

Thompson Island Pool Sediment PCB Sources



FINAL REPORT

GENhud 131

THOMPSON ISLAND POOL SEDIMENT PCB SOURCES

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SECTION 1 INTRODUCTION

Since 1990, the U.S. Environmental Protection Agency (USEPA) has been performing a reevaluation of the 1984 Superfund no-action decision for the PCB-containing sediments within the upper Hudson River. One principal objective of the reassessment is to determine the relative importance of the varied sources contributing to water column PCB loadings. This report provides a quantitative analysis of water column PCB sources within the TIP based on the extensive historical database of water and sediment PCBs generated by the state and federal governments and the more recent data sets generated by the General Electric Company (GE).

As a result of this work the following major conclusions can be drawn:

• During the 1990s, the amount of PCBs leaving the TIP was significantly overestimated due to a sampling bias at the routine sampling station located at the downstream limit of the TIP;

• The composition of water column PCBs attributed to the TIP sediments indicates that relatively undechlorinated PCBs are the principal source and that surface sediment pore water is the principal point of origin;

• PCB levels in the water column increase in a near linear fashion as water passes through the TIP, indicating a nearly uniform areal flux from sediments within the TIP; and

• Sediments downstream of the Thompson Island Dam (TID) contribute PCBs to the water column in a manner consistent with the TIP sediments (i.e., transfer from surface sediment pore water), increasing the water column loading by approximately 50% between TID and Schuylerville.

The analyses presented in this report demonstrate that surface sediments within all areas of the river contribute PCBs to the water column, not simply PCBs residing in "hot spot" areas. Comparison of dry weight sediment PCB concentrations, either at depth or at the sediment surface, gives a false impression of the relative importance of various sediments within the river. The surface

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sediment pore water PCB concentrations and, hence, the diffusive sediment PCB flux is controlled by PCB concentrations associated with the organic carbon component of the sediments. As these average organic carbon normalized PCB concentrations are similar within "hot spot" and non-"hot spot" areas, these areas contribute similarly to the water column PCB load. This finding has important implications for the development and evaluation of remedial strategies for the river.

The conclusions of this report are in many cases inconsistent with those reached by the USEPA in the Data Evaluation and Interpretation Report (USEPA, 1997). The differences are primarily due to the results of additional data collection since the release of the USEPA report and the application of a rigorous, quantitative PCB fate and transport modeling effort sponsored by GE. USEPA is in the process of developing a similar model.

This report has been prepared by Quantitative Environmental Analysis, LLC. (QEA) on the behalf of the GE to document the results of numerous field research, data analysis, and modeling efforts investigating the origin, fate, and transport of PCBs within the upper Hudson River. Section 2 provides a historical background of the Hudson River PCB problem and describes significant events that have impacted the observed temporal changes in water column PCB loadings. Section 3 describes the basic physical and chemical processes affecting PCBs in aquatic environments and their incorporation into a state-of-the-science PCB fate and transport model. Section 4 presents the results of field research, data analysis, and modeling studies conducted on the river over the last several years that are the basis for the conclusions presented above. Section 5 presents the summary, conclusions, and recommendations drawn from the analysis presented.

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SECTION 2 BACKGROUND

2.1 History

Over an approximate 30 year period, ending in 1977, two GE capacitor manufacturing facilities in Fort Edward and Hudson Falls, New York discharged PCB-containing wastewaters into the upper Hudson River. Much of the PCBs accumulated in sediments upstream of the former Fort Edward Dam located approximately 2 miles downstream of the Hudson Falls capacitor plant (Figure 2-1). Removal of this dam in 1973 by the owner (Niagara Mohawk Power Corporation) and subsequent high flow events resulted in the movement of large quantities of PCB-containing sediments downstream. Some of these sediments deposited further downstream in pools formed by dams along the Champlain Canal, which is coincident with the Hudson River channel (USEPA, 1984).

In the late-1970s, the New York State Department of Environmental Conservation (NYSDEC) undertook a number of studies to determine the concentration and distribution of PCBs in the water column, sediments, and biota of the upper Hudson River. As a result, they identified sediment "hot spot" areas defined as regions of the river containing sediments with PCB concentrations exceeding 50 parts per million (ppm). Forty of these "hot spots" were identified in the 40 mile stretch of the upper Hudson River between Fort Edward and Troy, N.Y. Twenty "hot spots" were located in the TIP, a six mile section of the river formed by the TID, which is the first dam downstream of the former Fort Edward Dam. In the early 1980's, the NYDEC proposed that the sediments from the TIP "hot spots" be removed and placed in a landfill in Ft. Edward, New York. Due to community opposition, the NYSDEC was unable to proceed with the project.

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In 1984, the USEPA placed the upper Hudson River on the Superfund National Priorities List and issued a Record of Decision (ROD). The ROD determined that the approximately 60 acres of shoreline PCB deposits upstream of the former Fort Edward Dam, formed when the pool elevation dropped approximately 20 feet due to the removal of the dam, were to be capped in-place to minimize direct contact with the exposed PCB-containing sediments. For the PCB-containing sediments within the TIP and downstream, an interim no-action decision was reached for a number of reasons, including: 1) declining PCB levels in water and fish as a result of source control measures on the plant sites and natural attenuation processes in the river, and 2) the unproven status of contaminated sediment removal technology (USEPA, 1984).

After the 1984 ROD, GE entered into agreements with the Federal government to implement the remnant deposits capping program. This was carried out between 1988 and 1991 (JL Engineering, 1992). In addition, GE implemented a water column monitoring program beginning in 1989 (Harza, 1990) to monitor the construction activities on the remnant deposits and to demonstrate that the remedy was functioning as intended¹. The NYSDEC continued to pursue a TIP "hot spot" dredging and landfill program, and in 1987 began the process of siting a local landfill, which ended in 1989.

In 1990, the USEPA reopened the 1984 no-action decision on the PCB-containing sediments of the upper Hudson River and initiated a reassessment remedial investigation and feasibility study (RRI/FS). Although GE was only one of two named potentially responsible parties (PRPs; the other being Niagara Mohawk Power Corp.), the USEPA decided to complete the RRI/FS using government contractors and funds. The complexity of the technical issues associated with assessing the origin, fate, and transport of PCBs in the system has delayed the original schedule of the RRI/FS, which is now scheduled for completion sometime after the year 2000.

¹This program and later variants provided much of the water column PCB data presented in this report.

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Although GE was not permitted to perform the RRI/FS for the USEPA, the company collected relevant scientific data that would enable: 1) a better understanding of PCB dynamics within the system, and 2) the development of a state-of-the-science PCB fate and transport model. The data collection program started in earnest during the spring of 1991 (O'Brien & Gere, 1993a, 1993b). A key component of the program was the routine (at least weekly) monitoring of water column PCB concentrations at a number of stations in the upper Hudson River, including (Figure 2-1):

•Route 27 Bridge in Hudson Falls (background station),

•Route 197 Bridge in Fort Edward (downstream of the plant sites and remnants deposits and upstream of the TIP), and

•the TID (downstream of the TIP).

This monitoring has continued and now provides a valuable data set to evaluate the temporal trends in water column PCBs in the upper Hudson River.

2.2 Hudson Falls and Allen Mill Remediation

During the routine monitoring performed by GE, a significant increase in water column PCB loading was detected after mid-September 1991. This loading originated upstream of the Fort Edward and downstream of the Route 27 Bridge stations (Figure 2-1). Within a weeks time, PCB levels within the river increased from less than 100 ng L⁻¹ to approximately 4000 ng L⁻¹ (O'Brien & Gere, 1993a). After significant investigation, the source of the increased water column PCB loading was attributed to the collapse of a wooden gate structure within an abandoned paper mill (Allen Mill) located adjacent to the Hudson Falls capacitor plant on Bakers Falls (O'Brien & Gere, 1994a; Figure 2-1, inset). The gate had kept water from flowing through a tunnel cut into bedrock below the mill, presumably since the mill's closure in the early 1900s. The tunnel contained oil phase PCBs that migrated there via subsurface bedrock fractures.

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In January 1993, with the cooperation of the Bakers Falls Hydroelectric Dam owner and the NYSDEC, the water flow through the mill was largely controlled. By Spring 1993, two of the three water ways within the mill were isolated from the river and planning for the removal of PCB containing material from within the Allen Mill commenced. Removal continued until the fall of 1995. Approximately 45 tons of PCBs were contained in the 3,430 tons of sediment removed from the Allen Mill (O'Brien & Gere, 1996a).

As part of the investigation and clean-up of the Allen Mill, dense non-aqueous phase liquid (DNAPL) seeps of PCBs were discovered within the exposed bedrock of the falls. In 1994, during the construction of the new dam at Bakers Falls, PCB DNAPL seeps were observed in the portion of the falls adjacent to the Hudson Falls plant site. A number of actions have been taken to contain and control these PCB seeps including grouting of bedrock fractures, manual collection of PCB oils, when accessible, and the operation and installation of pumping wells to hydraulically control the seeps. The release of PCB DNAPL through these bedrock seeps has declined in response to mitigation efforts, but has not ceased. While efforts are made to collect the material, uncollected oils are released into the river when the falls are inundated during elevated river flow events. Sediments and debris from the vicinity of the original wastewater outfall located immediately upstream of the dam and the area where the seeps are concentrated are being removed in an additional effort to control the seeps. This removal is scheduled for completion during the Summer of 1998.

In September 1996, divers discovered an additional area of PCB DNAPL seepage at the base of the Bakers Falls adjacent to the eastern shore in an area referred to as the plunge pool. A subaquatic collection system was installed to arrest the flow of the PCBs into the river. This seep produced approximately 0.5 pounds per day of PCBs. In January 1997, a ground water production well was installed on the shoreline upgradient from this seep in an effort to hydraulically control

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PCB discharges from the seep. This well produces significant quantities of PCB DNAPL and appears to have controlled discharges from the seep as PCB DNAPL has not been observed in the subaquatic collection system since the installation of the on-shore recovery well.

In addition to the activities to control riverbed PCB seeps and PCB movement from the Allen Mill, GE has conducted an intensive investigation and remedial program at the Hudson Falls plant site. DNAPL PCBs have been discovered in the fractured bedrock below the site. To date, over 3,000 gallons of oil have been removed from the subsurface. A series of 26 ground water pumping wells have been installed to create a hydraulic barrier between the site and the river, not only to collect PCB-containing ground water but also PCB-oil (GE, 1997). The effectiveness of this system in reducing PCB flux from the site to the river is being monitored by measuring PCB levels in the river, and through an assessment of the hydraulic capture zone created by the groundwater pumping system.

2.3 Upper Hudson River Water Column PCB Sources

Numerous upper Hudson River water column PCB sources have been identified and quantified using water column PCB data collected from four primary monitoring locations: the Route 27 Bridge, the Route 197 Bridge at Fort Edward, the western abutment at TID, and the Route 29 Bridge at Schuylerville (located approximately six miles downstream of the TIP).

2.3.1 Upstream of the plant sites

The background station at the Route 27 Bridge typically yields water column PCB concentrations of less than the method detection limit of 11 ng/l (ppt). While there are known PCB sources upstream of this sampling station, most notably Niagara Mohawk Power Corporation's

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Queensbury site, they do not appear to be significant sources of PCBs to the water column of the upper Hudson River. Water column PCBs at the Route 27 Bridge station are likely present at quantities between 1 and 11 ppt (USEPA, 1997).

2.3.2 Plant sites, Allen Mill, and remnant deposits

Potential external PCB sources between the Route 27 Bridge and the Route 197 Bridge in Fort Edward (Figure 2-1) include: the Hudson Falls capacitor site, the Allen Mill, the remnant deposits (including the site adjacent to the former Fort Edward Plant outfall area referred to as the 004 site) and the Fort Edward capacitor manufacturing site. The steep river bed grade in this reach of the river produces flow velocities that inhibit sediment deposition. Therefore, there are only limited areas of sediment accumulation in this portion of the river, and water column PCB loadings observed at the Fort Edward station generally reflect the activity of the external sources. This activity is illustrated in Figure 2-2 which presents the results of water column PCB measurements made at the Fort Edward station since the 1970s. Additionally, Figure 2-3 shows the PCB loading observed at this station during three spring high events in the 1990s. The following observations can be made from these data:

•PCBs have been present in samples collected from this station since the late-1970s,

•PCB levels declined between the late 1970s and late 1980s,

•PCB levels increased dramatically in September 1991 as a result of inputs from the Allen Mill,

•Remediation of Allen Mill and efforts to control PCB releases to the Hudson River reduced the large PCB loading observed during the 1991-1993 period, and

•PCB levels during the annual high flow period have declined in response to source control measures implemented at the mill and plant site.

These data indicate that a non-sediment PCB source has been active for many years. Even before the failure of the Allen Mill gate, a base load of PCB was entering the river, presumably from fractures in bedrock near the Hudson Falls site. Only recently has this base load of PCB been controlled. Although plant site sources still exist, it appears that remedial measures at the Hudson Falls plant site have reduced water column PCBs in this segment of the river to levels below those observed in the late-1980s. The current flux from the site is still being evaluated. Finally, these data indicate that the Allen Mill event, while transitory, represents the largest external PCB loading event, both in duration and magnitude, seen in this section of the river since the late-1970s.

2.3.3 Contaminated sediment deposits

The contaminated sediments within the upper Hudson River represent a source of PCBs to the water column. Within a given reach of the river, this source can be estimated as the difference in the product of PCB concentrations and flow between an upstream and downstream station². Figure 2-4 presents PCB loading between either Ft. Edward and Schuylerville (12 mile length of the river) or between Ft. Edward and TID (6 mile length of river). for the period 1980 to 1997. The earlier data (1980 to 1991) depicts loading over the longer reach (12 miles) and the later data (1991-1997) depicts loading over the TIP region only. Figure 2-5 presents the loading from the TIP alone between 1993-1997. These data indicate that:

•Through the 1980s, PCB loading from the contaminated sediments decreased from approximately 1 pound per day to approximately 0.25 pounds per day (although significant year-to-year variation is apparent);

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²This ignores any losses from the water column due to settling or volatilization which have been judged to be minor at low to moderate river flows.

