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PHASE 2 REPORT - REVIEW COPY
FURTHER SITE CHARACTERIZATION AND ANALYSIS

VOLUME 2D - REVISED BASELINE MODELING REPORT

HUDSON RIVER PCBs REASSESSMENT RI/FS

JANUARY 2000

UNITED STATES • ENVIRONMENTAL PROTECTION AGENCY •

For

U.S. Environmental Protection Agency
Region 2
and
U.S. Army Corps of Engineers
Kansas City District

Volume 2D - Book 1 of 4
Fate and Transport Models

TAMS Consultants, Inc.
Limno-Tech, Inc.
Menzie-Cura & Associates, Inc.
Tetra Tech, Inc.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 2
290 BROADWAY
NEW YORK, NY 10007-1866

January 25, 2000

To All Interested Parties:

The U.S. Environmental Protection Agency (EPA) is pleased to release the Revised Baseline Modeling Report for the Hudson River PCBs Superfund site. This report presents results and findings from the application of mathematical models for PCB transport and fate and bioaccumulation in the Upper Hudson River. This report provides predictions under baseline conditions, that is, without any remediation measures for the PCB-contaminated sediments in the Upper Hudson River.

The Revised Baseline Modeling Report incorporates changes made to the models based on comments received during the public comment period on the May 1999 Baseline Modeling Report (BMR) and from additional analyses that were conducted to refine the models for predicting future PCB levels in sediment, water and fish. EPA is also releasing a responsiveness summary for the BMR which provides readers with responses to significant comments, or directs them to the appropriate section of the Revised Baseline Modeling Report where the comment has been incorporated.

The Revised Baseline Modeling Report supercedes the May 1999 Baseline Modeling Report. EPA will evaluate if the revised modeling results would change the overall conclusions of the Human Health and Ecological Risk Assessments, and will update the risk and hazard values in the responsiveness summaries for the risk assessments, as necessary. The results of models used to calculate the loads leaving the Upper Hudson, which were subsequently utilized in the calculation of risks and hazards for the Mid- and Lower Hudson River, are presented in the Revised Baseline Modeling Report.

Because the Revised Baseline Modeling Report was prepared in response to public comment (with some additional analyses that were outlined in the May 1999 BMR), there is no public comment period on this document. Please remember that we will, of course, accept public comment on all aspects of the Reassessment during the comment period on the Proposed Plan.

The Revised Baseline Modeling Report is being peer reviewed by a panel of independent experts. The peer reviewers will discuss their comments on the Revised Baseline Modeling Report at a meeting that will be held on March 27 and 28, 2000 at the Sheraton Saratoga Springs Hotel and Conference Center. Observers are welcome and there will be limited time for observer comment.

If you need additional information regarding the Revised Baseline Modeling Report, please contact Ann Rychlenski, the Community Relations Coordinator for this site, at (212) 637-3672.

Sincerely yours,

William McCabe

for Richard L. Caspe, Director
Emergency and Remedial Response Division

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GLOSSARY

BAF	Biota Accumulation Factor
Bayesian updating	calibration procedure based on conditional probability in Bayes Rule (optimizes predicted distribution based on observed distribution).
BMR	Baseline Modeling Report
BSRE	Beale's Stratified Ratio Estimator
BURE	Beale's Unstratified Ratio Estimator
CEAM	Center for Exposure Assessment Modeling
CD-ROM	Compact Disc - Read Only Memory
cfs	Cubic feet per second
cm	Centimeter
Corp.	Corporation
DAR	Drainage Area Ratio
deg. C	Degree Celsius
DEIR	Data Evaluation and Interpretation Report
DOC	Dissolved Organic Carbon
DOSM	Depth of Scour Model
e.g.	For example
et al.	and others
FA	Flow Average (Phase 2 Water Column Monitoring Program)
FEMA	Federal Emergency Management Agency
foc	Fraction organic carbon
fps	Feet per second
g	Gram
GBTOX	Green Bay Toxic Chemical Model
GE	General Electric
GIS	Geographic Information System
GLI	Great Lake Initiative
HEC-2	US Army Corps of Engineers, Hydraulic Engineering Center, Surface Water Profile Model
HOC	Hydrophobic Organic Chemicals
HUDTOX	Hudson River Toxic Chemical Model
i.e.	That is
IADN	Integrated Atmospheric Deposition Network
kg	Kilogram
LDEO	Lamont-Doherty Earth Observatory
Likelihood profile	maximum likelihood estimation technique to determine parameters of prior and posterior distributions
LRC	Low Resolution Sediment Coring Report
m/s	Meters per second
mg/l	Milligrams per liter
mi^2	Square miles
MT	Metric Ton
MVUE	Minimum Variance Unbiased Estimator

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NAPL	Non-aqueous Phase Liquid
NPDES	National Pollutant Discharge Elimination System
ng/m^3	Nanograms per cubic meter
ng/l	Nanograms per liter
NGVD	National Geodetic Vertical Datum
NOAA	National Oceanic and Atmospheric Administration
NWS	National Weather Service
NYSDEC	New York State Department of Environmental Conservation
NYSDOH	New York State Department of Health
NYSDOT	New York State Department of Transportation
OC	Organic Carbon
PCBs	Polychlorinated Biphenyls
PMCR	Preliminary Model Calibration Report
Posterior distribution	optimized input distribution based on Bayesian updating calibration procedure; revised prior distribution
Prior distribution	empirical or likelihood-function-based probability distribution initially specified in FISHRAND before implementing any calibration procedure; "best guess"
RBMR	Revised Baseline Modeling Report
RMA-2V	Thompson Island Pool Hydrodynamic Model
ROD	Record of Decision
RPI	Rensselaer Polytechnic Institute
SS	Suspended Solids
TID	Thompson Island Dam
TIN	Triangulated Irregular Network
TIP	Thompson Island Pool
TSCA	Toxic Substances Control Act
TSF (tsf)	Temperature slope factor
TSS	Total Suspended Solids
ug/g (ppm)	Micrograms per gram (parts per million)
ug/L	Micrograms per liter
USACE	United States Army Corps of Engineers
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
WASP5	(USEPA) Water Quality Analysis Simulation Program, Version 4
TOXI5	Toxic Chemical Module in WASP5
WY	Water year

EXECUTIVE SUMMARY
REVISED BASELINE MODELING REPORT
JANUARY 2000

This report presents results and findings from the application of mathematical models for PCB physical/chemical transport and fate, as well as PCB bioaccumulation in the Upper Hudson River. The modeling effort for the Hudson River PCBs site Reassessment has been designed to predict future levels of PCBs in Upper Hudson River sediment, water and fish. This report provides predictions under baseline conditions, that is, without remediation of PCB-contaminated sediment in the Upper Hudson River (equivalent to a No Action scenario). The predicted sediment, water and fish PCB concentrations from the models are used as inputs in the Human Health and Ecological Risk Assessments. Subsequently, the models will be used in the Feasibility Study (the Phase 3 Report) to help evaluate and compare the effectiveness of various remedial scenarios.

The Revised Baseline Modeling Report (RBMR or Revised BMR) incorporates changes to the May 1999 Baseline Modeling Report (BMR) based on public comments and additional analyses, and supercedes the May 1999 report. The Revised BMR consists of four books. Books 1 and 2 are on the transport and fate models, with Book 1 containing the report text and Book 2 containing the corresponding tables, figures and plates. Similarly, Books 3 and 4 are on the bioaccumulation models, with Book 3 containing the report text and Book 4 containing the corresponding tables, figures and plates. Predictions of future PCB concentrations in sediment and water from the transport and fate models are used as input values for the bioaccumulation models. The bioaccumulation models forecast PCB concentrations in various fish species based on these inputs.

MODELING OBJECTIVES

The overall goal of the modeling is to develop scientifically credible models capable of answering the following principal questions:

- When will PCB levels in fish populations recover to levels meeting human health and ecological risk criteria under continued No Action?
- Can remedies other than No Action significantly shorten the time required to achieve acceptable risk levels?
- Are there contaminated sediments now buried that are likely to become "reactivated" following a major flood, possibly resulting in an increase in contamination of the fish population?

The work presented in this Revised BMR provides information relevant to the first and third questions. Forecasts regarding the potential impacts of various remedial scenarios, thus addressing the second question, will be presented in the Feasibility Study (the Phase 3 Report).

MODEL DEVELOPMENT

A large body of information from site-specific field measurements (documented in Hudson River Database Release 4.1), laboratory experiments and the scientific literature was synthesized within the models to develop the PCB transport and fate and the PCB bioaccumulation models. Data from numerous sources were utilized including USEPA, the New York State Department of Environmental Conservation, the National Oceanic and Atmospheric Administration, the US Geological Survey and the General Electric Company.

The proposed modeling approach and preliminary demonstrations of model outputs were made available for public review in the Preliminary Model Calibration Report (PMCR), which was issued in October 1996. The modeling framework of the PMCR was revised based on a peer review and public comment, as well as the incorporation of additional data. The baseline modeling effort and results were documented in the Baseline Modeling Report (BMR) issued in May 1999. USEPA decided to revise the BMR to reflect changes to the models based on public comment and additional analyses that were conducted. The Revised BMR includes model refinements, additional years of data, longer model forecasts, validation to an independent dataset, and additional model sensitivity analyses. This Revised BMR supercedes the May 1999 BMR.

Transport and Fate Models

HUDTOX - The backbone of the modeling effort is the Upper Hudson River Toxic Chemical Model (HUDTOX). HUDTOX was developed to simulate PCB transport and fate for 40 miles of the Upper Hudson River from Fort Edward to Troy, New York. HUDTOX is a transport and fate model, which is based on the principle of conservation of mass. The fate and transport model simulates PCBs in the water column and sediment bed, but not in fish. It balances inputs, outputs and internal sources and sinks for the Upper Hudson River. Mass balances are constructed first for water, then solids and bottom sediment, and finally PCBs. External inputs of water, solids loads and PCB loads, plus values for many internal model coefficients, were specified from field observations. Once inputs are specified, the remaining internal model parameters are calibrated so that concentrations computed by the model agree with field observations. Model calculations of forecasted PCB concentrations in water and sediment from HUDTOX are used as inputs for the forecasts of the bioaccumulation models (as described in Books 3 and 4).

Depth of Scour Model (DOSM) - The Depth of Scour Model was principally developed to provide spatially-refined information on sediment erosion depths in response to high-flow events such as a 100-year peak flow. The DOSM is a two-dimensional, sediment erosion model that was applied to the Thompson Island Pool. The Thompson Island Pool is characterized by high levels of PCBs in the cohesive sediments. DOSM is linked with a hydrodynamic model that predicts the velocity and shear stress (force of the water acting on the sediment surface) during high flows. There is also a linkage between the

DOSM and HUDTOX. Relationships between river flow and cohesive sediment resuspension were developed using the DOSM for a range of flows below the 100-year peak flow. These relationships were used in the HUDTOX model for representing flow-dependent resuspension.

Bioaccumulation Models

Three separate bioaccumulation models were developed in a sequential manner, beginning with a simple, data-driven empirical approach (Bivariate BAF Analysis), followed by a probabilistic food chain model, and ending with a time-varying, mechanistic approach (FISHRAND). The three approaches are complementary, with each progressively more complex model building on the results of the preceding, simpler effort. All three bioaccumulation models are presented in the Revised BMR; however, the FISHRAND model is the final bioaccumulation model that is used to predict future fish PCB body burdens.

Bivariate BAF Analysis - The Bivariate BAF (Bioaccumulation Factor) Analysis is a simple empirical approach that draws on the wealth of historical PCB data for the Hudson River to relate PCB levels in water and sediments (two variables, or "bivariate") to observed PCB levels in fish. This analysis is useful in understanding the relative importance of water and sediment sources on particular species of fish. As this empirical approach does not describe causal relationships, the analysis has limited predictive capabilities and accordingly was not used for forecasts.

Empirical Probabilistic Food Chain Model - The Empirical Probabilistic Food Chain Model is a more sophisticated representation of the steady-state relationships between fish body burdens and PCB exposure concentrations in water and sediments. The model combines information from available PCB exposure measurements with knowledge about the ecology of different fish species and the food chain relationships among larger fish, smaller fish, and invertebrates in the water column and sediments. The Probabilistic Model provides information on the expected range of uncertainty and variability associated with the estimates of average fish body burdens.

(FISHRAND) Mechanistic Time-Varying Model - The FISHRAND model is based on the peer-reviewed uptake model developed by Gobas (1993 and 1995) and provides a mechanistic, process-based, time-varying representation of PCB bioaccumulation. This is the same form of the model that was used to develop criteria under the Great Lakes Initiative (USEPA, 1995). The FISHRAND model incorporates distributions instead of point estimates for input parameters, and calculates distributions of fish body burdens from which particular point estimates can be obtained, for example, the median, average, or 95th percentile. FISHRAND was used to predict the future fish PCB body burdens for the Human Health and Ecological Risk Assessments.

MODEL CALIBRATION

The principal HUDTOX application was a long-term historical calibration for a 21-year period from 1977 through 1997. Consistent with the Reassessment principal questions, emphasis was placed on calibration of the model to long-term trends in sediment and water column PCB concentrations. However, a short-term hindcast calibration test was also conducted from 1991 to 1997 to establish model performance for certain individual PCB congeners.

Model applications included mass balances for seven different PCB forms: total PCBs, Tri+, and five individual PCB congeners (BZ#4, BZ#28, BZ#52, BZ#[90+101] and BZ#138). Total PCBs represents the sum of all measured PCB congeners and represents the entire PCB mass. Tri+ represents the sum of the trichloro- through decachlorobiphenyl homologue groups. Use of Tri+ as the historical calibration parameter allows for the comparison of data that were analyzed by congener-specific methods with data analyzed by packed-column methods (that did not separate the various PCBs as well and did not measure many of the mono- and dichlorobiphenyls). Therefore, use of the operationally defined Tri+ term allows for a consistent basis for comparison over the entire period for which historical data were available. Tri+ is also a good representation of the PCBs that bioaccumulate in fish.

The five PCB congeners were selected for model calibration based primarily on their physical-chemical properties and frequencies of detection in environmental samples across different media. These individual congener simulations help provide a better understanding of the environmental processes controlling PCB dynamics in the river by testing the model with PCBs with widely varying properties. BZ#4 is a dichloro congener that represents a final product of PCB dechlorination in the sediments. BZ#28 is a trichloro congener that has similar physical-chemical properties to Tri+. BZ#52 is a tetrachloro congener that was selected because of its resistance to degradation and based on its presence in Aroclor 1242, the main Aroclor used by General Electric at the Hudson River capacitor plants. BZ#[90+101] (a pentachloro congener) and BZ#138 (a hexachloro congener) represent higher-chlorinated congeners that strongly partition to solids in the river and bioaccumulate in fish.

The HUDTOX model calibration strategy can be considered minimal and conservative. It is minimal in that external inputs and internal model parameters were determined independently to the fullest extent possible from site-specific data and only a minimal number of parameters were adjusted during model calibration. It is conservative in that parameters determined through model calibration were held spatially and temporally constant unless there was supporting information to the contrary. Consistent with the Reassessment principal questions, emphasis was placed on calibration to long-term trends in sediment and water column PCB concentrations, not short transient changes or localized variations.

The 21-year historical calibration for Tri+ served as the main development vehicle for the PCB fate and transport model used in the Reassessment. This calibration was successful in reproducing observed long-term trends in water and sediment PCB concentrations over the 21-year period. This was primarily demonstrated through comparisons between model results and available data for long-term Tri+ surface sediment concentrations, in-river solids and Tri+ mass transport at low and high flows, and water column solids and Tri+ concentrations. Many different metrics were used collectively in a "weight of evidence" approach to demonstrate model reliability.

The calibration of the FISHRAND model was conducted by a process known as Bayesian updating. This approach optimizes the agreement between predicted distributions of fish concentrations from the FISHRAND model as compared to empirical distributions based on the data by adjusting three input distributions (percent lipid in fish, total organic carbon in sediment, and the octanol-water partition coefficient or K_{ow}). Initial input distributions (referred to as prior distributions) are specified based on site-specific data and values from the published scientific literature. The model is run and calculates the likelihood of obtaining an output distribution that matches observed measurements given the input distribution. The prior input distributions are then adjusted (within constraints of the data) and these adjusted distributions are referred to as posterior distributions. The focus of the calibration was on the wet weight concentrations (as opposed to the lipid-normalized concentrations) because the wet weight concentrations are generally of primary interest to USEPA and other regulators, the lipid content of any given fish is difficult to predict, and the model predicts fish body burdens on a wet weight basis and then lipid-normalizes. It was determined that, overall, the FISHRAND model predicts wet weight Tri+ PCB fish body burdens to within a factor of two, and typically significantly less than that.

Model Validation

Model validation is the comparison of model output to observed data for a dataset that was not included in the calibration of the model. A HUDTOX model validation was conducted to compare predicted and observed water column concentrations for Tri+ using a dataset acquired in 1998 for the Upper Hudson River by General Electric. Results indicated good agreement at both Thompson Island Dam and Schuylerville over an entire year, spanning a range of environmental conditions in the river. The validation was judged successful and it enhances the credibility of the model as a predictive tool.

Several approaches were used to validate the FISHRAND model. One method was to calibrate FISHRAND for one river mile, and then to run the model for a different river mile. Satisfactory agreement for both river miles implied model validity across locations in the Hudson River. In addition, a calibration was conducted using only part of the available dataset, and then the model results were compared with the remaining portion of the dataset. The posterior distributions obtained using only the partial dataset were compared to the posterior distributions obtained using the full dataset. Finally, the partial-data calibrated model was run for the forecast period and these results compared to the full-data calibrated model results. Good agreement across all three metrics implied confidence in the performance of the model.

MODEL FORECAST

In the Revised BMR, the HUDTOX model was run for a 70-year forecast period from 1998 through 2067 for Tri+. The forecast period was lengthened from the 21-year forecast in the May 1999 BMR for two reasons. First, the fish body burdens attained for the 21-year forecast presented risks and hazards above levels of concern as documented in the risk assessments (*i.e.*, the 21-year forecast was too short to predict when PCB concentrations in fish would decrease below levels of concern). Second, the 70-year forecast period was selected in order to provide exposure concentrations that can be used directly in the Monte Carlo analysis in the Human Health Risk Assessment. Tri+ was simulated because it reflects PCB congeners that bioaccumulate in fish and hence are key to the risk assessment.

In order to conduct forecast simulations with the HUDTOX model, it was necessary to specify future conditions in the Upper Hudson River for flows, solids loads, and upstream Tri+ loads. These model inputs are not easily predicted (similar to predicting the future weather), but reasonable estimates were made based on historical observations and current information regarding PCB loading trends.

The baseline forecast simulation was run for an assumed constant Tri+ concentration of 10 ng/L at the model's upstream boundary at Fort Edward. This level represented the annual average Tri+ concentration that was observed in 1997 and assumes that there will be no future load increases or reductions from upstream sources. In particular, it also assumes that the PCB migration from the GE Hudson Falls Plant site would not increase or decrease and that there would not be any type of event similar to the releases that occurred with the partial failure of the Allen Mill gate structure in 1991. Recognizing the uncertainty in this upstream load, model sensitivity runs were conducted for an assumed Tri+ concentration of zero (0 ng/L) to represent a lower bound on future loads due to the implementation of remedial measures upstream, and for an assumed concentration of 30 ng/L to reflect increased loads similar to observations in 1998.

Results from 70-year forecast simulations contain inherent uncertainty due to uncertainties in estimating future flow and solids loading conditions. Furthermore, various model input assumptions, while less influential in 21-year simulations, can become more important in 70-year forecast simulations. This uncertainty can be assessed and accounted for in USEPA's decision making by evaluating predictions across a range of alternate scenarios for these inputs. For this reason, model sensitivity runs were also conducted for three additional hydrologic conditions: plus/minus 50 percent changes in future tributary solids loads, a different assumption for the depth of particle mixing in the surface sediments, and different starting concentrations for Tri+ in the sediments.

Risk-based target levels for fish PCB body burdens have not yet been established. In the Feasibility Study, site-specific target levels to be protective of human health and the environment will be developed from the risk assessments. However, it is beneficial at this time to compare forecasted fish PCB levels against example target levels as a matter of perspective. The target levels used for this analysis provide several concentrations spanning two orders-of-magnitude. Again, these are not endorsements of these values for decision making. Appropriate values will be developed in the Feasibility Study for the site.

MAJOR FINDINGS

The primary objective of the modeling effort is to construct a scientifically credible tool to help in the understanding of PCB transport and fate and bioaccumulation in the Upper Hudson River, and to use that tool for making forecasts of what will happen in the future. As such, one of the major findings was that it was possible to construct models that simulate conditions that match the observed data reasonably well. Consequently, the model predictions can be reliably used to evaluate future ecological and human health risks and to assess the relative time it takes for the river to recover under various remedial scenarios.

There are numerous general observations about the river that are apparent from the mass balance exercises. Some important observations that impact the understanding of the system include:

- The river is net depositional for solids in Thompson Island Pool, and apparently also in downstream reaches;
- Solids loads are dominated by tributary inputs;
- PCB (Tri+) loads to the water column are dominated by sediment to water mass transfer under non-scouring flow conditions; and,
- Water column and PCB (Tri+) surface sediment concentrations are gradually declining due to reduced input loads and natural attenuation.

Beyond the general observations above, the model forecasts provide the following findings regarding PCBs in the Upper Hudson River. It should be noted that the findings below are made based on the evaluation of Tri+, and that some of the findings may differ for other mixtures of PCBs, such as total PCBs or individual congeners.

1. PCB (Tri+) concentrations in the surface sediment are forecasted to decline at annual rates of approximately 7 to 9 percent over the next two decades, consistent with long-term historical trends.

2. PCB (Tri+) loads from upstream of the model boundary at Fort Edward control the long-term responses of PCB (Tri+) concentrations in the water column and surface sediments, and accordingly, body burdens in fish.

   - For the first two to three decades of the model forecast, depending on location, the in-place PCB (Tri+) reservoir in the sediments and sediment-water transfer processes control responses of surface sediment concentrations.
   - Water column PCB (Tri+) concentrations are increasingly controlled by the upstream boundary at Fort Edward over the long term. The rate at which water

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column concentrations approach an asymptote depends upon the assumed magnitude of the upstream boundary load and location within the river.

3. Forecasted surface sediment PCB (Tri+) concentrations in several localized areas in the Stillwater reach and the Thompson Island Pool increase after 40 to 50 years, despite exponential-type decreases up to that time. These computed increases are due to relatively small annual erosion rates that eventually, over an extended length of time, expose PCB concentrations that were previously at depth.

   - The relative magnitudes of computed increases in surface sediment PCB (Tri+) concentrations are small within the context of long-term trends in historical concentrations.

   - The occurrence, magnitude and timing of these computed increases are dependent on forecast assumptions.

   - It is reasonable to assume that localized erosion occurs within the river, but at scales smaller than the spatial scale of the model. Therefore, the model may not accurately reflect the areal extent of such erosion or its timing.

4. Results of the 100-year peak flow show that a flood of this magnitude would result in only a small additional increase in sediment erosion beyond what might be expected for a reasonable range of annual peak flows.

   - The small sediment scour depths produced by the 100-year peak flow result in only very small increases in surface sediment PCB (Tri+) concentrations. These increases decline to values in the base forecast simulation (without the 100-year peak flow) in approximately four years.

   - Increases in water column PCB (Tri+) concentrations in response to a 100-year peak flow are very short-lived (on the order of weeks) and decline rapidly after occurrence of the event.

   - The 100-year event causes an increase of less than 30 kg (70 lbs) in cumulative PCB (Tri+) mass loading across the Thompson Island Dam by the end of the first year of the forecast. This increase represents approximately 13 percent of the average annual PCB (Tri+) mass loading across Thompson Island Dam during the 1990's.

5. The FISHRAND model results for the 70-year forecasts show that predicted wet weight PCB (Tri+) fish body burdens asymptotically approach steady-state concentrations. These concentrations are species-specific, depending on the relative influence of sediment versus water sources, and reflect the upstream boundary assumption. That is, the asymptotic value is lowest for the 0 ng/L upstream boundary condition and approximately an order of magnitude higher for the 10 ng/L upstream boundary condition. Under the 30 ng/L upstream boundary condition, the asymptotic value is approximately a factor of five higher than the 10 ng/L result.

6. FISHRAND model results show that PCB (Tri+) uptake in fish is predominantly attributable to dietary sources, with a smaller contribution from direct water uptake. Analysis of relative sediment and water contributions within the food chain yielded the following results. Brown bullhead are most sensitive to changes in sediment concentration and not very sensitive to changes in water concentration; largemouth bass are more sensitive to sediment concentrations than to water concentrations, but water plays a larger role than for brown bullhead; yellow perch are driven primarily by the water; white perch show greater sensitivity to sediment; and pumpkinseed and spottail shiner are sensitive to small changes in water concentration.

7. The time it takes to attain acceptable target levels in fish tissue is greatly dependent upon the target level selected. Target levels will be selected as part of the Feasibility Study for the site.

SUMMATION

The modeling effort for the Reassessment has provided USEPA with valuable insights regarding factors that control transport and fate and bioaccumulation of PCBs in the Upper Hudson River. Forecasted responses of water column and surface sediment PCB (Tri+) concentrations in the Upper Hudson River, as calculated by HUDTOX, are sensitive to changes in hydrology, solids loadings, sediment particle mixing depth and sediment initial conditions. Forecasted responses of fish body burdens using the FISHRAND model are sensitive to changes in lipid content of fish, total organic carbon in sediment, and the octanol-water partitioning coefficient (K_{ow}).

The models are useful tools for forecasting future sediment, water and fish PCB concentrations. The forecasts can be reliably used to evaluate future ecological and human health risks and to assess the relative time it takes for the river to recover under various remedial scenarios.

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Chapter 1

1. INTRODUCTION

1.1 PURPOSE OF REPORT

This volume is the fourth in a series of reports describing the results of the Phase 2 investigation of Hudson River sediment polychlorinated biphenyls (PCB) contamination. This investigation is being conducted under the direction of the U.S. Environmental Protection Agency (USEPA). This investigation is part of a three phase remedial investigation and feasibility study intended to reassess the 1984 No Action decision of the USEPA concerning sediments contaminated with PCBs in the Upper Hudson River. Figure 1-1 contains a location map for the Hudson River watershed. For purposes of the Reassessment, the area of the Upper Hudson River considered for remediation is defined as the river bed between the Fenimore Bridge at Hudson Falls (just south of Glens Falls) and Federal Dam at Troy, New York (Figure 1-2).

In December 1990, USEPA issued a Scope of Work for reassessing the No Action decision for the Hudson River PCB Site. The scope of work identified three phases:

- Phase 1 – Interim Characterization and Evaluation
- Phase 2 – Further Site Characterization and Analysis
- Phase 3 – Feasibility Study

The Phase 1 Report (USEPA, 1991) is Volume 1 of the Reassessment documentation and was issued by USEPA in August 1991. It contains a compendium of background material, discussion of findings and preliminary assessment of risks.

The Final Phase 2 Work Plan and Sampling Plan (USEPA, 1992) detailed the following main data collection tasks to be completed during Phase 2:

- High- and low-resolution sediment coring;
- Geophysical surveying and confirmatory sampling;
- Water column sampling (including transects and flow-averaged composites); and,
- Ecological field program.

The data available from the Phase 2 investigation and other historical datasets are documented in the Database Report (Volume 2A in the Phase 2 series of reports; (USEPA, 1995) and accompanying CD-ROM database. This database provides the validated data for the Phase 2 investigation. This Revised Baseline Modeling Report (RBMR or Revised BMR) utilized the Hudson River Database, Release 4.1b, which was updated in Fall 1998 (USEPA, 1998b).

This Revised Baseline Modeling Report is Volume 2D of the Reassessment documentation. It presents results and findings from application of mathematical models for PCB transport and fate, and PCB bioaccumulation in the Upper Hudson River.

There were two modeling reports preceding this RBMR in the Reassessment documentation. The Preliminary Model Calibration Report (USEPA, 1996) was issued for public review in October 1996. The purpose of the PMCR was to document the conceptual approaches, databases and preliminary calibration results for the transport and fate, and bioaccumulation models. The PMCR did not contain results for any forecast simulations with the preliminary models. The modeling approaches in the PMCR were reviewed by an independent peer review panel in September 1998. The modeling approaches were revised in response to comments from the peer review panel and from the public. The Baseline Modeling Report (USEPA, 1999c) was issued for public review in May 1999. The BMR contained model refinements recommended by reviewers, results from a long-term historical calibration of the transport and fate and bioaccumulation models, and results from forecast simulations designed to estimate long-term responses to continued No Action and impacts due to a 100-year peak flow. USEPA decided to revise the BMR to reflect changes in the models based on public comment and additional analyses that were conducted. The Revised BMR supercedes the May 1999 BMR.

The purpose of this Revised Baseline Modeling Report is to document:

- Additional model refinements;
- Sensitivity of the historical calibration;
- Model validation to an independent dataset;
- Longer (70-year) model forecasts for continued No Action; and,
- Sensitivity of forecast simulations for continued No Action.

1.2 Report Format and Organization

The information gathered and the findings of this phase are presented here in a format that is focused on answering questions critical to the Reassessment, rather than report results strictly according to Work Plan tasks. In particular, results are presented in a way that facilitates input to other aspects of the projects.

This report is presented in four books. Books 1 and 2 contain results and findings from the PCB transport and fate models. Book 1 contains the report text and Book 2 contains all tables, figures and plates for the transport and fate models. Books 3 and 4 contain results and findings from the PCB bioaccumulation models. Book 3 contains the report text and Book 4 contains all tables, figures and plates for the bioaccumulation models.

Books 1 and 2 contain results and findings for applications of PCB transport and fate models to existing historical data, and for forecast simulations designed to estimate both long-term responses to continued No Action and impacts due to a 100-year peak flow. Books 1 and 2 chapters are as follows:

- Chapter 1 herein provides the report introduction;
- Chapter 2 presents the overall conceptual approach used for the mathematical models and the relationships among individual models;
- Chapter 3 presents the hydrodynamic model used for Thompson Island Pool (TIP);
- Chapter 4 presents the Depth of Scour Model (DOSM) used to estimate masses of solids and PCBs eroded from cohesive and non-cohesive sediment areas in Thompson Island Pool (TIP) in response to peak flows;
- Chapter 5 presents the development of the Hudson River Toxic Chemical Model (HUDTOX) including conceptual framework, governing equations and spatial-temporal scales;
- Chapter 6 presents results from data synthesis tasks necessary to provide model inputs and to support processing and interpretation of model output;
- Chapter 7 presents results and findings from calibration of the HUDTOX model to historical data, including data collected as part of the USEPA Phase 2 investigation;
- Chapter 8 presents results and findings from forecast simulations with the HUDTOX model designed to estimate long-term responses to continued No Action and impacts due to a 100-year peak flow; and,
- Chapter 9 presents results from a model validation simulation using an independent dataset acquired in 1998 by General Electric.

1.3 PROJECT BACKGROUND

1.3.1 Site Description

The Hudson River PCBs Superfund site encompasses the Hudson River from Hudson Falls (river mile [RM] 198) to the Battery in New York Harbor (RM 0), a river distance of nearly 200 miles. Because of different physical and hydrologic regimes, approximately 40 miles of the Upper Hudson River, from Hudson Falls to Federal Dam (RM 153.9), is distinguished from the Lower Hudson River below Federal Dam. Emphasis was placed on Thompson Island Pool (TIP), a 6-mile portion of the river between Fort Edward and Thompson Island Dam (TID) (Figure 1-3), because a substantial amount of PCB-contaminated sediment is contained in this location.

1.3.2 Site History

Over a 30-year period ending in 1977, two General Electric (GE) facilities, one in Fort Edward and the other in Hudson Falls, NY, used PCBs in the manufacture of electrical capacitors. Various sources have estimated that between 209,000 and 1,300,000 pounds (95,000 to 590,000 kilograms [kg]) of PCBs were discharged between 1957 and 1975 from these two GE facilities (Sofaer, 1976; Limburg, 1984). Discharges resulted from washing PCB-containing capacitors and PCB spills. Untreated washings are believed to have been discharged directly into the Hudson from about 1951 through 1973 (Brown et al., 1984). No records exist on which to base estimates of discharges from the beginning of PCB capacitor manufacturing operations in 1946 to 1956; however, discharges during this period are believed to be less than in subsequent years. Discharges after 1956 have been estimated at about 30 pounds (14 kg) per day or about 11,000 pounds (5,000 kg) per year (Bopp, 1979, citing 1976 litigation; Limburg, 1984, citing Sofaer, 1976). In 1977, manufacture and sale of PCBs within the U.S. was stopped under provisions of the Toxic Substances Control Act (TSCA). PCB use ceased at the GE facilities in 1975 and only minor discharges (about 0.5 kg/day or less [Brown et al., 1984; Bopp, 1979]) are believed to have occurred during facility shutdown and cleanup operations through mid-1977 when active discharges ceased. GE had been granted a National Pollutant Discharge Elimination System (NPDES) permit allowing up to 30 lbs/day to be discharged during this period (Sanders, 1989). According to scientists at GE, at least 80 percent of the total PCBs discharged are believed to have been Aroclor 1242, with lesser amounts of Aroclors 1254, 1221 and 1016 (USEPA, 1997).

A significant portion of the PCBs discharged to the river adhered to suspended particulates and subsequently accumulated downstream in bottom sediments as they settled in the impounded pool behind the former Fort Edward Dam (RM 194.8), as well as in other impoundments farther downstream. Because of the proximity to the GE discharges, sediments behind the Fort Edward Dam were probably among the most contaminated to be found in the Hudson, although this was not well known in the 1970s. The Fort Edward Dam was removed in 1973 because of its deteriorating condition. During subsequent spring floods, the highly contaminated sediments trapped behind the Fort Edward Dam were scoured and transported downstream. Substantial portions of these sediments were stored in relatively quiescent areas of the river. These areas, which were surveyed by New York State Department of Environmental Conservation (NYSDEC) in 1976 to 1978 and 1984, have been described as PCB "hotspots". Exposed sediments from the former pool remaining behind the dam site, called the "remnant deposits", have been the subject of several remedial efforts.

PCB releases from the GE Hudson Falls Plant site near the Bakers Falls Dam have also occurred through migration of PCB oil through bedrock. The extent and magnitude of these releases are not well quantified. This release through bedrock continued until at least 1996, when remedial activities by GE brought the leakage under better control. Despite some evidence for its existence prior to 1991 based on U.S. Geological Survey (USGS) data, this leakage was not identified until the partial failure of the abandoned Allen Mill gate structure near the GE Hudson Falls plant site in 1991. This failure caused a large release of what were probably PCB-bearing oils and sediments that had accumulated within the structure. This failure also served to augment PCB migration from the bedrock beneath the plant to the river until remedial measures by GE over the period 1993 to 1997 greatly reduced the release rate. A more in-depth discussion of PCB sources is contained in the Data Evaluation and Interpretation Report (DEIR) (USEPA, 1997).

1.4 Modeling Goals and Objectives

The goal of the PCB transport, fate and bioaccumulation modeling was to assist in answering the following principal Reassessment questions:

1. When will PCB levels in fish populations recover to levels meeting human health and ecological risk criteria under continued No Action?

2. Can remedies other than No Action significantly shorten the time required to achieve acceptable risk levels?

3. Are there contaminated sediments now buried that are likely to become "reactivated" following a major flood, possibly resulting in an increase in contamination of the fish population?

The approach to the PCB transport and fate modeling was to develop and field validate a scientifically credible mass balance model that was capable of predicting future PCB concentrations in the water and sediments. The model would be used for evaluating and comparing the impacts of continued No Action, major flood events and various remedial scenarios. The model also provides water column and sediment PCB exposures for the PCB bioaccumulation model and the ecological and human health risk assessments.

The specific objectives of the transport and fate modeling work in this RBMR were the following:

- Develop a mass balance model for PCB levels in the water column and bedded sediments in the Upper Hudson River;

- Calibrate the mass balance model to available historical data, including data collected as part of the Phase 2 investigation;

- Conduct forecast simulations with the calibrated mass balance model to estimate long-term responses to continued No Action and impacts due to a 100-year peak flow; and

- Estimate short-term, fine-scale erosion of solids and PCBs in Thompson Island Pool in response to a 100-year peak flow.

Through these objectives, the modeling work in this Revised Baseline Modeling Report is directed at answering Reassessment questions pertaining to continued No Action (Question 1 above) and impacts of a major flood (Question 3). During Phase 3, the Feasibility Study, the models will be used for evaluation and comparison of the impacts of various remedial scenarios (Question 2).

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Chapter 2

2. MODELING APPROACH

2.1 INTRODUCTION

Mass balance models were developed for transport and fate of PCBs in the water column and bedded sediments, and for PCB bioaccumulation in fish. The report herein (Books 1 and 2) focuses only on the PCB transport and fate model, whereas the bioaccumulation model is described in Books 3 and 4. The spatial domain of these models was the Upper Hudson River between Fort Edward and Federal Dam at Troy (Figure 1-2). However, special emphasis was placed on Thompson Island Pond (TIP), a 6-mile portion of the river between Fort Edward and Thompson Island Dam (TID) (Figure 1-3), because this reach contains the highest PCB concentrations and a disproportionately high PCB mass reservoir relative to downstream reaches.

The following major sections are contained in Chapter 2:

- Section 2.2 presents the overall modeling framework used in this Reassessment;
- Section 2.3 describes the hydrodynamic model developed for Thompson Island Pool which was linked to the Depth of Scour Model and the HUDTOX model;
- Section 2.4 describes the Depth of Scour Model (DOSM) for Thompson Island Pool;
- Section 2.5 describes the Hudson River Toxic Chemical Model (HUDTOX) that was developed and applied to the Upper Hudson River between Fort Edward and Federal Dam at Troy;
- Section 2.6 describes the various applications conducted with the HUDTOX model; and,
- Section 2.7 presents an overview of the database used for model development and applications.

2.2 CONCEPTUAL APPROACH

The conceptual approach for the PCB transport and fate models of the Upper Hudson River was driven by the principal Reassessment questions:

1. When will PCB levels in fish populations recover to levels meeting human health and ecological risk criteria under continued No Action?
2. Can remedies other than No Action significantly shorten the time required to achieve acceptable risk levels?

3. Are there contaminated sediments now buried that are likely to become "reactivated" following a major flood, possibly resulting in an increase in contamination of the fish population?

Answers to the first two questions required reliable representation of long-term trends in water column and sediment PCB exposure concentrations to fish populations in the Upper Hudson River. To accomplish this objective, a mass balance model, HUDTOX, was developed to simulate water, solids and PCBs over the long-term historical period and a long-term forecast period. Inputs, outputs, and internal sources and sinks were balanced on a daily time scale in order to simulate long term conditions for the entire Upper Hudson River from Fort Edward to Troy, New York.

An answer to the third question required reliable representation of flow-driven sediment resuspension from highly contaminated areas, especially PCB "hotspots" associated with fine-grain, cohesive sediments. To accomplish this objective, a two-step approach was used. First, a fine-scale hydrodynamic and sediment scour model, DOSM, was used to estimate flow-driven resuspension of sediments and associated PCBs in Thompson Island Pool, the most heavily contaminated portion of the river, in response to a 100-year peak flow. Second, the PCB mass balance model, HUDTOX, was used to estimate water column and sediment responses in the entire Upper Hudson River to the same 100-year peak flow. The hydrodynamic and resuspension models provided an estimate of the likelihood that high PCB concentrations now buried in the sediments would become re-exposed due to flow-driven scour of the sediment bed. Results from the PCB mass balance model (HUDTOX) provided estimates of the resultant water column and sediment concentration responses due to flow-driven scour and subsequent transport and redistribution of contaminated sediments.

The operational framework for the Reassessment models is illustrated in Figure 2-1, which depicts the principal individual modeling components and their inter-relationships. In Figure 2-2, the specific information input to each of these models is also presented. The hydrodynamic model, the DOSM and HUDTOX comprise the transport and fate models. The Thompson Island Pool models consist of a coupled hydrodynamic and resuspension model (DOSM) for sediments. HUDTOX is the mass balance model that represents water, solids and PCBs in the entire Upper Hudson River, including Thompson Island Pool. There is a linkage module that serves to process output from the hydrodynamic model and the DOSM for use in HUDTOX. These transport and fate models are described in the following sections. The Bivariate Biota Accumulation Factor (BAF) Model and the bioaccumulation models (FISHPATH and FISHRAND) quantify linkages between PCB water column and sediment concentrations and fish body burdens. These models are the subject of Books 3 and 4, and not described herein.

Different models with different attributes were developed to most effectively answer the three Reassessment questions while balancing the issues of complexity, computational burden, supporting data and system characteristics. The Thompson Island Pool Hydrodynamic and Depth of Scour Models were more refined and complex, as necessary to answer the issue of episodic scour. Thompson Island Pool, although only 6 miles (15 percent) of the entire model domain, contains almost half of the PCB mass reservoir in the Upper Hudson (Tofflemire and Quinn, 1979) and the highest PCB concentrations. Hence, the Pool has been the focus of remedial considerations, and more specialized modeling was warranted. The same framework was not applied to the remainder of the river because substantially fewer supporting data were available, and the additional computational burden and model complexity were not warranted.

2.3 Hydrodynamic Model

The hydrodynamic model used for Thompson Island Pool was the U.S. Army Corps of Engineers RMA-2V. This model is two-dimensional and vertically-averaged. It was applied to Thompson Island Pool to provide velocity information for bottom shear stress calculations at the sediment-water interface using DOSM. It also provided flow routing, water depth, and velocity information to the HUDTOX model for Thompson Island Pool only. The hydrodynamic model includes explicit representation of the existing river geometry as well as the flood plains to account for overbank flow during flood events.

The hydrodynamic model was not directly integrated with the HUDTOX model. Hydrodynamic model results were spatially and temporally processed using a linkage module that transformed water velocities into flows that were routed among the HUDTOX model spatial segments in Thompson Island Pool. Water velocities were also transformed into applied shear stresses at the sediment-water interface for use in the DOSM. The hydrodynamic model was run to steady state for a range of different river flows, including the 100-year peak flow.

2.4 Depth of Scour Model

The DOSM is a two-dimensional, GIS-based model of sediment erosion that was applied to Thompson Island Pool. It is a specialized tool for providing spatially-refined information on sediment erodibility in response to high flows, including a catastrophic flood. It calculates sediment bed scour based on flow-induced shear stress and site-specific measurements of sediment properties and resuspension behavior. Information on applied shear stresses at the sediment-water interface was calculated based on output from the hydrodynamic model.

The DOSM was developed principally to answer questions related to the likelihood that flood-induced erosion of bottom sediment would reactivate buried PCB. It was first used as a stand-alone tool to provide mass estimates of solids and PCBs eroded, and depth of sediment bed scour, in response to a 100-year peak flow. A constant 100-year flow was simulated with the hydrodynamic model as a worst case scenario. This simulation produced a map of bottom shear stress throughout Thompson Island Pool for the 100-year flow. This shear stress map was used to compute estimates of depth of scour throughout the entire cohesive sediment bed in Thompson Island Pool. Based on various uncertainties in model inputs, DOSM also calculates a probability distribution for scour depth addressing the question of "likelihood". The relationship between cohesive sediment resuspension and applied shear stress was based on a formulation from the published literature and parameterized using site-specific measurements from Thompson Island Pool. The DOSM shear stress map was also used to compute an upper bound estimate of depth of scour that could be expected for the non-cohesive sediment area in Thompson Island Pool.

The DOSM was also used to develop relationships between river flow and cohesive sediment resuspension for use in the HUDTOX model. The hydrodynamic model was run for a range of flow conditions spanning typical summer flows to the 100-year flow. The DOSM was used to estimate cohesive sediment resuspension for each of these flow conditions, thus producing a family of resuspension-flow relationships. These relationships were used as input to the HUDTOX model to represent cohesive sediment resuspension across all flow conditions in the Thompson Island Pool portion of the River.

2.5 Mass Balance Model

HUDTOX is the principal transport and fate modeling tool in this Reassessment. HUDTOX is a time-variable, three-dimensional model that includes three types of mass balances: (1) a water balance; (2) a solids balance; and (3) a PCB mass balance. A water balance is necessary because PCB dynamics are influenced by river flow and mixing rates. A solids balance is necessary because PCB dynamics are influenced by the tendency of PCBs to sorb (attach) to both suspended and bedded solids in the river. Finally, a PCB mass balance is necessary to account for all inputs, outputs, and internal sources and sinks of PCBs in the river. HUDTOX has a fully-integrated representation of solids and PCB concentrations in the water column and bedded sediments.

The spatial scales of the HUDTOX model application were determined by the Reassessment questions and available site-specific data. HUDTOX was applied to the entire Upper Hudson River from Fort Edward to Federal Dam at Troy. Because a substantial amount of PCB-contaminated sediment is contained in Thompson Island Pool, this portion of HUDTOX included greater spatial resolution than the portion downstream of Thompson Island Dam. In the Pool, HUDTOX is two-dimensional in the water column and three-dimensional in the sediments. Between Thompson Island Dam and Federal Dam, HUDTOX is one-dimensional in the water column and two-dimensional in the sediments.

With respect to temporal scale, the HUDTOX model was developed to represent long-term average water column and sediment PCB exposure concentrations. It was not developed to represent short-term behavior associated with high flow events. The reason is that PCB body burdens in fish are driven primarily by long-term average exposure concentrations, not short-term, event-scale exposures. The model does, however, represent differences between low-flow and high-flow sediment resuspension processes, and differences between cohesive and non-cohesive sediment areas. In this sense the model was designed to capture both mean low-flow and mean high-flow solids and PCB dynamics.

In HUDTOX, hydraulic routing downstream of Thompson Island Dam was one-dimensional and was specified using USGS flow gage data at Fort Edward and estimated flows for downstream tributaries. In Thompson Island Pool, the two-dimensional flow routing was defined by the hydrodynamic model.

Sediment scour in HUDTOX was determined through use of output from DOSM. The hydrodynamic model results were used to calculate the bottom shear stress required for DOSM. Output from the DOSM was linked to HUDTOX in the form of relationships between flow and cohesive sediment resuspension. This linkage ensured internal consistency in representation of flow-dependent resuspension between these two models for cohesive sediment areas. In

Thompson Island Pool, the hydrodynamic, DOSM and HUDTOX models were linked in terms of flow routing, depth, velocity, applied shear stress and cohesive sediment resuspension. Neither the hydrodynamic model nor the DOSM was applied to the portion of the river below Thompson Island Dam. Average relationships for cohesive sediment resuspension developed from the DOSM in Thompson Island Pool were used in this portion of the river.

2.6 Mass Balance Model Applications

The HUDTOX mass balance model was applied in a structured sequence as follows:

- Historical calibration for Tri+ (sum of trichloro through decachloro homologue groups) for a 21-year period from 1977 to 1997;
- Hindcast applications for total PCB and five congeners for 1991 to 1997;
- Independent model validation for 1998;
- 70-year model forecasts from 1998 to 2067; and,
- Sensitivity analysis for the historical calibration and the forecast simulation periods.

Model applications included a total of seven different PCB forms: total PCBs, Tri+, and five congeners, BZ#4, BZ#28, BZ#52, BZ#[90+101] and BZ#138. Total PCBs represents the sum of all measured PCB congeners and is the only PCB form that completely represents total PCB mass. A limitation to the use of total PCBs is that data were available for only the period from 1991 to 1997. To extend the period of time for the HUDTOX historical calibration, Tri+ was used as a surrogate for total PCBs and served as the principal calibration and forecast model state variable. Tri+ represents the sum of only trichloro through decachloro homologue groups. Due to differences in analytical methods among individual datasets, Tri+ was the only internally-consistent PCB form that could be operationally defined to approximate total PCBs over the entire period from 1977 to 1997 (USEPA, 1998a). Tri+ was also an appropriate choice for calibration and forecast simulations because it represents the principal distribution of PCB congeners that bioaccumulate in fish.

The historical calibration was the principal development vehicle for the model, which was focused on representing long-term PCB trends in water and sediment for a 21-year period. Tri+ was the principal focus of the calibration because comparable measurements were available for the entire 21-year period. However, a subsequent 7-year hindcast application of the model to total PCB and five congeners provided a test of the historical calibration to Tri+. The calibrated model was then subjected to validation using an independent set of water column PCB data for 1998. Following successful validation of the model, 70-year forecast simulations were developed. The forecasts were intended to assess the long-term system responses to continued No Action and impacts due to a 100-year peak flow. Additionally, model performance over the historical calibration and forecast periods was assessed through sensitivity analyses.

The congener simulations were conducted to gain better understanding of the environmental processes controlling PCB dynamics in the river and to strengthen and support the long-term historical calibration. The five congeners were selected based primarily on their physical-chemical properties and frequencies of detection in environmental samples across different media. BZ#4 is a dichloro congener that represents a final product of PCB dechlorination in the sediments (USEPA, 1997). BZ#28 is a trichloro congener that has similar physical-chemical properties to total PCBs. BZ#52 is a tetrachloro congener that was selected as a normalizing parameter for congener patterns based on its presence in Aroclor 1242, the main Aroclor used by GE, and on its resistance to degradation or dechlorination in the environment (USEPA, 1997). BZ#[90+101] (a pentachloro congener) and BZ#138 (a hexachloro congener) represent higher-chlorinated congeners that are more strongly associated with suspended and bedded solids in the river.

2.7 Mass Balance Model Calibration

The calibration strategy can be described as minimal and conservative. It was minimal in the sense that external inputs and internal model parameters were determined independently to the fullest extent possible from site-specific data and only a minimal number were determined through model calibration. It was conservative in the sense that parameters determined through model calibration were held spatially and temporally constant unless there was supporting information to the contrary. Consistent with the Reassessment questions, emphasis was placed on calibration to long-term trends in sediment and water column PCB concentrations, not short transient changes or localized variations.

The following factors were found to be the most important in controlling long-term trends in sediment and water column Tri+ concentrations in the Upper Hudson River:

- Hydrology;
- External solids loads;
- External Tri+ loads;
- Tri+ partitioning;
- Sediment-water mass transfer under non-scouring flow conditions;
- Solids burial rates; and,
- Particle mixing depth in the sediments.

The first three of these factors are external inputs defined largely by data, and the last four factors are internal processes within the river defined by data, scientific literature and model calibration. Long-term solids burial rates were the principal factor controlling long-term Tri+ responses in the river. Partitioning controls the distribution of Tri+ mass between sorbed and truly dissolved phases, thus influencing sediment-water and water-air mass transfer rates, and bioavailability to fish. Sediment-water mass transfer under non-scouring flow conditions was found to be the principal source of Tri+ inputs to the water column. Particle mixing depth strongly influenced long-term responses and the vertical distribution of Tri+ in the sediments. With the exception of solids burial rates and particle mixed depth, all model inputs and parameter values were determined using site-specific data and were not adjusted during the model calibration.

Most of the effort during the HUDTOX model calibration consisted of determining solids burial rates. Solids burial rates were determined for the 21-year historical calibration for four major reaches, including Thompson Island Pool and three downstream reaches. The principal calibration constraints on solids burial rates were the following:

- Measured burial rates from dated sediment cores;
- Computed burial rates from a sediment transport model;
- Tri+ surface sediment concentration trends; and,
- In-river solids and Tri+ mass transport at high and low flows.

The historical calibration was conducted by applying simultaneous, mutual constraints on the coupled solids and Tri+ mass balances. Operationally, the approach consisted of adjusting four model parameters: gross settling velocities into cohesive and non-cohesive sediment areas; resuspension rates from non-cohesive sediment areas; depth of particle mixing in the sediment bed; and magnitude of sediment particle mixing.

2.8 Hudson River Database

All modeling work in this report utilized the extensive database that was created to support this Reassessment. The Database Report (USEPA, 1995) and accompanying CD-ROM database provides the validated data for the Phase 2 investigation. This Revised Baseline Modeling Report (RBMR) utilized the Hudson River Database, Release 4.1b, which was updated in fall 1998 (USEPA, 1998b). This database contains information from a large variety of different sources, including:

- New York State Department of Environmental Conservation (NYSDEC)
- New York State Department of Health (NYSDOH)
- New York State Department of Transportation (NYSDOT)
- General Electric Company (GE)
- Lamont-Doherty Earth Observatory (LDEO)
- Rensselaer Polytechnic Institute (RPI)
- U.S. Geological Survey (USGS)

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- National Oceanic and Atmospheric Administration (NOAA)
- National Weather Service (NWS)
- U.S. Environmental Protection Agency (USEPA).

To supplement the database in Release 4.1b, a portion of the 1997 USGS flow, suspended solids and PCB data were obtained directly from the USGS in Albany, New York. Where necessary and appropriate, information from the scientific literature and various technical reports was also used in this modeling work. These sources are cited in the report text.

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Chapter 3

3. THOMPSON ISLAND POOL HYDRODYNAMIC MODEL

3.1 OVERVIEW

The six-mile long Thompson Island Pool is a special area of focus in the Reassessment because it contains a disproportionate amount of the PCB mass (nearly half) in the 40-mile long portion of Upper Hudson River. Additionally, the highest PCB concentrations occur in the Pool. These factors have made the Pool a focus area for possible remediation. The Pool is also the most extensively sampled reach of the Upper Hudson. As a result of the special focus on the Pool and the greater data availability, a fine scale, two-dimensional hydrodynamic model was applied for the Pool to provide input to the PCB fate and transport model (Chapter 5) and the Depth of Scour Model (Chapter 4). The Depth of Scour Model uses fine scale velocity information from the hydrodynamic model to compute scour of sediments, especially under high flow conditions.

The Thompson Island Pool is defined as the reach of the Hudson River upstream from the Thompson Island Dam at RM 188.5 and downstream from the former Fort Edward Dam, as shown in Figure 3-1. The purpose of the hydrodynamic modeling effort for Thompson Island Pool was to provide information on bottom shear stresses at the sediment-water interface for the DOSM and HUDTOX models. Additionally, the model provided flow routing, depth and velocity information for the two-dimensional portion of the HUDTOX model in Thompson Island Pool.

The hydrodynamic model was used to calculate two-dimensional, vertically-averaged velocity fields for a range of different river flows, including the 100-year peak flow in the Hudson River, (estimated to be 47,330 cfs by Butcher, 2000a). The computation of a two-dimensional, vertically averaged velocity field is necessary to account for the lateral variability of the flow and resultant bed shear. The bed shear is used to compute the mass of cohesive sediments eroded in the Depth of Scour Model (DOSM). Because sediment properties and PCB concentrations are not uniformly distributed, the bottom shear stresses must be determined for each element used in the river model to correctly estimate Poolwide resuspension of PCBs.

The hydrodynamic model was applied for a range of steady flow conditions in the Thompson Island Pool. Transient effects due to storage and drainage were not included in the simulations because the historical flow record at Fort Edward shows that the Hudson River high flow events occur over several days, which gives the Pool enough time to establish approximate steady state conditions. This means simulation of transient water storage and drainage could be reasonably omitted from calculations of bottom shear at peak flow conditions. Additionally, the Depth of Scour Model (DOSM) presented in Chapter 4 requires only simulation of the peak flow hydraulic conditions to estimate solids resuspension losses from cohesive sediment bed areas during flood events. The credibility of the numerical simulation results was established by applying the model to events where the flow in the river had been measured. The model was run for the 100-year peak flow to provide the velocity field used by the DOSM.

The following major sections are included in Chapter 3:

3.2 Hydrodynamic Modeling Approach

3.3 Available Data

3.4 Hydrodynamic Model Calibration

3.5 Hydrodynamic Model Validation

3.6 Hydrodynamic Model Sensitivity Analyses

3.7 Conversion of Vertically Averaged Velocity to Bottom Shear Stress

3.8 Discussion of Results

3.2 Hydrodynamic Modeling Approach

The hydrodynamic model used to compute the flow is the US Army Corps of Engineers RMA-2V. RMA-2V uses the finite element method to compute vertically-averaged velocities and water surface elevations in the flow field. The model has been extensively studied and applied widely (Berger, 1990; Lin and Richards, 1993; McAnally et. al., 1984; and Richards, 1990). The selection of a two-dimensional, vertically averaged model and the density of the grid mesh were largely determined by the resolution needed to adequately define the flow field variations and river bathymetry, and hence, shear stress variation. The shear stress exerted on the river bottom is parameterized by the magnitude of the vertically averaged velocity and the depth of flow, as is described in Section 3.7

A short summary of the modeling procedure is as follows: A finite element grid was first constructed for the Thompson Island Pool section of the river and floodplain. RMA-2V uses a finite element procedure to solve the governing equations that describe the vertically-averaged velocities and water surface elevation. The boundary conditions consist of a specified upstream flow, the water elevation downstream and the resistance to flow. The downstream boundary was obtained from a rating curve developed for the stage-discharge gage near the Thompson Island Dam, and the resistance to flow is parameterized by Manning's 'n'.

3.2.1 Governing Equations

The RMA-2V model formulation is based on the conservation of mass and momentum equations in order to simulate water elevation and two-dimensional velocity. A brief description of the model equations and framework is provided here. A more rigorous presentation of the model is available in the user's manual.

The two governing equations for continuity of mass and momentum focus on three state variables, water elevation (h) and downstream and cross-stream velocity (u and v). To solve for these three variables, three equations are needed. Bottom stress is computed based on the vertically-averaged velocity using an additional equation. The equations are presented below.

