PHASE 2 REPORT - REVIEW COPY
FURTHER SITE CHARACTERIZATION AND ANALYSIS

# VOLUME 2D - BASELINE MODELING REPORT

## HUDSON RIVER PCBs REASSESSMENT RI/FS

MAY 1999

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

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

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

May 18, 1999

To All Interested Parties:

The U.S. Environmental Protection Agency (EPA) is pleased to release the 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.

The Baseline Modeling Report is the fourth of six volumes of the Phase 2 Report (Volume 2D) for the Hudson River PCBs Reassessment. The baseline modeling effort was broken out as a separate report to allow interested parties to comment on the modeling results that would be utilized in the Human Health and Ecological Risk Assessments, and subsequently, the Phase 3 Report or Feasibility Study. As with the previous Phase 2 Reports, it is important to recognize that the conclusions in this report do not yet determine whether or not remedial action is necessary for the PCB-contaminated sediments of the Upper Hudson. EPA must complete the Reassessment before an appropriate remedial decision can be made.

In their present forms, the models are useful tools for providing information on PCB exposure concentrations for the Human Health and Ecological Risk Assessments. Additional modeling efforts will be conducted to fine tune the model for predicting the time it takes for the system to recover. The results of these additional modeling efforts will be made available as part of the Responsiveness Summary for this report.

EPA will accept comments on the Baseline Modeling Report until **Wednesday, June 23, 1999.** Comments should be marked with the name of the report, the book number, and should include the report section and page number for each comment. Comments should be send to:

Douglas Tomchuk
USEPA - Region 2
290 Broadway - 19th Floor
New York, NY 10007-1866

Attn: BMR Comments

As with previous Reassessment reports, EPA will hold a Joint Liaison Group meeting on the date of release of this report, May 18, 1999, to discuss findings of the Baseline Modeling Report. The meeting is being held at 7:30 p.m. at the Marriott Hotel at 189 Wolf Road in Albany, New York, and is open to the general public. Notification of this meeting was sent to liaison group members, interested parties and the press several weeks prior to the meeting.

During the public comment period, EPA will hold a public availability session to answer questions from the public regarding the Baseline Modeling Report. The availability session will be held on Tuesday, June 15, 1999 at the Marriott Hotel in Albany, New York from 2:30 to 4:30 p.m. and from 6:30 to 8:30 p.m.

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

Sincerely yours,

Richard L. Caspe, Director
Emergency and Remedial Response Division

PHASE 2 REPORT - REVIEW COPY
FURTHER SITE CHARACTERIZATION AND ANALYSIS

# VOLUME 2D - BASELINE MODELING REPORT

## HUDSON RIVER PCBs REASSESSMENT RI/FS

MAY 1999

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


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

# Table of Contents

# PHASE 2 REPORT
# FURTHER SITE CHARACTERIZATION AND ANALYSIS
# Volume 2D – BASELINE MODELING REPORT
# HUDSON RIVER PCBs REASSESSMENT RI/FS

## CONTENTS

## BOOK 1 of 4

# PHASE 2 REPORT
# FURTHER SITE CHARACTERIZATION AND ANALYSIS
# Volume 2D – BASELINE MODELING REPORT
# HUDSON RIVER PCBs REASSESSMENT RI/FS

## CONTENTS

# PHASE 2 REPORT
# FURTHER SITE CHARACTERIZATION AND ANALYSIS
# Volume 2D – BASELINE MODELING REPORT
# HUDSON RIVER PCBs REASSESSMENT RI/FS

## CONTENTS



***Note:*** ***Book 3 and Book 4 Table of Contents is located in the respective books.***

# PHASE 2 REPORT
# FURTHER SITE CHARACTERIZATION AND ANALYSIS
# Volume 2D – BASELINE MODELING REPORT
# HUDSON RIVER PCBs REASSESSMENT RI/FS

## BOOK 2 of 4

## LIST OF TABLES

**BOOK 2 of 4**

## LIST OF TABLES (cont.)

## BOOK 2 of 4

## LIST OF FIGURES

## BOOK 2 of 4

### LIST OF FIGURES (cont.)

## BOOK 2 of 4

### LIST OF FIGURES (cont.)

## BOOK 2 of 4

### LIST OF FIGURES (cont.)

# PHASE 2 REPORT
# FURTHER SITE CHARACTERIZATION AND ANALYSIS
# Volume 2D – BASELINE MODELING REPORT
# HUDSON RIVER PCBs REASSESSMENT RI/FS

## BOOK 2 of 4

## LIST OF PLATES

## ACRONYMS

| | |
|---|---|
| BAF | Biota Accumulation Factor |
| 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 |
| LRSCR | Low Resolution Sediment Coring Report |
| m/s | Meters per second |
| mg/l | Milligrams per liter |
| $mi^2$ | Square miles |

# PHASE 2 REPORT
# FURTHER SITE CHARACTERIZATION AND ANALYSIS
# Volume 2D – BASELINE MODELING REPORT
# HUDSON RIVER PCBs REASSESSMENT RI/FS

## ACRONYMS

| | |
|---|---|
| MT | Metric Ton |
| MVUE | Minimum Variance Unbiased Estimator |
| 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 |
| 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) |
| Og/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

# BASELINE MODELING REPORT

## EXECUTIVE SUMMARY

### MAY 1999

This report presents results and findings from the application of mathematical models for PCB transport and fate and 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 Hudson River sediment, water and fish. This report provides predictions under baseline conditions, that is, without remediation (equivalent to a No Action scenario). The outputs from the models, baseline sediment, water and fish PCB concentrations will be used as inputs in the Human Health and Ecological Risk Assessments. Subsequently, the models will also be used in the Feasibility Study (the Phase 3 Report) to evaluate and compare the impacts of various remedial scenarios.

The Baseline Modeling Report (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 from the transport and fate models are used as input values for the bioaccumulation models.

**MODELING OBJECTIVES** - The overall goal of the modeling is to develop and field validate scientifically credible models in order to answer the following principal 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 work presented in this Baseline Modeling Report provides information relevant to the first and third questions. Predictions regarding the potential impacts of various remedial scenarios, the second question, will be conducted in the future and be presented in the Feasibility Study (the Phase 3 Report).

**MODEL DEVELOPMENT**

A large body of information from site-specific field measurements (as found in Hudson River Database Release 4.1), laboratory experiments and the scientific literature was synthesized within the models to develop the transport and fate and 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, a description of the data sets to be used for calibration, and demonstrations of model outputs were made available for public review in the Preliminary Model Calibration Report (PMCR), which was issued in October 1996. In addition, in September 1998, an independent peer review was held on the modeling approach. The modeling framework of the PMCR was revised based on the peer review and public comment. A major revision was the addition of a mechanistic bioaccumulation model, the Gobas Model, as described below. Because of the many uncertainties inherent in modeling bioaccumulation, EPA has used a weight-of-evidence approach employing three different bioaccumulation models at varying levels of complexity, ranging from empirical to mechanistic.

The following models were developed and calibrated for the Baseline Modeling Report:

**HUDTOX** - The backbone of the modeling effort is the Upper Hudson River Toxic Chemical Model (HUDTOX). The HUDTOX model covers the 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. It balances inputs, outputs and internal sources and sinks for the Upper Hudson River. Mass balances are constructed first for water, then sediment and then PCBs. External inputs of water, sediment and PCBs are specified from field observations. Once external inputs are specified, the internal model and system outputs, can be calibrated against field observations. Outputs of PCB concentrations in water and sediment from HUDTOX are used as inputs for the forecasts of the bioaccumulation models.

**Depth of Scour Model (DOSM)** - The Depth of Scour Model was developed to provide spatially-refined information on sediment erodibility in response to high-flow events such as a 100-year flood. The DOSM model is a two-dimensional, GIS-based sediment erosion model that was applied to the Thompson Island Pool. It is linked with the output from a hydrodynamic model that predicts the velocity and shear stress (force of the water acting on the sediment surface) during a flood. The model was also used to develop relationships between river flow and cohesive sediment resuspension. These relationships were used in the HUDTOX model for evaluating flow-dependent resuspension.

**Bivariate BAF Analysis** - The Bivariate BAF (Bioaccumulation Factor) Analysis for fish body burdens looks at the data for sediment and summer average water-column PCB concentrations (two variables or "bivariate") and compares them to measured PCB levels in fish tissue. This allows for the interpretation of the relative importance of water and sediment sources to a particular species of fish, in turn reflecting its feeding behavior. As the BAF calculated from this model does not take into account causal relationships, this analysis has limited predictive capabilities compared with the more mechanistic models, described below.

**Empirical Probabilistic Food Chain Model** - The Empirical Probabilistic Food Chain Model relies upon feeding relationships to link fish body burdens to PCB exposure concentrations in water and sediments. The model combines the information from available PCB exposure measurements with knowledge about the ecology of different fish species and the relationships among larger fish, smaller fish, and invertebrates in the water column and sediments. The Empirical Probabilistic Food Chain Model provides information on the expected range of uncertainty and variability around average body burden estimates (in contrast to the Bivariate BAF Analysis, which just provides the average body burden estimates).

**Gobas Mechanistic Time-Varying Model (FISHPATH and FISHRAND)** - As a result of the peer review for the Modeling Approach held in September 1998, it was determined that a time-varying, mechanistic model should be included in the suite of models being used to evaluate the potential for PCB uptake into fish tissue. Consequently, two additional mechanistic models were developed describing the uptake, absorption and elimination of PCBs in fish over time. The models are based on the approach of the peer-reviewed uptake model developed by Gobas (1993 and 1995). This is the same form of the model that was used to develop criteria under the Great Lakes Initiative (USEPA, 1995). Two versions of the model were developed for the Reassessment, a deterministic version (average body burdens) referred to as FISHPATH, and a probabilistic version (the average body burdens including estimates of uncertainty and variability, predominantly variability) referred to as FISHRAND. The predictions of future fish tissue concentrations from FISHRAND will be utilized for estimating potential risk in the Human Health and Ecological Risk Assessments.

## MODEL CALIBRATION

The HUDTOX model was calibrated for four different forms of PCBs: total PCBs, Tri+, BZ#4, and BZ#52. 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. This allows for the comparison of data that was 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 allowed for a consistent basis for comparison over the entire period for which historical data were available. BZ#4 is a dichloro congener that represents a final product of PCB dechlorination in the sediments. In addition, the physical and chemical properties of BZ#4 are different from the other forms of PCBs (*e.g.*, it is more soluble and has a lower partitioning coefficient), which adds to the rigor of the calibration. BZ#52 is a tetrachlorobiphenyl that was selected as a normalizing parameter for congener patterns based on its presence in Aroclor 1242, the main Aroclor used by General Electric at the Hudson River capacitor plants, and due to its resistance to degradation or dechlorination in the environment.

A long-term hindcasting application was conducted for Tri+ for the period of record, from 1977 to 1997. However, the period from 1977 to 1984 had limited PCB data for estimating external Tri+ loadings. The uncertainty introduced by this limited PCB data required that an additional PCB load be added in order for the model to match sediment concentrations in Thompson Island Pool in 1984 and water column observations downstream. Consequently, the long-term hindcast calibration for Tri+ was actually only conducted for the period from 1984 to 1997.

The period from 1991 to 1997 was the principal focus of the calibration effort because this period was relatively data rich in terms of parameters measured, spatial-temporal coverage and data quality. Applications for this period included all four PCB forms: total PCBs, Tri+, BZ#4, and BZ#52.

The HUDTOX model was successful in representing the hydraulics, solids and PCB dynamics of the Upper Hudson River over the historical period of record. This period was characterized by a significant transition from an early phase of high upstream PCB loads, followed by a long declining phase to present-day conditions with upstream PCB loads now very close to detection limits. Results from the HUDTOX calibration applications were consistent with the magnitudes and trends of the best available data for the historical period.

### MODEL FORECAST

The models were run for a forecast period of 21 years beginning January 1, 1998. The 21-year time frame was selected because it matched the time frame of the 1977 to 1997 hindcast. All flows, solids loadings and other external forcing functions were the same as those used in the hindcast, with the exception of PCB concentrations at Fort Edward. The initial PCB concentrations for the forecast were the same as the final PCB concentrations from the 1991 to 1997 calibration simulation. Forecast simulations were run for two different assumptions for PCB loadings at the upstream boundary at Fort Edward: first, water column PCB concentrations were held constant at a level equal to the annual average PCB concentration that was observed in 1997 (9.9 ng/l); and second, water column PCB concentrations were held constant at zero. Note that these simulations assume that there will be no future load increases from any upstream sources. In particular, it was assumed that during the forecasts PCB migration from the GE Hudson Falls Plant site would not increase and that there would not be any type of event similar to the releases that occurred with the alleged partial failure of the Allen Mill gate structure in 1991. Based on the expectation that the PCB load from the GE Hudson Falls Plant site would decrease in the future due to the implementation of remedial measures there, these forecasting simulations were designed to bound the estimates of system responses.

Appropriate target levels for fish 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 body burden levels against certain available criteria as a matter of perspective. These include: the 2 ppm wet weight Action Level used by the Food and Drug Administration (FDA) for regulating fish in commerce, and the Great Lakes Sport Fish Advisory Task Force values of 1.1 ppm wet weight for consumption of six fish meals per year, and 0.2 ppm wet weight for consumption of one fish meal per month. Again, these are not endorsements of these values for decision making, and appropriate values will be developed in the Feasibility Study for the site.

Forecasts using the mechanistic Gobas model, FISHRAND, were run only under the constant upstream boundary condition because predicted sediment and water exposure concentrations from HUDTOX were virtually the same for the constant and zero upstream boundary conditions, which would result in virtually the same body burden predictions. Species modeled were largemouth bass, brown bullhead, yellow perch, white perch and pumpkinseed. The reported time period for achieving target values for fish body burdens may extend beyond the 21-year forecast period after consideration of the uncertainty around the best estimated values.

## Major Findings

The primary objective in 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 a suite of models that generate output that matches the observed data reasonably well. Subsequent to this report, the model predictions can be used to evaluate ecological and human health risks and to assess the 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 USEPA's understanding of the system include: the tributaries along the length of the river contribute the vast bulk of the solids load carried by the system; the river is net depositional in the Thompson Island Pool and apparently also in the downstream reaches; and, the models indicate a gradual decline in the mass transport of PCBs down river over time.

Beyond the general observations above, the development of the models and the analysis of model outputs have provided USEPA with the following findings regarding PCBs in the Upper Hudson River:

1. The future projection for PCB concentrations in the water column is controlled by inputs from the sediment. Although the constant upstream PCB load in the forecast simulations contributes to the PCB concentration in the water column, the shape of the response curve is set by the sediment-to-water PCB fluxes.
   - Predicted PCB concentrations in the surface sediments are **not** controlled by PCB loads generated above Fort Edward. Sediment PCB concentrations are controlled primarily by sediment-to-water flux and exchange between deep and surface sediments.
   - Water column PCB concentrations are influenced by upstream PCB loadings, with the relative degree of influence increasing with time, due to declining PCB concentrations in the surficial sediments.
2. A 100-year peak flow event would not be expected to have substantial impacts on the recovery rate of the Upper Hudson River.
   - The models predict that approximately 60 kg (130 lbs.) of PCBs would be lost from the Thompson Island Pool in response to a 100-year peak flow (47,330 cubic feet per second).
   - Long-term, summer average PCB concentrations in the water column with and without the 100-year peak flow are virtually indistinguishable one year after the event. (Note that this does not account for potential impacts from PCBs that moved into the Lower Hudson River.)