•An increase in PCB loading, from approximately 0.25 pound per day to between 1 and 2 pounds per day occurred between 1989 and the early 1990s;

•The loading exhibits a seasonal pattern with the highest loading observed following the annual spring high flow period and the lowest loading observed in the winter;

•The PCB loading through the 1990s has not showed significant declines although the data contains significant year-to-year variations; and

•The lowest PCB loading since 1993 was observed in 1995, a year in which Spring flows were significantly lower than in other recent years.

While the decrease in PCB loading through the 1980s is consistent with natural recovery of the system through the burial of contaminated surface sediments with clean material, the cause of the apparent increase in loadings observed from this region of the river in 1991 is unclear. Several changes, both in the river monitoring program and the activity of external PCB sources occurred during this period. First, a monitoring station was added at the TID to assess PCB loadings directly from the TIP. Second, the PCB analysis scheme was changed from an Aroclor-based scheme that failed to detect the lowest chlorinated congeners to one that quantified the full spectrum of PCB congeners. Finally, over an approximately 18 month period beginning in 1991, the river experienced the largest external PCB loading since the late 1970s. Each of these changes may have exerted some influence on the observed PCB loadings from the TIP in the 1990s.

Estimates of PCB flux from TIP sediments, based on surface sediment conditions measured in the summer of 1991, cannot account for the PCB loadings observed from the TIP (HydroQual, 1995a)³. Possible causes for this apparent increase in PCB loading were presented in earlier reports and formed the basis for the data collection programs undertaken over the last few years (HydroQual,

³The TIP anomaly is defined as the excess PCB loading observed from the TIP since approximately 1992 that can not be accounted for by known PCB fate processes given the known PCB concentration of surficial sediments (HydroQual, 1995a).

et al., 1997a, 1997b, O'Brien & Gere 1997a, 1997b). The results of this work will be discussed in Section 4 of this report.

2.4 USEPA's Analysis of Water Column PCB Data

In association with the on-going RRI/FS of Hudson River PCBs, the USEPA issued a report in February 1997 that documented their interpretation of water column and sediment data collected in 1992 and 1993 (USEPA, 1997). The USEPA concluded that PCBs passing the TID during low flow conditions⁴ were the major source of PCBs to the freshwater Hudson. Additionally, the USEPA contended that sediments within "hot spot" areas of the TIP contribute the majority of PCBs passing the TID during low flow periods.

The USEPA's interpretation of the data did not recognize that the loading observed from the TIP could not be explained via known PCB fate and transport mechanisms given the level of PCBs within surface sediments (the TIP anomaly; GE, 1997). Moreover, the agency did not fully consider the temporal correspondence between the appearance of the excess loading, the upstream PCB loadings from the plant site areas, and the change in sampling and analytical methods. Based upon a qualitative assessment of the data, the agency offered three possible mechanisms for transfer of PCBs from the sediment to the water column:

1) sediment pore water diffusion of relatively undechlorinated PCBs partitioned from the particulate to the pore water phase,

2) groundwater-induced advective flux of sediment pore water PCBs within the TIP, and

3) resuspension of sediments contaminated with extensively dechlorinated PCBs deposited prior to 1984.

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⁴Less than 10,000 cfs at the USGS Fort Edward gauging station.

The USEPA did not conduct a quantitative mass balance evaluation to test these hypothesized mechanisms, but simply offered them as possible explanations for the observed loading from the TIP (USEPA, 1997). They deferred rigorous analysis of these mechanisms to the PCB fate and transport modeling phases of the project (USEPA, 1997).

The apparent impact of recent plant site loadings on PCB dynamics in the river, and the uncertainties expressed by the USEPA over mechanisms controlling such dynamics, underscores the need to develop a quantitative understanding of PCB origin, fate, and transport in the Hudson River system. It is only after such understanding is achieved that a technically defensible analysis of remedial alternatives for PCBs in Hudson River sediments can be developed. Recognizing this need, GE has conducted an extensive field research program and data analysis effort to identify and quantify the principal sources of PCBs in the system and the mechanisms controlling PCB fate and transport. Of particular concern was the anomalous PCB loading observed from the TIP.

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SECTION 3 QUANTITATIVE MODELING OF TIP SEDIMENT-WATER INTERACTIONS

To allow objective, quantitative evaluation of potential remedial measures in the Hudson River, GE has sponsored the development of state-of-the-science PCB fate, transport, and bioaccumulation models. This section describes the developmental state of these models, how well the model comports to existing data, and how model applications aided in the identification of the source of the PCB loading referred to as the TIP Anomaly.

3.1 Modeling Framework

A series of models have been developed to forecast changes in water column, sediment, and biota PCB levels in the upper Hudson River. Given initial sediment PCB concentrations and a time series of daily flows, total suspended solid (TSS), and PCB concentrations in the river at Fort Edward and each of the major tributaries, these models predict a time series of PCB concentrations in the water column, sediment, and biota. Four models are used: hydrodynamic, sediment transport, PCB fate, and PCB bioaccumulation (Figure 3-1). Sediment-water interactions of the TIP are driven by processes described in the hydrodynamic, sediment transport, and PCB fate models. Therefore, these models are the principal focus of this modeling discussion.

Hydrodynamics refers to the movement of water through the river and the friction or shear stress that this movement causes at the interface between the water and the sediment bed. A hydrodynamic model computes the velocity and depth of the river, as well as the shear stress at the sediment-water interface, in response to upstream flows and flows entering the river from tributaries. Sediment transport includes the movement of suspended and settled solids within the river and the settling and resuspension of solids that occurs at the sediment-water interface as a result of the shear caused by the moving water. A sediment transport model computes the concentration of solids in

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the water column and the rate at which sediment accumulates in the bed. PCB fate includes the transport of PCBs dissolved in the water or sorbed to solids, transfer between the dissolved and sorbed phases, transfer between the water and atmosphere, and degradation that occurs chemically or biochemically. A PCB fate model computes the concentrations of PCBs in the water column and sediment in general accordance with the equations presented in Appendix A.

The models are equations developed from the basic principles of conservation of mass, energy and momentum from laboratory and field studies of individual phenomena (§ A.1). The equations are general and can be applied to any river system. The application of the equations to a specific system such as the upper Hudson River involves the determination of appropriate values for each of the parameters in the equations. Site-specific data are the basis for assigning values, either directly or by the process of model calibration. Each of the models was calibrated and validated using a data record that extends from 1976 to the present. The extensive database that is available makes the Hudson River uniquely suited for the application of these models.

Two hydrodynamic models have been developed and calibrated and validated in order to provide the necessary hydrodynamic input for the sediment transport and PCB fate models. A twodimensional, vertically-integrated hydrodynamic model is needed to define the distribution of shear stresses at the sediment-water interface that controls sediment transport. By contrast, a onedimensional hydrodynamic model is sufficient to define the average transport of PCBs within the water column. The one-dimensional model is also more computationally efficient and was therefore used to drive long-term PCB fate simulations.

The sediment transport model uses the results of laboratory and field studies to describe the resuspension and deposition processes of cohesive and non-cohesive sediments. The model described here does not consider the resuspension of non-cohesive sediments. This process is

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included in ongoing modeling work. Results of the sediment transport model in the form of resuspension and deposition fluxes are used directly by the PCB fate model.

The PCB fate model includes mechanistic descriptions of the transport, transfer and reaction processes occurring in the river as described in § A.1 and presented in Figure 3-1. PCBs are assumed to partition between dissolved and particulate phases, with partitioning assumed to be rapid, such that equilibrium conditions are generally well approximated. The dissolved phase is composed of freely dissolved PCBs and PCBs sorbed to dissolved and colloidal organic matter. Freely dissolved PCBs are transferred from the water column to the atmosphere by volatilization across the air-water interface. Particulate-phase PCBs settle from the water column to the sediment bed, and are resuspended from the sediment bed into the water column. Dissolved PCBs are exchanged between the water column and sediment bed in accordance with the laws of diffusion, that is, from a region of higher concentration to one of lesser concentration, with the rate of transfer controlled by a mass transfer coefficient.

3.2 Model Calibration

3.2.1 Hydrodynamics

Applying the one- and two-dimensional hydrodynamic models to the upper Hudson River requires that the river be divided into discrete segments or grid elements. The eight dams on the river make it necessary to construct a separate grid system for each reach. The eight distinct hydrodynamic models, one for each reach, are linked together by running the system from Reach 8 (TIP) downstream to Reach 1. The downstream output of one reach provides the inlet boundary condition information for the adjacent downstream reach. The two-dimensional grid for the TIP is shown in Figure 3-2. While the two-dimensional model utilizes a variable, curvilinear grid, the one-

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dimensional model uses a constant grid spacing of 762 m (2,500 ft). Both models extend from Rogers Island at Fort Edward to the Troy Dam.

The hydrodynamic models were calibrated and validated using two sets of data. The first data set consists of water surface elevations measured at two locations in Reaches 1 to 7 and three locations in Reach 8 on November 28 and 29, 1990 (O'Brien & Gere, 1991). The mean flow rate at Fort Edward during this period was 7,860 cfs, with a maximum variation of less than 2 percent. One measurement was taken at the dam and the other was measured at an upstream location. Model calibration in each reach was conducted by fixing the dam stage height to the measured value and then adjusting model parameters until good agreement was achieved between the predicted and measured stage heights at the upstream location. In the one-dimensional model, Manning's coefficient (n) was the adjustable parameter; in the initial two-dimensional model the horizontal eddy viscosity (A_H) was the calibration variable and bottom friction coefficient (c_f) was assumed to have a constant value of 0.0025 in all reaches. The results of the calibration exercise demonstrated that, for a given flow rate, water surface elevation can be predicted with average errors of 8 and 1 percent for the one- and two-dimensional models, respectively. The two-dimensional model has been recalibrated using a variable friction coefficient related to sediment type.

Both models were validated using a second set of data consisting of stage height measurements collected in the TIP during the May 1983 flood. This flood had a peak flow at Fort Edward of 34,100 cfs, which corresponds to a recurrence interval of approximately 10 years. The stage heights were measured by NYSDOT personnel at staff gages 118 and 119 on the Hudson River/Champlain Canal. These staff gages approximately correspond to river stage heights at river miles 190.0 and 193.7. Values of the calibration parameters (i.e., n and A_H) were not changed during the model validation, the results of which are shown on Figures 3-3 and 3-4 for the one-dimensional and two-dimensional models, respectively.

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3.2.2 Sediment transport

The sediment transport model used the same grid as the two-dimensional hydrodynamic model to describe the upper Hudson River. The particle size distribution of suspended solids was approximated as two particle size classes in the model. Class 1 represents cohesive sediments (i.e., clays and silts with particle diameters of less than $62 \mu m$) while Class 2 is composed of coarser, non-cohesive sediments, primarily fine sands with diameters between 62 and $250 \mu m$. The deposition rate of the Class 1 particles was a function of shear stress and particle concentration. The deposition rate of the Class 2 particles was the product of particle concentration and an assumed settling velocity. Erosion potential parameters were determined from upper Hudson River data on the relationship between mass of resuspended sediment per unit of surface area and applied shear stress (HydroQual, 1995b).

The sediment transport model was calibrated using suspended solids data from the April 1982 flood. This flood had a peak flow rate of 27,700 cfs at Fort Edward, which corresponds to a return period of three to four years. The settling velocity of Class 2 sediments was set at 24 mm s⁻¹, which corresponds to a particle diameter of 200 μ m, and the tributary sediment loads were assumed to be composed of 35 percent Class 1 and 65 percent Class 2 sediments. Comparisons of predicted and observed TSS at Schuylerville, Stillwater, and Waterford for the April 1982 flood are presented in Figure 3-5. Predicted TSS concentrations at Schuylerville and Stillwater are in close agreement with measured values. However, the model under predicts TSS concentrations at Waterford during the peak of the flood. This under prediction is likely due to an underestimation of solids loading from the Hoosic River. More recent calibrations of the sediment transport model using new tributary solids loading data confirm this assessment of the preliminary model calibration presented in Figure 3-5.

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The calibrated sediment transport model was used to generate a relationship between the mass of sediment resuspended and flow rate for each of the eight reaches from Fort Edward to the Troy Dam. These relationships were then used in the PCB fate model to determine erosion rate in each model segment for a specified flow rate. In a similar manner, a relationship between the effective settling velocity and flow rate was developed from results of the sediment transport model.

3.2.3 PCB fate

The one-dimensional hydrodynamic model grid was used to model PCB fate. Daily values for river flow and water depth for the period from 1977 to 1996 were obtained from the hydrodynamic model. Rates of resuspension and deposition were obtained from the sediment transport model.

The sorption partition coefficient was determined from an analysis of dissolved and particulate PCB measurements taken by the USEPA as part of the Phase 2 field data collection program (USEPA, 1997). A 20°C value of 40,000 L kg⁻¹ dry sediment was used in the model. This value corresponds to an organic carbon normalized partition coefficient (K_{oc}) of 10^{5.4} L kg⁻¹ organic carbon.

Dissolved organic carbon in sediment pore water was included as a competitive sorptive phase. The partition coefficient for DOC was fixed at 10 percent of K_{oc} , based on an analysis of 1991 field data (O'Brien & Gere, 1993b).

The volatilization rate constant was calculated from two film theory using a Henry's Law constant of $3x10^{-4}$ atm-m³ mol⁻¹, a liquid film mass transfer coefficient calculated using the

O'Connor-Dobbins reaeration equation and a gas film mass transfer coefficient fixed at 100 m day⁻¹ (Equation A-8).

