration of PCBs dissolved in the water (M/L^3)
c_{air}	vapor phase PCB concentration in air (M/L^3)
c_s	concentration of PCBs in sediment pore water (M/L^3)
c_T	total PCB concentration (M/L^3)
c_w	concentration of PCBs dissolved in the water column (M/L^3)
D_S	molecular diffusivity of the PCBs in sediment pore water (L^2/T)
D_w	molecular diffusivity of the PCBs in water (L^2/T)
E_d	dispersion coefficient (L^2/T)
E_p	particle mixing coefficient (L^2/T)
f_d	fraction of total PCB in dissolved form
f_{dom}	fraction of total PCB sorbed to DOM
f_p	fraction of total PCB in particulate form
h	total water depth (L)
H	dimensionless Henry's Constant
H_T	Henry's Constant at temperature, T $(Pa \times m^3/mol)$
k_f	sediment pore water–water column mass transfer coefficient (L/T)
k_g	vapor phase mass transfer constant (L/T)
k_l	water phase mass transfer constant (L/T)
k_L	volatilization mass transfer coefficient (L/T)
K_{oc}	organic carbon normalized PCB partition coefficient (L^3/M)
K_p	adsorption partition coefficient (L^3/M)
m_s	concentration of particulate matter in sediment (M/L^3)
m_w	total suspended solids concentration (M/L^3)
p	particulate PCB concentration $[M/L^3]$
r	mass of PCBs/unit mass of solids (M/M)
R_S	sediment resuspension rate $(M/L^2 \times T)$
S_D	PCB flux between sediment pore water and water column $(M/L^3 \times T)$
S_R	PCB flux between sediment and the water column due to resuspension $(M/L^3 \times T)$
S_v	PCB flux due to volatilization $(M/L^3 \times T)$
t	time (T)
T	temperature $(°C$ or $°K$ depending on eq)
θ	porosity $(L^3$ water$/L^3$ total$)$
u	velocity $[L/T]$
u_z	velocity along the z-axis (L/T)
w_b	net deposition or burial velocity in sediment (L/T)
x	longitudinal distance
z	vertical distance

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