3. Although there has been net deposition of sediment in the Thompson Island Pool (as well as the entire upper Hudson), there have been losses of PCBs from the sediment. In other words, net deposition does not mean that PCBs will be unavailable to the water column. For example, from 1984 to 1994 (the same time frame analyzed in the Low Resolution Sediment Coring Report) the model estimated that 2000 kg of Tri+ were lost from the Thompson Island Pool sediment inventory, while at the same time 1.6 cm of net sediment deposition occurred on a poolwide basis.

4. There is a contribution of PCBs from the sediment that is not dependent on the flow of the river. Some of the processes that may cause non-flow dependent resuspension are: wind driven dispersion, bioturbation by benthic organisms, bioturbation by demersal fish, mechanical scour by propwash, boats and floating debris, and uprooting of macrophytes by flow, wind or biological action. Such a non-flow dependent load is important because the model calibration suggests that approximately 80 percent of the total PCB transport down the river from 1991 to 1997 took place during low-flow periods.

5. Forecasts for the FISHRAND model suggest that largemouth bass will achieve 2.0 ppm on an average wet weight basis between 2008 and 2014, with the best estimate of 2011 for river mile 189 (within the Thompson Island Pool), and between 2011 and 2019 (best estimate 2015) for river mile 168 (Stillwater) under constant upstream boundary conditions. Largemouth bass average values will not achieve target levels of 1.1 ppm or 0.2 ppm within the 21-year forecast period at these locations. In addition, the 95$^{th}$ percentile value (a statistically important value that is frequently used in evaluating a high-end risk and/or as part of the evaluation of uncertainty around the range of predicted values) will not achieve any of the target levels in the forecast period. Note that the target levels are for comparison purposes only, and that appropriate levels will be determined in the Feasibility Study.

6. Forecasts suggest that for river mile 189, average values for yellow perch will achieve 2.0 ppm between 2007 and 2014 (best estimate 2010), and 1.1 ppm between 2015 and 2021. 95$^{th}$ percentile values would not reach any of the targets within the forecast period. Average yellow perch values will achieve 2.0 ppm between 2008 and 2014 (best estimate 2011) for river mile168, but the lower target values and the 95$^{th}$ percentile values will be not reached within the forecast period.

7. For brown bullhead, the average fish body burden is forecasted to reach 2.0 ppm between 2014 and 2020 (best estimate 2017) at river mile 168. Within the 21-year forecast period, no other target levels will be achieved for average brown bullhead at river mile 168, and none of the target levels are achieved at river mile 189.

8. At river miles 157 and 154, forecasts for all species modeled achieved the FDA action level of 2 ppm by 2021, even at the 95$^{th}$ percentile value.

9. For all locations and species modeled, predicted average body burdens did not fall below 0.5 ppm within the 21-year forecast period.

**SUMMARY**

The principal processes that control contemporary PCB dynamics in the Upper Hudson River are hydraulics, external solids load, sediment-to-water fluxes, water-to-air fluxes and PCB fate in the bedded sediments. It appears that the river is currently on the tail of a long PCB washout curve controlled largely by the rate at which PCBs are being reduced in the upper mixed sediment layer. Consequently, forecasts of system responses depend on an accurate representation of processes controlling solids dynamics and PCB interactions across the sediment-water interface.

The forecasting results suggest that the water column and sediments of the Upper Hudson River will not have reached steady-state by 2018 (the end of the forecast period). At that time, even with constant upstream PCB loads, water concentrations still show a declining trend, suggesting that the sediments continue to be a source of PCBs to the system.

In their present forms, the models are useful tools for providing information on PCB exposure concentrations for the Human Health and Ecological Risk Assessments. Additional modeling efforts will be conducted to fine tune the model for predicting the time it takes for the system to recover. The results of these additional modeling efforts will be made available as part of the Responsiveness Summary for this report.

THIS PAGE LEFT BLANK INTENTIONALLY

# 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 (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 (TAMS/Gradient, 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 (TAMS/Gradient, 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 Database Report (Volume 2A in the Phase 2 series of reports; TAMS/Gradient, 1995) and accompanying CD-ROM database provides the validated data for the Phase 2 investigation. This Baseline Modeling Report (BMR) utilized the Hudson River Database, Release 4.1b, which was updated in Fall 1998 (TAMS et al., 1998a) The BMR is Volume 2D of the Reassessment documentation and is the fourth of a series of six reports describing the Phase 2 characterization and analysis activities. It presents results and findings from application of mathematical models for PCB transport and fate and bioaccumulation in the Upper Hudson River.

## 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 project.

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 these 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 these 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 long-term responses to continued No Action and impacts due to a 100-year peak flow. 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 TIP for a given peak flow. 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 development tasks that were necessary to provide model inputs and to support post-processing of model outputs. Chapter 7 presents results and findings from application of the HUDTOX model to existing historical data, including data collected as part of the Phase 2 investigation. Finally, 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.

## 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 their 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.

# Chapter 2

# 2. MODELING APPROACH

## 2.1. Introduction

The overall modeling approach in this Reassessment is based on the principle of conservation of mass. Models were developed for transport and fate of PCBs in the water column and bedded sediments, and for PCB bioaccumulation in fish populations. The spatial domain of these models was the Upper Hudson River between Fort Edward and Federal Dam at Troy (Figure 1-2). Emphasis was placed on 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.

Section 2.2 presents the overall modeling framework used in this Reassessment. Sections 2.3 and 2.4 describe the hydrodynamic model and the Depth of Scour Model (DOSM), respectively, that were developed and applied to TIP. 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. Section 2.7 presents an overview of the database used for model development and applications.

## 2.2. Conceptual Approach

The overall conceptual framework for the Reassessment models is illustrated in Figure 2-1. Depicted are the principal individual modeling components and their inter-relationships. The hydrodynamic model, the DOSM and HUDTOX comprise the transport and fate models. The linkage module serves only 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 Food Chain Model quantify linkages between PCB water column and sediment concentrations and fish body burdens. These models are the subject of Books 3 and 4.

## 2.3. Hydrodynamic Model

The hydrodynamic model is time-variable, two-dimensional and vertically-averaged. It was applied to TIP in steady state mode to provide hydraulic information for the HUDTOX model and information on bottom shear stresses at the sediment-water interface for the DOSM. The hydrodynamic model includes explicit representation of the flood plain to account for overbank flow during flood events.

The hydrodynamic model was not directly integrated with the HUDTOX model. Output from the hydrodynamic model was spatially and temporally processed using a linkage module that transformed water velocities into flows that were routed among the HUDTOX model spatial segments in TIP. Water velocities were also transformed into applied shear stresses at the sediment-water interface for use in DOSM and HUDTOX. 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 TIP. It is a specialized tool for providing spatially-refined information on sediment erodibility in response to flood events. Information on sediment physical properties and PCB concentrations was provided to the DOSM from field measurements. Information on applied shear stresses at the sediment-water interface was provided to the DOSM as output from the hydrodynamic model.

The DOSM was used in two different ways. First, the DOSM was used as a stand-alone tool to provide mass estimates of solids and PCBs eroded, and depth of sediment bed scour, in response a 100-year peak flow. Second, the DOSM was used to develop relationships between river flow and cohesive sediment resuspension. These relationships were used in the HUDTOX model in the form of algorithms describing flow-dependent cohesive sediment resuspension. To develop these relationships, the DOSM was run for a range of flows using output for applied shear stresses from the hydrodynamic model.

## 2.5. Mass Balance Model

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 substantial amount of PCB-contaminated sediment is contained in TIP, the TIP portion of HUDTOX included greater spatial resolution than the portion downstream of TID. In TIP, HUDTOX is two-dimensional in the water column and three-dimensional in the sediments. Between TID and Federal Dam it is one-dimensional in the water column and two-dimensional in the sediments.

Three types of mass balances are represented in HUDTOX: (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 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.

Output from the hydrodynamic model was used to provide hydraulic routing information for HUDTOX in TIP. Hydraulic routing downstream of TID was one-dimensional and was specified using USGS flow gage data at Fort Edward and estimated flows from downstream tributaries. Output from the DOSM was used to provide information on resuspension for HUDTOX in the form of flow-resuspension algorithms that were part of its dynamic solids mass balance. This linkage between the DOSM and HUDTOX ensured internal consistency in representation of flow-dependent resuspension between these two models for cohesive sediments. Output from HUDTOX for PCB concentrations in the water column and bedded sediments provided PCB exposure information for the ecological and human health investigations in the Reassessment.

## 2.6. Mass Balance Model Applications

Developmental applications and model calibrations were conducted with HUDTOX using historical data for the period January 1, 1977 to September 30, 1997. Differences in HUDTOX model applications were determined by model calibration strategy and data availability. In broad terms, the model calibration strategy involved testing HUDTOX over different physical conditions in the river, different PCB physical-chemical properties and different time frames. The calibrated model was used to conduct forecast simulations for a 21-year period 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.

HUDTOX applications included mass balances for four different PCB forms: total PCBs, Tri+, BZ#4 and BZ#52. 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 applications, Tri+ was used as a surrogate for total PCBs. 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 (TAMS et al., 1998b). BZ#4 is a dichloro congener that represents a final product of PCB dechlorination in the sediments (TAMS et al., 1997). 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 (TAMS et al., 1997). Because BZ#4 and BZ#52 have different physical-chemical properties, especially partitioning, their inclusion imposes tighter constraints on the HUDTOX model calibration and enhances its scientific credibility.

Most of the calibration effort was focused on the period 1991 to 1997 because this period was relatively data-rich in terms of parameters measured, spatial-temporal coverage and data quality. Applications for this period included all four PCB forms, total PCBs, BZ#4, BZ#52 and Tri+. To strengthen the scientific credibility of the model, a long-term hindcasting application was conducted for the period 1977 to 1997. This application included only Tri+ because this was the only one of the four PCB forms for which data were available over a long historical period. The principal emphasis in the hindcast application was on the period from 1984 to 1997 due to uncertainties in sediment PCB concentrations in 1977 and PCB inputs at Fort Edward between 1977 and 1984. The 21-year forecast simulations were conducted for total PCBs because total PCB concentrations are required for the ecological and human health risk assessments.

In the Preliminary Model Calibration Report (PMCR), short-term calibrations were conducted for five PCB congeners or groups of co-eluting congeners: BZ#4, BZ#28, BZ#52, BZ#90+101 and BZ#138. The period of simulation for these calibrations was from January 1 to September 30, 1993. In the present report the short-term calibrations for BZ#4 and BZ#52 were extended to include the period from 1991 to 1997. The scientific credibility of the HUDTOX model can be further strengthened by extending the short-term calibrations for BZ#28, BZ#90+101 and BZ#138. Calibration work with these three additional congeners is planned.

## 2.7. Hudson River Database

All modeling work in this report utilized the extensive database that was created to support this Reassessment. The Database Report (TAMS/Gradient, 1995) and accompanying CD-ROM database provides the validated data for the Phase 2 investigation. This Baseline Modeling Report (BMR) utilized the Hudson River Database, Release 4.1b, which was updated in fall 1998 (TAMS et al., 1998a). 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)
- 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.

# 3. THOMPSON ISLAND POOL HYDRODYNAMIC MODEL

## 3.1. Introduction

The Thompson Island Pool (TIP) 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 TIP was to provide hydraulic routing information for the HUDTOX model and information on bottom shear stresses at the sediment-water interface for the DOSM and HUDTOX. A 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 which is considered to be a flow of 47,330 cfs (Butcher, 1993). The computation of a two-dimensional vertically averaged velocity field is necessary to account for the lateral variability of the flow, which in turn allows for the estimation of a bed shear in the entire flow domain. The bed shear is used to compute the mass of cohesive sediments eroded in the 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 pool-wide resuspension of PCBs.

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, Richards (1990)). The choice of a two-dimensional vertically averaged model, and the density of the grid mesh was 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

The hydrodynamic model was applied for a range of steady flow conditions in the TIP. Transient effects due to storage and drainage were not included in the RMA-2V simulations because the HUDTOX model applies constant flow routing. The historical flow record at Fort Edward shows that the Hudson River high flow events occur over several days which gives the TIP enough time to establish steady state conditions. The credibility of the numerical 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 description of the hydrodynamic modeling effort is divided into eight sections. Section 3.2 describes the hydrodynamic modeling approach. Section 3.3 describes the input data required by the model to simulate TIP. Section 3.4 describes the model calibration. Section 3.5 describes model validation. Section 3.6 describes model sensitivity in response to changes in various model inputs. Section 3.7 outlines the conversion of the vertically averaged velocities computed by the model to the corresponding bed shear stresses. Finally, Section 3.8 contains a discussion of the model results.

## 3.2. Modeling Approach

A short summary of the modeling procedure is as follows. A finite element grid was first constructed for the TIP section of the river and floodplain. The 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 variables u and v, represent the vertically averaged velocity field in the downstream and cross stream directions respectively. The depth of flow is given by the variable, h. To solve for these three variables, three equations are needed. An additional relationship for the bottom stress is used to close the set of equations. These are as follows:

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$^2$] |
| $a_0$ | = | bottom elevation [L] |
| $C_f$ | = | flow roughness coefficient [dimensionless] |
| $n$ | = | Manning's 'n' channel roughness coefficient [dimensionless] |
| $E_{xx}$ | = | 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)] |
| $\rho$ | = | 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 the other forces for the Hudson River.

### 3.2.2. Computational Procedure

The RMA-2V model was first calibrated to the measured hydrodynamic data of 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 are as follows:

1) The flow field velocity and depth for each node were determined using RMA-2V;

2) The bed shear velocity u* for each node was determined from calculated velocity and depth at each node;

3) The bottom shear stresses were then calculated from the bottom shear velocities using the relation; and.

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

4) The calculated TIP velocities were used to determine the discharges for each HUDTOX segment.

### 3.3. Model Input 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, the use of 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 6000 nodes defining 3000 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 TIP channels. This is justified because velocities in the floodplain are much smaller than in the TIP 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. Conservation was achieved within approximately six percent and this was judged compatible with the requirements of the HUDTOX model. 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 it is judged that these changes 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 and 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 then 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. Forcing Functions

The principal forcing function of the model consists of the upstream boundary condition, which is the specified flow. The model was run for the eight different flows 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 they represent high flow events with a specified return period.

The model results for these eight flows were used in the DOSM to develop relationships between river flow and solids resuspension. These flows were specified at the most upstream transect of the model grid. This transect is approximately 500 feet upstream of Rogers Island.

### 3.3.4. Boundary Conditions

The boundary conditions of the model consist of the side-channel boundary condition and the downstream boundary condition. The side-channel boundary condition is the requirement that the velocity normal to the sides of the channel is 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 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 (TAMS et al., 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 engineering best judgment and a theoretical rating curve (Zimmie, 1985) was used to determine the water levels at Thompson Island Dam above these flows.