The vertical diffusion of PCBs between the pore waters of adjacent sediment segments was modeled using a diffusion coefficient of 1 cm² day⁻¹. A temperature dependent mass transfer coefficient with a value at 20°C of 2 cm day⁻¹ was used to model the exchange of PCBs between the pore water and the water column (Equation A-15).

Two external sources of PCBs were considered in the model. First, PCBs entering from upstream prior to 1991 were estimated from a correlation of PCB concentration with flow at Fort Edward based upon USGS data. Daily flows assigned at the upstream boundary were used to evaluate the associated PCB concentration, except on days when data were available; then the actual measured values were used. The correlation was modified over time to reflect the decrease in upstream PCB levels. From 1991 through 1996, the monitoring data at Fort Edward were used directly to define the upstream boundary concentration (Figure 2-2).

The second external PCB source was an empirically defined, exponentially decreasing load that was added to the TIP in the period between 1977 and 1983. The source of these PCBs has not been determined, but may have been related to leaching from dredge spoils deposited along the shoreline or a consequence of dredging activities.

Model calibration results for the March 1977 through September 1996 period are shown in Figures 3-6 through 3-9. Figure 3-6 compares temporal profiles of calculated and observed surface sediment (0-5 cm) PCB concentrations in TIP and downstream in the vicinity of Schuylerville, Stillwater, and Waterford. The declines in concentration between 1977 and 1991 that are predicted by the model are in general agreement with the observed declines. The model predicts a slightly

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greater decline in the TIP than the data (68% versus 60%). The model also underestimates the average concentration measured in 1984. This underestimation may be due to a sampling bias because the 1984 sampling program targeted areas of higher concentration. The methods used to average the data are currently under review to determine if alternate averaging methods should be employed.

Figure 3-7 compares the annual PCB load passing Waterford that has been estimated from the USGS PCB data with that computed by the model. The model picks up the overall trend in the data, as well as the year-to-year variations due to variations in river flow and associated resuspension.

Since the calibration of this model, an analytical bias has been identified in the water column PCB data appearing in Figure 3-7 (Tetra-Tech, 1997; HydroQual, 1998). This bias is associated with the analytical methods employed by the USGS. A preliminary analysis of the survey's laboratory records suggests that the historical water column data are biased low as the technique does not account for the entire compliment of mono- and dichlorinated PCBs within the samples (HydroQual, 1998). Preliminary estimates suggest the bias ranges from 10 - 40 percent and depends on the relative proportion of mono- and dichlorinated PCBs in the samples. Since, mono- and dichlorinated PCBs account for a significant portion of the total water column PCB loading occurring across the TIP, additional efforts are underway to more fully characterize this bias, and possibly correct a portion of the USGS database. Considering these limitations of the data, the absolute water column concentrations predicted by the model are of less importance than the model predicted change in water column levels over the 15 year monitoring period. The model accurately predicts the factor of five decline in measured water column PCB levels between 1976 and 1991.

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From 1991 to 1996, the data for calibration are largely restricted to the results of weekly monitoring of the water column at TID; although limited data are available from Schuylerville⁵. The comparison of the model to these data is less favorable than to the historical USGS water column data, even considering the bias in the USGS data. Figure 3-8 compares computed and observed water column PCB levels at Schuylerville for the period from 1989 through 1991. The model and data closely correspond in 1989, but the model underpredicts the observed levels in 1991. The comparison at TID for 1993 through 1996 demonstrates a consistent low bias by the model (Figure 3-9). The computed concentrations at TID are 300 to 500 percent lower than those measured. In contrast, the preliminary analysis of the bias in the USGS data appears to be less than 50 percent. Therefore, it is unlikely that the differences observed between model predictions and monitoring data can be solely attributed to the bias in the USGS data.

This difference between model projections and observed data was unexpected given the favorable comparison of model predictions to the data from 1977 to 1991, even considering the potential bias in the USGS data. Efforts to alter the model calibration to achieve water column levels consistent with the TID data were unsuccessful. No combination of reasonable rates of sediment-water interaction were able to reproduce both the long-term trends in sediment PCB levels and the TID water column PCB levels.

3.2.4 Summary of preliminary PCB fate and transport modeling

State-of-the-science hydrodynamic, sediment transport, and chemical fate models were developed to describe the PCB dynamics within the Hudson River system and to provide a means

⁵ Limited additional data collected by GE in 1991 and 1992 and the USEPA in 1993 are available for stations located downstream of the TID.

of predicting PCB concentrations in the different media into the future. The favorable comparison of the model predictions to observed field data between the late 1970s and 1991 indicated that the models provided a consistent and accurate assessment of the mechanisms controlling PCB fate in the system over this period. The degradation of the model calibration to water column data collected after 1991 suggested that the models did not accurately account for the varied sources and processes affecting PCB dynamics within the TIP region of the river. Another PCB source(s), loading mechanism(s), or data inadequacy(s), not accurately represented by the models, was controlling PCB loading observed from the TIP region of the river.

A number of hypotheses were developed to explain these observations and were tested through a rigorous analysis of existing field data and the development and execution of a field research program (HydroQual, 1996, 1997a, 1997b, O'Brien & Gere, 1995, 1997b). These efforts are describe in Section 4.

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SECTION 4 EVALUATION OF ALTERNATIVE HYPOTHESES FOR ANOMALOUS PCB LOADING WITHIN TIP

During 1996 and 1997, GE conducted an extensive field research program and data analysis effort to evaluate different hypotheses for the anomalous PCB loading observed within the TIP. As described in Section 3, known and understood PCB fate and transport mechanisms could not account for the entire loading observed from the TIP region of the river. An alternative PCB source, loading mechanism, or data inadequacy was required to account for this anomalous loading. The hypotheses considered to explain the loading anomaly fell into three general categories:

• additional mechanism of PCB exchange between sediments and water column,

- additional PCB sources, and
- erroneous estimates of PCB flux due to biased sampling.

The USEPA advanced the hypothesis of alternative mechanisms for PCB exchange between sediments and the water column in their Data Evaluation and Interpretation Report (DEIR; USEPA, 1997) and Preliminary Model Calibration Report (PMCR; USEPA, 1996) developed as part of their ongoing RRI/FS. In the DEIR, the USEPA hypothesized that either groundwater induced advective flux or resuspension of dechlorinated sediments in addition to diffusive flux mechanisms may account for the loading observed at TID. During preliminary model calibration, the USEPA invoked all of these mechanisms to transport PCBs from surface sediments into the overlying water column to account for the TID loading. Data analysis conducted by GE and documented in formal comments on these reports does not support these mechanisms as possible explanations for the observed anomalous loading (GE, 1997). GE undertook a field research program designed to evaluate the plausibility that these mechanisms can contribute significantly to the observed loading from the TIP.

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The hypothesis that additional PCB sources may have been introduced into the TIP and were responsible for the anomalous loading was considered in light of recent PCB DNAPL loadings to the river. DNAPL PCBs within fractured bedrock underlying the GE Hudson Falls Plant site (O'Brien & Gere, 1996a) is believed to have migrated through bed rock fractures and accumulated in waterways within the 150 year old Allen Mill (O'Brien & Gere, 1994a). Collapse of a wooden gate structure within the mill is believed to have resulted in the transport of PCB DNAPL into the Hudson River during September 1991 and until flow through the waterways was controlled in January 1993 (O'Brien & Gere, 1994a). Although these sources were controlled by remedial measures (O'Brien & Gere, 1996a), PCB DNAPL from the plant site continued to enter the river directly through fractures in the river bed until remedial measures on the plant site mitigated these sources. The temporal correspondence of the mill loadings and the increase in PCB loadings from the TIP suggested the mill loadings as the causative factor. For this hypothesis to be true, PCBs must have passed the Fort Edward sampling station (Figure 2-1) undetected and then been deposited within the pool. This could occur if PCBs enter the river between sampling events or are transported as part of the bed load passing under sampling devices. PCB DNAPL transport was evaluated in a field research program sponsored by GE (HydroQual, 1997c).

The hypothesis that biased sampling may have resulted in erroneous estimates of PCB flux into or out of the TIP was considered as a possible cause of the TIP anomaly. For this hypothesis to be true, PCBs must have either; 1) entered the headwaters of the TIP undetected by the routine water column monitoring program and, following transport through the TIP, been detected within samples collected at the sampling station downstream of the TIP at TID, or 2) been unrepresentatively elevated within samples collected from the shore-based station located at TID. Data from limited sampling conducted during the early 1990s from the eastern and western shore areas at TID were in general agreement, supporting the representativeness of the western shore-based sampling location (O'Brien and Gere, 1996c). This hypothesis was further tested during extensive

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field efforts conducted in 1996 and 1997 and appears to be the principal cause of the anomalous loadings.

The results of specific field research programs and data analysis efforts evaluating these different hypotheses for the observed anomaly are presented below.

4.1 Additional Mechanism of PCB Exchange Between Sediments and Water Column

The hypothesis that additional mechanisms of PCB exchange between the sediments and the overlying water column were responsible for the anomalous loading was evaluated through an intensive data evaluation effort as well as field research. The effect of long-term elevated PCB flux from the sediments either as a result of surface sediment erosion or ground water advection, was assessed within a mass balance framework. The results of these analyses were presented in comments to the USEPA on their DEIR (GE, 1997). Additionally, in-field groundwater advection measurements were made and the resulting groundwater velocities were compared to those required to sustain the anomalous loading as presented in the USEPA PMCR (1996). Moreover, low flow water column TSS measurements were made through the TIP to assess the possibility that sediment resuspension may be contributing to the observed loading under low flow conditions. Finally, quantitative sediment transport modeling, based on state-of-the-science cohesive sediment transport theory, was conducted to estimate low-flow sediment resuspension and test the plausibility that this mechanism is contributing to the TIP anomaly.

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4.1.1 Effect of long-term high flux on sediment PCB inventory

A mass balance calculation was performed to test the hypothesis that the anomalous PCB loading could be attributed to surface sediment PCB transport processes, either surface sediment resuspension or ground water advection. In this calculation, the net increase in PCBs between Rogers Island and the TID was assumed to originate from PCBs in the surface sediments of the TIP, defined conservatively as 0-8 cm. No vertical mixing was assumed between surface sediments and deeper sediments. The inventory or mass of PCB homologs within the surface sediments ($M_{j,ss}$) was estimated using the results of USEPA's reanalysis of the 1984 sediment data (USEPA, 1997) as follows:

$$M_{i,ss} = C_{i,ss} \rho_{ss} z_{ss} A_{tip}$$
(4-1)

where:

 $C_{j,ss}$ is the average concentration of PCB homolog j within the surficial sediments (0-8 cm) as calculated from 1984 data (M M⁻¹),

 ρ_{ss} is the density of surface sediments (M L⁻³),

 z_{ss} is the depth of the surface layer (L), and

 A_{tip} is the surface area of the TIP (L²).

The surface sediment area of the TIP $(2.0 \times 10^6 \text{ m}^2)$ and the density of surface sediments (0.77 g cm^{-3}) were developed from information provided by the USEPA (USEPA, 1997). Annual total loadings of PCB homologs (j) across the TIP ($W_{tip,j}$) were calculated using measured annual paired loadings from Rogers Island and the TID from 1993 to 1996 (O'Brien & Gere, 1994b, 1995, 1996b, 1997c) in accordance with the following expression:

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$$W_{tip, j} = \frac{\sum_{i=1}^{n} Q_{fe, i} * (C_{tid, i, j} - C_{ri, i, j})}{n} \times 365$$
(4-2)

where:

 $Q_{fe,i}$ is the daily average flow at the USGS Fort Edward gauging station for day i (L³ T⁻¹), $C_{tid,i,j}$ is the concentration of PCB homolog j on day i at the TID station (M L⁻³),

 $C_{ri,ij}$ is the concentration of PCB homolog j on day i at the Rogers Island station (M L⁻³), and

n

is the number of paired samples collected at the Rogers Island and TID stations for the year in question.

The calculated average annual total PCB loadings across the TIP, calculated as the sum of homolog loadings, are presented in Table 4-1. The average annual load ranged from a low of 84 kg yr⁻¹ in 1995 to a high of 407 kg yr⁻¹ in 1996. The four year average loading is 248 kg yr⁻¹.

Table 4-	1. Average	Annual T	Total PCB	Loading	Across T	IP from	1993 to 1	1996.

Year	No. of Paired Samples	Average PCB Load		
		(kg yr ⁻¹)		
1993	49	202		
1994	34	297		
1995	45	84		
1996	57	407		
Average	46	248		

The depletion of 1984 surface sediment PCBs was estimated simply by dividing the estimated 1984 surface sediment mass of PCB homologs by the annual flux rate as calculated above using paired Rogers Island and TID data and projecting into the future. The year in which the surface sediments would become depleted of homolog j (Yr_i) was calculated as follows:

$$Yr_{j} = \frac{M_{j, ss}}{W_{j, tip}} + 1984$$
(4-3)

The results are presented in Table 4-2 below⁶.

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⁶This calculation is conservative since historical flux rates were likely greater than those measured in the 1990s because the higher surface sediment PCB concentrations in the 1980s would have resulted in higher flux rates than those observed in the 1990s.

Homolog	Mass of PCBs in TIP Surface Sediments in 1984 ¹ (MT)	Load from TIP (MT yr ⁻¹)	Year in Which Surface Sediment Reservoir Depleted
Mono	0.58	0.055	1995
Di	1.40	0.117	1996
Tri	1.00	0.062	2000
Tetra	0.41	0.016	2009
Penta	0.13	0.002	2040
Total	3.52	0.25	-

 Table 4-2.
 Surface Sediment PCB Inventory Depletion Under Average 1993-1996 TIP PCB loadings.