1. Continuity

$$\frac{\partial h}{\partial t}+\frac{\partial(uh)}{\partial x}+\frac{\partial(vh)}{\partial y}=0 \qquad \textbf{(3-1)}$$

2. Linear Momentum

a. x-direction (longitudinal) momentum

$$\frac{\partial u}{\partial t}+u\frac{\partial u}{\partial x}+v\frac{\partial u}{\partial y}=-g\frac{\partial(h+a_0)}{\partial x}-C_f q\frac{u}{h}+\frac{1}{\rho}\left(E_{xx}\frac{\partial^2 u}{\partial x^2}+E_{xy}\frac{\partial^2 u}{\partial y^2}\right) \qquad \textbf{(3-2)}$$

b. y-direction (transverse) momentum

$$\frac{\partial v}{\partial t}+u\frac{\partial v}{\partial x}+v\frac{\partial v}{\partial y}=-g\frac{\partial(h+a_0)}{\partial y}-C_f q\frac{v}{h}+\frac{1}{\rho}\left(E_{yx}\frac{\partial^2 v}{\partial x^2}+E_{yy}\frac{\partial^2 v}{\partial y^2}\right) \qquad \textbf{(3-3)}$$

3. Bottom Friction Coefficient

(English Units)

$$C_f=\frac{gn^2}{(1.486)^2 h^{(1/3)}} \qquad \textbf{(3-4)}$$

(Metric Units)

$$C_f=\frac{gn^2}{h^{(1/3)}} \qquad \textbf{(3-5)}$$

where:

h	=	water depth [L]
u	=	vertically-averaged flow velocity in the x-direction (longitudinal) [L/T]
v	=	vertically-averaged flow velocity in the y-direction (lateral) [L/T]
x	=	distance in the longitudinal direction [L]
y	=	distance in the lateral direction [L]
t	=	time [T]
g	=	acceleration due to gravity [L/T^2]
a_o	=	bottom elevation [L]
C_f	=	bottom friction coefficient [dimensionless]
n	=	Manning's 'n' channel roughness coefficient [T/L$^{1/3}$]
E_{xx}	=	normal turbulent exchange coefficient in the x direction [M/(LT)]

E_{xy}	=	tangential turbulent exchange coefficient in the x direction [M/(LT)]
E_{yy}	=	normal turbulent exchange coefficient in the y direction [M/(LT)]
E_{yx}	=	tangential turbulent exchange coefficient in the y direction [M/(LT)]
ρ	=	water density [M/L^3]
q	=	velocity magnitude = $(u^2 + v^2)^{1/2}$ [L/T].

The Coriolis apparent force and the force imposed by wind stress have been neglected here because these forces are small compared to forces induced by gravitation and friction.

3.2.2 Computational Sequence and Linkages

The hydrodynamic model for the Thompson Island Pool was not incorporated directly in either the HUDTOX model or the Depth of Scour Model because its calculations could be performed independently. As a result, output from the hydrodynamic model needed to be linked to the other models.

The RMA-2V model was first calibrated to the measured hydraulic data for the river, with Manning's 'n' as the primary calibration parameter. River data, such as river stage-discharge relations for the upstream (Lock 7) gaging station, were used to calibrate the model. Other data, such as velocity measurements made by the USGS during high flow events, were also used to validate the model results.

The specific steps used in the modeling procedure to provide information to the other models are as follows:

1. The flow field, velocity and depth for each node were calculated using the RMA-2V model for a range of flow conditions, and bottom shear velocities (u^*) were computed from depth and vertically-averaged velocity.

2. The Depth of Scour Model calculates the bottom shear stress from the bottom shear velocities using the relation:

$$\tau = \rho \left(u^*\right)^2$$

3. Intersegment flows between the larger HUDTOX segments were defined by integrating velocity field results from the hydrodynamic model at the various corresponding nodes.

3.3 AVAILABLE DATA

The hydrodynamic model RMA-2V requires specific input data describing the hydraulic conditions of the system chosen for simulation. These input data consist of the grid used for the computation, Manning's 'n' to parameterize the bottom friction, the forcing functions or upstream boundary conditions, and the downstream and side-channel boundary conditions. These are described below.

3.3.1 Model Grid

The RMA-2V model uses a six-node triangular element scheme to describe the physiography of the TIP system. The model grid consists of approximately 6,000 nodes defining 3,000 elements. Each node is defined by an x-y coordinate and its corresponding elevation. The depth associated with each grid node for the main channel is based on the bathymetric survey performed by General Electric in 1991 (O'Brien & Gere, 1993b). Figure 3-2 shows the finite element grid used in the model calibration. The finite element grid in the floodplain was constructed using elevations taken from the USGS topographic maps. As seen in Figure 3-2, the grid in the floodplain is much coarser than in the Thompson Island Pool channels. This is justified because velocities in the floodplain are much smaller than in the Pool channels and do not vary as much. The nodes of the finite element grid in the main channel are located approximately every 50 feet across the River (laterally) and approximately 300 feet along the channel (longitudinally).

During the course of model calibrations and runs, it was necessary to refine the grid so that the water mass was conserved at the various transects corresponding with HUDTOX segment boundaries. Conservation was achieved within a few percentage points for each transect. This level of accuracy was sufficient to allow post-processing of the RMA-2V results to meet the mass balance of water requirements for the HUDTOX model without significantly affecting the routing of advective flows through segments in the Thompson Island Pool. The refining of the grid consisted of eliminating isolated nodes along the sides of the flow and smoothing the bottom elevations. These changes were minor and had little impact on the calculated overall velocity field.

3.3.2 Manning's 'n'

The input parameter, Manning's 'n', expresses the river's hydraulic resistance to flow. Conceptually, resistance to flow reflects the character of the sediments and the nature of the flow pathways. This parameter is commonly a calibration parameter, because its value cannot be determined accurately from a measurement of the physical dimensions of the river or from a description of the sediment type. Two site-specific hydraulic flow modeling studies, Zimmie (1985) and FEMA (1982), had been conducted previously; the Manning's 'n' values can be expected to be near the values used in these studies. Table 3-1 contains the Manning 'n' values used in these two studies.

For this study, the values of Zimmie were used initially and subsequently calibrated to best fit the recorded observations of the river, especially those at high flow. The sensitivity of the model to changes in this parameter is discussed below in Section 3.6.1.

3.3.3 Boundary Conditions

The principal input to the model is the upstream boundary condition, the incoming flow. The model was run for the eight different flows at Fort Edward shown in Table 3-2. The first four flows are of interest because the concentration of suspended sediment in the river was sampled when they occurred. The fifth flow is of interest because it is the highest flow recorded in TIP after the Fort Edward dam was removed in 1973. The final three flows are of interest because

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they represent high flow events with a specified return period. The model results for these eight flow simulations were used in the DOSM to develop relationships between river flow and cohesive sediment resuspension.

Other boundary conditions of the model consist of the side-channel boundary condition and the downstream water elevations. The side-channel boundary condition is the requirement that the velocity normal to the sides of the channel be zero. This is implicitly performed in the RMA-2V model. The downstream boundary condition consists of specifying the water surface elevation at the most downstream transect, which is the Thompson Island Dam. The downstream boundary must be specified as an elevation in order to incorporate the backwater effects of the dam into the model.

The downstream boundary surface elevation was taken from the rating curve for USGS Gage 118, which is located just above Thompson Island Dam. The rating curve was developed from a regression analysis performed on the discharge-water level data accumulated during the 11 year period of 1983 to 1993 (USEPA, 1997). Examination of this rating curve showed that the regression is good for flows up to 30,000 cfs; however, the third-order polynomial developed in the regression fails to accurately predict increasing river elevations for flows above 30,000 cfs. Refined extrapolation using best engineering judgment and a theoretical rating curve (Zimmie, 1985) was used to determine the water levels at Thompson Island Dam above these flows.

3.4 Hydrodynamic Model Calibration

The hydrodynamic model calibration approach consisted of specifying an appropriate value for the turbulent exchange coefficients based on literature values and then varying the Manning's 'n' so that computed river levels agree with elevations from the upstream rating curve. The agreement with the upstream rating curve was assessed for each flow input at the most upstream transect of the grid. Note that only one value of Manning's 'n' was used for the entire length of the main channel, because there are no physical data on which to base a variation of Manning's 'n'. The upstream rating curve used for comparing to model output during calibration was USGS Gage 119, near Lock Number 7, which is near the southern tip of Rogers Island (Figure 3-1).

Because the calculation of velocity is of primary interest for larger flows on the Hudson River, the calibration first focused on the flow of 30,000 cfs, which is the highest flow for which the rating curves for both USGS Gage 119 (upstream) and USGS Gage 118 (downstream) are substantiated. The Manning's 'n' values were calibrated for 30,000 cfs and were then used in the model to predict water elevations for lesser flows. These predicted water elevations were then compared with the elevations from the Gage 119 elevations.

The turbulent exchange coefficients were set to 4,790 Pa-sec (100 lb-sec/ft^2) which is within the range of longitudinal turbulent dispersion (K_{ij}) values measured in a variety of rivers (Fischer et.al., 1979). The measured dispersion numbers can be directly translated into turbulent momentum exchange coefficients, since for most turbulent flows the turbulent Prandtl number (E_{ij}/K_{ij}) equals 1.0 (Tennekes and Lumley, 1972).

As described above, the model was primarily calibrated for the flow of 30,000 cfs. The Manning's 'n' values for the final calibration were 0.020 for the main channel and 0.060 for the floodplain. The model computed the same river water surface elevation as was observed at Gage 119 using these Manning's 'n' calibration values. Table 3-3 shows this result, along with the comparison of model output vs. rating curve water levels for lesser flows. The elevations in the table are listed in feet relative to the National Geodetic Vertical Datum (NGVD).

Comparing the last two columns in Table 3-3 shows that the model's results are slightly higher than the rating curve for the smaller flows, implying that the calibrated Manning's 'n' might be somewhat low for the lower-flow cases. It is possible that the rating curve used in the calibration was biased at either low or high flow, making calibration difficult across the entire flow range. Nevertheless, it was judged that a higher value could not be justified, given the model's close fit for 30,000 cfs, (a higher Manning's 'n' would unacceptably increase the model's prediction of the upstream water surface in that case).

The excellent model fit at the calibration flow of 30,000 cfs, along with good results from two validation exercises described below, provide confidence in using the model to simulate high-flow events.

3.5 Hydrodynamic Model Validation

There were two additional and independent sources of information used to verify the calibration results. The first source is the Hudson River velocity measurements made in the Thompson Island Pool by the USGS. The second source is the flood study conducted by FEMA. A comparison of model results with these sources of information is discussed below.

3.5.1 Rating Curve Velocity Measurements

The USGS periodically measures the flow in the Hudson River in the Thompson Island Pool to develop and update the river's rating curves. For the rating curve located at Scott Paper, which is upstream of Rogers Island, the flow is measured by measuring the depth and velocity at numerous points over the cross-section of the river at Rogers Island. These data are taken at the bridges over the Hudson River on both sides of Rogers Island. The model's simulated velocities can be compared to these measured velocities as a check on the accuracy of the model.

The model was run for the discharge (29,800 cfs) that was measured on April 18, 1993. The velocities computed by the model for locations along the cross-section of the river were approximately equal to or slightly lower than measured. For example, the river velocities measured in the middle of the channel by the USGS were approximately 4.3 feet per second (fps), while the model computed velocities of approximately 4.1 fps. These values are sufficiently close for validation. It should be noted that since the velocities were measured from a bridge, it is to be expected that the measured velocities are slightly higher than the computed ones, since the bridge piers will cause a localized acceleration in the flow. Constraints on model resolution inhibit the ability to capture these localized effects on the flow.

3.5.2 FEMA Flood Studies

The Federal Emergency Management Agency (FEMA) regularly conducts studies to predict the flood elevations in rivers for flows of various return periods. The results of the study conducted by FEMA in 1984 for the Upper Hudson River were used as an additional validation of the credibility of the model. The 100-year flow used by FEMA (52,400 cfs) is greater than the 100-year flow used in this study (47,330 cfs) so that a direct comparison of 100-year flood elevations was not initially possible. Estimates of the 100-year flow magnitude are different due to use of different datasets and estimation methods. However, the model was also run for the 100-year FEMA flow of 52,400 cfs, and the model predicted a river elevation at Fort Edward of 130.4 ft. NGVD (National Geodetic Vertical Datum, formerly Sea Level Datum of 1929). The FEMA flood study using the HEC-2 program predicted a river elevation of 130.7 ft. NGVD. These results are comparable considering that the two models reflect a slightly different representation of the river hydraulics.

The RMA-2V model developed here was also run for 52,400 cfs with a Manning's 'n' of 0.030 for the main channel and 0.075 for the floodplain (approximately the same as the FEMA study). This resulted in a predicted river elevation of 131.7 ft. Most importantly, the river velocities do not vary appreciably for the various representations. Therefore, the model results are judged to be comparable to those produced from the FEMA flood study.

3.5.3 100-Year Peak Flow Model Results

The model was used to simulate the 100-year peak flow of 47,330 cfs. The predicted river elevation at the downstream tip of Rogers Island was 128.6 ft. This elevation is slightly lower than the extrapolated rating curve's elevation of 129.1, but is reasonably close.

The vertically-averaged velocity field produced by RMA-2V for the 100-year peak flow is shown in Figure 3-3. The velocity magnitudes are reflected by the length of the vectors in accordance with the scale provided near the bottom of the figure. The vectors in the floodplain that have no visible tail indicate slow moving water in the overbank area. A vector was printed where the water depth was greater than zero, even if the velocity was small, to indicate the extent of the flow.

The RMA-2V velocity field was used to compute the shear stresses in the DOSM within the normal river banks of the Thompson Island Pool, not in the floodplain. Floodplain simulation was only included to ensure an appropriate representation of the in-river, vertically-averaged velocity field.

3.6 Hydrodynamic Model Sensitivity Analyses

The sensitivity of the model to the principal inputs was evaluated by varying the finite element grid size, the Manning's 'n', and the turbulent exchange coefficient. The model's sensitivity to the grid size was checked by running the model for a flow of 40,000 cfs with a finite element grid having approximately two times the number of elements as the baseline finite element grid. The results obtained with the larger grid resolution were essentially the same as the smaller grid and, therefore, it was concluded that the finite element grid used here was of sufficient resolution to simulate the river flow. The sensitivity of the model to the Manning's 'n' and the turbulent exchange coefficient was measured by the effect on the predicted water elevations for the 100-year peak flow at the downstream tip of Rogers Island (Gage 119). The sensitivity results are presented in the following discussion.

3.6.1 Manning's 'n'

The Manning's 'n' was varied from 0.015 to 0.035 for the main channel and 0.040 to 0.080 for the floodplain. These values of 'n' are consistent with what has been previously used for this reach of the Hudson (Zimmie, 1985; FEMA, 1982), and with literature values (Chow, 1959; Hicks and Mason, 1998). The model was run for the 100-year peak flow of 47,330 cfs; the results are contained in Table 3-4. These results indicate that changes in Manning's 'n' do not significantly affect results from the calibrated model. It is also evident that the main channel Manning's 'n' generally affects the results much more than the floodplain Manning's 'n', as would be expected because most of the flow occurs in the main channel. The model insensitivity to Manning's 'n' is due to the fact that the flows are large and the system is strongly forced. The accurate prediction of stages and velocities in this flow regime depends more on having an accurate representation of the depth of the main channel and the flood plains.

3.6.2 Turbulent Exchange Coefficient

The four turbulent exchange coefficients, E_{xx},, E_{xy}, E_{yx}, and E_{yy} were all set to a value of 4,790 Pa-sec (100 lb-sec/ft^2) in the baseline run. Table 3-5 shows the effects of varying these turbulent exchange coefficient values on the water surface elevation at Rogers Island.

It can be concluded that variations in turbulent viscosities do not affect the river elevation dramatically, especially evidenced by the small increase in the river elevation for each doubling of the coefficients. The model predicts higher elevations for higher turbulent exchange coefficients in much the same way that it would predict higher elevations with a larger Manning's 'n'. Both the Manning's 'n' and the turbulent exchange coefficients parameterize energy loss in the system. This means that if higher turbulent exchange coefficients were used in the calibration, then a lower Manning's 'n' would be required to obtain an equally good agreement with the observed rating curve. Given these results, it was judged that a turbulent exchange coefficient of 100 lb-sec/ft^2 was reasonable and that further calibration was not required.

3.7 Conversion of Vertically-Averaged Velocity to Bottom Shear Stress

Conversion of the vertically-averaged River velocities, as obtained from the RMA-2V model, to bottom shear stresses is required to compute resuspension of Thompson Island Pool bed sediments in the DOSM and HUDTOX models. Several formulations were investigated. One of these formulations computes shear stress directly from the vertically-averaged velocity, while the other three provide computed values of bottom shear velocity, $u*$, for use in computing shear stress as $\tau = \rho \left(u^*\right)^2$. The four methods, with a short description of each, are presented below.

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1. Smooth wall log velocity profile

This conversion method (Thomas and McNally, 1990; Schlichting, 1979) derives from the assumption that the vertical velocity profile at any point in the river conforms to the "smooth wall log velocity profile". The following equation describes this velocity profile:

$$\frac{u}{u^*} = 2.5\ln\left(\frac{3.32 u \mathrm{d}}{\nu}\right) \qquad \textbf{(3-6)}$$

where:

u	=	vertically-averaged velocity [L/T]
u^*	=	shear velocity [L/T]
d	=	depth of flow [L]
ν	=	kinematic viscosity [L^2/T].

The applicability of this relation to the Upper Hudson River is suspect, because it is known that the bottom of the river is not hydraulically smooth.

2. Gailani Method

This empirical method was used by Gailani (Gailani et al., 1991) for the Lower Fox River, as follows:

$$\frac{\tau_b}{\rho_0} = 0.003\, u^2 \qquad \textbf{(3-7)}$$

where:

τ_b	=	bottom shear stress [M/L/T^2].
ρ_0	=	reference density [M/L^3].

3. Rough wall log velocity profile

$$\frac{u}{u^*} = 6.25 + 2.5\ln(\mathrm{d}/\mathrm{k}) \qquad \textbf{(3-8)}$$

where:

u	=	vertically averaged velocity [L/T],
u^*	=	shear velocity (friction velocity) [L/T],
d	=	depth of flow [L],
k	=	equivalent Nikuradse roughness [L].

This relation (Thomas and McNally, 1990) describes the velocity profile for a rough wall river flow, which is typically the condition for river flows. The only free parameter for this equation is k, the roughness factor. This parameter can be estimated from the Manning's roughness (Chow, 1960): for 'n' = 0.02, k was determined to be 0.04 feet.

4. Manning shear stress equation

The fourth formulation, the Manning shear stress equation was selected for use in the Depth of Scour Model. It involves a combination of the cross-section average velocity and bottom shear stress equations (Thomas and McNally, 1990). Specifically, the bed shear velocity is expressed as:

$$u^* = \frac{\sqrt{g} \cdot u \cdot n}{(1.486)d^{1/6}} \qquad \text{(English Units)} \qquad \mathbf{(3\text{-}9)}$$

$$u^* = \frac{\sqrt{g} \cdot u \cdot n}{d^{1/6}} \qquad \text{(Metric Units)} \qquad \mathbf{(3\text{-}10)}$$

The channel average velocity is defined from the one-dimensional Manning equation, which is given below, as:

$$u = \frac{1.486}{n} R^{2/3} S^{1/2} \qquad \text{(English Units)} \qquad \mathbf{(3\text{-}11)}$$

$$u = \frac{1}{n} R^{2/3} S^{1/2} \qquad \text{(Metric Units)} \qquad \mathbf{(3\text{-}12)}$$

The definition of the cross-sectional average shear stress (τ_0), can be written as,

$$\tau_o = wRS = \rho\, gRS \qquad \mathbf{(3\text{-}13)}$$

where:

u	=	channel averaged velocity [L/T],
n	=	Manning's 'n' [$T/L^{1/3}$] ,
g	=	acceleration due to gravity [L/T^2],
ρ	=	density of fluid [M/L^3]
w	=	weight of the water (ρg) [$M/L^2/T^2$],
R	=	hydraulic radius [L],
S	=	the slope of the river [dimensionless].

The definition of the friction velocity u^* can be combined with Equation 3-13 to yield;

$$u^* = \sqrt{\frac{\tau_0}{\rho}} = (gRS)^{1/2} \qquad \mathbf{(3\text{-}14)}$$

For flow in a wide open channel, the wetted perimeter is approximated by the depth (R ≈ d). Combining this assumption with Equations 3-12 and 3-14 will yield Equation 3-10.

Results comparing the model calculations using the four different methods are presented in Figure 3-4, which shows the variation of shear stress with the average vertical velocity among methods. In Figure 3-4, the depth used to calculate the conversion for methods 1,2 and 4 was 10 feet. As seen in Figure 3-4, Method 1, the smooth wall velocity profile, and Method 2, the Gailani method, yield the smaller shear stresses, especially at higher flows. Methods 3 and 4, the rough wall and Manning's methods respectively, yield appreciably higher values for stress at high velocity flows. Method 4 (Manning's) was chosen to estimate shear stress because it is consistent with the RMA-2V approach, and it provides the most critical (highest) estimates of bottom shear stress for the DOSM.

The shear stress field for the Thompson Island Pool 100-year peak flow, as computed by the Manning method using the velocity field shown in Figure 3-3, is plotted in Figure 3-5. Maximum stresses are observed in the flood plain, which is to be expected since the depths of the flow are smaller and the Manning's 'n' is 0.06, compared to 0.02 in the main channel.

3.8 Discussion of Results

The calibrated RMA-2V model is a good representation of Thompson Island Pool hydraulics for various flow regimes. This conclusion is based on the good agreement found between model output for water levels and rating curve results at Lock 7, and the good agreement between model output for velocities and those measured by the USGS. The model's ability to simulate flows well above the calibration flow, 30,000 cfs, is supported by the reasonable agreement between the 100-year peak flow predictions by this model and the FEMA model, and also by the lack of sensitivity of high-flow results to changes in internal model parameters.

The sensitivity analyses show that the RMA-2V model is not appreciably sensitive to changes in the calibration parameters. However, the analysis of the conversion of the flow field output (vertically-averaged velocity and depth) to river- bed shear stress shows that shear stress can vary significantly at high flow, depending on the conversion method used. The lower bound estimate for the smooth wall profile is not applicable. However, the other three methods are potentially valid and provide similar results. The most conservative method, that method which predicts the largest shear stress given the magnitude of the vertically-averaged velocity, was chosen to provide shear stress to the DOSM. However, overall differences among the three methods are approximately less than 30 percent.

4. THOMPSON ISLAND POOL DEPTH OF SCOUR MODEL

4.1 OVERVIEW

The Depth of Scour Model (DOSM) is a two-dimensional model of sediment erosion depth that was applied to Thompson Island Pool. This model was developed as a stand-alone tool specifically to address one of the three principal study questions:

- Are there contaminated sediments now buried that are likely to become "reactivated" following a major flood, possibly resulting in an increase in contamination of the fish population?

The DOSM formulations were also integrated into the HUDTOX mass balance model, providing consistency between these two models in Thompson Island Pool for cohesive sediment resuspension.

The DOSM has different formulations for cohesive and non-cohesive sediment scour. Cohesive sediment scour is calculated on the basis of site-specific measurements of resuspension properties for Thompson Island Pool cohesive sediments. Non-cohesive sediment scour depth is computed via formulations available in the scientific literature, using sediment physical property data for the Pool. Scour depth calculations in each sediment type for the Thompson Island Pool are based on the depth of scour equations, linked to steady-state hydrodynamic model predictions of overlying water velocity (Chapter 3).

The cohesive scour depth calculations are probabilistic estimates. The 5th to 95th percentile estimates were used to define the "likelihood" that buried contaminated sediments are reactivated in a flood. However, the mean estimate at each location is used in HUDTOX transport and fate simulations. For non-cohesive scour depths, only a singular theoretical estimate is available. Both cohesive and non-cohesive estimates assume that the flow condition of interest persists long enough to achieve the estimated scour depth. For cohesive sediments, laboratory observations show that maximum scour will occur within approximately one hour for all flow conditions. The time to maximum scour cannot be determined for non-cohesive sediment in the DOSM framework and hence, the model calculations are viewed as an upper bound.

The DOSM is used to answer the principal study question presented above by estimating probable ranges of sediment scour depth expected in cohesive sediment areas with the occurrence of a 100-year flood event in Thompson Island Pool. These depth of scour ranges are compared to vertical PCB sediment concentration profiles at five specific locations. Additionally, these ranges are used to estimate PCB mass and sediment eroded from cohesive sediments through a poolwide application of DOSM. Cohesive sediment areas are of special interest relative to the non-cohesive sediment areas due to their higher levels of contamination. Observed PCB hotspots generally coincide with cohesive sediment areas and exhibit the highest buried PCB concentrations.

The DOSM cohesive sediment resuspension algorithms are also used in the HUDTOX mass balance model (described in Chapter 5). Although the DOSM does not account for transport or redeposition of scoured sediment and PCBs, the HUDTOX mass balance model does. The HUDTOX model incorporates cohesive sediment resuspension algorithms obtained through application of the DOSM model to a range of flow conditions. Median values were used from the probabilistic DOSM model application. Equations were developed to relate the predicted cohesive sediment mass scoured to flow at Fort Edward for each HUDTOX cohesive sediment segment in Thompson Island Pool. Through this approach, consistency between the DOSM and HUDTOX models is achieved for cohesive sediment resuspension. In contrast to cohesive sediments, time to maximum scour for non-cohesive sediments is uncertain. Therefore the DOSM non-cohesive sediment scour depths were viewed as an upper bound estimate, with actual resuspension values calibrated in HUDTOX.

The findings from the Depth of Scour Model application show that the expected impact of a 100-year flood on surface sediment PCB concentrations in the Thompson Island Pool is small because computed scour does not expose higher concentrations of PCB in the sediments. Results suggest that the 100-year event is not an important concern from the standpoint of a potential remediation decision for PCBs in the Thompson Island Pool. Specific findings are presented at the end of this chapter. These findings were corroborated by HUDTOX simulation of long-term response to a 100-year peak flow, presented in Chapter 8.

The following major sections are included in Chapter 4:

4.2 DOSM Model Development

4.3 DOSM Parameterization

4.4 DOSM Application

4.5 Major DOSM Findings

Section 4.4 presents results of the DOSM estimates regarding depth of scour, likelihood of "reactivating" buried PCBs at the five high resolution core locations, and an estimate of the mass of PCB eroded from cohesive sediment areas due to a 100-year peak flow.

4.2 DOSM Model Development

4.2.1 Conceptual Approach

Two categories of information are necessary to compute the depth of erosion and total mass of solids eroded from bedded sediments for a high-flow event. First, the hydrodynamic conditions at the sediment-water interface need to be specified. The primary forcing function for entrainment of bottom sediments into the flowing water is the shear stress exerted at the sediment-water interface by flowing water. The Thompson Island Pool Hydrodynamic Model yields estimates of vertically-averaged flow velocities at a fine spatial resolution. Bottom shear stresses are computed from the velocities by a simple formula (Section 3.7). Second, the physical-chemical properties of the bedded sediments greatly influence the magnitude and rate of entrainment of sediments for a given event, and the resulting depth of scour. These are specified from data.

Entrainment mechanisms can be classified into two distinct categories based on sediment bed properties. The main parameters affecting the entrainment of non-cohesive sediments include grain size and shape (and their distributions), the applied shear stress, bed roughness, and specific weight. Bed sediments that are primarily fine grained and/or possess a high clay content exhibit interparticle effects that are cohesive in nature. The resulting entrainment properties are very different from non-cohesive sediments. Since the toxic contaminants of interest (PCBs) are associated preferentially with fine grained sediments, this distinction is of considerable importance. Each approach is described separately below.

4.2.2 Formulation for Cohesive Sediments

4.2.2.1 Background

Particle diameter has a significantly lower influence on the entrainment characteristics of cohesive sediments compared to electrochemical influences. Relatively small amounts of clay in the sediment-water mixture can result in critical shear stresses far larger than those in non-cohesive materials of similar size distribution (Raudkivi, 1990). Previous studies on the entrainment of cohesive sediments hypothesize that the scour magnitude is primarily influenced by the excess applied shear stress (i.e., the difference between the applied shear stress and the critical shear stress of the surficial sediments), and the state of consolidation (or age after deposition) of the bed sediments (Partheniades, 1965; Mehta et al., 1989; Xu, 1991). The mass of material resuspended can be expressed in the following functional form:

$$M = f(\tau - \tau_c;\ \text{age, other sediment properties}) \qquad \textbf{(4-1)}$$

where M is the mass of material resuspended, τ is the applied shear stress, and τ_c is the bed critical shear stress. The function f has been expressed in a variety of different forms, including linear, (e.g. Partheniades, 1965), exponential, (e.g. Parchure and Mehta, 1985), and the power relationship, (e.g. Lick et al., 1995; Gailani et al., 1991).

4.2.2.2 Basic Equations

Lick et al. (1995), proposed an erosion equation based on statistical analysis of laboratory and field data. This work forms the basis of DOSM calculations for cohesive sediments and is expressed as follows:

$$\varepsilon = \frac{a_0}{t_d^n} \times \left(\frac{\tau - \tau_c}{\tau_c} \right)^m \qquad \textbf{(4-2)}$$

where:

ε = the net total amount of material resuspended (g/cm^2);
τ = the applied shear stress (dynes/cm^2);
τ_c = the bed critical shear stress (dynes/cm^2);
t_d = the time after deposition (days); and
a_0, n, and m = empirical constants.

The empirical constants a_0, n, and m are obtained through fitting of Equation 4-2 to experimental data. The critical shear stress, τ_c, is also determined through experimentation. The depth of scour can then be calculated as:

$$z_{scour} = \frac{\varepsilon}{C_{bulk}} \tag{4-3}$$

where Z_{scour} is the depth of scour (cm), and C_{bulk} is the dry bulk sediment density (g/cm^3). These equations have been applied to site-specific data for several rivers (Fox, Detroit, and Buffalo) by McNeil (1994).

4.2.2.3 Reparameterization to a Probabilistic Model

The reassessment study asks if buried contaminated sediments are "likely" to become reactivated following a major flood. To address this issue of likelihood, the resuspension formulation was adapted to provide probabilistic calculations of scour, as described below.

If the value of τ_c is assumed to have been defined from resuspension experiments, while the other parameters are unknown, then Equation 4-2 can be reduced from five parameters to two using a dimensionless shear stress parameter, τ':

$$\varepsilon = A \times (\tau')^m \tag{4-4}$$

where:

τ' = $(\tau - \tau_c) / \tau_c$,
A = a_0/t_d^n

Equation 4-4 can be linearized as follows:

$$\ln(\varepsilon) = \ln(A) + m \times \ln(\tau') \tag{4-5}$$

Therefore, a linear regression may be performed to fit a straight line to data for erosion vs. dimensionless shear stress in "log-log" space. The slope obtained from this regression will correspond to the exponent "m" from Lick's equation, while the intercept will correspond to the logarithm of the lumped term a_0/t_d^n. Characterization of the distribution of errors around this regression will allow estimation of the uncertainty in erosion predictions due to uncertainty in measured resuspension properties.

Given a regression line with normally distributed residuals, prediction limits for new observations (for a given value of the independent variable) fall on a Student-t distribution (Neter et. al., 1990). For large sample sizes, the Student-t distribution is approximately normal. Predicted values for new observations are therefore calculated as percentiles of normal distributions, in log-log space. The resulting predicted distribution in ordinary space (again, for given values of shear stress) is log-normal, and is calculated according to Equation 4-6.

$$\varepsilon = \exp\left(A + m \times \ln(\tau') + u\right) \tag{4-6}$$

where:

$$u = Z \times \sqrt{MSE \times \left[1 + \frac{1}{ns} + \frac{(\ln(\tau') - X_{avg})^2}{\sum_i (X_i - X_{avg})^2}\right]}$$

and

τ'	=	$(\tau-\tau_c) / \tau_c$,
exp	=	exponentiation operator
Z	=	a value of the standard normal distribution variable
MSE	=	mean square error of regression
ns	=	number of data used in the regression
X_{avg}	=	mean of the natural log dimensionless shear stresses
X_i	=	a particular natural log dimensionless shear stress value.

Division of the erosion by the bulk density gives the depth of scour in centimeters, as shown in Equation 4-3.

4.2.2.4 Calculation of PCB Erosion

Equations 4-3 and 4-6 define a probabilistic model for predicting bottom cohesive sediment mass erosion and depth of scour as a function of shear stress and sediment physical properties. The model is probabilistic in that it presents a range of depth of scour estimates with associated probabilities based on the variability in experimental resuspension measurements. For a given scour depth, an estimate of the PCB erosion from cohesive sediments can then be estimated as a function of sediment PCB concentration using Equation 4-7.

$$P = \frac{S \times C_{PCB}}{\left(\frac{1000mg}{1g}\right)} \tag{4-7}$$

where:

P	=	quantity of PCBs eroded from cohesive sediments (g)
S	=	mass of solids eroded from cohesive sediments (kg)
C_{PCB}	=	average cohesive sediment surficial PCB concentration (mg/kg).

In a stand-alone application of DOSM used to evaluate the impact of a 100 year peak flow, average surficial sediment PCB concentrations were used to provide a conservative screening estimate of eroded PCB. However, in long-term forecasts with HUDTOX, model simulations of PCB in individual PCB layers was used, rather than surficial averages.

4.2.3 Formulation for Non-cohesive Sediments

4.2.3.1 Background

Net erosion of non-cohesive sediments occurs when the sediment transport capacity of the flow exceeds the actual sediment burden being carried by the flow. A flow will have transport capacity for a *particular* particle diameter (size class) when the shear stress applied to those particles by the flow exceeds the critical shear stress of the particle size class. The transport capacity of the flow is inversely related to the particle size; hence, differential scouring takes place, with the smaller particles being removed in greater proportion than the larger particles. The particle size distribution of the bed surface then shifts progressively towards larger particles. If sufficient large particles are present that cannot be transported under the flow conditions, the bed surface will come to consist primarily of the larger particles, with the smaller particles underneath sheltered from scour. This layer of coarse particles, called the armor layer, may persist until higher flows and their associated shear stresses erode it, causing further coarsening and the establishment of a new armor layer. The armor layer can be degraded by vertical mixing with the parent bed material and replenishment of fine material via deposition from the water column.

4.2.3.2 Equations

Borah (1989) gives equations for the depth of scour that will occur before the establishment of an armor layer. His formulation assumes a well-mixed surface layer with constant particle specific gravity, but different particle sizes. After a scour event and armoring, the result is a single surface layer of the smallest non-transportable particle size. The formulation may be viewed as conservative because the potential for finer particles to be trapped (hiding) in the armor layer is ignored. This means that the mass of sediment scoured to achieve armoring may be high because the fine particles that may be trapped are assumed to be scoured in order to achieve armoring. An active layer thickness is defined as:

$$T = \frac{D_a}{(1-\phi)P_a} \tag{4-8}$$

where T is the thickness of the active layer (cm); D_a is the smallest armor size (cm); ϕ is the porosity of the bed material; and P_a is the fraction of all the armor sizes present in the bed material. D_a is computed using a modified version of the Shields Curve (Shields, 1936; van den Berg and van Gelder, 1993). The scour depth is then computed as:

$$E = T - D_a \tag{4-9}$$

where E is the scour depth (in cm). These equations have been applied and the results validated for laboratory (Little and Mayer, 1972) and field (Karim and Kennedy, 1982) data.

4.2.4 Time Scale of Erosion Estimates

The cohesive sediment scour calculations result in a mass estimate at the peak flow for an event assuming that the event peak shear stress is established essentially instantaneously. Experiments by Lick et al. (1995) indicate that this mass is eroded over the time scale of approximately one hour. The non-cohesive computations provide a mass estimate corresponding to scour down to the armoring depth. However, the time required to reach armoring depth cannot be directly calculated with the available models. Model predictions for non-cohesive sediments should therefore be considered "upper bound" estimates, as they are based upon the assumption that the flood event is of sufficient duration to allow erosion to proceed all the way down to the armoring depth. This upper bound estimate is suitable for determining the likelihood that the buried contamination can be "reactivated", but it is not suitable for direct use in HUDTOX. Hence, non-cohesive sediment resuspension rates in HUDTOX were calibrated.

4.3 DOSM PARAMETERIZATION

4.3.1 Data

4.3.1.1 Distribution of Types of Bottom Sediment

The bedded sediments in Thompson Island Pool were differentiated as cohesive and non-cohesive based on side-scan sonar profiles of fine and coarse sediments (Flood, 1993). The analysis of sonar and sediment data suggested that the results of the 500 kHz digital image (i.e. mean digital number, or DN) can be successfully correlated to mean grain size. It was found that DN values less than about 40 generally correspond to finer grain sizes (mean size less than about 4 phi) while DN values greater than about 60 generally correspond to coarser sediments (coarse sand, gravel). For the purpose of characterizing the sonar images, sediment type is described as "finer" for DN less than 40, or as "coarse" or "coarser" for DN greater than 60.

The sonar maps were qualitatively divided into several categories including "coarse", "coarser", "finer", "island", and "rocky". These maps were digitized into a GIS coverage by TAMS Consultants, Inc. No sediments described as "coarse" were listed for Thompson Island Pool. The two sediment categories considered for this analysis to be significant sources of potentially erodible materials (due to magnitude of area and/or substrate type) were "coarser" – representing non-cohesive sediments – and "finer" – representing cohesive sediments. The area of non-cohesive sediments in Thompson Island Pool is approximately three times that of cohesive sediments.

4.3.1.2 Resuspension Experiments

Data used to parameterize the DOSM for cohesive Thompson Island Pool sediments were obtained from resuspension experiments described in a report by HydroQual (1995). This report contained two different sets of experimental data.

The first dataset came from an annular flume study, wherein sediments from three different locations in Thompson Island Pool were transported to a laboratory at the University of California at Santa Barbara and subjected to two types of experiments involving shear stress. Multiple shear stress tests were conducted by filling the flume with sediment, allowing it to compact for 1, 3, or 14 days with the flume at rest, and running (i.e., rotating) the flume at successively higher levels of shear stress, with steady state suspended sediment concentrations

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achieved (as indicated by concentration measurements at 30 minute intervals) before each shear stress increase. A continuous flow test was conducted by filling the flume with sediment and running it continuously for 47 days at a shear stress of about one dyne/cm^2, except that on several days the shear stress was increased to 5 dynes/cm^2 for two hours. Also, one multiple shear stress test similar to those described above was conducted.

The purpose of these experiments was to investigate the effects of bed compaction and to estimate the value of the critical shear stress, within the framework of the Lick equation, Equation 4-2. Based upon these laboratory flume experiments, HydroQual (1995) concluded that: 1) the critical shear stress was approximately 1.0 dyne/cm^2, 2) the maximum time since deposition (t_d) was 7 days (i.e., after 7 days no further significant bed compaction takes place), and 3) the exponent, n, for t_d was 0.5.

Although laboratory-derived values were used in the DOSM, there are environmental factors that were not accounted for in the laboratory experiments. Critical shear stresses from resuspension can vary seasonally due a number of factors. These include disturbance of sediments by benthic organisms, generation of gases from decomposition of organic matter, and uprooting of macrophytes. Also, the bed surface in the river may be much more varied than the planar surfaces achieved in the laboratory annular flume experiments. Nonetheless, these laboratory data were the best available information.

The second set of sediment resuspension measurements described in HydroQual (1995) consisted of field studies using a portable resuspension device, commonly called a shaker. Surficial sediment cores were collected at 20 cohesive sediment locations in Thompson Island Pool and 8 locations downstream; each location had one (Thompson Island Pool) or two (downstream) sets of three cores each. Each core was subjected to a shear stress in the shaker and the resulting resuspension potential was determined. The field study produced 107 resuspension potential-shear stress data pairs for the Hudson River, with 60 measurements specific to Thompson Island Pool. The shear stresses used in the field study ranged from 5 to 11 dynes/cm^2. Observed sediment erosion rates in Thompson Island Pool ranged from 0.06 to 28.84 mg/cm^2.

From the Thompson Island Pool-specific data, HydroQual (1995) assumed a Thompson Island Poolwide constant value of 3 for m, and back-calculated the core-specific values for a_0 necessary to produce the observed erosion. The methodology used to determine the value for m was not provided. HydroQual reported a mean value and standard deviation for a_0 of 0.071 (in units of mg- day$^{1/2}$/cm^2) and 0.062, respectively, excluding certain results deemed to be outliers.

4.3.1.3 Non-Cohesive Particle Size Distributions

The Borah formulation described above (Equations 4-8 and 4-9) requires sediment data on particle size distribution, particle density, and wet bulk density (to calculate porosity). Unfortunately, a large percentage of the cores had missing or incomplete data for one or more properties. This obstacle was overcome in two ways: 1) missing data on particle density and bulk density were replaced by random deviates from the distributions found for the existing data, and 2) particle size distributions, which were occasionally incomplete on the large-particle end, were extrapolated by plotting the data for each core as ln(size) vs. ln(fraction) and extending the curves smoothly (this was done for 81 cores with data to extrapolate). The distribution used for particle density was normal with a mean of 2.438 g/cm^3 and a standard deviation of 0.262. The distribution used for wet bulk density was normal with a mean of 1.452 g/cm^3 and a standard deviation of 0.212; random deviates greater than 1.8 or less than 1.04 were rejected on the grounds of physical improbability and were replaced with new deviates. Particle size distributions were extrapolated as far as size fraction 2.7 percent or size 20 mm.

The data synthesis procedures (extrapolations and data substitutions) contribute to uncertainty. However, it was judged that more uncertainty would result from ignoring the sample datasets entirely where one parameter was missing.

4.3.1.4 1984 Cohesive Sediment PCB Concentration

The DOSM was used separately from HUDTOX to develop a conservative estimate of PCB mass and associated sediment eroded from cohesive sediment areas in response to a 100-year peak flow. This was accomplished by using the 1984 NYSDEC sediment PCB data from grab samples and coarsely-segmented sediment cores. Surface sediment core sections for these data were on average about 10 inches thick. The mean cohesive sediment surface sediment PCB concentration is approximately 32.5 mg/kg (USEPA, 1998a). This value was applied to the DOSM cohesive sediment elements, which are the same as the hydrodynamic model elements in Figure 3-2. The depth of scour in each element at the 100-year flow was converted to PCB mass eroded using this concentration.

Use of the 1984 median surface concentration results in a conservatively high estimate of PCB mass likely to be eroded under a future 100-year event for the following reasons:

1. The surface concentrations at the present have decreased significantly from those observed in 1984; and

2. The coarse vertical segmentation of the 1984 core samples likely resulted in an over-estimate of mean surface concentrations because peak concentrations are buried.

It should also be noted that the 1984 NYSDEC data do not represent total PCB and therefore do not provide an estimate of total PCB mass eroded. These data more closely represent the sum of the tri- and higher-chlorinated congeners, which is discussed in detail in Section 6.3.3.

Results of the mass erosion estimates from cohesive sediment are presented below in Section 4.4.3.1

4.3.2 Parameterization for Cohesive Sediments

There are several assumptions inherent in the application of Equations 4-3 and 4-6 to the shaker data for parameterization of the DOSM. These include:

- The value for critical shear stress obtained from the annular flume study is constant and applies throughout Thompson Island Pool;

- The sediment cores used in the resuspension studies represent an unbiased random sample of Thompson Island Pool cohesive sediments;

- The experimental shear stress values are exact;

- The statistical model is valid for extrapolation to higher values of shear stress than were used experimentally; and,

- The bulk density, at a specific location, used for converting erosion to depth of scour can be represented as a single number.

All statistical analyses were conducted using SYSTAT® Version 6.0 for Windows® (SPSS, 1996), and only data from Thompson Island Pool were considered. A linear regression of natural log erosion (in mg/cm^2) vs. natural log τ' produced an intercept (A) value of -3.829 and a slope (m) value of 2.906 (Figure 4-1). Of 60 Thompson Island Pool data points, two outliers were deleted; 58 data points were used. The outliers were identified solely on the basis that their Studentized residuals were too large (absolute value greater than 3.0). The regression R-squared value was 0.541, and p-values for both the regression constant and the slope were <0.00001. An analysis of the residuals strongly indicated that they could be assumed to be normally distributed. It was concluded on the basis of these and other statistical indications that the use of linear regression was supported by the data.

The value of 2.906 obtained for m is similar to the value of 3 reported by HydroQual (1995). Assuming from the flume studies that the maximum time since deposition (t_d) was 7 days, and the exponent, n, for t_d was 0.5, the lumped term corresponds to a value of a_0 of 0.0575. This value is well within one standard deviation of the value reported by HydroQual (1995), (Section 4.3.1.2).

4.3.3 Parameterization for Non-cohesive Sediments

The Borah formulation described previously was used to develop a relationship between depth of scour and shear stress for the various size fractions in each core sample. The data points were plotted on a log-log plot. One linear relationship was found for shear stresses below about 5 dynes/cm^2, and another for shear stresses above 5 dynes/cm^2 (Figure 4-2).

Data for determining particle size distributions are not available throughout Thompson Island Pool, but shear stresses are available on a fine scale. A predictive relationship between armoring depth and shear stress was sought. Assuming that the core particle size distributions are typical of particle size distributions throughout Thompson Island Pool, the relationships between armoring depth and shear stress discussed above can be considered predictive, even where the particle size distribution is unknown. Therefore, a linear regression was performed to fit the 355 data points above 5 dynes/cm^2 (shear stresses lower than 5 would not be, of course, as significant in producing erosion) to Equation 4-10.

$$\mathbf{ln}(Depth, cm) = A + m \times \mathbf{ln}(ShearStress, dynes/cm^2) \qquad \textbf{(4-10)}$$

A constant (A) value of -1.6335 and a slope (m) value of 1.2407 were found. The R-squared value was 0.5, and the p-values were less than 0.00001. The spread around the regression line is considerable, encompassing approximately two orders of magnitude. This is not unexpected, since a similarly large spread was observed for the cohesive sediment correlation. The graph of armoring depth vs. shear stress, with the regression line shown, is provided in Figure 4-2.

4.4 DOSM APPLICATION

4.4.1 Application Framework

An ARC/INFO-based Geographical Information System (GIS) (ESRI, 1997) was utilized to associate sediment and hydrodynamic properties with geographic locations and areas in Thompson Island Pool. Computations made use of shear stresses estimated at the nodal locations where flow field information was available from the Thompson Island Pool Hydrodynamic Model (Chapter 3). The sediments were spatially differentiated into cohesive and non-cohesive areas, as described in Section 4.3.1, with separate analyses conducted for each sediment type.

It is important to note that the DOSM, as a stand-alone model, has not been designed to simulate the subsequent transport and redeposition of eroded sediments. It evaluates only the mass of bottom sediments potentially mobilized at a specified peak flow. The HUDTOX mass balance model includes a dynamic representation of solids and PCB transport and fate in the water column and bedded sediments.

The DOSM was used to develop relationships between river flow and cohesive sediment resuspension in Thompson Island Pool that were subsequently used in the HUDTOX model to compute flow-dependent cohesive sediment resuspension. Details of the development of these equations are presented in Section 5.2.3.2. The relationship between the DOSM and HUDTOX ensures internal consistency in representation of flow-dependent resuspension for cohesive sediments between these two models. Use of the non-cohesive sediment scour equations to determine non-cohesive resuspension rates in HUDTOX was not possible due to limitations of the theoretical formulations. As discussed in Section 4.2.4, the non-cohesive armoring equation only represents the maximum potential scour and the actual armoring depth depends on the dynamic characteristics of the flood hydrograph.

4.4.2 Probabilistic Model Application to High Resolution Coring Sites

As discussed above, a Monte Carlo approach was used to assess probability of sediment scour depths based on the variability in site-specific measurements of cohesive sediment resuspension properties. This was done specifically for cohesive sediment locations where USEPA collected high-resolution sediment core PCB profiles, and the range of probable scour depths was compared to these profiles to assess the likelihood that higher PCB concentrations would be uncovered in response to scour under a 100-year flow event. Probabilistic calculations were not conducted for non-cohesive sediments because the method already provides an upper-bound calculation.

As part of the Phase 2 monitoring program, sediment cores were taken at five locations in areas containing cohesive sediments in Thompson Island Pool, and analyzed at a high vertical resolution. These sediment cores exhibited fairly high long-term sediment burial rates and showed peak PCB concentrations in excess of 2,000 ug/g (dry weight). Core collection locations were specifically established in highly depositional areas of the River. Although these five locations are not necessarily representative of PCB profiles in cohesive sediments in the entire Pool, they were used because each site contained detailed measurements of sediment physical-chemical properties that were required for a finely resolved analysis of resuspension potential. Location-specific inputs consisted of predicted shear stress at each coring location and sediment bulk density measured for each core. Table 4-1 lists location-specific input data for each of the five cores. For depths greater than 2 cm, core average values of dry bulk density were used for calculating depths of scour.

Table 4-2 contains summary results for each of the five sediment core locations. The predicted median depths of scour for the five locations, shown in the second column of Table 4-2, range from less than 0.08 (HR-19) to almost 4 cm (HR-25). The third and fourth columns in Table 4-2 show the range of predicted scour depths encompassing the middle 90 percent of expected values (i.e. 5th to 95th percentile) for each core location. By comparing the depth of scour estimates in Table 4-2 with the input data in Table 4-1, one can see that bottom shear stress is a very strong determinant of erodibility in these cohesive sediments.

The median predicted depth of scour provides information on quantities of solids that can potentially resuspend during an event; however, this information alone does not define the quantity of PCBs that can potentially resuspend. The last column in Table 4-2 contains the observed depth of the total PCB peak at each of the five core locations. By comparing median predicted depths of scour and observed depths of PCB peaks, a more complete picture of potential PCB erodibility emerges. These results are depicted graphically in Figure 4-3, which show the total PCB (as originally measured) profiles with depth for each of the five sediment cores, along with the 5^{th}, 50^{th} and 95^{th} percentile predicted depth of scour for each of the five core locations. Results indicate that Core HR-25 is likely to experience scour of sufficient magnitude to substantially erode the PCB peak at that location. However, even if erosion occurs at the 95^{th} percentile depth, PCB peaks at the other four locations are predicted to be unscoured (i.e. the PCB peaks are likely to stay intact after a 100-year peak flow event).

4.4.3 Poolwide Model Application

4.4.3.1 Cohesive Sediments

Equations 4-3 and 4-6 can conveniently be used to estimate the total mass of solids remobilized from cohesive sediments throughout Thompson Island Pool, and the mean depth of scour in cohesive sediments, by means of a Monte Carlo Analysis. The cohesive sediment areas of Thompson Island Pool were subdivided into polygons of constant shear stress and dry bulk density by intersecting coverages for these properties in the GIS system discussed in Section 4.4.1. The Monte Carlo technique was employed to calculate the depth of scour and the mass scour by randomly varying parameters in the resuspension equation according to variability in the site-specific resuspension measurements. Poolwide results for mass scour were obtained by summing the results at all locations, while an area-weighted average was calculated as the mean depth of scour. The calculation was repeated many times to get a valid statistical distribution of results.

Monte Carlo calculations were performed with the Crystal Ball® computer program (Decisioneering, Inc., 1996). Depth and mass of scour were computed together, with 3,000 repetitions conducted; a sensitivity analysis of the number of repetitions demonstrated that 3,000 repetitions were adequate to produce consistent results. The results were plotted as cumulative percent vs. mean depth of scour or mass of scour, respectively. Expected values for mean depth and mass of scour were estimated by the mean of the Monte Carlo trials and are shown in Table 4-3.

Figure 4-4 shows the results for mean depth of scour. Most of the predictions fall into the range of about 0.3 to 0.4 cm. There is, therefore, a high probability that a future 100-year peak flow would result in a mean depth of scour of between 0.3 and 0.4 cm. Figure 4-5 shows the results for total solids scoured. Most of these predictions fall into the range of about 1,500,000 to 2,000,000 kg. There is, therefore, a high probability that a future 100-year peak flow would result in a mass scour of between 1,500,000 and 2,000,000 kg.

The PCB concentration in Thompson Island Pool surficial sediments was estimated to be 32.5 mg/kg (USEPA, 1998a). Using this concentration value in Equation 4-6 with the above estimate of 1,500,000 to 2,000,000 kg of solids erosion provides an approximate range of gross PCB erosion of 49 to 65 kilograms. This is a conservative estimate due to the use of the 1984 PCB data, as discussed in Section 4.3.1.4. The range of solids scoured represents uncertainty due to variability in sediment properties. This range could be applied to a more recent estimate of surface sediment concentrations to get a more refined estimate of the range of expected PCB mass scoured.

4.4.3.2 Non-Cohesive Sediments

Equation 4-9 was applied using estimated shear stresses in non-cohesive sediment areas. For the 100-year peak flow, the mean, non-area-weighted Thompson Island Pool non-cohesive sediment armoring depth is 13.1 cm. Therefore, 13.1 cm is an estimate of the expected average upper bound erosion from non-cohesive sediment areas in Thompson Island Pool resulting from a 100-year peak flow. Upper bound estimates of erosion at specific non-cohesive sediment locations throughout Thompson Island Pool ranged from 1.5 to 42 cm. This estimate of erosion in non-cohesive sediment areas is fundamentally different from, and not directly comparable to, the above estimates of erosion in cohesive sediment areas. Those cohesive estimates are predictive of the actual erosion expected to occur under the specified conditions, including an uncertainty band for the prediction. It is reasonably certain that the actual erosion would be less than the non-cohesive sediment erosion estimate, perhaps much less. Given the difference in the nature of the estimates, it is not surprising that the 13.1 cm upper bound on the average erosion from non-cohesive sediment areas of Thompson Island Pool substantially exceeds the 0.317 cm expected value of the mean depth of scour from cohesive sediment areas of Thompson Island Pool. If this upper bound scour depth were achieved in non-cohesive sediments, *some* areas *might* result in increased surface sediment PCB concentrations based on observations of the PCB distribution in the various sediment PCB datasets. For example, the 1977 NYSDEC sediment core data and 1991 GE composite core data show that higher PCB concentrations exist below the surface sediment layer in non-cohesive sediments. This can be observed from inspection of Figures 6-34 and 7-21 through 7-23, which present data used in the development of sediment initial conditions and model calibration datasets.

4.5 DOSM FINDINGS

The Depth of Scour Model (DOSM) was developed for Thompson Island Pool specifically to address the likelihood of a 100-year flood event uncovering buried high concentrations of PCBs due to erosion of surface sediments. Two separate applications of the DOSM model were conducted to address this question. These applications found that:

5. A probabilistic calculation of 100-year peak flow scour depths at the five USEPA high resolution sediment coring locations in Thompson Island Pool; and,

6. A conservatively high estimate of total PCB mass eroded during a 100-year peak flow from cohesive sediments in the Pool.

These results lead to the following major findings:

- Predicted scour depths under 100-year peak flow conditions are small and will not result in significant remobilization of buried sediments in Thompson Island Pool cohesive sediments;

- Non-cohesive scour depths could only be computed as an upper bound because the time to armoring is very uncertain and could not be determined in the DOSM framework. If this upper bound were achieved, scour in non-cohesive sediment areas may result in increased surface sediment PCB concentrations in some areas;

- Even at the 95th percentile of scour depth, the 100-year peak flow does not cause scour to elevated PCB concentrations at the high-resolution sediment core locations; and,

- Based on a conservative estimate of the mass of PCBs resuspended under a 100-year peak flow, the 100-year flow will result in only a slightly larger amount of PCBs resuspended than may be expected during typical annual high flow events.

5. FATE AND TRANSPORT MASS BALANCE MODEL DEVELOPMENT

5.1 INTRODUCTION

Chapter 5 describes the development of the Hudson River Toxic Chemical Model (HUDTOX), the principal transport and fate modeling tool in this Reassessment. This chapter presents the conceptual framework and the governing equations for model state variables and process mechanisms as well as details on the computer hardware and software operating environment. The following major sections are included in Chapter 5:

5.2 General Model Approach

5.3 Water Transport

5.4 Solids Dynamics

5.5 PCB Dynamics

5.6 Model Spatial Segmentation

5.7 Model Implementation

5.2 MODEL APPROACH

5.2.1 Introduction

HUDTOX is the principal transport and fate modeling tool in this Reassessment. HUDTOX is a time-variable, three-dimensional mass balance model. It is a fully-integrated representation of solids and PCB concentrations in the water column and bedded sediments. HUDTOX was applied to the entire Upper Hudson River from Fort Edward to Federal Dam at Troy. Because a disproportionate amount of PCB-contaminated sediments is contained in Thompson Island Pool (TIP), and because there is substantially more data available for the Pool HUDTOX included greater spatial resolution for the Thompson Island Pool than for the river downstream of Thompson Island Dam (TID). In the Pool, HUDTOX is two-dimensional in the water column and three-dimensional in the sediments. Between Thompson Island Dam and Federal Dam, it is one-dimensional in the water column and three-dimensional in the sediments.

The principal model application was a long-term historical calibration for a 21-year period from 1977 to 1997 for Tri+ PCBs. Short-term hindcast applications were also conducted from 1991 to 1997 in order to test the long-term historical calibration for several PCB forms (5 congeners, and total PCBs) exhibiting a range of physical-chemical properties (e.g., sorption to solids, Henry's Law constants, molecular weights, etc.). The calibrated model was also used to conduct a validation simulation with an independent dataset acquired in 1998 for the Upper Hudson River. Calibration parameters were not changed in this validation exercise. The calibrated model was then used to conduct forecast simulations for 70-year periods beginning in 1998. These forecast simulations were intended to estimate long-term system responses to continued No Action and impacts due to a 100-year peak flow.

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5.2.2 Conceptual Framework

Three different mass balances are represented in HUDTOX: (1) a water balance; (2) a solids balance; and (3) PCB mass balances. A water balance is necessary because PCB dynamics are influenced by river flow rates and mixing rates. A solids balance is necessary because PCB dynamics are influenced by the tendency of PCBs to sorb, or attach, to both suspended and bedded solids in the river. Finally, a PCB mass balance itself is necessary to account for all sources, losses and internal transformations of PCBs in the river.

HUDTOX represents PCBs in both the water column and bedded sediments. PCBs in each medium are comprised of three phases:

- Truly dissolved;
- Bound to dissolved organic carbon (DOC); and,
- Sorbed to total solids.

Organic carbon is the principal sorbent compartment for hydrophobic organic chemicals in aquatic systems. A time-dependent mass balance was developed for the suspended and bedded solids, and organic carbon fractions were assigned to these solids based on data. Dissolved organic carbon (DOC) was not simulated in the mass balance. Instead, concentrations were held constant in the sediment bed and the water column. These concentrations were developed from site-specific data and specified as model inputs.