## 3.4. Model Calibration

The calibration approach consists of determining an appropriate value for the turbulent exchange coefficients and then varying the Manning's 'n' so that the river levels computed by the model agree with the river levels predicted by the upstream rating curve for each flow input at the 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 Gage 119, near Lock Number 7, which is near the southern tip of Rogers Island (Figure 3-1).

Because this component of the study is primarily interested in 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 Gage 119 (upstream) and 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$^2$), based on the guidelines given in the RMA-2V manual (Thomas and McNally, 1990). Specifically, the guidelines given in the manual suggest a range of values from 479 to 4, 790 Pa-sec (10 to 100 lb-sec/ft$^2$), and the stage and discharge results proved to be relatively insensitive to variations within this range of values.

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).

As seen when comparing the last two columns in Table 3-3, the model's results are slightly higher than the rating curve for the smaller flows, implying that the calibrated Manning's 'n' appears to be somewhat low for the lower-flow cases. Nevertheless, it was judged that a higher value could not be justified, given the model's close fit for 30,000 cfs, because a higher Manning's 'n' would 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. Model Validation

There were two additional and separate sources of information used to validate the calibration results. The first source is the Hudson River velocity measurements made in the TIP by the USGS. The second source is the flood study conducted by FEMA. A comparison between 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 TIP 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. Using these data, the model's simulated velocities can be compared to the 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 that were 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. Even though these values are sufficiently close for validation, it should be noted that the measured velocities were expected to be slightly higher, because the bridges from which the velocity measurements are taken constrict the flow, causing localized higher velocities. The model does not include the localized effect of flow restriction due to bridge piers.

### 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 check 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. However, the model was eventually 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 (with higher Manning 'n' values) predicted a river elevation of 130.7 ft. NGVD. These results are comparable and each model reflects 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 the FEMA flood studies.

### 3.5.3. 100-Year Peak Flow Model Results

The model was run for the 100-year peak flow of 47,330 cfs, and 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.

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. Examining the flow patterns provides a visual check on the model performance. This velocity field was used to compute the shear stresses for the DOSM.

## 3.6. 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 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. Sensitivity to Manning's 'n'

The Manning's 'n' was varied over a reasonable range for the main channel and the floodplain. The model was run for the 100-year peak flow of 47,330 cfs and 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 will depend 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. The RMA-2V manual provides guidelines in choosing values for these coefficients. These guidelines are: 1) in general, there is a tendency for these coefficients to be assigned at values that are too high rather than too low; and 2) most rivers without flow reversal will have coefficients in the range of 479 to 4,790 Pa-sec (10 to 100 lb-sec/ft$^2$). Table 3-5 shows the effects of varying these turbulent exchange coefficient values in the calibrated model.

It can be concluded that variations 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. This means that if higher turbulent exchange coefficients were used in the calibration, then a lower Manning's 'n' would be used to obtain equally good agreement with the observed rating curve. Given these results, it was judged that a turbulent exchange coefficient of 100 was reasonable and that further calibration was not required.

## 3.7. Conversion of Vertically Averaged Velocity to Shear Stress

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

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 follows the smooth wall log velocity profile. The following equation describes this velocity profile.

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

where:

| | | |
|---|---|---|
| $u$ | = | vertically averaged velocity |
| $u*$ | = | shear velocity |
| $d$ | = | depth of flow |
| $\nu$ | = | kinematic viscosity. |

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

2) Gailani Method

This method was used by Gailani (Gailani et al., 1991), for the Fox River

$$\tau_b = 0.003\ u^2 \quad \textbf{(3-7)}$$

where:

$\tau_b$ = bottom shear stress.

This relation is based on empirical approach.

3) Rough wall log velocity profile

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

where:

| | | |
|---|---|---|
| $u$ | = | vertically averaged velocity. |
| $u*$ | = | shear velocity (friction velocity). |
| d | = | depth of flow. |
| k | = | equivalent Nikuradse roughness. |

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

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

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

This shear stress conversion (Thomas and McNally, 1990) above is based on combining equations which represent cross-section average velocity and bottom shear stress. Specifically, the one-dimensional Manning equation for channel averaged velocity which is given below as,

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

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

The definition of the cross-sectional average shear stress ($\tau_0$), can be written as,

$$\tau_o = wRS = \rho gRS \qquad \textbf{(3-13)}$$

where:

| | | |
|---|---|---|
| $u$ | = | channel averaged velocity, |
| n | = | Manning's 'n' , |
| g | = | acceleration due to gravity, |
| w | = | weight of the water ($\rho$g) , |
| $R$ | = | hydraulic radius, |
| $S$ | = | the slope of the river. |

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

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

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

Note that although normally both equations are only valid for the whole cross-section of the river, the finite element model, RMA-2V, actually uses the above formulations in local flow field calculations.

Figure 3-4 shows the variation of shear stress with the average vertical velocity for the four different 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, yields 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 would provide the most conservative estimate for the DOSM.

The shear stress field for the Thompson Island Pool 100-year peak flow as computed by Method 4 using the velocity field shown in Figure 3-3, is plotted out Plate 3-1. 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 as compared to 0.02 in the main channel.

### 3.8. Discussion

The calibrated RMA-2V model is a reasonable representation of TIP 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, depending on the conversion method used. 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.

THIS PAGE LEFT BLANK INTENTIONALLY

# Chapter 4

# 4. THOMPSON ISLAND POOL DEPTH OF SCOUR MODEL

## 4.1. Introduction

The Depth of Scour Model (DOSM) is a two-dimensional, GIS-based sediment erosion model that was applied to Thompson Island Pool. It is a specialized tool for providing spatially-refined information on sediment erodibility in response to flood events. The DOSM was used as a stand-alone tool to provide gross mass estimates of solids and PCBs eroded, and depth of sediment bed scour, in response to a 100-year peak flow. The DOSM does not account for subsequent transport or redeposition of eroded material. The primary use for the DOSM in this study was to develop relationships between river flow and cohesive sediment resuspension. These relationships were used in the HUDTOX model in the form of algorithms describing flow-dependent resuspension.

The DOSM is based on separate empirical erosion equations for cohesive and non-cohesive sediments; the equations are fully predictive for cohesive sediments but give only upper bound estimates for non-cohesive sediments. The DOSM application for the 100-year peak flow was designed to address the following questions:

1. What is the range of expected scour depths in TIP?,
2. How do these depth of scour ranges compare to observed depth profiles of PCB concentrations at five Phase 2 high resolution coring sites?; and
3. What is the expected range of total PCB and solids mass eroded from cohesive sediments throughout TIP?

The DOSM was designed to address the question of the potential risk of resuspension of PCBs from the deeply buried sediments of TIP in response to a "catastrophic" flood event. The model provides quantitative and qualitative information to estimate this risk. It was used to estimate the total mass of solids and PCBs eroded for the 100-year peak flow (hydrodynamic modeling of this peak flow is discussed in Chapter 3). In addition, more detailed estimates of local scour at selected locations in TIP were conducted. As part of the Phase 2 monitoring program, sediment cores were taken at five locations in areas containing cohesive sediments in TIP and analyzed at a high vertical resolution. These sediment cores showed peak PCB concentrations in excess of 2,000 ug/g (dry weight). The vertical resolution of PCB data at these locations allows a more detailed investigation of the potential risk of scour in response to large events. These analyses were carried out, including an explicit consideration of the uncertainties in the resulting estimates.

Section 4.2 describes the development of the DOSM, including model conceptualization and formulation for cohesive and non-cohesive sediments. Section 4.3 describes the parameterization of the DOSM, including a description of the data available to support the model and how it was used for parameterization. Section 4.4 describes the application of the DOSM, including 1) comparison of predicted ranges for depth of scour at each of the five Phase 2 high resolution coring sites with observed PCB concentration profiles, 2) poolwide computations for total mass of PCBs and solids remobilized from cohesive sediments throughout TIP, and 3) determination of the mean depth of scour in cohesive and non-cohesive sediments.

## 4.2. DOSM Model Development

### 4.2.1. Conceptualization

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 is the shear stress exerted at the sediment-water interface by flowing water. The TIP Hydrodynamic Model yields estimates of velocities at a fine spatial resolution. Bottom shear stresses are computed from the velocities by a simple formula (Section 3.7). Second, the physico-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.

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 which are primarily fine grained and/or possess a high clay content exhibit interparticle effects which 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.

### 4.2.2. Formulation for Cohesive Sediments

**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:

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

where M is the mass of material resuspended, $\tau$ is the applied shear stress, and $\tau_c$ is the bed critical shear stress. The function f has been expressed in a variety of different forms ranging from linear, e.g. Partheniades (1965), exponential, e.g. Parchure and Mehta (1985), and the power relationship developed by Lick and co-workers, e.g. Gailani et al. (1991).

## Basic Equations

Lick et al. (1995), based on statistical analysis of laboratory and field data, proposed an erosion equation of the following form:

$$\varepsilon = \frac{a_0}{t_d^n} \times \left( \frac{\tau - \tau_c}{\tau_c} \right)^m \qquad \textbf{(4-1)}$$

where $\varepsilon$ is the net total amount of material resuspended (g/cm$^2$); $\tau$ is the applied shear stress and $\tau_C$ is the bed critical shear stress (dynes/cm$^2$); $t_d$ is the time after deposition; and $a_0$, n, and m are empirical constants.

The depth of scour can then be calculated as:

$$Z_{scour} = \frac{\varepsilon}{C_{bulk}} \qquad \textbf{(4-2)}$$

where Zscour is the depth of scour (cm), and Cbulk 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.

## Reparameterization to a Probabilistic Model

If the value of $\tau_C$ is known or assumed, while the other parameters are unknown, then Equation 4-1 can be reduced from five parameters to two using a dimensionless shear stress parameter $\tau'$:

$$\varepsilon = A \times (\tau')^m \qquad \textbf{(4-3)}$$

where:

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

Equation 4-3 can be linearized as follows:

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

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.

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., 1985). 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 4-5.

$$\varepsilon = \mathbf{exp}\left(A + m \times \mathbf{ln}\left(\tau'\right) + u\right) \qquad \textbf{(4-5)}$$

where:

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

and

| | | |
|---|---|---|
| $\tau'$ | = | $(\tau - \tau_c) / \tau_c$, |
| **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 cm, as shown in Equation 4-2.

**Calculation of PCB Erosion**

Equations 4-2 and 4-5 define a probabilistic model for predicting mass erosion and depth of scour as a function of shear stress and sediment physical properties. An estimate of the poolwide PCB erosion from cohesive sediments can then be determined as a function of sediment PCB concentration using Equation 4-6.

$$P = \frac{S \times C_{PCB}}{\left(\frac{1000mg}{1g}\right)} \qquad \textbf{(4-6)}$$

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). |

### 4.2.3. Formulation for Non-cohesive Sediments

**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 as a result of the flow exceeds the critical shear stress of the particle size class. When the flow continuously has excess transport capacity the bed is scoured as transportable particles are entrained when exposed at the bed surface. Because the transport capacity of the flow is inversely related to the particle size, 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 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 smaller particles sheltered underneath them. 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.

**Equations**

Borah (1989) gives equations for the depth of scour that will occur before the establishment of an armor layer, assuming a well mixed surface layer with constant particle specific gravity, and that a monolayer of the smallest nontransportable particle present in the bed material will be created. The formulation is conservative in that the potential for finer particles to be trapped (hiding) in the armor layer is ignored. An active layer thickness is defined as:

$$T = \frac{D_a}{(1-\phi)P_a} \tag{4-7}$$

where T is the thickness of the active layer (cm); $D_a$ is the smallest armor size (cm); $\phi$ 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:

$$E = T - D_a \tag{4-8}$$

where E is the scour depth. 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. Temporal Scale

The cohesive computations result in a mass estimate for the entire event assuming that the event peak shear stress is established 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 result in a mass estimate corresponding to scour down to the armoring depth. The temporal scale 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.

## 4.3. DOSM Parameterization

### 4.3.1. Data

**Distribution of Types of Bottom Sediment**

The bedded sediments in TIP were delineated 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 "coarser", "finer", "island", and "rocky". These maps were digitized into a GIS coverage by TAMS Consultants, Inc.. 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. No sediments described as "coarse" were listed for Thompson Island Pool. The area of non-cohesive sediments in TIP is approximately three times that of cohesive sediments.

**Resuspension Experiments**

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

The first data set came from an annular flume study, wherein sediments from three different locations in TIP 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 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 4-1. 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.

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 TIP and 8 locations downstream; each location had one (TIP) 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 TIP. The shear stresses used in the field study ranged from 5 to 11 dynes/cm$^2$. Observed sediment erosion rates in TIP ranged from 0.06 to 28.84 mg/cm$^2$.

From the TIP-specific data, HydroQual (1995) assumed a TIP-wide constant value of 3 for m, and back-calculated 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.

**Non-Cohesive Particle Size Distributions**

The Borah formulation described above requires sediment data on particle size distribution, particle density, and wet bulk density (the last as a means to get porosity). An obstacle encountered in using the core data was that some 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% or size 20 mm.

Two limitations of the above method are: 1) extrapolations and data substitutions contribute to model uncertainty, and 2) the method would require modification to handle correlations, if any, between the physical property distributions.

**Sediment PCB Concentration**

As an illustrative example, the DOSM was used to estimate a range for the mass of PCBs eroded from the sediments of TIP in response to a specified peak flow. To use the DOSM for this example, it was required that sediment PCB concentration be specified as a model input. The median value of samples of the cohesive sediment surficial total PCB concentrations (TAMS et al., 1998a) was found to be 32.5 mg/kg. This value was used to approximate the surficial cohesive sediment PCB concentration throughout TIP, although it does not take into account variation of PCB concentration with location and time.

### 4.3.2. Parameterization for Cohesive Sediments

There are several assumptions inherent in the application of Equations 4-2 and 4-5 to the shaker data for parameterization of the DOSM. These include:

- The value for critical shear stress imputed from the annular flume study applies throughout TIP.
- The sediment cores used in the resuspension studies represent an unbiased random sample of TIP 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.
- 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 TIP were considered. A linear regression of natural log erosion (in mg/cm$^2$) vs. natural log $\tau'$ produced an intercept (A) value of -3.829 and a slope (m) value of 2.906 (Figure 4-1). Of 60 TIP 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 outliers were: 1) erosion 0.06 at shear stress 5; and 2) erosion 0.47 at shear stress 11. The regression R-squared value was 0.541. 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 (Section 4.3.1.2) reported by HydroQual.

### 4.3.3. Parameterization for Non-cohesive Sediments

The Borah formulation was used to calculate an armoring depth – shear stress data point for each size fraction of each core with a particle size distribution (core CG-23 was excluded because it produced several outliers). That is to say, a given size fraction corresponds to a minimum particle size which requires a minimum shear stress to scour, and for which an armoring depth is calculated as the depth achieved when all smaller particles are scoured from the active layer. 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 TIP, 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 TIP, 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 4-9.

$$\mathbf{ln}(Depth, cm) = A + m \times \mathbf{ln}(ShearStress, dynes / cm^2) \qquad \mathbf{(4\text{-}9)}$$

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 4-3.