1) The mass of PCB homologs was calculated by multiplying the average PCB homolog distribution of the 1994 low resolution cores (USEPA, 1995) and the estimates of TIP PCB mass obtained by statistical analysis of the 1984 NYSDEC data (USEPA, 1997).

This mass balance calculation indicates that, if surface sediments of the TIP were the sole source of PCBs contributing to the apparent loading increase observed over the TIP, then the mono, di, and tri homologs present within the surficial sediments in 1984 would be entirely depleted by the year 2000. This is particularly significant since the current water column measurements show a continuing source of mono- and dichlorinated PCBs from the TIP. Moreover, sediment sampling by both GE in 1991 (O'Brien & Gere, 1993b) and the USEPA in 1992 (USEPA, 1997) and 1994 (USEPA, 1995) indicate that significant reserves of PCB remain within the surface sediments of the TIP. Therefore, on a mass balance basis, the PCB loadings observed from the TIP between 1993 and 1996 cannot be representative of long-term surface sediment-water exchange processes. Another source of PCBs, possibly related to upstream sources, or data inadequacies as discussed below must be contributing to the observed loading from the TIP in the 1990s.

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4.1.2 Measurement of ground water seepage rates

Direct field measurements of ground water seepage rates provided data with which to evaluate the hypothesis that ground water advection may be responsible for the anomalous PCB load detected in the TIP. This effort was prompted by the USEPA's invocation of a groundwater mechanism in the PMCR to account for the anomalous PCB loadings (USEPA, 1996). The mechanism of groundwater advection of PCBs from the sediments to the water column is described in detail in Appendix A, and a complete description of the groundwater investigation is documented elsewhere (HSI GeoTrans, 1997).

Direct measurement of groundwater seepage has been widely employed as a means of assessing the hydraulic and chemical interactions between groundwater and surface water, and to examine spatial and temporal patterns of groundwater seepage (Lee, 1977; Lee and Cherry, 1978; and Woessner and Sullivan, 1984; Gallagher et al., 1996). The seepage meters employed to monitor groundwater seepage within the Hudson River were modeled after the original design by Lee (1977), with modifications to reduce the potential for measurement biases that have been documented in the literature (e.g., Belanger and Montgomery, 1992, Shaw and Prepas, 1989). Seepage meters consisted of a cylindrical stainless steel vessel equipped with two ¼ inch Teflon bulkhead fittings, a Teflon air sampling bag equipped with a release valve, and ¼ inch Teflon tubing (HydroQual, 1997b; Figure 4-1). Two seepage meters were deployed at each of the six locations depicted in Figure 4-2. Measurements were taken at multiple sites within the TIP and one downstream site to allow delineation of spatial trends in groundwater seepage rates. Multiple seepage rate measurements were conducted over approximately a one month period between late May and late June 1997. This period was immediately after the annual spring high flows and snow melt, when hydraulic gradients between the groundwater system and the river were expected to be at their greatest.

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The seepage meter study produced pronounced temporal and spatial patterns in groundwater seepage (HSI GeoTrans, 1997). Average seepage rates declined over the monitoring period from a high of 0.18 L m² hr⁻¹ in late May to a low of -0.03 L m² hr⁻¹ in mid June (Figure 4-3). A decreasing temporal trend occurred in measurements collected within the headwaters of the TIP at Site S1 (Figure 4-2). This observation is consistent with the reduction in hydraulic gradient observed in piezometers installed adjacent to the seepage meters (HSI GeoTrans, 1997) and that expected in response to seasonal changes in surface water and groundwater elevations.

Within the TIP, ground water seepage increased with distance upstream of the TID (Figure 4-4). This is expected since the hydraulic gradients near the TID would be affected by the artificial increase in surface water elevation produced by the dam. Seepage measurements were generally positive (flux of groundwater into the Hudson River) at sites S1 through S3 (Figure 4-4) located 3-5 miles upstream of the TID (Figure 4-2). In contrast, groundwater flow was consistently negative at site S5 (Figure 4-4) located just one mile upstream of the TID (Figure 4-2).

The groundwater seepage investigation produced temporal and spatial patterns in groundwater seepage that were consistent with both independent measurements of hydraulic gradients between the surface water and groundwater systems and our understanding of the Hudson River system. Piezometers installed adjacent to the seepage meters generally yielded hydraulic gradients indicative of water movement in the same direction measured within the seepage meters (HSI GeoTrans, 1997). Moreover, spatial and temporal patterns in groundwater seepage were consistent with those expected in response to both seasonal changes in surface water and groundwater elevation and the artificially elevated surface water condition at the downstream limit of the TIP as a consequence of the TID. However, the ground water seepage rates were, on average, approximately an order of magnitude lower than the value assumed during preliminary calibration of the USEPA PCB fate and transport model ($1.3 \text{ Lm}^{-2} \text{ hr}^{-1}$; USEPA, 1996; Figures 4-3 and 4-4).

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Ground water induced PCB flux from the sediments to the water column of the TIP were estimated as the product of groundwater seepage flow developed from the ground water seepage measurements and estimates of sediment pore water PCB concentrations in accordance with Equation A-19. The total groundwater flow was estimated as the product of the average volumetric seepage flux and the total area of the TIP. The mean surficial sediment pore water PCB concentration was calculated from the 0-5 cm section of sediment cores collected in 1991 based upon equilibrium partitioning concepts described in Equations A-13 and A-14. The organic carbon-based PCB partition coefficient was calculated using USEPA water column partitioning data (USEPA, 1997) and corrected for temperature using temperature correction functions (GE, 1997). The pore water dissolved organic carbon concentration was calculated as the mean surficial sediment (0-5 cm) TIP dissolved organic carbon measurements from the 1991 sediment survey (O'Brien & Gere, 1993b), and the equilibrium constant describing partitioning between freely dissolved PCBs and PCBs adsorbed to dissolved organic carbon was assumed equal to 0.1 K_{ee}.

Applying the parameter values in Table 4-3 to Equations A-13, A-14 and A-19 yielded groundwater induced PCB flux measurements of approximately 30 g day⁻¹. Assuming these seepage measurements represent an average seepage flux for the entire year, groundwater induced PCB loading contributes an estimated 11 kg yr⁻¹ of PCBs to the water column. This represents approximately 4% of the average PCB loading observed from the TIP between 1993 and 1996 (Table 4-2). These estimates are conservatively high due to the assumption that the spring 1997 measurements are representative of groundwater flux for the entire year, even though they were collected during a period in which the hydraulic gradient between surface water and ground water was expected to be at its greatest. Based on these measurements and calculations, groundwater induced PCB flux cannot account for the anomalous loading observed from the TIP.

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 Table 4-3. Parameters Used to Calculate Groundwater Induced Advection of PCBs from

 Surface Sediments to the Water Column.

Parameter	Description	Value (units)
K _{oc}	organic carbon-based PCB partition coefficient	10 ^{5.4} (L kg ⁻¹)
K _{doc}	dissolved organic carbon PCB partition coefficient	10 ^{4.4} (L kg ⁻¹)
C_s/f_{oc}	organic carbon normalized surficial sediment (0-5 cm) PCB concentration	2110 (mg kg oc ⁻¹)
m _{doc}	pore water dissolved organic carbon concentration	33.7 (mg L ⁻¹)
Q _{avg}	average measured ground water seepage rates	0.04 (L m ⁻² hr ⁻¹)
A _{tip}	area of the TIP	$2.0 \times 10^6 (\mathrm{m}^2)$

4.1.3 Estimates of low to moderate flow sediment bed resuspension

The hypothesis that low to moderate flow sediment resuspension may be contributing to the observed PCB loading from the TIP was assessed using the calibrated hydrodynamic and sediment transport model described in Section 3. The approach included the following:

• calculation of the total mass of sediment resuspended at different flow rates as the sum of the mass of sediment eroded from the different hydrodynamic/sediment transport model grid elements, and

• calculation of PCB resuspension at different flow rates as the product of the mass of sediment resuspended and surficial sediment PCB concentrations calculated as the area-

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weighted average of the 0-5 cm sections collected in 1991 (21.8 mg/kg; O'Brien & Gere, 1993b).

Additionally, field measurements of TSS through the TIP during the elevated loading period were collected and analyzed to test the predictions of the sediment transport model.

At flow rates less than 10,000 cfs, sediment, and consequently PCB, resuspension is minimal (Table 4-4 and Figure 4-5). At the average annual river flow rate of approximately 5,000 cfs at Fort Edward, the estimated mass of sediment erosion is approximately 6 kg⁷. Using the average 0-5 cm PCB data collected in 1991 (O'Brien & Gere, 1993b), this corresponds to an estimated PCB erosion of only 0.12 grams. It is only after river flow rates approach 10,000 cfs that sediment bed erosion significantly contributes to water column PCB loading. This is consistent with our understanding of sediment erosion processes, which predict no resuspension at bottom shear stresses less than the critical shear stress as described in § A.2.2.

The critical shear stress established for the cohesive sediments of the TIP is 1 dyne cm⁻² (HydroQual, 1995b). The lack of significant bed erosion at flows less than 10,000 cfs indicates that there are only limited areas within the TIP where shear stresses exceed 1 dyne cm⁻² at these flows. This is reflected in the data presented in Table 4-4. At 5000 cfs, less than 0.5% of the cohesive sediment bed area within the TIP is subject to sheer stresses greater than 1 dyne cm⁻². This increases to approximately 1% at flows of 10,000 to 20,000 cfs (Table 4-4). Moreover, negligible resuspension from the non-cohesive sediment bed occurs at flow rates below 10,000 cfs; the non-cohesive bed is not mobilized and fine sands cannot be resuspended because of bed armoring effects caused by coarse sands and gravels.

⁷Sediment bed erosion is not represented as a rate (M T^1) since erosion occurs instantaneously (see Appendix A).

River Flow ¹ (cfs)	Cohesive Bed Eroded ² (%)	Mass of Sediment Eroded ³ (kg)	Mass of PCBs Eroded ⁴ (g)
2500	.05	1.09e-03	2.37e-05
5000	.32	5.92e+00	1.29e-01
6000	.75	1.64e+02	3.57e+00
7000	.80	1.78e+02	3.88e+00
8000	.84	3.25e+02	7.08e+00
9000	.87	4.92e+02	1.07e+01
10000	.89	1.32e+03	2.88e+01
15000	.95	1.32e+04	2.88e+02
20000	.96	5.61e+04	1.22e+03

Table 4-4. Estimates of TIP Sediment and PCB Erosion as a Function of River Flow.

1) Flow at the headwaters of the TIP at Fort Edward, N.Y.

2) Percent of TIP sediment surface area subject to erosion under different river flows as calculated using the hydrodynamic and sediment transport model described in Section 3.

3) Mass of sediment eroded under the different flow conditions as calculated using the hydrodynamic and sediment transport model described in Section 3.

4) Estimates of PCB erosion calculated by multiplying the mass of sediment eroded by the 1991 area-weighted mean surface sediment (0-5 cm) PCB concentration within the TIP (21.8 mg/kg; O'Brien & Gere, 1993b).

The lack of significant sediment bed erosion at low to moderate river flows was also observed in field studies conducted on the river in 1996 and 1997 (O'Brien & Gere, 1998). Time of travel surveys, consisting of sampling at stations located along lateral transects established every 0.25 to 0.5 miles between Rogers Island and TID (Figure 4-6), yielded TSS concentrations that were

generally less than 5 mg L^{-1} and did not produce patterns indicative of sediment bed erosion (Figure 4-7). During these studies, water column samples were collected from upstream to downstream so as to correspond with the flow of river water as it traversed the TIP and should have detected regions of the river subject to erosive conditions at the sampled flows.

The hypothesis that low flow sediment resuspension is contributing to the TIP anomaly can not be supported by sediment fate and transport theory or field data. The application of state-of-thescience hydrodynamic and sediment transport models predicts insignificant sediment bed erosion under the low to moderate flow conditions under which the TIP anomaly has been observed. Field measurements of TSS support these predictions. Therefore, the USEPA hypothesized mechanism of low-flow sediment resuspension cannot explain the TIP anomaly.

4.2 Additional PCB Sources

The second general hypothesis to explain the anomalous TIP PCB loading considers the possibility that additional PCB DNAPL loadings from the Allen Mill and Hudson Falls Plant site are entering or have entered the TIP without being detected at the Rogers Island sampling stations. Potential DNAPL loading mechanisms include:

• preferential transport of PCB laden sediments and PCB DNAPL along the sediment-water interface,

• pulse loading of PCBs associated with the periodic flooding of the Bakers Falls plunge pool as a result of the operation of the Adirondack Hydro Development Corporation's (AHDC) turbines or during elevated flow events, and

• transport of oil-soaked sediment into the TIP at the time of the Allen Mill collapse.

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These hypothesized PCB sources were the subject of an extensive field research program sponsored by GE in 1996 and 1997.

4.2.1 Simulation of PCB oil transport

The hypothesis that PCB DNAPL loadings may be transported from the plant site areas into the TIP was examined in a field research program that simulated the fate of PCB DNAPL in the river. The program included the direct discharge of a conservative tracer with properties similar to PCB DNAPL into the river near Hudson Falls and tracking of the tracer downstream. The details of this study have been documented elsewhere (HydroQual, 1997c). In summary, the study included:

• injection of 20 pounds of fluorescent particles (Figure 4-8) with a density similar to that of Aroclor 1242 into the river from the AHDC Hydroelectric Plant,

• collection of daily composites of water column and bed load particle samples in specially designed sampling devices (Figure 4-9) at or near routine water column monitoring stations for three days following fluorescent particle injection,

• analysis of water column and bed load particle samples for fluorescent resin particle concentration,

• calculation of the total mass of fluorescent particles passing each station over the three day period by scaling up the mass of particles trapped within the sampling devices to reflect the entire river cross section, and

• development of fluorescent particle mass balances to evaluate particle transport and, by inference, the transport of PCB DNAPL within the Hudson River.