HUDTOX computes time-dependent mass balances for two state variables: solids and PCBs (total PCBs, Tri+, and congeners BZ#4, BZ#28, BZ#52, BZ#[101+90], or BZ#138, depending on the particular application). It assumes that within each model spatial segment a local equilibrium exists among the three different PCB phases. It computes the PCB distribution among these phases by applying an organic carbon-based partition coefficient to the organic carbon concentration of each sorbent (dissolved and particulate organic carbon). This local equilibrium assumption allows the mass balance model to compute only a single PCB state variable while still representing the specific process kinetics operating on each PCB phase. For example, only the solids-sorbed PCBs will settle; therefore, the settling velocity determined through the solids mass balance is applied to only the solids-bound phase of PCBs within each spatial segment. On the other hand, only truly dissolved PCBs can exchange across the air-water interface; hence, that process is applied to only dissolved phase PCBs in water column segments at the air-water interface.

Figure 5-1 contains a conceptual diagram for HUDTOX that illustrates PCBs in the water column and surface sediment spatial segments. This diagram displays the three phases into which PCBs can be partitioned, as well as the model processes which are applied to either the whole PCB form or to an individual PCB phase. Thus, each arrow into or out of a given control volume (or spatial segment) represents a distinct source or sink flux process that operates on the PCB state variable and forms its full mass balance equation for that segment. The simultaneous solution of those mass balance equations permits quantification of the relationship between external inputs and within-system concentrations of PCBs over space and time.

5.2.3 Governing Equations

This section presents a summary of the state variables and processes in the HUDTOX mass balance model. The HUDTOX model is a modified version of the USEPA WASP toxic chemical model WASP5/TOXI5. The equations and framework are essentially the same except for two major enhancements; one relates to handling of sediment bed segments under erosion and scour, and the second relates to sediment scour formulations.

The HUDTOX model code was originally developed using an earlier version of the WASP model (WASP4/TOXI4) which was later updated by EPA to reflect coding changes and various enhancements. The primary source for documentation of the updated WASP5/TOXI5 model is Ambrose et al. (1993). This document can be obtained via the Internet by downloading it from the USEPA Center for Exposure Assessment Modeling (CEAM) web site located at "*http://www.epa.gov/epa_ceam/wwwhtml/ceamhome.htm.*" The HUDTOX model description presented in this section is a summarized version of the WASP5/TOXI5 documentation contained in Ambrose et al. (1993). Details are presented for those processes in HUDTOX that were modified from the WASP5/TOXI5 model. Unless specifically noted, the HUDTOX model processes are identical to those in the WASP5/TOXI5 model.

The mass balance for the HUDTOX model accounts for all user-specified material entering and leaving the system by external loading, advective and dispersive transport, settling and resuspension, and physical, chemical, and biological transformations. The generalized HUDTOX mass balance (partial differential) equation for an infinitesimally small fluid volume in three-dimensions is:

$$\frac{\partial C}{\partial t} = -\frac{\partial}{\partial x}(U_x C) - \frac{\partial}{\partial y}(U_y C) - \frac{\partial}{\partial z}(U_z C)$$
$$+ \frac{\partial}{\partial x}\left(E_x \frac{\partial C}{\partial x}\right) + \frac{\partial}{\partial y}\left(E_y \frac{\partial C}{\partial y}\right) + \frac{\partial}{\partial z}\left(E_z \frac{\partial C}{\partial z}\right)$$
$$+ S_L + S_B + S_K \qquad \textbf{(5-1)}$$

where:

C =	concentration of the water quality constituent state variable, mg/L (g/m^3) [M/L^3]
t =	time, days [T]
U_x, U_y, U_z =	longitudinal, lateral, and vertical advective velocities, m/day [L/T]
E_x, E_y, E_z =	longitudinal, lateral, and vertical diffusion (dispersion) coefficients, m^2/day [L^2/T]

S_L = direct and diffuse loading rate, g/m^3-day [M/L^3/T]
S_B = boundary loading rate (including upstream, downstream, sediment, and atmospheric), g/m^3/day [M/L^3/T]
S_K = total kinetic transformation rate; positive indicates a source, negative indicates a sink, g/m^3/day [M/L^3/T].

By expanding the infinitesimally small control volumes into larger adjoining "segments" and specifying transport, loading, and transformation parameters, HUDTOX implements a finite-difference form of Equation 5-1 to solve for the concentration of each water quality state variable over time. A one-dimensional simplification of Equation 5-1 may be expressed by assuming vertical (z-domain) and lateral (y-domain) homogeneity:

$$\frac{\partial}{\partial t}(AC) = \underbrace{\frac{\partial}{\partial x}\left(-U_x AC + E_x A\frac{\partial C}{\partial x}\right)}_{\text{Term 1}} + \underbrace{A\,(S_L + S_B)}_{\text{Term 2}} + \underbrace{A\,S_K}_{\text{Term 3}} \qquad \textbf{(5-2)}$$

where:

A = cross-sectional area, m^2 [L^2]

This equation represents the three major classes of water quality processes:

- Transport (term 1);
- External loading (term 2); and,
- Transformation (term 3).

These processes, which describe the fate of each HUDTOX solids and PCB model state variable, are discussed in the following paragraphs. The finite-difference derivation of the general WASP mass balance equations and the specific solution technique implemented to solve these equations are described in Ambrose et al. (1993).

5.3 Water Transport

The physical transport of water column solids and PCBs in HUDTOX is governed principally by advective flow and dispersive mixing in the water column. Each are described below. Advective water column flows are important because they control the downstream transport of dissolved and particulate pollutants in many water bodies. In addition, changes in velocity and depth resulting from variable flows can affect such kinetic processes as reaeration, volatilization, and photolysis. HUDTOX tracks each separate inflow specified by the user from its point of origin and through each segment until it exits the model network. For each inflow, the user must supply a continuity or unit flow response function (i.e., flow routing) and a time function. For the HUDTOX model, the flow routing information is based upon the RMA-2V results for the Thompson Island Pool two-dimensional water column segmentation grid. The advective flows are simply routed directly through the one-dimensional HUDTOX segmentation existing downstream of the Thompson Island Pool. Representation of short-term transient effects due to storage and drainage were deemed unimportant considering the goal of the HUDTOX model, which was to describe long-term PCB concentration trends.

The flow continuity function describes how various flow inputs are routed throughout the model network. The time function describes the temporal variability of the inflow. The actual flow between segments that results from a given inflow is the product of the time function and the continuity function. If several inflow functions are specified between any segment pair, then the total flow between segments is computed as the sum of the individual flow functions. In this manner, the effect of several tributaries joining, density currents, and wind-induced flow patterns can be described in a simple manner.

Hydraulic relating describing depth and velocity to stream flow are based on formulations developed by Leopold and Maddox (1953) which describe empirical observations of the velocity and depth to stream flow relationship. These relationships, which are used for determining chemical air-water mass transfer rates (gas phase absorption and volatilization), are described in Ambrose et al. (1993). For the Thompson Island Pool portion of the Upper Hudson River, the HUDTOX model coefficients describing this relationship were developed from the RMA-2V hydrodynamic model described in Chapter 3. The relationship for downstream reaches was developed using correlations between surface water elevations and flow (USEPA, 1997). Note that these relationships are only used to affect chemical gain or loss within a water column model segment (through volatilization); they do not affect water volume or advective or dispersive transport of chemicals between model segments.

Dispersive water column exchanges significantly influence the transport of dissolved and particulate pollutants by mixing between water of different concentrations. In rivers, longitudinal dispersion can be an important process in diluting peak concentrations that may result from dynamic (unsteady) loads or spills. Natural or artificial tracers such as dyes, salinity, conductivity or heat (temperature) are often used to calibrate dispersion coefficients for a model network.

The dispersive exchange between HUDTOX segments i and j at time t is given by:

$$\frac{\partial M_i}{\partial t} = \frac{E_{ij}(t) \cdot A_{ij}}{L_{cij}}(C_j - C_i) \tag{5-3}$$

where:

M_i = mass of constituent (state variable) in segment i, g [M]

C = total constituent (state variable) concentration, mg/L (g/m^3) [M/L^3]

$E_{ij}(t)$ = dispersion coefficient time function for exchange "ij", m^2/day [L^2/T]

A_{ij} = interfacial area shared by segments i and j, m^2 [L^2]

L_{cij} = characteristic mixing length between segments i and j, m [L] .

The exchange coefficient may also be expressed as a mass transfer velocity by dividing the dispersion coefficient by the characteristic mixing length:

$$v_{ij}(t) = \frac{E_{ij}(t)}{L_{cij}} \qquad \textbf{(5-4)}$$

where:

$v_{ij}(t)$ = mass transfer rate for exchange "ij", m/day [L/T] .

5.4 SOLIDS DYNAMICS

HUDTOX calculates sediment and PCB concentrations for every segment in a model grid that includes surface water, surficial sediment bed, and underlying sediment bed layers. During simulation, solids are treated as a conservative constituent that is advected and dispersed through water column segments, settles to and resuspends from surficial sediment segments, and moves through the subsurface bed through burial/scour of the surficial bed or through particle mixing. Due to large uncertainties in externally contributed solids loads (see Chapter 6), internal production and decay of water column biotic solids through primary production was not included in the HUDTOX model calibration application to the Upper Hudson River. The contributions of primary production and decay of solids is dwarfed by the high upstream and tributary solids loads.

5.4.1 Solids Gross Settling

HUDTOX differs from WASP5/TOXI5 with respect to gross settling of suspended solids from the water column to the sediment bed in order to capture effective differences in settling characteristics between cohesive and non-cohesive sediment areas. Constant settling velocities (not dependent on flow or other factors) are specified in HUDTOX with different rates specified for cohesive and non-cohesive sediment areas. Settling velocities are constant for each sediment type throughout the river under all flow conditions. This approach was developed to be consistent with the model calibration strategy presented in Chapter 7. The differences between cohesive and non-cohesive settling velocities arise as a result of lower resuspension and higher deposition for cohesive sediment areas relative to non-cohesive sediment areas. Lower resuspension occurs in cohesive sediment areas due to lower flow velocities and shear stress in these areas. Due to the lower flow velocities in cohesive sediment areas, higher deposition occurs relative to non-cohesive areas.

The rationale and approach for specification of the cohesive and non-cohesive settling rates specified for HUDTOX in this RBMR calibration is presented in Chapter 7 of this report.

5.4.2 Cohesive Sediment Flow-Driven Resuspension

The algorithm for flow-driven resuspension of cohesive sediments used in the DOSM (Equation 4-5) was incorporated into the HUDTOX model. Total sediment erosion (ε , mg/cm^2) is incrementally applied to the rising side of the flood hydrograph. Non-linear correlations were developed relating the DOSM-predicted sediment erosion in each segment as a function of flow measured at Fort Edward. Equations of the following form were fit to DOSM results correlating the mass of cohesive sediment erosion to flow:

$$\varepsilon = \alpha_1 + \alpha_2 \times Q_x^{\alpha_3} \tag{5-5}$$

where:

ε = cohesive sediment erosion, mg/cm^2
Q_x = advective flow in 1000's of cfs
α_1 = empirical constant fit to DOSM results, mg/cm^2
α_2 = empirical constant fit to DOSM results, mg/cm^2/1000 cfs
α_3 = empirical constant fit to DOSM results, dimensionless.

The cohesive sediment erosion is converted to an effective resuspension rate (v_{rH}, m/day) in the HUDTOX model over each model time step during the rising side of a flood hydrograph. Computational time steps in the model vary between approximately 5 and 25 minutes. This approach is consistent with observations by Lick et al. (1995) that most resuspendable material is mobilized in approximately one hour.

In the HUDTOX model, resuspension occurring over previous model time steps within an increasing hydrograph is tracked such that total cumulative erosion equals the amount computed using the maximum shear stress during that event. This mass flux tracking occurs in an incremental fashion. The amount eroded during any given model time step being dependent on the change in flow and the cohesive sediment solids concentration (dry bulk density). The total amount of sediment erosion is limited by the maximum predicted erosion (ε_{max}) associated with the peak flow. Flow-driven resuspension effectively stops depleting the existing sediment bed once the peak flow is reached and that cohesive sediment armoring is assumed to have occurred.

HUDTOX also includes a recovery period (t_{rec}, days) in which the maximum erosion constraint prevents subsequent near-term smaller floods from eroding bedded cohesive sediments that have reached an armored condition. Any solids depositing on the sediment bed during the recovery period are allowed to erode based on Equation 5-5, but only to the extent that freshly deposited material is available. Once the recovery period is ended, no differentiation is made between freshly deposited solids and older "bedded" solids in the surficial sediment layer. At this point, all the surficial sediments are again subject to scour based on Equation 5-5 (i.e., armoring of the cohesive sediment bed ceases). Model applications employing the Lick resuspension formulation for cohesive sediments have generally used a recovery or "sediment aging" timeframe of 7 days for the surficial sediment layer (Gailani et al., 1991; Ziegler et al., 1994). Lick et al. (1995) cites a range of 1 to 28 days for the consolidation process (i.e., the consolidation or "aging" of fresh sediments to a condition consistent with sediments lying below this recently deposited material) to take place based on experiments using sediments from various freshwater river systems.

5.4.3 Non-Cohesive Sediment Resuspension

In contrast to cohesive sediments, the DOSM model only provides a single, upper-bound estimate of scour for non-cohesive sediments. The single estimate is characterized as an upper-bound because it occurs when armoring is achieved and is a function of deposition and time over which peak shear stresses are experienced (Chapter 4). Consequently, the non-cohesive scour formulation from DOSM was not incorporated into the HUDTOX model.

The representation of the flow-driven resuspension of non-cohesive sediments in HUDTOX was developed for the calibration strategy presented in Chapter 7. This strategy attempts to describe mean high and low-flow solids dynamics. It is represented in HUDTOX model by specification of a constant high-flow resuspension velocity operative during scouring conditions. Non-cohesive sediment scour is considered insignificant below specified flow thresholds, which are spatially variable in the model. Thus, non-cohesive resuspension rates switch between zero and the specified high flow resuspension rate.

No attempt has been made in HUDTOX to simulate armoring conditions in the non-cohesive sediments. The calibration approach relies on accurately capturing the long-term behavior of the system based on solids burial rates, surface sediment PCB concentration trends, and in-river mass transport of solids and PCBs, rather than description of event dynamics which vary over small time scales. This is consistent with the overall objective of this modeling study presented in Chapter 1. Chapter 7 presents the calibration approach and a discussion of the model parameters specified to simulate non-cohesive resuspension during high flow scouring conditions. These parameters include: the transition flow between scouring and non-scouring conditions for each reach of the river, and the calibrated non-cohesive resuspension rate for scouring flow conditions.

5.4.4 Sediment Bed Particle Mixing

Bioturbation and other physical processes can result in vertical mixing of solids (and sorbed chemicals) within the bedded sediment. Particle mixing rates tend to be site-specific and can vary seasonally due to temperature influences on biological activity (e.g. McCall and Tevesz, 1982). Sediment bed particle mixing is an important model consideration.

Sediment mixing processes are represented in HUDTOX by effective particle diffusion coefficients. The resulting particle diffusion transfer between sediment layers induces a flux of sorbed contaminants between sediment layers in the model. The direction of flux is determined by the concentration gradient between layers. The form of the particle mixing equation is similar to that represented by Equation 5-3, but with the concentration gradient expressed in terms of the solids concentrations (and sorbed chemical concentrations) in the sediment layers across which the flux takes place. Particle mixing rates are not subjected to temperature influences in the model.

The parameterization of particle mixing in HUDTOX requires specification of the depth over which particle mixing occurs and the effective particle diffusion rates between sediment layers. Specification particle mixing depths and particle diffusion rates is presented in Chapter 6 and further developed in Chapter 7.

5.4.5 Scour and Burial

The HUDTOX model uses an improved sediment bed handling approach from that in WASP5/TOXI5. The HUDTOX approach maintains and allows the formation of a distinct vertical chemical profile through the bedded sediments. This modified sediment bed handling routine is a better representation of transport of PCB mass through the sediment bed because it maintains the integrity of the deeply buried sediment layers as burial or scour occurs. The standard WASP5/TOXI5 model can exhibit significant numerical dispersion over long simulation periods, leading to a "smearing" of vertical contaminant profiles.

To insure the maintenance and formation of a distinct vertical profile, the following modifications were made to WASP5/TOXI5: 1) use of a quasi-Lagrangian sediment bed handling routine; and, 2) use of an archival stack of deep sediment layers as a dynamic boundary condition to track PCB mass beneath the computational grid. The following paragraphs describe the implementation of this alternative bed handling through a set of modifications to the WASP5/TOXI5 scour and burial processes.

The revised sediment bed handling routine maintains the integrity of the deeply buried sediment profile as sedimentation and erosion occur. With the revised framework, the surficial sediment layer volume varies over time due to deposition and resuspension. Thus variation continues until either erosion or burial is triggered based on the volume (or equivalently, the thickness) reaching a specified minimum or maximum level. For burial, the trigger is based on a doubling of the surficial sediment thickness. Erosion is triggered by depletion (or near depletion) of the original surficial sediment volume. Essentially, the HUDTOX model bed handling implements a quasi-Lagrangian (or floating frame of reference) approach to burial and scour versus the WASP/TOXI5-based quasi-Eulerian (fixed frame of reference) approach.

Figures 5-2 and 5-3 illustrate the manner in which HUDTOX implements respectively scour and burial of surface sediment segments. In the HUDTOX bed handling framework, burial results in no numerical mixing of chemicals to deeper sediments, because the surface sediment segment is simply split into two and renumbering of the segments is triggered whenever its volume doubles. Erosion of the surface sediments still provides a degree of mixing between the surface sediments and the immediate segment below. The degree of this mixing is dependent on the amount of sediment remaining in a surface segment once it has been effectively depleted. However, no additional mixing occurs through the deeper sediment segments as a result of the HUDTOX bed handling procedure. These deeper segments are subject to renumbering when erosion occurs, but they still maintain their original pre-erosion characteristics. As described in the previous discussion of particle mixing, HUDTOX allows user-specified vertical mixing (via particle mixing and/or diffusion) through the active sediment bed to represent the effects of bioturbation and other processes (e.g., ice scour, propagation of bed load waves, prop wash, etc.) which serve to maintain partially mixed conditions through some depth of the sediment bed. Thus, the degree of vertical "smearing" of sediment concentration profiles is user-controlled, rather than being dependent upon the sedimentation time utilized in the standard WASP5/TOXI5 model framework.

In order to provide long-term tracking of sediment layer PCB concentration, and allow possible future exposure of deeply buried PCBs, a second modification of the WASP5/TOXI5 framework maintains an "archival" stack of deep sediment layers beneath the existing simulated bed segments. A user-defined reserve stack of deep sediment layers can be specified to underlie the existing simulated bed segments with distinct stacks for each surface sediment segment. In essence, the archive stacks provide a dynamic boundary condition for the bottom sediments. The stacks are not part of the computational grid, except to the extent that layers are moved between the stack and the model grid to compensate for burial or erosion of the surface sediment segments. The process of constituent decay is not represented in the archive stack.

When erosion results in a surface sediment segment being depleted, then "renumbering" of the segments is triggered as previously described. Additionally, the top layer of the archival stack is then incorporated within the computational grid as a new bottom sediment segment. During periods of deposition, the surface layer is allowed to grow in thickness (the bed solids density is kept constant) until renumbering is triggered, based on a doubling of the surface sediment volume. The surface segment is then split into two layers and the sediment segments are renumbered accordingly. Additionally, the bottom sediment layer is removed from the computational grid and placed on the top of the archive sediment stack. The archive stack is allowed to grow or shrink as needed in response to burial or erosion of the surface sediment segments. A significant advantage of using the sediment archive stack relates to its minimal effect on the computational requirements and execution speed of the model. This allows for improved vertical resolution of the sediment bed without excessively increasing memory and runtime requirements.

The HUDTOX approach for sediment scour and burial requires that the upper portion of the sediment bed be composed of vertical layers of equal thickness at the beginning of the model computations. This insures that long periods of scour and deposition will not cause changes to the basic physical characteristics (e.g. original volume and thickness) of the surface layer sediments when deposition or scour triggers the bed handling mechanism.

5.5 PCB Dynamics

In the environment, organic chemicals may transfer across the different environmental media (air, water, and sediment) and may be degraded and/or transformed by a number of physical-chemical and biological processes. Cross-media PCB transfer processes within the HUDTOX model framework include equilibrium sorption and volatilization (air-water exchange). PCBs may also be transformed within HUDTOX through degradation as expressed by a first-order rate equation to represent the effect of dechlorination and/or destruction as a net mass loss over time. PCB dechlorination or degradation processes are not represented in the HUDTOX model for this application to the Upper Hudson River. Other chemical transformation processes (hydrolysis, photolysis, and chemical oxidation) are included within the overall WASP5/TOXI5 framework. Detailed descriptions of these processes are contained in Ambrose et al. (1993).

5.5.1 Equilibrium Sorption

Sediment particle dynamics are important in controlling the transport, transformation and fate of PCBs in aquatic systems due to the tendency of PCBs to sorb, or bind, to both suspended and bedded solids (Eadie and Robbins, 1987). Karickhoff et al. (1979) and Karickhoff (1984) have shown that organic carbon is the principal sorbent compartment for hydrophobic organic chemicals, such as PCBs, in aquatic systems. In addition to organic carbon in particulate form, dissolved organic carbon (DOC) can also be an important sorption compartment in determining

PCB fate (Eadie et al., 1990; Bierman et al., 1992). Partition coefficients are used to characterize the distribution of chemical among three apparent phases: dissolved, particulate-bound, and DOC-bound.

The assumption of equilibrium partitioning in a natural system is reasonable when PCB sorption kinetics are rapid relative to other processes affecting water and sediment concentrations. There is some evidence of non-equilibrium conditions in the mainstem of the Upper Hudson River; however, a detailed investigation by USEPA (1997) found that the assumption of equilibrium partitioning was a valid approach for the spatial-temporal scales in the HUDTOX model applications. Section 6.9 provides further information on the available site-specific data for estimating the partition coefficients used for the PCB forms in the HUDTOX model.

The partition coefficients depend upon characteristics of the chemical and the sediments or DOC on which sorption occurs. PCBs are non-polar, hydrophobic, organic compounds. The sorption of these compounds correlates well with the organic carbon fraction (f_{OC}) of the sediment. Rao and Davidson (1980) and Karickhoff et al. (1979) developed empirical expressions relating equilibrium coefficients to laboratory measurements, leading to reliable means of estimating appropriate values. Dissolved organic materials are typically assumed to be composed entirely of organic carbon ($f_{OC} = 1$). The partitioning expressions implemented in the HUDTOX model are:

$$K_p = f_{oc} \times K_{POC} \quad \textbf{(5-10)}$$

$$K_B = 1.0 \times K_{DOC} \quad \textbf{(5-11)}$$

where:

K_p = Solids partition coefficient, L_W/kg_{solid} [L^3/M].

K_{POC} = particulate organic carbon partition coefficient, L_W/kg_{OC} [L^3/M]

f_{oc} = organic carbon fraction of sediment, kg_{OC}/kg_{solid} [M/M].

K_B = DOC-bound partition coefficient, $L_w/kg_{DOC\text{-sorbent material (or DOM)}}$ [L^3/M]

K_{DOC} = dissolved organic carbon partition coefficient, L_W/kg_{DOC} [L^3/M].

The dissolved organic carbon (DOC) partition coefficient, K_{DOC}, is commonly estimated as K_{POC} times a binding efficiency factor based on analysis of field data measurements of each chemical phase.

HUDTOX differs from WASP5/TOXI5 in that it includes temperature-dependent partitioning, as well as segment-specific parameters which allow for both spatial and compartmental (i.e., water column vis-à-vis sediment bed) variations in partitioning. The dependence of partitioning on temperature was developed and presented in the DEIR (USEPA, 1997). The general form of the resulting empirical relationship, applicable to both the particulate and DOC partition coefficients, is represented by:

$$\log K_{p,T} = \log K_{p,25} + tsf \times \left(\frac{1}{T - T_0} - \frac{1}{25 - T_0} \right) \quad \textbf{(5-12)}$$

where:

$K_{p,25}$ = partition coefficient at 25°C, L/kg
T = water temperature, °C
T_0 = Absolute zero temperature (0 °K) = -273.15 °C
tsf = temperature slope factor, °K.

The HUDTOX model can include particle interaction effects on solids partition coefficients using the approach proposed by DiToro (1985). This approach is described in Ambrose et al. (1993). Analysis of site-specific data for the Upper Hudson River indicated that particle interaction effects on PCB partitioning were minimal (USEPA, 1997). Consequently, none of the present HUDTOX applications included particle interaction effects on PCB partitioning.

The total chemical concentration is the sum of the three phase concentrations:

$$C = C_w^{'} n + C_s^{'} M_s + C_B^{'} B \tag{5-13}$$

where:

$C_w^{'}$ = concentration of dissolved chemical in water, mg/L $_{water}$
n = porosity ($Volume_{water}$ / $Volume_{water + solids}$), L_{water}/L
$C_s^{'}$ = concentration of solids-sorbed chemical on a mass basis, mg/kg_{solid}
M_s = concentration of solids, kg_{solids}/L
$C_B^{'}$ = concentration of DOC-bound chemical on a mass basis, mg/kg_{DOC}
B = concentration of DOC, kg_{DOC}/L.

The dissolved fraction f_d is given by:

$$f_d = \frac{C_w^{'} n}{C} = \frac{1}{1 + K_B B^{'} + K_p M_s^{'}} \tag{5-14}$$

The particulate (solids-sorbed) and DOC-bound fractions, respectively f_p and f_b, are given by:

$$f_p = \frac{C_s^{'} M_s}{C} = \frac{K_p M_s^{'}}{1 + K_B B^{'} + K_p M_s^{'}} \tag{5-15}$$

$$f_b = \frac{C_B^{'} B}{C} = \frac{K_B B^{'}}{1 + K_B B^{'} + K_p M_s^{'}} \tag{5-16}$$

where:

$M_s^{'}$ = M_s/n = solids concentration on a water volume basis, kg_{solid}/L_W
$B^{'}$ = B/n = DOC concentration on a water column basis, kg_{DOC}/L_W

These fractions are determined in time and space throughout a simulation from the partition coefficients, internally calculated porosities, simulated solids concentrations, and externally-specified DOC concentrations. Bulk volumetric concentrations for each phase (C_w for dissolved, C_p for particulate chemical, and C_B for DOC-bound chemical) are simply determined from the product of each relative fraction and the total chemical concentration.

5.5.2 Air-Water Exchange

Air-water exchange, or volatilization, is the mass transfer of a chemical across the air-water interface as dissolved chemical attempts to equilibrate with the gas phase concentration of that chemical in the atmosphere. In HUDTOX the air-water mass transfer exchange rate, S_V, is a function of dissolved chemical gradient between the liquid and vapor phase by the following equation:

$$\frac{\partial C}{\partial t}\Big|_{volat.} = S_v = \frac{K_v}{D}\left(f_d C - \frac{C_a}{\frac{H_T}{RT_K}} \right) \tag{5-17}$$

where:

S_V = air-water chemical mass transfer rate, g/m^3/day
K_V = air-water chemical transfer rate, m/day
R = universal gas constant, 8.206×10^{-5} atm m^3/mole °K
T_K = water temperature, °K
H_T = Henry's Law constant at temperature T (°C), atm m^3/mole.
D = depth (m) C_a = atmospheric chemical concentration (g/m^3)

Equilibrium occurs when the ratio of the atmospheric partial pressure of a chemical to its dissolved concentration in the water column equals its temperature-corrected Henry's Law constant. Atmospheric partial pressure is expressed as a boundary condition in HUDTOX and the determination of its value is described in Chapter 6.

HUDTOX employs the same two-layer resistance model (Whitman, 1923) utilized by WASP5/TOXI5 to calculate the air-water exchange rate. This model assumes that two "stagnant films" exist at the air-water interface, bounded by well-mixed compartments on either side. The air-water mass transfer rate is controlled by the combined effect of liquid and gas phase resistance described by the following equation:

$$K_V = (R_L + R_G)^{-1} = \left[K_L + \left(K_G \frac{H_T}{RT_K} \right)^{-1} \right]^{-1} \tag{5-18}$$

where:

K_V = Air-water chemical transfer rate, m/day
R_L = liquid phase resistance, day/m

R_G = gas phase resistance, day/m
K_L = liquid phase transfer coefficient, m/day
K_G = gas phase transfer coefficient, m/day

Diffusion of chemical through the liquid (water) layer is driven by concentration differences, whereas the gas (air) layer diffusion is controlled by partial pressure differences. The Henry's Law constant generally increases with increasing vapor pressure and decreases with increasing solubility of a compound. Therefore, highly volatile compounds that have low solubility are likely to exhibit mass transfer limitations in water (i.e., high liquid phase resistance). Similarly, mass transfer in air is limited (i.e., high gas phase resistance) when chemical compounds are relatively nonvolatile and have high solubility.

Air-water exchange is usually smaller in lakes and reservoirs than in relatively turbulent rivers and streams. Gas exchanges in rivers and river-reservoir systems can also be significantly enhanced by the highly turbulent conditions created as water flows through and/or over dams. The present HUDTOX model does not account for the possible gas exchange losses of PCBs to the atmosphere as water flows through the various run-of-the-river dams along the Upper Hudson River between Fort Edward and Federal Dam at Troy. The significance of gas exchange at dams on PCB dynamics in the Upper Hudson River is evaluated in the data analysis discussions presented in Chapter 6 of this report.

Air-water exchange in HUDTOX is the same as in WASP5/TOXI5 (Ambrose, et al., 1993) with two exceptions that are described in the following paragraphs.

The chemical-specific Henry's Law constant (H) is assumed to describe the equilibrium between the gas phase and dissolved liquid phase at the boundary between the two layers. In HUDTOX, the Henry's Law constants are temperature corrected according to the empirical relationship presented by Achman et al. (1993) in the following equation:

$$\log H_T = \log H_{25} \frac{\left(7.91 - \frac{3414}{(T - T_0)}\right)}{\left(7.91 - \frac{3414}{(25 - T_0)}\right)} \qquad \textbf{(5-19)}$$

where:

H_T = Henry's Law constant at temperature T, atm m^3/mole
H_{25} = Henry's Law constant at 25 °C, atm m^3/mole
T_0 = Absolute zero temperature = -273.15 °C
T = Temperature, °C.

As in WASP5/TOXI5, HUDTOX uses a constant gas film transfer coefficient of 100 m/day, typically applied to flowing waterbodies such as the Upper Hudson River. HUDTOX differs from WASP5/TOXI5 in that it directly adapts the O'Connor-Dobbins oxygen reaeration formula, as opposed to the Covar method which selects rates from a range of formulation (including

O'Connor-Dobbins) depending on predicted water depth and current velocity within a river cross-section to predict a chemical-specific liquid film air-water transfer rate:

$$K_L = \left(\frac{D_w u}{D}\right)^{1/2} \times 8.64x10^4 \tag{5-20}$$

where:

K_L = liquid film air-water transfer rate, m/day
D = water depth, m
u = water velocity, m/sec
D_w = diffusivity of chemical in water, m^2/sec

The O'Connor-Dobbins formula internally adjusts the air-water transfer rate to determine a chemical-specific liquid film rate based on the chemical-specific diffusivity:

$$D_w = 22.0E\text{-}09 / (MW)^{2/3} \text{, as per Ambrose et al. (1993).} \tag{5-21}$$

where:

MW = molecular weight of the chemical, g/mole

A detailed description of the two-layer resistance model used in HUDTOX and WASP5/TOXI5 is contained in Ambrose et al. (1993).

5.5.3 Dechlorination

Although the HUDTOX model framework allows for dechlorination and other degradation processes, these loss processes were assumed to be zero in the HUDTOX model calibration presented herein. Rationale for this approach is presented in Chapter 6. Dechlorination may be accommodated in the HUDTOX model in a variety of ways (e.g., first-order decay) through the use of standard WASP5/TOXI5 degradation mechanisms. However, accurate representation of dechlorination pathways from degradable higher chlorinated PCB congeners to specific lesser chlorinated PCB congeners would be an extremely difficult task to undertake in a modeling effort of this scale. Dechlorination is also not expected to be a significant loss mechanism for PCB mass in the Upper Hudson River for future conditions.

5.5.4 Sediment-Water Mass Transfer of PCBs

In river systems, non-flow dependent sediment-water exchange of contaminants, including PCBs, can result from many different physical and biological processes, which are discussed in Chapter 6. These processes include molecular diffusion in porewater as well as biologically- and hydrodynamically-enhanced transfer of both porewater and particulate phase PCBs to the water column. The net effect is observed as changes in PCB loading to the water column. The individual processes have not been directly measured or quantified for the Upper Hudson River, and not all of them are well understood. The combined effect of these processes is evident, however, in observed concentration changes of PCBs in the water column.

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Non-flow dependent sediment-water mass transfer processes are represented in HUDTOX by effective particulate and/or porewater diffusion mass transfer rates. These rates move porewater and particulate chemical across the sediment-water interface based on concentration gradients of these phases between these compartments. HUDTOX represents diffusive exchanges of dissolved and DOC-bound PCBs between sediment porewater and the overlying water column with a diffusion equation similar to Equation 5-3, but with the concentration gradient expressed in terms of the dissolved and DOC-bound PCB concentrations in the porewater:

$$\frac{\partial M_i}{\partial t} = \frac{E_{ij}(t)\cdot A_{ij}\cdot n_{ij}}{L_{ij}/n_{ij}}\left(\frac{f_{dj}C_j}{n_j} - \frac{f_{di}C_i}{n_i}\right) \qquad \textbf{(5-22)}$$

where:

M_i = mass of chemical constituent (state variable) in segment i, g [M]

C_i, C_j = total chemical concentration in segments i and j, mg/L (or g/m^3) [M/L^3]

$E_{ij}(t)$ = diffusion coefficient time function for exchange "ij", m^2/day [L^2/T]

A_{ij} = interfacial area shared by segments i and j, m^2 [L^2]

Lc_{ij} = characteristic mixing length between segments i and j, m [L] .

f_{d_i}, f_{d_j} = dissolved or DOC-bound fraction of chemical in i and j [dimensionless]

n_{ij} = average porosity at interface "ij", L_W/L (volume of water/volume total solution) [dimensionless]

Depending on the PCB concentration gradients, porewater diffusion may be a source or sink for the water column.

HUDTOX can represent mass transfer of PCBs from the particulate phase in the sediment to the overlying water column, without net mass transfer of associated solids, via application of a mass transfer coefficient applied directly to the particulate phase PCBs in the upper sediment layer.

Specific alternative approaches (i.e., porewater only versus combined porewater and particulate phase transfer) for specifying PCB sediment-water mass transfer exchanges within the HUDTOX model were investigated using data-based mass balances (see Chapter 6), and through the use of model simulations presented in Chapter 7 for a range of PCB forms.

5.6 Model Spatial Segmentation

5.6.1 Water Column Segments

The HUDTOX water column spatial segmentation was developed to capture the effects of the principal factors that influence spatial patterns of water column and sediment PCB concentrations within the Upper Hudson River. A total of 47 water column segments were represented from Rogers Island (RM 194.6) to Federal Dam (RM 153.9) at Troy (Figure 5-4, Parts A through D).

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The criteria for developing the water column segmentation grid were driven by locations of:

- Major tributaries to the Upper Hudson River;
- Lock and dam structures along the river;
- Phase 2 and historical water quality sampling stations;
- USGS gaging stations; and,
- Sediment PCB "hotspots" along the river.

Hydrographic survey data collected by GE during 1991 (O'Brien & Gere, 1993b) were used to estimate HUDTOX model segment cross-sections. The TAMS/Gradient Team also conducted hydrographic measurements within a portion of the Upper Hudson River; however, the GE data provides more complete coverage. No significant differences were found between the two datasets in reaches of the river covered by both surveys, including Thompson Island Pool. Consequently the GE data were used exclusively in determining river cross-section geometry for HUDTOX.

A two-dimensional segmentation for the water column was developed within Thompson Island Pool to better resolve potential differences in impacts from cohesive and non-cohesive sediment areas. The 28 water column segments within the Pool are configured as three lateral segments across the river, except at Rogers Island, with longitudinal resolution on the order of ½ to ¾ of a mile (Figure 5-5). At Rogers Island the east and west river channels are each represented by one lateral segment. Figure 5-6 presents a schematic representation of the HUDTOX model grid that includes references to geographical locations. Output from the RMA-2V hydrodynamic model for a flow of 8,000 cfs at Fort Edward was used to provide flow-routing information for this two-dimensional segmentation grid within the Pool. An evaluation of the variation in flow through the HUDTOX segments at a given TIP cross-section for different upstream flows showed only minor variations, so the flow routing pattern was held constant over the entire range of flows simulated (also see Section 5.2.3.1).

The 19 one-dimensional water column segments between Thompson Island Pool and Federal Dam were developed to capture the impacts of hydrologic features of the river, including dams and locations of tributary inputs. The water column segmentation was also specified based on locations of sediment PCB "hotspots". Consequently, the longitudinal resolution of these segments is variable, ranging from less than one mile to greater than four miles. The geometry of the HUDTOX water column segmentation is presented in Tables 5-1a and 5-1b. Figure 5-7 illustrates how the HUDTOX water column segment depths vary from upstream to downstream, indicating the important impacts of the lock and dam systems on river geometry.

5.6.2 Sediment Segments

Tables 5-2a and 5-2b present the spatial configuration and geometry of the HUDTOX surface sediment segmentation (layer 1), including the assignment of cohesive and non-cohesive sediment areas. Historically delineated sediment PCB "hotspots" are not explicitly represented by

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individual model segments. The finer model grid in Thompson Island Pool does, however, better represent these areas than it does in segments downstream of the Thompson Island Dam. As such, care must be taken in the use of the model for simulating future responses to remedial scenarios that focus on bedded sediment areas which may be much smaller than the model segmentation spatial scale. The longitudinal variation in cohesive sediment abundance in the HUDTOX model is depicted in Figure 5-8 and was developed according to the procedure described in the following paragraphs.

Surface sediment segment areas for the HUDTOX model were computed using two GIS coverages. First, a GIS coverage developed from side scan sonar studies conducted as part of the USEPA Phase 2 investigation (USEPA, 1997) was used to define sediment segments within TIP and downstream to the Northumberland Dam (RM 183.4). The side scan sonar measurements were used to distinguish river bottom areas of finer (representing cohesive solids) and coarser (representing non-cohesive solids) sediments. Rocky and mounded bed areas identified by the river bottom coverage were excluded from the sediment segmentation grid, as were all islands.

Two additional criteria were used in developing the sediment segmentation from the side scan sonar data:

- Water column segments underlain by 15 percent or more cohesive sediment area were assigned both cohesive and non-cohesive sediment segments, unless they contained more than 85 percent cohesive sediment area, in which case only a cohesive sediment segment was assigned; and,

- Water column segments underlain by less than 15 percent cohesive sediment area were assigned only non-cohesive sediment segments.

The second GIS coverage was based on GE's 1997 sediment bed type sampling between Northumberland Dam and Federal Dam (QEA, 1998). This coverage was used to define the HUDTOX sediment segmentation in reaches of the Upper Hudson River that were not covered by the side scan sonar surveys.

These two GIS coverages of sediment type were intersected with the HUDTOX water column segments to develop a two-dimensional picture of the surface sediments, and to define 27 cohesive and 43 non-cohesive sediment segments for the Upper Hudson River between Fort Edward and Federal Dam. Figure 5-4 (Parts A through D) depicts the two sediment types underlying each water column segment for the entire upper river. Figure 5-5 provides a large-scale view of the same information within just TIP, which was represented with 15 cohesive and 27 non-cohesive surface sediment segments.

A vertical discretization of two centimeters was used for the HUDTOX sediment segmentation to provide adequate resolution of vertical PCB profiles for simulating sediment-water interactions and long-term system responses. This resolution also provides flexibility in the use of HUDTOX model output for PCB sediment exposures in terms of an "active" surface sediment layer for the bioaccumulation models. A summary of the HUDTOX surficial sediment segmentation geometry is provided in Tables 5-2a and 5-2b. The model grid includes sediments down to 26

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cm (13 layers), resulting in a total of 1035 water column and sediment segments in the entire model grid.

5.7 Model Implementation

The HUDTOX model was developed from the USEPA WASP toxic chemical model framework. The model was originally constructed from the WASP4/TOXI4 version of the code and subsequently modified to include relevant code corrections and changes that were implemented by USEPA in the WASP5/TOXI5 version. The WASP5 model is documented in Ambrose et al. (1993) and is distributed by the Center for Exposure Assessment Modeling (CEAM) at the USEPA Environmental Research Laboratory, Athens, Georgia.

The HUDTOX model FORTRAN source code was compiled and run using Lahey FORTRAN 90 (Version 4.50b, Lahey Computer Systems, Inc.) for personal computers running Microsoft DOS or Windows (95, 98 or NT) operating systems. Development, testing and application of the HUDTOX model was conducted on IBM-PC compatible computers. The computer hardware system requirements vary, depending on the type of HUDTOX model simulations being conducted. A Pentium II microprocessor (266 Mhz or higher), 64 Megabytes of RAM, and available disk storage space of 1.0 Gigabyte are minimum requirements for the simulations presented in this report. As a general indication of model execution speed, a 21-year simulation from 1977 to 1997 required on the order of 10 hours of real time on a 450 Mhz Pentium II computer. This simulation included a model grid consisting of 1035 spatial segments and computational time steps ranging from 0.0027 to 0.019 days over the 21-year simulation period. Most model calibration and forecast simulations were conducted on 600 Mhz Pentium III computers.

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6. DATA DEVELOPMENT FOR MODEL APPLICATIONS

6.1 INTRODUCTION

The development and application of the HUDTOX PCB mass balance model relied on the extensive site data obtained from the database created to support this Reassessment RI/FS (USEPA, 1995) and other sources. This chapter presents the organization and analysis of the available data to specify required model forcing functions, initial conditions, rate coefficients, and state variable parameters. Additionally, observed spatial and temporal PCB concentration trends are presented to support model calibration, which is the topic of Chapter 7.

The following major sections are included in Chapter 6:

6.2 Available Data

6.3 Model Application Data Sets

6.4 Flow Balance

6.5 Mainstem and Tributary Solids Loads

6.6 Mainstem and Tributary PCB Loads

6.7 Sediment Initial Conditions

6.8 Water Temperature

6.9 Partitioning

6.10 Volatilization

6.11 Sediment Particle Mixing

6.12 Dechlorination

6.13 Sediment-Water Mass Transfer

Sections 6.4, 6.5 and 6.6 present development of the 21-year daily flow, solids and PCB inputs to the model. Section 6.7 presents development of beginning sediment PCB concentrations for the entire river from 1977 data for the historical calibration and 1991 data for the short-term hindcast applications. Sections 6.8 through 6.13 discuss the specification of various parameter values and other inputs to the model based on available data.

6.2 AVAILABLE DATA

The Hudson River is one of the most extensively monitored PCB contamination sites. The system has been studied extensively and monitored almost continuously over a period of more than 20 years. The various monitoring studies have provided numerous water column and sediment datasets useful to modeling PCB fate and transport in the system. Most of these data have been compiled by TAMS in the Hudson River Database, which was created to support this Reassessment.

The development and application of the HUDTOX model relied extensively on the Hudson River Database, in addition to data obtained from other sources. The Hudson River Database Report (USEPA, 1995) and accompanying CD-ROM database provides the validated data for the Phase 2 investigation. This Revised Baseline Modeling Report (RBMR) utilized Release 4.1b of the CD-ROM database, which was updated in fall 1998 (USEPA, 1998b). The Hudson River Database contains information from a large variety of different sources, including:

- New York State Department of Environmental Conservation (NYSDEC)
- New York State Department of Health (NYSDOH)
- New York State Department of Transportation (NYSDOT)
- General Electric Company (GE)
- Lamont-Doherty Earth Observatory (LDEO)
- Rensselaer Polytechnic Institute (RPI)
- U.S. Geological Survey (USGS)
- National Oceanic and Atmospheric Administration (NOAA)
- U.S. Environmental Protection Agency (USEPA).

In addition to the Hudson River Database, site specific information was also obtained from a number of other sources, which are presented in the bulleted list below.

- An update to the GE database, dated 12 October 1998, was supplied by Kerry A. Thurston of O'Brien & Gere.
- To supplement the records available in Release 4.1b of the database, a portion of the 1997 USGS flow, suspended solids and PCB data were obtained directly from the USGS in Albany, New York (email to Penelope Moskus from Brian Wolorby on 8/12/98).
- Additional water column dissolved organic carbon data reported by J. Vaughn (1996), were used in addition to the measurements by GE and USEPA contained in the database.
- The 1998 GE Sediment sampling program data are not included in Release 4.1b although these data were also used. The poolwide average surface sediment PCB concentrations reported by QEA (1999) from these data were used as additional model calibration points for surficial sediment PCB concentrations in Thompson Island Pool (TIP) (Chapter 7).

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- Atmospheric PCB concentration data from the Integrated Atmospheric Deposition Network (IADN) station at Point Petre, Ontario (Hoff, et al. 1996) were obtained to specify atmospheric PCB concentrations in the HUDTOX model.

Where necessary and appropriate, information from the scientific literature and various technical reports was also used to specify values for model process coefficients. These sources are cited in the report text.

The Data Evaluation and Interpretation Report (DEIR) (USEPA, 1997) and the Low Resolution Sediment Coring Report (LRC) (USEPA, 1998a) are companion reports to this Revised Baseline Modeling Report (RBMR). The DEIR contains a literature review of current and historical PCB water column data, and an evaluation of geochemical fate of PCBs in the sediments of the Upper Hudson River. The LRC contains an assessment of current and historical inventories of sediment PCBs in the Upper Hudson River. The reader is referred to these companion reports for additional details on the available datasets for this Reassessment.

6.3 Model Application Datasets

The development and application of the HUDTOX model is based on the extensive sediment and water column monitoring datasets collected by primarily by the USEPA, USGS, NYSDEC, and the General Electric Company. A summary of the various data collection activities through 1994 is provided in the Hudson River Database Report (USEPA, 1995). In addition to the long-term record of PCB concentrations in water and sediment available from the combined datasets, a number of specific, focused studies were conducted by USEPA and GE. The data from these studies provide additional insight into processes affecting PCB fate and transport in the system, which supported parameterization of key processes in the HUDTOX model. This section provides an overview of the primary model application datasets and their use in the HUDTOX modeling effort.

6.3.1 Sediment Datasets

The primary sediment datasets used in this modeling effort are the sediment sampling surveys conducted by:

- NYSDEC in 1976-78 (Tofflemire and Quinn, 1979) and 1984 (Brown et al., 1988);
- GE in 1991 (O'Brien and Gere, 1993) and 1998 (O'Brien and Gere, 1999); and
- USEPA in 1992 and 1994 (DEIR and USEPA, 1998b).

The NYSDEC 1976-78, NYSDEC 1984, GE 1991 and the GE 1998 surveys are comprehensive assessments of PCB levels in the sediments. The NYSDEC 1976-78 and GE 1991 studies sampled the complete extent of the river from Fort Edward to Federal Dam, whereas, the NYSDEC 1984 survey was limited to Thompson Island Pool. The GE 1998 study extensively sampled Thompson Island Pool and included focused coring at a limited number of locations downstream as well. The USEPA 1994 studies were aimed at assessing PCB concentrations in a relatively small number of discrete areas in Thompson Island Pool and a few hotspot locations downstream.

Model initial conditions for sediment PCB concentrations for the 1977-1997 historical calibration were established from 1976-78 NYSDEC sediment PCB data, referred to as the 1977 NYSDEC data throughout this report (Section 6.7). The average surface sediment concentrations from the 1984, 1991, and 1998 datasets served as calibration targets for the historical calibration. The GE 1991 and 1998 data were considered primary calibration targets for surface sediments. The 1984 NYSDEC data and the 1994 USEPA low-resolution sediment core data were not primary calibration points for surface sediment PCBs because these data contain measurements of surface concentrations averaged over large depth intervals.

The sediment survey in Thompson Island Pool by GE in 1998 attempted to 'repeat' portions of the 1991 O'Brien and Gere, and 1994 USEPA sediment surveys (QEA 1999). Average concentrations for cohesive and non-cohesive sediments were computed for the 0-5 cm sediment layer and reported by QEA (1999). As the raw 1998 sediment data were obtained in a later phase of this project, the reported concentrations were used as additional model calibration targets for the Thompson Island Pool.

The "Low Resolution" sediment dataset collected by USEPA in 1994 provides assessments of sediment concentrations at approximately 20 locations in Thompson Island Pool (15 small zones and 4 near shore locations) and in 7 hotspots downstream of Thompson Island Pool. In addition, the USEPA data provide high-resolution core analyses at 28 selected locations in the Upper and Lower Hudson collected in 1992. The USEPA data are not extensive enough to serve as primary calibration information for the model. The main use of the 1994 USEPA sediment data was to assess changes in PCB levels relative to the 1984 measurements by NYSDEC at specific locations, which is a principal topic in the LRC (USEPA, 1998a). The high-resolution core data analyses included radionuclide dating, providing an estimate of sediment accumulation rates at specific locations (USEPA, 1997).

The sediment sampling effort conducted by USEPA included mapping of fine and coarse sediment grain size using side scan sonar images from Fort Edward to the Northumberland Dam (Flood, 1993). A qualitative sediment bed mapping survey was conducted by GE to characterize locations of fine and coarse sediment deposits between Northumberland Dam and Federal Dam (QEA, 1998a). The combined side scan sonar and qualitative bed mapping data were used to develop the model sediment segmentation (Section 5.3) and to classify some sediment samples for the purpose of determining fine and coarse sediment average PCB concentrations.

The GE 1991 and USEPA datasets included congener analysis in the water and sediments, which are available in the Hudson River Database, whereas the NYSDEC PCB analysis reported concentrations as Aroclors. The GE 1991 data were used to specify sediment initial conditions for modeling individual congeners and total PCBs over the period 1991 to 1997 (Section 6.7).

The GE 1991 data included measurement of porewater PCB and dissolved organic carbon data. These data were used to estimate in-situ sediment-water partition coefficients for individual congeners and the historical calibration state variable, Tri+. The development of the partition coefficients for Tri+ and congeners is presented in the DEIR (USEPA, 1997). The application of the partition coefficients estimated from these data is discussed in detail in Section 6.9.

A summary of the sediment datasets and their use in this modeling effort is summarized in Table 6-1.

6.3.2 Water Column Data

The principal water column datasets used for solids and PCBs in this modeling effort were the following:

- Long-term monitoring data collected at Fort Edward, Schuylerville, Stillwater and Waterford from 1977 to 1997 (collected by USGS, USEPA and GE)
- Thompson Island Dam data from 1991 to 1997 (collected by USEPA and GE)
- Mainstem and tributary solids data from the spring 1994 high flow survey (collected by USEPA)
- Mainstem data from the USEPA Phase 2 monitoring program in 1993
- High flow sampling data in 1997 (collected by GE)
- Thompson Island Pool float study data in 1996 and 1997 (collected by GE)
- Thompson Island Dam bias study data (collected by GE).

The long-term water column monitoring by USGS at Fort Edward, Schuylerville, Stillwater and Waterford, combined with the more recent sampling by GE and the USEPA at these and other locations, provides an extensive history of water column PCB and TSS concentrations in the Upper Hudson River. Monitoring of PCB and TSS concentrations by the USGS commenced in 1977 and continues to the present. The USGS data, combined with the more frequent data from the GE monitoring beginning in 1991, and the USEPA Phase 2 data collected in 1993 to 1994, allow specification of PCB and TSS loading at Fort Edward and the tributaries. In addition, these combined datasets permit development of in-river load estimates of PCB and TSS at Stillwater and Waterford over the entire historical calibration period. The long-term record of solids and PCB concentration measurements at Thompson Island Dam (1991 - 1997), Schuylerville (1977 - 1993), Stillwater (1977 - 1997) and Waterford (1977 - 1997) serve as principal calibration datasets for the HUDTOX modeling effort.

The GE water column monitoring data, which spans the period 1991 to the present, provides a high frequency monitoring dataset at Fort Edward and Thompson Island Dam, in addition to periodic data collected at downstream locations. GE also has conducted a number of specialized monitoring studies which provide insight into processes affecting PCB transport, localized sources of PCB loading and seasonal patterns in PCB fluxes.

The high flow event sampling in March and April of 1994 by USEPA represents the most extensive high flow solids monitoring dataset. Samples were collected during the only period over which tributary and mainstem TSS concentrations were measured simultaneously during a high flow event. While this dataset provides the most constrained assessment of solids dynamics over the course of a high flow event, PCBs were not simultaneously measured during this sampling event and a significant fraction of the total tributary flow was not measured for this period.

The USEPA also conducted a number of water column sampling surveys to assess PCB concentrations, sources, and transport in the system. Six of these surveys were down-river transects in which composite samples were collected over approximately two-week periods over six months spanning a range of seasonal conditions in the river. A series of seven sampling events occurring approximately monthly at 13 stations was also conducted in which sampling was timed to monitor the same parcel of water through the system. These USEPA Phase 2 data provide additional information about the spatial and seasonal patterns of PCB transport in the river and provide a determination of sediment-water partitioning behavior. Interpretation of the Phase 2 data and development of partitioning relationships from these data is presented in the DEIR (USEPA, 1997).

6.3.3 Conversion of PCB Data in Historical Calibration Datasets

Different sediment and water datasets used different analytical methods, which required various data adjustments in order to make the datasets comparable for use in the HUDTOX model calibration. The historical modeling state variable was the sum of tri and higher chlorinated congeners (denoted Tri+ in the remainder of this report). Individual congeners and total PCB could not be used for the historical calibration because neither congener analyses nor equivalent total PCB quantitations are available in the historical datasets. Individual Aroclors were also not consistently quantified between datasets. Additionally, Aroclors and total PCBs were considered unsuitable state variables for historical calibration because shifts in congener patterns due to weathering and/or dechlorination may result in variations in partitioning behavior. The Tri+ quantity could be determined in all datasets and was selected for the historical calibration. Tri+ was an attractive choice for a historical modeling state variable not only because it is consistently identified among datasets, but also because its composition is relatively less variable throughout the system than PCB forms including mono- and dichloro-biphenyls. Methods were previously developed (USEPA, 1998a, Butcher, 2000b) to convert the various PCB quantifications into estimates of the Tri+ concentration for each dataset. These methods are summarized for each dataset below.

6.3.3.1 USGS Water Column Data

The USGS water column data represent whole water analyses, with PCBs quantified using Aroclor standards. Packed column analysis was used until 1987, when data began to be analyzed

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with capillary columns. Approximately coincident with the USGS switch from packed column analysis to capillary column analysis beginning in 1987, a limited number of Aroclor standards were used relative to the earlier years.

Split sample analysis between USGS and Phase 2 data supported use of the USGS-reported total PCB concentration from the packed column analysis as a direct measure of the Tri+ sum. A regression relating USGS total PCB to the Tri+ sum gives a good linear fit with an intercept not significantly different from zero (USEPA, 1997). Thus, the USGS packed-column total PCB results were used directly as Tri+ through 1987.

Re-analysis of 60 USGS sample chromatograms by QEA (Rhea and Werth, 1999) supported use of the USGS reported Aroclor 1242 results or, when 1242 results are not available, use of Aroclor 1248 as the best representation of Tri+ concentration in the USGS data after 1987.

6.3.3.2 1976-1978 NYSDEC Sediment Data

Total PCBs were reported by O'Brien and Gere for the 1976-1978 sediment dataset. These were based on Aroclor analysis using a limited number of packed column peaks, which tended to miss the mono- and di-homologues. Based on reconstruction of the 1976-1978 total PCB results from USEPA Phase 2 sediment congener data, a regression between the Tri+ concentration and the 1977-1978 total PCB concentrations produced a zero-intercept model with which to estimate Tri+ concentrations from these data (Equation 6-1). Details of this analysis are presented in USEPA, 1998a and Butcher, 2000b.

$$\text{Tri+}\ (1977) = 1.131 \times [\text{Aroclor } 1016 + 1254] \qquad \textbf{(6-1)}$$

6.3.3.3 1984 NYSDEC Sediment Data

Total PCB concentrations reported for the 1984 sediment data were reported by NYSDEC as the sum of estimated concentrations of Aroclors 1242, 1254, and 1260. A constant conversion factor was determined to correct these data to a basis consistent with the Tri+ quantitation in the Phase 2 data (Equation 6-2). The analysis conducted to develop this conversion is presented in detail in USEPA, 1998a.

$$\text{Tri+}(1984) = 0.944 \times (1984 \text{ NYSDEC total PCBs}) \qquad \textbf{(6-2)}$$

6.3.3.4 GE Water Column and Sediment Data

The majority of GE water column results and all of the GE sediment data collected in 1991 include congener-specific analyses and homologue fractions. Tri+ concentrations were computed as the sum of tri-through deca-homologue concentrations.

6.3.3.5 USEPA Water Column and Sediment Data

All of the USEPA water column and sediment data include congener concentrations and calculated homologue concentrations. Tri+ concentrations were computed as the sum of tri-through deca-homologue concentrations.

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6.3.4 Data conversion for Total PCB and Congeners

While the primary calibration state variable in the long-term historical calibration is Tri+, short term hindcast applications over the period Jan. 1, 1991 through Sept. 30, 1997 were additionally conducted with individual congeners and total PCBs to test the Tri+ historical calibration.

Five congeners were selected for modeling based on physical and chemical properties and frequency of detection in all media types (sediment, water and biota). These five congeners are BZ#4 (a di-chlorobiphenyl), BZ#28 (tri-chlorobiphenyl), BZ#52 (tetra-chlorobiphenyl), BZ#101+90 (co-eluting penta-chlorobiphenyls) and BZ#138 (hexa-chlorobiphenyl).