## 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 TIP. Computations made use of shear stresses estimated at the nodal locations where flow field information was available from the TIP 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, fully-integrated 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 solids resuspension that were subsequently used in the HUDTOX model in the form of resuspension algorithms for flow-dependent resuspension. The relationship between the DOSM and HUDTOX ensures internal consistency in representation of flow-dependent resuspension for cohesive sediments between these two models.

### 4.4.2. Model Application to High Resolution Coring Sites

The DOSM was applied to compare expected scour depths in TIP for the 100-year peak flow to observed depth profiles of PCB concentrations at five Phase 2 high resolution coring study sites. Although these sites were not necessarily representative of PCB profiles in cohesive sediments in the entire TIP, they were used because they were identified as cohesive sediment sites by the TAMS/Gradient Team and 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 values for each of the five cores. Average values of dry bulk density somewhat higher than the surficial (0-2 cm) values shown in this table were used for calculating depths of scour greater than two cm.

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.

Median predicted depth of scour provides information on quantities of solids that can potentially resuspend during an event; however, this information alone does not tell us 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 Figures 4-4 through 4-8, 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. Model Application Poolwide

#### Cohesive Sediments

Equations 4-2 and 4-5 can conveniently be used to estimate the total mass of solids remobilized from cohesive sediments throughout TIP, and the mean depth of scour in cohesive sediments, by means of a Monte Carlo Analysis. The cohesive sediment areas of TIP 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 as the values of random variables at each location. 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 3000 repetitions; a sensitivity analysis of the number of repetitions demonstrated that 3000 repetitions was adequate to produce consistent results. The results were plotted as cumulative percent vs. mean depth of scour or mass 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 4-9 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 4-10 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 total PCB concentration in TIP surficial sediments was estimated to be 32.5 mg/kg (TAMS et al., 1998a). Using this concentration value with the above estimate of 1,500,000 to 2,000,000 kg of solids erosion in Equation 4-6 provides an approximate range of gross PCB erosion of 49,000 to 65,000 grams. The actual amount of PCBs eroded by a 100-year peak flow would depend upon the amount of PCBs in the sediments at the time the flood occurred and upon areal and depth variations in PCB concentration.

**Non-Cohesive Sediments**

Equation 4-9 was applied to estimated shear stresses in non-cohesive sediment areas. For the 100 year peak flow, the mean, non area-weighted TIP non-cohesive sediment armoring depth is 13.1 cm. Therefore 13.1 cm is an upper bound estimate of the expected average erosion from non-cohesive sediment areas in TIP resulting from a 100-year peak flow. Upper bound estimates of erosion at specific non-cohesive sediment locations throughout TIP 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 that would occur under the specified conditions, including an uncertainty band for the prediction. The non-cohesive sediment erosion estimate is a value for which it is reasonably certain that the actual erosion would be less than that value, 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 TIP substantially exceeds the 0.317 cm expected value of the mean depth of scour from cohesive sediment areas of TIP. Relative estimates of erosion from cohesive and non-cohesive sediment areas can best be made using the HUDTOX model which contains a dynamic, full-integrated representation of solids dynamics.

THIS PAGE LEFT BLANK INTENTIONALLY

# Chapter 5

# 5. MASS BALANCE MODEL DEVELOPMENT

## 5.1. Introduction

Chapter 5 contains the development of the Hudson River Toxic Chemical Model (HUDTOX), the principal transport and fate modeling tool in this Reassessment. Section 5.2 presents the model approach, including the conceptual framework and the governing equations for model state variables and process mechanisms. Section 5.3 presents the spatial segmentation grid on which the HUDTOX model was applied for the Upper Hudson River. Section 5.4 presents information on model implementation, including details on the hardware and software operating environment.

## 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 substantial amount of PCB-contaminated sediments is contained in TIP, the TIP portion of HUDTOX included greater spatial resolution than the portion downstream of TID. In TIP, HUDTOX is two-dimensional in the water column and three-dimensional in the sediments. Between TID and Federal Dam it is one-dimensional in the water column and two-dimensional in the sediments.

Developmental applications and model calibrations were conducted with HUDTOX using historical data for the period 1977 to 1997. Differences in HUDTOX model applications were determined by model calibration strategy and data availability. In broad terms, the model calibration strategy involved testing HUDTOX over different physical conditions in the river, different PCB physical-chemical properties and different time frames. The calibrated model was used to conduct forecast simulations for a 21-year period 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.

### 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. Since organic carbon is the principal sorbent compartment for hydrophobic organic chemicals in aquatic systems, the approach was to first conduct a time-dependent mass balance for the suspended and bedded sorbent solids, and then to assign organic carbon fractions to these solids. Dissolved organic carbon (DOC) was not simulated in the mass balance, rather, concentrations were held constant in the sediment and the water column.

HUDTOX computes time-dependent mass balances for two state variables: solids and PCBs (total PCBs, Tri+, BZ#4, or BZ#52, 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. 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 upper 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 as a function of 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 HUDTOX model code was originally developed using an earlier version of the WASP model (WASP4/TOXI4) that was updated by EPA to reflect coding error corrections and various enhancements. The primary source for documentation of the 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 only those HUDTOX processes that were modified from the original 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 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:

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

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).

## Water Transport

Advective water column flows directly control the 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 and a time function. The continuity function describes the spatial extent of the inflow response as it varies 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.

Discharge coefficients describing depth and velocity from stream flow are based on formulations developed by Leopold and Maddox (1953) which describe empirical observations of the velocity-depth-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 TIP portion of the Upper Hudson River, the HUDTOX model coefficients describing this relationship were developed from the RMA-2V hydrodynamic model described in Chapter 4. The relationship for downstream reaches was developed using correlations between surface water elevations and flow (TAMS et al., 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 advective or dispersive transport of chemicals between model segments.

Dispersive water column exchanges significantly influence the transport of dissolved and particulate pollutants in such water bodies as lakes, reservoirs, and estuaries. In rivers, longitudinal dispersion can also 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:

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

where:

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

$C$ = total constituent (state variable) concentration, mg/L (g/m3) [M/L$^3$]

$E_{ij}(t)$ = exchange / 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:

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

where:

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

**Solids Dynamics**

HUDTOX uses a finite difference form of the mass balance relationship expressed by Equation 5-1 to calculate sediment and chemical mass and 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.

Solids Gross Settling

HUDTOX differs from WASP5/TOXI5 with respect to gross settling of suspended solids from the water column to the sediment bed. Gross settling in HUDTOX is represented as a flow-dependent process. This approach attempts to capture well-known behavior in rivers whereby increasingly larger, faster-settling particles are entrained as flow increases above a resuspension threshold. The gross settling mechanism in HUDTOX is similar to the empirical relationship used to model particle settling in other river systems (Gailani et al., 1991; Gailani et al., 1996; Ziegler and Nisbet, 1994).

In HUDTOX, gross solids settling speed progresses from a constant low flow value ($v_{sL}$, m/day) to a constant high flow value ($v_{sH}$) between user-specified low and high flow thresholds ($q_{CTL}$ and $q_{CTH}$, cms). These functions are implemented in HUDTOX on a water column segment-specific basis so that reach-specific characteristics affecting the settling speed-flow relationship can be incorporated within these flow-dependent functions.

Cohesive Sediment Flow-Driven Resuspension

The algorithm for flow-driven resuspension of cohesive sediments from the DOSM was incorporated into the HUDTOX model. Total sediment erosion ($\varepsilon$ , mg/cm$^2$) applied to the rising limbs of the flood hydrograph were converted into erosion rates. Non-linear correlations were developed relating the DOSM-predicted sediment erosion in each segment as a function of flow measured at Fort Edward. The erosion was correlated to flow by fitting equations of the form:

$$\varepsilon = \alpha_1 + \alpha_2 \times Q_x^{\alpha_3} \qquad \textbf{(5-5)}$$

where:

$\varepsilon$ = cohesive sediment erosion, mg/cm$^2$
$Q_x$ = advective flow in 1000's of cfs
$\alpha_1$ = empirical constant fit to DOSM results, mg/cm$^2$
$\alpha_2$ = empirical constant fit to DOSM results, mg/cm$^2$/1000 cfs
$\alpha_3$ = empirical constant fit to DOSM results, dimensionless.

The cohesive sediment erosion is converted to an effective resuspension rate ($v_{rE}$, m/day) in the HUDTOX model over each model time step during the rising limb of a flood hydrograph. Because computational time steps in the model are on the order of 30 minutes or less, 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 during an increasing hydrograph is tracked such that total erosion equals the amount computed using the maximum shear stress during the event. Tracking occurs in an incremental fashion, dependent on the change in flow and the cohesive sediment solids concentration (or dry bulk density). The total amount of sediment erosion is limited by the maximum predicted erosion $\varepsilon_{max}$ associated with the peak flow. This flow-driven resuspension effectively stops once the peak flow is reached under the assumption that cohesive sediment armoring has occurred.

HUDTOX also represents a recovery period ($t_{rec}$, days) for the maximum erosion rate to prevent subsequent near-term smaller floods from eroding cohesive sediments that have reached an armored condition.

Non-Cohesive Sediment Flow-Driven Resuspension

The DOSM provides only an upper-bound estimate of non-cohesive resuspension occurring during a flood event because it does not account for armoring as a function of time and deposition of suspended material to the bed. Consequently, the algorithm for non-cohesive resuspension in the DOSM was not incorporated into the HUDTOX model. Flow-driven resuspension of non-cohesive sediments has been incorporated into the HUDTOX model in an empirical manner under the assumption that the rate of erosion is controlled by: bottom shear stress, the critical bottom shear stress, armoring of the sediment bed, and a recovery from armoring of the non-cohesive sediment bed. Armoring occurs when the largest particles that can be resuspended by a specific flow are removed from the surface layer, leaving larger non-resuspendable particles. Armoring can persist until either a higher flow occurs that can resuspend larger particles or the armored layer is degraded due to mixing with the parent bed or deposition of fine material from the water column. Vertical mixing processes may also serve to mix the armored layer with the parent bed material and restore the particle size grading to pre-armored conditions.

The resuspension rate when the bottom shear stress is greater than the critical shear in non-cohesive sediments is described by:

$$V_{rH} = \beta_3 \times \left( \frac{\tau - \tau_c}{\tau_c} \right) \quad \textbf{(5-6)}$$

where:

$V_{rH}$ = high flow resuspension rate, m/day
$\tau$ = bottom shear stress, dynes/cm$^2$
$\tau_c$ = critical shear stress, dynes/cm$^2$
$\beta_3$ = empirical constant, m/day.

The resuspension rate when the bottom shear stress is less than or equal to the critical shear in non-cohesive sediments is described by:

$$V_{rH} = 0 \quad \textbf{(5-7)}$$

The bottom shear is specified as a function of flow:

$$\tau = \beta_1 \times Q_x^{\beta_2} \quad \textbf{(5-8)}$$

where:

$Q_x$ = advective flow in 1000's of cfs
$\beta_1$ = empirical constant fit to hydrodynamic model results
$\beta_2$ = empirical constant fit to hydrodynamic model results.

Armoring effectively increases the critical shear stress over time when bottom shear is above the specified critical value. Degradation of the armored layer returns the critical shear stress to a steady baseline value, $\tau_{c0}$, representative of the particle grading in the parent bed. Representation of the armoring process incorporated in HUDTOX assumes that degradation of the armored layer back to the composition of the parent bed occurs in a linear fashion with complete recovery at a constant time, $t_{rec}$. An empirical relationship describing this process is implemented in HUDTOX as follows:

$$\frac{d\tau_c}{dt} = \beta_5 \times \max(\tau - \tau_c, 0) - \beta_6 \times (\tau_c - \tau_{c0} \quad \textbf{(5-9)}$$

where:

$Q_x$ = advective flow in 1000s of cfs
$\beta_5$ = critical shear "bed armoring" rate for non-cohesive sediments, $day^{-1}$
$\beta_6$ = critical shear "bed recovery" rate for non-cohesive sediments, $day^{-1}$
$\tau_{c0}$ = initial baseline (steady) critical bottom shear stress, dynes/cm$^2$
$\tau_c = \tau_{c0}$ at time t = 0.0.

This relationship is used to adjust the bottom critical shear stress, $\tau_c$, in the non-cohesive sediments at each time step during a model simulation. During non-event conditions, the critical shear approaches the baseline value, $\tau_{c0}$, within a time period determined by the specified "recovery" rate.

Background (Non-Flow-Dependent) Sediment Resuspension

The HUDTOX model includes background, non-flow-dependent solids resuspension. There were two reasons for including this process. The first reason was that even under a condition of zero net advective flow, there are physical processes in the river that cause solids flux (and flux of sorbed PCBs) from the sediment bed to the overlying water column. Some of these processes include wind-driven dispersion, bioturbation by benthic organisms (Thomas et al., 1995; Thibodeaux et al., 1990), bioturbation by demersal fish, mechanical scour by propwash, boats and floating debris, and uprooting of macrophytes by flow, wind or biological action.

The second reason was that most contemporary mass balance models (including HUDTOX) represent flow-dependent resuspension of cohesive sediments using Equation 4-1 by Lick et al. (1995). The parameters in this equation are empirically-derived. Using results from laboratory flume experiments, HydroQual (1995) concluded that the critical shear stress parameter in Equation 4-1 for cohesive sediments in TIP was 1.0 dynes/cm$^2$. This value was used as the critical shear stress for cohesive sediment resuspension in both DOSM and HUDTOX. Recent experimental results by Zreik et al. (1998) claim to achieve better accuracy of critical shear measurements at very low flows and suggest that critical shear stress for cohesive sediment resuspension might actually be closer to 0.1 dynes/cm$^2$. Consequently, the non-flow-dependent background resuspension in HUDTOX may be considered to represent resuspension that occurs under low flow conditions that generate bottom shear stresses between 0.1 and 1.0 dynes/cm$^2$.

There is precedent for using a non-flow-dependent background sediment resuspension rate in contaminated sediment transport and fate models. A similar "background resuspension" process was used by Velleux et al. (1996) to represent sediment resuspension in a PCB mass balance model for the Fox River. Velleux, et al. suggest that the apparent resuspension rate for this process can range from 0 to 0.3 cm/yr.

Sediment Particle Mixing

Bioturbation and other physical processes discussed above can result in mixing of solids (and sorbed chemicals) between different layers within the bedded sediment. Investigators in other studies have estimated effective biodiffusion coefficients ranging from approximately 1-100

$cm^2/yr$ (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. These sediment mixing processes are represented in HUDTOX by particle mixing exchange coefficients which range from 36.5 $cm^2/yr$ between the top two sediment layers (0-2 and 2-4 cm) to 0.365 $cm^2/yr$ between sediment layers three and four (4-6 and 6-8 cm) (see Table 7-1). Operationally, some degree of sediment particle mixing occurs to a depth of 8 cm in HUDTOX. The form of this particle mixing 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.

Scour and Burial

The HUDTOX model uses an improved sediment bed handling approach from that in WASP/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 WASP/TOXI5: 1) implementation of an alternative sediment bed handling routine; and, 2) implicit specification of a dynamic boundary condition in an archival stack of deep sediment layers. The following paragraphs describe the implementation of this alternative bed handling through a set of modifications to the WASP5/TOXI5 scour and burial processes.