The results of the three day fluorescent particle mass balance appear in Figure 4-10. Of the 9.1 kg of particles injected into the river near the Hudson Falls Plant site (RM 196.9), an estimated 73% (6.6 kg) was transported downstream to the Fort Edward station (RM 194.4). These

calculations suggest that an estimated 27% (2.5 kg) of the fluorescent particle mass released into the river was retained between the particle injection point and the Fort Edward station. This pattern of particle retention continued downstream, as approximately 18% of that injected (1.6 kg) was retained within the river between the Fort Edward and Rogers Island sampling stations. Over the three day study, only an estimated 2% (0.1 kg) of the particles were transported downstream of the Thompson Island station (Figure 4-10). These data indicate that 98% of the particles injected in the river near the Hudson Falls plant site were retained in the river upstream of Thomson Island.

Fluorescent particles retained upstream of the Fort Edward station consisted predominantly of the smallest particle size class (19-38 μ m) and the two size classes greater than 190 μ m (Figure 4-11c). This distribution was calculated as the difference between the mass of particles injected (Figure 4-11a) and the mass of particles passing the Fort Edward station (Figure 4-11b), on a size class basis. The apparent retention of the smaller particles between the injection point and the Fort Edward station may be the combined result of: 1) under sampling of smaller particles by the 100 μ m mesh of the *in situ* filtration devices and, 2) loss of particles near the injection point. The larger particles retained upstream of the Fort Edward station likely settled within the river near the injection point as they were never detected downstream.

Several inferences with regard to the transport and fate of PCB DNAPL within the Hudson River may be drawn from the fluorescent particle data. First, PCB DNAPL droplets in excess of 190 μ m will likely be sequestered near the discharge point where they would be subject to dissolution. Mobilization of these droplets downstream may be limited at flows less than the 7000 cfs observed during this study, but may occur under higher flow conditions. Such temporary storage is demonstrated by the presence of fluorescent particles in sediment bed load samples collected during the spring high flow event of April 1997 (HydroQual, 1997c). Second, PCB DNAPL existing in the river over the particle size range tested (19-380 μ m) would be deposited upstream of

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the TID. That is, little, if any DNAPL would be transported downstream of the TIP. Once within these sediments, DNAPL would be subject to other fate determining processes such as dissolution, diffusion, advection, and partitioning onto sediment solids.

The PCB DNAPL transport study provides a unique data set from which to infer the fate of PCB DNAPL loadings within the Hudson River system. The fluorescent particles employed during this study possessed a density similar to that of PCB DNAPL oils found on the Hudson Falls plant site and a particle size distribution believed to be representative of DNAPL oil droplets within the river (HydroQual, 1997c). As such, the behavior of these particles was considered to represent PCB DNAPL fate and transport in the system. Several conclusions regarding PCB DNAPL were drawn from the results of this study:

• PCB DNAPL with droplet sizes greater that approximately 200 μ m entering the river under low river flow conditions will be sequestered near the point of entry into the system,

• PCB DNAPL sequestered in the river may be mobilized during high flow events, possibly as part of the sediment bed load, and

• PCB DNAPL transported into the TIP will be deposited within the surface sediments of the TIP.

The results of the PCB DNAPL study generally support the hypothesis that PCB DNAPL loadings from the Hudson Falls plant site (§1.2) may have contaminated the surface sediments of the TIP. This may have been occurring throughout the 1980s. However, it is unclear whether this mechanism has been contributing to the anomalous loading observed from the TIP during the 1990s.

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4.2.2 High flow water column and sediment bed loading

The results of the DNAPL study suggest that PCBs may be transported from the vicinity of the Hudson Falls plant site and into the TIP as a pulse loading within the water column or within the sediment bed load during periods of high flow. To evaluate this hypothesis, high flow water column and sediment bed load sampling was conducted on the Hudson River during the spring high flow period of 1997 (O'Brien & Gere, 1998). The approach included:

• water column sampling and analysis for PCBs and TSS from the Fort Edward and TID stations along the rising and falling limb of the spring high flow event hydrograph between April 6 and 9, 1997, and

•sediment bed load sampling and analysis for PCBs within the east and west channel of Rogers Island (Figure 2-1) during the high flow event using a specially designed bed load sampling device (Figure 4-12).

Water column samples were collected as vertically integrated composite samples consisting of discrete samples collected from three depths in the east and west channels of Rogers Island at Fort Edward and as discrete grab samples collected in a stainless steel vessel at TID.

During the 1997 spring high flow period, instantaneous flows at the Fort Edward gauging station increased from approximately 9,000 cfs on April 6 to a maximum flow rate of approximately 19,400 cfs on April 8, 1997 (Figure 4-13a). These flows produced only modest increases in TSS levels (Figure 4-13b), as TSS concentrations never exceeded 12 mg/L, indicating that the event did not produce bottom sheer stresses capable of causing significant sediment resuspension. Water column total PCB concentrations also remained low during the high flow event, ranging between 10 and 30 ng/L (Figure 4-13c). At peak flow, water column concentrations represent a PCB loading of 1.3 kg/day at the Fort Edward station (Figure 4-13d).

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The PCB loadings observed during the 1997 high flow period represent a significant reduction in high flow event driven PCB transport in the system compared to similar events sampled in 1992 and 1993 immediately following external PCB loadings to the system (Figure 2-3). The 1992 and 1993 spring flood events produced maximum PCB loadings of approximately 50 lbs/day and approached the loadings observed in the late 1970s. These observations indicate:

• high flow events were an important mechanism transporting PCBs downstream from the plant site regions of the river and into the TIP during the early 1990s, and

• remedial measures conducted on the plant site (§1.2) appear to have mitigated PCB discharges to the river and significantly reduced high flow PCB transport in 1997 (Figure 2-3).

Flow event-driven transport of sediments and associated PCBs along the sediment-water interface (sediment bed loading) does not appear to be a significant mechanism by which PCBs are transported into the TIP. Particulate phase PCB concentrations of sediment bed load samples collected from both the east and west channel of Rogers Island contained less than 15 mg/kg PCBs (Figure 4-14), and two of the three samples collected contained less than 5 mg/kg PCBs. These concentrations are significantly lower than the water column particulate phase PCB concentrations measured at Fort Edward by the USEPA in 1993 and the average surface sediment (0-5 cm) PCB concentrations measured in 1991. These data indicate that sediment bed loading in 1997 was not a significant contributor to the PCB loading into the TIP.

Based upon the high flow data collected in 1997, flow event driven water column and sediment bed load PCB transport do not appear to be significant mechanisms for continued pulse loadings of PCB from the plant site regions and into the TIP. However, the high flow events in the early 1990s did mobilize significant PCB loads into the system. These loadings may have contributed to PCB DNAPL transport into the TIP as the results of the DNAPL transport study (§

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4.2.1) indicate that PCB oils transported downstream of the plant site would be deposited in the TIP. This mechanism may have contributed to the elevated TIP loadings observed following the Allen Mill loading event by elevating surface sediment PCB concentrations. Additionally, PCB loading via this mechanism may have contributed to TIP surface sediment PCB contamination prior to the mill event. However, the results of the 1997 high flow study indicate that remedial measures conducted on the Hudson Falls plant site and the Allen Mill have mitigated these sources to the river and greatly reduced the transport of PCB into the TIP. Hence, to the extent that flow event driven pulsed loadings contributed to the TIP load in the early 1990s, their effect should be greatly diminished in the future.

4.2.3 Pulse loadings during periodic flooding of Bakers Falls plunge pool

Pulse loadings during periodic flooding of the Bakers Falls plunge pool as a result of the operation of the AHDC hydroelectric facility is another possible source of PCBs to the TIP. The trash rack assemblies that protect the turbines from debris transported through the intake raceway require cleaning every few days. During this process, flow through the facility ceases and the racks are pneumatically cleaned of debris, which is carried by water flow through a bypass structure along the western shore of Bakers Falls and into the plunge pool. Due to the reduced flow through the hydroelectric facility, the surface water elevation of the pool upstream of Bakers Falls increases and spills over the dam. This inundates the falls and provides additional waters for flushing of PCBs downstream.

The periodic flooding of Bakers Falls was considered as a possible source of PCBs to the TIP due to the PCB DNAPL seeps located within fractures in the bed rock outcroppings of the falls and within the plunge pool. A specific monitoring program was designed to assess the relative contribution of this PCB source to the TIP loading anomaly (O'Brien & Gere, 1997a).

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The approach used to monitor the impact of hydrofacility operation on PCB transport in the system included (O'Brien & Gere, 1997a):

• release of rhodamine WT dye into the plunge pool prior to trash rack washing activities at the hydroelectric facility,

• monitoring of the dye front and collection of samples representing water flushed from the pool at three locations: the plunge pool, Fort Edward, and the TID, and

• analysis of collected samples for PCBs and TSS.

Three hydrofacility operation monitoring events were conducted; one in September 1996 and two in June 1997.

The periodic flushing of Baker Falls appears to have a significant effect on the PCB concentrations found within the plunge pool (Figure 4-15). During two of the three sampling events, PCB concentrations within the plunge pool increased substantially from near the method detection limit of 11 ng/l before inundation of the falls to approximately 400 ng/l (June 9, 1997) and 130 ng/l (June 23, 1997) after falls inundation. These data suggest that PCB DNAPL that accumulates on the bedrock outcrops of the falls, is transported into the plunge pool as water flows over the falls. The magnitude of the release from the falls is difficult to assess from the plunge pool data due to uncertainties over flow characteristics of the pool. Therefore, the impact of the loading from the falls was assessed by examining the transport of these PCBs downstream at the Fort Edward station.

Periodic loading of PCBs as a result of hydroelectric facility operations had little effect on PCB loadings into the TIP. Although water column PCB concentrations at the Fort Edward station increased in response to the loadings from the plunge pool, these increases were relatively small (Figure 4-15). Moreover, there was no evidence of any correlation between the PCB levels observed

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within the plunge pool and those observed at Fort Edward. The largest increase in PCB concentrations in the plunge pool was observed during the June 9, 1997 sampling event. In contrast, PCB concentrations from the Fort Edward station on this date increased only slightly. Therefore, the total mass of PCB transported downstream as a result of this loading mechanism is not sufficient to appreciably increase PCB loading observed at the Fort Edward station.

Data collected in association with the hydrofacility operations monitoring indicate that periodic inundation of Bakers Falls provides relatively insignificant PCB loads into the TIP. Hence, this mechanism is not likely responsible for anomalous loadings from the TIP.

4.2.4 Localized PCB source areas within TIP

PCB DNAPL loadings from the Hudson Falls plant site area and the Allen Mill during the early 1990s (§ 2.2) may have contaminated surface sediments within localized regions of the TIP. This hypothesis was generally supported by the PCB DNAPL study which indicated that oil phase PCBs entering the river within the vicinity of the Hudson Falls plant site would be transported downstream and deposited in the TIP (§4.2.1). To assess the importance of this potential cause of the TIP anomaly, time-of-travel surveys were conducted through the TIP. These surveys were designed to monitor a single mass of water as it traveled through the pool. In this way, localized areas potentially contributing a disproportionate quantity of PCBs to the water column load could be detected.

Detailed information regarding the methods employed for the TIP time-of-travel studies is provided elsewhere (O'Brien & Gere, 1998). In summary, the surveys consisted of sampling along lateral transects established every 0.25 to 0.5 miles between Rogers Island and TID, with sampling stations at three positions across each transect: east shore, west shore, and center channel (Figure 4-

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6). Transects were sampled from upstream to downstream so as to correspond with the flow of river water. Stations along each transect were sampled simultaneously. Time-of-travel between each transect was estimated from flow information retrieved from the USGS gauging station located in Fort Edward (1996) and by monitoring a pulse of dye injected into the river (1997). A total of four time of travel surveys were conducted: two in September 1996 and two in June 1997. Samples from each station consisted of vertically stratified composite samples collected from three depths and were analyzed for PCBs and TSS.

The four TIP time of travel surveys exhibited similar spatial trends in total PCB concentration within the center channel (Figures 4-16 and 4-17). PCB concentrations were generally at or near the method detection limit of 11 ng/L at the Rogers Island sampling station and increased gradually to approximately 30 ng/l over the first 2 miles of the TIP, to river mile 193. Over the four mile section of the TIP between river mile 193 and 189, center channel PCB concentrations increase by approximately 40 to 60 ng/L. At average flows of approximately 4,000 cubic feet per second (cfs) observed during the surveys, this increase represents a mass loading rate of 0.4 - 0.6 kg day⁻¹. These mass loading rates represent sediment areal flux rates of approximately 0.3 to 0.4 mg m⁻² day⁻¹ across this region of the TIP. This mass loading rate is generally consistent with the load expected from observed 1991 surface sediment PCB concentrations. It does not appear that any additional load, other than that attributed to surface sediments, is required to achieve the observed water column PCB concentrations between river miles 193 and 189.

The TIP survey results indicate elevated PCB concentrations in waters along the eastern and western shoreline. These occasional high values do not necessarily indicate the presence of an area of elevated PCB flux from the sediments. Rather, they appear to be the result of lateral variations in river flow. For example, pronounced increases in water column PCB concentrations along the eastern shore across from the Snook Kill (Figure 4-18; Transect 12) can be attributed to a change in

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hydrodynamics in this region of the river. The elevated concentrations occur downstream of a group of small islands that impede river flow along the eastern shore (Figure 4-6). Field measurements of flow velocities in this region of the river indicate the high concentrations were measured in backwater areas (O'Brien & Gere, 1998). Under these conditions, surface sediments at the same PCB concentration as upstream areas and exhibiting the same areal PCB flux would produce higher water column PCB concentrations. This phenomenon was observed along several of the near shore areas (Figure 4-18).