In the GE congener quantitations, all five of the congener state variables co-elute with other congeners. BZ#28, 52 and 138 co-elute, respectively, with BZ#50, 73 and 163, all of which are minor congeners not quantitated by USEPA. The BZ#28, 52 and 138 concentrations in the GE data were used directly as measures of these congeners, ignoring the co-eluting, minor congeners. BZ#101 and BZ#90 co-elute in both the GE and the USEPA congener results and were not separated for modeling purposes. For the co-eluting BZ#4 and BZ#10 congeners, the average BZ#4/BZ#10 ratio determined in TIP water column and sediment samples presented by Hydroqual (1997) was used to compute BZ#4 concentrations in the GE water column and sediment data.

The GE database contains total PCB data analyzed by three different methods, which are referred to as the capillary column method (PCB_cap), the USGS method (PCB_usgs), and the Webb and McCall method (PCB_wm). The majority of the GE samples were analyzed using capillary columns, although a relatively small number of samples had only a USGS or Webb and McCall result reported. The method to be used was selected as follows: use PCB_cap result if available, or else use the PCB_usgs if available, and if neither PCB_cap or PCB_usgs are available, use PCB_wm.

6.4 Flow Balance

6.4.1 Overview

The HUDTOX model is based on the principle of conservation of mass. Mass balances of flow, solids and PCBs are represented in the model. HUDTOX requires specification of all tributary and upstream flow inputs, in addition to external solids and PCB loads. The purpose of this section is to describe the development of daily flow inputs from upstream at Fort Edward and from tributaries and direct drainage flows for the calibration period (January 1, 1977 through September 30, 1997). Tributary inflows are specified for eight significant tributaries and four direct drainage inputs between Fort Edward and Federal Dam at Troy. Direct drainage flows were computed for drainage areas not included in the eight tributary watersheds and they are treated as additional tributary flows. The Fort Edward daily flow estimates were based on USGS flow gage data at Fort Edward. The Hoosic River and Mohawk River flow inputs were taken from continuous USGS records available for these tributaries. Ungaged tributary and direct drainage flows were estimated based on the Hoosic River flow records or other available USGS stream flow data in the Upper Hudson watershed.

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Daily flow estimates for mainstem Hudson River locations downstream of Fort Edward were based on the sum of Fort Edward, tributary and direct drainage flow inputs. These synthesized flow time series were used for developing cumulative in-river solids and PCB load estimates to supplement the primary, long term sampling stations for use in model calibration (Sections 6.5 and 6.6).

6.4.2 Flow Data

Mainstem and tributary flow gages in operation during the study period are summarized in Table 6-2. The locations for these flow gages are shown in Figure 6-1. The Fort Edward gaging station (USGS # 01327750) was operational for the entire study period, whereas major gaps exist in daily flow records for the other mainstem stations. Reported USGS daily flow data for the Stillwater (USGS # 01331095) and Waterford (USGS # 01335754) stations are flagged by USGS as estimated values beginning in September 1992 at Stillwater and July 1992 at Waterford. This was due to construction activities that began in 1992 and continued through at least 1995 (USGS Water Resources Data 1993; and, Charles Fluelling, NYS Thruway, personal communication, February 27, 1997). The daily flows at Stillwater continued to be reported as estimates through the end of 1997 because this gage remained out of operation until that time. The only direct tributaries gaged for the entire study period are on the Hoosic (USGS # 01334500 at Eagle Bridge) and Mohawk Rivers (USGS # 01357500 at Cohoes, and # 01357499 at Crescent Dam). Stream flow data are available at two locations in the Fish Creek watershed: Kayaderosseras Creek (USGS # 01330500), and Glowegee Creek (USGS # 01330000). USGS flow monitoring at the Kayaderosseras Creek station was discontinued in 1995.

The ungaged tributary drainage area is a large percentage of the drainage area between Fort Edward and Waterford. The drainage area of tributaries feeding the Hudson River between Fort Edward and Waterford equals 1,794 mi^2. Only 33 percent of this area is gaged (Kayaderosseras Creek near West Milton (90 mi^2) and Hoosic River at Eagle Bridge (510 mi^2). Approximately 67 percent of the watershed area between Fort Edward and Waterford is ungaged. Flows draining ungaged watersheds were estimated as described in Section 6.4.

The Mohawk River is a large gaged tributary to the Hudson River (3,450 mi^2) which enters between Waterford and Federal Dam at Troy. The drainage area of tributaries feeding the Hudson River between Fort Edward and the Federal Dam at Troy equals 5,244 mi^2. Accounting for the gaged Mohawk River, Hoosic River and Kayaderosseras Creek drainages (3,450 + 510 + 90 = 4,050 mi^2), 77 percent of the tributary between Fort Edward and the Federal Dam at Troy (5,244 mi^2) is gaged.

Flood frequency analysis (Log Pearson Type III) was conducted based on 1930 to 1991 flows at Fort Edward by Butcher (2000a). As the period of record at Fort Edward commences in 1977, this analysis made use of flows estimated from the sum of flows measured upstream in the Hudson River at Hadley, NY (USGS gage # 01318500) and Sacandaga River (USGS gage # 01325000) for the period before 1977. The estimated 5, 50, and 100 year return frequency flows at Fort Edward based on this analysis are 30,126 cfs, 43,671 cfs and 47,330 cfs, respectively (Figure 6-2). The peak daily average flow at Fort Edward during the model calibration period occurred in 1983 (34,100 cfs), which has an estimated return frequency of approximately 11 years. In 1976, the year prior to the simulation period, a 37-year flow of approximately 42,000 cfs occurred, only 11 percent lower than the estimated 100 year flow.

6.4.3 Flow Estimation Methods

To specify daily upstream and tributary daily flow inputs to the HUDTOX model, daily average USGS flow records were used where possible and ungaged inflows estimated by relationship to these data. Upstream flow at Fort Edward was specified directly from the USGS data, without modification. Mohawk River flows (sum of daily flows at Cohoes and the Crescent Dam diversion), and the Hoosic River flows measured at Eagle Bridge were also used without modification. The USGS Fort Edward flow time series from 1977 to 1997 is shown in Figure 6-3.

Ungaged tributary flows were estimated using the drainage area ratio (DAR) method. This approach relates measured flows to unmeasured flows in similar watersheds by assuming equal flow yield per unit area of watershed. Based on gaged tributary flows, ungaged flows are computed using the ratio of watershed drainage areas (Equation 6-3).

$$Q_{ungaged\_tributary} = Q_{gaged\_tributary} \cdot \left(\frac{DA_{ungaged\_tributary}}{DA_{gaged\_tributary}} \right) \qquad \textbf{(6-3)}$$

where:

$Q_{ungaged\_tributary}$ = ungaged tributary flow

$Q_{gaged\_tributary}$ = gaged tributary flow

$DA_{ungaged\_tributary}$ = ungaged tributary drainage area

$DA_{gaged\_tributary}$ = gaged tributary drainage area.

The DAR approach was used to estimate all ungaged tributary and direct drainage flows based on USGS flow rate data from Kayaderosseras Creek, Glowegee Creek or the Hoosic River at Eagle Bridge. The ungaged area includes the Hoosic River watershed downstream of Eagle Bridge. Reference tributaries for each watershed in which flows were estimated were selected based on consideration of similarities in land use, topography, location and watershed size. Tributary watershed areas were estimated by digitizing the watershed boundaries from USGS topographical maps in a GIS (Table 6-3). All estimated tributary and direct drainage flows between Fort Edward and river mile 180 (just downstream of Schuylerville) were based on Kayaderosseras Creek or Glowegee Creek flow data, and those downstream of river mile 180 were based on Hoosic River at Eagle Bridge flow data (Table 6-3). The Kayaderosseras Creek gaging station is located in the upper portion of the watershed drained by Fish Creek (Figure 6-1). USGS flow monitoring at the Kayaderosseras Creek station was discontinued in 1995. Flow data collected on Glowegee Creek were used after 1995. The Glowegee Creek gage is located in the upper reaches of the same watershed as Kayaderosseras Creek and has a relatively small drainage area (26 mi^2).

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Direct application of the DAR approach does not result in flows from individual tributaries that are mutually constrained in the sense that these estimates may not sum to observed flows at downstream locations in the Upper Hudson River. USGS flow estimates at Stillwater and Waterford were used to constrain estimated tributary flows in order to achieve a long-term seasonal average flow balance between Fort Edward and Waterford. Comparison of the estimated flows at Stillwater and Waterford for 1993 to the flow estimates presented in the DEIR (USEPA, 1997) showed the DEIR estimates to be substantially higher during low flow. Correlation of the DEIR summer average flow estimates with cumulative precipitation data revealed that the DEIR estimates were biased high (USEPA, 1999a). Consequently, the DEIR flow estimates were not used in any of the HUDTOX model applications and the USGS estimates at Stillwater and Waterford were used exclusively.

The seasons used in the seasonal flow balance were defined as follows:

- Spring: March, April, May
- Summer: June, July, and August
- Fall: September, October, and November
- Winter: December, January, and February

The seasonal mean flow computed by summing the Fort Edward and estimated tributary flows was compared to the seasonal mean flow from the USGS gages at Stillwater and Waterford over the period from March 1, 1977 to June 30, 1992 (Table 6-4). This period was used because all three gages (Fort Edward, Stillwater and Waterford) were operational. After September 1992, the gages at Stillwater Dam and Lock 1 at Waterford were influenced by dam construction activities and flows reported by USGS after this date are estimated.

The seasonal mean flows at Fort Edward, Stillwater and Waterford were computed from the USGS data over the period March 1, 1977 to June 30, 1992. Seasonal mean flow, increases in seasonal mean flow, and computed watershed flow yield between these locations are presented in Table 6-5. The ungaged tributary flows estimated by the DAR method were scaled using an adjustment factor, α, for season, j, in order to be achieve a long-term seasonal average flow balance between Fort Edward and Stillwater (Equation 6-4) and between Stillwater and Waterford (Equation 6-5). Equations 6-4 and 6-5 were solved for the adjustment factors (the α terms) for each season.

$$\left(\overline{Q}_{Still} - \overline{Q}_{FE}\right)_j = \left(\alpha_{FE-Still}\right)_j \sum \beta_i \left(\overline{Q}_{reference}\right)_j \qquad \textbf{(6-4)}$$

$$\left(\overline{Q}_{Watfd} - \overline{Q}_{Still}\right)_j = \left(\alpha_{Watfd-Still}\right)_j \sum \beta_i \left(\overline{Q}_{reference}\right)_j \qquad \textbf{(6-5)}$$

where:

$\alpha_{FE\text{-}Still}$	= seasonal adjustment factor for season j and for tributaries between Fort Edward and Stillwater
$\alpha_{Still\text{-}Watfd}$	= seasonal adjustment factor for season j and for tributaries between Stillwater and Waterford
$Q_{reference}$	= flow of gaged reference tributary
β_i	= drainage area proration factor for tributary i

As discussed above, the drainage area proration factor for tributary i is the ratio of the ungaged to the gaged (or reference) tributary watershed areas (Equation 6-6).

$$\beta_i = DA_{ungaged\_tributary} / DA_{gaged\_tributary} \qquad \textbf{(6-6)}$$

The mean seasonal flows, drainage area proration factors and seasonal adjustment factors are presented in Table 6-5.The seasonal flow adjustment resulted in average tributary flows that sum to the average flows at Stillwater and Waterford for the period considered in the flow balance.

The required adjustment for the ungaged tributary flow between Stillwater and Waterford was much less than 1.0 in the summer and fall (Table 6-5). This indicates that the extrapolation of the Hoosic River flows gaged at Eagle Bridge to ungaged tributaries using the DAR approach resulted in a significant overestimate of incremental flows during summer and fall in the reach from Stillwater to Waterford. It is possible that differences in watershed geology may cause different base flow behavior relative to higher flows in the Hoosic River compared to the smaller tributaries whose flow was estimated based on the Hoosic flow. Evaporative and other losses from the Hoosic River between Eagle Bridge and the Hudson may be significant during the summer and fall, which could result in an overestimate of the ungaged Hoosic River flows between Eagle Bridge and Hudson River for these periods.

To evaluate resulting tributary flows estimated in the manner described above, resulting flows at Stillwater and Waterford computed by summing the Fort Edward and tributary flows were plotted versus the USGS flow data (Figure 6-4). Generally, daily flow estimates were within 30 percent of the USGS estimates, however, during some high flow events, estimated flows differed by over 30 percent from the USGS flow. This was is not surprising, considering the DAR approach, which assumes that unit hydrograph responses seen at Eagle Bridge and Kayaderosserass Creek are instantly translated from the whole watershed to the Stillwater and Waterford gages. Thus the flow discrepancies are explained in part by relative timing of flood pulses.

To minimize error associated with estimating mainstem Hudson River flows during high flow events, an adjustment was applied for high flows differing by more than 30 percent from the USGS data. The USGS gage readings during the 1977 to 1992 period were assumed to be accurate within 30 percent during high flow events. Estimated tributary flows were adjusted to achieve agreement within 30 percent of the USGS flows when flow at Fort Edward was greater than 10,000 cfs. When the difference between estimated and USGS-reported flows was greater than 30 percent, the tributary flows were reduced according to their percent flow contribution at mean flow. This produced flow estimates within 30 percent of the USGS data for flows greater than 10,000 cfs at Fort Edward.

6.4.4 Results of Flow Balance

Analysis of the flow balance developed for the HUDTOX application period of January 1, 1977 to September 30, 1997 produces mean flows at Fort Edward, Schuylerville, Stillwater and Waterford of 5,248 cfs, 6,117 cfs, 6,603 cfs and 8,106 cfs, respectively. Mean Upper Hudson River flows increase 54 percent from Fort Edward to Waterford. The Fort Edward flow represents 79 percent and 65 percent of the average flow at Stillwater and Waterford, respectively. During this period, the estimated peak flows at Fort Edward, Schuylerville, Stillwater and Waterford are 34,100, 40,200, 46,800 and 70,500 cfs, respectively. Peak flows at Fort Edward and Schuylerville occurred in 1983, while at Stillwater and Waterford, peak flow occurred in 1977. The 1983 flow has an estimated return frequency at Fort Edward of approximately 11 years.

Figure 6-5 presents a summary of average daily flows for the study period, by tributary and mainstem station. The three largest tributaries in order of decreasing mean flow are the Mohawk River, Hoosic River and Batten Kill. Average flows increase by a factor of 1.2 and 1.5 from Fort Edward to Stillwater and Fort Edward to Waterford, respectively. Flows over Federal Dam, the downstream extent of the model are a factor of 2.5 larger than Fort Edward flows.

A plot of estimated flow contributions from each source along the river allows visualization of relative magnitude of the various tributary inputs (Figure 6-6). Approximately 35 percent of the flow volume at Waterford is due to tributary inputs entering between Fort Edward and Waterford. The Fort Edward flow represents about 65 percent of the flow past Waterford. The Hoosic River and Batten Kill are the largest sources, providing 16 percent and 7 percent of the flow at Waterford, respectively. At Federal Dam, approximately 62 percent of the total flow is from tributaries, with the Mohawk being the largest source, providing 41 percent of the total flow at Federal Dam. Only 38 percent of the flow at Federal Dam is from the Fort Edward flow during the 21-year study period.

6.4.4.1 Validation of the Flow Estimation Approach

While the above tributary and mainstem flow balance was determined for the period from March 1, 1977 to June 30, 1992, the adjustment factors in Table 6-5 were applied to the DAR-estimated tributary flows for the entire HUDTOX application period from January 1, 1977 to September 30, 1997. As a measure of accuracy, the estimated daily flows at Stillwater and Waterford were compared to the reported USGS daily flows and average annual flows. After 1992, the USGS flows are also estimated values at Stillwater and Waterford.

Estimated and USGS-reported flows were compared on a daily and average annual basis. The estimated and USGS-reported average annual flow passing Stillwater and Waterford was compared for each year of the calibration period (Table 6-6). Results indicate that mean annual flows are within 7 percent at Stillwater and 9 percent at Waterford. Percent differences for the 1993-1997 period, which is outside of the flow balance period, are consistent with the 1977 to 1992 flow balance period. The difference between estimated and USGS-reported average flow over the entire calibration period is about 1 percent at each location. Scatter plots of daily estimated versus USGS-reported flows at Stillwater and Waterford also show fairly good agreement for the 1993-1997 period, generally within about 30 percent (Figure 6-7). Inspection of the estimated and USGS-reported daily flow hydrograph also suggests that the flow estimation approach produced good results for this period (Figure 6-8). Based on the good agreement between the estimated and USGS-reported flows for the entire calibration period, the flow estimation method described above was considered to give good results that were acceptable for modeling purposes.

6.4.4.2 Application of Estimated Flows in Modeling

The USGS -reported flow at Fort Edward and the synthesized daily average flow time series for tributaries were input as discrete daily time functions in the HUDTOX model.

To compute in-river mass loads of solids and PCBs for comparison to model output, the estimated daily flow time series at TI Dam, Schuylerville, Stillwater and Waterford were used, instead of the USGS flow estimates, which are available at Stillwater and Waterford.

6.4.4.3 Summary of Flow Balance

Approximately 20 percent of the total tributary flow inputs to the HUDTOX model were estimated. Between Fort Edward and Waterford, approximately 60 percent of the tributary flows were estimated. Ungaged drainage areas between these stations accounts for 67 percent of the total tributary drainage area. Tributary flow estimates used the DAR approach, relating unmeasured flows to measured flows on Kayaderosseras Creek (substituting with Glowegee Creek after 1995), and the Hoosic River. Flow estimates were adjusted to achieve a seasonal water balance from 1977 to 1992 between Fort Edward and Stillwater and between Stillwater and Waterford. Based on comparison to USGS data, corrections were made to estimated flows during high flow periods to be within 30 percent of USGS flows. Estimated flows were compared to USGS-reported flows at Stillwater and Waterford, which are estimated by USGS, for the period 1992 to 1997 with good results. The estimated flows were used to specify flow inputs to the HUDTOX model and to develop in-river mass flux estimates for solids and PCBs, which is explained in the following sections.

Daily average flows over the study period increase by approximately a factor of 1.2 and 1.5 from Fort Edward to Stillwater and Fort Edward to Waterford, respectively. While the Fort Edward flow is the largest single flow input upstream of Waterford, the Mohawk River flow is larger than the Fort Edward flow and is the largest inflow between Fort Edward and Federal Dam.

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6.5 Mainstem and Tributary Solids Loads

6.5.1 Overview

The HUDTOX model requires specification of solids and PCB inputs, analogous to the specification of flow inputs from upstream and tributary sources. Daily average solids loading to the HUDTOX model from upstream at Fort Edward and from all tributary inputs was estimated for the entire calibration period: January 1, 1977 through September 30, 1997.

Total suspended solids (TSS) concentrations were not measured at all locations, or continuously throughout the calibration period, requiring estimation of a significant fraction of the total solids loading. Daily sampling frequency was approximately 11 percent at Fort Edward for the calibration period. Data was especially limited for tributaries, for which daily TSS monitoring frequency is less than 2 percent for those tributaries that were monitored. In addition, only 71 percent of the watershed area was monitored for TSS, requiring estimation of TSS loads from the other 29 percent of the watershed with no data.

As a consequence of the limited data available, resulting estimates of tributary loads are very uncertain. Initial estimates of tributary solids did not result in a solids balance for the mainstem Upper Hudson River. The sum of upstream and tributary loads were significantly lower than in-river estimates at Stillwater and Waterford. As a result, assumptions were required regarding in-river solids dynamics which led to adjustment of solids loads to achieve a long-term solids balance. Significantly more solids data are available at low and high flows for the main Thompson Island Pool tributaries (Snook Kill and Moses Kill), which allows estimation of solids loads to the Thompson Island Pool with more certainty than to downstream reaches. The significant uncertainty associated with the estimation of tributary solids loads downstream of Thompson Island Pool is addressed through model sensitivity analysis (Chapter 7).

Apparent decreases on solids loads over time at Fort Edward were observed during the calibration period. The solids loading was observed to be lower for given flows at Fort Edward after 1990, compared before 1990. In developing estimates of the Fort Edward solids loads, separate rating curves were developed for these periods based on this observation.

6.5.2 Solids Data

The available solids data for the mainstem and tributary stations are summarized in Tables 6-7 and 6-8, respectively. The locations of these solids sampling stations are shown in Figure 6-9. More frequent solids concentration data were available for mainstem stations than tributary stations, with no tributary solids data available prior to 1988. In addition, as illustrated in Figure 6-10, only 71 percent of the watershed area between Fort Edward and Waterford was monitored for solids, thus requiring estimation of solids loads from 29 percent of the total watershed area in the Upper Hudson River. Furthermore, for the 71 percent of the watershed area that was monitored, only very limited data are available for most of the tributaries. Generally, tributary samples were collected for only a short period of time during the 21-year study period. Solids samples were collected for mainstem and tributary stations on only 24 percent and 1 percent, respectively, of the total days in the 21-year simulation period.

An extensive record of suspended solids concentration data is available at Fort Edward, Stillwater and Waterford over the 21-year study period. Although numerous measurements are available, sampling frequency was sporadic during certain time periods.

Due to differences in sample collection methods between GE and USGS, there is uncertainty as to whether or not these datasets are comparable, especially at Fort Edward. The GE samples were collected by O'Brien & Gere by a number of methods. For the GE 1991 Thompson Island Pool Suspended Solids Study, a Manning automatic sampler was used to collect samples from an intake tube positioned at mid-depth (O'Brien & Gere, May 1993a). In the other GE studies, TSS samples were obtained using a 1.2-liter Kemmerer sampler to collect depth-composited samples either at 3-foot depth intervals throughout the water column (e.g. O'Brien & Gere, May 1993b), or at surface, mid-depth and deep sample depths (e.g. O'Brien & Gere 1998). The USGS TSS sampling method collected a continuous depth-integrated sample throughout the entire water column (personal communication 10/29/99, Ken Pearsall USGS, Albany New, York).

During periods when a strong vertical gradient in TSS concentrations existed, it is possible that the GE sampling approach may have resulted in a low bias in measured TSS concentration relative to TSS measurements obtained by the USGS sampling method. This potential is greatest during periods of high flow, due to possible occurrence of bed load. This may also affect estimates of PCB loading because the GE samples were analyzed for both TSS and PCB.

Relative differences in GE and USGS TSS concentrations were assessed several ways. First, daily average GE and USGS TSS concentrations between 5/10/91 and 4/9/97 were paired on the basis of date, resulting in 30 daily average data pairs. Scatter plots of the daily average pairs were developed for daily average flows above and below 10,000 cfs (Figure 6-11). Based on observation of the TSS/flow correlation and in-river PCB data, flow of approximately 10,000 to 11,000 cfs is considered to be an approximate threshold above which resuspension becomes significant in the river. Inspection of these scatter plots suggests that GE and USGS TSS measurements may be biased relative to each other, but in different directions at high and low flow. At low flow, GE TSS measurements appear to be significantly greater than USGS measurements. At high flow, the opposite may occur, at least for concentrations greater than 10 mg/L. These observations are not well supported due to the limited number of data pairs available and uncertainty as to exact times of collection. A second approach to investigating differences in USGS and GE data was to group the data by flow range and test for statistically significant differences in mean concentrations in each flow range. Two-sample and paired sample statistical tests were done at low flow (less than 10,000 cfs) and at high flow (greater than 10,000 cfs). The results of these tests tended to confirm what was observed in the above scatter plots: the GE measurements were higher at low flow, while the USGS measurements were higher at high flow.

The GE data represents a significant percentage of the total available daily average TSS measurements at Fort Edward (40 percent) for use in computing the upstream TSS loading. While comparison of USGS and GE data suggest that these data may have biases relative to each other, the limited data pairs available do not support discrimination between these datasets. The data were combined for use in computing Fort Edward TSS loads (Section 6.5).

6.5.3 Methods for Estimating Solids Loads

Solids loading estimates were based on sediment rating curves developed for the upstream load at Fort Edward, all tributary inputs and for long-term mainstem Hudson River TSS sampling stations. The mainstem Hudson River solids load estimates downstream of Fort Edward were used to develop a long-term solids balance for the river and for comparison to model output. The solids rating curves relate observed TSS concentrations to flow and thus describe solids loading as a function of flow. The general form of the rating curve is presented below (Equation 6.7)

$$TSS = aQ^b \qquad \textbf{(6-7)}$$

where:

Q = flow

a,b = fitting parameters

Using measured daily average TSS concentrations where available and concentrations estimated from rating curves for days on which no measurements were taken, daily average TSS loads were computed for the HUDTOX calibration period: January 1, 1977 through September 30, 1997. The daily solids load time series computed for Fort Edward and the tributaries were input directly into the HUDTOX model. The estimated in-river sediment loads passing Stillwater and Waterford were used as model calibration targets.

6.5.3.1 Mainstem Solids Loads

To develop suspended solids rating curves for the mainstem Hudson River sampling stations, daily average TSS concentrations were plotted versus daily average flow. Suspended solids concentrations are generally correlated with flow at Fort Edward, Stillwater and Waterford, with a stronger dependence of solids concentration on flow observed at higher flows (Figure 6-12). The relationship between solids concentration and flow is distinctly different at flows above approximately 1.0 to 1.5 times the average flow at each location. The flow at which the relationship between TSS and flow changes at each station is referred to as the flow cut-point. Regression equations were developed for each station that describe the relationship between TSS and flow above and below the flow cut-point.

A non-linear least squares regression approach was used to fit the data above and below the flow cut-point. An alternative approach considered was the Minimum Variance Unbiased Estimator (MVUE) method of Cohn et al. (1989). Comparison of results from these two methods shows that differences are small (Figure 6-13). The non-linear least squares regression approach has benefit of being applied using commonly available software rather than requiring special computer code.

The approach taken consisted of two phases. The first phase, using log-transformed data, simultaneously developed linear regression equations and refined the specification of the flow cut-point so as to obtain a continuous function relating TSS concentrations to flow over the entire flow range of interest. The second phase eliminated transformation bias by using non-linear least squares regression of the un-transformed data; retaining the first phase cut-point at the cost of a discontinuity in the TSS prediction at the cut-point. This process described above is presented below in more detail.

1. An initial cut-point was selected based on visual inspection of the TSS – flow plots.

2. The (log-transformed) data above and below the flow cut-point were fit with a linear least squares regression equation of the form ln(TSS) = A + B * ln(Q), where A and B are the equation parameters.

3. The value of Q for which the low flow and high flow equations were equal at the cut-point was computed.

4. Step 2 was repeated with the value of Q computed in step 3.

5. Steps 2 through 4 were repeated until convergence was obtained.

6. The (un-transformed) data above and below the cut-point were fit with a non-linear least squares regression equation of the form $TSS = aQ^b$, where a and b are the equation parameters. However, if the relationship between TSS and flow was not significant, the arithmetic average TSS was used.

The resulting rating curve equations for each station are presented below. The equations fit data below and above the cut-point, respectively.

Fort Edward	Q_{cut} = 10,829 cfs	$Q < Q_{cut}$: $TSS = 1.767 \times Q^{0.08624}$	**(6-8a)**
		$Q \geq Q_{cut}$: $TSS = 1.431E\text{-}8 \times Q^{2.101}$	**(6-8b)**
Schuylerville	Q_{cut} = 3,866 cfs	$Q < Q_{cut}$: $TSS = 3.79$	**(6-9a)**
		$Q \geq Q_{cut}$: $TSS = 0.0004238 \times Q^{1.13}$	**(6-9b)**
Stillwater	Q_{cut} = 7,555 cfs	$Q < Q_{cut}$: $TSS = 0.0122 \times Q^{0.6937}$	**(6-10a)**
		$Q \geq Q_{cut}$: $TSS = 4.555E\text{-}6 \times Q\ 1.595$	**(6-10b)**
Waterford	Q_{cut} = 9,799 cfs	$Q < Q_{cut}$: $TSS = 0.06739 \times Q^{0.5287}$	**(6-11a)**
		$Q \geq Q_{cut}$: $TSS = 8.489E\text{-}9 \times Q^{2.213}$	**(6-11b)**

Subsequent to development of rating curves based on all available data for the calibration period, investigation of possible changes over time in the solids load at Fort Edward was pursued. This was undertaken primarily in response to comments received from NOAA personal at the June 16 Science and Technical Committee Meeting, Albany, NY. Investigation of possible decreases in Fort Edward solids loading over the calibration period is prudent considering a number of possible factors, including: 1) washout and consolidation of former Fort Edward Dam impoundment sediments in the river; and 2) stabilization of the remnant deposit areas.

To initially assess whether the relationship between TSS and flow changed at Fort Edward over the calibration period, rating curves were developed as described above for the first five years (January 1, 1977 through December 31, 1982) and the last 5 years (January 1, 1993 through September 30, 1997) of the calibration period. Results indicated that there was a statistically significant reduction in TSS concentrations at both high and low flow between these two periods. This suggested it was necessary to account for the decrease in TSS loading in order to achieve the best estimate at Fort Edward over the calibration period. This required specification of time intervals over which to represent the change in solids loads.

Reductions in solids erosion over time from bedded sediments and the exposed remnant deposit areas were considered possible factors contributing to observed decreases over time in solids load at Fort Edward. A review of site information related to erosion of the former Fort Edward Dam sediments was used to estimate a reasonable time stratum. A number of sources document high erosion rates and solids loading to Thompson Island Pool following removal of the Fort Edward Dam. Various stabilization activities were conducted within the calibration period that were designed to reduce erosion of the former dam sediments.

Over the period July 1973 to April 1976, following removal of the Fort Edward Dam in 1973, approximately 1.0 million cubic yards of PCB laden sediments were washed downstream into Thompson Island Pool (NUS 1984). It is likely that significant erosion continued to occur after 1976. In 1978, areas of highly contaminated river-bank sediment that were exposed following the removal of the Fort Edward Dam were stabilized from a highly erodable state (Brown et al. 1988). The five discrete remnant sediment deposit areas upstream of Fort Edward identified by NUS (NUS 1984) were sources of sediment and PCBs until containment of the remnant deposit sediments in the fall of 1990. Following containment activities in 1990, PCB loading from the remnant deposit sediments appears to be small, if any (O'Brien & Gere 1996).

To account for changes in the TSS to flow relationship in specifying solids loads at Fort Edward, 1990 was considered a reasonable boundary for the two time strata. While decreases in solids loads also likely occurred before 1990, the stabilization activities completed by GE at the remnant deposit areas in the fall of 1990 provides a logical time stratum for investigating changes in solids loads.

The daily average TSS data at Fort Edward were grouped before and after Dec. 31, 1990 and tested for statistical difference at both high and low flow. Results indicate that there is a significant difference in the solids rating curves that were developed following the procedure presented above. Resulting Fort Edward rating curves for the pre and post 1990 periods are presented below and in Figure 6-14, for flows below and above the cut-points, respectively.

1977-1990 $\quad Q_{cut} = 10{,}100$ cfs $\quad Q < Q_{cut}$: TSS = $0.0674Q^{0.5024}$ **(6-12a)**

$Q \geq Q_{cut}$: TSS = $9.505\text{E-}7Q^{1.701}$ **(6-12b)**

1991-1997 $\quad Q_{cut} = 12{,}100$ cfs $\quad Q < Q_{cut}$: TSS = 3.23 **(6-13a)**

$Q \geq Q_{cut}$: TSS = $8.202\text{E-}11Q^{2.592}$ **(6-13b)**

These equations were used to compute cumulative suspended sediment loading at Fort Edward over the HUDTOX calibration period: January 1, 1977 to September 30, 1997. To illustrate the estimated change in loads before and after 1991, the average annual solids loading for each period were compared, showing 38% percent difference for the earlier and later periods, respectively. Part of this difference is attributable to differences in flow. The two largest flow events in the calibration period (1977 and 1983) occurred before 1991.

Because the time stratification approximately coincides with the time that TSS data became available from the GE studies, it is reasonable to consider the influence of data source on the observed decrease in solids loading. One way to assess the influence of data source is to investigate the justification for time stratification based the USGS data alone. It is not practical to attempt this with the GE data because GE data collection began in 1991.

Possible support for time stratification based only on the USGS data was investigated two ways. First, the USGS data at Fort Edward was time (before and after Dec. 31, 1990) and flow stratified (above and below 10,000 cfs) and the high and low flow data groups were compared for each period. This assesses whether there is a difference in mean concentrations at high and low flow between the two periods, although differences due to flow effects are not accounted for. Secondly, to account for the influence of flow on observed differences, TSS data from the two time periods were paired on the basis of flow. Typically, paired data had differences in flow of less than 1 percent. TSS data that could not be closely matched on the basis of flow were excluded from this paired comparison. The second approach addresses the question of whether the average difference in TSS concentrations between the two time periods is significantly different from zero while removing the obscuring influence of flow. The following statistical tests were done using Systat 8.0 (Systat 8.0 Statistics, 1998. SPSS, Inc.):

- Two-sample t-tests with logarithmically transformed data;
- Mann-Whitney U tests;
- Paired samples t-tests with logarithmically transformed data; and,
- Wilcoxon Signed Ranks tests.

For both low and high flows, all tests indicated that USGS TSS measurements for the later time period decreased relative to the earlier time period. The differences were found to be substantial, both in absolute terms and in terms of statistical significance (i.e. $p<0.05$ in all cases). These results show that the use of time stratification in computing the Fort Edward solids load is supported, at both high and low flows, regardless of whether or not the GE data are included. Inclusion of the GE data in developing the time stratified rating curves tends to increase computed TSS loads at low flow and decrease computed TSS loads at high flow. Use of the GE data was considered appropriate considering the large number of GE data available, uncertainty as to potential differences between the two datasets, and the observed changes in the USGS TSS/flow relationships independent of the GE data. In spite of observed differences between GE

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and USGS data, the use of time stratification in the rating curve is supported based on the finding that both the USGS dataset and the combined USGS-GE dataset show statistically significant decreases in concentration over time.

The time stratified rating curves developed based on all the available data (Equations 6-12 and 6-13) were used to compute TSS loads at Fort Edward for the model calibration. To develop the daily loading time series for the model calibration, measured daily average TSS concentrations were used where available, and TSS concentrations were computed using the rating curves for days upon which TSS was not measured.

In order to develop a long-term solids balance for the Upper Hudson River, cumulative solids loads at Stillwater and Waterford were computed in the same manner as described for Fort Edward. While decreases in TSS concentrations over time were also observed at Stillwater and Waterford at low flow, no statistically significant differences were observed at high flows. Based on this observation, the use of time-stratified ratings curves was not well supported at Stillwater and Waterford, and was not used in the calculation of solids loads at these locations. Estimates of in-river solids loads at Stillwater and Waterford were used in model calibration and in developing a long-term solids balance for the river (Section 6.5).

The solids rating curves at Fort Edward (Equations 6-8a and 6-8b), Stillwater (Equation 6-10a and 6-10b), and Waterford (Equation 6-11a and 6-11b) were used to estimate TSS concentration for days where measurements were not available. This allowed estimates of daily TSS loads at these locations for the entire calibration period (1977-1997).

6.5.3.2 Tributary Solids Loads

A major obstacle to estimating tributary solids loads was that available solids data were very limited. This factor, combined with uncertainty in estimated tributary flows (Section 6.4) resulted in poorly constrained estimates of tributary solids loading. There is significant uncertainty in the resulting tributary load estimates, especially downstream of Thompson Island Pool.

The general approach used for estimating tributary TSS loads was similar to that adopted for the Fort Edward load. TSS rating curves were developed to relate TSS concentrations to flow. Similar to the pattern observed at the mainstem stations, tributary solids concentrations were positively correlated with flow and the tributary rating curves generally exhibited a cut-point above which the slope of the relationship increases (Figure 6-15). The average flow of each tributary was observed to reasonably approximate the flow cut-point above which TSS concentrations increase significantly in each tributary. Below the average flow, TSS concentrations were generally not flow dependent or only weakly flow dependent, so average TSS concentrations were specified below average flow.

Many tributaries were not monitored for suspended solids concentration. Unmonitored tributaries represent 29 percent of the drainage area between Fort Edward and Waterford. For unmonitored tributaries, the TSS rating curves developed for the monitored tributaries were applied. Each unmonitored tributary was matched with a monitored tributary based on consideration of land use distribution, watershed size, topography and location (Table 6-9). The rating curve for Moses Kill was used to estimate solids loads for all unmonitored drainage areas between Fort Edward and Stillwater. The Hoosic River rating curve was applied for unmonitored drainages between Stillwater and Waterford. Loads for each of the unmonitored tributaries were scaled to account for differences in drainage area from the reference tributary.

In two cases, unmonitored drainage areas were reduced in the estimate of solids loading to account for sediment trapping. The unmonitored drainage area between Fort Edward and TI Dam includes the Champlain Canal, which is fed by Bond Creek and water diverted from the Hudson upstream of Fort Edward (Art Murphy, NYS Canal Corporation, personal communication). The canal is highly regulated and during high flow is allowed to overflow, delivering water to the Hudson via overland flow. This likely results in solids retention in the canal. The effective drainage area of the Champlain canal was assumed to be 8 mi^2, 26 percent of the canal's watershed area (31 mi^2). Fish Creek drains Saratoga Lake, which receives tributary runoff from the bulk of the Fish Creek watershed. It was assumed that 80 percent of the tributary solids load from Fish Creek watershed was retained in Saratoga Lake. Therefore, 90 mi^2 of the 245 mi^2 watershed was considered in computing tributary solids loads.

The flow-dependent rating curve coefficients developed for each tributary are presented in Table 6-10. As discussed above, constant concentrations were specified below the average flow.

Resulting tributary solids loads from application of the tributary TSS rating curves in the manner described above were evaluated in the context of a solids balance for the mainstem Upper Hudson River. The period chosen for the solids balance was Jan. 1, 1977 to Jun. 30, 1992 because all mainstem river flow gages were operational during this time. Limiting the mass balance to this period was intended to reduce error associated with flows reported as estimates by USGS after 1992.

A comparison of annual average mainstem solids yields for the drainage area at Stillwater and Waterford to tributary solids yield (Table 6-11) shows that mainstem yields are about a factor of two larger than the estimated tributary yields. Table 6-12 presents the mainstem solids load increments between Fort Edward, Stillwater and Waterford. Estimated solids loads passing Stillwater and Waterford are 1.7 and 2.0 times larger than the sum of Fort Edward and upstream tributary solids loads. Assuming the mainstem in-river solids load estimates are accurate, the observed increases in in-river solids loads must be explained by either:

- additional external loads, from tributary inputs or other sources;
- internal production of solids from primary production; or,
- net erosion of the sediment bed between Fort Edward and Waterford.

External sources other than tributary load inputs are assumed negligible and estimates of possible contributions of solids from primary production were insignificant. Therefore, if estimated tributary solids loads are assumed accurate, this implies that resuspension accounts for the observed increases and that the Upper Hudson River is on average net erosional between Fort Edward and Waterford.

Considering that the Upper Hudson is an impounded system with six dams over the 40 miles between Fort Edward and Waterford, it was considered unlikely that the river is net erosional over this reach. Typically, river impoundments experience net deposition. Required navigational dredging over the extent of the Upper Hudson also suggests that the river is depositional, however, erosion-derived sediment from other areas of the river could be responsible for required navigational dredging in the main channel. Based on the assumption that the river was net depositional on a reach basis, it was concluded that tributary loads were likely underestimated and required upward adjustment to achieve a long-term solids balance with observed loads passing Stillwater and Waterford.

6.5.3.3 Development of Long-term Solids Balance

Development of a long-term solids balance for the Upper Hudson is possible for reaches to which upstream and downstream in-river solids loads are known. For each reach, the sum of upstream loads, tributary loads and internal sources (resuspension or primary production) must equal the estimated in-river load. As discussed above, primary production contributions (from algal growth) and solids loads from external sources, excluding tributary inputs, (such as possible point source or other direct loads to the water column) were assumed insignificant in developing the solids balance. Thus, the solids balance required that upstream loads, tributary loads, and net solids loads from the sediment sum to the estimated in-river loads leaving each reach. Unless solids loads to the system being modeled are equal to solids transport out of the system, internal solids dynamics are unconstrained in the model. For example, if upstream and tributary loads are estimated without consideration of net solids exchange with the sediment bed, calibration of the model to observed in-river loads may result in unrealistic predictions of bed behavior.

In adjusting tributary solids loads to achieve a long-term solids balance, all impounded reaches of the Upper Hudson river from Fort Edward to Waterford were assumed to be net depositional over decadal time scales, even if there might be localized areas within reaches that are net erosional. Estimated solids loads passing Fort Edward, Stillwater and Waterford were assumed to be accurate.

Depositional loads to each reach were estimated and tributary TSS loads were increased between Thompson Island Dam and Waterford to equal the sum of observed loads at Waterford and the estimated depositional load. Tributary solids loads to Thompson Island Pool from Snook Kill, Moses Kill and direct drainage inputs were not adjusted. These tributary load estimates are based on sufficient TSS and flow data such that their solids loads are reasonably well known. The Mohawk River suspended solids loads were also not adjusted because insufficient data exist at Federal Dam to evaluate the solids balance between Waterford and Federal Dam.

A measure of the depositional load is the long-term average sediment burial velocity. Measurements of burial velocity were obtained by USEPA using radionuclide sediment core dating at 5 locations between Federal Dam and Fort Edward (USEPA, 1997). Two of these locations are in TIP. These measured burial velocities represent long-term average deposition at the core sites, however, these locations were generally positioned in low energy, highly depositional areas and are not considered representative of reach-wide average conditions. Therefore, estimation of sediment burial rates or reach-specific solids trapping efficiency was necessary. Solids trapping efficiency can be used to compute the average burial rate based on sediment density as shown later below.

Calculations of solids burial rates were available from a sediment transport model (SEDZL) developed for the Upper Hudson River by General Electric Company (GE) contractors (QEA, 1999). Flow and solids loading inputs to SEDZL were developed through discussion with the USEPA in the development of the HUDTOX model. As a result, the SEDZL inputs are nearly identical to the inputs described in this report. Initial sediment transport simulations conducted by GE were used to compute burial rates (and solids trapping efficiency) by reach for use in computing the tributary solids loads. Final results indicated that initial input assumptions were reasonable. The SEDZL simulation period was nearly the same as the HUDTOX 21-year historical calibration period. This sediment transport model was based on the same cohesive sediment resuspension formulations and site-specific data used to develop the Depth of Scour Model (DOSM) presented in Chapter 4. This model also used theoretical formulations for non-cohesive sediment armoring based in part on the non-cohesive sediment scour calculations in the DOSM. Earlier versions of SEDZL have been successfully applied on other similar river systems (e.g. Ziegler and Nisbet, 1994, Pawtuxet River, R.I.; Galiani et al. 1996, Buffalo River, N.Y.). Details of the SEDZL sediment transport model development and application to the Upper Hudson River are provided elsewhere (QEA, 1999).

Available SEDZL calibration results suggest the GE sediment transport model achieved reasonable agreement with estimated burial rates at the USEPA high-resolution sediment core sites (QEA, 1999). Results were within a factor of two with measured solids burial rates from all but one of the high resolution sediment cores. Agreement was within a factor of five for the remaining sediment core. The burial rate results from this sediment transport model contain uncertainty, however, due to large uncertainty in model inputs, especially tributary solids loads downstream of Thompson Island Pool. These uncertainties affect long-term solids burial rates in both cohesive and non-cohesive sediment areas. These limitations notwithstanding, burial rates from the SEDZL sediment transport model were considered reasonable estimates. Downstream of Thompson Island Pool, these estimates are affected by high uncertainty as would be any estimates that could be made, due to the limitations of the tributary flow and solids data.

Based on the above considerations, the reach-specific estimates of TSS trapping efficiency from the GE sediment transport model presented in Table 6-13 were used to develop the long-term solids balance for Jan. 1, 1977 through 1997. The trapping efficiency estimates by reach were area-weighted to determine trapping efficiencies for TI Dam to Stillwater (8.47 percent) and Stillwater to Waterford (3.66 percent) reaches. Solids depositional loads to the sediments in each reach were computed from the trapping efficiency and used to back-calculate total tributary loading to the each reach. The trapping efficiency is generally related to the depositional load as shown in Equation 6-14.

$$\text{Depositional load(kg/d)} = \left(\begin{matrix} \text{upstream load} \\ + \text{tributary load} \end{matrix} \text{(kg/d)} \right) \times \text{trapping efficiency (\%)} \quad \textbf{(6-14)}$$

In order to determine depositional loads to each reach, calculation of tributary loads and upstream loads was done in succession for Thompson Island Pool, Thompson Island Dam to Stillwater, and Stillwater to Waterford. In Thompson Island Pool, the available data for tributaries (Snook Kill and Moses Kill) was sufficient to compute loads directly from data-based rating curves. A long-term data-based solids balance could not be conducted explicitly for Thompson Island Pool because Thompson Island Dam sampling began in 1991. Based on the successful calibration of the SEDZL model to available data at the dam (presented by QEA, 1999), the Thompson Island Pool trapping efficiency estimate is assumed reasonably accurate for use in computing the Thompson Island Dam solids load. This was estimated by multiplying the TIP trapping efficiency estimate (8.8 percent) and the sum of tributary and upstream loads (Equation 6-15). The incremental load computed for the Thompson Island Dam to Stillwater reach (Equation 6-16) was apportioned to each tributary based on the percent of total tributary watershed area, excluding watershed area draining to the upstream portion of river (Table 6-2), as shown below.

Thompson Island Dam to Stillwater solid balance:

$$L_{TID} = (1\text{-}.088) \times (L_{FE} + L_{Snook} + L_{Moses} + L_{DD}) \quad \textbf{(6-15)}$$

$$\Delta L_{trib,TID\text{-}Still} = \frac{L_{Still}}{1 - \%trap} - L_{TID} \quad \textbf{(6-16)}$$

$$L_i = \Delta L_{trib,TID\text{-}Still} \times \left(\frac{DA_i}{DA_{TID-Still}} \right) \quad \textbf{(6-17)}$$

where:

L_{FE}, L_{TID}, L_{Still}	= TSS load at Fort Edward, TI Dam, Stillwater
L_{snook}, L_{Moses}, L_{DD}	= tributary TSS load from Snook, Moses, and direct drainage
$\Delta L_{trib,\ TID\text{-}Still}$	= incremental load from tributaries between TI Dam and Stillwater
L_i	= total load apportioned to tributary *i* in the solids balance
DA_i	= drainage area of tributary *i*
$DA_{TID\text{-}Still}$	= total incremental drainage area from TI Dam to Stillwater
$\%trap$	= solids trapping efficiency

In order for rating curve tributary load estimates to equal the apportioned load to each tributary, an upward adjustment in the data based curves was required. The largest uncertainty in tributary TSS load estimates was assumed to be in the high-flow portion of the rating curve. Therefore, the tributary rating curve *b* coefficient (Equation 6-18) was adjusted iteratively until the resulting load equaled the specific value of L_i computed for each tributary. The constant low-flow concentrations were not adjusted.

$$\left\{\begin{matrix} Q > \overline{Q}, \text{ TSS } = a \times Q^b \\ Q \le \overline{Q}, \text{ TSS } = c \end{matrix}\right\} = L_i \tag{6-18}$$

where:

c = constant low flow TSS concentration based on data average

Tributary loads between Stillwater and Waterford were adjusted in the same fashion. The resulting exponent in the rating curve equation, b, for each tributary ranged from 1.1497 for the Fish Creek to 2.236 for Deep Kill (Table 6-10).

Resulting increases in tributary solids loads to achieve the long-term solids balance were significant. Tributary loads between Thompson Island Dam and Stillwater were increased by a factor of 2.46. Between Stillwater and Waterford, tributary loads were increased by a factor of 1.91. The adjusted rating curves required to achieve the solids balance are shown with the data and data-based rating curves to demonstrate the required adjustments at high flow (Figure 6-15). While the adjusted Hoosic River rating curve looks reasonable, the adjustment of the Batten Kill rating curve does not agree well with the limited available data. However, considering the limited data available and the fact that the Batten Kill flow is estimated based on a much smaller tributary, there is considerable uncertainty in the TSS versus flow relationship observed for Batten Kill. Flow phasing errors (timing of peak flows) based on relating Batten Kill flow to Kayaderosseras Creek flow may have significantly affected the Batten Kill rating curve.

6.5.4 Results

A long-term solids balance was developed for the period Jan. 1, 1977 through September 30, 1997. The Fort Edward solids rating curve and the tributary rating curves adjusted to achieve the solids balance were applied to develop daily time series inputs to the HUDTOX model for the calibration period. Annual average mainstem and tributary solids loads for the calibration period are presented in Figure 6-16.

Results show that annual average sediment load increases by a factor of 2.8 between Fort Edward and Stillwater and by a factor of 5.7 between Fort Edward and Waterford over the calibration period. In comparison, average flow increases by a factor of only 1.2 and 1.5 percent between these locations, respectively. Watershed TSS yield increases by a factor of 2.1 and 3.5 moving downstream from Fort Edward (10.7 MT/yr-mi^2) to Stillwater (22.2 MT/yr-mi^2) and Waterford (37.4 MT/yr-mi^2), respectively.

To illustrate relative sediment load contributions, percent of annual average solids loads for low and high flow periods, "non-event" and "event", respectively, are plotted in sequence from upstream to downstream (Figure 6-17). This plot shows that high and low flow tributary solids contributions are about the same and also illustrates the importance of tributary loads downstream of Thompson Island Dam. The Batten Kill load is about the same magnitude as the Fort Edward load and the Hoosic River load is approximately twice as large as the Fort Edward load. Without accounting for depositional losses, at Stillwater and Waterford, only 36 and 17 percent, respectively, of the external solids load entering the river is attributed to Ft. Edward.

Only 5 percent of the suspended solids load at Federal Dam enters the system at Fort Edward, due to the large contribution from the Mohawk River.

The distribution of mainstem solids loads over the range of observed flows was analyzed to understand the relative importance of high and low flow solids transport (Figure 6-18). At Fort Edward, Stillwater and Waterford approximately 55, 50, and 70 percent of the TSS transport occurs below two times the average flow ($Q/Q_{avg} = 2.0$). At Fort Edward, two times the average flow, 10,496 cfs, is approximately equal to the high/low flow strata used to specify the TSS rating curves, 10,000 cfs.

6.5.5 Summary of Solids Load Estimates

Mainstem solids load estimates were developed for Fort Edward, Stillwater and Waterford using rating curves developed using non-linear least squares fitting. At Fort Edward, time stratification in the load estimates was based on observed changes in the TSS to flow relationship between the 1977-1990 and 1991-1997 periods. Annual average sediment loads for the 1991-1997 period are 40% percent lower than the loads for the 1977-1990 period at Fort Edward. The time-stratified solids rating curves for the 1991-1997 period are considered the best estimates of future TSS loading at Fort Edward (Chapter 8).

Tributary loads were initially computed using rating curves based on the limited available tributary data. These results required adjustment for tributaries between Stillwater and Waterford to achieve a long-term solids balance from 1977 to 1992 consistent with the assumed depositional character of the Upper Hudson River. Estimates of solids trapping efficiency by reach developed by QEA (1999) using the SEDZL sediment transport model were used to compute tributary loads between these locations. The data based tributary rating curves were scaled up at high flow to achieve the necessary TSS loading increase. Results produced tributary solids yields in reasonable agreement with literature ranges (Table 6-14), although the adjusted rating curves did not agree with the limited data in all cases (Figure 6-15). Final tributary load estimates between Thompson Island Pool and Waterford are considered very uncertain.

The solids balance achieved for the 1977-1992 period gave good results for the entire calibration period when compared to estimated solids fluxes passing Stillwater and Waterford. Results show that mainstem solids loads increase by a factor of 5.7 from Fort Edward to Waterford. This illustrates the significance of tributary loads, which are very uncertain due to limited tributary solids and flow data. The large degree of uncertainty in these estimates imparts significant uncertainty to the model calibration below Thompson Island Dam (Chapter 7).

6.6 Mainstem and Tributary PCB Loads

6.6.1 Overview

Application of the HUDTOX model requires specification of all external flow inputs, solids loads and PCB loads. Just as flow (Section 6.4) and solids loading (Section 6.5) time series were developed for the calibration period, upstream and tributary loading time series were developed for the seven PCB state variables: total PCB, Tri+, BZ#4, BZ#28, BZ#52, BZ#90&101, and

BZ#138. Tri+ load estimates were developed for the long-term historical calibration period, January 1, 1977 through September 30, 1997. Load estimates for total PCB and the five congener state variables were estimated for the short-term hindcast period: April 1, 1991 through September 30, 1997. To aid in model calibration, estimates of in-river fluxes were also developed for Tri+ at Schuylerville, from 1977-1992; Stillwater and Waterford from 1977 to 1997; and, for Tri+ and Total PCB at Thompson Island Dam from 1991-1997. In developing the Thompson Island Dam PCB load estimates, a correction was applied to measurements taken at the west shore station to correct for observed biases in these data (QEA, 1998b). The in-river load estimates were calculated solely for comparison to model output and do not represent additional loads to the model.

6.6.2 PCB Data

6.6.2.1 Data Availability for Estimating PCB Loads

Mainstem Upper Hudson River PCB data were available from the USGS (1977-present), GE (1991-present) and from the USEPA 1993 Phase 2 investigation (1993). While the USGS dataset represents an extensive historical record of PCB concentrations, due to analytical and sampling limitations these data can only be used to develop approximate estimates of water column PCB load (USEPA, 1997). As discussed in Section 6.3.3.2, there is uncertainty associated with the USGS PCB quantitation and the translation of these quantitations to estimates of the long-term calibration state variable, Tri+.

The most extensively sampled mainstem stations in the model domain are Fort Edward, Thompson Island Dam, Schuylerville, Stillwater and Waterford. Exact sample collection locations varied at these stations, especially at Fort Edward. Samples collected in the vicinity of Fort Edward by the various USGS, GE and USEPA Phase 2 data collection efforts were grouped to represent Fort Edward concentrations. The same was done for the other stations.

The data available from each source at the primary mainstem sampling stations are summarized for Tri+ by year in Table 6-15 and for total PCB and congeners in Table 6-17. Significantly fewer data are available for tributaries, with only Batten Kill, Hoosic River and the Mohawk River actually being sampled for PCB (Table 6-16). Additionally, no tributary PCB data are available prior to 1991. Figure 6-19 presents the location of the long-term PCB monitoring stations on the mainstem Upper Hudson River and the tributary sampling stations within the study area.

The long-term combined dataset from USGS, GE and USEPA represents good coverage of the high and low flow regimes. Figure 6-20 shows the distribution of data over the range of sampled flows.

The USGS PCB data are reported as Aroclor quantitations or the sum of Aroclor quantitations and neither individual congener nor complete unbiased total PCB concentrations are available from these data. Thus the total PCB and congener data are limited to the GE and USEPA data collection periods, which began in 1991. Congener data are available for all five congener state variables, however, at Fort Edward BZ#4 and 138 were quantified in only about half of the

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samples in which total PCB was quantified. BZ#28, 52, and 101+90 were quantified in nearly all of the samples in which total PCB was quantified.

While continuous sampling was conducted at Fort Edward and Thompson Island Dam from 1991 through 1997, GE and USEPA conducted little or no sampling at stations downstream of Thompson Island Dam from 1993 to 1997. As a result, a continuous record of PCB concentrations over the calibration period (1977-1997) is only available for Tri+ at Fort Edward, Stillwater, and Waterford. Sampling at Schuylerville by USGS ended in 1992.

6.6.2.2 Thompson Island Dam West Shore Station Bias Correction

As summarized in QEA (1998b), an apparent sampling bias was discovered in fall of 1997 in PCB measurements from the routine monitoring station located on the west shore of Thompson Island Dam. A significant fraction of the GE and USEPA data at Thompson Island Dam were collected from stations on the west shore. The samples collected at this station are not always representative of the average PCB concentration leaving the pool, hence the term "bias", and must be corrected for use in mass balance analysis.

The bias appears to be related to contribution of PCB from nearshore contaminated sediments under conditions of incomplete lateral mixing. The magnitude of the bias, in terms of percent difference between the west shore and center channel locations, is related to flow conditions and upstream PCB concentration. During high flow periods sufficient lateral mixing occurs to prevent any significant lateral gradients at the dam. During periods of high PCB loading at Fort Edward, the relative contribution of the nearshore hotspots is smaller.

After discovery of the west shore station bias, GE modified its monitoring program to better quantify the magnitude of the bias (O'Brien & Gere, 1998). The modified program included collection of samples further upstream and downstream of Thompson Island Dam, in the center channel of the river, and on lateral transects. These data allowed assessment of the relative degree of bias over different flow and upstream loading conditions. An analysis conducted by USEPA, (USEPA, 1999b) indicated that the ratio of west shore to center channel Tri+ concentrations approached unity for concentrations and flows at Fort Edward greater than 15 ng/L and 4,000 cfs, respectively. For flows less than 4,000 cfs and concentrations less than 15 ng/L at Fort Edward, a significant high bias exists for the west shore concentrations relative to the center channel. Segregating the observed ratios by these criteria produces the results in Table 6-18, which also presents results for total PCB based on an identical analysis. These values were used to "bias-correct" the west shore observations to better represent mean concentrations leaving Thompson Island Pool, based on Fort Edward concentration and flow conditions. The bias-corrected west shore concentrations were used when center channel observations were not available to compute PCB loads at Thompson Island Dam and for comparison to model output.

6.6.2.3 Data Development for Computing PCB Loads

The combined USGS, GE, and USEPA water column PCB datasets were reduced to daily average values for estimating daily average PCB loads. On numerous occasions, multiple samples were collected at these locations on the same day, especially at Fort Edward and

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Thompson Island Dam. Daily average concentrations were computed for days on which multiple measurements were reported. In computing daily average concentrations, the Phase 2 flow-average concentrations (which are from 15-day composite samples) were only used if no discrete measurements were available from GE or USGS.

Exact sample collection points at the mainstem sampling stations varied between and within agencies. Data from the various sample collection points at the primary sampling stations were combined to provide a record of concentrations at each location. At Fort Edward, samples were collected from the east and west channel of Rogers Island. Where same day measurements were taken in each channel, these were averaged. Otherwise, data from east or west channel, included with data from various other studies in the direct vicinity of the northern tip of Rogers Island were included in estimating PCB loads at Fort Edward.