In simple terms, the revised sediment bed handling routine eliminates the sedimentation time step as a "burial/scour" trigger and maintains the integrity of the deeply buried sediments as sedimentation and erosion occur. With the revised framework, the surficial sediment layer volume varies 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.

Figures 5-2 and 5-3 illustrate the manner in which HUDTOX implements scour and burial of surficial sediment segments. In the HUDTOX bed handling framework, burial results in no numerical mixing of chemicals to deeper sediments, because the surficial sediment segment is simply split into two and renumbering of the segments is triggered whenever its volume doubles. Erosion of the surficial 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 surficial segment once it has been effectively depleted. However, no additional mixing occurs through the deeper sediment segments. These deeper segments are subject to renumbering when erosion occurs, but they still maintain their original pre-erosion characteristics.

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 WASP/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 surficial 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 surficial sediment segments. The process of decay is not currently allowed in the archive stack, but it could easily be added in future applications because the time at which a segment is added to the archival stack is also tracked. Although the HUDTOX model framework allows for dechlorination and other degradation processes, these loss processes were assumed to be zero in the HUDTOX applications presented herein.

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 surficial layer is allowed to grow in thickness (the bed solids density is kept constant) until renumbering is triggered, based on a doubling of the surficial sediment volume. The surficial 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 surficial 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. 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.

The HUDTOX scour/burial approach also requires the computational upper portion of the bed to be composed of layers of equal thickness. This insures that long periods of scour and deposition will not result in a change to the basic physical characteristics (e.g. the original volume and thickness) of the surface sediments.

**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 physico-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 currently represented in the HUDTOX model. 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).

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). Karickoff (1979; 1984) has 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: truly dissolved, particulate-bound, and DOC-bound.

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 used in HUDTOX are:

$$K_p = f_{oc} \times K_{poc} \tag{5-10}$$

$$K_B = 1.0 \times K_{doc} \tag{5-11}$$

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].

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

The dissolved organic carbon (DOC) partition coefficient, $K_{doc}$, is typically 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. This dependence was developed and presented in the DEIR (TAMS et al., 1997). The general form of the resulting empirical relationship, applicable to both the particulate and DOC partition coefficients, is represented by:

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

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 Di Toro (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 (TAMS et al., 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/kg 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:

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

$$f_b = \frac{C_B B}{C} = \frac{K_B B'}{1 + K_B B' + K_p M_s'} \qquad \textbf{(5-16)}$$

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.

Air-Water Exchange

Air-water exchange 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. 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 7.

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:

$$K_v = (R_L + R_G)^{-1} = \left[ K_L + \left( K_G \frac{H_T}{RT_K} \right)^{-1} \right]^{-1} \qquad \textbf{(5-17)}$$

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
$R$ = universal gas constant, $8.206 \times 10^{-5}$ atm m$^3$/mole °K
$T_K$ = water temperature, °K
$H_T$ = Henry's Law constant at temperature T (°C), atm m$^3$/mole.

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. Future work is planned to investigate the significance of gas exchange at dams on PCB dynamics in the Upper Hudson River.

Air-water exchange in HUDTOX is the same as in WASP5/TOXI5 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:

$$\log H_T = \log H_{25} \frac{\left(7.91 - \frac{3414}{(T - T_0)}\right)}{\left(7.91 - \frac{3414}{(25 - T_0)}\right)} \tag{5-18}$$

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 used for 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:

$$K_a = \left( \frac{D_w u}{D} \right)^{1/2} \times 8.64 \times 10^4 \qquad \textbf{(5-19)}$$

where:

$K_a$ = reaeration velocity, m/day
$D$ = water depth, m
$u$ = water velocity, m/sec
$D_w$ = diffusivity of oxygen in water, $m^2$/sec.

The computed rearation rate is adjusted to determine a chemical-specific liquid film air-water transfer rate based on the ratio of molecular weights:

$$K_L = K_a \left( MW_{O_2} / MW \right)^{1/2} \qquad \textbf{(5-20)}$$

where:

$MW$ = molecular weight of the chemical, g/mole
$MW_{O_2}$ = molecular weight of the oxygen molecule (as $O_2$) = 32 g/mole.

Tsivoglu and Wallace (1972) show this ratio to be constant regardless of the level of turbulence in the receiving water body. A detailed description of the two-layer resistance model used in HUDTOX and WASP5/TOXI5 is contained in Ambrose et al. (1993).

Sediment-Water Mass Transfer of PCBs

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 x $10^{-6}$ $cm^2$/sec, estimated that mass transfer rates due to molecular diffusion applied to the dissolved phase of a chemical in sediment pore water would be on the order of 0.02 cm/day. Application of this mass transfer rate to pore water concentrations of PCBs will result in a relatively small mass flux from sediments to water.

Numerous sediment studies have shown that molecular or Brownian diffusion is not the only mechanism driving sediment-water exchange. Greatly enhanced sediment-water mass transfer of chemicals like PCBs has been shown to occur as a consequence of mixing processes within the upper 2-10 cm of bottom sediments (see above discussion on sediment particle mixing). Several authors have shown that by continually replacing sediment particles at the interfacial boundary with new sediment particles and associated pore water from deeper layers, these mixing 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). For example, 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 pore water chemical) mass transfer rate would be approximately 12 cm/day.

In river systems, sediment mixing can result in sediment-water mass transfer of both pore water and particulate phase PCBs. HUDTOX represents diffusive exchanges of dissolved and DOC-bound PCBs between sediment pore water 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 pore water. Depending on the PCB concentration gradients, pore water diffusion may be a source or sink for the water column. .

Sediment mixing in rivers can also result in sediment-water mass transfer of particulate phase PCBs 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). HUDTOX represents this net 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 (Table 7-5).

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.

### 5.3. Model Spatial Segmentation

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 was represented from Rogers Island (RM 194.6) to Federal Dam (RM 153.9) at Troy (Figure 5-4, Parts A through D).

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;
- Known, significant sources of direct PCB loading to the river;
- Phase 2 and historical water quality sampling stations;
- USGS gaging stations; and,
- Sediment PCB "hot spots" 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 data sets in reaches of the river covered by both surveys, including TIP. 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 TIP to better resolve potential differences in impacts from cohesive and non-cohesive sediment areas. The 28 water column segments within TIP 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 TIP. The flow routing pattern was held constant over the entire range of flows simulated.

The 19 one-dimensional water column segments between TIP and Federal Dam were developed to capture the impacts of hydrologic features of the river, including dams, as well as sediment PCB "hot spots". 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. Tables 5-2A and 5-2B present the spatial configuration and geometry of the HUDTOX sediment segmentation, including the assignment of cohesive and non-cohesive sediment areas. 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. The longitudinal variation in cohesive sediment abundance in the HUDTOX model is depicted in Figure 5-8.

Surficial sediment segment surface 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 (TAMS et al., 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 % or more cohesive sediment area were assigned both cohesive and non-cohesive sediment segments, unless they contained more than 85 % cohesive sediment area, in which case only a cohesive sediment segment was assigned; and,
- Water column segments underlain by less than 15 % 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 surficial 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 surficial sediment segments. The longitudinal variation in cohesive sediment abundance within the Upper Hudson River is depicted in Figure 5-8.

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

### 5.4. 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 personal 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 personal 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.

# Chapter 6

# 6. DATA DEVELOPMENT

## 6.1. Introduction

The applications of the HUDTOX mass balance model required a large effort to organize and process primary data for use as model input and for model calibration targets. This chapter contains a summary of the data development effort. Section 6.2 presents an overview of the Hudson River Database. Section 6.3 presents summaries of the principal water column and sediment datasets used in the modeling analysis. Section 6.4 describes synthesis of river flow data and development of external loadings and in-river mass fluxes for solids and PCBs. External loadings were the most important model inputs and in-river mass fluxes were important model calibration targets.

## 6.2. Hudson River Database

All modeling work in this report utilized the extensive database that was created to support this Reassessment. The Database Report (TAMS/Gradient, 1995) and accompanying CD-ROM database provides the validated data for the Phase 2 investigation. This Baseline Modeling Report (BMR) utilized Release 4.1b, which was updated in fall 1998 (TAMS et al., 1998a). 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)
- 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.

The Data Evaluation and Interpretation Report (DEIR) (TAMS et al., 1997) and the Low Resolution Sediment Coring Report (LRSCR) (TAMS et al., 1998b) are companion reports to this Baseline Modeling Report (BMR). 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 LRSCR 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 complete details on the available datasets for PCBs and associated parameters in this Reassessment.

### 6.3. Model Application Datasets

From the standpoint of mass balance model applications, the most comprehensive datasets for the Upper Hudson River were acquired during 1991 to 1997. Data for tributaries are very sparse compared to data for the mainstem. The most extensive long-term monitoring for solids and PCB concentrations was conducted at Fort Edward, Thompson Island Dam, Schuylerville, Stillwater and Waterford. Data for solids and PCBs were also collected at other locations as part of specialized, short-term studies. The principal sediment datasets were collected by NYSDEC in 1976-1978 and 1984, by GE in 1991-1997 and by USEPA in 1992 and 1994.

#### 6.3.1. Water Column Datasets

The principal water column datasets used for solids and PCBs were the following:

- Long-term monitoring data collected 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).

Data from these various studies is included in the TAMS/Gradient Phase 2 database, Release 4.1b (TAMS et al., 1998a).

These water column data were used to estimate external loadings of solids and PCBs at the upstream boundary (Fort Edward) and for tributaries to the mainstem portion of the river, both of which are required for HUDTOX model input. In-river mass fluxes of solids and PCBs were also estimated for use as model calibration targets. Concentration time series throughout the calibration period and down-river concentration profiles on specific days were also derived from the data for comparisons between model output and field observations. These data were also used to specify model initial conditions.

#### Bias in Thompson Island Dam PCB Data

As summarized in QEA (1998), an apparent sampling bias was discovered in fall of 1997 in PCB measurements from the routine monitoring station located on the west shore of TID. The samples collected at this station are not always representative of the average PCB concentration leaving the pool due to apparent influences of a local PCB hot spot near the west shore just above the dam, hence the term bias. The bias appears to be related to incomplete lateral mixing between the west shore and center channel of the river during periods of low flow. 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 loading. During high flow periods and/or periods of high PCB loading at Fort Edward, the localized contribution of the hot spot upstream of the west shore station appears to be smaller. Presumably, during high flow periods, sufficient lateral mixing occurs to destroy any significant lateral gradients in the river. After discovery of the west shore station bias, GE continued to conduct a monitoring program designed to better quantify the magnitude of the bias. This monitoring program included collection of samples further upstream and downstream of TID and on lateral transects.

When the TID PCB data were processed for use in model calibration, 34 paired west shore-center channel samples collected by GE were available. These data pairs were used to develop a method for bias-correcting PCB concentrations measured at the west shore monitoring station in order to quantify PCB mass leaving TIP. Monthly bias-correction factors were computed as monthly average percent differences between west shore and corresponding center channel or downstream concentrations for total PCBs and Tri+. No sample pairs were available to establish the existence of a sampling bias at high flows, thus the bias was assumed not to exist at flows above 10,000 cfs. The computed monthly average bias correction factors were applied to individual west shore data collected at flows below 10,000 cfs. This analysis did not consider the effect of upstream load in controlling the magnitude of the bias. Further investigation of the TID bias is planned. Specifically, the magnitude and temporal pattern of the bias will be investigated as a function of both upstream flow and PCB load at Fort Edward.

**Potential Bias in USGS Water Column PCB Data**

An analytical bias exists in the USGS water column dataset that was not accounted for in development of historical PCB loads and model calibration targets. The bias is inherent in the analytical technique used by USGS to measure PCBs. The USGS methods use manufactured Aroclor standards that contain small percents by weight of mono- and di-homologues. This introduces bias into samples containing a relatively high percentage of these homologues. The bias affects samples collected downstream of Fort Edward more than the Fort Edward samples due to the higher fractions of mono- and di-homologues in downstream samples resulting from dechlorination in the sediments. Samples collected at Fort Edward are more similar to the source Aroclor material than downstream samples because they have not undergone the same degree of dechlorination.

General Electric provided USEPA with their quantification of this analytical bias (Rhea and Werth, 1999). These GE results suggest that the USGS data at stations downstream of Fort Edward are biased low by 4 to 70 percent. The impact of this bias might not be large, however, due to the high number of samples near detection limits. Future work is planned to further investigate this bias and its significance to the HUDTOX model results.

### 6.3.2. Sediment Datasets

The principal sediment datasets used for solids and PCBs, and for physical characterization, were the following:

- 1976-1978 NYSDEC data
- 1984 NYSDEC data
- 1991 GE data
- 1992 USEPA high resolution coring data
- 1994 USEPA low resolution coring data.

These datasets were used to specify model initial conditions and model calibration targets. Table 6-1 summarizes the uses of these primary datasets in development and application of the HUDTOX model. Sediment PCB concentrations were computed for cohesive and non-cohesive sediments. Table 6-2 presents the areas of cohesive and non-cohesive sediments that were estimated for different reaches in the river.

### 6.4. External Loadings and Mainstem Mass Fluxes

The HUDTOX model is based on the principle of conservation of mass. It balances inputs, outputs and internal sources and sinks for the Upper Hudson River. Three separate mass balances are represented in HUDTOX: (1) a water balance; (2) a solids balance; and (3) a PCB balance. Before the HUDTOX model can be applied, all external inputs for water, solids and PCBs must be specified from field observations. During the calibration process, internal model parameters are adjusted in order to balance these external inputs against field observations for internal sources, sinks and reservoirs, and for system outputs. The purpose of this section is to describe the development of external inputs for water, solids and PCBs, and of mainstem solids and PCB mass fluxes required for the model calibration process.

Daily average river flow estimates were developed for the mainstem and tributaries in the Upper Hudson River between Fort Edward and Federal Dam at Troy for the period January 1, 1977 through September 30, 1997. Daily average suspended solids (SS) and Tri+ load estimates were also developed in association with these historical flow estimates. Daily average loads for total PCBs and congeners BZ#4 and BZ#52 were estimated for the period April 1, 1991 through September 30, 1997.

#### 6.4.1. Water Balance

The HUDTOX model required specification of all hydraulic inflows in the form of daily time series. These inflows included upstream flow at Fort Edward and flows from all important tributaries between Fort Edward and Federal Dam at Troy. These time series were developed for mainstem Hudson River locations and 12 tributaries for the period January 1, 1997 to September 30, 1997. The daily flow estimates were based on available USGS flow gage data.

Mainstem and tributary flow gages in operation during the study period are summarized in Table 6-3. The locations for these flow gages are shown in Figure 6-1. The Fort Edward gaging station was operational for almost the entire study period (March, 1977 to the present), whereas major gaps exist in daily flow records for the other mainstem stations. Final USGS daily flows for the Stillwater and Waterford stations are flagged as estimated values from October 1992 onward due to construction activities that began that year and continued through at least 1995

(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 tributaries gaged for the entire study period were located on the Hoosic and Mohawk Rivers.