To illustrate the backwater effect, consider a section of the river having a sediment area A_s (L²). Water flows into and out of this section of the river at a rate of Q (L³ T⁻¹). Assume water flowing in does not contain PCBs and the only water column source is diffusion from contaminated sediments (J_s: M L⁻² T⁻¹). At steady state, the PCB concentration in water leaving this area (C_{out} :M L⁻³) can be calculated as:

$$C_{out} = \frac{J_s A_s}{Q}$$

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Given a uniform areal PCB flux rate of $0.4 \text{ mg m}^2 \text{ day}^{-1}$ and a sediment area of 100,000 m² (the approximate area of the eastern river channel between transects 10 and 12), the PCB concentration in water traveling over this sediment would increase in inverse proportion to the river flow rate, as shown in Table 4-5.

Flow Rate (cfs)	C _{out} (ng/L)
10	1635
50	327
100	164
500	33
1000	16

 Table 4-5. Relationship between river flow rate and PCB concentration considering a constant sediment flux rate.

To further demonstrate the importance of river hydrodynamics in determining spatial patterns of water column PCB concentrations, the two-dimensional hydrodynamic model described in Section 3 was used to estimate river flow velocities within the TIP. These results are presented in Figure 4-19 for a total river flow rate of 4380 cfs⁸. The model predicts the greatest river flow velocities within the center channel, with lower velocities along the shorelines, a pattern consistent with the field measurements described above. The impact of spatially varying flow velocities on observed water column PCB concentrations was simulated by:

•applying a spatially uniform flux of a conservative substance from the sediments to the water column,

•calculating water column concentrations for each of the model grid elements, and

•normalizing water column concentrations to the average concentration passing TID⁹.

⁸The average flows for the TIP time-of-travel surveys.

⁹In this way the influence of hydrodynamics on the predicted water column concentrations can be observed independent of the actual flux used in the calculation.

The results of these calculations appear in Figure 4-19 and demonstrate that given a uniform sediment flux rate, water column concentrations are dependent on river hydrodynamics. The largest concentrations occur in regions with the slowest flow velocities. This simplified representation of a uniform sediment source underscores the importance of understanding small-scale differences in river hydrodynamics when interpreting the spatial patterns in water column PCB loading observed during the time of travel surveys.

In addition to river hydrodynamics, spatial patterns in water column PCB concentrations depend upon spatial variations in sediment PCB flux. The flux of PCBs from surface sediments to the water column depends on the organic carbon normalized PCB concentration, the sediment-water exchange coefficient, and the PCB partition coefficient as described using Equations A-10 to A-15 (Appendix A). Regions of the river with equal surface sediment organic carbon normalized PCB concentrations and composition contribute equally to the water column PCB load. Data gathered by the NYSDEC in 1984 indicate that mean organic carbon normalized PCB concentrations are similar inside and outside the sediment "hot spot" areas (Table 4-6; Figure 4-20)¹⁰. Moreover, organic carbon normalized PCB concentrations were similar for both coarse grained and fine grained sediments collected in 1991 from the TIP (Table 4.6). Therefore, coarse grained and fine grained sediment areas and "hot spot" and non-"hot spot" areas are expected to have similar sediment pore water PCB concentrations and, through the process of sediment diffusion, similar areal PCB fluxes. Such conditions would produce the pattern of gradually increasing water column PCB concentrations observed within the center channel during the time-of-travel surveys conducted in 1996 and 1997 (Figures 4-16 and 4-17). Thus, the differences in water column PCB concentration between the center channel and the near-shore zones are not evidence that "hot-spots" dominate the PCB flux.

¹⁰In this analysis, 1984 organic carbon concentrations were estimated as 40% of the reported volatile solids concentration.

In fact, the sediment data suggest that the non-"hot spot" areas dominate because they constitute the vast majority of the river bottom. Localized variations in river hydrodynamics are the likely cause of the concentration variations observed during the time-of-travel surveys.

Table 4-6. TIP Organic Carbon Normalized Surface Sediment PCB Concentrations: 1) Both Inside and Outside NYSDEC "Hot Spots" in 1984 (0-2.5 In.), and 2) for Coarse Grained and Fine Grained Sediments Collected in 1991 (0-5 cm).

Sediment Survey	Location/ Sediment Type	# Observations	Mean PCB Concentration (mg/kg oc)	Std. Deviation (mg/kg oc)
1984 NYSDEC	Inside "Hot Spots" ¹	155	2045	2069
	Outside "Hot Spots"	177	2030	1827
1991 GE	Coarse Sediments	16	2941	1824
	Fine Sediments	41	2185	2265

1) These statistics excludes one sample collected in 1984 which contained 331,000 mg PCB/kg oc.

The TIP time-of-travel surveys did not reveal any localized regions of elevated surface sediment PCBs within the pool that are disproportionately contributing to the water column PCB load. Elevated water column PCB concentrations along several of the near shore areas have been, at least partially, attributed to localized changes in the hydrodynamics. PCB loadings characterized using center channel data uninfluenced by localized hydrodynamics depict an approximately uniform increase in PCB mass loading that is consistent with surface sediment exchange processes and the 1991 surface sediment PCB concentrations. These observations are discussed further in §4.3 below.

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4.3 Erroneous Estimates of PCB Flux Due to Biased Sampling

The hypothesis that biased sampling may have resulted in erroneous estimates of PCB flux into or out of the TIP was considered as a possible cause of the TIP anomaly. Biased low estimates of PCBs transported into and/or biased high estimates of PCB transported out of the pool could have produced the anomaly. Initial assessments of the routine monitoring stations located along the Route 197 Bridge in Fort Edward and the western wing wall of the TID suggested that samples collected from these stations provided reasonably representative estimates of PCB loading into and out of the TIP, respectively (O'Brien & Gere, 1993a; HydroQual, 1995a). Nonetheless, this hypothesis was further tested during extensive field efforts conducted in 1995, 1996, and 1997.

4.3.1 Route 197 Bridge in Fort Edward

The approach for assessing the representativeness of the Fort Edward monitoring station involved the simultaneous collection of water column samples from the routine monitoring station and at stations across a transect perpendicular to river flow located approximately 0.5 miles upstream (Figure 4-21). The transect was located in a region of the river characterized by shallow, vertically well mixed, and swift moving waters to minimize the potential for vertical stratification of water column PCBs due to particle size sorting or sediment bed loading. Nonetheless, samples were collected from two depths: near the air-water interface (0-3 inches of water column) and the sediment-water interface (3-6 inches from the sediment bed; O'Brien & Gere, 1996c). Samples along the transect were collected as temporal composites with equal volume aliquots collected every hour over a six hour period. Samples were collected from the routine monitoring station on the same day as the transect samples as an equal volume composite of samples collected at three depths from both the east and west channel of Rogers Island (O'Brien & Gere, 1996c). Sampling was performed twice during the fall of 1995 (September 17 and October 3, 1995).

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The routine monitoring station located at the Fort Edward station provides reasonably representative data for assessing the PCB loading into the TIP. Results of the transect study indicate that PCB concentrations of samples collected from the routine monitoring station agree well with samples collected across the transect located 0.5 miles upstream (Figure 4-22). PCB concentrations in transect samples were generally within 25% of the concentrations found in samples collected from the routine station. Furthermore, the transect monitoring indicates that PCBs within this reach of the river, and under the flow conditions sampled, are both vertically and laterally mixed (Figure 4-22). There was no significant difference between PCB concentrations within the shallow or deep samples collected at the transect stations nor any significant trend in PCB concentration across the river (Figure 4-22).

These data indicate that routine monitoring at the Fort Edward station provides reasonable data upon which to base estimates of PCB loading into the TIP. Therefore, it is not likely that biased sampling at the Fort Edward station contributed to the TIP anomaly.

4.3.2 Thompson Island Dam

The approach for assessing the representativeness of the TID monitoring station involved the simultaneous collection of water column samples from the center channel of the river at a location approximately 1000 feet upstream of the dam and from the routine station at the western wing wall of the dam. The results of the time-of-travel surveys indicated that samples from this center channel station accurately represent average PCB concentrations within this section of the river and are uninfluenced by localized changes in hydrodynamics that may bias samples collected along the shoreline (§4.2.4). Additional sampling was conducted from the eastern wing wall of the dam and from stations located immediately downstream of the dam within the western and eastern channels of the river at Thompson Island (Figure 4-23). Sampling and analysis methods generally followed

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the protocols described within the sampling and analysis plans (O'Brien & Gere, 1997a, 1997b). Generally, where water column depth permitted, samples consisted of vertically integrated composites made up of discrete aliquots collected from three depth intervals (0.2, 0.5 and 0.8 times the total depth) using a stainless steel Kemmerer Bottle sampler. Where water depth restricted the use of the Kemmerer Bottle, grab samples were collected using a stainless steel beaker. Several of the sampling rounds also consisted of temporal composites consisting of discrete aliquots collected over a several hour period and composited. Finally, the sampling occurred from upstream to downstream with the timing corresponding to the estimated time-of-travel of a parcel of water between the stations. Water column samples were analyzed for PCBs and TSS.

The TID monitoring program found that the routine shoreline sampling station at TID-west (Figure 4-23) consistently yielded PCB concentrations in excess of those observed from the center channel station. Fifteen pairs of samples were collected from the center channel of the river and TID-west between September 1996 and November 1997. In all pairs, the samples from the TID-west station contained higher PCB concentrations (Table 4-7 and Figure 4-24). The difference between the samples ranged from 3 to 167 ng/L representing between a 6 and 163% increase (Table 4-7 and Figure 4-24). The increase observed between the two stations does not appear to be the result of resuspension of contaminated sediments since there does not appear to be any significant bias in TSS concentrations between the two stations (Figure 4-25).

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Date	Center Channel (ng L ⁻¹)	TID-west (ng L ⁻¹)	Difference (ng L ⁻¹)	% Difference ¹
18Sep96	54	142	88	163
25Sep96	50	53	3	6
29Oct96	50	102	52	104
4Jun97	84	113	29	35
17Jun97	105	272	167	159
30Jun97	175	271	96	55
14Jul97	92	190	98	107
28Jul97	67	116	49	73
13Aug97	50	90	40	80
9Sep97a	64	107	43	67
9Sep97b	70	90	20	29
10Sep97	52	94	42	81
01Oct97	65	72	7	11
10Oct97	74	82	8	11
16Oct97	83	87	4	5
Mean	76	125	50	66
Std. Dev.	32	67	46	52

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¹ Percent difference calculated (TID-west - center channel)/center channel * 100.

The difference in PCB levels between the two stations suggested that either: 1) one or both sampling stations were biased and unrepresentative of average PCB concentration in water passing

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the TID, or 2) the sediments between the center channel station located approximately 1000 feet upstream of the dam and the dam were contributing, on average, approximately half the total PCB load observed over the entire TIP (Table 4-7). A second phase of the monitoring program was conducted to evaluate this.

Phase 2 of the TID monitoring program involved the collection of water column samples from numerous locations both upstream and downstream of the TID during four sampling events in August and September, 1997. As with the other sampling events, samples from the TID-west station contained higher PCB concentrations than those collected upstream at the center channel station (Figure 4-26). The center channel samples produced PCB concentrations consistent with the generalized PCB loading pattern observed throughout the TIP as observed during the time-of-travel surveys (§4.2.4). Similarly, water column samples collected downstream of the dam in both the western and eastern channels were consistent with center channel samples collected upstream of the dam, and were significantly lower than concentrations along the shoreline at the dam. PCBs in samples downstream of the dam within the western and eastern channels were, on average, 34% lower than in samples collected from the dam. These data clearly indicate that the routine samples collected from the TID-west station are not representative of average concentrations passing the TID.

Water column monitoring conducted by the USEPA from the western shoreline upstream of the TID likely contains a bias similar to that of the TID-west station. On October 1, 10, and 16, 1997 water column samples were collected from a western shoreline station upstream of the TID from a location close to that sampled by the USEPA during their water column transect and flow averaged sampling studies. These samples produced PCB concentrations significantly higher than those collected from the more representative center channel stations upstream and downstream of the dam (Figure 4-26). These data provide strong evidence that the TIP PCB flux estimates developed by the USEPA are based upon biased data.

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Water column monitoring downstream of TID at Fort Miller¹¹ and Schuylerville, NY provides further evidence that the routine TID-west station and the USEPA TID station produces biased high PCB concentrations. Samples from the Fort Miller and Schuylerville stations contained PCB concentrations consistent with both the measurements at the stations downstream of the TID and our understanding of PCB dynamics in the river (Figure 4-27). The sediments within river reaches between TID and Fort Miller, and Fort Miller and Schuylerville contain PCBs at levels that should produce water column PCB loadings through sediment-water exchange mechanisms under low flow conditions (O'Brien & Gere, 1993b). The monitoring conducted since August 13, 1997 between Fort Edward and Schuylerville produces an approximately linear increase in PCB loadings with river mile (0.1 lb mi⁻¹ day⁻¹; Figure 4-27), indicating that the sediments of the TIP are contributing no more PCBs than adjacent reaches downstream.

In contrast, low flow loading estimates developed from USEPA water column transect data produce a spatial pattern of PCB loading that is inconsistent with the spatial patterns of sediment PCB levels and our understanding of sediment-water interactions (USEPA, 1997; Figure 4-28). Samples collected by the USEPA during August 1993 produced a spatial pattern of PCB loading that suggested the loading from the TIP was elevated compared to adjacent reaches of the river, as the calculated loading at the TID exceeded that measured at the Schuylerville station (Figure 4-28). This is inconsistent with spatial patterns of PCB loading observed during the same season in 1997 using data from stations considered to be free of sampling bias (Figure 4-28). This analysis provides further evidence that the loading estimates developed by the USEPA and presented in the DEIR (USEPA, 1997) overestimate PCB loading from the TIP.