PCB concentrations reported as non-detect were assigned a value of one-half the detection limit concentration. Detection limits vary among datasets. Although the USGS laboratory reports a theoretical quantitation limit of 0.01 μg/L through 1983, the practical quantitation limit was often considered to be 0.1 μg/L because of the small size of the water samples (Bopp et al., 1985). With water year 1984, the practical quantitation limit was lowered to 0.01 μg/L, however, the data were often reported as if they adhere to the previous quantitation limit through 1984 and 1985. In 1986, the quantitation limit began to be consistently reported as 0.01 μg/L. For the purposes of this project, USGS data in the printed Water Resources Data, New York and the USGS/Albany NWIS database were cross-checked to recover original quantitations at the 0.01 μg/L theoretical quantitation limit where possible. For the majority of the GE data, the detection limit was reported as 11 ng/L. The Phase 2 results include reported detection limits for non-detect values and an adjusted value for non-detects based on a treatment procedure (USEPA, 1989) for non-detect values put forth by EPA.

6.6.2.4 Overview

Calibration of the HUDTOX model to daily average PCB concentrations required specification of daily average PCB loads at Fort Edward and from tributaries. Thus, it was necessary to develop estimates of daily average loads at Fort Edward and for the tributaries for input to HUDTOX over the 21-year historical calibration period. While estimates of daily average PCB load passing the downstream stations were used for comparison to model output, these were developed on a daily basis for consistency with the Fort Edward load estimation and to develop estimates for the entire 21-year period. Estimates of annual PCB load at the long-term sampling stations are presented in the DEIR for part of the historical calibration period (USEPA, 1997). The annual load results computed from the sum of estimated daily loads (Section 6.6.3) are compared to the DEIR estimates.

In order to develop loads for Tri+, it was necessary to estimate concentrations for long periods of time between 1977 and 1991 that contained very few measurements. The estimated loads for these periods have high uncertainty. Sampling frequency was sufficiently high from 1991-1997 at Fort Edward and Thompson Island Dam that load estimates for the period 1991-1997 are considered more accurate than estimates for 1977-1991, with the exception of the period following the collapse of the Allen Mill gate structure at the Hudson Falls plant site. This event led to episodic elevated PCB loading in late 1991 and early 1992 that was probably not fully captured by routine sampling.

Loads of total PCB and the five congener state variables were also determined at Fort Edward for the short-term hindcast period (Jan. 1, 1991 to Sept. 30, 1997). In cases where congeners were not quantified while total PCB was quantified, congener concentrations were estimated based on their average observed mass percent in total PCB measurements.

This section presents the development of the mainstem Upper Hudson River load estimates for Tri+ over the period January, 1 1977 to September 30, 1997 and for total PCB and congeners BZ#4, BZ#28, BZ#52, BZ#90&101 and BZ#138 over the period January 1, 1991 to September 30, 1997.

6.6.2.5 Mainstem Tri+ Loads 1977-1997

In-river PCB loads were estimated at the primary long-term USGS monitoring locations, most importantly, at Fort Edward, the upstream boundary of the HUDTOX model. Specification of PCB loading at Fort Edward was done on a daily average basis, consistent with the input frequency of flows and solids loading.

Estimates of annual historical PCB loads at Fort Edward, Schuylerville, Stillwater and Waterford based on the USGS data are presented in the DEIR (USEPA, 1997). These estimates were based on application of two methods: the ratio estimator by Cochran (1977), and the averaging estimator presented by Dolan et al. (1981). An overview of these and other methods is presented by Preston et al. (1991). While these methods are suitable for estimating annual loads, estimates of daily average PCB load were sought for simulating PCB dynamics in HUDTOX on daily time scales. The HUDTOX calibration includes comparison to daily average PCB concentration measurements. To develop a method for estimating daily average PCB loads, flow-dependent regression relationships were explored, as was linear interpolation of measured concentrations and use of seasonal average concentrations by year.

Regression methods were eliminated because no significant relationships were observed among PCB concentration, flow and suspended solids concentration. Relationships between these parameters at Fort Edward were explored for 2-year intervals to reduce confounding effects of long-term reductions in concentrations (e.g. Figures 6-21 and 6-22). Elevated PCB loads do appear to be partially correlated with flow and TSS concentrations, however, significant variability in the correlations is observed at high and low-flow conditions. These observations did not support use of flow-based regression methods.

Based on exclusion of regression methods, a combination of linear interpolation of measured concentrations between sampling dates and use of seasonal average concentrations by year was selected. The appropriateness of either of these individual methods depends on data availability. During periods of low data frequency, linear interpolation has a significant potential for bias due to the presence of high or low measurements that have biases relative to mean concentrations. During high sampling frequency, linear interpolation may more accurately describe daily loads when concentrations are changing as a result of seasonal effects or upstream source activity.

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Prior to 1991, a combination of seasonal average concentrations by year and linear interpolation was used to estimate daily PCB concentrations at Fort Edward. Beginning in 1991, GE began regular monitoring of PCBs at Fort Edward and data availability over the period 1991 to 1997 was considered sufficient to support linear interpolation of measured concentrations over time for all PCB forms modeled.

During the earlier historical period, large data gaps exist and data collection was sparse, especially from 1977 to 1984. Due to the limited amount of data available during various times in the calibration period, seasonal average concentrations were used in lieu of the linear interpolation approach. Seasonal average concentrations were computed during each year and applied in the respective individual years. Periods of application of each approach were specified based on inspection of the PCB concentration time series at Fort Edward. Figure 6-23 presents the daily average measured and estimated PCB concentrations at Fort Edward. Inspection of this figure reveals the time periods selected for application of each method. The black line on this figure shows estimated concentrations based on the data, shown as symbols.

One complication in the use of linear interpolation is the apparent occurrence of random "pulse" loading events of PCBs at Fort Edward, identified through inspection of the Ft. Edward daily average concentrations. These pulses occasionally occur in conjunction with high flow events. Two such examples are presented in Figure 6-24. On May 9, 1994 a concentration of 130 ng/L was observed at Fort Edward and concentrations measured 3 days before and 3 days after this measurement both showed concentrations less than 15 ng/L. On April 25, 1983 a concentration of 900 ng/L was observed three days following and two days preceding measurements less than 20 ng/L.

The occurrence of these pulse load events appears only partially correlated with flow. Due to very high concentrations, however, these events can contribute large mass loading of PCBs to Thompson Island Pool. The use of linear interpolation during periods of infrequent sampling sometimes exaggerated the apparent contribution of pulse loads that were characterized by only a single or very few data points. Interpolation in these situations caused estimated loads to be strongly affected by individual high concentration measurements for long periods of time prior to and following the measurements. This was considered unreasonable based on inspection of the high frequency data collected by GE beginning in 1991. These data suggest that these pulse load events are of short duration, on the order of days rather than weeks. Based on these observations, the pulse loading events were assigned a duration of 6 days, assuming that the measured value captured the peak concentration. Seasonal average values were then applied for the periods before and after these events to the preceding and following measurements.

Considering the low sampling frequency, it is very likely that many pulse load events were missed, which introduces large uncertainty into the PCB load estimates, considering the large magnitude of observed pulse loads. It is noteworthy that a single measured pulse load in 1992 was responsible for 19 percent of the estimated total PCB load in that year alone. The uncertainty due to pulse loads is further exacerbated in the early historical period by the fact that sampling frequency was lowest during the period when PCB loads were at their highest levels.

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Estimates of daily average in-river Tri+ loads at Thompson Island Dam, Schuylerville, Stillwater and Waterford were computed using the same approach as that implemented for Fort Edward. These loads were estimated for comparison to model output. Periods over which interpolation was used varied among stations due to variations in sampling frequency among stations.

6.6.2.6 Tributary Tri+ Loads 1977-1997

Due to extremely limited data, tributary PCB loads were estimated in a different manner from mainstem loads. For the monitored tributaries, Batten Kill, Hoosic River and Mohawk River, the average PCB concentration was calculated and the assumption was made that this concentration remained constant for the entire study period (Table 6-19). Measured concentrations were substituted when available. Because the three monitored tributaries were also the only tributaries with known PCB dischargers, it was assumed that these tributaries would have higher PCB concentrations than the other tributaries in the study area. The Tri+ concentrations in the unmonitored tributaries were assumed to equal the lowest recorded Tri+ concentration from the three monitored tributaries, 0.17 ng/l.

These values were assumed to represent background concentrations for the unmonitored tributaries. It is possible that historical tributary PCB concentrations were higher, however, the relative contribution of tributary PCB loads compared to the upstream PCB load at Fort Edward is small (less than 5 percent) and has negligible impact on the HUDTOX model predictions.

6.6.2.7 Tri+ Load Results 1977-1997

To evaluate results, total annual Tri+ loads estimated for each mainstem station are compared to annual loads presented in the DEIR by USEPA (1997) (Table 6-20, Figure 6-25). The DEIR annual load estimates are based on application of a flow-stratified version of the ratio estimator developed by Cochran (1977). This comparison recognizes that comparison to the DEIR estimates is affected for some periods by use of different Tri+ concentration and flow data. Nonetheless, the DEIR load estimates provide a reasonableness check against the estimates developed as describe above because the DEIR estimates were based on a different method.

The DEIR estimates used Tri+ concentrations estimated from the USGS data that do not reflect the more recent approach developed by Rhea and Werth (1998) to account for analytical bias in these data. Therefore, based on the average effect of the bias correction, the DEIR estimates are estimated to contain a high bias of approximately 14 to 16 percent relative to the estimates presented here. Comparison of the DEIR estimates at the mainstem stations to those developed herein for the period 1977-1990 shows that on a cumulative loading basis, the DEIR values are on average 18 to 26 percent larger on an annual basis, consistent with the approximate magnitude of the analytical bias correction. This comparison suggests that the loads estimated here are consistent with the DEIR estimates, after accounting for the analytical bias.

Several important observations can be made from inspection of the estimated annual Tri+ loads over the simulation period. It is clear that a significant declining trend in Tri+ loads past all of the mainstem stations occurred over the period 1977 to 1997 (Figure 6-26). While, the overall trend is clearly declining, estimated loads show large year to year variability (some years' loads

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are greater than previous years). Of particular note is the large increase in Tri+ loads in 1983-84 and 1991-92. The large temporary increase in PCB load in 1991-92 is associated with the failure of the Allen Mill gate structure in September 1991 (USEPA, 1997). The 1983 load increase reflects high spring floods occurring in that year.

Average daily loads at Fort Edward over the period 1980-1984 were approximately 1.21 kg/d compared to an average of 0.45 kg/d for 1985-1990. Following an increase in loads in 1991-1992 due to the Allen Mill event, loads continued to decline. Average loading at Fort Edward for the period 1994-1997 was 0.24 kg/d. The 1997 Fort Edward daily average load was about 0.8 kg/d.

A conspicuous result is that the estimated Tri+ load passing Fort Edward is much lower than estimated PCB loads passing Schuylerville, Stillwater and Waterford in 1977, 1978, and 1979, relative to the remainder of the simulation period (Figure 6-26). This suggests that either large unmeasured external loads were entering the river upstream of Schuylerville, or that the sediment contribution of Tri+ between Fort Edward and Schuylerville was very large during this period. It is possible that additional sources were active during this period, perhaps from land-disposed PCB laden sediments near the river. The low sampling frequency at Fort Edward may also have missed significant high concentration events, resulting in an underestimate of the Fort Edward load. The most likely explanation, however, is that large amounts of unstable contaminated sediment deposits, released by the 1973 dam removal at Fort Edward, were available for mobilization within the Thompson Island Pool in this period. It should be noted, however, that the period of highest upstream loading, from 1977 to 1983, contains only 22 percent of the 801 daily average measurements at Fort Edward. In 1977, when loads were the second highest of any year in the calibration, only 3 samples were collected. Due to the high uncertainty in Fort Edward loads in the late 1970's and early 1980's, comparison of model results to downstream data was discounted during this period (Chapter 7).

An important understanding gained from interpreting the estimated loads is that the majority of PCB transport occurs during non-flood flow periods. The term "low flow" is used throughout this report to refer to non-flood flows less than 10,000 cfs at Fort Edward, which is approximately twice the average flow. Low flow periods are characterized by relatively low sediment scour, although approximately 50% of the total solids transport occurs at low flow. By comparison, between 65 and 70% of PCB transport in the Upper Hudson River occurs at low flow (Figure 6-27).

Analysis of Tri+ PCB load gain across Thompson Island Pool also shows the significance of sediment-water exchanges at low flow (Figure 6-28). For the period 1993-1997, between 60 and 70 percent of the Tri+ load gain across Thompson Island Pool occurs during the summer months, June through August, when flows are typically very low. This observation does not diminish the significance of high flow events in mobilizing PCBs due to flow-dependent resuspension, however, it does suggest that flow-dependent resuspension is not the dominant process controlling sediment-water PCB mass fluxes in the Upper Hudson River. This focuses attention on the importance of low flow sediment to water PCB mass transfer processes, which is discussed in Section 6.12.

A plot of relative contributions of tributaries to the cumulative Tri+ load over the calibration period is presented in Figure 6-29. Tributary loads are insignificant relative to upstream loads.

6.6.2.8 Mainstem and Tributary Total PCB and Congener Loads 1991-1997

Specification of daily upstream and tributary PCB loads was also required for the hindcast application period, Jan.1, 1991 to Sept. 30, 1997. Sampling frequency was approximately biweekly at Fort Edward and Thompson Island Dam for ice-free conditions during this period. In winter months, sampling frequency was approximately monthly. At Stillwater and Waterford, sampling by GE and USEPA provided total PCB and congener measurements through 1993. Daily average loads of total PCB and the five congener state variables (BZ#4, BZ#28, BZ#52, BZ#90+101, and BZ#138) were estimated by linear interpolation of daily average values at Fort Edward over this period. For total PCB daily average loads were also estimated by interpolation at Thompson Island Dam for comparison to model output (Chapter 7). As discussed in Section 6.3, a correction was developed for the Thompson Island Dam data to account for the observed bias in the west shore sampling station measurements. Because sampling frequency was lower and the sampling period much shorter at Stillwater and Waterford, daily average loads were not estimated for total PCB and congeners at these locations.

The estimated loads of congeners BZ#28, BZ#52, and BZ#90+101 are considered known to within the certainty of the estimated total PCB load because the number of data points used was nearly the same as for total PCB. BZ#4 and BZ#138, however, have reported quantitations greater than zero for only 42 and 34 percent of the total PCB results, respectively in Release 4.1b of the Hudson River Database. Zero, or non-detects were frequent for BZ#4 and BZ#138 when other congeners were measured in fairly high concentrations. Concentrations of BZ#4 and BZ#138 were estimated based on observed ratios to total PCB. Evaluation of these ratios at Fort Edward showed a seasonal pattern, with BZ#4 mass fraction highest in the summer months and BZ#138 showing the opposite behavior. This probably reflects enhanced sediment-water release of BZ#4 during summer months from contaminated sediment deposits upstream of Fort Edward. This may also reflect enhanced mobilization of heavier congeners during resuspension events upstream of Fort Edward, based on an observed negative correlation of the BZ#4 mass fraction with flow.

An additional observation was that in 1991 and 1992, average BZ#4 fractions (0.035) were approximate to that in Aroclor 1242 (0.0313), which is the primary source material of the Fort Edward PCB load. In the other years where congener data are available (1993, 1996, and 1997) BZ#4 mass fractions were significantly higher, on average about 0.09 (Figure 6-30). Some measurements showed BZ#4 fractions greater than 0.25. These observations probably reflect the release of fresh Aroclor 1242 material during the Allen Mill event. In light of these observations, the monthly average ratios to total PCB for the period 1991-1992 and 1993-1998 were used to estimate BZ#4 and BZ#138 concentrations when total PCB was quantified but the congener results reported as zero.

The same approach as used in developing tributary loads for Tri+ was used for specifying tributary loads for Total PCB. The average measured concentrations was used for monitored tributaries, while the minimum measured concentration (0.51 ng/l) in the monitored tributaries was assigned to the unmonitored tributaries (Table 6-19). Tributary loads for individual congeners were assumed insignificant and specified as zero.

6.6.3 Total PCB and Congener Load Results 1991-1997

Annual average total PCB and congener loads computed at Fort Edward are presented in Table 6-21. Consistent with the long-term declining trend in Tri+ loads observed at all mainstem stations, the total PCB and congener loads at Fort Edward are also observed to decline over the period 1992-1997 following the increase in load associated with the Allen Mill gate structure event in the fall of 1991 (Figure 6-31).

Comparison of total PCB loads at Fort Edward and Thompson Island Dam shows that annual average total PCB load gain across Thompson Island Pool is approximately a factor of two larger than the load gain of Tri+. The difference is primarily due to the release of BZ#4 from Thompson Island Pool sediments, which is not reflected in the Tri+ load gain.

6.6.4 Summary of PCB Load Estimates

Daily average estimates of PCB loads at Fort Edward, TI Dam, Stillwater and Waterford were developed for use in the long term historical calibration and short-term hindcast applications. Tri+ loads were developed for the long-term calibration, from January 1, 1977 to September 30, 1997, using a combination of linear interpolation and seasonal averages of measured concentrations by year. Seasonal average values were specified during periods where data sampling frequency was too low to support linear interpolation. Total PCB and congener load estimates were developed for the short-term hindcast period, January 1, 1991 to September 30, 1997, using linear interpolation. Total PCB loads for this period were estimated at Fort Edward and at Thompson Island Dam. Congener loads were only estimated at Fort Edward. The Thompson Island Dam total PCB loads were developed for comparison to model output. Monitored tributaries were assigned the average measured concentrations. For unmonitored tributaries, loads were specified for total PCB and Tri+ based on the minimum measured concentrations from monitored tributaries. During the historical calibration period, tributary PCB loads represent less than 3 percent of the total loading of PCB between Fort Edward and Waterford.

The resulting daily average PCB loads estimated as described above were used to develop input time series of PCB loads for the HUDTOX model at Fort Edward and all 12 tributaries. Estimated loads at Thompson Island Dam, Stillwater and Waterford were used for comparison to model output.

PCB load estimates at Fort Edward are very uncertain in the first few years of the historical calibration period and again in the fall of 1991 due to low sampling frequency during periods of high, fluctuating loads. Based on observation of high concentrations at Schuylerville, the Fort Edward load may have been under-estimated or other sources may have been active from 1977 to about 1984. An additional source of uncertainty in the Fort Edward load arises from the apparent occurrence of random pulse loading events, which are suspected to be only partially captured by available data.

Load results show overall, a strong declining trend in upstream PCB loads from the late 70s to the late 90s, with a noticeable temporary interruption in 1991 due to the Allen Mill event. Currently, Fort Edward loads and load gain through the system are comparable to loads observed approximately 10 years ago in the late 1980s.

Analysis of PCB loads estimated at Fort Edward and Thompson Island Dam shows that approximately 60 percent to 70 percent PCB loading at Fort Edward, and PCB load gain across Thompson Island Pool, occurs at flows less than 10,000 cfs at Fort Edward.

6.7 SEDIMENT INITIAL CONDITIONS

6.7.1 Overview

The HUDTOX model requires specification of initial PCB concentrations, in addition to sediment specific weight (mass of dry solids per unit volume), sediment particulate organic carbon content (f_{OC}) and sediment dissolved organic carbon concentrations (DOC). This section presents specification of initial PCB concentrations in 1977 and specific weight. Specification of sediment f_{OC} and DOC concentrations is presented in Section 6.9, which also includes specification of partition coefficients.

Sediment initial conditions for Tri+ are developed from the 1977 NYSDEC sediment dataset. Average concentrations were determined on a dry weight concentration basis for specific sediment layer intervals over discrete areas of the river corresponding to individual segments, or groups of segments in areas of limited data. Concentrations were averaged over 2 cm intervals in the sediment bed to develop concentrations for each HUDTOX sediment layer, down to 26 cm. Sediment specific weight was established based on the USEPA Phase 2 low resolution coring data. Average values were determined for cohesive and non-cohesive sediment for the entire river.

6.7.2 Sediment Specific Weight

Specific weight is defined as the mass of dry solids per unit volume of wet sediment, or the sediment solids concentration. The HUDTOX model requires specification of sediment specific weight as an initial condition, which is held constant through the simulation (See Chapter 5).

Sediment specific weight values for the HUDTOX sediment layers have been determined using a subset of the USEPA Phase 2 low resolution sediment core data for which specific weight was estimated as wet bulk density times percent solids. Some of the reported data were excluded due to anomalous values for bulk density, percent solids or both. A total of 535 specific weight measurements from 169 sediment cores were used (there are values for multiple core slices at most locations).

An attempt was made to incorporate the following three criteria used by Zeigler and Nisbet (1994) to identify cohesive sediments:

1. $d_{50} < 250\ \mu m$;

2. percent clay and silt > 15%; and,

3. percent moisture > 75% .

The percent moisture values were deemed unsuitable for this purpose, therefore, samples were classified as cohesive or non-cohesive based on criteria #1 and #2, using the ASTM sediment classifications provided in the Hudson River Database. The sediment classifications (up to 3 classes are identified based on visual description or grain size) are associated with a descriptor (either abundant, some, trace, or few) indicating relative abundance of the associated material. The descriptors provided for each sample were used to infer grain size and the percent clay and silt.

Samples classified as fine sand, silt, clay, or organics were assumed to meet the criteria of $d_{50} <$ 250 μm, except those containing "some" coarse sand and/or gravel. Fine sand samples having "some" or "abundant" silt, clay, or organics were assumed to meet criterion #2 and were considered cohesive. A total of 30 fine sand samples having "few", "trace" or no silt, clay, or organics were classified as non-cohesive. All other samples were classified as non-cohesive. This resulted in a total of 366 samples classified as cohesive and 169 samples classified as non-cohesive.

Specific weight values were grouped by sediment type (cohesive and non-cohesive) for top core sections, which have an average depth of 10 inches. Mean specific weights for cohesive (0.84 g/cc) and non-cohesive (1.38 g/cc) sediments were selected to represent the sediment specific weight in HUDTOX.

The cohesive sediment average specific weight (0.84 g/cc) is 37 percent lower than the average specific weight for non-cohesive sediment (1.38 g/cc). The difference in specific weights of the cohesive and non-cohesive sediments determined from the TAMS low resolution sediment cores is mainly due to differences in porosity (average porosity is 0.59 for cohesive and 0.37 for non-cohesive), which accounts for approximately 93 percent of the difference in specific weights. The difference in particle density (average particle density is 2.16 for cohesive and 2.22 for non-cohesive) contributes approximately 5 percent of the difference in specific weight.

6.7.3 1977 Tri+ Initial Conditions

6.7.3.1 1977 NYSDEC Sediment Data

Initial conditions were developed from the 1977 NYSDEC data. These data were collected from a sediment coring and grab sampling program spanning the Upper Hudson River from the Bakers Falls area to Troy. The most extensive sampling occurred in Thompson Island Pool. Approximately 30 samples were collected north of Fort Edward, and 24 samples downstream of Federal Dam at Troy, falling outside of the HUDTOX model domain. Approximately 40 other samples lacked location data (river mile or northing/easting coordinates) and were not usable for developing sediment initial conditions. A total of 961 sample locations, consisting of 623 grab samples and 338 core samples were available within the HUDTOX domain.

A number of the 1977 samples were excluded from use in specifying initial conditions due to anomalies in the data. A group of grab samples all reported to be located at river mile 189.2 and having very high PCB concentrations were considered suspect and dropped, as was a group of grab samples reported to have been collected at river mile 156.5 on December 27, 1977. No documentation could be found supporting this December sampling event (QEA, 1999). One additional sample was excluded, ID number 30291, which had a very high PCB concentration and was surrounded in close proximity by samples with much lower concentrations.

The 1977 NYSDEC data core sample depths varied widely. Surficial layer sectioning ranged from 1.5 cm to 56 cm, with an average of 7.5 cm. Grab samples were taken by a Shipek sampler and usually obtained a 0-5 inch depth composite (Tofflemire and Quin, 1979). The average surface sample depth of core and grab samples combined is 10.9 cm.

The 1977 NYSDEC samples were not analyzed for solids specific weight. Measurement of principal fraction-phi, %gravel, %sand, %silt, %clay, %total solids, % volatile solids and texture is reported for many samples, however numerous samples do not have results for one or more of these parameters.

6.7.3.2 Methods

HUDTOX requires specification of initial conditions as bulk concentrations (mass of PCB per unit bulk volume of sediment). Average dry weight Tri+ concentrations (mass of PCB per mass of dry solids) were computed from the 1977 NYSDEC sediment data. In order to specify sediment initial conditions on a bulk concentration basis, average dry weight PCB concentrations were computed for cohesive and non-cohesive sediment from these data and multiplied by the sediment specific weight values (Section 6.7.2).

Samples were classified as cohesive or non-cohesive following hierarchy of methods, dependent on the parameters reported for each sample (Table 6-22). After classification of the individual core sections according to the criteria in Table 6-22, all core sections in each core were assigned the cohesive/non-cohesive classification of the top-most section. The samples classified as cohesive or non-cohesive were mapped to the HUDTOX water column segments based on location information.

To specify sediment Tri+ initial conditions, the NYSDEC 1977 data were averaged horizontally and vertically for cohesive and non-cohesive sediment types in each HUDTOX layer. The vertical segmentation scheme employs 2 cm layers throughout the modeled portion of the sediment bed (0-26 cm).

The core section and grab sample data were mapped onto the HUDTOX vertical sediment layer segmentation using a length-weighted-average calculation for each sample:

$$C_j = \frac{\sum_{i=1}^{n} C_i l_i}{\sum_{i=1}^{n} l_i} \tag{6-19}$$

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where:

C_j = concentration of layer j (mg/L)
C_i = concentration of sample i in layer j (mg/Kg)
l = length of section i in layer j (cm)
n = number of sections extending into layer j

Once each sample was mapped onto the vertical segmentation intervals, using equation 6-19, average Tri+ concentrations were computed for specific intervals of the river based on data availability. For some portions of the river, data falling in multiple adjacent water column segments were grouped and averaged together, by sediment layer interval and sediment type. Average concentrations were computed for each group. The Thompson Island Pool water column segments were divided into 7 averaging groups, and the segments downstream of Thompson Island Pool were divided into 10 averaging groups (Table 6-23).

6.7.3.3 1977 Initial Condition Results

The 1977 initial condition surficial sediment Tri+ concentrations for cohesive and non-cohesive segments are shown in Figure 6-32. Maximum concentrations of both cohesive sediment, 290 mg/kg, and non-cohesive sediment, 44 mg/kg, occurs in Thompson Island Pool (Figure 6-33). Minimum concentrations are 7.2 mg/kg for cohesive sediment and 3.3 mg/kg for non-cohesive sediment, occurring just below Stillwater Dam and below the Lock 1 Dam, respectively. The vertical profiles computed for each segment are shown in Figure 6-34 with plus and minus two standard errors. Inspection of the vertical profiles shows that peak concentrations typically occur at depths less than 12 cm. The vertical profiles do not show a significant gradient with depth, which is attributed to the variable surface core section thickness used in the sampling, ranging from 1.4 to 46 cm. The average surface sediment sample thickness is 7.5 cm with a standard deviation of 6.3 cm.

6.7.4 1991 Initial conditions and model calibration targets

Sediment initial conditions for total PCB, Tri+ and the congener state variables were computed from the 1991 GE composite sediment sampling data for use in the short term hindcast application conducted from Jan. 1, 1991 to Sept. 30, 1997. Tri+ concentrations were also used as model calibration targets.

6.7.4.1 Data

In the GE 1991 composite sampling survey, approximately 520 individual samples were collected in Thompson Island Pool and approximately 480 from Thompson Island Dam to Federal Dam. The Thompson Island Pool was divided into 6 sub-reaches, in which 5 to 12 composites samples were collected. The composites generally contain on the order of 10 to 20 individual samples collected over a range of ¼ mile or more. Thus, the 1991 data do not represent individual cohesive or non-cohesive sediment deposits. Individual sediment core samples were grouped as fine or coarse sediments in the laboratory after determination of sediment type based on texture and bulk density. After sectioning into 0-5, 5-10, and 10-15 cm layers, the individual layer sections were composited in each group and analyzed for PCB. As

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discussed in Section 6.3, sediment BZ#4 concentrations were estimated from the co-eluting BZ#4&BZ#10 sum.

6.7.4.2 Methods

The calculation of 1991 concentrations involved vertically mapping concentrations on the 2 cm model sediment layer intervals as conducted for the 1977 NYSDEC data using equation 6-19. The constant core sectioning employed in the 1991 survey resulted in interpolation at only two depths, 5 cm and 10 cm. Grab samples were assumed to represent 10 cm.

Each sample in the composite was assigned the composite concentration for each sediment layer. The composite samples were classified as cohesive or non-cohesive based on the fine/coarse designation assigned to the composite samples during collection. Similar to the approach employed for the 1977 NYSDEC data, samples in adjacent water column segments were grouped by sediment type based on data availability (Table 6-24).

6.7.4.3 1991 Initial Condition Results

The longitudinal (down-river) surface sediment concentration profiles computed for each PCB state variable from the GE 1991 data are presented with the data in Figures 6-35 through 6-38. Down-river trends show that PCB concentrations in Thompson Island Pool and between Thompson Island Dam and Schuylerville are very elevated relative to concentrations observed downstream of Stillwater. This trend has persisted from 1977, where a similar pattern is observed in Tri+ concentrations (Figure 6-32). Examination of congener concentrations shows that BZ#4 concentrations exhibit a larger decrease relative to the heavier congeners. Congener concentrations normalized to BZ#52 concentrations show that the ratio of BZ#4/BZ#52 drops markedly at Schuylerville (Figure 6-39), while ratios of the heavier congeners increase. This is attributed to in-place dechlorination of sediment PCBs between Fort Edward and Schuylerville. Decreased BZ#4 concentrations downstream of Schuylerville may be related to weathering processes, whereby heavier congeners are preferentially delivered to downstream sediments via deposition and loss of the lighter more mobile congeners via volatilization or export over Federal Dam.

Poolwide average surface sediment concentrations in TIP are shown for each state variable in Table 6-25.

6.7.5 Summary

Sediment initial conditions were computed in 1977 from the NYSDEC data for the historical calibration period for Tri+ and in 1991 from the GE composite sampling data for the short-term hindcast period. Sediment conditions were computed for all seven PCB state variables in 1991 (total PCB, Tri+, BZ#4, BZ#28, BZ#52, BZ#90+101, and BZ#138). The Tri+ concentrations were used as model calibration targets for the long-term historical calibration, while the other PCB forms were used as initial conditions for shorter-term 1991-1997 simulations. Concentrations were mapped onto sediment segment layers according to Equation 6-19. Average concentrations for cohesive and non-cohesive sediment concentrations were computed for

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specific intervals of the river, based on data availability. Due to the averaging approach taken, the specified initial conditions do not represent discrete PCB hotspots in many areas.

Based on the specified initial conditions for the congeners, BZ#4 represents the largest fraction of the total PCB mass in Thompson Island Pool and between Thompson Island Dam and Schuylerville, approximately 25 percent. Below Lock 5 at Schuylerville the concentration of BZ#4 declines significantly and at Waterford, the BZ#4 mass fraction is on the order of 5 percent.

6.8 WATER AND AIR TEMPERATURES

A number of processes represented in the HUDTOX model are temperature dependent. These include: partitioning, volatilization and porewater diffusion rates. A large number of in-situ water temperature data are available from the USEPA and GE datasets. No in-situ temperature data were available for sediments. The sediment bed temperatures were assumed to follow the water column temperature. Sediment temperatures are likely to be damped relative to surface water temperatures by heat exchange with groundwater and underlying bedrock, however, no data exist with which to evaluate this.

Monthly-average water column temperatures were computed for the primary Upper Hudson River sampling locations for application in HUDTOX. Some smoothing of the monthly average curves at each station was required (Figure 6-40). The annual time series represented by the monthly average was used to describe the HUDTOX calibration and forecast application periods. The monthly time series specified at each station was applied to segments between station midpoints. For example, the Thompson Island Dam temperature series applies to the downstream half of Thompson Island Pool and half the distance to the Schuylerville sampling station.

Year to year variations in mean monthly water temperatures are fairly small. The largest year to year variability appears to occur during April and May for which the standard deviation of observations is approximately 30 to 50 percent (in degrees Celsius), depending on location. Peak monthly average temperature occurs in July. During non-winter months, water temperature generally exhibits a continual increase from Ft. Edward downstream to Waterford. In July, at peak temperature, the mean water column temperature increases 3.6 °C, from Ft. Edward (24.2 °C) to Waterford (27.8 °C) as shown in Figure 6-41. During the winter months, the entire river is about the same temperature. Minimum mean monthly temperature is 1.1 °C in January.

Temperature gradients between near shore and center channel may exist due to a number of factors, which may result in positive or negative gradients. Shallow, near shore areas of the river can experience more solar heating due to slower velocities and depth, which may serve to increase temperatures relative to the center channel. Groundwater inflows may serve to decrease near shore temperatures relative to the center channel and likely cause sediment temperatures to lag water column temperatures.

Very little data exist with which to evaluate possible temperature gradients between center channel and shallow near shore areas. In HUDTOX, no lateral temperature gradients are represented.

Monthly average air temperature data were obtained from the NOAA-NCDC daily summaries for Glens Falls/Warren County, New York.

6.9 PARTITIONING

6.9.1 Overview

In natural systems the fate and transport of PCBs and other hydrophobic chemicals is largely controlled by their degree of partitioning to sediment particles and dissolved organic matter (DOC-bound). While sorption and desorption are complex processes, often the dissolved phase and particle phase concentrations are assumed to be in equilibrium. This assumption is reasonable when sorption kinetics are rapid relative to other processes affecting concentrations. Two-phase and three-phase models of equilibrium partitioning assume that measured concentrations in one phase can be used to predict concentration in the other phase(s).

The equilibrium partitioning assumption was evaluated by USEPA (1997) and found to be valid for the Upper Hudson River. TAMS computed particulate concentrations predicted from measured dissolved concentrations using two-phase partition coefficients and compared results to observed values throughout the Upper Hudson River over a range of environmental conditions. The predictions were unbiased for the majority of samples and average difference between the predictions and observations was 45 percent, and only 33 percent for stations downstream of Thompson Island Dam. Results for data collected near Fort Edward suggest non-equilibrium conditions at this station. These predictions represent a high degree of accuracy relative to similar reported studies and suggest it is possible to predict the phase distribution of PCB congeners to within about 33 percent for the freshwater Hudson below Thompson Island Dam. Equilibrium assumptions were proposed to be adequate to represent fate and transport of PCBs in the Hudson (USEPA,1997).

Development of two-phase and three-phase equilibrium partition coefficients for 64 congeners are presented in the DEIR. Three-phase partition coefficients were estimated using numerical optimization from USEPA Phase 2 water column data and 1991 GE sediment composite data, both of which report particulate and apparent dissolved (truly dissolved plus DOC-sorbed) concentrations. The reader is referred to the DEIR for details of those analyses. Partition coefficients computed from water column data are considered to be more accurate than partition coefficients computed between sediment and porewater due to differences in analytical and sample collection methods. There is, however, considerable uncertainty in the determination of three-phase partition coefficients in both media. Results show that for the lightest congeners, the DOC-bound fraction may comprise up to 50 percent of the total PCB concentration in the water column, but is generally less than 10 percent for congeners constituting Tri+. In the sediments, results suggest that a significant fraction of the porewater concentration is associated with DOC for all congeners. The mono- and di-chlorinated congeners exhibit different partitioning behavior than the other congeners in that their K_{poc} and K_{doc} (see Equations 5-10 and 5-11) values are of approximately the same order of magnitude. Further, because of their lower partition coefficients, porewater concentrations of mono- and di-chlorinated congeners are enhanced relative to the heavier congeners, which may facilitate greater sediment-water transfer of these congeners via porewater. Enhanced flux of these congeners relative to the heavier congeners may also occur due to the presence of elevated DOC, considering the differences in ratios of K_{poc} to K_{doc} for the heavy and light congeners (USEPA, 1997).

Three-phase equilibrium partitioning was adopted for HUDTOX based on two considerations. First, because of the importance of the DOC phase in affecting the phase distributions of the lighter congeners, it is necessary to use three-phase partitioning to properly account for the ratios between sediment-water transfer of congeners in porewater. A sensitivity analysis presented in the DEIR (USEPA, 1997) suggests that dissolved and DOC-bound concentrations are likely to be of the same order of magnitude. Second, truly dissolved chemicals are thought to be more readily bioavailable than those sorbed to DOC and accounting for the DOC fraction may provide a better estimate of exposure to biota.

The HUDTOX model applies three-phase equilibrium partitioning equations presented in Section 5.2 (Equations 5-10 and 5-11). In these equations, the K_{poc} and K_{doc} values for congeners and Tri+ are temperature corrected according to the temperature correction slope factor (Equation 5-12) recommended for all congeners in the DEIR (USEPA, 1997). The temperature correction is log-linear and a 10-degree C change in temperature reduces partition coefficients by 28 percent.

In addition to the three-phase partition coefficients presented for congeners in the DEIR, three-phase coefficients were also developed by USEPA, 2000 for Tri+, following the same approach. To compute total PCB partition coefficients, mass-weighted values from Tri+ and the mono- and di-chlorinated congeners were used. The mass weighting used average congener and Tri+ mass fractions in the USEPA and GE water column data. Details of this analysis are presented below.

Application of the three-phase partitioning model requires specification of the fraction of organic carbon (f_{OC}) in suspended and bedded sediment particles, as well as concentrations of DOC in the water column and sediment porewater. For bedded sediments, average f_{OC} values were computed from the GE 1991 composite sediment data based on sediment type and location. For the water column f_{OC} was found to be correlated with flow. A function relating water column f_{OC} to flow was applied in HUDTOX. Average sediment DOC concentrations were also computed from the GE data based on sediment type and location. Water column DOC concentrations were observed to be relatively invariant in the Upper Hudson throughout the year and exhibit small differences between locations. Average DOC concentrations were computed from the GE, Phase 2, and J. Vaughn (1996) data. The development of the f_{OC} and DOC concentrations for sediment and water are presented in detail below.

Based on the specified parameters influencing partitioning of PCB, typical phase distributions of PCB in the Upper Hudson River are presented for winter and summer low and high flow conditions.

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6.9.2 Partition Coefficients

The three-phase partition coefficients developed based on the UPEPA Phase 2 water column for Tri+ and congeners BZ#4, BZ#28, BZ#52, BZ#90&101, and BZ#138 are used in HUDTOX (Table 6-26). These partition coefficients are temperature corrected in the HUDTOX model according to the temperature correction slope factor developed for all congeners in the DEIR (Equation 5-12).

Consistent with the equilibrium assumption employed in the HUDTOX model, a single partition coefficient was applied for the whole Upper Hudson River. Non-equilibrium conditions appear to occur in some of the Phase 2 data, particularly at Fort Edward, resulting in higher apparent partition coefficient estimates than downstream. Partition coefficient estimates were corrected for the possible presence of non-equilibrium samples by use of the median of individual estimates to describe the central tendency of observations. Partitioning at Thompson Island Dam and downstream locations appears to be generally at equilibrium conditions for tri- and higher-chlorinated congeners, however, for mono-, di-, and tri-chlorinated congeners, there appears to be some local non-equilibrium at Thompson Island Dam (possibly associated with sediment-water transfer of predominately the dissolved phase for these congeners).

Generally, the Phase 2 data do not indicate a clear distinction between partitioning behavior among stations and differences among stations are likely attributable to variations in organic carbon concentration and water temperature (USEPA, 1997).

In addition to Tri+ and the five congeners, total PCB is an additional HUDTOX state variable. Partition coefficients were not developed for total PCB as part of the DEIR or LRC investigations. To estimate K_{POC} and K_{DOC} for total PCB, a mass weighting approach was adopted using values determined for Tri+ and the mono- and di-chlorinated congeners. The average mass fraction of total PCB represented by Tri+, BZ#1, BZ#4, and BZ#8 were computed at Fort Edward, Thompson Island Dam, Schuylerville, Stillwater and Waterford from the USEPA Phase 2 data and the GE data (Table 6-27). Because these mass fractions do not sum to unity due to exclusion of other mono- and dichlorobiphenyls for which partition coefficients were not calculated, the mass fractions were normalized by the total mass represented by these congeners and multiplied by their respective partition coefficients to compute a mass-weighted value for total PCB as described by Equation 6-20.

$$K_{poc} = \frac{(K_{poc}X)_{BZ\#1} + (K_{poc}X)_{BZ\#4} + (K_{poc}X)_{BZ\#8} + (K_{poc}X)_{Tri+}}{X_{BZ\#1} + X_{BZ\#4} + X_{BZ\#8} + X_{Tri+}} \qquad \textbf{(6-20)}$$

where:

X = mass fraction for each PCB form
K_{poc} = particulate organic carbon partition coefficient (l/kg)

This procedure was repeated for K_{DOC}, resulting in K_{POC} and K_{DOC} estimates for each of the five stations listed above (Table 6-28, Figure 6-42). The shift in the congener distribution toward the mono- and di- fraction due to gain of these constituents across Thompson Island Pool and loss downstream of Thompson Island Dam is evident in the pattern of results. While partition coefficients for individual congeners and Tri+ exhibit some spatially variability (probably related to differences in dissolved organic carbon and temperature, as discussed above), the changing composition of total PCB is an additional factor contributing to spatial variability and uncertainty in the total PCB partition coefficient. This was a consideration in deciding not to calibrate to total PCB concentrations, but rather to focus the calibration on Tri+ and use additional congener calibrations to strengthen the Tri+ calibration. This is discussed in Chapter 7.

To determine a single value of K_{POC} and K_{DOC} for total PCB for application in HUDTOX, the station values were distance-weighted using the distance between midpoints of each location divided by the total distance between upstream and downstream locations. The Waterford value was assumed to represent the reach from Waterford to Federal Dam in the distance weighting (Table 6-29). While the Fort Edward value may be affected by non-equilibrium conditions (see above), it receives a fairly small distance weighting factor and does not significantly affect the result. The log K_{poc} and log K_{doc} values determined by this method for total PCB are 5.64 and 4.22, respectively.

Sediment three-phase partition coefficients were also estimated by USEPA (1997) from the 1991 GE composite sediment sampling data. These estimates were subsequently updated to account for corrections to analytical biases in the GE data (Table 6-26). While the GE data allowed estimates of sediment partition coefficients, a number of important factors in the sampling and analysis procedures affect the quality of these estimates. Samples were frozen prior to analysis, which may alter all phases of the matrix (USEPA, 1997), and field blank contamination affected 87 percent of the PCB analyses. These limitations suggest that the accuracy of the GE estimates are low compared to the values estimated from the USEPA Phase 2 water column data. Therefore, the Phase 2 water column estimates were chosen to describe both sediment and water column partitioning behavior in HUDTOX. Application of the water column estimates may have contributed to difficulty in calibrating the model to individual congeners, which is discussed in Chapter 7.

6.9.2.1 Water Column Organic Carbon Concentrations

The HUDTOX model employs three-phase equilibrium partitioning formulations (Equations 5-13 through 5-16), which compute PCB distribution among particulate organic matter, dissolved organic carbon (DOC) and water (Section 5.2). In these equations, the concentration of particulate organic material is computed as the sediment solids concentration times the fraction of organic carbon in the sediment particles, f_{OC}. Values for f_{OC} and DOC are specified separately for the water column and sediments. Values for both of these parameters were determined from site-specific data and specified as model inputs. The determination of water column f_{OC} and DOC values considered spatial and temporal patterns in data. This section presents the development of these parameters for the water column. The next section presents development of the sediment f_{OC} and DOC values.

6.9.2.2 Water Column DOC

In addition to the USEPA Phase 2 data and the GE monitoring data, water column DOC measurements were also available from investigative studies conducted at Rensselaer Polytechnic Institute (Vaughn 1996). The GE water column organic carbon data required extensive filtering due to numerous inconsistencies among reported TSS, TOC and DOC concentrations in the dataset. Measurements were only used for samples meeting the following criteria: [TOC] < [TSS] and, [TOC] ≥ [DOC]. This resulted in use of 17 percent of the 421 samples for which TSS, TOC and DOC concentrations are reported in the Release 4.1b of the Hudson River Database. Table 6-30 summarizes the number of data used from each source by mainstem Hudson River location, along with a statistical summary of the data at each location.

Dependencies of DOC concentration on flow, season, and location were investigated with the combined USEPA, GE and J. Vaughn datasets. Consistent with the findings in the DEIR based on the USEPA Phase 2 data, DOC was observed to be slightly negatively correlated with flow, and only weakly correlated with temperature (and season). The observed decrease in mean concentrations in the spring is explained by the dependence on flow. The lowest DOC concentrations tend to occur coincident with the highest flows and lowest temperatures during the snowmelt runoff period (Figure 6-43). A plot of the DOC versus river mile suggests some dependence of DOC concentration on location, which is also evident in the mean values (Figure 6-44). Differences between locations are generally small. Mean values at the primary mainstem locations (Ft. Edward, Thompson Island Dam, Schuylerville, Stillwater and Waterford) differ by a maximum of 14 percent.

Even considering the slight negative correlation of DOC on flow and temperature, DOC concentrations are relatively invariant in the Upper Hudson River. Maximum deviations from mean concentration at each location is less than 30 percent (excluding a possible outlier of 0.94 mg/L at Stillwater from USEPA Transect 4). Specification of mean values by reach was judged to give adequate representation of DOC concentrations in the model. The DOC data were grouped into the four reaches presented below for the purpose of specifying mean DOC concentrations (Table 6-31).

6.9.2.3 Water Column f_{OC}

Water column f_{OC} values were specified based on estimates available from the USEPA Phase 2 data and the GE data. As discussed above, filtering of the GE dataset was required in order to identify samples with reported TSS, total organic carbon (TOC), and DOC concentrations consistent with each other. This resulted in use of only 17 percent of the 421 samples for which TSS, TOC and DOC concentrations are reported in the Release 4.1b of the Hudson River Database. The GE data reports concentrations for TSS, TOC and filterable TOC (labeled TOC_f in the database). For each sample, particulate organic carbon (POC) concentration was computed as TOC – TOC_f. Subsequently, f_{OC} was computed as POC /TSS.

In the USEPA Phase 2 studies, POC was not measured directly in the water column. However, weight-loss-on-ignition (WLOI) data were reported and can be used to estimate POC (USEPA, 1997). The Phase 2 data contain WLOI data at two temperatures, 375 °C and 450 °C (for

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Transect 1 only), however a conversion factor was developed so that all WLOI data could be converted to a common temperature. Based on zero-intercept regression analysis using sediment data, $WLOI_{375}$ can be converted to organic carbon weight fraction as (USEPA, 1997):

$$f_{OC} = 0.611 * WLOI_{375} \quad \textbf{(6-21)}$$

$$WLOI_{375} = WLOI_{450} * 0.864 \quad \textbf{(6-22)}$$

The combination of f_{OC} estimates obtained from the USEPA and GE data resulted in 24 to 296 measurements at the primary mainstem sampling locations.

Results in the DEIR (from analysis of the Phase 2 data) show that f_{OC} is significantly correlated to flow but not to location at a 95 percent confidence level. Based on this observation the dependence of f_{OC} on flow was analyzed to develop a functional relationship for the HUDTOX model. The data were plotted versus flow normalized by mean flow at each location (Figure 6-45). While f_{OC} is clearly negatively correlated with flow, there is significant variability in f_{OC} across the range of flows sampled, with the greatest variability observed at low flow. A power function regression analysis was used to fit the data as a function of normalized flow. This produces a model which generally describes f_{OC} well at high flows, but has limited predictive ability at low flow due to significant variability in the observations. This function was applied in the HUDTOX model to compute f_{OC} as a function of flow (Equation 6-23).

$$f_{OC} = 0.175 \times \left(\frac{Q}{\overline{Q}}\right)^{-0.3687} \quad \textbf{(6-23)}$$

For application in HUDTOX, the average flow of each model segment was computed for segment below TIP by using segment specific flow, Q, and the average flow of total flow estimated upstream flow inputs, $\overline{Q}$.

Evaluating the behavior of this equation over the range of flows modeled shows that at the lowest flow conditions, f_{OC} is approximately 0.22 and 0.08 at the low and high end of the flow range, respectively. At the average flow, f_{OC} is 0.175.

6.9.2.4 Sediment Organic Carbon Concentrations

Average sediment fraction of organic carbon (f_{OC}) values and porewater dissolved organic carbon (DOC) concentrations were developed from GE and USEPA Phase 2 data. The HUDTOX model requires specification of these input values, which determine PCB phase partitioning in the three-phase partitioning calculations. The data were segregated by sediment type (cohesive or non-cohesive) and location in the River and average concentrations were determined for each sediment type over intervals of the River that were dependent on data availability and apparent spatial trends in these values. The specification of (f_{OC}) and DOC values is described below.

6.9.2.5 Porewater DOC

The sediment DOC measurements available from the GE 1991 Sediment Sampling and Analysis Program (O'Brien and Gere, 1993) were used to specify DOC concentrations by reach in the

HUDTOX model. The Phase 2 sediment studies did not measure porewater DOC concentrations. The GE DOC data are measurements of filterable TOC obtained from sediment core composites. A total of 86 sediment DOC measurements are available from Fort Edward to Federal Dam.

Spatial differences along the river and between fine and coarse sediment areas were investigated. When plotted versus river mile, the data show a trend of increasing porewater DOC concentrations with distance downstream from Fort Edward (Figure 6-46). The GE samples were composited by sediment type and composites are identified as being from coarse or fine sediments. The available DOC data are biased toward fine sediment composites, with only a small percentage of the DOC measurements being from coarse sediment. Based on the distinction of coarse and fine sediments in the GE composites, and the limited number of coarse sediment DOC data available, no distinction between fine and coarse sediment DOC concentrations is supported.

Considering that fine and coarse sediments were observed to have different organic carbon content, correlation between sediment f_{OC} and DOC was investigated as an alternate approach to investigating differences in porewater DOC concentration between fine and coarse sediment. A scatter plot of sediment DOC versus f_{OC} shows no correlation between these two parameters. Thus, DOC was specified on river mile intervals, with no distinction between fine and coarse sediment, as shown in Figure 6-46.

6.9.2.6 Sediment f_{OC}

Sediment f_{OC} values were specified using data from the GE 1991 Sediment Sampling and Analysis Program (O'Brien and Gere, 1993). While measurements of sediment f_{OC} concentrations are also available from the USEPA Phase 2 data, the GE 1991 data are extensive enough to provide a good estimate of mean f_{OC} values throughout the Upper Hudson River. The GE composites consisted of fine and coarse sediment collected over intervals of about 2 miles downstream of Thompson Island Pool and about 1 mile in Thompson Island Pool. The composite data were assigned river mile location corresponding to the approximate midpoint of the sampling interval and plotted versus river mile to investigate changes in f_{OC} along the river (Figure 6-47). Sediment organic carbon content was observed to decline with distance downstream from Ft. Edward. Measured values ranged from 6.9 to 0.3 percent for fine (cohesive) sediment and 4.6 percent to 0.2 percent for coarse (non-cohesive) sediments with the highest values being measured in Thompson Island Pool.

The data were grouped by river mile interval to compute average fine and coarse sediment concentrations for specification in HUDTOX (Table 6-32). The f_{OC} values specified in HUDTOX range from 3.7 percent to 1.6 percent for fine sediment and from 1.3 percent to 0.7 percent for coarse sediment.

6.9.2.7 Distribution of PCBs in sediment and water

Based on the specified parameters influencing the partitioning calculations in the HUDTOX model, typical phase distributions of PCBs in sediment and water are presented below for all PCB state variables, along with the approximate range of distributions that may result in the

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model. Parameters controlling the three-phase partitioning include: K_{POCc}, K_{DOC}, f_{OC}, DOC, and temperature.

Waterford was chosen to illustrate the typical summer and winter, high and low-flow ranges of water column partitioning behavior because it experiences the largest changes in temperature (1.1 °C to 27.8 °C), and the largest range of observed suspended solids concentration. Typical low and high-flow TSS concentrations of 5 and 100 mg/L were chosen for this illustration. Similarly, typical high and low flow f_{OC} values specified are 22 and 8 percent, respectively. Water column DOC was specified as 4.01 mg/L.

The range of partitioning behavior due to the range of parameter values specified for this illustration is presented for each state variable, using water column and sediment 3-phase partitioning coefficients (Table 6-33). Note that results are independent of the actual PCB concentration. Results are displayed as percent of PCB in each phase: truly dissolved, DOC-bound and sorbed to particulate organic carbon. The apparent dissolved phase includes truly dissolved and DOC-bound PCBs.

6.9.2.8 Partitioning Summary

Partitioning behavior of PCB to particulate matter and colloids is represented in HUDTOX through the application of equilibrium three-phase partitioning equations that compute distribution of PCB among water, dissolved organic carbon and particulate organic carbon. The equilibrium assumption was evaluated by USEPA (1997) and found to be reasonable for the Upper Hudson River, although evidence of non-equilibrium conditions was observed. This primarily affected Fort Edward and TI Dam concentrations. Three-phase partition coefficients for Tri+ and congeners estimated from USEPA Phase 2 water column data were specified for HUDTOX. Partition coefficients were not varied spatially. Results suggest that with accurate representation of temperature, f_{oc} and DOC it is possible to predict phase distributions of individual congeners to within 45 percent for the Upper Hudson River upstream of Thompson Island Dam and to within 33 percent below Thompson Island Dam.

Because estimates of partition coefficients for total PCB were not available from previous investigations, these were estimated based on mass weighting of values determined for Tri+ and mono and di-chlorinated congeners. Estimates were computed for the primary sampling stations between Fort Edward and Waterford. A spatial pattern in results was observed, consistent with the relative changes in congener distributions through the system. These results were distance weighted to obtain an estimate for total PCB for the entire system. Considering that total PCB is used only for estimating total PCB transport and is was not used for primary calibration of the HUDTOX model, uncertainty in total PCB partitioning behavior does not affect the calibration.

6.10 VOLATILIZATION

6.10.1 Overview

Air-water exchange by volatilization is a transport pathway for water-borne PCBs in the Upper Hudson that is explicitly represented in the HUDTOX model. Whereas Chapter 5 presents the

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empirical model formulations used in the computation of air-water exchange, this section presents specification of chemical-specific and hydrodynamic parameters affecting the rate of volatilization. An assessment of volatilization losses at dam cascades is also presented, with the conclusion that this process is not large enough to warrant explicit representation in the HUDTOX model.

6.10.2 Volatilization Mass Transfer

Volatilization affects PCB transport in the Upper Hudson by serving as a net loss pathway for water column borne PCB in the truly dissolved phase. Air-water exchange of truly dissolved PCB occurs across the air-water interface of the entire river and is enhanced by induction of air in cascades such as falls over dams.

The rate of volatilization tends to be chemical specific and is determined by Henry's Constant. Volatilization is enhanced by hydrodynamically-induced and wind-driven shear stresses at the water surface. Due to temperature dependencies, volatilization is also seasonally dependent, exhibiting higher rates during warm temperature periods. Liquid phase and air-phase resistances control the rate of volatilization, which are dependent on the concentration and diffusivity of PCB in each phase.

Volatilization rates are computed in HUDTOX according to the O'Connor Dobbins formulation presented in Chapter 5. This equation computes volatilization mass transfer coefficients across the air-water interface based on water column depth and velocity, temperature, and chemical specific properties, including atmospheric concentrations, molecular weight and Henry's constant. Enhanced volatilization due to cascades at dams is not represented in the model based on a determination that this processes is of small importance in affecting PCB transport in the system. This determination is summarized below.

Also presented in this section are estimates of Henry's constant and molecular weight obtained from literature sources and site-specific data.

6.10.2.1 Henry's Constant and Molecular Weight

Chemical-specific properties, Henry's Constant (H) and molecular weight (MW) were estimated for each PCB state variable. Values for H and MW are presented for a wide range of PCB congeners. For Tri+ and total PCB, estimates of these parameters were developed for specific locations by mass weighting congener results based on the average mass fraction of each congener.

Henry's coefficients were obtained for individual congeners from Brunner et al. (1990). The H values in units of (atm-m^3/mol) are presented in Table 6-34 and Figure 6-48. Average congener mass fractions for the primary Upper Hudson sampling stations were computed from the GE and USEPA data (Tables 6-35 and 6-36). Based on these results, individual congener H values were mass-weighted to arrive at a value for each location specific to the GE and USEPA datasets (Table 6-37 and Figure 6-49). A weighted average of these values for each location was computed based on the number of samples in each dataset used to determine average congener

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mass fractions. Results reveal a down-river pattern in H that reflects the shift in congener distributions through the system. H values are highest at Thompson Island Dam, reflecting the gain in mono- and di-homologues across Thompson Island Pool. The final values for each location were then distance weighted by the distance between sampling midpoints to arrive at a final value of H for total PCB (1.85e-4) and Tri+ (1.69e-4) for application to the entire Upper Hudson (Table 6-38).

MW is constant for each congener in a given homologue group and is a fixed quantity. MW values are presented in the DEIR (Table 4-8) for each homologue group. MW was computed for total PCB and Tri+ by mass-weighting congener values in an identical manner as done to estimate H. Results of this calculation are presented in Tables 6-39 and 6-40, and illustrated in Figure 6-50.

A summary of the H and MW values specified for each state variable is presented in Table 6-41.

6.10.2.2 Film Transfer Coefficients

As described in Chapter 5 (Section 5.2.3), air-water chemical exchange (or volatilization) rates in HUDTOX are determined through application of the stagnant layer "two-film" theory. As a result, overall volatilization rates (K_V) are controlled by liquid-phase (K_L) and gas-phase (K_G) exchange coefficients acting in series (see Equation 5-18). Since these coefficients function in a series fashion (with K_G being adjusted by a chemical- and temperature-dependent Henry's Law Constant), the smallest of these two factors may be considered to be "controlling" (or limiting) the overall volatilization rate. However, even the non-limiting factor may still have a substantial effect on the volatilization rate under conditions when both are of similar magnitudes.