**Methods**

Gaged daily average USGS flows were used directly where available, and when reported to be accurate, to estimate upstream and tributary flows. These included flow gage data from USGS stations at Fort Edward, the Mohawk River (sum of daily flows at Cohoes and the Crescent Dam diversion), and the Hoosic River at Eagle Bridge. The entire Fort Edward flow time series reported by USGS was used without modification. Ungaged tributary flows were estimated by applying average flow per unit area from nearby, gaged tributaries that drained similar watersheds. Because the Hoosic River flows were gaged at Eagle Bridge, upstream of the mouth, these flows were adjusted to the mouth to account for the ungaged portion of the Hoosic River watershed using a drainage area ratio (DAR) approach (Equation 6-1):

$$Q_{tribX} = Q_{Gagedtrib} \cdot \left( \frac{DA_{tribX}}{DA_{Gagedtrib}} \right) \qquad \textbf{6-1}$$

where:

$Q_{tribX}$ = ungaged drainage tributary flow
$Q_{Gagedtrib}$ = gaged tributary flow
$DA_{tribX}$ = ungaged tributary drainage area
$DA_{Gagedtrib}$ = gaged tributary drainage area.

Equation 6-1 was used to estimated all ungaged tributary flows. Similarities in land use, topography and location were considered when selecting a reference tributary. Tributary drainage areas were estimated by digitizing the watershed boundaries in a GIS and are presented in Table 6-4. Also presented in this table are the gaged reference tributaries used in the DAR approach for each ungaged tributary.

The DAR approach does not result in flows from individual tributaries that are mutually constrained. Long-term USGS flow estimates at Stillwater and Waterford were used to check the internal consistency of flows in the Upper Hudson River. 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 6-5). This period was used because all three gages (Fort Edward, Stillwater and Waterford) were operational. After October 1992, the gages at Stillwater and Waterford were influenced by dam construction activity. The ungaged tributary flows estimated by the DAR method were scaled, as necessary, by their percent contributions to the total ungaged area in order to be consistent with the long-term seasonal average flows at Stillwater and Waterford. This approach achieved a seasonal mean flow balance between Fort Edward and Stillwater and between Stillwater and Waterford. The daily flow estimates assigned to direct drainage and ungaged portions of tributaries between Fort Edward and Waterford represent approximately 27 percent (1,258 $mi^2$ of a total 4,611 $mi^2$) of the Upper Hudson River drainage basin area between these locations.

The mean seasonal flows presented in Table 6-5 were used to calculate a factor, $\alpha$, by which the DAR-estimated tributary flows were multiplied so that the sum of the seasonally-averaged tributary flows equaled the difference in the seasonally-averaged, gaged USGS inflows (upstream flow + gaged tributary flows) and seasonally-averaged, USGS outflow (downstream flow) between the main gauging stations (Fort Edward, Stillwater, and Waterford. The seasonal flow adjustment factor, $\alpha$, was calculated for the Fort Edward to Stillwater reach based on the seasonal average flow difference and tributary DARs. This factor was then applied to the DAR-estimated tributary flows in this reach to give the seasonally-adjusted flows. The same calculations were performed for the Stillwater to Waterford reach. The reach-specific seasonal flow adjustment factors, $\alpha$, are summarized in Table 6-6.

The required adjustment for the ungaged tributary flow between Stillwater and Waterford was much less than 1.0 in the summer and fall. This indicates that the extrapolation of the Hoosic River flows gaged at Eagle Bridge using the DAR approach gives a significant overestimate of incremental flows during summer and fall from Stillwater to Waterford, and possibly the Hoosic River at the mouth. It is possible that differences in watershed geology may cause different base flow behavior relative to higher flows in the Hoosic River than in the smaller tributaries draining directly to the Hudson River. Evaporative and other losses from the Hoosic River between Eagle Bridge and the Hudson may be significant during the summer and fall, which may result in an overestimate of the Hoosic River flows to the Hudson River for these periods.

Note that 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 6-6 were applied to the DAR-estimated tributary flows for the entire HUDTOX application period from January 1, 1977 to September 30, 1997.

**Results**

The tributary flows estimated in the manner described above were summed and added to the Fort Edward flows to develop an estimated daily flow time series for comparison to the measured USGS flows at Stillwater and Waterford. In general, the estimated values compared well: however, during some high flow events the LTI flow estimate differed by over 30 percent from the USGS flow. This was not unexpected because the seasonal correction applied to the tributary flows can not capture all events due to localized precipitation or snowmelt in the ungaged tributaries that might not have occurred in the gaged tributaries or vice versa. Because the USGS gage readings during the 1977 to 1992 period were assumed to be accurate within 30 percent during high flow events, the LTI-estimated tributary flows were adjusted to within 30 percent of the USGS gaged flows where differences greater than 30 percent occurred.

In summary, although approximately 67 percent of the tributary flows were estimated, estimates of daily mainstem flows at Stillwater and Waterford differ by no more than 30 percent from the measured daily USGS flows and in general, agreement was within 10 percent. For the period between March 1, 1977 and June 30, 1992, estimated cumulative flows equal 100 percent and 99.7 percent, respectively, of the measured cumulative USGS flows at Stillwater and Waterford.

Analysis of the estimated flow contributions from each source indicate that most of the flow volume measured at Federal Dam enters the Upper Hudson River from tributaries between Fort Edward and Federal Dam. Of the total flow over the 21-year study period, approximately 38 percent of the flow at Federal Dam enters the system at Fort Edward with 62 percent coming from tributaries (Figure 6-2). The Hoosic and Mohawk Rivers contribute most of the tributary flow (10 percent and 41 percent, respectively). Figure 6-3 presents a summary of average daily flows for the study period, by tributary and mainstem station.

The estimated daily flow time series at Stillwater and Waterford, instead of the measured USGS flows, were used to compute in-stream fluxes of solids and PCBs for the HUDTOX model. This was done to maintain consistency with upstream and tributary flow inputs to the model. The estimated flows at Stillwater and Waterford after October 1992 were assumed to be reasonable, based on the flow balance achieved from March 1, 1977 to June 30, 1992. Comparison of the estimated flows at Stillwater and Waterford for 1993 to the flow estimates presented in the DEIR (TAMS et al., 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. Consequently, the DEIR flow estimates were not used in any of the HUDTOX model applications.

### 6.4.2. Mainstem and Tributary Solids Loads

Daily average suspended solids (SS) load estimates were developed for the mainstem and tributaries in the Upper Hudson River for the period January 1, 1977 through September 30, 1997. Because suspended solids loads were estimated based on both flow measurements and solids concentration data, the stations selected for load estimation were either nearby or the same as those selected for flows. 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 6-4.

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 6-5, 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.

### Methods for Mainstem Solids Loads

An extensive record of suspended solids concentration data are 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. To develop accurate estimates of solids loads, the following three methods were used in different combinations:

1) A modified ratio estimator approach;

2) A flow-stratified minimum variance unbiased estimator (MVUE) regression approach; and,

3) Use of monthly average suspended solids concentrations with daily average flow.

The modified ratio estimator approach was based on Beale's Stratified Ratio Estimator (BSRE) (Beale, 1962) which computes ratios of load to flow and then stratifies by flow to separate periods with similar ratios. The MVUE (Cohn et al., 1989) develops a statistical relationship between measured concentrations and flows and then uses this relationship to estimate concentrations on days for which only a flow measurement is available. Loads were estimated using monthly average concentrations and daily average flows for periods that did not contain sufficient data to apply the BSRE or during which there were no significant relationships between concentration and flow. In general, the approach to load estimation in the Upper Hudson River followed Preston, et al. (1989, 1992) who conducted retrospective studies with comprehensive sets of field measurements to evaluate various ratio estimators, regression methods and averaging methods.

**Results for Mainstem Solids Loads**

Suspended solids concentrations were generally well-correlated with flow at Fort Edward, Stillwater and Waterford, with stronger correlations observed at higher flows (Figure 6-6). Flow-stratified regressions were also conducted at these three stations. First, high and low flow data were separated based on the approximate breakpoint observed in the concentration-flow correlation plots. Then a flow-stratified regression analysis was conducted for each station by calculating the mean concentration for all solids concentration data collected below a flow cutpoint and then conducting a MVUE regression analysis on the mean daily flow (Q) and solids concentration data above the cutpoint flow. The equations developed for the mainstem stations are summarized below, with the high flow regression equations incorporating the MVUE bias correction factor.

| | | |
|---|---|---|
| 1) Fort Edward SS (mg/L) | = 3.6 | when $Q \leq 11{,}000$ cfs |
| | = 9E-09 x $Q^{2.15}$ | when $Q > 11{,}000$ cfs |
| 2) Stillwater SS (mg/L) | = 5.1 | when $Q \leq 13{,}000$ cfs |
| | = 1E-06 x $Q^{1.74}$ | when $Q > 13{,}000$ cfs |
| 3) Waterford SS (mg/L) | = 7.5 | when $Q \leq 16{,}000$ cfs |
| | = 2E-08 x $Q^{2.12}$ | when $Q > 16{,}000$ cfs |

Daily solids load estimates were obtained by multiplying estimated daily solids concentrations, computed as shown above, by daily average flow. Measured USGS flows were used at Fort Edward and the estimated flows (see Section 6.4.1) were used at Stillwater and Waterford.

Based on comparisons of results among different methods, solids loads at Fort Edward were estimated using a MVUE regression approach, while the modified ratio estimator was used to estimate solids loads at Stillwater and Waterford. It should be noted that these methods were used to estimate loads only on days for which no concentration measurements were available. In constructing the actual daily loading time series used for input to the HUDTOX model, estimated loads were replaced with observed loads on days where paired measurements of flow and concentration were available.

### Methods for Tributary Solids Loads

A major obstacle to estimation of tributary solids loadings was that available data were very limited, especially for solids concentrations. Many tributaries had little or no suspended solids concentration data. For those tributaries having data, a correlation between concentration and flow was sought in order to estimate concentration as a function of flow. This sort of regression analysis is also referred to as a rating curve approach. The tributary data are too sparse to support application of the ratio estimator approach that was used in calculation of the mainstem solids fluxes. 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 breakpoint above which the slope of the relationship increases. For each monitored tributary, the average solids concentration was calculated below the average flow and a MVUE regression was developed between flow and solids concentration above average flow, which generally approximated the observed flow breakpoint.

Unmonitored tributaries comprise 29 percent of the drainage area between Fort Edward and Waterford. Each unmonitored tributary was matched with a monitored tributary that had a watershed with similar land use distribution, topography and location (Table 6-9). Watershed size was also considered. The rating curve for the reference tributary was then applied to the matched unmonitored tributary using flows specific to the unmonitored tributary.

### Results for Tributary Solids Loads

The cumulative mainstem solids loads and annual average mainstem solids yields for the drainage area at Fort Edward, Stillwater and Waterford were computed (Table 6-10) and compared to the tributary load and yield (Table 6-11). Results show larger solids load gain between mainstem stations than contributed by the estimated tributary solids loads. The computed watershed yields based on solids load gain between the mainstem stations is nearly a factor of two larger than the estimated tributary yields. This implies that more solids are passing Stillwater and Waterford than can be explained by upstream loads at Fort Edward plus estimated tributary solids loads based on the rating curves. This large discrepancy in the Upper Hudson River solids balance required a resolution in order to develop consistent external solids load inputs for the HUDTOX model.

## 6.4.3. Development of Long-Term Average Solids Balance

In order to calibrate the HUDTOX mass balance model for solids, it was necessary to achieve a long-term solids balance that reconciles external solids loads, outgoing solids fluxes, and internal sources (resuspension and primary production) and sinks (deposition). If external loads and outgoing fluxes are reasonably well known, the mass balance model can be used to reconcile internal processes with these inputs and outputs. Without good estimates of incoming and outgoing solids loads, the internal solids dynamics (source and sink processes) will be unconstrained. In order to achieve a long-term solids balance for the Upper Hudson River, it was necessary to determine whether the estimated upstream and tributary solids loads could be reconciled with those at Stillwater and Waterford to produce an internally consistent representation of solids dynamics in the system.

**Methods**

In determining the most probable explanation for the solids load discrepancy, estimated loads passing Fort Edward, Stillwater and Waterford were assumed to be accurate. Based on results in the PMCR, the contribution to solids loading by internal primary production was assumed to be insignificant. Remaining possible explanations are underestimation of external loads, including tributary and possible bank erosion loads, or net erosion of the sediment bed. Experience with other similar river systems suggests that the impounded reaches in the Upper Hudson River are net depositional over long periods of time, even if there might be localized areas that are net erosional. Nevertheless, the possibility of net solids erosion as an explanation for the solids load discrepancy has not been dismissed. Future work is planned to investigate alternate scenarios for solids dynamics in the Upper Hudson River, including net erosion as a source for the observed gain in solids loadings.

To develop tributary solids loads for the HUDTOX model applications presented herein, it was assumed that tributary loads developed from the limited available data were underestimates of the true tributary solids loads. As a global constraint, it was assumed that the Upper Hudson River from Fort Edward to Waterford was net depositional over the historical study period. It should be noted that a solids balance for TIP based solely on available measurements confirmed that the pool was, in fact, net depositional. Available data for tributaries to TIP (Snook Kill and Moses Kill) were more extensive than available data for downstream tributaries, especially during high flows. Consequently, solids loads for these tributaries were assumed to represent true solids loads.

The approach used to develop tributary solids loads for the HUDTOX model was to assume that the net depositional condition observed in TIP also existed for reaches downstream of TID. Tributary solids loads developed from the limited available data were adjusted upward to be consistent with this global constraint. The incremental loads were apportioned to each subwatershed within a reach based on tributary drainage area (Table 6-12). These upward adjustments were applied only to tributaries downstream of TID and not to any external solids loads to TIP.

The first step in the approach was to assume a range of net deposition rates for cohesive and non-cohesive sediment in each reach downstream of TIP (Table 6-13). A reach-wide average long-term sediment burial velocity was estimated using the range and the average of assumed sediment burial velocities and the areas of cohesive and non-cohesive sediments. Depositional solids loads were then computed using sediment bulk density (Table 6-13). The depositional loads were used to compute the solids trapping efficiency of each reach below TIP by dividing by total upstream load. The trapping efficiency in TIP was computed directly from observations and no adjustment of TIP tributary loads was conducted. During data-rich periods in 1993, 1994, and 1997 reasonable solids mass balances could be constructed for TIP based on measured concentrations and estimated flows at Fort Edward, Snook Kill, Moses Kill and TID. Based on the solids trapping efficiencies for these three periods, which ranged from 9 to 28 percent, a solids trapping efficiency of 15 percent was specified for TIP (Table 6-14). For the TID to Stillwater portion of the river, the total external solids loads were computed as the sum of direct tributary loads plus the TID load. The TID load was computed as the sum of all external loads to TIP times 0.85. The trapping efficiency for this reach was computed as the depositional load divided by the sum of tributary loads and the TID load. The trapping efficiency of the Stillwater to Waterford portion of the river was computed in a similar manner (Table 6-14).

Using the solids trapping efficiency estimates presented in Table 6-14, the incremental solids loads required between TID and Stillwater and between Stillwater and Waterford were computed. The required load increments were then allocated to the tributaries on a drainage area basis by increasing the high flow slope coefficient on the rating curves as shown in Table 6-15.