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¹¹The Fort Miller sampling station is located approximately two miles downstream of the TID.

4.3.3 Possible mechanism for the observed bias at TID-west

The observed bias at TID-west may be the result of incomplete lateral mixing. The region immediately upstream of the TID along the east and west shorelines consist of emergent aquatic vegetation beds that may be hydraulically isolated from the main stream of the river. PCB concentrations in these waters are likely elevated in comparison to PCBs in the center channel samples as the diffusive flux from sediments is integrated into a smaller volume of water. Shear forces along the boundaries of these water masses may promote the transport of waters containing higher PCB concentrations within a thin band along the shorelines. This thin band of water may be what is sampled from the shoreline locations at the TID and what was sampled by the USEPA during its transect and flow averaged sampling studies of 1993 (USEPA, 1997). This hypothesis is supported by two-dimensional hydrodynamic model estimates of river flow velocities (described in $\S3.2.1$) which identify a region of river flow immediately upstream of the TID that is lower than that in the main channel of the river. Additionally, application of a spatially uniform flux of a conservative substance from the sediments to the water column (§4.2.4), produces normalized concentrations at the TID west station that are in excess of that observed across the face of the dam (Figure 4-29). These data demonstrate that river hydrodynamics play an important role in the representativeness of the samples collected from the TID-west station. Nonetheless, it is apparent that the routine sampling station located at the western wing wall of the TID produces PCB concentrations that are not representative of the average PCB concentration across the TID.

4.3.4 Composition of the sediment PCB source

The composition of the summer low-flow (June - August 1997) average TIP load was calculated as the difference in water column derived PCB congener peak loading across the TIP using unbiased data collected from Fort Edward and the vicinity of the TID. The source of this

loading was assessed by calculating the required composition of a surface sediment source, assuming equilibrium partitioning between sediments and pore waters and a diffusive mass transport mechanism. Specifically, the approach included:

1) Calculation of TIP water column PCB peak (based on a DB-1 capillary column) loadings from paired Fort Edward (C_{fe}) and unbiased TID water column PCB data (C_{tid}) in accordance with the following equation:

$$W_{wc} = Q_{fe}(C_{tid} - C_{fe})$$

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where:

 Q_{fe} is Fort Edward flow (L³ T⁻¹), and

2)Calculation of the sediment-phase PCB composition assuming the load calculated using Equation 4-5 originates from surface sediments and is transported to the water column via diffusional processes. This load was calculated by substituting W_{wc} for W_d in Equation A-15 (Appendix A), solving for C_s on a DB-1 peak basis, and calculating the congener peak and homolog distributions. The parameters used in the calculation are summarized in Table 4-8.

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Parameter	Description	Value	Units	Source
K _t	Sediment-water Exchange Coefficient	2	cm day ⁻¹	GE Model Calibration
A _s	Surface Sediment Area	2x10 ⁶	m ²	GE Hudson River GIS
m _{doc}	Pore Water DOC	33.7	mg L ⁻¹	GE 1991 Sediment Survey
K _{oc}	Temperature Corrected Partition Coefficient	Varies w/ Temp. and Congener Peak	L kg ⁻¹	USEPA Phase 2 Data as calculated in GE (1997)
f _{oc}	Fraction Organic Carbon	1.82	%	GE 1991 Sediment Survey
K _{doc}	DOC Partition Coefficient	0.1 K _{oc}	L kg ⁻¹	_

Table 4-8. Parameters Used in the Calculation of Surface Sediment PCB	Source Sign	ature.
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The homolog distribution of the summer low flow TIP load appears in Figure 4-30a. On average, the homolog distribution of the TIP load consists of approximately 55% mono- and dichlorinated PCBs (Figure 4-30a). Back calculating the particulate-phase PCB concentration of surface sediments yields the average homolog distribution in Figure 4-30b. This PCB source best matches the surface sediment PCB composition as represented by the 0-2 cm sections of the USEPA high resolution cores collected from the TIP in 1992 (Figure 4-31a). In contrast, the source of the TIP load does not appear to match the composition of PCBs found at depths greater than 8 cm (Figure 4-31b). This analysis indicates that the source of the TIP PCB load is surface sediments as expressed through a diffusive flux mechanism.

4.4 New Paradigm for Sediment-Water PCB Exchange in the TIP

The discovery that a sampling bias at the TID-west station was responsible for the anomalously high PCB loading estimates from the TIP sets up a new paradigm for sediment-water interactions in the upper Hudson River: PCB loading patterns within the river are consistent both with conventional sediment-water exchange mechanisms and PCB concentrations and compositions found within the surface sediments. In response to loadings emanating from sediments throughout the upper Hudson River, primarily by way of diffusion, water column PCB concentrations increase approximately linearly with distance downstream. The observations of elevated loadings from the TIP following the release of PCBs from the plant site areas appear primarily to be the result of biased high PCB levels in samples collected from the TID-west station. This discovery now allows calculations of PCB fate and transport in the river to proceed without invoking extraneous PCB sources or unsupported sediment-water exchange mechanisms to account for the observed loadings.

The discovery of the sampling bias at the TID-west station invalidates conclusions drawn by the USEPA regarding TIP sediment loadings. In the DEIR, the USEPA concluded that the measured TIP load originated from the TIP sediments (USEPA, 1997). Based upon the unbiased sampling conducted since the fall of 1997, it appears that a significant portion of this loading was due to the sampling bias. The USEPA also stated that PCB transport downstream of the TIP was conservative, with little or no change in water column PCB loads with distance downstream. This pattern was produced by the biased high PCB data collected at the TID station. Unbiased data collected since the fall of 1997, produces a gradual increase in water column PCB loading between Fort Edward and Schuylerville as water flows over downstream PCB deposits (Figure 4-27).

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SECTION 5 SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

5.1 Summary

A state-of-the-science model of PCB fate and transport has been configured to represent the upper Hudson River system and calibrated using extensive field data from the study area. The ability of the model to represent the short-term and long-term changes in water column and sediment PCB levels over the period from 1977 to 1991 indicates that the model provides a reliable, quantitative representation of the significant mechanisms in the upper Hudson River that affect the fate and transport of PCBs. However, comparison of the model to water column monitoring data from the TID for the period from 1991 to 1996 suggested that the model underestimated the increase in PCB levels between Rogers Island and the TID. Efforts to alter the model calibration to achieve water column levels consistent with the TID data were unsuccessful. This failing of the model led to the formation of hypotheses regarding additional PCB sources and biased sampling.

5.2 Conclusions

An extensive field sampling program and data analysis effort designed to address the various hypotheses regarding TIP PCB loading sources revealed five major conclusions:

1. The water column concentrations measured at the TID overestimated the average PCB concentration in water passing this location. The shoreline sampling location is influenced by a quiescent backwater immediately upstream that tended to result in higher PCB concentrations than the cross-sectional average concentration. Unbiased data collected in the main channel upstream and downstream of the TID indicate that cross-sectional average concentrations are approximately 1.5

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times lower than those measured at the shoreline stations. The unbiased data indicate that sediments within the TIP contribute between a 0.5 and 1 lb/d of PCBs to the water column.

2. <u>PCB levels increase in a linear fashion as water passes through the TIP, indicating a nearly</u> <u>uniform areal flux from sediments within the pool</u>. The spatial patterns in water column PCB loading indicate that the diffusive flux of PCBs from sediments is similar across the TIP. This is due to the similarity of surface sediment organic carbon-normalized PCB concentrations that produce spatially invariant areal PCB flux.

3. <u>The composition of the TIP PCB load is consistent with the surface sediment PCB</u> composition considering equilibrium partitioning and sediment pore water exchange processes. During the summer low flow period, the composition of the TIP load closely resembles that which would result from equilibrium partitioning and pore water exchange with the surface sediments of the TIP. The composition is inconsistent with pore water exchange with sediments containing extensively dechlorinated PCBs such as those buried within the hot spot regions of the river.

4. <u>Water column PCB loadings increase as water travels downstream of the TIP</u>. The spatial patterns in water column PCB loading developed from unbiased data are consistent with known and understood sediment-water exchange mechanisms and surface sediment PCB concentrations. The conclusions drawn by the USEPA regarding the origin and fate of the TIP sediment source are not supported by the unbiased data. The biased data overestimate the magnitude and importance of the TIP sediment source.

5. While a significant portion of the TIP anomaly can be explained by sampling bias at the TID station, it is still possible that the Allen Mill event increased PCB levels in surface sediments within the TIP. Care must be taken when calibrating the long term fate and transport models to even

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the unbiased data currently being collected as they may be affected by elevated surface sediment concentrations resulting from the mill loadings. Calibration to the corrected USGS data may provide a means to determine if the Allen Mill event did increase the surface sediment concentrations within the TIP. This would allow more accurate estimates of the sediment to water mass transfer coefficient and yield more reliable estimates of future water column PCB concentrations.

6. Based on observations of DNAPL in the river bed at Bakers Falls, the extent of DNAPL presence at the Hudson Falls site, and the results of the DNAPL transport study, it is possible that PCB DNAPL from the plant entered the river throughout the 1980s and was deposited in surface sediments of the TIP. Since this mechanism and PCB loading is not represented in the PCB fate and transport models, the models may not accurately describe what is occurring in the river. For example, surface sediment mixing, sediment water exchange, and PCB partitioning may be sensitive to an underestimation of surface sediment loading. However, the 1997 high flow data indicate that remedial activities at the site have successfully controlled the movement of DNAPL from the plant site into the river. This suggests that recovery rates may be accelerated over those observed in the late 1980s. The on-going water column monitoring program will provide data from which to evaluate the recovery rate of the river. Moreover, as it has been seven years since the last extensive survey, additional sediment sampling within the TIP may yield important information on the impact of the Allen Mill event and subsequent recovery on surface sediment PCB concentrations.

5.3 Recommendations

1. The analytical bias in PCB concentrations reported by the USGS for monitoring stations south of Ft. Edward during the mid to late 1980's should be assessed and corrected before the data are used in model calibration. If this data set is not corrected, the impact of the Allen Mill PCB

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loadings on surface sediment PCB concentrations within TIP may be indeterminable, resulting in considerable uncertainty in model projections.

2. <u>Model calibration needs to be based on at least 1 year of data from the unbiased sampling</u> <u>station located immediately downstream of TID.</u> GE began collecting this data as well as data from Schuylerville last September. This is necessary given the strong seasonal variability in the PCB loading from the TIP observed in the existing data set.

3. <u>Consideration should be given to performing additional sampling and analysis for PCBs</u> in <u>TIP sediments</u>. Extensive surveys were conducted in 1977, 1984, and 1991. Given the uncertainty over the impact of the Allen Mill event on surface sediment PCB concentrations and the amount of time that has transpired since the last survey, this data would be useful in model calibration and increasing the reliability of the projections.

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FIGURES





Figure 2-1. Map of Hudson River from Glens Falls to Thompson Island Dam.





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Figure 2-4.

Temporal Trends in Mean Annual Low Flow Water Column PCB Loading from Thompson Island Pool (1980-1997).

Note: Data for flow < 10,000 cfs at Fort Edward plotted; High loads from 9/91 to 12/91 are excluded.



Figure 2-5.

Temporal Trends in Mean Monthly Low Flow Water Column PCB Loading from Thompson Island Pool (1993-1997). Note: Data for flow < 10,000 cfs at Fort Edward plotted.



Figure 3-1.

Models, State Variables, and Kinetic Processes for PCB Dynamics.

General Electric Company Hudson River Project





Figure 3-2. Sediment Transport Model Grid for Thompson Island Pool.





1-D Hydrodynamic Model Predictions and Data: Stage Height During 1983 Flood.



Figure 3-4. 2-D Hydrodynamic Model Predictions and Data: Stage Height During 1983 Flood.

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Figure 3-5. Model-Predicted and Observed TSS Concentrations at Schuylerville, Stillwater, and Waterford.



Comparison of Computed and Observed Surface (0-5 cm) Sediment PCB Levels in Four Areas of the Upper Hudson River.



Figure 3-7.

Comparison of Estimates of the Annual PCB Load Passing Waterford, NY Computed from the USGS Data (symbols) and from the Daily Model Results (lines).

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Schuylerville



Figure 3-8.

Comparison of Computed and Observed Water Column PCB Levels at Schuylerville for the Years 1989 - 1991.

Thompson Island Dam Calibration, x1197-9



TIME (years)

Figure 3-9.

Comparison of Computed and Observed Water Column PCB Levels at Thompson Island Dam for the Years 1993 - 1996.



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Figure 4-1.

Schematic of Groundwater Seepage Meter.



Figure 4-2. Locations of Spring 1997 Groundwater Seepage Monitoring Stations.



Figure 4-3.

Temporal Trends in Measured Groundwater Seepage into Thompson Island Pool.



Figure 4-4.

Spatial Trends in Measured Groundwater Seepage into Thompson Island Pool.



Figure 4-5. Model-Predicted Sediment Bed Resuspension as a Function of Flow Rate.



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Note: Lateral averages plotted; open squares represent PCRDMP samples at west wingwall of TID. Spatial Profile of TSS Concentrations for 1997 Time of Travel Surveys.





Total Suspended Solids [mg/L]

Total Suspended Solids [mg/L]

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Figure 4-8.

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Epifluorescent Photograph of Fluorescent Particles within Natural Sediment at Approximately



SIDE ELEVATION VIEW NOT TO SCALE



Figure 4-9. Schematic of *In-Situ* Particle Filtration Device.



Fluorescent Particle Mass Balance for PCB DNAPL Transport Study.







Figure 4-12.

Schematic of Passive Bed Load Sampling Device.





Figure 4-14.

Particulate PCB Concentrations for the Fort Edward Station.