In the Upper Hudson River, flow and environmental conditions largely determine whether the liquid-phase or gas-phase coefficient has a more limiting effect on volatilization. The gas-phase tends to be limiting during cooler conditions (because K_G decreases with temperature) as well as during higher flow conditions (because K_L generally increases with flow). Conversely, the liquid-phase tends to more limiting on volatilization during lower flow (average and below) periods and especially as water temperatures warm up (e.g., summer low flow conditions). Differences in chemical-specific diffusivity (D_w) across the range of PCB congeners evaluated in this modeling study can change the limiting phase between liquid and gas.

Determination of the liquid-phase transfer coefficient (K_L) for a specific river cross-section using the O'Connor-Dobbins reaeration formulation (Equation 5-20) requires both depth and velocity. Table 6-42 provides the Leopold and Maddox (1953) coefficients that were specified for each HUDTOX river cross-section to estimate velocity and depth as a function of flow. Note that depths were estimated for average flow conditions and assumed to be constant due to the mitigating effects of dams on water level variations as flow changes.

6.10.2.3 Atmospheric PCB Concentrations

Given the air-water mass transfer rates, air-water flux depends on the gradient between the dissolved water phases and the atmospheric gas phase; therefore, computation of this flux

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requires specification of the atmospheric gas phase boundary condition. For this boundary condition an annual average value was estimated for Tri+ from 1977-1997 and for total PCBs and the two congeners from 1991-1997. The procedure for setting this boundary condition involved establishing a recent reference concentration based on measurement of total PCBs in the atmosphere and back projecting from that reference value to obtain estimates of historical levels. The nearest and most recent reference value was the 1992 annual average atmospheric gas phase total PCB value of 170 ± 86 pg/m^3 determined by Hoff *et al.* (1996) at the Integrated Atmospheric Deposition Network (IADN) station at Point Petre, Ontario. Historical concentrations were determined by scaling this value to a curve developed using PCB profiles collected in dated (1940-1981), ombrotrophic peat bogs (Rapaport and Eisenreich, 1988) and observed water column PCB load decay rates for rivers draining Lake Michigan watersheds from 1981-present (Marti and Armstrong, 1990). This scaling process produced a curve which reflects the synthesized time series of atmospheric total PCB concentration from 1977-1997 (Figure 6-51). Also included in Figure 6-51 as a check on this approach, are seasonal data reported by NYSDEC (undated) and data from Buckley and Tofflemire (1983), both of which represent air sampled in the vicinity of the Upper Hudson River. Additionally, the line representing historical atmospheric PCB concentrations estimated by Mackay (1989) in conducting a modeling analysis for Lake Ontario is included.

Ideally, the estimate of historical atmospheric concentrations for congeners or the Tri+ mixture would be made by applying measured ratios of these constituents to the hindcast total PCBs. This was possible for estimating BZ#4 and BZ#52 levels by using ratios reported by Hornbuckle (personal communication, 11/18/98) for samples collected over Lake Michigan. For Tri+, a ratio was determined by assuming the atmospheric gas phase concentrations for both Tri+ and total PCBs in 1992 were in equilibrium with the dissolved phase in the water column and computing a gas phase Tri+/total PCB ratio for 1992 on that basis. Then Tri+ was hindcast using the same scaling curve as was used for total PCBs in Figure 6-51. The resulting HUDTOX boundary condition values used for these PCB state variables are presented in tabular form on Figure 6-51.

6.10.3 Gas Exchange at Dams

A method of estimating gas exchange at river cascades presented by Cirpka et al. (1993) was overviewed in the DEIR (USEPA, 1997) and air-water transfer of Tri+ based on this equation was assessed by QEA (1999). For chemicals with small Henry's constants this model can be expressed as (QEA 1999):

$$c_d = \left(\frac{1}{1+\frac{GH}{Q}} \right) c_u + \left(\frac{\frac{GH}{Q}}{1+\frac{GH}{Q}} \right) \frac{c_{air}}{H} \qquad \textbf{(6-24)}$$

where:

G/Q = ratio of entrained air flow rate to river flow rate
c_d = concentration downstream of cascade
c_u = concentration upstream of cascade

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The air flow to river flow ratio is can be estimated from the cross-section dimensions of the fall and the river flow rate (c.f. McLachlan et al. 1990). For the two river cascades (shown as a series of small drops) studied in Cirpka et al. (1990) these ratios were about 0.03 to 0.07 for cascades of approximately 1 to 2 meters. The falls over dam weirs on the Upper Hudson are approximate to these heights, varying from about 2 to 6 m, although the nature of the falls are somewhat different from the cascades in Cirpka et al. (1990), equation 6-24 is assumed to provide a reasonable estimate of air-water mass transfer for the dams on the Upper Hudson River. Based on this equation, QEA (1999) estimated maximum concentration reductions due to loss at dams to be less than 3% for Tri+.

Because volatilization at dams is estimated to have a small impact on water column concentrations, it was not included in the HUDTOX model.

6.11 Sediment Particle Mixing

Vertical mixing of sediment particles and associated porewater in the sediment bed arises from bioturbation and other physical processes. The activities of infaunal organisms inhabiting the surface sediments, called bioturbation, include: burrow and tube excavation and their ultimate collapse or infilling, ingestion and excretion of sediment, plowing through the surface sediment, and building of mounds and digging of craters (Boudreau, 1997). As discussed in Chapter 5, particle mixing is represented as a diffusional process in HUDTOX. The model requires as input, specification of a depth over which mixing occurs, and an associated mixing rate, or particle diffusion rate.

No direct evidence is available for particle mixing rates in the Upper Hudson River, however, Olsen et al. (1981) determined surface particle diffusion rates of approximately 1 cm^2/yr in Foundry Cove and Lents Cove in the Lower Hudson River. This is a relatively low rate compared to the ranges typically observed, which is about from 1 to 100 cm^2/yr (e.g. Boudreau 1997, Matisoff 1982). More specifically, Aller (1982) estimated bioturbation-induced particle mixing rates in Narragansett Bay to range from 5 to 32 cm^2/yr, Brownawell (1986) estimated a biodiffusion coefficient of 9.4 cm^2/yr in Buzzards Bay, and Thibodeaux et al. (1990) estimated biodiffusion coefficients of 9-13 cm^2/yr. These authors suggest that bioturbation-induced particle mixing can occur to a depth of 6-10 cm and that benthic organism density and associated mixing generally decreases with depth from the sediment surface.

Particle mixing depths are often estimated by inspection of vertical concentration profiles of tracer material, often radionuclides such as ^{210}Pb, ^{137}Cs, or ^{7}Be. Observation of contaminant profiles can also provide an indication of mixed depth. Finely section sediment cores collected by USEPA in 1992 and by GE in 1998 (QEA 1999) provide a means to qualitatively assess mixed depths. Inspection of ^{137}Cs and PCB profiles at five high-resolution core sites in the Upper Hudson River, shown in Figure 3-53 in the DEIR (USEPA, 1997), suggests mixed depths may be greater than 20 cm in some locations.

Figures 6-52a-c, presented by QEA (1999), show PCB concentration profiles for 27 sediment cores collected in 1998. Mixed depths appear to vary widely, with a number of cores showing little or no gradient to 10 cm or more. Non-cohesive sediments are likely less mixed due to lower bulk density, larger grain sizes, and reduced sediment deposition relative to cohesive sediments. Due to the variability in mixed depths and particle mixing rates, there is large uncertainty associated with the parameterization of particle mixing in the model.

Considering the uncertainty in sediment mixing depth, this parameter was considered a calibration parameter and was varied spatially to achieve reasonable fits to long-term sediment trajectories (Chapter 7).

6.12 DECHLORINATION

Anaerobic and aerobic dechlorination processes have the potential to alter PCB congener distribution in the water column and sediments. These processes are of particular concern for the historical calibration as the state variable, Tri+, is subject to potential mass loss due to dechlorination in the sediments. The influence of dechlorination on the sediment inventory of PCBs has been extensively assessed as presented in the DEIR (USEPA, 1997). This assessment compared congener patterns in the sediment to known source material (primarily Aroclor 1242 at Fort Edward) and found little evidence for extensive dechlorination. Results showed minimal aerobic dechlorination and suggested that anaerobic dechlorination of Hudson River sediments is limited to meta- and para- chlorines, which limits its ability to reduce sediment PCB mass. The DEIR concluded that dechlorination mass losses are theoretically limited to 26 percent in Hudson River sediment. Dechlorination losses of more than 10 percent were limited to concentrations greater than 30 mg/kg and below this level, dechlorination losses were frequently observed to be zero, compared to the original Aroclor 1242 source material. Sediments as old as 35 years were found with little or no dechlorination. No sediments were found with dechlorination mass loss greater than 25 percent, based on change in molecular weight, and the median mass loss was 7 percent since the time of PCB deposition. The mean mass loss was 8 percent.

Based on the interpretations provided by USEPA (1997) in the DEIR, which are partially summarized above, the overall impact of dechlorination on the historical and future fate of sediment PCB reservoirs in the Upper Hudson is small. Therefore, the HUDTOX model does not include representation of dechlorination processes.

6.13 SEDIMENT-WATER MASS TRANSFER

6.13.1 Overview

Sediment to water PCB mass transfer in the HUDTOX model occurs due to either porewater diffusion, particulate phase mass transfer, or by sediment resuspension, as discussed in Chapter 5. During high flow periods, sediment resuspension can be the dominant sediment-water transfer mechanism, however, under low flow conditions resuspension contributions can be small relative to other mechanisms giving rise to transfer of PCB from sediment to water. These include numerous processes that act on particulate and dissolved phase PCBs. Possible transfer mechanisms for the dissolved phase include:

- molecular diffusion of dissolved phase PCB in porewater;
- diffusion of colloid-bound PCBs in porewater;

- groundwater advection up through the sediment bed;
- hydrodynamically induced advective pumping; and,
- biologically enhanced porewater transport.

Non flow dependent transfer mechanisms may act on particulate phase PCBs, resulting in subsequent desorption to the water column at the sediment-water interface. These processes may include:

- bioturbation by benthic organisms;
- emergence and uprooting of macrophytes;
- physical disturbance from wind waves or fish activity; as well as,
- direct desorption from surface sediments to the water column.

The magnitude of these various processes can vary seasonally as a function of temperature and climatological conditions. Biologically enhanced sediment-water transfer of PCBs is temperature dependent due to increased biological activity during warm temperatures. Groundwater advection transfer will vary with the groundwater hydraulic gradient. Measurements of groundwater seepage in the Upper Hudson River indicated large spatial and temporal variability, ranging from negative (river losses) to positive groundwater inflows. The highest groundwater inflow rates were measured in late May and early June (HSI Geotrans 1997). In the absence of any physical disturbance of the upper sediment layer (*e.g.*, bioturbation, advection or dispersion), exchange of PCBs between the sediments and water takes place by molecular diffusion (for dissolved material) or Brownian diffusion (for colloidal bound material). Valasaraj et al. (1997), using a water diffusivity of 5.6×10^{-6} cm^2/sec, estimated that mass transfer rates due to molecular diffusion applied to the dissolved phase of a chemical in sediment porewater would be on the order of 0.02 cm/day. Application of this mass transfer rate to porewater concentrations of PCBs results in a relatively small mass flux from sediments to water.

Direct desorption of particulate phase PCBs and subsequent transfer to the water column can be enhanced by bioturbation of surface sediments via the following sequence of processes: first, particles can be transported by mixing processes from depth to the sediment-water interface; second, while residing briefly at this interface, particles can desorb a fraction of the sorbed PCB before being mixed back into deeper sediments; and finally, desorbed PCB can move through the benthic boundary layer into the overlying water column (Portielje and Lijklema, 1999; Thibodeaux, 1996). Several authors have shown these processes can increase effective chemical mass fluxes across the sediment-water interface by a factors of 10-1000 (*e.g.*, Thibodeaux, 1996; Nadal, 1998; Thoms et al., 1995; Reible et al., 1991). Horn et al. (1979) suggested that this non-flow-dependent sediment-water exchange process is important for PCBs in the Hudson River. They further suggested that approximately half of PCB transport in the Hudson River occurs at low to moderate flows and is not the result of solids scour from the sediment bed. In comparison to their calculation of molecular diffusion mass transfer of 0.02 cm/day, Valasaraj et al. (1997)

estimated that a biodiffusion (bioturbation-induced mass transfer of porewater chemical) mass transfer rate would be approximately 12 cm/day.

Analysis of low flow PCB load gain of across TIP reveals that sediment-water transfer mechanisms are occurring at rates much greater than those typically associated with molecular diffusion. This indicates that transfer mechanisms other than molecular diffusion are operative at high rates under low flow conditions. While individual sediment-water transfer processes (such as those listed above) have been extensively studied and measured in other systems (*e.g.*, Thibodeaux, 1996), direct measurement of these processes has not been conducted for the Upper Hudson River. Due to a lack of site-specific information, development of a process-level model to describe low-flow sediment to water mass transfer was not supported. Therefore, an empirical modeling approach was adopted to describe effective sediment-water mass transfer of PCB under low flow conditions.

A seasonally-variable mass transfer rate coefficient operating on porewater PCBs was derived from observations of PCB load gain across Thompson Island Pool under low flow. This effective mass transfer coefficient (k_f) represents the combined effect of all the various processes contributing to low-flow sediment-water transfer of PCBs. The k_f time series derived from observations describes the average low-flow mass transfer occurring during specific intervals over which average values were computed. This approach provides a reasonable estimate of mean behavior and was used successfully in the historical calibration to Tri+.

In attempting to apply the calibrated Tri+ model to individual congeners, it was found that a single porewater PCB mass transfer coefficient could not be used to simultaneously model multiple PCB congeners. Differences in sediment-water partitioning behavior apparently cause differences in observed effective sediment water mass transfer coefficients for individual congeners. Calibration to individual congeners could have been achieved by deriving congener-specific mass transfer coefficients, however, this would have essentially resulted in multiple calibrations that are not mutually consistent. In order to maximize use of the congener simulations in evaluating the historical calibration to Tri+, a modeling approach was sought that could simultaneously describe sediment-water mass transfer for the range of congener partitioning behavior represented by the five congeners chosen for modeling.

Analysis of congener patterns in sediment porewater, on sediment particles and in the Thompson Island Pool load gain suggested that the low flow load gain is dominated by particle-based processes. This analysis also suggested that separation of the porewater and particulate phase mass transfer processes <u>may</u> provide a model capable of describing a range of PCB congeners simultaneously, with varying only congener-specific chemical properties in model inputs. Separate mass transfer coefficients for the particulate and dissolved phases were therefore derived such that the combined contribution to overall sediment-water mass transfer resulted in the same amount. This was done by picking a ratio between these processes that optimized agreement with the observed congener distribution in the water column at Thompson Island Dam.

This approach, while subject to a number of large uncertainties, permitted a reasonable simulation of all five congener state variables, in addition to the principal state variable, Tri+.

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The historical Tri+ calibration was run with the separate particulate and porewater mass transfer coefficients and compared to the calibration achieved with the single k_f function. Results are presented in Chapter 7.

Because results for simulations with the computed porewater and particulate mass transfer coefficients showed good performance for BZ#28 and BZ#52, the two congeners most like Tri+, the historical calibration to Tri+ based on the k_f series was accepted as the model calibration (Chapter 7) and used for model forecasting (Chapter 8).

The analysis of sediment-water mass transfer rates is summarized below.

- To describe low-flow sediment-water transfer of Tri+ for the historical calibration, an empirical modeling approach was used due to a lack of site-specific information on individual processes.
- A seasonally-variable mass transfer rate coefficient was computed from observations of low flow load gain across Thompson Island Pool, which was used in the historical calibration to Tri+.
- The application of the model to individual congeners provided insights as to the relative importance of dissolved phase versus particulate phase mass transfer processes.
- While representation of these processes provided better agreement to individual congener data, results for Tri+ tended to confirm the historical calibration based on the effective porewater mass transfer coefficient.

This section presents the development of the effective mass transfer function, k_f, and subsequent investigation of sediment-water transfer of congeners. Sensitivity analysis are presented in Chapter 7 that explore the significance of implementing separate particulate and porewater mass transfer processes to describe congener load gain.

6.13.2 Calculation of k_f for Tri+

6.13.2.1 Data

The seasonally-variable low flow effective mass transfer coefficient, k_f, was derived from observations of Tri+ load gain across Thompson Island Pool under non-resuspending conditions. Observations of low flow load gain, determined from paired (same day) daily average PCB concentrations at Fort Edward and Thompson Island Dam, were segregated by flow and TSS concentrations. Based on the observed knee in the TSS-flow correlation at approximately 10,000 (Figure 6-12), sediment resuspension is considered significant at flows above 10,000 cfs. Below 10,000 cfs, PCB load gain observations coincident with TSS less than or equal to 10 mg/L were assumed to minimally affected by sediment resuspension. To evaluate this assumption, the relationship between same-day TSS concentrations at Thompson Island Dam and Fort Edward was examined (Figure 6-53). The correlation exhibits high variability, with approximately equal distribution about the 1:1 line, suggesting that on average, TSS transport may be considered conservative in Thompson Island Pool at flows less than 10,000 cfs and TSS less than 10 mg/L. A regression of these data suggest that at very low concentrations, TSS is slightly higher at Thompson Island Dam, however, at concentrations above about 3 mg/L, concentrations at Thompson Island Dam are lower than at Ft. Edward. The apparent lack of significant resuspension contributions in these data suggests that use of data under these conditions for computing low-flow sediment-water mass transfer coefficients is reasonable. Due to the elevated loading of PCBs observed at Fort Edward beginning in September, 1991 from the Allen Mill gate failure, none of the 1991-92 data were used in any of the evaluations of mass transfer rates. The large pulse loading of PCBs influenced PCB loads at Fort Edward for the later part of 1991 and early 1992. The effect of this load on surface sediment concentrations in Thompson Island Pool is unknown, imparting additional uncertainty to calculations of load gain across Thompson Island Pool for this period, therefore the mass transfer analysis was limited to observations collected from 1993 through 1997. Observations of load gain across the Thompson Island Pool for this period were based on daily average PCB concentrations at Fort Edward and Thompson Island Dam. At Thompson Island Dam, the bias-corrected concentrations were used, as described in Section 6.3.

The effective sediment-water mass transfer coefficient relates observations of low flow load gain to surficial sediment concentrations. In order to make use of the 1993 –1997 observations of load gain, estimation of corresponding sediment concentrations was required. The surficial sediment concentration for Tri+ was estimated for each year by applying a first order rate of decline computed from observed poolwide average surficial sediment concentrations from 1991 to 1998 ($k = {}^-0.076\ yr^{-1}$). The 1991 average concentrations were computed from the 0-5 cm layer concentrations in GE 1991 composite sediment data, which were collected before the Allen Mill Event occurred in the fall of 1991. This event increased surface sediment concentrations by an unknown amount and produced a noticeable increase on observed PCB load gain across Thompson Island Pool . The average Poolwide 1998 sediment surface sediment concentrations reported by QEA for cohesive and non-cohesive sediment (1999) were used. The unknown perturbation of sediment concentrations from the Allen Mill Event in 1991 imparts uncertainty to the estimated rate of sediment concentration declines from 1991 to 1998. Estimated poolwide sediment and porewater concentrations for all modeled PCB groups using this approach are shown in Table 6-43 and 6-44.

6.13.2.2 Approach

To compute the effective mass transfer coefficient for Tri+, Thompson Island Pool was represented as a single control volume and the following mass balance equation for the water column was employed to relate observed load gain to sediment concentrations (Equation 6-25).

$$k_f = \frac{1}{A_s}\left(\frac{(QC)_{TID} - (QC)_{FE}}{C_{PW}}\right) \cdot 244.659 \qquad \textbf{(6-25)}$$

where:

k_f = effective mass transfer rate (cm/day)
QC_{TID} = product of flow and concentration at TI Dam, (cfs · mg/L)

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QC_{FE} = product of flow and concentration at Fort Edward, (cfs · mg/L)
C_{pw} = Apparent porewater Tri+ concentration (mg/L)
A_s = Surficial sediment area (m^2)
244.659 = Conversion factor to cm/day

Application of this simplistic mass balance calculation implies the following assumptions.

1. The time of travel between upstream and downstream locations is less than one day and therefore samples collected at Fort Edward and TI Dam on the same day can be reasonably assumed to represent the same parcel of water.

2. Volatilization losses across TIP do not significantly affect the observations of low flow load gain.

3. The gradient of porewater to water column concentrations can be approximated with the porewater concentration. Because porewater concentrations are typically at least 1 to 2 orders of magnitude greater than water column concentrations, this assumption is valid.

For consistency between the calculation of k_f values and implementation in HUDTOX, sediment surface area was calculated based on the model segmentation. The percentage of cohesive and non-cohesive sediment area were used to determine area weighted average values for sediment properties, such as: bulk density, porosity, f_{OC}, and DOC concentration (Table 6-45). To compute the porewater PCB concentration, the 3-phase partitioning equations presented in Chapter 5 were employed with the input values in Table 6-43 and the Phase 2 water column partition coefficients. Partition coefficients were temperature-adjusted according to the water column temperature time series in the model (Section 6.8).

Equation 6-25 was solved for each individual observation of paired (same day) concentrations at Fort Edward and Thompson Island Dam, censored as described in the above section. The k_f values for Tri+ ranged from -1.0 to 65 cm/d. Negative results occurred for days where lower concentrations were observed at Thompson Island Dam than at Fort Edward. This affected 7 percent of the observations and these results were excluded in developing the effective mass transfer function. (Figure 6-54)

6.13.2.3 k_f Results

Individual values of k_f were plotted versus Julian day to discern the average seasonal pattern in low flow load gain for the 1993-1997 period. The k_f values were distinctly higher in summer months relative to most of the year (Figure 6-54). Observed high values in March and April (Julian days ~60-120) maybe a result of resuspension activity during the spring runoff period, either preceding these data, or not represented by the associated TSS measurements. The average mass transfer rate in specific time intervals was used to develop a variable k_f annual time series, which was incorporated into the HUDTOX model. The approximate mean value (10.2 cm/d) of the low temperature period, September through April, was applied for these months. The resulting k_f series shows that from early May to mid June, k_f increases from about 10 to 25 cm/d and declines to about 10 cm/d at the end of August (Table 6-46, Figure 6-55). The seasonal dependence on the low-flow mass transfer rate is clearly evident, with the peak mass transfer occurring in mid June. The causal factors leading to the peak rate occurring in mid June are poorly understood. Peak water column temperature is observed in July (Figure 6-41). It is notable that the timing of the peak mass transfer rates are generally coincident with the timing of the highest measured groundwater influx rates (HSI Geotrans, 1997).

6.13.2.4 Implementation in HUDTOX

The sediment-water transfer of porewater PCBs is computed in HUDTOX by Equation 5-22. To correctly implement the k_f time series in HUDTOX, Equation 5-22 was rearranged to achieve the same form of expression of the mass transfer coefficient as in Equation 6-26. This shows that k_f is equal to the following terms.

$$kf = \frac{E \cdot n_{ij}}{L_{ij} \cdot n_j} \qquad \textbf{(6-26)}$$

The HUDTOX model input describing the transfer rate is the dispersion coefficient, E. Therefore, Equation 6-26 was solved for E for each value of k_f in the annual time series and the resulting series for E was input to HUDTOX. The mixing length, L_{ij}, was specified as 0.02 m. The average porosity between sediments and water (n_{ij}) computed based on the average sediment porosity of 0.527 and water column porosity of ~1.0 is 0.7635.

6.13.3 Analysis of congener and total PCB mass transfer coefficients

The k_f series developed as presented above for Tri+ was used in the historical 1977-1997 calibration. Following the historical calibration to Tri+, the HUDTOX model was tested through short-term hindcast applications to total PCB and five congeners (BZ#4, BZ#28, BZ#52, BZ#90+101, and BZ#138) for 1991 to1997. BZ#4 exhibits the largest deviation in environmental behavior relative to Tri+ and BZ#4 is not a component of Tri+. All of the other congeners are included in Tri+. BZ#4 is the least hydrophobic of these congeners and also has the highest volatility.

Initial investigations revealed that the porewater mass transfer coefficient, k_f, developed for Tri+ was not applicable to all congeners. This is apparent through comparison of observed effective sediment-water mass transfer rates for total PCB and the five congeners. These rates were estimated following the same approach as for Tri+ explained in the previous section (Figure 6-56) and plotted versus the k_f values for total PCB. Sediment concentrations used in calculation of k_f for congeners were computed as described above (Table 6-43 and 6-44). Results for BZ#4 show significantly lower k_f values relative to the other results. BZ#28 results were in best agreement with total PCB results, although still noticeably higher. Tri+, BZ#52, 101+90 and 138 show higher values relative to total PCB. Thus, the k_f for total PCB over-predicts BZ#4 load gain, while under-predicting load gain for Tri+, BZ#28, 52, 90+101, and 138. The differences in apparent k_f values among congeners is also shown through comparison of results for 14 selected days on which quantitations were available for all five congeners at Fort Edward and Thompson Island Dam (Figure 6-57).

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An objective of modeling congeners was to evaluate the Tri+ calibration for PCBs exhibiting different environmental behavior. While congener-specific mass transfer coefficients could have been developed for the short-term hindcast applications, this would have somewhat diminished the use of the model for this purpose because in effect individual calibrations would be developed for each congener. Therefore, the sediment-water mass transfer processes were investigated through use of the congener data with the goal of representing sediment-water mass transfer processes in a consistent manner across all PCB groups modeled (i.e. Tri+, Total PCB and individual congeners). This would allow simultaneous application of the Tri+ calibration to all congeners, varying only congener-specific chemical properties.

Differences in partitioning behavior among congeners was considered in order to explain differences in effective mass transfer rates. The water column partition coefficients estimated from the USEPA Phase 2 water column data are compared to the estimates from the GE 1991 sediment data in Figure 6-58. The estimates of effective k_f values for individual congeners used pore water congener concentrations estimated through application of the sediment partition coefficients from the GE 1991 sediment data. Large differences in estimated sediment-water partitioning coefficients exist for the lighter congeners, while the heavier congeners show approximately the same values in the water and sediment. While initially congener-specific estimates of k_f used sediment partition coefficients, use of the water column values to compute effective mass transfer values did not result in convergence of these values among congeners. This suggests that there are factors other than influences of sediment-water partitioning on pore water PCB concentrations controlling the relative flux of congeners out of the sediments.

Observation of the relative distributions of PCBs in pore water, surface sediments, and in the water column at Thompson Island Dam suggest that a pore water source alone cannot account for the observed congener patterns in the water column. This is illustrated through comparison of the expected pore water distribution in sediment pore water, the measured distribution on particulate sediments, and measured distribution in the Thompson Island Pool PCB load gain for 15 congeners (Figure 6-60). These congeners are those for which 3-phase partition coefficients were estimated from the Phase 2 water column data and the GE 1991 sediment data (USEPA 1997). Inspection of the congener distribution in these three compartments suggests that a combination of dissolved phase and particulate phase pathways is required to match the observed congener pattern at Thompson Island Dam.

Using pore water transfer only (represented by k_f) means that relative sediment-water flux of the congeners under non-resuspending conditions is fixed by their relative concentrations and sediment-water partitioning, which does not appear to be the case. By implementation of a particulate transfer mechanism in the description of sediment-water mass transfer, the relative flux of congeners from the sediments is determined not only by concentrations and partition coefficients, but also by the relative ratio of the particulate and pore water transfer mechanisms.

The mechanisms contributing to enhanced sediment-water transfer of PCBs are due to physical perturbations of the surficial sediments (see list of possible mechanisms above), and are largely independent of chemical properties (assuming dynamic desorption effects are small). The effect of these processes, however, varies by congener due to differences in partitioning behavior. Therefore, modeling the relative sediment-water flux ratios of the congeners may be possible by representing the relative contribution of dissolved and particulate phase PCBs and congener-specific partition behavior. It was postulated that the mechanisms affecting sediment particles at the sediment-water interface was resulting in desorption of PCBs from the sediment to the water column. The relative degrees of desorption among congeners was assumed to occur in ratios determined by equilibrium phase partitioning on suspended solids in the water column.

6.13.4 Estimation of Particulate and Pore water Mass Transfer Rates

As discussed above, in estimating separate mass transfer rates for particulate and pore water pathways, the sediment partition coefficients derived from the GE 1991 sediment data were used. Differences in mass transfer among PCB congeners were assumed to be due only to chemical specific properties. That is, the resulting rates reflect differences among congeners resulting directly from differences in their partitioning behavior.

Similar to the development of k_f for pore water mass transfer, separation of pore water and particulate transfer processes was also represented by simple mass transfer coefficients, which combine to produce the total sediment-water flux for Tri+ computed by k_f.

The load gain represented by the effective mass transfer (k_f) can be assumed to represent the sum of the load gain of particulate pathway processes and the load gain of pore water pathway processes as in the equation below:

$$\Delta L_p + \Delta L_d = \Delta L_{kf} \qquad \textbf{(6-27)}$$

where:

ΔL_p = load gain from particulate pathway
ΔL_d = load gain from pore water pathway
ΔL_{kf} = total load gain produced by the effective mass transfer rate

The individual load terms in this equation can be expressed in terms of their respective mass transfer rates (Equation 6-28).

$$\left(k_p \cdot A_s \cdot C_p \cdot \rho \cdot d_f\right) + \left(k_d \cdot A_s \cdot C_d\right) = \left(k_f \cdot A_s \cdot C_d\right) \qquad \textbf{(6-28)}$$

where:

k_p = particulate mass transfer rate (cm/day)
k_d = pore water mass transfer rate (cm/day)
k_f = effective mass transfer rate (cm/day)
A = surficial area (m^2)
Cp = particulate PCB concentration in the sediment (mg_{PCB}/Kg_{solid})
ρ = sediment dry bulk density (Kg_{solid}/L_{bulk})
C_d = apparent dissolved PCB concentration ($mg_{PCB}/L_{porewater}$)
d_f = fraction dissolved in the water column

This equation assumes the water component of the concentration gradients are negligible. The d_f term reflects the assumption that desorption occurs from sediment particles according to equilibrium partitioning in the water column (based on partition coefficients estimated from the

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Phase 2 water column data). The k_d and k_p terms can be solved for through specification of R. This produces two equations and two unknowns, from which values of k_p and k_d can be determined (Equation 6-29, 6-30).

$$k_p = \frac{k_f \cdot C_d}{C_p \cdot \rho + R \cdot C_d} \tag{6-29}$$

$$R = \frac{k_d}{k_p} \tag{6-30}$$

The value of R was determined through congener pattern matching. An initial value of R was specified and k_d and k_p were solved for using equation 6-29 and 6-30. Then, the relative percent load gain (RP_I) for each of the 15 congeners) for which water column and sediment partition coefficients were estimated (Table 6-47) was computed according to Equation 6-31.

$$RP_i = \frac{\left[\left(k_p \cdot A_s \cdot C_p \cdot \rho \cdot d_f\right) + \left(k_d \cdot A_s \cdot C_d\right)\right]_i}{\sum_{i=1}^{15} \left[\left(k_p \cdot A_s \cdot C_p \cdot \rho \cdot d_f\right) + \left(k_d \cdot A_s \cdot C_d\right)\right]_i} \tag{6-31}$$

The RP values were plotted for each congener, representing the computed congener distribution in the TIP load gain, which was matched to the observed distribution. R was optimized to minimize cumulative squared error between computed and observed RP for each of the 15 congeners as shown in Figure 6-60 for summer and non-summer periods.

The value of R was 710 for summer conditions (June through August) and 725 for non-summer conditions (September through May). The resulting mass-transfer coefficients for each modeled congener are shown in Table 6-47. These rates were used in short-term hindcast applications presented in Chapter 7. Results showed that this approach gave reasonable results, however, did not completely explain differences in sediment-water mass transfer between congeners.

7. MASS BALANCE MODEL CALIBRATION

7.1 OVERVIEW

Chapter 5 presented development of the Hudson River Toxic Chemical Model (HUDTOX) which included the conceptual framework, governing equations and spatial-temporal scales. Chapter 6 presented the organization and analysis of available data to specify the required model forcing functions, initial conditions, rate coefficients and state variables. This chapter presents results from calibration of the HUDTOX model to site-specific data for solids and PCB state variables. It also includes results from sensitivity analyses for important model inputs and process mechanisms. The calibration results in this chapter provide the foundation for use of the HUDTOX model in conducting forecast simulations to estimate long-term responses to continued No Action and impacts due to a 100-year peak flow in Chapter 8.

The principal model application was a long-term historical calibration for Tri+ for a 21-year period from 1977 to 1997. The historical calibration was tested through short-term hindcast applications for total PCBs and five individual congeners from 1991 to 1997. Consistent with the Reassessment questions, emphasis was placed on calibration to long-term trends in sediment and water column PCB concentrations. Additional, independent model validation is described in Chapter 9.

The following major sections are included in Chapter 7:

7.2 Calibration Strategy

7.3 Solids Dynamics

7.4 Historical Tri+ Calibration

7.5 Sensitivity Analyses

7.6 1991-1997 Hindcast Applications

7.7 Calibration Findings and Conclusions

The model was successful in its primary objective, representation of long-term trends in PCB behavior in the Upper Hudson River. This was best demonstrated by comparison to 21-year trends in surface sediment Tri+ concentrations and in-river solids and Tri+ mass transport. Tests of model performance conducted for the 1991-1997 data-intensive period were also successful in demonstrating model reliability. Localized and transient discrepancies between the model and data were viewed as having minimal significance to the model's reliability for long-term forecasting as required for the Reassessment. Many different metrics were used to demonstrate model reliability and they should be used collectively in a "weight of evidence" approach.

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7.2 CALIBRATION STRATEGY

The calibration strategy can be described as minimal and conservative. It was minimal in the sense that external inputs and internal model parameters were determined independently to the fullest extent possible from site-specific data (as presented in Chapter 6), and only a minimal number of parameters were determined through model calibration. It was conservative in the sense that parameters determined through model calibration were held spatially and temporally constant unless there was supporting information to the contrary.

A 21-year historical calibration was the principal development vehicle for the model. The calibration focused on representing long-term Tri+ trends in water and sediment. The Tri+ form was the principal focus of the calibration because comparable measurements were available in all calibration datasets. Tri+ is the sum of the tri and higher chlorinated PCB congeners. Details of selection of Tri+ as the principal state variable are presented in Chapter 6. Also presented in Chapter 6 is the development of all inputs for model flows and loadings for the calibration period.

The following factors were the most important in controlling long-term trends in sediment and water column Tri+ concentrations in the Upper Hudson River:

- Hydrology;
- External solids loads;
- External Tri+ loads;
- Tri+ partitioning;
- Sediment-water mass transfer under non-scouring flow conditions;
- Solids burial rates; and,
- Particle mixing depth in the sediments.

The first three of these factors are external inputs largely defined by data, and the last four are internal processes within the river defined by data, scientific literature and calibration. Long-term solids burial rates were the principal factor controlling long-term Tri+ trends in the river. Partitioning controls the distribution of Tri+ mass between sorbed and dissolved phases, thus influencing sediment-water and water-air mass transfer, and bioavailability to fish. Sediment-water mass transfer under non-scouring flow conditions was found to be the principal source of Tri+ inputs to the water column. Particle mixing depth strongly influenced long-term responses and the vertical distribution of Tri+ in the sediments. With the exception of solids burial rates and particle mixed depth, all model inputs and parameter values were determined using site-specific data and were not adjusted during the model calibration.

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The principal datasets used in calibration of HUDTOX were the following:

- Tri+ surface sediment concentration trends;
- Measured solids burial rates from dated sediment cores;
- Computed solids burial rates from a sediment transport model;
- In-river solids and Tri+ mass transport at high and low flows; and,
- Solids and Tri+ water column concentrations.

The historical calibration was conducted simultaneously for solids and Tri+. Operationally, the approach consisted of adjusting four model parameters: gross settling velocities into cohesive and non-cohesive sediment areas; resuspension rates from non-cohesive sediment areas; depth of particle mixing in the sediment bed; and, magnitude of sediment particle mixing.

Based on the flow balance and solids loads developed in Chapter 6, solids and Tri+ dynamics in HUDTOX were calibrated to achieve long-term results consistent with the calibration datasets listed above. In the simultaneous solids and Tri+ calibration, primary emphasis was placed on representing long-term historical rates of decline for Tri+ in the water column and surface sediments from 1977 to 1997. The calibration sought to describe mean high and low flow solids and Tri+ dynamics in the river. Calibration to short-term event dynamics was not emphasized because detailed representation of short-term event impacts was not necessary to answer the principal Reassessment questions.

The model calibration was tested with a short-term 1991-1997 hindcast application for total PCBs and five congeners (BZ#4, BZ#28, BZ#52, BZ#[90+101] and BZ#138). The physical-chemical properties of the five congeners span a wide range of partitioning and volatilization behavior. These important differences in environmental behaviors provided opportunity to test the rigor of the Tri+ calibration, especially sediment-water and air-water exchange processes. For example, model results for a highly volatile congener may be more sensitive to errors in sediment-water exchange than a less volatile congener. Likewise, model results for a strongly partitioning congener may be more sensitive to errors in particle-based PCB processes such as settling than a weaker partitioning congener.

7.3 Solids Dynamics

7.3.1 Calibration Approach

Solids dynamics in the Upper Hudson River are strongly driven by hydrology and external solids loads. Hydrology and external solids loads were developed in Chapter 6 using data-based balances for tributary and mainstem flows and solids mass transport. Internal processes of settling and resuspension largely determine the long-term PCB fate in the sediment bed. Long-term sediment burial or erosion rates are determined by the net effect of deposition and resuspension processes. The calibration approach for solids dynamics in HUDTOX consisted of adjusting constant gross settling velocities for cohesive and non-cohesive sediment areas, and resuspension rates from non-cohesive sediment areas. Flow-driven resuspension from cohesive sediment areas was computed internally in the model using algorithms based on the Depth of Scour Model.

Solids burial rates were determined by model calibration using the following principal constraints:

- Measured burial rates from dated sediment cores;
- Computed burial rates from a sediment transport model;
- Tri+ surface sediment concentration trends; and,
- In-river solids and Tri+ mass transport at high and low flows.

The first two constraints are described below.

Information on solids burial rates was available from two sources: first, measurements from eight high resolution sediment cores (USEPA, 1997); and second, results from SEDZL, a coupled hydrodynamic-sediment transport model for the Upper Hudson River (Quantitative Environmental Analysis, 1999). There are limitations to the high-resolution sediment cores that preclude direct use of these data as calibration inputs. The cores are few in number and are not considered representative of average solids burial rates on the spatial scale of the HUDTOX model. Furthermore, measurements from these cores represent burial rates only in cohesive sediment areas. Therefore these data were used as upper bounds on burial rates and as only one of four sources of calibration guidance.

The calibration of solids dynamics in the model was also guided by computed solids burial rates from SEDZL, a coupled hydrodynamic-sediment transport model for the Upper Hudson River developed by General Electric Company contractors (QEA, 1999). Flow and solids load inputs to the SEDZL model were developed using essentially the same methods and data as development of flow and load inputs to HUDTOX and hence, results are transferable. The SEDZL results were in general agreement with estimated burial rates from the USEPA high-resolution sediment cores (QEA, 1999). SEDZL results were within a factor of two of measured burial rates from all but one of the high-resolution sediment cores. Agreement was within a factor of five for the remaining sediment core. The SEDZL model results contain uncertainty, however, due to limited data and large uncertainty in model inputs (especially solids loads downstream of Thompson Island Pool). These uncertainties affect long-term solids burial rates in both cohesive and non-cohesive sediment areas. These limitations notwithstanding, results from the SEDZL model were considered reasonable and the best available estimates of solids burial rates on a reach-average basis.

Ultimately, solids burial rates were determined through model calibration using available site specific information for the four principal constraints listed above. The model calibration led to additional upward adjustment of low flow solids loadings between Schuylerville and Waterford, beyond the estimates presented in Chapter 6. This adjustment was considered to be within the

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large range of uncertainty in tributary loadings estimated from the sparse available data for the major tributaries downstream of the Thompson Island Dam.

7.3.2 Solids Calibration Results

Values for all solids calibration input parameters are presented in Tables 7-1 and 7.2. The calibration of the solids dynamics is demonstrated for:

- Long-term solids burial rates;
- In-river solids mass transport at low and high flow;
- Water column solids concentration time series from 1977 to 1997;
- Solids mass balances for the Spring 1994 high-flow event;
- Water column solids concentrations during several high flow periods; and,
- Scatter plots and cumulative probability distributions of solids concentrations at low and high flow.

Each is discussed below.

7.3.2.1 Burial Rates

Model calibration results for long-term, reach-average burial rates in cohesive and non-cohesive sediment areas are presented in Figure 7-1. Over the calibration period, the HUDTOX model represents the Upper Hudson River as a whole to be net depositional, based on the assumption underlying development of tributary solids loads in Chapter 6. Computed solids burial rates are generally an order of magnitude larger in cohesive sediments (0.24 to 1.50 cm/yr) than in non-cohesive sediments (0.04 to 0.10 cm/yr). No results for cohesive sediments are reported for the Federal Dam reach because this reach consists almost exclusively of non-cohesive sediment areas and it was represented as completely non-cohesive in the HUDTOX model.

Reach average results for cohesive and non-cohesive sediment areas were compared to the SEDZL model results, one of four primary calibration constraints. Model burial rates were generally consistent with SEDZL results except where differences were necessary to achieve simultaneous agreement with Tri+ surface sediment concentrations and solids dynamics. This resulted in somewhat lower burial rates for Thompson Island Pool than those computed by the SEDZL model. In Thompson Island Pool, solids burial rates for cohesive and non-cohesive sediment areas in the HUDTOX calibration were 0.65 and 0.07 cm/yr, respectively. In the SEDZL calibration, the corresponding solids burial rates were 0.81 and 0.03 cm/yr (QEA, 1999).

7.3.2.2 High and Low-flow Solids Loads

In addition to achieving agreement with solids burial rates and long-term surface sediment Tri+ trends, another important calibration test was comparison to estimated high and low flow solids mass transport in the river. These mass transport values can be viewed as in-river solids loads. Results were stratified using a river flow of 10,000 cfs at Fort Edward to represent the approximate cutpoint above which flow-dependent resuspension is observed (See Figure 6-12). Flows below and above 10,000 cfs are referred to as "low flow" and "high flow", respectively, throughout this report. Use of a single flow cutpoint is a simple and convenient way to evaluate model behavior under resuspension and non-resuspension conditions, however, recognize that no single flow cutpoint completely separates these conditions at all locations in the River.

There is good agreement between model and data-based estimates of the solids loads at Stillwater and Waterford for both high and low flows (Figure 7-2). This suggests the model is representing average high and low flow behavior for the historical calibration period. Estimated solids loads were based on the rating curves presented in Chapter 6, which were not developed for Thompson Island Dam. There was not a strong relationship between solids concentration and flow in the available data at this location. At Stillwater and Waterford, differences are less than four percent for both low and high flow. In-river solids loads are split almost equally between high and low flow conditions, consistent with observations presented in Section 6.5.

It must be noted that initial calibration efforts were not successful in reconciling estimated tributary solids loads with solids and Tri+ water column concentrations and in-river solids loads below Thompson Island Pool at low flow. Calibration analyses indicated that decreasing gross solids settling velocities or increasing solids resuspension velocities produced results that were not in good agreement with Tri+ surface sediment concentrations or water column concentrations. Upward adjustment of low flow tributary solids loads downstream of Thompson Island Pool provided better agreement with both Tri+ and solids concentrations, and also improved model agreement with long term sediment Tri+ concentrations. Solids loads were adjusted by adding a total constant additional load of 40 MT/day to the Schuylerville-Stillwater and Stillwater-Waterford reaches. These adjustments represent increases of 26 and 17 percent, respectively to the total tributary loads for these two reaches. The magnitude of this adjustment was considered to be within the large range of uncertainty in estimation of tributary solids loads below TIP.

7.3.2.3 Water Column Solids Concentrations

The model calibration was evaluated by comparing computed water column suspended solids concentrations to long-term data over the 21-year calibration period and short-term intensive data during four high-flow events. Each is described below.

The calibrated model results for water column solids over the 21-year calibration period show reasonable fit at both high and low flow observations across the entire period at Thompson Island Dam, Schuylerville, Stillwater and Waterford (Figure 7-3 a and b). Results shown for the first model segment downstream of Fort Edward represent solids loading inputs at the upstream boundary and are shown only for reference. Note that data are only available for Thompson Island Dam from 1991 to 1997. The solids concentrations throughout the year, and especially during high flow events were found to be strongly driven by hydrology and external solids loads. Solids concentrations are much higher in reaches below Thompson Island Pool and reflect the much higher external solids loads to this portion of the river (Section 6.5). Both computed and

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observed peak concentrations generally range between 50 and 100 mg/l at TID and Schuylerville, and between 100 and 400 mg/l at Stillwater and Waterford.

Although the calibration strategy focused on accurate representation of long-term Tri+ trends and mean high and low flow solids dynamics, it is of interest to assess model performance for high flow events when flow-dependent resuspension is important. Suspended solids results for the spring high flow periods during 1983, 1993, 1994 and 1997 are shown in Figures 7-4 through 7-7. These four events are among the most extensively sampled events in the calibration period. Results are of particular interest in 1993 and 1994 because sampling frequencies were higher than in 1983 or 1997.

In general, timing of computed and observed concentration peaks is in fair agreement. This is largely because water column solids concentrations are strongly driven by hydrology and external solids loads, especially during high flows. The computed peak concentrations at times tend to be lower than observed peak concentrations. This is especially evident at Stillwater. This is not unexpected considering the model calibration strategy of capturing mean high flow solids dynamics. There is good agreement between computed and observed concentrations at Thompson Island Dam during spring 1994, a period during which daily measurements were available.

The model calibration to peak concentrations at Stillwater appears weakest, but may be partially explained by errors in estimated tributary flow, especially for Batten Kill. While solids concentrations were measured for Batten Kill over much of the 1994 event, Batten Kill flows were estimated based on Kayaderosseras Creek flows, which drain a much smaller watershed and thus are expected to exhibit a more "flashy" response to precipitation or snowmelt (See Section 6.4). Closer agreement occurs at Thompson Island Dam, shown for the 1994 and 1997 events.

7.3.2.4 Spring 1994 High Flow Event Solids Mass Balance

The model calibration was also evaluated by comparing model-estimated and data-estimated solids mass balances for Thompson Island Pool during the spring 1994 high flow event. This is the only reach in the Upper Hudson River for which there exists a well-constrained solid mass balance for mainstem and tributary solids loads. For the 33-day period (March 29 to April 30) encompassing this event, measurements were available for flows and water column concentrations for the two major tributaries and upstream inputs. This permitted development of an input-output solids mass balance for this event. The model-based estimate of 400 MT net erosion during this event agrees within three percent of the data-based estimate of 411 MT.

7.3.2.5 Further Model-Data Comparisons

To provide insights into model behavior and the limits of model capability, calibration results are also shown by comparison of computed and observed water column solids concentrations using scatter plots and cumulative probability functions for model results and data stratified by flow. Presentation of results in this manner shows the model performance in describing individual data. However, it must be recognized that the model calibration approach was not aimed at describing the full range of observed event-scale behavior. The solids calibration sought to describe mean low and high flow behavior. Considering this, model agreement with mean or median concentration results is of more interest than a good fit across the range of observed behavior. In fact, the model may be expected to show offsetting errors at the high and low end of each flow range.

Scatter plot results for Thompson Island Dam, Stillwater and Waterford are shown in Figures 7-8 and 7-9 for low and high flows, respectively. The model and data mean values are shown on these figures by the horizontal and vertical crossed lines, as is the 1:1 correspondence line. Even on log-log scale, the high variability in agreement between model and data is evident. Inspection of these plots shows that the model tends to over compute low concentrations and under compute high concentrations in each flow range, an expected result of the model because it is calibrated to mean low and high flow behavior. Note that the model and data means intersect at the 1:1 line (meaning they are nearly identical) for both high and low flows. Agreement is best for Stillwater and Waterford. At Thompson Island Dam, the model appears to be biased slightly low under low flow conditions and slightly high at high flow conditions.

Probability distributions provide similar insights as the scatter plots. Computed and observed cumulative probability distributions for solids concentrations at Thompson Island Dam, Stillwater and Waterford are presented in Figures 7-10 and 7-11 for low and high flows, respectively. The same observations regarding model behavior can be made in these figures as the scatter plots. At Stillwater and Waterford, the computed and observed median values tend to agree, which was the intent of the calibration, while the model shows offsetting biases at low and high concentrations of each flow range. At Thompson Island Dam, the model results are good at low flow, however, show considerably higher concentrations than were observed at high flow.

While the model agreement with data at high flow for Thompson Island Dam is not ideal, the overall significance of this to use of the model for the Reassessment is small. Fish PCB levels do not respond at any significant level to short-term event concentrations. The model was successfully calibrated to estimates of long-term solids burial rates and sediment Tri+ concentrations. The water column Tri+ concentrations that affect fish levels are determined largely by sediment-water transfer mechanisms that are not flow driven, and by upstream Tri+ loadings at Fort Edward. Therefore, additional model calibration to high flow dynamics was deemed unnecessary for the Reassessment.

7.3.3 Components Analysis for Solids

Over the 21-year calibration period, the HUDTOX model represents the Upper Hudson River as a whole to be net depositional, based on the assumption underlying development of tributary solids loads. The computed average bed elevation change in Thompson Island Pool over the 21-year calibration period is approximately 4.5 cm (Figure 7-12). Computed annual average burial rates in cohesive and non-cohesive sediment areas from Fort Edward to Federal Dam are shown over specific river mile intervals in Figure 7-13. Burial rates in cohesive sediments range from 0.24 to 1.49 cm/yr while burial rates in non-cohesive sediments do not exceed 0.10 cm/yr. Computed burial rates in cohesive sediment areas are approximately an order of magnitude greater than those computed in non-cohesive sediment areas.

A 21-year solids mass balance components analysis from the calibrated model is shown in Figure 7-14 for the four major reaches in the Upper Hudson River. These four reaches represent the river from Fort Edward to Thompson Island Dam, Thompson Island Dam to Schuylerville, Schuylerville to Stillwater, and Stillwater to Waterford. All four reaches are computed to be depositional over the 21-year calibration period. There is a computed net load gain to the water column of 3,043 x 10^3 MT (497 percent) between Fort Edward and Waterford. Contributions to solids load gain are dominated by tributary loads. Gross sediment resuspension accounts for only 21 percent of the total solids inputs to the water column. Tributary loads (including Fort Edward) and sediment resuspension contribute 4,183 x 10^3 MT (79 percent) and 1,128 x 10^3 MT (21 percent), respectively, between these locations.

It is noteworthy that approximately 80 percent of computed solids inputs to the water column are due to external sources and only approximately 20 percent are due to sediment resuspension. Furthermore, these proportions change only slightly when solids mass balance components analyses are conducted separately for high and low flows. It can be concluded that although sediment resuspension is important, water column solids concentrations and in-river solids loads are driven primarily by hydraulics and solids loads from upstream and tributary sources, even under high flow conditions.

7.3.4 Solids Calibration Summary

The calibration approach for solids dynamics in the historical calibration consisted of adjusting constant gross settling velocities into cohesive and non-cohesive sediment areas, and resuspension rates from non-cohesive sediment areas. These parameters were adjusted to meet the simultaneous constraints of long-term Tri+ concentrations in the surface sediments, solids burial rates, in-river solids loads, water column solids concentrations, and long-term water column Tri+ concentrations. The HUDTOX model represents the Upper Hudson River as a whole to be net depositional from 1977 to 1997, based on the assumption underlying development of tributary solids loads. Computed solids burial rates in cohesive sediment areas are approximately an order of magnitude greater than those computed in non-cohesive sediment areas. Computed in-river solids loads are split almost equally between high and low flow conditions.

There is a computed net solids load gain to the water column of 497 percent between Fort Edward and Waterford over the 21-year historical calibration. Contributions to solids load gain are dominated by tributary loadings. Computed tributary loadings (including Fort Edward) and gross sediment resuspension contribute 79 and 21 percent, respectively to total solids inputs between these locations. Although sediment resuspension is important, water column solids concentrations and in-river solids loadings are driven primarily by hydraulics and solids loadings from upstream and tributary sources, even under high flow conditions.

The model calibration was demonstrated as successful for purposes of simulating general solids behavior in the Upper Hudson River. Model performance was deemed satisfactory based on:

- Model computed solids burial rates;
- Model computed high and low flow solids loads;

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- Representation of the intensely-sampled spring 1994 high flow event; and,
- Statistical comparisons of model mean performance.

Additionally, it must be recognized that the HUDTOX calibration was conducted simultaneously for solids and Tri+ and hence, further support of the calibration is evidenced in the next section describing Tri+ results.

7.4 Historical Tri+ Calibration

7.4.1 Calibration Approach

Although the solids and Tri+ calibrations were conducted simultaneously, the Tri+ model calibration results are presented separately and involved some considerations that did not affect the solids model. For example, sediment mixed layer depths and mixing rates do not affect water column suspended solids concentrations, however, these parameters have important impacts on long-term surface sediment Tri+ concentrations. Mixing rates, however, are somewhat less influential than long-term solids burial rates.

In addition to simultaneous use of the calibration datasets for solids dynamics, the additional principal constraints for Tri+ in the historical calibration were:

- Tri+ surface sediment concentrations;
- Solids burial rates;
- In-river Tri+ mass transport at high and low flows; and,
- Tri+ water column concentrations.

As discussed in Section 7.3, the application of simultaneous, mutual constraints on solids and Tri+ ensured consistency between the solids and Tri+ mass balances in the model. However, greater emphasis was placed on trends in sediment and water column Tri+ concentrations, because these were the primary objectives of the model calibration.

The historical calibration was conducted on a reach-average spatial scale. Operationally, the calibration approach consisted of adjusting only four model parameters: gross settling velocities into cohesive and non-cohesive sediment areas; resuspension rates from non-cohesive sediment areas; depth of particle mixing in the sediment bed; and, magnitude of sediment particle mixing. No chemical-specific parameters were adjusted during the Tri+ calibration. External loads, partitioning, sediment-water mass transfer and air-water mass transfer rates were determined solely by Tri+ physical-chemical properties and site-specific data, as described in Chapter 6.

Specification of Tri+ partitioning behavior has significant influence on the model calibration. The model uses three-phase equilibrium partitioning equations that require specification of organic carbon concentrations. Values for site-specific organic carbon input parameters to the model (determined in Chapter 6) are summarized in Table 7-3. Input values for Tri+ process

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coefficients and state variable properties are presented in Table 7-4. Values for all solids calibration input parameters were presented previously in Tables 7-1 and 7.2.

7.4.2 Tri+ Calibration Results

Results for the Tri+ calibration are presented in a series of comparisons between computed and observed values which include:

- Long-term surface sediment Tri+ concentrations;
- Longitudinal and vertical profiles for Tri+ sediment concentrations;
- Water column Tri+ concentration time series from 1977 to 1997;
- In-river Tri+ loads at low and high flow;
- Scatter plots of water column Tri+ concentrations at low and high flow;
- Cumulative probability distributions of Tri+ concentrations at low and high flow; and,
- Water column Tri+ concentrations during several high flow periods.

7.4.2.1 Long-Term Sediment Tri+ Concentrations

The principal calibration metric was comparison of computed and observed long-term Tri+ concentration trajectories in surface sediments (as shown in Figures 7-15 a-e). These figures show reach-wide average concentrations for five river reaches. Model results are shown for surface sediments, which correspond to the first two sediment layers (0-2 and 2-4 cm). Computed results for deeper sediments are also shown as average concentrations over depth intervals corresponding to the respective sediment datasets.

In addition to the 1977 initial condition data, sediment data were collected in 1991 (for the entire Upper Hudson) and 1998 (mainly for Thompson Island Pool). The vertical resolution of these data (0-5 cm surface layers) permits direct comparison with HUDTOX results for the top two sediment layers in the model. Other sediment data were also collected by USEPA and NYSDEC, but these data did not resolve the 0-5 cm surface layer. As a result, model comparisons to sediment data collected by NYSDEC in 1984 (average depth of approximately 25 cm, TIP only) and by USEPA in 1994 (average depth of approximately 23 cm) are displayed as concentrations averaged over deeper layers.

Computed and observed concentrations in each reach are expressed in terms of area-weighted averages for cohesive and non-cohesive sediments. Data are presented as mean values plus and minus two standard errors (2 SE) which corresponds to the 95 percent confidence interval about the mean. The model trajectories in Figures 7-15a through 7-15e represent Tri+ concentrations for the surface layer. Symbols denote model output averaged over layers corresponding to the average depths of the 1984 and 1994 data.

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Model results show very good agreement between computed and observed surface sediment Tri+ concentrations in TIP for both cohesive and non-cohesive sediment areas (Figure 7-15a). Computed concentrations in surface sediments decline by 89 and 80 percent, respectively, in these sediment areas over the historical period from 1977 to 1997. These declines correspond to annual first-order loss rates of approximately 11 and 8 percent, respectively. Declines in surface sediment Tri+ concentrations occur due to burial to deeper sediment layers and sediment-water transfer processes. Agreement with depth-averaged concentrations in 1984 and 1994 is also good, although the vertical scales are coarse and data variability is high. This suggests that the model is accurately accounting for changes in the Tri+ mass reservoir in the sediments of Thompson Island Pool.

There is also generally good agreement between computed and observed surface sediment Tri+ concentrations and deeper concentrations below Thompson Island Dam (Figures 7-15b through 7-15e). A notable exception is for non-cohesive sediments in the Schuylerville reach in 1991 (Figure 7-15b) where data are higher than the model. It is speculated that either the sampling and/or compositing processes used for these data may have incorporated high measured concentrations that were not representative of reach-average conditions. The 1991 non-cohesive sediment data for this reach appear unrepresentative when compared to the 1994 data and the overall declining trend observed at other locations in the river. Hence this discrepancy was viewed as a likely data anomaly and not a model deficiency.