In summary, the tributary suspended solids load adjustments were performed for tributaries entering the Upper Hudson River between Thompson Island Dam and Waterford. The tributary loads to Thompson Island Pool were not adjusted because sufficient suspended solids data exist for both Snook and Moses Kill to define the suspended solids rating curve sufficiently well that the loads are considered accurate. The Mohawk River suspended solids loads were not adjusted because insufficient data exist at Federal Dam to evaluate the solids balance between Waterford and Federal Dam.

Following the adjustment to tributary loads, the resulting equations in Table 6-15 were used to compute tributary solids loads for input into HUDTOX based on flows estimated in Section 6.4.1. In constructing the input load time series, measured suspended solids loads were used in place of predicted loads on days where paired flow and concentration data were available.

**Results**

Using the tributary solids load time series constructed as described above. average annual tributary loads were computed (Table 6-16). Results show that in general. tributary loads between TID and Waterford were adjusted upward by a factor of 2.5, relative to load estimates based on the unmodified rating curves. This required adjustment is large and it illustrates the large uncertainty regarding solids dynamics in the Upper Hudson River below Thompson Island Dam. To evaluate the reasonableness of the adjustments. the resulting tributary watershed yields were computed and compared to available information. While the yields are relatively large. they are well within ranges reported in the literature.

Tributary yields were also compared to the yield computed at stations on the mainstem Upper Hudson River (Figure 6-7). This comparison reveals an increase in yield moving from Fort Edward downstream. The mainstem yields computed based on in-river data are much lower than the tributary yields; however, this is expected considering the ability of the mainstem to capture solids via deposition. Apparent yields computed at these stations do not reflect the total loading due to the large degree of deposition that might occur.

Evaluation of the relative contribution of tributary suspended solids loads to the Upper Hudson River indicates the large contribution of the tributaries (Figure 6-8). Only 5 percent of the suspended solids load at Federal Dam enters the system at Fort Edward, with 95 percent entering from tributaries. Table 6-17 presents a temporal summary of solids loads that shows seasonality of load differences from TID to Waterford, based on mainstem load calculations. The comparison is made to the seasonal tributary loads, estimated using the equations in Table 6-15. Results in this table confirm that application of a correction factor to the exponent on the high flow regression equation caused the additional tributary loads to be delivered during the season in which the load differences between mainstem stations were actually observed.

### 6.4.4. Mainstem and Tributary PCB Loads

Application of the HUDTOX model requires specification of all external inputs of water, solids and PCBs. Just as loading time series were developed for water (Section 6.4.1) and suspended solids (Section 6.4.2), external loading time series were developed for the four PCB state variables: total PCB, Tri+, BZ#4 and BZ#52. In order to apply the HUDTOX model, daily average loading estimates were developed for Fort Edward and the 12 tributaries represented in the model. Tri+ loads were estimated over the hindcast calibration period, January 1, 1977 through September 30, 1997. Total PCB, BZ#4, and BZ#52 loads were estimated over the April 1, 1991 through September 30, 1997 calibration period. To aide in model calibration, in-river fluxes of PCBs were developed at mainstem Upper Hudson River stations where data availability permitted. The in-river flux estimates were calculated solely for the purpose of model calibration and were not used as external loads to the model.

It should be noted that Tri+ and total PCB concentrations measured at the west shore of TID were bias-corrected (Section 6.3.1) prior to estimating mass fluxes across TID. The bias correction applied did not take into account the effect of the upstream load measured at Fort Edward in determining the magnitude of the bias. Future work is planned to further investigate this bias. Furthermore, the USGS data were not adjusted to account for the analytical bias in these data (Section 6.3.1) and future work is also planned to investigate the significance of this bias.

Summaries of PCB data availability for tributary stations are presented in Table 6-18. PCB data sources consisted of the USGS (1977-present), the USEPA Phase 2 investigation (1993) and GE (1991-present). Table 6-18 highlights the fact that tributary data are very limited, with only the Batten Kill, Hoosic River and Mohawk River being sampled for PCBs. In addition, no tributary PCB data exist prior to 1991. Figure 6-9 presents the location of the PCB sampling stations within the study area.

Several data processing steps were taken prior to PCB load estimation. The first step was to assign a value equal to one-half the detection limit for any values reported as being less than the detection limit. Second, for the data from the USEPA Phase 2 flow-average surveys (16 days duration), reported concentrations were assigned to each of the days over which the sample was collected. Finally, for days with multiple concentrations, an average daily value was used for load estimation.

### Methods

Similar to the development of external solids loads for the HUDTOX model, several different methods were also considered for estimating daily average external PCB loads. The scarcity of measured PCB concentrations over the historical calibration period required estimation of the external loads and in-river fluxes of PCBs during a major part of the calibration period. This introduces substantial uncertainty into the calibration of the model during data-poor periods, especially from 1977 to 1984.

Regression methods were eliminated because no significant relationships were found among flow, PCB concentration and suspended solids concentration. Beale's ratio estimators, both stratified (BSRE) and unstratified (BURE), and the seasonal average methods were eliminated because none of these methods reproduced actual observed PCB loads with sufficient accuracy when predicted and observed loads were compared. Furthermore, data frequency was too low for application of the BURE during large portions of the study period. A combination of linear interpolation and year-specific, seasonal average concentrations was adopted as the method of choice to construct both daily PCB loading time series at Fort Edward and in-river fluxes at Thompson Island Dam, Schuylerville, Stillwater and Waterford.

The available time series of water column PCB data were reviewed for each station and separated into time periods where sufficient data frequency existed to support interpolation. For those periods where interpolation did not appear reasonable, seasonal average concentrations were computed during each year and applied in the respective individual years. The periods over which interpolation was used varied among stations due to variations in sampling frequency among stations.

One complication in the use of linear interpolation is the apparent occurrence of random "pulse" loads of PCBs at Fort Edward. These pulse loads appear to be largely unrelated to flow and they can contribute significant mass of PCBs to TIP. The use of linear interpolation during periods of infrequent sampling sometimes exaggerated the apparent contribution of pulse loads that were characterized by only one or two data points. Interpolation in these situations caused incoming concentrations to be strongly affected by individual high concentration measurements for long periods of time prior to and following the measurements. To account for this effect, the approximate duration of these pulse loads was estimated by inspection of the concentration time series. It appeared that the typical time scale for high-concentration events was on the order of only several days. Therefore, during periods of infrequent sampling, best professional judgment was used in substituting year-specific, seasonal average concentrations for interpolated concentrations several days prior to and following individual high concentration measurements. Year-specific seasonal average concentrations were used where necessary in place of interpolation because the data show both seasonal trends within a year and decreasing concentrations over time (Figure 6-10). It should be noted that substitution of seasonal average concentrations was necessary only for Tri+. Sufficient data frequency was available for total PCBs, BZ#4 and BZ#52 and the interpolation-based loads were used without modification.

Due to extremely limited data, tributary PCB loads were estimated in a different manner from mainstem locations in the Upper Hudson River. 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. 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 PCB concentrations in the unmonitored tributaries were assumed to equal the lowest recorded PCB concentration from the three monitored tributaries. These concentrations were 0.17 ng/l for Tri+, 0.51 ng/l for total PCBs, 0.0 ng/l for BZ#4 and 0.03 ng/l for BZ#52. These values were assumed to represent background concentrations for the unmonitored tributaries. It is likely 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 very small and has negligible impact on the HUDTOX model calibration.

**Results**

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. Most of the total external load of PCBs to the system is upstream loading at Fort Edward, with tributaries contributing only a few percent of the total load (Figure 6-13). Cumulative PCB load profiles past TID, Schuylerville, Stillwater and Waterford were also developed for use as calibration targets for the HUDTOX model.

The PCB loads estimated here for the HUDTOX model compare favorably with previous PCB load estimates developed in the DEIR (TAMS et al., 1997). The DEIR estimates were developed at an annual time scale, whereas the estimates developed for the HUDTOX model were daily average time series. The DEIR estimates included Fort Edward (1977 to 1994), Schuylerville (1977 to 1989), and Stillwater and Waterford (1977 to 1993). When the present daily loading time series are expressed in terms of cumulative loads (Figure 6-14) and annual loads (Table 6-21 and Figure 6-15) they agree to within approximately 12 percent of the DEIR loads for corresponding years and station locations.

Several important observations can be made from inspection of the annual Tri+ loads over the simulation period. First, a significant overall declining trend in Tri+ loads past all of the mainstem stations is evident over the period 1977 to 1997 (Figure 6-11). Second, the trend is not monotonic and during some years, loads are much larger than the previous year. Of particular note are Tri + loads in 1983-84 and 1991-92. The large, temporary increase in PCB load in 1991-92 is probably associated with the failure of the Allen Mill gate structure in September 1991 (TAMS et al., 1997). Consistent with the long-term declining trend in Tri+ loads observed at all mainstem stations, total PCBs, BZ#4, and BZ#52 loads at Fort Edward are observed to decline over the period 1992-1997 following the increase in load associated with the Allen Mill gate structure event (Figure 6-12). Third, 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. This suggests that either the contribution of Tri+ from sediments between Fort Edward and Schuylerville was very large during this period, or the external Tri+ loads are underestimated either at Fort Edward or to the reach between these two locations. Both of these are likely possibilities and are discussed in presentation of the HUDTOX calibration (Chapter 7).

An important understanding gained from interpreting the estimated daily PCB loads is that the majority of PCB transport occurs during low flow periods. Low flow periods are characterized by relatively low sediment scour and transport as opposed to high flow events. During 1991 to 1997, between 81 and 94 percent of the estimated daily PCB load is delivered at flows less than 11,000 cfs at Fort Edward (Table 6-19). A similar pattern is observed when PCB load at Fort Edward is stratified by suspended solids concentrations (Table 6-20). Based on the estimated PCB loads at the various mainstem stations, an important conclusion is that most of the PCB transport in the Upper Hudson River occurs during periods of low flow and low suspended solids concentrations. This focuses attention on the importance of non-flow-dependent sediment-water mass transfer processes. 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 most important process controlling long-term, in-river PCB mass fluxes in the Upper Hudson River.

An unresolved issue in estimating PCB loads in the Upper Hudson River is that of stochastic pulse loads due to apparent releases from the GE Hudson Falls site and loads from flow-driven resuspension between Hudson Falls and Fort Edward. It is not clear that sampling frequencies for water column PCBs were sufficiently high to capture all of these loads, especially before 1991 when most of the historical cumulative mass loading occurred. There could have been significant additional loads delivered to the system during periods of low sampling frequency that were not captured by the sampling. The significance of these potential "missing loads" is difficult to determine; however, it is noteworthy that a single measured pulse load in 1992 was responsible for 19 percent of the total PCB load in that year alone. Recent monitoring data (O'Brien & Gere, 1999) for a high flow event that occurred in the Upper Hudson River in January 1998 appear to indicate that there are PCB sources above Rogers Island that can be activated by high river flows. Future work is planned to investigate the significance of these sources and their potential implications for forecast simulations with the HUDTOX model.

The issue of pulse loads is further exacerbated by the fact that when PCB loads to the Upper Hudson River were at their highest levels, PCB water column sampling frequencies were at their lowest. Most of the historical cumulative Tri+ load occurred between 1977 and 1983 (Figure 6-11); however, of the total number of water column PCB samples taken between 1977 and 1997 at Fort Edward (801), only 22 percent (173) were taken between 1977 and 1983. Furthermore, only three samples were taken during 1977, a year in which PCB loads were estimated to be the second-highest in the entire historical period of record.

THIS PAGE LEFT BLANK INTENTIONALLY

# Chapter 7

# 7. MASS BALANCE MODEL CALIBRATION

## 7.1. Introduction

Before applying a site-specific model such as HUDTOX in a forecast mode, it is necessary to first calibrate the model to existing field observations. Model calibration involves adjusting a process model's coefficients within an acceptable range of values – this acceptable range generally depends on experience with other similar systems and reported literature values – until the model captures the observed spatial and temporal behavior of the state variables and processes (system observables) in the system. Deterministic, process-oriented mass balance models are a simplified representation of the full complexity of the actual system. In that regard, models of this type are designed to describe the behavior of those processes and state variables that are important to the problem under consideration. If such a site-specific model can be formulated and parameterized (*i.e.*, calibrated) to simulate the system observables of interest for a period approaching that of the desired forecast period, then this model is considered usable for making forecasts of system behavior in response to different remedial alternatives.

This section reports on the approach and results of the calibration exercise. Section 7.2 describes the calibration strategy and resulting metrics for model calibration. Section 7.3 presents a detailed summary of model parameters which, in combination with model configuration to the physical system, flows, and loads of solids and PCBs, provided the most scientifically justifiable and internally consistent calibration to available data. Sections 7.4 and 7.5 present the calibration results and a diagnostic component analysis of those results, respectively.

## 7.2. Calibration Strategy

The calibration strategy was driven by a desire to use available observations in the model domain in a way that would optimize our confidence in using the model to make accurate long-term forecasts of the behavior of PCBs in the river in response to both No Action and potential remediation alternatives. The strategy also followed a generally accepted principle of proceeding sequentially from balancing water to solids (sorbents) and finally to the PCBs. The long-term flow balance was based on USGS measurements at Fort Edward and estimated tributary flows (Section 6.4.1). Once the solids dynamics were calibrated, an attempt was made to calibrate the PCB dynamics without changing the parameters that govern solids dynamics. Ultimately, however, it is desirable to obtain a scientifically credible and internally consistent calibration for **both** solids and PCBs. Achieving this goal often requires some iteration between solids and PCB calibration. In effect, PCBs can serve as a "tracer" for solids because under many conditions solids and PCBs tend to be mutually constrained, especially during resuspension events.

The calibration proceeded from short-term applications to longer-term applications. If used judiciously, high-resolution, short-term data sets can provide useful information to sufficiently constrain parameters that control the long-term behavior of a system. Small biases that are not detectable in short-term simulations can manifest themselves when simulations are carried out over long time periods, which is the requirement of this overall modeling analysis.

An important reality of model calibration should be recognized. Virtually all process-oriented water quality models are under-determined (*i.e.*, they have more calibration coefficients (degrees of freedom) than state variables); therefore, for complex models such as HUDTOX often there is not a unique set of model coefficients that will give the "best" fit to the observed data. Trade-offs often exist between two processes that cause the same change in a given state variable. For example, sediment resuspension and pore-water diffusion can both transfer PCBs from the sediments to the water column. If water column PCB concentration is the only calibration metric, then the same transfer rate can be achieved with a range of parameter values for these two processes. On the other hand, if water column suspended solids are also included as a calibration metric, then the range of parameter values for these two processes is more tightly constrained because one of them transfers solids to the water column and the other does not. With this understanding, the model calibration strategy was conceived to use metrics that provided the most constraint on the calibration possible with the available data. For example, system-specific process rate measurements (*e.g.*, field shaker resuspension experiments) were used to derive estimates of process parameters governing resuspension. The model calibration process was also constrained by formulating model processes in theoretically sound ways, so that the process coefficients had as much physical meaning as possible. Even with the constraints imposed by mechanistic process descriptions, calibration of the HUDTOX model required scientific judgment in specifying process coefficients and many sensitivity analyses were conducted to understand state variable responses to each parameter.