Figure 4-15.

Water Column PCB Concentrations at Bakers Falls Plunge pool and Fort Edward from Hydrofacility Monitoring Program.



HUDSON RIVER PROJECT 1996 Time of Travel Survey

Sector Sector





HUDSON RIVER PROJECT 1997 Time of Travel Survey





Figure 4-18.

Comparison of West, Center, and East Channel PCB Concentrations at Select Transects from the 1996 and 1997 Time of Travel Surveys.




Figure 4-20.

1984 Organic Carbon Normalized Surface Sediment PCB (0-2.5 in.) Concentration within the TIP.





Figure 4-22.

Water Column PCB Concentrations Within the Vicinity of Fort Edward from the 1995 River Monitoring Test.





Figure 4-24.

Comparison of PCB Concentrations Upstream of Thompson Island Dam and at the West Wingwall.

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Comparison of TSS Concentrations Upstream of Thompson Island Dam and at the West Wingwall.



Figure 4-26. Comparison of PCB Concentrations Within the Vicinity of Thompson Island Dam.

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Contraction







Spatial Profile of Average Low Flow PCB Loading for 1993 EPA Data and 1997 GE Data

Figure 4-28.

Spatial Profile of Upper Hudson River PCB Loading During Summer Low Flow Period for EPA (August 1993) and GE Data (August 1997).





Homolog Group

Mean +/- 95% Confidence Interval for June to August 1997Upstream Station:Fort EdwardDownstream Stations:TIP 18C and TID PRW-2

Figure 4-30.

PCB Homolog Distribution of Water Column Delta Load Across the TIP and Calculated Sediment Source Required to Produce Water Column Load by Equilibrium Partitioning.





Comparison of PCB Peak Compositions for Calculated Diffusional Sediment Source (1997 Summer Average) with Sediments from 1992 EPA High Resolution Cores Collected from TIP.

APPENDIX A



APPENDIX A CONCEPTUAL MODEL OF TIP PCB DYNAMICS

A.1 PCB Mass Balance

The conceptual model of PCB dynamics in TIP is presented graphically in Figure A-1. PCBs in the water column are present in three phases: 1) freely dissolved, 2) sorbed to particulate matter, and 3) bound to dissolved organic carbon (DOC). The relative distribution among these water column PCB phases is described by equilibrium partitioning concepts. TIP water column PCB concentrations are affected by external loadings from the upstream plant site areas, loadings from sediment sources, advective transport to downstream reaches, and exchange with the atmosphere via volatilization. A brief description of these mechanisms and processes with respect to their importance in TIP PCB dynamics is described below.

A.1.1 Partitioning

Total water column PCBs are expressed as the sum of the dissolved, particulate-bound, and DOC-bound fractions. Equilibrium partitioning, with local linear sorption is used to describe the distribution among these phases. Particulate phase PCBs are bound to the organic carbon fraction of the water column suspended solids and are in equilibrium with the freely dissolved phase. The organic carbon partition coefficient is used to characterize the distribution between these two phases as follows:

$$C_{p} = C_{d} K_{oc} f_{oc} m_{ss}$$
(A-1)

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where:

 C_p is the water column particulate PCB concentration (M L⁻³),

 C_d is the water column dissolved PCB concentration (M L⁻³),

 K_{oc} is the PCB organic carbon partition coefficient (L³ M⁻¹),

 f_{∞} is the organic carbon fraction of water column particulates (M M⁻¹), and

 \mathbf{m}_{ss} is the water column suspended solids concentration (M L⁻³).

PCBs sorbed to water column DOC (C_{doc} ; M L⁻³) are in equilibrium with the freely dissolved phase, as described by the following equation:

$$C_{doc} = C_d K_{doc} m_{doc}$$
(A-2)

where:

 K_{doc} is the PCB dissolved organic carbon partition coefficient (L³ M⁻¹), and m_{doc} is the water column dissolved organic carbon concentration (M L⁻³).

Total TIP water column PCBs can be written in terms of the dissolved phase concentration:

$$C_{tip} = C_d \left(1 + K_{oc} f_{oc} m_{ss} + K_{doc} m_{doc} \right)$$
(A-3)

where:

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is the total PCB concentration in the TIP water column (M L^{-3}).

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A.1.2 External loadings

External PCB loadings to the TIP potentially exist anywhere water flows into the system. The magnitude of an external PCB loading depends on the flow rate and PCB concentration of the contributing source:

$$W_{e} = Q_{e}C_{e} \tag{A-4}$$

where:

External loadings result from sources such as tributaries, industrial discharges, and sewer outfalls.

A.1.3 Sediment sources

PCBs within the TIP sediments contribute to water column PCBs through three mechanisms: 1) bed resuspension, 2) pore water diffusion, and 3) groundwater advection. The sediment PCB load is the product of the mass flux due to each mechanism listed above and the surface area of PCBcontaminated sediments. The total loading from TIP sediment sources (W_s ; M T⁻¹) is therefore the sum of the flux from these three loading mechanisms taken over the sediment area (A_s ; L²)

$$W_s = A_s \left(J_r + J_d + J_{gw} \right) \tag{A-5}$$

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where:

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J _r	is the sediment PCB resuspension flux (M L ⁻² T),
J _d	is the sediment PCB pore water diffusive flux (M L ⁻² T), and
J_{gw}	is the sediment PCB groundwater advective flux (M L^{-2} T).

The physical and chemical processes that govern the sediment PCB flux ascribed to these mechanisms are described in Section A.2.

A.1.4 Settling

PCBs are lost from the water column via settling. In this process, particulate phase PCBs settle from the water column and are deposited on surficial sediments. PCB mass loss from the water column due to settling is parameterized with the mean settling velocity:

Settling Loss =
$$v_{c} C_{p} A_{c}$$
 (A-6)

where:

 v_s is the mean particulate settling velocity (L T⁻¹).

A.1.5 Advection

Water column PCBs within the TIP are affected by advection from the upstream to the downstream reaches as a consequence of water movement through the TIP. Advective mass transport is the product of the PCB concentration and the river discharge. Upstream loadings and downstream transport are summed to produce the net advective PCB mass transport:

Net Advection =
$$QC_{yn} - QC_{tin}$$
 (A-7)

where:

Q is the Hudson River discharge within TIP ($L^3 T^{-1}$), and C_{up} is the water column PCB concentration flowing into TIP (M L⁻³).

In the modeling framework discussed in Section 3, the measured PCB load passing the Fort Edward station was treated as a boundary condition. This loading was calculated as the product of the flow and PCB concentration of water passing the Fort Edward station. In this manner, external PCB loadings to the river from sources upstream of the TIP including the remnant deposits, Allen Mill loadings, river bed DNAPL seeps, and sediment sources were incorporated into the modeling assessment.

A.1.6 Volatilization

Volatilization is the net mass exchange across the air-water interface and is driven by a concentration gradient between the air and water phases. Since atmospheric concentrations are considerably lower than the TIP water column concentrations, volatilization represents a PCB loss mechanism. The volatilization flux is expressed in general terms as the product of the dissolved phase PCB concentration and the volatilization mass transfer velocity. The net volatilization mass transfer is the product of the volatilization flux and the surface area of the air-water interface:

$$Volatilization \ Loss = v_{u} C_{d} A_{u}$$
(A-8)

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where:

 v_v is the volatilization mass transfer velocity (L T⁻¹), and

 A_w is the surface area of the air-water interface (L²).

A.1.7 Governing equation

The governing mass balance equation to describing PCB dynamics in TIP can be expressed as: the time rate of change of PCB mass is equal to the sum of PCB sources less the sum of PCB sinks within the TIP. PCB sources include external loadings, internal sediment sources, and advection from upstream. PCB sinks include advection to downstream, settling, and volatilization. Assuming constant volume (V), the governing mass balance equation can be expressed as:

$$V\frac{\partial C_{tip}}{\partial t} = \sum C_e Q_e + A_s \left(J_r + J_d + J_{gw}\right) - v_s C_p A_s + Q C_{up} - Q C_{tip} - v_v C_d A_w$$
(A-9)

where:

t is time (T), and V is the TIP volume (L^3) .

The overall mass balance equation contains concentrations in terms of total, dissolved, and particulate PCBs. Using the partitioning relationships presented in section A.1.1, the mass balance may be expressed in terms of total water column PCBs. The mass balance equation presented above is coupled with similar expressions for upstream and downstream reaches, resulting in a system of equations for the entire river reach being modeled. Furthermore, the particulate phase and sediment source terms require coupling of the water column and sediment solids and PCB mass balance equations.

$$\frac{\partial C}{\partial x} \approx \frac{C_d' - C_{d,tip}}{\Delta x}$$
(A-11)

where:

 C_d is the pore water PCB concentration (M L⁻³); Δx is the surface sediment mixing depth (L).

Grouping the porosity, diffusion coefficient, and mixing depth into a bulk exchange coefficient, and expressing the sediment flux in terms of mass loading, results in the following expression:

$$W_{d} = k_{f} A_{s} \left(C_{d}^{\prime} - C_{d,tip} \right)$$
(A-12)

where:

 W_d is the water column PCB load from sediment pore water diffusion (M T⁻¹), and k_f is the sediment diffusion exchange coefficient (L T⁻¹).

Equilibrium kinetics with local linear sorption is assumed to describe the partitioning between the freely dissolved pore water PCBs, and PCBs sorbed to sediment organic carbon:

$$C_{d} = \frac{C_{s}}{K_{oc}f_{ac}}$$
(A-13)

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where:

 C_s is the dry weight surface sediment PCB concentration (M M⁻¹).

Sediment pore water PCBs are the sum of freely dissolved and DOC-bound fractions:

$$C_d' = C_d \left(1 + m_{doc} K_{doc} \right) \tag{A-14}$$

where:

 m_{doc} is the sediment pore water dissolved organic carbon concentration (M L⁻³).

Since the sediment pore water PCB concentration is typically much larger than the water column concentration, the water column concentration can be neglected in the resulting sediment diffusive loading equation:

$$W_{d} = k_{f} A_{s} \left(1 + m_{doc} K_{doc} \right) \frac{C_{s}}{f_{oc} K_{oc}}$$
(A-15)

The equation shown above states that the diffusive loading is proportional to the surface sediment concentration and surface area of PCB-containing sediments. Although surface sediment PCBs within the TIP are not spatially homogeneous, the diffusive loading equation can be used with area-weighted averages for organic carbon normalized PCB concentrations to calculate the net TIP flux.

A.2.2 Sediment resuspension

Resuspension or bed scour is the process by which surface sediments are mobilized and resuspended into the water column in response to shear forces produced by water movement over the bed. Only a finite amount of material can be resuspended from a cohesive sediment bed that is exposed to a constant bottom shear stress. This phenomenon, referred to as bed armoring, has been observed and quantified in numerous laboratory studies (Tsai and Lick, 1987; Parchure and Mehta, 1985). The amount of fine grained sediment that is resuspended (ϵ ; M L⁻²) at a given shear stress (τ ; F L⁻²) is given by the following empirical expression:

$$\varepsilon = \alpha \left(\frac{\tau - \tau_0}{\tau_0}\right)^m \qquad \tau \ge \tau_0$$
 (A-16)

where:

α is a system constant dependent on time since material was deposited as determined from field studies,

 τ_0 is the critical shear stress below which sediment is not subject to resuspension (F L⁻²),

At $\tau < \tau_0$, ε is equal to zero. Equation A-16 determines the net resuspension at a given shear stress.

The flux of sediment resuspended from the TIP at a given flow rate is dependent on the spatially varying bottom shear stress $(\tau_{i,j})$ as calculated using a two-dimensional hydrodynamic model. Using estimates of ε within each of the model grid elements, the maximum total mass of PCBs resuspended at a given flow (W_r) can be calculated as follows:

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$$W_r = \sum_{i=1}^n \varepsilon_i A_i C_i$$

(A-17)

where:

 ϵ_i is the mass of sediment eroded from hydrodynamic grid element i (M L⁻²),

 A_i is the area of grid element i (L²), and

 C_i is the surface sediment PCB concentration within grid element i (M M⁻¹).

This loading is distributed evenly over an assumed 1 hour resuspension period.

A.2.3 Groundwater advection

Groundwater advection occurs due to a hydraulic gradient within a porous media. One dimensional groundwater flow is described by Darcy's Law, in which the flow is related to the hydraulic gradient and the hydraulic conductivity of the media:

$$Q_{gw} = -KA_s \frac{\partial h}{\partial x}$$
(A-18)

where:

 Q_{gw} is the upward groundwater flow (L³ T⁻¹),

 A_s is the area perpendicular to flow (L²),

K is the sediment hydraulic conductivity (L T^{-1}), and

 $\partial h/\partial x$ is the vertical hydraulic gradient (L L⁻¹).

The upward flow of groundwater through surface sediments and into the TIP water column results in a net PCB loading. As groundwater travels through PCB-contaminated sediments, the interstitial pore water reaches an equilibrium with the solid-phase PCBs. Therefore, the net

groundwater advective PCB loading to the TIP water column is the product of the upward groundwater flow and the surface sediment pore water PCB concentration:

$$W_{gw} = Q_{gw} C_d^{\prime}$$
(A-19)

where:

 W_{gw} is the groundwater advective PCB loading to the water column (M T⁻¹).

The total internal sediment PCB loading within the TIP is the sum of the loadings from surface sediment pore water diffusion, sediment resuspension scour, and groundwater advection. Since the total sediment PCB loading varies both spatially and temporally, it is important to gain an understanding of the factors that influence the relative importance of these three loading mechanisms. These processes were considered in the quantitative modeling framework described in Section 3, and several field studies described in Section 4 were conducted to examine each loading mechanism.

QEA

Figure A-1.

Conceptual Model of PCB Dynamics in the Hudson River.