Computed concentrations in surface sediments in reaches downstream of Thompson Island Pool decline by 91 to 97 percent in cohesive sediment areas and by 82 to 93 percent in non-cohesive sediment areas. These declines correspond to annual first-order loss rates of 11 to 14 percent in cohesive sediment areas and 8 to 12 percent in non-cohesive sediment areas.

7.4.2.2 Longitudinal and Vertical Sediment Profiles

Another way to compare computed and observed sediment concentrations is to assess results at smaller spatial scales along the longitudinal axis of the river and in the vertical. Figure 7-16 contains comparisons of computed and observed depth-averaged (0 to 25 cm) Tri+ concentrations for 1984 in Thompson Island Pool in the longitudinal direction. Because the HUDTOX model represents three lateral spatial segments in Thompson Island Pool, multiple results for computed and observed values are shown at some locations. The model captures changes in Tri+ concentrations at depth along the length of TIP in both cohesive and non-cohesive sediments. This demonstrates that model is representing the approximate magnitude of changes in the sediment Tri+ mass reservoir in TIP.

Figures 7-17 through 7-19 contain comparisons of computed and observed depth-averaged Tri+ concentrations in 1991 (0 to 5 cm, 5 to 10 cm and 10 to 23 cm) from Fort Edward to Federal Dam. The two upper reaches (Thompson Island Pool and Schuylerville) between river miles 193 and 183 are more heavily contaminated than the three lower reaches (Stillwater, Waterford and Federal Dam) between river miles 183 and 153. Computed values cluster well around most of the data values for the 0-5 cm layer in both the upper and lower reaches. Model results are generally good for the 5-10 cm layer with the exception of a high bias (approximately a factor of two) in the very lower reaches between river miles 163 and 153. Model results are not as good for the 10-26 cm layer, especially in the lower reaches. Results for this layer reflect the fact that grab samples do not represent this depth interval and hence there are fewer data with which to estimate reach-average concentrations.

7.4.2.3 Water Column Tri+ Concentrations

Figure 7-20 (a and b) shows comparisons between computed and observed Tri+ concentrations in the water column at Thompson Island Dam, Schuylerville, Stillwater and Waterford for the full historical period from 1977 to 1997. Figure 7-20c shows an expanded view of results at Thompson Island Dam where flows, solids and Tri+ can all be balanced with the most confidence. Again, results at Fort Edward represent Tri+ loading inputs at the upstream boundary and are shown only as a reference. Note that Tri+ detect limits changed in the mid 1980s, showing an apparent sudden drop in minimum concentrations in the river. Comparisons between computed and observed results are confounded by inconsistent temporal coverage among stations, changes in detection limits, datasets acquired by different organizations, a bias-correction applied to data from the west shore of Thompson Island Dam, and revised estimates of Tri+ concentrations applied to post-1986 USGS data. These factors are discussed in detail in Chapter 6.

Long-term declining trends in observed Tri+ concentrations are captured by the model. Magnitudes and seasonal trends at Thompson Island Dam are well represented by the model, however, data are available only between 1991 and 1997. In general, model results tend to be higher than observations during the mid-1980s at Schuylerville, Stillwater and Waterford, and again during the mid-1990s at Stillwater and Waterford. There appears to be better agreement between computed and observed values for the GE data, especially at Thompson Island Dam from 1991 to 1997 and at Schuylerville for 1991 and 1992.

Achieving consistency between computed and observed values at Thompson Island Dam and downstream locations was a particular concern of the calibration, as the model was often higher than the USGS data at Stillwater and Waterford. Sensitivity analyses on volatilization, sediment-water mass transfer rates and gross settling velocities did not achieve sufficient reductions in water column Tri+ concentrations. Increasing settling velocity and decreasing sediment-water mass transfer rates resulted in over-estimating surface sediment Tri+ concentrations.

This prompted consideration of potential differences between USGS and GE datasets for Tri+. Potential bias between the USGS and GE data could perhaps explain why the model is well calibrated to GE data at Thompson Island Dam, but over-estimating relative to USGS data downstream. Figure 7-21 shows same-day comparisons between USGS and GE data for Tri+ at Fort Edward, Stillwater and Waterford. These results suggest that the GE measurements may be biased high relative to the USGS measurements; however, these results are not conclusive.

7.4.2.4 High and Low-flow Tri+ Loads

The ability of the model to distinguish between low and high flow contributions to overall Tri+ mass transport was assessed in similar manner as done in the solids calibration. Results of comparisons for model-estimated and data-estimated in-river Tri+ loads at Thompson Island

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Dam, Schuylerville, Stillwater and Waterford are contained in Figure 7-22. The cumulative Tri+ load estimates are provided, although these estimates are uncertain due to data limitations. Perhaps of more interest is the relative contributions of low and high flow to overall transport, shown in the bottom panel of the figure. Note that data for Thompson Island Dam are limited to the period from 1991 to 1997 and that there are no data for Schuylerville after 1993 (see Figure 7-20a). Consequently, the Tri+ mass loads in the top panel of Figure 7-30 correspond to 1991-1997 for Thompson Island Dam, 1977-1992 for Schuylerville and 1977-1997 for Stillwater and Waterford.

Results show that the model accurately computes the relative high and low flow Tri+ loads at all locations, and in addition shows good agreement with the estimated cumulative loadings. The maximum difference in fractional distribution of Tri+ load between high and low flow strata is less than seven percent in all cases. It is of interest to note that 70 to 80 percent of in-river Tri+ loads at TID and 60 to 70 percent of Tri+ loads below TIP occur during low flow conditions. This is in contrast to in-river solids loads which are split almost equally between high and low flow conditions (Figure 7-2).

Model performance is also illustrated through comparisons of computed and observed values over the course of several high flow events. Although the model was not developed specifically as an event scale model, it does include cohesive resuspension formulations based on site-specific measurements of resuspension behavior (See Chapters 4 and 5). Resuspension of cohesive sediment has higher potential to impact water column concentrations because of the much higher Tri+ concentrations relative to non-cohesive sediments. The ability of the model to represent water column Tri+ concentrations over high-flow events is observed by inspection of results for spring high flow periods during 1983, 1993, 1994 and 1997 (Figures 7-23 through 7-26). These results for Tri+ correspond to the results for solids concentrations in Figures 7-4 through 7-7.

It is more difficult to compare computed and observed Tri+ concentrations during high flow periods than solids concentrations because no high-frequency sampling was conducted for Tri+ concentrations during high flows. Nonetheless, results show that the model does generally represent the temporal event-scale variability shown in the Tri+ concentration data. Both model and data exhibit nearly order-of-magnitude increases in water column concentrations in response to flow impacts.

7.4.2.5 Further Model-Data Comparisons

As was done for the solids calibration, scatter plots and cumulative probability distributions are presented to provide insights into model behavior and the limits of model capability. Again it should be recognized that the model calibration approach was not aimed at describing the full range of observed event-scale behavior. The Tri+ calibration sought to describe long-term Tri+ concentrations in surface sediments and mean low and high flow behavior in the water column. Considering this, model agreement with mean or median concentration results is of more interest than a good fit across the range of observed behavior. Given the high variability in measured Tri+ concentrations, even within a given year, comparison of computed and observed values on a point-by-point basis is of marginal value in assessing the calibration. A number of other factors also preclude use of such comparisons in assessing model accuracy, including changes in analytical methods and detection limits, a bias-correction applied to data from the west shore of Thompson Island Dam, and revised estimates of Tri+ concentrations applied to post-1986 USGS data. These factors are discussed in detail in Chapter 6.

Comparisons between computed and observed Tri+ concentrations using scatter plots stratified by river flow are shown in Figures 7-27 and 7-28. The model and data mean values are shown on these figures by the horizontal and vertical crossed lines, as is the 1:1 correspondence line. A river flow of 10,000 cfs at Fort Edward is used to represent the cutpoint between low and high flow, with the rationale explained in the previous section. Results are good at Thompson Island Dam, showing reasonable agreement between model and data mean values, and close correspondence across the range of observed values. A similar behavior as for solids was observed for the Tri+ concentration scatter plots at Schuylerville, Stillwater and Waterford. This is due in small part to the solids calibration approach, however, these results are also affected by the above-mentioned high bias in the calibration results compared to measured Tri+ concentrations downstream of Thompson Island Dam.

Comparisons between computed and observed probability distributions for Tri+ concentrations over the entire calibration period stratified by river flow (Figures 7-29 and 7-30) show similar results as the scatter plots, but are also affected by the complicating factors mentioned above. At Thompson Island Dam, the model computes observed PCB concentrations with good accuracy over the full range of observed concentrations. Similar to observations from the time series results and scatter plots, results for Stillwater and Waterford also indicate that the model is weaker at Stillwater and Waterford.

7.4.3 Components Analysis for Tri+

A Tri+ mass balance components analysis from the calibrated model is shown in Figure 7-31 for the four major reaches in the Upper Hudson River. These are the same four reaches for which the solids mass balance components analysis was conducted (Figure 7-14). Over the 21-year historical period there is a computed Tri+ net load gain to the water column of 9,141 kg (39 percent) between Fort Edward and Waterford. Most of this load gain (74 percent) occurs in the first two reaches, TIP and Schuylerville.

Contributions to Tri+ load gain are dominated by non-flow-dependent sediment-water mass transfer. Computed total inputs of Tri+ to the water column from 1977 to 1997 were 26,597 kilograms. External loads (99 percent from Fort Edward) contributed 6,657 kg (25 percent), flow-dependent sediment resuspension contributed 6,722 kg (25 percent) and non-flow-dependent sediment-water mass transfer contributed 13,218 kg (50 percent) of the Tri+ inputs between Fort Edward and Waterford. Total losses of Tri+ from the water column were 10,759 kg. These losses consisted of 9,496 kg (88 percent) from gross settling and 1,263 kg (12 percent) from volatilization.

It is noteworthy that 75 percent of computed Tri+ inputs to the water column are due to internal sources and not external loads. This is in sharp contrast to results for solids in which approximately 80 percent of computed sources to the water column was due to external loads.

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Results from Tri+ mass balances conducted separately for high and low flows indicate that internal sources are responsible for at least 70 percent of computed inputs to the water column. The principal difference between low and high flow Tri+ mass balances is the relative importance of non-flow-dependent sediment-water mass transfer versus flow-driven resuspension. At low flow, non-flow-dependent sediment-water mass transfer is responsible for 61 percent of computed Tri+ inputs to the water column and flow-dependent resuspension is responsible for 14 percent. At high flow, this relationship is reversed and the computed contributions are 12 percent and 60 percent, respectively.

Computed cumulative Tri+ mass load gains between mainstem stations from 1991 to 1997 are shown in Figure 7-32. This period represents recent historical conditions and conditions in the river for the early portion of the forecast simulations for No Action. Gains in Tri+ mass are computed between all four mainstem stations. During 1992 and 1993, load gains are reduced in the two upper reaches due to large increases in upstream Tri+ loads from failure of the Allen Mill gate structure in September 1991. In the lower two reaches Tri+ mass is lost from the water column during 1992 and 1993. After 1993, upstream Tri+ loads decline and the influence of sediment-water mass transfer begins to control Tri+ mass load gains between stations. These load gains appear to increase with time as upstream Tri+ loads continue to decline through the mid-1990s.

7.4.4 Comparison to Low Resolution Sediment Coring Report (LRC) Results

As part of the Reassessment, USEPA (1998a) conducted an investigation of the change in sediment PCB inventories in Thompson Island Pool between 1984 and 1994. This investigation involved a comparison of results from the extensive 1984 NYSDEC survey with results from a series of matched sediment cores collected by USEPA in 1994. Inventories from a set of 60 sampling locations in Thompson Island Pool were compared on a point-to-point basis to provide a quantitative indication of the direction and magnitude of change in the sediment PCB inventory. This analysis was subsequently revised to include comparisons based on localized sediment areas as opposed to point-to-point comparisons (USEPA, 1999a and b). Results from the revised analysis indicated that the best unbiased mean estimate of mass loss of Tri+ from the sediments within historic hotspot areas was 45 percent, with an uncertainty range from 4 to 59 percent. It was estimated that dechlorination was responsible for approximately 5 percent of the mean mass loss. The remaining loss was interpreted as a loss of the Tri+ hotspot inventory either to the overlying water column or through redistribution of contaminated sediments within TIP. Another conclusion from this LRC analysis was that there was no evidence of extensive widespread burial of historically contaminated sediments in the Pool.

Although HUDTOX and LRC findings are in general agreement, a direct comparison of results is not possible due to the different assumptions and spatial scales between these two approaches. The LRC analysis included only cohesive sediment areas that were historically known to be more contaminated than average Thompson Island Pool sediments, whereas the HUDTOX model includes both cohesive and non-cohesive sediment areas over the full range of sediment inventories estimated to reside in the Pool. The LRC analysis does not account for Tri+ mass loss that would be transported downstream of Thompson Island Pool or redeposited in non-cohesive sediment areas, or in less contaminated cohesive sediment areas. The HUDTOX model accounts for the full mass balance cycle including transport and fate downstream of Thompson Island Pool, and redeposition in the Pool.

An approximate comparison of results suggests consistency among the HUDTOX, DEIR and LRC analyses. A components analysis of the Tri+ historical calibration indicated that 1,288 kg of Tri+ was lost from the Thompson Island Pool sediment inventory between 1984 and 1994. Most of this loss was due to Tri+ mass transport across Thompson Island Dam and a small portion was due to volatilization. If the Tri+ inventory in 1984 is taken to be approximately 14,500 kg (USEPA, 1997), then this mass loss out of the pool corresponds to approximately 9 percent. This value is within the range of the 4 to 59 percent estimate of mass loss from historical hotspots in the LRC analysis. As an independent check on both of these approaches, the annual rate of net export of Tri+ from the Pool was estimated to range between 0.36 and 0.82 kg/day over the period April 1991 to October 1995 (USEPA, 1997). Assuming a value of 0.59 kg/day, the net export of Tri+ from the Pool sediments between 1984 and 1994 would be 2,153 kg which corresponds to a mass loss of 15 percent of the 1984 inventory. Because of its focus on hotspots, the LRC does not distinguish between loss over Thompson Island Dam and redistribution to less contaminated areas within the pool. When coupled with the LRC findings, HUDTOX and the DEIR also suggest that there has also been a significant amount of redistribution of Tri+ mass within Thompson Island Pool from historical hotspots.

With respect to lack of extensive widespread burial of historically contaminated sediments in TIP, the HUDTOX model results are again consistent with results from the LRC analysis. Results in Figure 7-12 indicate that the increase in sediment bed elevation in Thompson Island Pool between 1984 and 1994 computed by the HUDTOX model is approximately 2.0 cm. This is a poolwide result and it should be understood that there are differences between cohesive and non-cohesive sediment areas within the Pool (Figure 7-13). From results in Figure 7-1 the computed increase in bed elevation for cohesive sediments in Thompson Island Pool over 10 years is approximately 6.5 centimeters. Furthermore, it should be understood that in the actual river there is variability within the individual model spatial segments and that certain areas can be erosional and not depositional. Nonetheless, a net sedimentation rate of 6.5 cm over 10 years is small compared to the surface layer depth of 23 cm (9 in) in the LRC sediment cores. Considering the differences in spatial and temporal scales of the two approaches, it can be concluded that the HUDTOX model and the LRC are in qualitative agreement with respect to the question of widespread burial of historically contaminated sediments in Thompson Island Pool.

7.4.5 Tri+ Calibration Summary

Summarizing to this point, the calibration approach for Tri+ in the historical calibration consisted of adjusting only four model parameters: gross settling velocities into cohesive and non-cohesive sediment areas; resuspension rates from non-cohesive sediment areas; depth of particle mixing in the sediment bed; and, magnitude of sediment particle mixing.

Computed Tri+ concentrations in surface sediments declined by 89 and 80 percent, respectively, in the cohesive and non-cohesive sediment areas of Thompson Island Pool between 1977 and 1997. These declines correspond to annual first-order loss rates of approximately 11 and 8 percent, respectively. Computed surface sediment concentrations in reaches downstream of

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Thompson Island Pool decline by 91 to 97 percent in cohesive sediment areas and by 82 to 93 percent in non-cohesive sediment areas over this period. These declines correspond to annual first-order loss rates of 11 to 14 percent in cohesive sediment areas and 8 to 12 percent in non-cohesive sediment areas. Declines in surface sediment Tri+ concentrations occur due to burial to deeper sediment layers and sediment-water transfer processes.

Computed results indicate that 70 to 80 percent of in-river Tri+ loads at Thompson Island Dam and 60 to 70 percent of in-river Tri+ loads below TIP occur during low flow conditions. This is in contrast to in-river solids loads which are split almost equally between low and high flow conditions. This finding supports the calibration strategy of focusing on long-term average behavior and not on short-term dynamics associated with high flow events.

There is a computed Tri+ net load gain to the water column of 139 percent between Fort Edward and Waterford between 1977 and 1997. Most of this load gain occurs in the Thompson Island Pool and Schuylerville reaches. Contributions to Tri+ load gain are dominated by non-flow-dependent sediment-water mass transfer. Computed external loads (99 percent from Fort Edward), flow-dependent sediment resuspension, and non-flow-dependent sediment-water mass transfer contribute 25, 25 and 50 percent, respectively, to total Tri+ inputs to the water column. Gross settling and volatilization accounted for 88 and 12 percent, respectively, of the total computed losses from the water column. It is noteworthy that 75 percent of computed Tri+ inputs to the water column are due to internal sources and not external loads. This is in sharp contrast to results for solids in which 80 percent of computed sources to the water column was due to external loads.

7.5 Sensitivity Analyses

Sensitivity analyses were conducted with the calibrated HUDTOX model to evaluate model responses due to uncertainties in important model inputs and calibration parameters. The analysis elucidates model behavior and identifies parameters which are important in determining Tri+ exposure concentrations. The approach was to change a particular model input or calibration parameter, and then re-run the model for the 21-year historical calibration period. Results were evaluated in terms of changes in long-term Tri+ concentrations in surface sediments and the water column, relative to base calibration values, and changes in Tri+ mass loadings at mainstem stations and Federal Dam. The sensitivity analyses were designed to assess perturbations to the base calibration and they do not represent attempts to re-calibrate the model with different model inputs or calibration parameters.

Sensitivity analyses were conducted for the following model inputs and calibration parameters:

- Solids loads at Fort Edward and tributary solids loads;
- Tri + partition coefficients;
- Tri+ sediment-water mass transfer coefficients;

- Solids burial rates via variation of gross settling velocity in cohesive sediment areas;
- Particle mixing in sediments;
- Sediment initial conditions for Tri+; and,
- Henry's Law Constant affecting volatilization of Tri+.

Table 7-5 contains an inventory of all sensitivity analyses conducted, and results for Tri+ mass loads at mainstem stations and Federal Dam.

Model calibration results are sensitive to uncertainties in sediment particle mixing depth in non-cohesive sediments, Tri+ partitioning, solids burial rates, non-flow-dependent sediment-water mass transfer rates, tributary solids loads and sediment initial conditions. The calibration was not especially sensitive to differences in solids loadings at Fort Edward computed by time-stratified versus non-time-stratified loading methods, or to changes in Henry's Law Constant.

7.5.1 Solids loadings

During calibration of the HUDTOX model a key forcing function driving Tri+ exposure concentrations was external solids loads to the system. Hence, upstream solids loads at Fort Edward and the tributary solids loads were varied separately and results discussed below.

7.5.1.1 Solids loads at Fort Edward

Solids loadings at the upstream boundary at Fort Edward were developed in Section 6.5. A time-stratified regression approach was used to develop these loadings for the model calibration because a significant difference in solids-flow relationships was observed pre- and post-1990. A sensitivity analysis was conducted for solids loadings at Fort Edward that was determined using a non-time-stratified regression approach. Both of these approaches were conducted using the same solids concentration and flow data. Although the two approaches used the same data, they produced solids loadings that were distributed differently in time. The non-stratified approach produced solids loadings that were lower than the stratified approach early in the historical period (1977 to 1990) but higher in the latter part of the period (1990 to 1997).

Results in Figures 7-33 and 7-34 indicate that sediments are responsive only in TIP and not at Waterford, and that only the trajectory in the cohesive sediment area of TIP is responsive. Two reasons for these results are that solids burial rates in cohesive sediment areas are higher than those in non-cohesive areas, and that most of the solids loadings downstream of TIP are from tributaries and not Fort Edward. The response of cohesive sediments in TIP is consistent with the lower solids loadings produced by the non-stratified approach early in the historical calibration period. With increasing time, the two trajectories converge and arrive at approximately the same Tri+ concentrations at the end of the calibration period. Water column concentrations were not sensitive to changes in solids loadings due to application of the non-stratified regression approach and graphical results are not shown. Results in Table 7-5 indicate that changes in-river Tri+ loadings and loadings over Federal Dam are small (approximately 3 percent).

7.5.1.2 External Tributary Solids Loads

Approximately 80 percent of the solids loadings to the Upper Hudson River between Fort Edward and Federal Dam are delivered by tributaries. To assess the sensitivity of model calibration these external solids loads were incremented and decremented by 50 percent and compared to the base calibration. Figures 7-35 and 7-36 show the results of this analysis for surface sediment Tri+ concentrations in Thompson Island Pool and the reach from Schuylerville to Waterford. Results in TIP are not particularly sensitive to changes in tributary solids loads because the loadings at Fort Edward are the principal loads for that reach (see section 7.5.1.1).

The results downstream of TIP however, show a significant sensitivity to these load changes. Concentrations in cohesive areas show widely different sediment trajectories throughout the simulation period. Due to lower net settling velocities in the non-cohesive areas the trajectories are not far apart in the earlier part of the historical simulation. However, for the case where tributary loads were 50 percent smaller several segments in the non-cohesive areas become net erosional and consequently expose buried Tri+ concentrations in the latter part of the simulation. This behavior also occurs in the forecast simulations (run with base tributary loads) and is discussed at length in Chapter 8. Figure 7-37 shows the water column Tri+ concentrations at Thompson Island Dam and at Waterford for these sensitivity runs. As expected, concentrations at TID are insensitive to changes in tributary solids. Concentrations at Waterford are much higher when tributary loads are reduced by 50 percent and slightly lower when the loads are increased by 50 percent.

7.5.1.3 Tributary Solids Loads Based on the Original Rating Curves

The details of the methods and data used to compute the external solids loads to the system are discussed in detail in Chapter 6 of this report. Since the original rating curves for the tributary solids loads were adjusted to determine the final calibration tributary loads a sensitivity analysis was conducted with the original unadjusted rating curves. Figure 7-38 and 7-39 show the results for this sensitivity run compared with base calibration results. Again results in TIP are insensitive to changes in tributary solids loads. Downstream of TID in general higher sediment Tri+ concentrations would be observed if the original rating curves were employed. In particular note that several non-cohesive segments tend to be erosional and expose buried Tri+ concentrations for this sensitivity run. The resultant Tri+ concentrations in the non-cohesive areas are inconsistent with the observed concentrations. Figure 7-40 shows that the water column concentrations are also significantly higher downstream of TIP.

7.5.2 Partition Coefficients

A value of log K_{POC} = 5.845 was used as the partition coefficient for Tri+ in the historical calibration (Table 7-4). An analysis by Butcher et al. (1998b) indicated that the range of observed partition coefficients in the Upper Hudson River was approximately 5.4 to 6.6. Sensitivity analyses were conducted using these two values of log K_{POC} for Tri+.

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Results in Figures 7-41 and 7-42 indicate that sediment response trajectories are very sensitive to these variations in partitioning. The response trajectories for both of these variations violate the principal sediment calibration constraints (reach average cohesive and non-cohesive Tri+ concentrations in 1991 and 1998) in TIP for cohesive and non-cohesive sediments. Response trajectories at Waterford for higher partitioning are in better agreement with observations than base calibration results. Water column concentrations (Figure 7-43) are also sensitive, however, the sensitivity of these responses declines with time.

Sediment water exchange processes in the model were parameterized as a mass transfer rate from the dissolved and DOC phases in the sediment porewater. Thus, any changes to the partition coefficient directly changes the porewater concentrations and thus affects the flux out of the sediments. In addition, the larger the concentration, the greater the proportional flux out of the sediments. Hence, for example the behavior observed in Figure 7-43. In the early part of the historical simulation for the case of the lowered partition coefficients, the flux out of the sediments is very large and results in water column exposure much greater than the base case. However, this large flux depletes surficial sediment reservoirs and in the latter part of the historical simulation the concentrations are closer to the base case (and in some locations even smaller). For the higher partition coefficient the reverse is true. Hence, Figure 7-43 shows the sensitivity results crossing each other in the water column.

It is noted here that the empirically determined mass transfer coefficient was dependent on the choice of the partition coefficient. A change in the partition coefficient would necessitate re-computation of this parameter to achieve the same net flux out of the sediments. Hence, though the numerical value of the mass transfer parameter is dependent on the choice of the partition coefficient, the base calibration result in TIP would not be any different were a different value of the partition coefficient utilized.

7.5.3 Sediment-Water Mass Transfer Rates

To assess the sensitivity of historical calibration results to this important mechanism two approaches were undertaken: first, variation of the seasonally dependent rate between upper and lower bounds; and second, specification of different rates between the cohesive and non-cohesive sediment areas.

7.5.3.1 Variation of Sediment-water Transfer Rate

Figure 7-44 contains the time series used in the model calibration for non-flow-dependent sediment-water mass transfer rates. This time series was determined using data-based, site-specific mass balances (Section 6.13) and was not adjusted during the model calibration. The estimated range of uncertainty in this time series is shown in Figure 7-44 and corresponds to approximately plus and minus 50 percent. Sensitivity analyses were conducted for this range of values about the base time series.

Results in Figures 7-45 and 7-46 indicate that sediment responses are sensitive to these variations in sediment-water mass transfer. The Tri+ surface sediment responses violate the principal calibration constraints in non-cohesive sediments in TIP, and remain within approximately two

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standard errors of the constraints in the cohesive sediments. The response trajectory for non-cohesive sediments at Waterford for the lower sediment-water mass transfer rate is in better agreement with observations than base calibration results. Water column concentrations (Figure 7-47) are also sensitive, however, the sensitivity of these responses declines with time. Results in Table 7-5 indicate that in-river Tri+ mass loadings and loadings over Federal Dam are sensitive to changes in sediment-water mass transfer. Loadings over Federal Dam change by approximately 10 percent in response to variations in sediment-water mass transfer rates.

The data to determine the mass transfer rates is confined primarily to TIP. It is uncertain if the same rates are operative throughout the Upper Hudson River. Thus, water column exposure concentrations downstream of TID and the export of PCBs over Federal Dam to the Lower Hudson River contain uncertainties due to this assumption in the historical calibration.

7.5.3.2 Differences in Sediment Water Transfer between Cohesive and Non-Cohesive Areas

The base HUDTOX model calibration assumes that the sediment-water exchange processes are identical for cohesive and non-cohesive sediment areas. Even though the exact mechanisms which govern these processes are unclear, a hypothesis with some merit is to consider the possibility of higher exchange in cohesive sediment areas as compared to the non-cohesive sediment areas. The reasons are discussed in Chapter 6 and include, for example the observation of greater benthic activity and mixing in cohesive areas as compared to non-cohesive areas.

A sensitivity run was conducted by assuming that the mass transfer rate is twice as large in the cohesive sediment areas as compared to the non-cohesive sediment areas. However, the overall net flux from the entire sediment bed was constrained as previously by the data-based Tri+ mass balance. The results are shown in Figures 7-48 and 7-49 and are compared to the base model calibration. As expected the surface sediment Tri+ trajectories are shifted below the base case in the cohesive areas and shifted higher in the non-cohesive areas. Thus, if this hypothesis were to be incorporated into the model calibration it would require revisions to the base model parameter choices. Water column results as expected show no effect since the same net flux out of the sediments was maintained.

7.5.4 Burial Rates in Cohesive Sediments

The gross settling velocity into cohesive sediments in the model calibration was 4.15 m/day (Table 7-1). This parameter was adjusted during the model calibration and its value was determined by the principal calibration constraints. Sensitivity analyses were conducted in which gross settling velocity was varied so as to produce plus and minus 50 percent changes in solids burial rates in TIP cohesive sediment areas. Although these sensitivity analyses were conducted by varying gross settling velocity, the effect of this variation is the same as if external solids loadings were varied. The reason is that there is a direct relationship between external solids loadings and solids burial rates in the river.

Results in Figures 7-50 and 7-51 show responses of solids burial rates to the sensitivity analyses conducted. Although only the gross settling rate into cohesive sediment areas was varied, burial

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rates respond in both cohesive and non-cohesive areas because solids are redistributed due to the dynamics of settling and resuspension. Solids burial rates respond in opposite directions, increasing in cohesive sediment areas and decreasing in non-cohesive sediment areas because external solids loadings were not changed.

Results in Figures 7-52 and 7-53 indicate that sediment Tri+ trajectories are sensitive to these variations in solids burial rates. The principal model calibration constraints are violated in the cohesive sediment areas of TIP, however, responses for lower settling velocities are in better agreement with observations in cohesive sediments at Waterford than in the base calibration. Water column concentrations are more responsive at Waterford than in TIP (Figure 7-54). Results in Table 7-5 indicate that in-river Tri+ mass loadings and loadings over Federal Dam are sensitive to changes in solids burial rates. Loadings over Federal Dam change by approximately 10 to 15 percent in response to these variations in solids burial rates.

7.5.5 Particle Mixing in Sediments

Sediment particle mixing in the model was determined on the basis of observed sediment core depth profiles, judgments on distributions of biological activity and model calibration to long-term Tri+ concentration trajectories in the sediments. Table 7-1 presents model calibration values for particle mixing depths and mixing rates. Particle mixing depths were 10 cm in cohesive sediments in all reaches, 6 cm in the non-cohesive sediments in TIP and 4 cm in the non-cohesive sediments downstream of TID. The most uncertain of these values is mixing depth in non-cohesive sediment areas in reaches downstream of TID. Some reaches achieved calibration constraints better with 4 cm depth of mixing while other areas were better at 6 cm depth of mixing. To avoid use of differing parameters in the calibration the choice of 4 cm was selected for all reaches downstream of TID. This sensitivity analysis presents results for the case of non-cohesive sediments mixed to a depth of 6 cm for all reaches downstream of TID.

Results in Figures 7-55 through 7-58 indicate that sediment trajectories are sensitive to these changes. The deeper mixing depths and higher mixing rates contribute additional Tri+ mass to the surficial sediment layer by upward mixing from deeper contaminated layers. Modeled historical trajectories are more consistent with this choice of mixing depth in the reaches at Stillwater and Waterford. The calibration choice of 4 cm yields better results than a mixing depth of 6 cm in the non-cohesive sediments in the Federal Dam reach. Based on this sensitivity analysis a choice of 6 cm mixing in the non-cohesive sediments downstream of TID appears reasonable and may represent an alternate choice for the historical calibration.

7.5.6 Sediment Initial Conditions

There is large uncertainty in the 1977 data used to specify sediment initial concentrations for Tri+ in the historical calibration. Figure 6-32, 6-33, and 6-34 show the variability in the available historical data for 1977. In many locations concentrations measured in 1977 can vary by an order of magnitude or more. Hence, sensitivity analyses were conducted for variations of plus and minus one standard error about mean values for Tri+ concentrations in cohesive and non-cohesive surface sediments in the 1977 data.

Results in Figures 7-59 and 7-60 indicate that sediment trajectories are sensitive to these variations in initial conditions, especially early in the historical calibration period. With increasing time the sensitivity response trajectories converge closely to the base model calibration trajectories. At the end of the calibration period, differences are small between the sensitivity results and the base calibration. Both sensitivity trajectories agree reasonably well with the model calibration targets in 1998 in TIP. Water column responses (Figure 7-61) follow the same trends as sediment responses. Results in Table 7-5 indicate that in-river Tri+ mass loadings and loadings over Federal Dam are sensitive to changes in initial conditions. Loadings over Federal Dam change by approximately 20 percent in response to variations in sediment initial conditions.

7.5.7 Henry's Law Constant

Among the parameters which affect volatilization of Tri+ there is some uncertainty associated with the choice if the Henry's Law constant. The historical calibration used a value of 1.69E-04 atm m^3/mole. A sensitivity analysis was conducted to assess the sensitivity of the model to choices of 1.93E-04 and 0.68E-04 atm m^3/mole. This range was established based on published literature. Water column results at Thompson Island Dam and at Waterford are shown in Figure 7-62. Results show that the modeled exposure concentrations are insensitive to the choice of this parameter.

7.6 1991-1997 HINDCAST APPLICATIONS

7.6.1 Overview

Following successful calibration of the HUDTOX model to Tri+ over the 21-year historical calibration period, the model calibration was tested with short-term hindcast applications for the period 1991 to 1997 to five congeners and total PCB. The five congeners chosen for these applications (BZ#4, BZ#28, BZ#52, BZ#[90+101] and BZ#138) have different physical-chemical properties, spanning a wide range of partitioning and volatilization behavior. The primary objective of the individual congener applications was to strengthen and support the long-term Tri+ historical calibration, and thereby, the use of the model in addressing the principal questions of the Reassessment.

The differences in environmental behavior among the five congeners provides an opportunity to test the rigor of the Tri+ calibration, especially sediment-water and air-water exchange processes. For example, model results for a highly volatile congener may be more sensitive to errors in sediment-water exchange than a less volatile, strongly partitioning congener. Conversely, model results for a strongly partitioning congener may be more sensitive to errors in particle-based PCB processes such as settling and resuspension than a weaker partitioning congener.

Overall, the short-term hindcast applications to congeners demonstrate that the Tri+ historical calibration is technically sound and appropriate for use in the Reassessment. The Tri+ historical calibration was confirmed in that the two congeners whose physical-chemical properties most closely resemble Tri+ (BZ#28 and BZ#52) were accurately represented using the same model parameters as the Tri+ historical calibration. While changes to the model (discussed below) may permit better simultaneous representation of all five PCB congeners, these changes do not enhance model performance for Tri+. Therefore, the Tri+ historical calibration was judged technically sound based on the calibration results presented above and on the confirmatory results presented below for BZ#28 and BZ#52.

7.6.2 Approach

The approach to the congener hindcast applications was to use the same flow and solids mass balances as in the Tri+ historical calibration, along with input loads for total PCBs and the individual congeners. Total PCB and congener loads were developed in Chapter 6, in addition to sediment initial conditions based on the 1991 GE composite data. All of the same model parameters used for the Tri+ historical calibration were used initially for the total PCB and congener applications, with the exception of those that were chemical-specific. These chemical-specific parameters include only Henry's Law constant, molecular weight and partition coefficients (Table 7-4). Partition coefficients for total PCBs and the five congeners were developed in Section 6.9.

Initial 1991 to 1997 results showed that the empirical sediment-water mass transfer coefficient developed for Tri+ (Chapter 6) was not applicable to BZ#4. The Tri+ sediment-water mass transfer coefficient produced unreasonably high sediment-water transfer of BZ#4. An analysis of apparent sediment-water mass transfer rates for all congeners revealed large differences, seemingly related to differences in sediment-water partitioning. This led to estimation of separate particle-based and porewater sediment-water mass transfer coefficients, which allowed a reasonable simultaneous representation of sediment-water mass transfer for all congeners. Details of the development of these coefficients is presented in Chapter 6.

7.6.3 Results

Model testing through the short-term hindcast applications was accomplished by comparison of computed congener and total PCB concentrations to water column observations. As discussed above, initial simulations used the same empirical sediment-water mass transfer coefficient developed for Tri+ (Chapter 6). Results of these initial simulations, shown for BZ#4, BZ#28, and BZ#52 from 1991 to 1992 at Thompson Island Dam, revealed that while the model performed well for BZ#28 and BZ#52, the BZ#4 sediment-water mass transfer was too high (Figure 7-63). Water column BZ#4 concentrations were significantly higher than the data for the first two years of the forecast. This is due to rapid loss of BZ#4 from the sediments, evidenced by a comparison of the BZ#4, BZ#28, and BZ#52 sediment concentration trends for these three congeners (Figure 7-64).

To determine whether potential differences between measured water column and sediment partition coefficients was contributing to the over-prediction of BZ#4, simulations using partition coefficients from the 1991 sediment data were conducted. Sediment partition coefficients were used as computed from the GE 1991 sediment core composite data (USEPA, 1997), however, they were considered less reliable than the estimates from the Phase 2 water column data. This is because the GE 1991 samples were frozen and composited prior to analysis, likely altering PCBs in porewater measurements. Results showed that use of the sediment partition coefficients mav

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improve model fit to BZ#4. This indicated sediment-water transfer for this congener is over-computed using the Tri+ mass transfer coefficient.

This led to incorporation of the separate particle and porewater-based sediment-water mass transfer coefficients, as described in Chapter 6, which generally improved model for BZ#4 and total PCB while also showing reasonable results for the other congeners. Results are demonstrated several ways:

- Model versus data concentration time series at several locations for 1992 to 1997;
- Comparison to congener concentrations and congener ratios to BZ#52 in the GE 1996 and 1997 float study surveys which measured down-river profiles in Thompson Island Pool; and,
- Comparison of down-river congener ratios to BZ#52 from Fort Edward to Waterford.

These are each discussed below.

Computed water column concentrations for each congener are compared to observations at Thompson Island Dam for the period 1991 through 1997 (Figure 7-66). Results are shown in Figure 7-67 (a to f) for Schuylerville, Stillwater and Waterford for the period 1991 through 1993. Very little data are available below Thompson Island Dam after 1993. The model shows very good comparison to observed concentrations of BZ#28 and BZ#52, the two congeners with environmental behavior most similar to Tri+. Results are also good for total PCB and BZ#4, although summer time concentrations are slightly below observed values. Performance for BZ#[101+90] and BZ#138 is very good at Schuylerville, however, the model under-computes at Stillwater and Waterford. This may be due to differential settling losses of these congeners as a result of their stronger partitioning behavior.

Overall, based on the specification of separate particulate and porewater mass transfer pathways, the model does reasonably well for simulating BZ#28, BZ#52, BZ#4 and total PCB. Performance is weaker for BZ[101+90] and BZ#138, however, the best agreement with BZ#28 and BZ#52 is a confirmation of the historical calibration because these congeners have the most similar environmental behavior to Tri+.

A unique series of datasets was collected by GE in the summer of 1996 and 1997 that provide a useful evaluation of the model performance on a small spatial scale. These data were collected from boats at a large number of sequential locations, floating down through Thompson Island Pool. The down-river profile of PCB concentrations in these data show the highest PCB load gains over high sediment concentration areas and consequent changes in the congener pattern. Model results were compared to observed concentrations and the ratio of congener concentrations to BZ#52 concentrations. BZ#52 was chosen as a normalizing congener for evaluating the congener pattern because it is consistently present in higher concentrations and is a stable congener. Results are shown BZ#4, BZ#28 and BZ#[90+101] in Figure 7-68 (a to d). The

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model describes the shift in congener ratios across the Pool reasonably well, representing both the down-river concentration profiles and the observed higher release of BZ#4 relative to the other congeners.

In addition to evaluation of the down-river profile comparisons in Thompson Island Pool using the above float study data, comparisons were also made to the down-river profile of the BZ#28 to BZ#52 ratio using data for Fort Edward, Thompson Island Dam, Schuylerville, Stillwater and Waterford. The ratios were evaluated for summer and non-summer conditions (Figure 7-69), as well as high and low flow conditions (Figure 7-70). These results show that the model captures the BZ#28/BZ#52 ratio reasonably well for the entire Upper Hudson River over these seasonal and flow conditions.

To assess the significance of the alternative parameterization of sediment-water mass transfer rates on the historical calibration, the calibration simulation was run with these rates. That is, the historical calibration was re-run with non-flow-dependent sediment-water mass transfer decomposed into separate particle-based and porewater-based pathways. Results showed that this did not alter the performance of Tri+ in the historical calibration. Cohesive sediment concentrations were insensitive to use of the separate porewater and particulate transfer pathways, however, the rate of decline in non-cohesive sediment concentrations was slowed, resulting in concentrations somewhat higher than the observed values in 1991.

7.6.4 Hindcast Applications Summary

The short-term hindcast applications confirmed the Tri+ historical calibration because use of the exact same parameter set used for the historical calibration resulted in very good predictions of observed BZ#28 and BZ#52 concentrations. The hindcast applications revealed that alternate specification of the sediment-water mass transfer coefficient was required to allow simultaneous simulation of all congeners; however, these changes resulted in somewhat poorer calibration to non-cohesive sediment concentration trends in the historical Tri+ calibration. While investigations conducted in the hindcast applications to individual congeners provided insights into sediment-water mass transfer behavior, no changes to the Tri+ historical calibration were supported. Model performance in the hindcast applications was strongest for BZ#28 and BZ#52, the congeners whose environmental behavior most closely resembles that of Tri+. Testing of the historical calibration through short-term hindcast applications to individual congeners strongly supported the technical soundness of the Tri+ historical calibration and use of the calibrated HUDTOX model in the Reassessment.

7.7 Calibration Findings and Conclusions

The HUDTOX 21-year historical calibration to Tri+ served as the main development vehicle for the PCB fate and transport model to be used this Reassessment. This calibration was successful in reproducing observed long-term trends in water and sediment PCB concentrations over the 21-year period. This was primarily demonstrated through comparisons between model results and available data for the following parameters:

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- Long-term solids burial rates;
- Long-term Tri+ surface sediment concentrations;
- In-river solids and Tri+ mass transport at low and high flows;
- Water column solids and Tri+ concentrations;
- Solids mass balance for the Spring 1994 high flow event; and,
- Testing of the historical calibration through short-term hindcast applications to individual congeners.

Many different metrics were used to demonstrate model reliability and they were used collectively in a "weight of evidence" approach.

The following factors were found to be the most important in controlling long-term trends in Tri+ responses in the Upper Hudson River:

- Hydrology;
- External solids loads;
- External Tri+ loads;
- Tri+ partitioning;
- Sediment-water mass transfer under non-scouring flow conditions;
- Solids burial rates; and,
- Particle mixing depth in the sediments.

The first three of these factors are external inputs largely determined by site-specific data, and the last four are internal processes within the river.

The principal findings and conclusions from the calibration analyses are the following:

- The HUDTOX model represents the Upper Hudson River as a whole to be net depositional from 1977 to 1997, based on the assumptions underlying development of tributary solids loads. Computed solids burial rates in cohesive sediment areas are approximately an order of magnitude greater than those computed in non-cohesive sediment areas;
- Computed in-river solids mass loads are split almost equally between high and low flow conditions;

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- There is a computed net solids load gain to the water column of 497 percent between Fort Edward and Waterford over the 21-year historical calibration; computed tributary loadings (including Fort Edward) and gross sediment resuspension contribute 79 and 21 percent, respectively, to total solids inputs between these locations;

- Although sediment resuspension is important, water column solids concentrations and in-river solids loads are driven primarily by hydraulics and solids loads from upstream and tributary sources, even under high flow conditions;

- Computed Tri+ concentrations in surface sediments declined by 89 and 80 percent, respectively, in the cohesive and non-cohesive sediment areas of Thompson Island Pool between 1977 and 1997. These declines correspond to annual first-order loss rates of approximately 11 and 8 percent, respectively;

- Computed Tri+ concentrations in surface sediments in reaches downstream of Thompson Island Pool decline by 91 to 97 percent in cohesive sediment areas and by 82 to 93 percent in non-cohesive sediment areas. These declines correspond to annual first-order loss rates of 11 to 14 percent in cohesive sediment areas and 8 to 12 percent in non-cohesive sediment areas;

- Computed results indicate that 70 to 80 percent of in-river Tri+ loads at Thompson Island Dam and 60 to 70 percent of in-river Tri+ loads below Thompson Island Pool occur during low flow conditions;

- There is a computed Tri+ net load gain to the water column of 139 percent between Fort Edward and Waterford over the 21-year historical calibration; most of this Tri+ load gain occurs in the Thompson Island Pool and Schuylerville reaches;

- Computed external loads (99 percent from Fort Edward), flow-dependent sediment resuspension, and non-flow-dependent sediment-water mass transfer contributed 25, 25 and 50 percent, respectively, to total Tri+ inputs to the water column during the 21-year historical calibration;

- Gross settling and volatilization accounted for 88 and 12 percent, respectively, of the total computed losses of Tri+ from the water column;

- Testing of the 21-year historical calibration for Tri+ through short-term hindcast applications to individual congeners strongly supported the technical soundness of the historical calibration, and use of the calibrated HUDTOX model in the Reassessment;

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- Model calibration results are sensitive to uncertainties in solids burial rates, Tri+ partitioning, non-flow-dependent sediment-water mass transfer rates, tributary solids loads, sediment particle mixing depth, and sediment initial conditions; and,

- Model calibration results were not especially sensitive to uncertainties in solids loadings at Fort Edward or to volatilization, as influenced by uncertainties in Henry's Law Constant.

Based on the above tests of model performance and reliability, the HUDTOX model is considered adequately calibrated for predicting long-term PCB responses in the Upper Hudson River, which is the primary use of the model in the Reassessment.

8. FORECAST SIMULATIONS FOR NO ACTION

8.1 OVERVIEW

In 1984 the U.S. Environmental Protection Agency (USEPA) issued an interim decision of No Action concerning PCB contaminated sediments in the Upper Hudson River. In December 1990, USEPA issued a Scope of Work for a Reassessment of the 1984 No Action decision. The modeling work presented in this report is part of Phase 2 of the three-phase Remedial Investigation and Feasibility Study being conducted for the Reassessment. The HUDTOX model was developed to answer two of the three principal study questions posed in the Reassessment:

- When will PCB levels in fish populations recover to levels meeting human health and ecological risk criteria under continued No Action?
- Can remedies other than No Action significantly shorten the time required to achieve acceptable risk levels?

Question one is addressed in this chapter through prediction of the future course of PCB concentrations in the Upper Hudson River using the HUDTOX model developed and calibrated as described in Chapters 5 through 7. Question two will be addressed through application of the HUDTOX model in Phase 3, the Feasibility Study. The third principal study question:

- Are buried contaminated sediments likely to become "reactivated" following a major flood, possibly resulting in an increase in contamination of the fish population?

was answered through use of the Depth of Scour Model (Chapter 4) and HUDTOX.

The Depth of Scour Model (DOSM) presented in Chapter 4 was developed specifically to address the third principal question of the Reassessment. The DOSM computes the depth of scour expected under peak flow conditions and was used to evaluate the likelihood that buried PCB sediments would become reactivated. However, DOSM does not account for subsequent longer-term transport and redistribution of resuspended sediment and PCBs. Hence, the DOSM formulations for cohesive sediment resuspension were incorporated into the HUDTOX model, and HUDTOX was used to calculate the long-term system response to a flood induced resuspension event. HUDTOX was not designed to simulate short-term transient events, hence the focus of the 100-year peak flow simulation with HUDTOX is on long-term system response.

The No Action simulation was conducted for a 70-year forecast period beginning January 1, 1998. The 70-year water and sediment concentrations computed by the model were provided as input to the fish bioaccumulation modeling effort (presented in Books 3 and 4 of the Revised Baseline Modeling Report) and the Human Health Risk Assessment, which are also being conducted under this Reassessment. The results of the No Action forecast and 100-year peak flow simulations are presented in this chapter, along with the design and implementation of these scenarios. An important aspect of the forecast simulations is that the load at the upstream boundary at Fort Edward was specified as a constant PCB (Tri+) concentration, ranging from zero to 30 ng/L, the average concentration in 1998. Also presented are results of sensitivity analyses conducted for upstream solids loading conditions.

The following major sections are included in Chapter 8:

8.2 No Action Forecast Simulation Design

The forecast state variable for the No Action simulation and the 100-year flow simulation is Tri+, the sum of the tri through decachlorinated PCB homologues. This PCB group was the principal model calibration parameter. This PCB group was selected for the historical calibration and forecasts because it provided a consistent basis for comparison among the site-specific datasets over the historical period, and because it is a good represention of the distribution of PCB congeners that bioaccumulate in fish.

In order to conduct forecast simulations with the HUDTOX model, it was necessary to specify future conditions in the Upper Hudson River for flows, solids loads, and Tri+ loads. Estimates were made based on historical observations and current information regarding PCB loading trends.

It is important to recognize that forecast results have inherent uncertainty due to uncertainties in estimating future flow and loading conditions. This uncertainty can be assessed and accounted for in management decision making by evaluating predictions across a range of alternate scenarios for these inputs. To the extent that one or another scenario may be considered the most likely, it is possible to compute a best estimate of future PCB concentration trends with the model.

Presented in the next few subsections are discussions of forecast model inputs for the flow hydrograph, solids loads, PCB loadings, model initial (start-up) conditions, and specifications of the other inputs.

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8.2.1 Hydrograph

Specification of daily flow inputs at Fort Edward and all tributaries was required for the 70-year No Action forecast simulation. Flow inputs were based on the historical 1977-1997 Fort Edward and tributary hydrographs presented in Chapter 6. To construct the 70-year forecast flow inputs, randomly selected annual hydrographs from the 1977-1997 period were linked sequentially until a continuous 70-year daily flow series was produced. If the average flow over the synthesized 70 years was within 10 percent of the average flow of the actual 1977-1997 period, the hydrograph was accepted for possible use in the No Action forecast. This process was repeated to produce four randomly generated 70-year Fort Edward hydrographs. For each of the four hydrographs developed for Fort Edward, corresponding tributary hydrographs were used (See Chapter 6), tributary flows were assembled sequentially in the same order as the Fort Edward hydrograph to produce 70-year flow inputs for all tributaries.

The four sets of alternative Fort Edward and tributary hydrographs developed above were assessed by conducting No Action forecast simulations with each and selecting the one producing the approximate median result. The hydrograph selected for forecast modeling is presented in Table 8-1 and Figure 8-1. The other three alternative hydrographs were used to show sensitivity of the forecast predictions to the choice of hydrograph in Section 8.6.1.

8.2.2 Solids Loads

Solids loads play an important role in determining Tri+ concentrations in the river, due to burial of PCB in the sediment bed by solids deposition. As with flow, future solids loads are uncertain and forecast inputs are best based on historical data. As discussed in Chapter 6, upstream solids loading relationships at Fort Edward changed over time. Comparison of solids rating curves for 1991 through 1997 data and for 1977 through 1990 data indicate that solids loading decreased over time. This suggests that future solids load estimates at Fort Edward may be best estimated by the solids rating curves developed for the period 1991-1997, Equation 6-13. This equation was used with the forecast hydrograph selected as described in the preceding section, to compute solids loads at Fort Edward for the baseline No Action forecast.

Sensitivity of the forecast simulations to the method of developing the solids rating curve at Fort Edward was assessed using Equation 6-8, which is based on all available data from 1977 to 1997. These results are presented in Section 8.6.2.

8.2.3 PCB Loads

Specification of Tri+ loads at Fort Edward has a large influence on forecast results of Tri+ concentrations in the Upper Hudson River. However, due to the variable nature of Tri+ loading at Fort Edward, specification of future loading conditions is very uncertain. In spite of extensive remediation of upstream sources conducted by GE over the last decade, PCB loading continues from contaminated sediment deposits and direct discharge of PCB oil through bedrock fissures (USEPA, 1997). While average loads generally continue to decline, high concentrations continue to be periodically observed at Fort Edward. For example on January 10, 1998 a concentration of 190 ng/L was observed at Fort Edward during the spring high-flow event and a

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concentration of 85 ng/L was observed on September 9, 1998 during a period of low flow (Figure 8-2). Pulse loads due to these periodic high concentrations have been observed in the past and the total annual load delivered to Thompson Island Pool has been estimated to be as much as 660 kg/year based on analysis of data from 1977 to 1998 (QEA 1999).

Year to year variability in PCB loads at Fort Edward are seen in Figure 8-3 for 1991 through 1997 (and previously shown in Figure 6-26 for 1977 through 1997). Available data collected by GE in 1997 and 1998 show that annual average Tri+ concentrations were about 9.9 ng/L and 30.4 ng/L, respectively (based on using one-half detect limit concentrations for non-detect values).

As a result of the uncertainty associated with estimates of future Tri+ loads at Fort Edward, baseline No Action forecasts were conducted with a range of assumptions that may reasonably bound future behavior. Simulations were run with constant Tri+ concentrations of zero, 10 and 30 ng/L specified for the incoming flows at Fort Edward. The 30 ng/L simulation represents an upper bound for the 70-year forecast based on the assumption that future annual average concentrations will not increase substantially above 1998 observed average levels. The 10 ng/L simulation roughly approximates the 1997 Tri+ loads and approximates the analytical detection limit. The zero boundary sensitivity provides a lower bound for simulation and assumes complete upstream remediation. Based on the average flow, a constant concentration of 10 ng/L Tri+ produces an annual load of about 47 kg/yr at Fort Edward, and 30 ng/l produce a load of 141 kg/yr.

All downstream tributary Tri+ loads were assumed to be negligible and set to zero for the forecast simulations because historical concentrations were very low. This assumption may be significant in calculating loads to the Lower Hudson River (over Federal Dam). Conditions in the Mohawk River are particularly important because of its large flow; however, the Mohawk River enters just above the downstream boundary of the model and it has little impact on model results for the Upper River. For a Lower Hudson River assessment, different assumptions for tributaries (especially the Mohawk River) might be considered, but these were not the focus of this report. Any independent estimates of Tri+ loading to the Lower Hudson River from the Mohawk River could simply be added to the HUDTOX estimates of load over Federal Dam.

8.2.4 Initial Conditions for the Forecast

Sediment initial conditions for the 1998 through 2067 forecast simulations were based on the end results of the 1991 through 1997 model hindcast application. In effect, this corresponds to initializing the forecast simulations with measured conditions in 1991. This approach utilizes the most recent, reliable and comprehensive dataset to begin the model forecasts. In particular, in terms of accuracy, vertical resolution and spatial coverage for the Upper Hudson River, the 1991 sediment measurements represent the best match between available sediment data and model requirements. The initial conditions for the forecast are presented on a reach-average basis for cohesive and non-cohesive sediments in Table 8-2. These concentrations are model results on the last day of the simulation from January 1, 1991 to September 30, 1997.

8.2.5 Specification Of Other Model Inputs

In addition to specification of flows, solids loads and Tri+ loads, the forecast simulation required specification of air and water temperatures and atmospheric Tri+ concentrations. The same annual air and water temperature series applied in the model calibration (Section 6.8) were repeated for the forecast simulations. Atmospheric Tri+ concentrations were assumed to be zero for the entire forecast period. All other model inputs remained the same as those in the historical Tri+ calibration.

8.3 NO ACTION FORECAST RESULTS

As discussed in Section 8.2.3, there is large uncertainty in estimated upstream Tri+ concentrations entering Thompson Island Pool at Fort Edward over the forecast period. Consequently, a single most likely estimate of future concentrations is not presented. Rather, a likely range of estimates is presented, bounded by results based on specification of constant 30 ng/L and zero Tri+ concentrations at Fort Edward. An additional simulation was done with a concentration of 10 ng/L, the approximate analytical detection limit. Results of the 70-year No Action forecast simulation are presented for:

- Surface sediment (0-4 cm) Tri+ concentration time series for the whole Upper Hudson River (Figure 8-4,a-e);
- Annual average and summer average water column Tri+ concentration time series for the long-term monitoring stations (Figures 8-6, a and b; and 8-7, a and b); and,
- Annual Tri+ mass loading to the Lower Hudson River over Federal Dam (Figure 8-9, a and b).

These results are discussed in the subsections below.

8.3.1 Forecast Results: Surface Sediment PCB Concentrations

Several important observations are made from the No Action forecast results for surface sediment PCB concentrations (Figure 8-4, a-e). First, the influence of the upstream PCB load on surface sediment PCB concentrations is immediately apparent. Following the first few years of the forecast period, large separation occurs between the three upstream Tri+ load scenarios (zero, 10, and 30 ng/L Tri+ at Fort Edward). For the zero Tri+ loading simulation, concentrations in the sediment and water column exhibit a continual decline, at a rate of between 7 and 8 percent per year. This rate is consistent with observed historical trends. For the simulations using constant upstream concentrations of 10 ng/L and 30 ng/L, similar recovery rates are initially observed, however, upstream loads control sediment concentrations by about 2030.

All three loading simulations show concentrations approaching various asymptote values throughout the river. For the zero Tri+ loading simulation, surface sediment concentrations asymptotically approach zero. For the simulations using constant upstream concentrations of 10 ng/L and 30 ng/L, results asymptotically approach a quasi steady-state concentration determined by the upstream load and processes acting on Tri+ in the river. This is not a true equilibrium because the declining sediment releases still have minor effects on concentrations, and natural variability causes year to year fluctuations. The quasi steady-state concentrations approached in Thompson Island Pool cohesive sediment for the 30 ng/L and 10 ng/L are approximately 1.8 mg/kg and 0.7 mg/kg, respectively. Respective non-cohesive sediment concentrations in Thompson Island Pool level off at about 0.75 mg/kg and 0.27 mg/kg for these simulations. In downstream reaches, asymptote concentrations are slightly lower due to "clean" tributary flow and solids load inputs as well as volatilization losses.

The 70-year forecast results showed increases in surface sediment concentrations in localized areas in Thompson Island Pool (Figure 8-4a) and Stillwater Pool (Figure 8-4c) as a result of small *long-term* average sediment erosion in some model segments that eventually exposes Tri+ contamination in deeper layers. These results do not occur in response to singular high flow events. This response was not observed during the calibration period, although erosional behavior did occur. This behavior is predicted to occur 40 to 50 years in the future because of the long-term impact of small sediment erosion rates in certain locations. These computed increases in surface sediment Tri+ concentrations serve to slow or interrupt apparent rates of recovery. However, due to factors described later below, the exact timing and magnitude of the events are dependent on forecast assumptions.

In year 2044, two of the 15 cohesive sediment segments in the Thompson Island Pool (below water column Segments 10 and 25, Figure 5-5) increase approximately 0.4 mg/kg and again in 2051 by about 0.3 mg/kg. The minimum poolwide average cohesive sediment concentration before the increase in 2044 ranges from 0.27 mg/kg for the zero upstream loading simulation to 1.92 mg/kg for the simulation with a constant Tri+ concentration of 30 ng/L at Fort Edward. Non-cohesive sediments in the Stillwater reach (below water column Segments 37, 38 and 39, Figure 5-4c) also experience a series of increases, most notably in 2039 when concentrations rise by about 0.4 mg/kg. Prior to this increase, average non-cohesive concentrations ranged from 0.03 to 0.47 mg/kg for the zero and 30 ng/L Fort Edward Tri+ simulations, respectively.

These results are manifested as relatively sharp rises in surface concentrations that occur when buried sediments of higher concentration are incorporated into the mixed layer due to erosive loss of the surface sediment layer. Gradual increases are also observed in non-eroding surface sediments downstream due to transport and subsequent deposition from upstream sediment erosion. The relative magnitude of these increases is very small when compared in the context of historical observations (Figure 8-5, a-e). These forecasted increases will be considered during the development of the Feasibility Study.

The actual occurrence, magnitude and timing of the predicted increases in surface sediment concentrations is uncertain due to the uncertainty in future conditions, especially tributary solids loads. Also, the occurrence of these increases may be in part due to solids dynamics in the model calibration and/or the specification of sediment initial conditions that would not be apparent in 21-year historical calibration period. Solids burial rates, which were determined by model calibration, determine the net erosional or depositional nature of each sediment area in the model. Solids burial rates are strongly driven by external solids loadings. Variations in these solids inputs, which may be within calibration uncertainty, can result in slight net deposition instead of slight net erosion for these localized areas. However, it is equally possible that such variations could enhance the occurrences of predicted increases. Also, alternate specification of the sediment initial condition profile and/or the mixed layer depth may reduce the magnitude of these events. These possibilities are assessed through sensitivity analysis, presented below.

Model results indicating that not all areas of the river are net depositional is a reasonable expectation and is corroborated by independent modeling and data analysis. The computed erosional behavior of some areas of the river is not unique to HUDTOX. The HUDTOX solids results are based on a calibration guided, in part, by calculations from the SEDZL sediment transport model (QEA, 1999). The SEDZL model also computed some areas of both cohesive and non-cohesive sediments to be net erosional over the historical calibration period from 1977 to 1997. This is discussed in more detail in Chapter 7.

General findings of the Low Resolution Sediment Coring Report (USEPA, 1998a) seem to also offer corroborative support for the findings of the forecast simulations that localized sediment areas in the river are experiencing long-term erosional behavior. The general conclusion from the Low Resolution Sediment Coring Report that burial is not sequestering PCBs on a widespread basis is borne out to some extent by the results observed in the model. It is likely that there are localized areas of continuing scour and PCB erosion on scales smaller than the HUDTOX model segmentation. The HUDTOX results may not show these areas to be net erosional because they fall within larger model segments that are on average (across the whole segment), net depositional. While the findings presented in the Low Resolution Sediment Coring Report are based on analyses at much finer spatial scales than the HUDTOX calculations, results are comparable in a general sense and seem to indicate that long-term burial may not effectively sequester buried PCBs at all locations in the river.

8.3.2 Forecast Results: Water Column PCB Concentrations

Forecasted annual average and summer average water column concentrations are also presented for all three loading simulations at Thompson Island Dam, Schuylerville, Stillwater and Waterford in Figures 8-6 (a and b) and 8-7 (a and b). These results show large separation in water column Tri+ concentrations throughout the system under the different assumptions regarding PCB loads at Fort Edward. For the zero Tri+ concentration assumption at upstream boundary, water column concentrations decline to less than 10 ng/L within 10 years at all locations. With upstream concentrations at Fort Edward set to 30 ng/L and 10 ng/L, water column concentrations at Thompson Island Dam begin to level off around 2015 to about 27 ng/L and 9 ng/L Tri+ respectively. Downstream, annual average concentrations level off at lower values due to dilution from tributary inputs and losses from the water column.

Water column concentration results show significant year to year variability, caused by variability in flows and solids loading. The noticeable difference in average concentrations observed in the third year of the forecast period versus those in the first two years is due to differences in summer flow conditions (Figure 8-7). Computed summer average Tri+ concentrations in 2000 are much lower than in 1998 and 1999 because summer time flows were higher, diluting inputs of Tri+ from the sediment. This point is illustrated below in the simulations showing model sensitivity to choice of forecast hydrograph.

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The predicted increases in surface sediment Tri+ concentrations in Thompson Island Pool and in non-cohesive sediments in the Stillwater reach do not significantly impact the water column concentrations. This is because water column concentrations are being driven by upstream Tri+ loads at the time the sediment increases occur. Additional Tri+ inputs due to the increased surficial sediment concentrations is small relative to the upstream load contribution.

Figure 8-8 (a and b) presents the forecasted water column PCB concentrations along with the historical calibration concentrations. At this temporal scale, forecasted increases in water column concentrations in the Stillwater and Waterford reaches are very small. From a transport and fate standpoint, these increases may be considered insignificant; however, they may be important in a potential remediation decision.

8.3.3 Forecast Results: PCB Loads to the Lower Hudson River

Annual and cumulative forecasted Tri+ loads over Federal Dam to the Lower Hudson River are also presented for all three upstream PCB loading simulations (Figure 8-9 a and b). Tri+ loads to the Lower Hudson River mirror water column concentration declines and decrease from approximately 150 kg/yr to less than 10 kg/yr by about 2015 under assumptions where Tri+ loading at Fort Edward ceases in 1998 (0 ng/L boundary concentration). For the upstream load simulations based on 30 ng/L and 10 ng/L Tri+ concentrations at Fort Edward, loads continue to decline until about 2015 and then essentially level off at about 125 kg/yr and 45 kg/yr, respectively. These loads assume zero downstream tributary inputs which may be an important consideration especially for the Mohawk River at the downstream boundary of the model.

8.4 100-YEAR PEAK FLOW SIMULATION DESIGN

As discussed in Section 8.1, one of the principal questions of this Reassessment concerns the possibility that deeply buried contaminated sediments might become "reactivated" during a major flood, possibly resulting in an increase in PCB contamination of the fish population. The available historical data for the Upper Hudson River can not provide a direct answer to this question because there were no very large floods during the period 1977 to 1997. The peak flow during this period was 35,200 cfs in May of 1983, a 15-year peak flow. The 100-year peak flow in the Upper Hudson River at Fort Edward is estimated to be 47,330 cfs (Butcher, 2000a). The Depth of Scour Model presented in Chapter 4 was developed specifically to address this question, through application to the Thompson Island Pool. The 100-year flood impacts were also assessed for the whole Upper Hudson River through application of the HUDTOX model.

8.4.1 Specification of the 100-year Flood Hydrograph and Loadings

In the 100-year peak flow simulation, the HUDTOX model was run for a 70-year forecast simulation identical to the No Action forecast with the exception of a peak flow corresponding to the 100-year flood peak imposed in the spring of the first year. The 100-year flood simulation was conducted with zero PCB loading at Fort Edward and compared to the corresponding No Action simulation to maximize the observation of an effect. External solids loads were not increased during simulation of the 100-year peak flow, but remained the same as in the continued No Action simulation. This design was a single factor, worst-case experiment in which the only

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differences between continued No Action and the 100-year peak flow would be due to changes in flow-dependent sediment resuspension. This design was a worst-case scenario because the peak flow was placed in the first year of the simulation when sediment contamination was greatest and because there was no increase in external loads of "clean" solids to sorb PCBs in the water column or enhance PCB burial rates.

Figure 8-10 illustrates the base flow at Fort Edward during the continued No Action simulation and the scaling of the first spring peak to match the 100-year peak flow. The value of 12,000 cfs for the maximum spring peak in 1988 (the hydrograph for 1988 was randomly selected to represent the hydrology of the first year of the 70-year forecast) was nearly half of the historical average spring peak flow of 21,339 cfs at Fort Edward. Due to the relatively quiescent nature of this spring flood during the first year of the forecast, daily flows at Fort Edward were scaled by applying exponential trends to the rise and fall periods between March 26 and April 18. The 1988 peak spring flow in the time series was scaled up from 12,000 cfs to a value of 47,330 cfs on April 5, approximately a factor or four. The duration, rise and fall of the 100-year flow in this modified hydrograph were generally consistent with other observed peak flows in the 21-year historical period. The rise period from 50 percent of the peak flow was approximately five days, and the fall period to 50 percent of the peak flow was just under seven days. This modified hydrograph represents a 100-year peak flow but does not necessarily represent the duration, rise and recession characteristics of an actual 100-year flood event.

8.5 100-Year Peak Flow Simulation Results

Table 8-3 presents the impact of the 100-year peak flow on sediment bed solids in Thompson Island Pool (TIP) and downstream reaches of the Upper Hudson River. Cohesive sediments in the Pool were computed to be scoured with a net bed elevation decline of approximately 0.28 cm (on a poolwide average basis). The poolwide average non-cohesive sediment bed elevation declined by approximately 0.05 cm. Some individual HUDTOX cohesive and non-cohesive sediment segments experienced higher erosion depths. As noted above and in the discussion of the HUDTOX calibration, resuspension of non-cohesive sediment is treated in a relatively simple fashion so these predictions are more uncertain for simulation of event impacts.

The small erosion depths predicted throughout the Upper Hudson in response to the 100-year peak flow produce only minor fluctuations in surface sediment concentrations. This finding is in agreement with the findings reported in Chapter 4 from the separate DOSM application to cohesive sediments in Thompson Island Pool.

The 100-year event does not produce increased surface sediment concentrations of the nature observed later in the 70-year forecast. This is because the increases observed in the forecast are a result of long-term net erosional behavior that over time works to expose buried concentrations. The incremental impacts of the 100-year event on the long-term erosion depth speeds the occurrence of these increases by about one year relative to the No Action forecast.

Differences in water column Tri+ concentrations between the No Action scenario and imposition of a 100-year flood event are of relatively short duration. A comparison of predicted water column concentrations between the 100-year peak flow and No Action is shown for Thompson

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Island Dam and Federal Dam in Figures 8-11 and 8-12, respectively. Although a significant increase in water column Tri+ levels occurs during the event due to resuspension, the differences are short-lived and decline to a fairly insignificant levels fairly rapidly once the event is completed. The impact of the 100-year peak flow on surface sediment levels (i.e., the top 2 HUDTOX sediment layers) was minimal. Cohesive sediment Tri+ concentrations in the TIP increased marginally (on the order of 0.1 ppm), and then decline nearly back to No Action forecast levels within less than 4 years. Impacts on non-cohesive surface sediment contamination levels were insignificant.

Figure 8-13 shows the impact on Tri+ mass loading at various locations in the Upper Hudson River caused by imposing the 100-year peak flow on the base No Action scenario. The event causes an increase of slightly less than 26 kg (57 lbs.) in cumulative Tri+ mass loading across Thompson Island Dam by the end of the first year of the forecast. This increase represents approximately 13 percent of the average annual Tri+ mass loading across Thompson Island Dam during the 1990s. The Tri+ mass loading increase at Federal Dam during the first year was approximately 73 kg (161 lbs.)

Also note that almost all of the increase in Tri+ mass loading over No Action levels depicted by Figure 8-13 occurs during the course of the flood event (March 26 through April 18). In general, the in-river mass loading effect of the 100-year peak flow is very short-lived. Subsequent (post-first year) increases over the No Action predictions generally amount to less than 2 kg per year at Thompson Island Dam and downstream locations, and this impact eventually declines to negligible levels.

A similar analysis of 100-year peak flow impacts was conducted by General Electric (QEA, 1999). Both analyses used the same peak daily average flow for the 100-year event. On the basis of predicted sediment scour depths, results for these two modeling analyses were comparable when corrected for the flood plain effects, which were not included in the GE model.

8.6 Sensitivity Analysis

Results of sensitivity analyses are provided for the No Action forecast simulation to illustrate the impact of the assumptions made regarding future flow and solids loading conditions. In addition, sensitivity analyses for non-cohesive sediment particle mixed depth and sediment initial conditions are presented to show the influence of these parameters on the magnitude of the increases in surficial sediment concentrations observed in the No Action forecast results. All sensitivity results presented here are compared to the No Action forecast based on specification of a constant Tri+ concentration of 10 ng/L at Fort Edward.

8.6.1 Sensitivity to Specification of Forecast Hydrograph

To demonstrate the forecast sensitivity to the choice of simulation hydrograph, No Action forecasts were conducted with three alternative synthetic 70-year hydrographs in addition to the baseline forecast hydrograph. These hydrographs were developed as described in Section 8.2.1. Sensitivity results are presented for surface sediment Tri+ concentrations (8-14 a-e) and annual average water column concentrations (Figure 8-15 a-b).

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In general, specification of the forecast hydrograph does not change either the long-term rates of decline in concentrations or the quasi steady-state concentrations based on the 10 ng/L Tri+ concentration at Fort Edward. Hydrograph choice does, however, significantly affect the timing of the computed increases in surface sediment Tri+ concentrations. In Thompson Island Pool, surface sediment concentration increases due to sediment erosion occur as early as 2013 versus 2044 with the baseline forecast hydrograph. In non-cohesive sediments in the Stillwater reach, timing of the largest increase in sediment concentrations is affected by about 13 years among the four hydrographs.

The water column results from the alternative hydrographs show significant year-to-year variability relative to each other, although the overall trends are the same. The impact of the hydrograph on the forecast results does show notable differences in the first few years of the forecast period. However, these differences are based on the choice of forecast hydrograph. The apparent rate of recovery is different over the first few years, but then overall trends normalize to similar conditions for all 4 simulations.

8.6.2 Sensitivity to Solids Loads at Fort Edward

The magnitude of solids loading plays an important role in determining future Tri+ concentrations in the Upper Hudson River. As discussed in Section 8.1.1.2, the specification of future solids loads at Fort Edward was estimated by the solids rating curve developed for the 1991-1997 period. The possibility that solids loads may occur at a level observed during earlier periods of the historical calibration cannot be excluded. To assess the significance of this on forecast results, a sensitivity analysis was conducted with a solids rating curve based on all available historical data from 1977 to 1997 at Fort Edward (Equation 6-8).

Results indicate that higher solids loads at Fort Edward produce a faster rate of decline of Tri+ surface sediment concentrations and concentrations asymptotically approach a slightly lower quasi steady-state concentration with the upstream load (Figure 8-16). The higher solids loads also result in more solids deposition and delay the occurrence of the predicted concentration increases in cohesive surface sediments. Overall the impact of using the solids rating curve estimated based on the 1991 to 1997 period relative to use of the 1977 to 1997 period is small.

8.6.3 Sensitivity to Tributary Solids Loads

The solids mass balance described in Chapter 6 estimated tributary solids loads downstream of Thompson Island Pool from limited available data. This solids balance was premised on the assumptions that the Upper Hudson River below TIP was net depositional over the 21-year historical calibration period, and that solids trapping efficiencies estimated using data for TIP could also be applied to reaches downstream of TIP. To show the sensitivity of the forecast results to tributary solids loads, sensitivity analyses were conducted with 50 percent upward and downward adjustments to all tributary solids loads to the river.

The result of 50 percent increases and decreases in tributary solids loads is generally to speed and slow rates of Tri+ concentration declines, respectively. Responses in Thompson Island Pool (Figure 8-17a) are smaller than responses in downstream reaches (Figure 8-17b, e) because

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tributaries account for most of the solids inputs to downstream reaches and only a small portion of solids loadings to TIP. The occurrence, magnitude and timing of computed increases in surface sediment Tri+ concentrations are strongly influenced by changes in solids loadings. Increases of 50 percent in tributary solids loadings cause the complete disappearance of computed increases in Tri+ concentrations. Decreases of 50 percent in tributary solids loadings cause increases in both the frequency and magnitude of computed increases in Tri+ concentrations. Furthermore, new increases in Tri+ concentrations are now computed to occur in the surface sediments of the Waterford and Federal Dam reaches (Figure 8-17d, e). The 50 percent adjustments to tributary solids loads in this sensitivity analysis are considered to be within the uncertainty of the load estimates, therefore, these alternative results are all considered plausible. Use of the forecast results in decision making should consider the possibility that long-term erosional behavior downstream of Thompson Island Pool may occur on a more frequent basis than indicated by the baseline forecast results, or may not occur at all depending on future solids loadings.

8.6.4 Sensitivity to Particle Mixing

The sediment mixed layer depth and particle mixing rate are parameters for which direct measurements are not available. In the historical calibration and the base forecast simulation, sediment mixed layer depths were 10 cm and 6 cm, respectively, in the cohesive and non-cohesive sediment areas of Thompson Island Pool. In reaches downstream of TIP, sediment mixed layer depths were 10 cm and 4 cm, respectively, in cohesive and non-cohesive sediment areas. Initial estimates of sediment particle mixed depths were guided by available information from vertical profiles of sediment Tri+ concentrations, and then adjusted as part of the model calibration process. A sensitivity analysis to non-cohesive sediment mixed layer depth was conducted for the forecast by changing the mixed layer depth from 4 to 6 cm in reaches downstream of TIP. This was done primarily to assess sensitivity of computed sediment Tri+ concentration increases in the Stillwater reach. These simulations used sediment initial conditions for 1991-1997 simulations also computed with mixed layer depth set to 6 cm.

Results indicated slower declines in surface sediment Tri+ concentrations in all reaches downstream of TIP (Figure 8-18 a-e), compared to the baseline No Action case. These responses were due to greater upward mixing of Tri+ mass from the depth interval between 4 and 6 centimeters. The computed increase in surface sediment Tri+ concentration in the non-cohesive sediments of the Stillwater reach was approximately 20 percent less than the increase in the base forecast simulation. Water column Tri+ concentrations are shown in Figure 8-19 at Stillwater.

8.6.5 Sensitivity to Sediment Initial Conditions

Sediment initial conditions for the 1998 through 2067 forecast simulations were based on the end results of the 1991 through 1997 model hindcast application. In effect, this corresponds to initializing the forecast simulations with measured conditions in 1991. This approach utilizes the most recent, reliable and comprehensive dataset to begin the model forecasts. In particular, in terms of accuracy, vertical resolution and spatial coverage for the Upper Hudson River, the 1991 sediment measurements represent the best match between available sediment data and model requirements. An alternate approach would have been to use the end results of the 1977 through

1997 historical calibration. This would correspond to initializing the forecast simulations with measured conditions in 1977.

A forecast sensitivity analysis was conducted to investigate the impacts of changes in sediment initial conditions. This analysis involved initializing the forecast simulation with measured conditions in 1977. The principal result from this sensitivity analysis was that computed increases in surface sediment Tri+ concentrations in TIP and the Stillwater reach were magnified relative to computed increases in the base forecast simulation (Figure 8-20 a-e). Water column Tri+ concentration increases were also magnified (Figure 8-21 a, b). This indicates that the magnitudes of computed increases in surface sediment Tri+ concentrations during the forecast simulations depend on the temporal history of Tri+ vertical concentration profiles in the sediments.

8.7 Exposure Concentrations for August 1999 and December 1999 Risk Assessments

The HUDTOX model was developed and refined over a period of years, and EPA conducted the risk assessments for the Reassessment concurrently with this modeling effort. Accordingly, EPA used the most updated version of HUDTOX and the latest model results that were available at the time the risk assessments were conducted. The processing of HUDTOX results for linkage with the FISHRAND bioaccumulation model is discussed in Book 3 of this report.

The computed total PCB concentrations in water and surface sediment in the No Action forecast from the May 1999 BMR were used in the August 1999 Ecological Risk Assessment and the Human Health Risk Assessment for the Upper Hudson River. These results are based on initial conditions in sediment specified from the 1991 GE composite data set and 10 ng/L PCBs in water at the upstream boundary (see, Appendix A).

The computed Tri+ concentrations in water and surface sediment in the No Action forecast from this RBMR report were used in the December 1999 Ecological Risk Assessment for Future Risks in the Lower Hudson River and the Human Health Risk Assessment for the Mid-Hudson River. These results are based on initial conditions in sediment specified from the 1977 data set and 10 ng/L PCBs in water at the upstream boundary (see, Appendix A).

8.8 Principal Findings and Conclusions

Several important conclusions were drawn from the No Action and 100-year peak flow simulations provided in this report. The conclusions drawn from these simulations are based on the No Action forecast and 100-year event applications of the HUDTOX model that was successfully calibrated to long-term trends of water column and surface sediment Tri+ concentrations. Findings and conclusions from the No Action forecast, the 100-year event simulation and the selected sensitivity analyses are addressed in the sections below.

8.8.1 No Action Forecast

The principal findings and conclusions from the No Action forecast simulations are the following:

- Forecasted surface sediment Tri+ concentrations continue to decline at approximately 7 to 9 percent per year over the next two decades, consistent with long-term historical trends.

- Forecasted surface sediment Tri+ concentrations eventually reach levels determined by upstream boundary Tri+ loadings at Fort Edward. Under the assumptions in the forecast simulations, this occurs after the first two decades of the forecast period. For the first two decades, the in-place Tri+ reservoir in the sediments and sediment-water transfer processes control long-term responses of surface sediment concentrations.

- Forecasted water column Tri+ concentrations continue to decline for the first one to two decades and are very sensitive to Tri+ loading at Fort Edward. Based on specification of constant Tri+ concentrations of 10 ng/L and 30 ng/L at Fort Edward, the Fort Edward load begins to control average annual water column responses after 12 to 15 years.

- Declines in Tri+ loads to the Lower Hudson River mirror water column Tri+ declines. They reach a quasi steady-state asymptote of 45kg/yr and 125 kg/yr for the 10 and 30 ng/L Tri+ concentration assumptions at Ft. Edward.

- Surface sediment Tri+ concentrations in localized areas in Thompson Island Pool and the Stillwater reach are forecasted to increase 40 to 50 years in the future. These computed increases occur due to the long-term consequences of small sediment erosion rates that eventually expose Tri+ contamination originally present in deeper sediment layers.

- The relative magnitudes of computed increases in surface sediment Tri+ concentrations are small within the context of long-term trends in historical concentrations; however, they may be important in a potential remediation decision. The occurrence, magnitude and timing of these computed increases are dependent on forecast assumptions.

- Forecasted responses of water column and surface sediment Tri+ concentrations in the Upper Hudson River were sensitive to changes in hydrology, solids loadings, sediment particle mixing depth and sediment initial conditions. Long-term responses were most sensitive to changes in tributary solids loadings and sediment mixing depth. Computed increases in surface sediment Tri+ concentrations were most sensitive to changes in tributary solids loadings and sediment initial conditions.

The No Action forecast findings are affected by uncertainty in upstream Tri+ loads. In general, if Tri+ loads stay at or below levels observed in the past few years (1997 through 1999), surface sediment Tri+ concentrations are expected to show declines consistent with historical rates. Model forecasts show that concentration declines are likely to exhibit half-lives of about 7 to 10 years. In other words, every 7 to 10 years, concentrations will decrease by 50 percent. However, beyond two decades, forecasted surface sediment Tri+ concentrations will reach levels determined by the assumed constant upstream boundary concentrations at Fort Edward.

8.8.2 100-Year Peak Flow Simulation

The principal findings and conclusions from the 100-year peak flow simulation are the following:

- Results of the 100-year peak flow simulation show that a flood of this magnitude would result in only a small additional increase in sediment erosion beyond what might be expected for a reasonable range of annual peak flows. A 100-year peak flow is 39 percent larger than the peak flows included in the base No Action forecast simulation.

- The small sediment scour depths produced by the 100-year peak flow result in only very small increases in surface sediment Tri+ concentrations. These increases are short-lived and decline to values in the base forecast simulation (without the 100-year peak flow) in approximately four years.

- Increases in water column Tri+ concentrations in response to a 100-year peak flow are very short-lived and decline rapidly after occurrence of the event. The event causes an increase of 26 kg (57 lbs) in cumulative Tri+ mass loading across Thompson Island Dam by the end of the first year of the forecast. This increase represents approximately 13 percent of the average annual Tri+ mass loading across Thompson Island Dam during the 1990s.

- The occurrence of a 100-year peak flow is not likely to have a substantial effect on the future course of Tri+ concentrations in the water or sediments of the Upper Hudson River relative to the base No Action forecast simulation.

Results from simulation of a 100-year peak flow with HUDTOX are consistent with those reported for the Depth of Scour Model in Chapter 4.

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9. HUDTOX VALIDATION

9.1 OVERVIEW

Model validation is the process of confirming the ability of a model to predict observed behavior using datasets that are independent of the datasets used to calibrate the model. Validation is a test of the scientific rigor of a model and of its utility as a predictive tool. Should a model fail a validation exercise, its predictive ability is suspect. Conversely, should a model's predictions compare well with validation datasets, its suitability for forecasting is considered validated and conclusions drawn from model predictions are strengthened. With this in mind, a validation of the HUDTOX model was pursued using an independent dataset collected after the calibration period.

Water column data collected by GE in 1998 were available to conduct an independent validation of the HUDTOX model. These data are not included in Release 4.1b of Hudson River Database, the main data source for the modeling work presented in this report. The GE 1998 data include PCB measurements of water column and sediment concentrations. A portion of these data are presented in O'Brien and Gere 1999a and 1999b. Validation of the model to the water column dataset provided an assessment of the sediment-water mass transfer processes in the model.

Observed sediment concentrations served as the primary calibration targets for the 1977 to 1997 historical calibration. The calibrated model predicts the observed sediment concentrations in 1998 reasonably well. However, year to year changes in sediment concentrations are small. Therefore, focus of the validation testing of HUDTOX was on the water column data for 1998, available at Fort Edward, Thompson Island Dam and Schuylerville. Model results for 1998 agreed very well with the observed seasonal variations in water column data.

9.2 VALIDATION APPROACH

The validation simulation was conducted for the period of January 1, 1998 through September 30, 1998 because USGS flow records extending beyond this date were not available when this analysis was conducted. Beyond specification of 1998 flows and loads, all other model input in this validation runs were unchanged from the historical calibration.

Tributary solids loads and input hydrographs were calculated based on USGS flow data, solids data, and solids to flow regressions used in the calibration. The major tributaries which contribute significant solids and flow (Hoosic River and the Mohawk River) are all located downstream of the two locations where 1998 data was available for comparison to model output. Thus, any uncertainty in assumptions for these sources should not significantly affect the results of this validation exercise. Improved estimates of solids loads from Batten Kill would make the comparisons of model output and data at the Schuylerville location slightly more accurate.

Linear interpolation of Fort Edward Tri+ concentrations was used to specify the upstream boundary condition for the validation. Computed surficial sediment concentrations at the end of the model calibration period were specified as sediment initial conditions, the same as described in Chapter 8 for the No Action simulation. All other model parameters and coefficients were identical as employed in the calibration period simulations.

9.2.1 Validation Results

Year to year changes in surface and sediment concentrations are small and hence 1998 sediment conditions were not used as a primary measurement of validation. In fact, 1998 sediment data were used in the historical calibration in Chapter 7. However, water column PCB concentrations can vary significantly year to year, season to season or even day to day due to changes in hydrology, loads, and sediment effects.

Water column PCB observations are available for Tri+ at Fort Edward, Thompson Island Dam and Schuylerville. The sampling frequency was approximately weekly with a few exceptions. Model results were compared with these data by visual inspection of time series concentrations. Results are shown for the last three years of the calibration period and the validation period, 1998 (Figures 9-1 and 9-2). Model comparisons to just the 1998 data are presented in Figure 9-3.

Good agreement is observed between model results and observations. The model generally reproduces the observed concentrations through the entire 1998 validation period. Figures 9-4 and 9-5 show scatter diagrams comparing model output and data at Thompson Island Dam and Schuylerville on a monthly average basis. Based on the good agreement of the model with observed concentrations at Thompson Island Dam and Schuylerville, the HUDTOX model validation appears reasonably successful. While the extent of this validation period does not necessarily lead to a validation of the model's ability to make accurate long-term projections of exposure concentrations, it does provide a test of the model to represent annual fluxuations in water column PCB concentrations outside of the calibration period. This tends to strengthen the model's utility as a predictive tool.

9.2.2 Validation Summary

The model validation was conducted by comparing predicted water column Tri+ concentrations to observed concentrations in 1998. Results indicate good agreement between predicted and observed concentrations at both Thompson Island Dam and Schuylerville over an entire year, spanning a range of environmental conditions. The validation is considered successful and it enhances the model's credibility as a predictive tool for use in assessing the future course of the river's recovery from historical contamination under continued No Action.

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References

REFERENCES

Achman, D.R., B.J. Brownawell, L. Zhang, 1996. "Exchange of polychlorinated biphenyls between sediment and water in the Hudson River Estuary." *Estuaries.* 19(4): 950-965.

Achman, D.R., K.C. Hornbuckle, and S.J. Eisenreich, 1993. "Volatilization of Polychlorinated Biphenyls from Green Bay, Lake Michigan." *Environmental Science and Technology.* 24(1), pp. 75-.

Aller, R.C., 1982. "The effects of macrobenthos on chemical properties of marine sediment and overlying water." In Animal-sediment Relations, The Biogenic Alteration of Sediments. P.L. McCall and J.J.S. Tevesz (eds.), Plenum Press, NY.

Ambrose, R.B., Jr.; T.A. Wool; and J.L. Martin, 1993. "The Water Quality Analysis Simulation Program, WASP5 – Part A: Model Documentation." Environmental Research Laboratory, Office of Research and Development, USEPA, Athens, Georgia.

Baun, K., 1982. "Alternative Methods of Estimating Pollutant Loads in Flowing Water." Tech. Bulletin 133, Dept. Natural Resources, Madison.

Beale, E.M.L., 1962. "Some uses of computers in operational research." *Industrielle Organisation.* 31: 51-52.

Berger, R.C., 1990. "Mass Conservation In The RMA2V Code." *Hydraulic Engineering: Proceedings of the 1990 National Conference,* San Diego, CA, July 30-31, 1990. American Society of Civil Engineers, Boston Society of Civil Engineers Section, Boston, MA, 2, 873-878.

Bierman, V.J., Jr.; J.V. DePinto; T.C. Young; P.W. Rodgers; S.C. Martin; and R. Raghunathan, 1992. "Development and Validation of an Integrated Exposure Model for Toxic Chemicals in Green Bay, Lake Michigan." Large Lakes and Rivers Research Branch Environmental Research Laboratory – Duluth. U.S. Environmental Protection Agency.

Bopp, R.F., 1979. "The geochemistry of polychlorinated biphenyls in the Hudson River." Ph.D. Dissertation. Columbia University. Univ. Micro. Intern. 8008704, 191 pp.

Bopp, R.F., H.J. Simpson, and B.L. Deck, 1985. "Release of Polychlorinated Biphenyls from Contaminated Hudson River Sediments." Final Report NYS C00708 to NYSDEC, Albany, New York.

Borah, D. K., 1989. "Scour Depth Prediction Under Armoring Conditions", *Journal Hydraulic Engineering* 115(10), p. 1421.

Boudreau, B.P., 1997. Diagenetic Models and Their Implementation. Springer Verlag, Berlin, Heidelberg. 414 pp.

Brown, J.F Jr., R.E. Wagner and D.L. Bedard, 1984. "PCB Transformations in Upper Hudson Sediments." *Northeastern Environmental Science* 3:184-189.

Brown, M P.; M. B. Werner; C.R. Carusone, M. Klein, 1988. "Distribution of PCBs in the Thompson Island Pool of the Hudson River; Final Report of the Hudson River PCB Reclamation Demonstration Project Sediment Survey." May 1988.

Brownawell, B., 1986. "The Role of Colloidal Organic Matter in the Marine Geochemistry of PCBs". Ph.D. dissertation. Woods Hole Oceanographic Institution, Woods Hole, MA. WHO1-8619-19.

Brunner, S. E. Hornung, H. Santi, E. Wolff, and O.G. Piringer, 1990. " Henry's Law Constants for Polychlorinated Biphenyls: Experimental Determination and Structure - Property Relationships." *Environmental Science Technology* 24(11): 1751-1754.

Buckley, E.H. and T.J. Tofflemire, 1983. "Uptake of Airborne Polychlorinated Biphenyls in Foliage." *Science* 216: 520-522.

Butcher, J.B.,2000a. "Flood Frequency Analysis, Fort Edward at Rogers Island Gage, Hudson River. Memorandum" from J.B. Butcher of Cadmus to: V. Bierman, S. Verhoff, Limno-Tech Inc.; E. Garvey, TAMS; and, D. Merrill, Gradient, Inc. June 18, 1993.

Butcher, J.B., 2000b. Memorandum from J.B. Butcher of Tetra Tech to V. Bierman and S. Hinz of Limno-Tech, Inc. and E. Garvey and A. DiBernardo of TAMS Consultants, Inc. regarding Historic Sediment PCB Data Conversions dated June 9, 1998.

Butcher, J. B., E. A. Garvey and V. J. Bierman, Jr., 1998. Equlibrium Partitioning of PBC Congeners in the Water Column : Field Measurements From the Hudson River. Chemosphere, Vol. 36, No. 15, pp. 3149-3166.

Capel, P.D. and S.J Eisenreich, 1990. "Relationship between chlorinated hydrocarbons and organic carbon in sediment porewater." *Journal of Great Lakes Research* 16(2): 245-257.

Chapra, S.C., 1997. Surface Water-Quality Modeling, McGraw Hill. New York, New York.

Chow, V.T., 1959. Open-Channel Hydraulics, McGraw-Hill. New York, New York

Chow, V.T., 1960. Open-Channel Flow, McGraw-Hill. New York, New York.

Cochran, W.G., 1977. Sampling Techniques, 3rd ed. John Wiley and Sons, Inc. New York, New York.

Cohn, T.A.; L.L. DeLong; E.J. Gilroy; R.M. Hirsch; and D.K. Wells, 1989. "Estimating constituent loads." *Water Resources Research* 25(5): 937-942.

Decisioneering, Inc., 1996. *Crystal Ball® Version 4.0 User Manual.* 2530 S. Parker Road, Suite 220, Aurora, CO 80014 U.S.A.

DiToro, D.M., 1985. "A particle interaction model of reversible organic chemical sorption" . *Chemosphere* 14(10):1503-1138.

Eadie, B.J. and J.A. Robbins, 1987. "The role of particulate matter in the movement of contaminants in the Great Lakes." Advances in Chemistry Series No. 216, Sources and Fates of Aquatic Pollutants. R.A. Hites and S.J. Eisenrech (eds.), American Chemical Society. Chapter 11.

Eadie, B.J.; N.R. Moorehead, and P.F. Landrum, 1990. "Three-phase partitioning of hydrophobic organic compounds in Great Lakes waters." *Chemosphere.* 20(1-2): 161-178.

Eadie, B.J., N.R. Moorehead, J. Val Klump, P.F. Landrum, 1992. "Distribution of hydrophobic organic compounds and particulate organic matter in Green Bay waters." *Journal of Great Lakes Research* 18(1): 91-97.

ESRI, 1997. *ARC/INFO Version 7.1.2.* Environmental Systems Research Institute, Inc., Redlands, California.

Federal Emergency Management Agency (FEMA), 1982. *Flood Insurance Study for the Town of Ft. Edward, New York, Washington County.* Washington, D.C.

Fischer, et al., 1979 Mixing in Inland and Coastal Waters, Academic Press, Inc. San Diego, CA.

Flood, R.D., 1993. "Analysis of Side-Scan Sonar, Bathymetric, Subbottom, and Sediment Data from the Upper Hudson River between Bakers Falls and Lock 5." State University of New York at Stony Brook, Marine Science Research Center. Report to TAMS Consultants, Inc. for the Hudson River PCB Reassessment RI/FS. (Original Report September, 1993; Report Errata March, 1994).

Gailani, J., C.K. Ziegler, and W. Lick, 1991. "Transport of suspended solids in the lower Fox River." *Journal of Great Lakes Research* 17(4): 479-494.

Gailani, J., W. Lick, C.K. Ziegler, and D. Endicott, 1996. "Development and calibration of a fine-grained sediment transport model for the Buffalo River." *Journal of Great Lakes Research* 22(3):765-778.

Hicks D.M. and P.D. Mason, 1998. "Roughness Characteristics of New Zealand Rivers" *National Institute of Water and Atmospheric Research Ltd.* Water Resources Publication. September.

Hoff, R.M., W.M.J. Strachan, C.W. Sweet, 1996. "Atmospheric deposition of toxic chemicals to the Great Lakes: A review of data through 1994." *Atmospheric Environment* 30(20):3505-3527.

Horn, E.G., L.J. Hetling, and T. J. Tofflemire, 1979. "The problem of PCBs in the Hudson River." *Ann. N.Y. Acad. Sci.* 320: 591-609.

HydroQual, Inc, 1995. "The Erosion Properties of Cohesive Sediments in the Upper Hudson River." General Electric Company.

HydroQual, Inc, 1997. "Development of Corrections for Analytical Biases in the 1991-1997 GE Hudson River PCB Database." Prepared for General Electric Company, Albany, New York. June 1997.

Karickhoff, S.W., D.S. Brown, and T.A. Scott, 1979. "Sorption of hydrophobic pollutants on natural sediments." *Water Resources.* 13: 241-248.

Karickhoff, W.W. 1984. "Organic pollutant sorption in aquatic systems." *Journal of Hydraulic Engineering.* 110: 707-735.

Karim, M. F., and J. F. Kennedy, 1982. "IALLUVIAL: A computer-based flow and sediment routing model for alluvial streams and its application to the Missouri River", Report No. 250, *Iowa Institute of Hydraulic Research,* Iowa City, Iowa.

Leopold, L.B., and T. Maddox, 1953. "The Hydraulic Geometry of Stream Channels and Some Physiographic Implications." Professional Paper 252, U.S. Geological Survey, Washington, D.C.

Lick, W., J. McNeil, Y. Xu, and C. Taylor, 1995. 'Resuspension Properties of Sediments from the Fox, Saginaw, and Buffalo Rivers." *Journal of Great Lakes Research,* International Association for Great Lakes Research. 21(2):257-274.

Limburg, K.E., 1984. "Environmental Impact Assessment of the PCB Problem: A Review." *Northeastern Environmental Science.* 3(3/4):122-136.

Lin, H. J., and D.R. Richards, 1993. "Numerical Model Investigation of Saugus River and Tributaries, Massachusetts, Flood Damage Reduction," *Technical Report HL-93-5,* U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Little, W. C., and P. G. Mayer, 1972. "The role of sediment gradation on channel armoring." *School of Civil Engineering, Georgia Inst. of Tech.,* Atlanta, GA.

MacKay, D., 1989. "Modeling the Long-Term Behavior of an Organic Contaminant in a Large Lake: Application to PCBs in Lake Ontario." *Great Lakes Research.* 15(2): 283-297.

Mackay, D., W.Y. Shiu, and K.C. Ma, 1992. Illustrated Handbook of Physical-Chemical Properties and Environmental Fate of Organic Chemicals. Monoaromatic Hydrocarbons, Chlorobenzenes, and PCBs. Volume 1. Lewis Publishers, Ann Arbor, MI.

Marti, E.A. and D.E. Armstrong, 1990. "Polychlorinated Biphenyl Levels in Lake Michigan Tributaries." *Journal of Great Lakes Research.* 16(3): 396-405.

Matisoff, G., 1982. Mathematical models of bioturbation. In Animal-sediment Relations, The Biogenic Alteration of Sediments. P.L. McCall and J.J.S. Tevesz (eds.), Plenum Press, NY. pp. 289-330.

McAnally, W H., Jr.; J. V. Letter, Jr.; J. P. Stewart; N. Brogdon; N. James, Jr.; T.W. Anthony, 1984. "Columbia River Hybrid Modeling System," *Journal of Hydraulic Engineering* 110(3), 300-311.

McCarl, P. L. and M. J. S. Tevesz, 1982. "The effects of benthos on physical properties of freshwater sediments." In: Animal-Sediment Relations: The Biogenic Alterations of Sediments. Eds. P.L. McCall and M. J. S. Tevesz, Plenum Press, New York.

McNeil, J. D., 1994. "Measurements of the Resuspension and Erosion of Sediments in Rivers." Ph.D. dissertation. University of California at Santa Barbara.

Mehta, A.J., E.J. Hayter, W.R. Parker, R.B. Krone, and A.M. Teeter, 1989. "Cohesive sediment transport. 2. Application." *Journal of Hydraulic Eng*ineering 115 (8), pp. 1094-1112.

Nadal, E.O., 1998. "Evaluation of physical/chemical mechanisms controlling PCB release from river sediments." Ph.D. dissertation. Department of Civil and Environmental Engineering, Carnegie Institute of Technology, Carnegie Mellon University.

Neter, J., W. Wasserman, and M. H. Kutner, 1990. Applied Linear Statistical Models. Third Edition, Irwin, IL 60430.

New York State Department of Environmental Conservation. "New York State Toxics Air Monitoring Report" by Department of Environmental Conservation Division of Air Resources 1982-1984. Bureau of Air Quality Surveillance, Bureau of Air Research.

NUS, 1984. "Volume 1, Feasibility Study, Hudson River PCBs Site, New York. April, 1994." EPA Contract No. 68-01-6699. Table 4-12, pp 4-13.

O'Brien & Gere Engineers, Inc., 1993a. "Hudson River Project Sampling and Analysis Program; 1990 Sediment Sampling and Analysis Program." Prepared for General Electric Company, May 1993.

O'Brien & Gere Engineers, Inc., 1993b. "Data Summary Report, Hudson River Project 1991 Sediment Sampling and Analysis Program." Prepared for General Electric Company Corporate Environmental Programs. O'Brien and Gere Engineers, Inc., Syracuse, New York.

O'Brien & Gere Engineers, Inc., 1993c. "1991 Hydrographic survey of the Upper Hudson River Hudson River project sampling and analysis program." General Electric Company, Corporate Environmental Programs. Albany, New York.

O'Brien & Gere Engineers, Inc., 1993d. "Hudson River Project 1991-1992 Sampling and Analysis Program Temporal Water Column Monitoring Program." General Electric Company, Corporate Environmental Programs. Albany, New York.

O'Brien & Gere Engineers, Inc., 1995. "1994 Post Construction Remnant Deposit Monitoring Report." Syracuse, NY: O'Brien & Gere Engineers, Inc. November 1995.

O'Brien & Gere Engineers, Inc., 1996. "1995 Post Construction Remnant Deposit Monitoring Report". Syracuse, NY: O'Brien & Gere Engineers, Inc.

O'Brien & Gere Engineers, Inc., 1998. "Hudson River Project 1996-1997 Thompson Island Pool Studies." Syracuse, NY: O'Brien & Gere Engineers, Inc. February 1998

O'Brien & Gere Engineers, Inc., 1999. "1998 High Flow Monitoring Program, Hudson River Project." General Electric Company, Corporate Environmental Programs. Albany, New York.

Olsen, C.R., H.J. Simpson, T.H. Peng, R.F. Bopp and R.M. Trier, 1981. "Sediment mixing and accumulation rate effects on radionucleide depth profiles in Hudson estuary sediments." *J. Geophys. Res.*, 86:

Parchure, T.M., and Mehta, A.J., 1985. "Erosion of soft cohesive sediment deposits." *Journal of Hydraulic Engineering.*, ASCE, 111(10), 1308-1326.

Partheniades, E., 1965. "Erosion and deposition of cohesive soils." *Journal Hydraulic Division,* ASCE, 91 (HY1), pp 105-138.

Phillips, P.J. and D.W. Hanchar, 1996. "Water Quality Assessment of the Hudson River Basin in New York and Adjacent States- Analysis of Available Nutrient, Pesticide, Volatile Organic Compounds, and Suspended-Sediment Data, 1970-90," U.S. Geological Survey, Water-Resources Investigations Report 96-4065.

Portielje, R. and L. Lijklema, 1999. "Estimation of sediment-water exchange of solutes in Lake Veluwe, The Netherlands." *Water Research* 33(1): 279-285.

Preston, S.D., V.J. Bierman, Jr., and S.E. Silliman, 1989. "An evaluation of methods for the estimation of tributary mass loads." *Water Resources Research.* 25(6): 1379-1389.

Preston, S.D., V.J. Bierman, Jr., and S.E. Silliman, 1992. "Impact of flow variability on error in estimation of tributary mass loads." *Journal of Environmental Engineering* 118(3): 402-419.

Quantitative Environmental Analysis, LLC, 1998a. "Sediment Bed Mapping Study of the Upper Hudson River from Northumberland Dam to Troy Dam." Prepared for the General Electric Company. Final Report.

Quantitative Environmental Analysis, 1998b. "Thompson Island Pool Sediment Coring Program – Field Sampling Plan". General Electric, Albany, New York.

Quantitative Environmental Analysis, 1999. "PCBs in the Upper Hudson River; Volume 2; A Model of PCB Fate, Transport, and Bioaccumulation." Prepared for General Electric, Albany, New York. May 1999.

Rao, P.S., and J.M. Davidson, 1980. "Estimation of Pesticide Retention and Transformation Parameters Required for Nonpoint Source Pollution Models." In *Environmental Impact of Nonpoint Source Pollution.* Ann Arbor Sciences, Ann Arbor, Michigan, pp. 23-67.

Rapaport, R.A. and S.J. Eisenreich, 1988. "Historical Atmospheric Inputs of High Molecular Weight Chlorinated Hydrocarbons to Eastern North America. *Environmental Science Technology.* 22(8): 931-941.

Raudkivi, A.J., 1990. Loose Boundary Hydraulics. 3rd edition. Pergamon Press.

Reible, D.D., K.T. Valsaraj, and L.J. Thibodeaux, 1991. Chemodynamic models for transport of contaminants from sediment beds. In The Handbook of Environmental Chemistry, Vol. 2, part F. Hutzinger, O. (ed). Springer-Verlag, Berlin. pp. 185-228.

Rhea, J. and M. Werth, 1999. "Phase 2 Evaluation of Analytical Bias in the USGS Water Column Database." Technical Memorandum from Quantitative Environmental Analysis to John Haggard, General Electric. March 22, 1999. 12 pp.

Rhea, J. and M. Werth, 1999. "Memorandum from James Rhea and Michael Werth to John Haggard", GE Corporate Environmental Programs, Albany, NY. Phase 2 Evaluation of Analytical Bias in the USGS Water Column Database. March 22, 1999.

Richards, D.R., 1990. "Flow Separation Around A Solitary Dike; Eddy Viscosity and Mesh Considerations." *Hydraulic Engineering: Proceedings of the 1990 National*

Conference, San Diego, CA, July 30-31, 1990. American Society of Civil Engineers, Boston Society of Civil Engineers Section, Boston, MA, 2, 867-872.

Sanders, J. E., 1989. The PCB-Pollution Problem in the Upper Hudson River: From Environmental Disaster To "Environmental Gridlock," Northeastern Environmental Science, Vol. 8, No. 1

Schlichting, H., 1979, Boundary-Layer Theory. McGraw-Hill, New York, New York.

Shields, A., 1936. "Anwendung der Ahnlichkeitsmechanik und der Turbulenzforschung auf die Geschiebebewegung", *Mitteilungen der Preussischen Versuchsanstalt fur Wasserbau und Schiffbau*, No. 26, Berlin, Germany.

Sofaer, A.D., 1976. "Interim Opinion and Order in the Matter of Alleged Violations of the Environmental Conservation Law of the State of New York by General Electric Co., Respondent." *NYSDEC File No. 2833.* February 9, 1976, Albany, New York.

SPSS Inc., 1998. *SYSTAT® Version 8.0 for Windows® Statistics.* 444 North Michigan Avenue, Chicago, IL 60611 U.S.A.

Tennekes, H., and Lumley J.L., 1972. A First Course in Turbulence The MIT Press, Cambridge, MA.

Thibodeaux, L.J., 1996. Environmental Chemodynamics: Movement of Chemicals in Air, Water, and Soil. John Wily & Sons, Inc., New York.

Thibodeaux, L.J., D.D. Reible, W.S. Bosworth, L.C. Sarapas, 1990. "A theoretical evaluation of the effectiveness of capping PCB contaminated New Bedford Harbor Sediment." Final report. Hazardous Substance Research Center, Louisiana State University, Baton Rouge, LA.

Thomann, R.V., and J.A. Mueller, 1987. Principles of Surface Water Quality Modeling and Control. Harper & Row, New York, New York.

Thomas, W. A. and W.H. McNally, Jr., 1990. "User's manual for the generalized computer program system: open-channel flow and sedimentation, TABS-2." US Army Engineer Waterways Experiment Station, Vicksburg, Mississippi.

Thoms, S.R., G. Matisoff, P.L. McCall, and X. Wang, 1995. "Models for alteration of sediments by benthic organisms." Final technical report for Project 92-NPS-2, prepared for Water Environment Research Foundation, Alexandria, VA.

Thurston, Kerry A., 1998. "Database Transmittal 10/13/98 (0612.246)." E-mail from Kerry A. Thurston, O'Brien & Gere Engineers, Inc. to John Haggard, General Electric regarding GE database update as of October 12, 1998.

Tofflemire, T.J., and S.O. Quinn, 1979. "PCB in the Upper Hudson River: Mapping and Sediment Relationships". NYSDEC Technical Paper No. 56. March 1979. NYSDEC, Albany, New York.

Tsivoglou, E.E. and J.R. Wallace, 1972. "Characterization of Stream Reaeration Capacity" EPA-R3-72-012. U.S. Environmental Protection Agency, Washington, D.C.

U.S. Environmental Protection Agency, (US EPA). 1989. "Statistical Analysis of Groundwater Monitoring Data at RCRA Facilities – Interim Final Guidance." EPA/530-SW-89-026.

U.S. Environmental Protection Agency, (USEPA), 1991. "Phase I Report - Review Copy. Interim Characterization and Evaluation" Volume 1. Hudson River PCBs Reassessment RI/FS. Prepared for USEPA, Region II by TAMS Consultants, Inc. and Gradient Corporation, August 1991.

U.S. Environmental Protection Agency, (USEPA), 1992. "Final Phase 2 Work Plan and Sampling Plan." Hudson River PCBs Reassessment RI/FS. Prepared for USEPA, Region II by TAMS Consultants, Inc. and Gradient Corporation, September 1992.

U.S. Environmental Protection Agency, (USEPA), 1995. "Further Site Characterization and Analysis, Volume 2A Database Report." Phase 2 Report - Review Copy. Hudson River PCBs Reassessment RI/FS. Prepared for USEPA, Region II by TAMS Consultants, Inc. and Gradient Corporation, October 1995.

U.S. Environmental Protection Agency, (USEPA), 1996. "Preliminary Model Calibration Report. Phase 2 Report, Further Site Characterization and Analysis Volume 2B". Hudson River PCBs Reassessment RI/FS. USEPA Region II. Prepared for USEPA by Limno-Tech, Inc., Menzie Cura and Associates, Inc., and The CADMUS Group, Inc., October 1996.

U.S. Environmental Protection Agency, (USEPA), 1997. "Further Site Characterization and Analysis, Volume 2C - Data Evaluation and Interpretation Report." Hudson River PCBs Reassessment RI/FS. Prepared for the USEPA by TAMS Consultants, Inc., The Cadmus Group, Inc. and Gradient Corporation, February, 1997.

U.S. Environmental Protection Agency, (USEPA) 1998a. "Further Site Characterization and Analysis" Volume 2C-A – Low Resolution Sediment Coring Report, Hudson River PCBs Reassessment RI/FS. Prepared for USEPA, Region II and the U.S. Army Corps of Engineers, Kansas City District by TAMS Consultants, Inc., Gradient Corporation and Tetra Tech, Inc., July 1998.

U.S. Environmental Protection Agency, (USEPA), 1998b. "CD-ROM Database for the Hudson River PCBs Reassessment RI/FS, Phase 2 Report Further Site Characterization and Analysis Database Report", Volume 2A, Release 4.1b. Prepared for USEPA, Region

II and the U.S. Army Corps of Engineers, Kansas City District by TAMS Consultants, Inc., August, 1998.

U.S. Environmental Protection Agency (USEPA), 1998c. "Hudson River PCBs Reassessment RI/FS Responsiveness Summary for Volume 2A: Database Report, Volume 2B: Preliminary Model Calibration Report, Volume 2C: Data Evaluation and Interpretation Report." Prepared for USEPA and the U.S. Army Corps of Engineers, Kansas City District by TAMS Consultants, Inc.; Limno-Tech, Inc.; Tetra Tech, Inc.; Menzie Cura & Associates, Inc., December 1998.

U.S. Environmental Protection Agency (USEPA), 1999a. "Responsiveness Summary for Volume 2C-A Low Resolution Sediment Coring Report, Addendum to the Data Evaluation and Interpretation Report, Book 1 of 2". Hudson River PCBs Reassessment RI/FS. Prepared for USEPA, Region II and the U.S. Army Corps of Engineers, Kansas City District by TAMS Consultants, Inc., and Tetra Tech, Inc., February 1999.

U.S. Environmental Protection Agency (USEPA), 1999b. "Responsiveness Summary for Volume 2C-A Low Resolution Sediment Coring Report, Addendum to the Data Evaluation and Interpretation Report, Book 2 of 2." Hudson River PCBs Reassessment RI/FS. Prepared for USEPA, Region II and the U.S. Army Corps of Engineers, Kansas City District by TAMS Consultants, Inc. and Tetra Tech, Inc., February 1999.

U.S. Environmental Protection Agency (USEPA), 1999c. "Further Site Characterization and Analysis, Volume 2D – Baseline Modeling Report, Book 2 of 4." Hudson River PCBs Reassessment RI/FS. Prepared for USEPA by Limno-Tech, Inc., Menzie-Cura & Associates, Inc., and Tetra Tech, Inc., May 1999.

U.S. Environmental Protection Agency, (USEPA). 1999d. "Phase 2 Report – Review Copy. Further Site Characterization and Analysis. Volume 2F- Human Health Risk Assessment." Hudson River PCBs Reassessment RI/FS. Prepared for USEPA, Region II and the U.S. Army Corps of Engineers, Kansas City District by Gradient Corporation, August, 1999.

U.S. Environmental Protection Agency, (USEPA), 1999e. "Phase 2 Report – Review Copy. Further Site Characterization and Analysis, Volume 2E – Baseline Ecological Risk Assessment, Hudson River PCBs Reassessment RI/FS." Prepared for USEPA by TAMS Consultants, Inc., and Menzie-Cura & Associates, Inc., August 1999.

U.S. Environmental Protection Agency, (USEPA). 1999f. "Phase 2 Report – Review Copy. Further Site Characterization and Analysis. Volume 2F–A Human Health Risk Assessment for the Mid-Hudson River." Hudson River PCBs Reassessment RI/FS. Prepared for USEPA, Region II and the U.S. Army Corps of Engineers, Kansas City District by TAMS Consultants, Inc. and Gradient Corporation, December, 1999.

U.S. Environmental Protection Agency, (USEPA). 1999g. "Phase 2 Report – Review Copy. Further Site Characterization and Analysis. Volume 2E–A Baseline Ecological

Risk Assessment for Future Risks in the Lower Hudson River." Hudson River PCBs Reassessment RI/FS. Prepared for USEPA, Region II and the U.S. Army Corps of Engineers, Kansas City District by TAMS Consultants, Inc. and Menzie-Cura & Associates, Inc., December, 1999.

U.S. Environmental Protection Agency, (USEPA), 2000. "Responsiveness Summary for Volume 2D - Baseline Modeling Report, Phase 2." Hudson River PCBs Reassessment RI/FS. Prepared for USEPA, Region II and the U.S. Army Corps of Engineers by TAMS Consultants, Inc., Limno-Tech, Inc., Menzie-Cura & Associates, Inc., Tetra Tech, Inc., January, 2000.

USGS, 1969. "Time-of-Travel Study Upper Hudson River – Fort Edward, NY to Troy Lock and Dam, Troy NY." RI-10. Prepared by Harold L. Shindel, US Geological Survey, US Department of the Interior, Washington DC.

USGS, 1993. "Water Resources Data Report" for New York, Volume 1.

Valsaraj, K.T., L.J. Thibodeaux, and D.D. Reible, 1997. "A quasi-steady-state pollutant flux methodology for determining sediment quality criteria." *Environmental. Toxicology & Chemistry.* 16(3):391-396.

van den Berg, J., and A. van Gelder, 1993. "Prediction of Suspended Bed Material Transport in Flows Over Silt and Very Fine Sand", *Water Res. Res.*, Vol. 29 No. 5 pp. 1393-1404.

Vaughn, J.A., 1996. "Dissolved Organic Carbon Dynamics in the Upper Hudson River Basin," thesis presented to Rensselaer Polytechnic Institute, Troy New York, in partial fulfillment of the requirements for the degree of Master of Science.

Wagner, L.A., 1982. Drainage Areas Of New York Streams, By River Basins: A Stream Gazetteer. U. S. Geological Survey Water Resources Investigations Open File Report 81-1055. U. S. Department of the Interior.

Wasserman N. J., and M. H. Kutner, 1985. Applied Linear Statistical Models, 2nd Ed., Richard D. Irwin, Inc.

Whitman, W.G., 1923. "The two-film theory of gas adsorption." *Chemical and Met. Engineering.* Vol. 29, 147 pp.

Xu, Y., 1991. "Transport properties of fine-grained sediments." Ph.D. dissertation. University of California at Santa Barbara.

Ziegler, C.K. and B. Nisbet, 1994. "Fine-grained sediment transport in Pawtuxet River, Rhode Island." *Journal Hydraulic Engineering.* 120(5):561-576.

Zimmie, 1985. "Assessment of erodibility of sediments in the Thompson Island Pool of the Hudson River." Final Report to the Office of Special Projects, New York State Department of Environmental Conservation. US EPA Grant No. C-36-1167-01.

Zreik, D.A., B.G. Krishnappan, J.T. Germaine, O.S. Madsen, and C.C. Ladd, 1998. "Erosional and mechanical strength of deposited cohesive sediments." *Journal of Hydraulic Engineering*, ASCE, 124(111):1076-1085.