### 7.2.1. Solids Calibration Strategy

Once the flows in the system have been specified, the first step in the calibration process is to calibrate the solids dynamics. Calibration of solids dynamics in HUDTOX required *a priori* specification of all external solids loading rates (Section 6.4.2), including the upstream load at Fort Edward. Given flows and solids loads, the parameters controlling water column settling, bottom sediment resuspension from both cohesive and non-cohesive sediment areas, and resulting bottom sediment accumulation and/or erosion were adjusted within scientifically reasonable values until suspended solids concentration, mass fluxes, and sediment accumulation rates in the modeled system compared best with observations.

The first step in the solids calibration was to parameterize solids settling and resuspension using the short-term, high-frequency TSS data collected by RPI during the spring of 1994. This sampling program was designed to capture daily variation in solids loads and concentrations in the system in response to spring high flow events associated with snowmelt and rainfall runoff events. There are also relatively high-frequency data for Fort Edward, TID, Stillwater and Waterford during the entire 1991-1997 period (and for Schuylerville in 1991 only). Therefore, by next modeling the entire 1991-1997 period, we were able to compare model predicted concentrations with available data during both high-flow and summer low-flow periods in this data set in order to verify appropriate behavior of the solids dynamics during a range of flow conditions occurring in sequence.

Once a satisfactory short-term calibration for solids was obtained, the model with the same solids parameters was applied to the long-term solids data set between 1977-1997 (a 21-year hindcast). This long-term historical simulation is driven by daily flow and estimated daily external (tributaries and upstream boundary) loadings of TSS. The cumulative solids flux profiles at several points below Fort Edward was an important metric for this part of the calibration. The model was also tested for its ability to capture the long-term net solids accumulation or erosion rates in each reach of the river in cohesive and non-cohesive sediment areas; these rates of solids sediment accumulation must be reasonable relative to observed burial of historical inputs of PCBs to the system. These two additional constraints were used to refine the settling and resuspension parameterization so that river solids dynamics were captured during both low-flow and high-flow event periods. This accurate determination of the long-term sediment-water solids exchange rate is very important in modeling long-term PCB dynamics.

In summary the metrics used in the solids calibration step included:

1. Water column concentration time series of TSS at several locations within the mainstem of the river;

2. Cumulative TSS mass flux time profiles at major locations along the mainstem (TID, Stillwater, Waterford); and,

3. Solids burial rates in cohesive and non-cohesive sediment areas.

This phased data-model comparison approach presented the best opportunity to parameterize how settling and resuspension from both cohesive and non-cohesive sediment regions vary as a function of flow and season.

### 7.2.2. PCB Calibration Strategy

Following the TSS model calibration, an attempt was made to calibrate HUDTOX to the PCB data by adjusting PCB fate and transport process parameters without altering the solids dynamics. However, as mentioned above, since the transport and fate of hydrophobic organic compounds is closely tied to solids dynamics, minor readjustments to the solids calibration were made in order to produce the most scientifically credible and internally consistent calibration for both TSS and PCBs.

Once the solids dynamics of the system and external loads of PCBs have been specified (Section 6.4.4), there are a limited number of processes available for calibration of the PCB model: air-water exchange; sediment-water exchange by mass transfer and resuspension; partitioning; particle mixing rates in sediments; and sediment dechlorination rates (a consideration in modeling historical hindcast for Tri+). Among other environmental factors, these process rates are dependent on the physical-chemical properties (molecular weight, $K_{oc}$, Henry's Law Constant) of the chemical under investigation. Therefore, average properties were attributed to the congener mixture under investigation when modeling either total PCBs or Tri+.

For the calibration of HUDTOX, four different PCB state variables were used in conjunction with the data sets described in Chapter 6. During the period from 1991-1997 total PCBs, BZ#4, BZ#52 and Tri+ were analyzed. Because of the different properties of the two congeners measured in the data sets from this period, we were able to constrain individual process (sediment-water exchange, air-water exchange, partitioning, solids settling and resuspension) that might otherwise not be constrained when simply modeling total PCBs or Tri+.

For the long-term hindcast runs (1977-1997), the state variable was Tri+. This is the only PCB state variable for which data are available over the entire historical period. Unfortunately, as described in Section 6.4.4, data for estimating external loading of Tri+ was most scarce between 1977 and 1984, a period when loadings entering the river above Rogers Island were still very high compared to post-1990s loadings.. This important data uncertainty required special consideration for the 1977-1984 model period. The HUDTOX model was run for this period simply as a means of generating initial sediment concentrations in the reaches of the river downstream of Thompson Island pool (which were not measured in the 1984 NYSDEC sediment sampling) for the actual historical calibration period of 1984-1997. This analysis approach required an upward adjustment in data-based PCB loading at Fort Edward during the 1977-84 period by an amount that was necessary to match the measured cumulative Tri+ flux at Schuylerville over the period. Consequently, the long-term hindcast calibration for Tri+ was actually conducted only for the period from 1984 to 1997.

In summary, the PCB calibration strategy has been an iterative process that produced internally consistent simulations of the solids model metrics mentioned above as well as the following PCB metrics:

1. Water column concentration space and time profiles;

2. PCB mass cumulative flux profiles at key locations along the mainstem of the river (TID, Schuylerville, Stillwater, Waterford) and under both high and low flow conditions; and,

3. Sediment PCB concentration profiles (surficial sediment changes over time and vertical profiles at selected locations).

Again, the juxtaposition of PCB behavior during high and low flow periods in more recent, high-frequency data sets (1991-1997) was also important for the iterative PCB calibration.

### 7.3. Calibration Parameters

This section presents the values of parameters for both solids and PCBs used in the base model calibration. Datasets used to develop water column and sediment initial conditions were described in Section 6.3. Flows and loadings of solids and PCBs for model calibration were presented in Section 6.4. A presentation of the results of the calibration process relative to the above metrics will follow in Section 7.4.

#### 7.3.1. Solids Dynamics Parameters

The solids dynamics calibration deals with establishing those parameters that govern the processes of settling, resuspension, and sediment burial in the system. As discussed in Chapter 5, the solids dynamics sub-model within HUDTOX is a time-dependent mass balance of a single suspended solids type in the water column (represented by average particle properties of the river's suspended solids). But in the bottom sediments, the model does distinguish between cohesive and non-cohesive sediment areas; of course, this distinction, along with hydraulic conditions, impacts the spatial distribution of sediment resuspension and burial rates.

Presented in Table 7-1 are the HUDTOX solids model calibration parameters and the values obtained for the base calibration. Gross settling from the water column into the sediments is modeled as a flow-dependent process, as described in Section 5.2.3. The shape of the functionality is shown in Figure 7-1; gross settling velocities and flow thresholds presented in this figure are those determined for the Thompson Island Pool (upstream of RM 182.3). This functionality attempts to capture well-known river behavior, where increasingly larger, faster settling particles are entrained in the flow as it increases above a resuspension threshold. There is an upper bound on settling velocity that is essentially limited by the size distribution of particles being washed into the system from its drainage basin. Since the flow-velocity relationships change as one moves downstream, these parameters have been established on a reach-specific basis according to cumulative drainage area as indicated in Table 7-2.

There are two types of bottom sediment resuspension in HUDTOX: flow-driven resuspension (large in magnitude, but short in duration) and low-level continuous background resuspension that occurs as a result of a variety of processes that generate turbulence at the sediment-water interface in the absence of high flows. The mechanisms giving rise to this process and its potential rate have already been discussed in Section 5.2.3. The background resuspension is included as a constant value that is different for cohesive and non-cohesive sediment areas (Table 7-1). The background resuspension values (0.2 mm/yr for cohesive sediments and 0.4 mm/yr for non-cohesive sediments) are small relative to the maximum potential value of 3.0 mm/yr suggested in Velleux et al. (1996). While the rates used here have very little impact on the solids calibration, they provide an important source of PCB mass flux from the sediments that is necessary to calibrate observed water column concentrations under low flow conditions.

Flow-driven resuspension is formulated differently for cohesive and non-cohesive sediment, as described in Section 5.2.3. Table 7-3 contains the calibration parameters for these two event-driven resuspension processes. The mechanistic description for flow-driven resuspension from cohesive sediments is the same as that used in the Depth of Scour Model (Chapter 4). An empirical equation was formulated for non-cohesive sediment to describe resuspension as a function of applied shear stress and its time history. This equation simulates the process of sediment armoring during high flow and "recovery" from armoring (Chapter 5).

In order to visualize the different responses of cohesive and non-cohesive sediments to a high-flow period, the parameterization in Table 7-3 has been used to plot the model-computed gross settling velocity and resuspension velocities for both cohesive and non-cohesive sediments in model Segment 21 (TIP - see Figure 5-6) during the spring 1994 high-flow period (Figure 7-2). Cohesive sediment resuspension responds to an increase in bottom shear stress above a critical value by eroding a fixed amount that is a function of the incremental shear stress above the previous value. No resuspension from cohesive sediments takes place on the falling limb of a hydrograph within a specified period that was determined through calibration. For non-cohesive sediments increases in the shear stress above the critical shear stress also produce resuspension; however, the critical shear stress for non-cohesive sediments is time-variable and depends on the previous history of erosion and deposition in the bed. As smaller particles get eroded and only larger particles are left behind, the effective critical shear stress for resuspension increases (*i.e.*, armoring takes place). This armored bed takes some time to recover (*i.e.*, for effective critical shear stress to decline as a result of smaller particle deposition); and overlapping events may produce a smaller resuspension velocity for the second event even though its flow is higher than the first. This phenomenon is displayed in Figure 7-2 during the April 14-18 period.

### 7.3.2. PCB Model Parameters

Parameters for the PCB mass balance model – those required in addition to the solids dynamics parameters described above – are presented in Tables 7-4 and 7-5. Two important forcing functions ($f_{oc}$ and DOC concentrations) that have a bearing on PCB transport and fate must be specified *a priori* in HUDTOX. The values specified for these parameters in water and sediments are presented in Table 7-4; these values have been specified on the basis of field observations as listed in the table.

Several of the PCB model parameters are temperature dependent: therefore, two important forcing functions in the model are air and water temperature. Air temperature was determined over the 1977-1997 model period from monthly average data at Glens Falls, NY as depicted in Figure 7-3. Shown in Figure 7-4 are the monthly average water temperatures in the four reaches of the model domain; these temperatures were determined from the TAMS/Gradient Phase 2 Database TAMS et al. (1998a).

The first four items in Table 7-5 (molecular weight, Henry's Law constant, and organic carbon normalized partition coefficient) can be thought of as fundamental chemical properties, although the organic carbon normalized partition coefficients are somewhat dependent on the nature of the organic carbon in the system. Initial estimates of these attributes were based on the recommendations from the congener distribution analysis conducted by TAMS/Gradient (1996); however, some adjustment, especially for partitioning, was necessary to account for site-specific conditions.

The molecular weight for the two congeners was computed on the basis of knowing their elemental composition. The molecular weights for Tri− and total PCB were based on assumptions regarding their congener distributions relative to Aroclors 1242 and 1248 (TAMS/Gradient, 1996; Mackay *et al.* 1992). Since Tri+ does not contain mono- or dichlorobiphenyls, its molecular weight (set at the mid-point between 1242 and 1248) is larger than total PCBs.

Henry's Law Constants were also based on measured values reported in the literature. Values for BZ#4 and BZ#52 were taken from congener-specific measurements made by Brunner *et al.* (1990). The Tri+ value was again determined by selecting a value mid-way between those reported by Mackay *et al.* (1992) for Aroclor 1242 and 1248. The Henry's Law Constant for total PCBs was the same value used for the PMCR.

Some calibration flexibility is available for setting the organic carbon normalized partition coefficients. The approach was to begin with the values arrived at by the theoretical analysis performed in the DEIR (TAMS et al., 1997). It was then recognized that some adjustment of these values could be made during the calibration process, especially for total PCBs and Tri+. A range of ±0.5 log units for the congener mixtures was permitted in the calibration, so long as the theoretical relationships among congeners and congener mixtures was not violated. In other words, the ranks for $K_{poc}$ in decreasing order should be BZ#52 > Tri+ > total-PCB > BZ#4. In the absence of empirical measurements for $K_{doc,}$ the DOC binding constants were set to 10 percent of the respective $K_{poc}$; this practice is within the range of values (1 to 10 percent) obtained for PCBs in natural systems by other researchers (Eadie *et al.* 1992; Capel and Eisenreich, 1990). All partition coefficients were assumed to be temperature dependent with the same temperature slope factor (tsf) determined by TAMS et al. (1997).

Air-water mass transfer rates were determined using a Whitman two-film theory, with the liquid film mass transfer rate being dependent on oxygen mass transfer as determined according the O'Connor-Dobbins formulation (Section 5.2.3) and adjusted for the PCB molecular weight and for variation in water temperature (Chapra, 1997; Thomann and Mueller, 1987). The gas film mass transfer rate was set to a constant value of 100 m/day, as recommended by Ambrose *et al.* (1993) for fluvial systems.

Given the air-water mass transfer rates, air-water flux depends on the gradient between the dissolved water phases and the atmospheric gas phase (Section 5.2.3); therefore, computation of this flux 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 7-5). Also included in Figure 7-5 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 7-5. The resulting HUDTOX boundary condition values used for these PCB state variables are presented in tabular form on Figure 7-5.

Sediment dechlorination rates were not included in this modeling exercise, primarily for two reasons. First, because of the uncertainty in determining the external PCB loading from 1977-1984, any loss of sediment PCBs due to dechlorination during that period would be masked by the arbitrary load increment required to attain 1984 sediment inventories in TIP. Second, TAMS et al. (1998b) estimated that the sediment reservoir in TIP had lost approximately 10 percent of its mass between 1984-1994 due to dechlorination. Sensitivity analysis in combination with an estimate of the uncertainty in PCB loading during this period suggested that data were insufficient to discern between no dechlorination and a sediment decay rate of approximately 1 percent per year. In the interest of parsimony, it was therefore decided to neglect the effect of sediment dechlorination on Tri− and total PCBs for this analysis. The need to include this process in model forecast simulations will be further investigated.

Finally, HUDTOX contains two processes that serve to exchange PCBs between the sediments and the overlying water and between upper mixed sediment layers without causing any net solids transport. The two processes are: diffusive mass transfer of pore water PCBs and sediment-to-water mass transfer from particulate phase PCBs. Based on the assumption that bioturbation, mechanical scour and other turbulence-generating phenomena in the surface sediments are the driving forces for both of these processes (Section 5.2.3), the following constraints were established in calibrating these rates:

1. The maximum rates should occur for the PCB exchange between the upper sediment layer and the overlying water; PCB exchange between layer 1 (0-2 cm) and layer 2 (2-4 cm) should be lower than across the sediment-water interface and it should decrease to strictly molecular diffusion of pore water PCBs below the bioturbation zone;

2. The rates should be seasonally variable with highest rates during summer, biologically active periods;

3. Based on the reanalysis of the TIP sediment source congener signature (Tetra-Tec, Inc. and TAMS Consultants, Inc., 1998), PCBs in both pore water and the particulate phase should contribute to sediment-water mass transfer; and,

4. The final calibration values should be within the range of values employed in other modeling applications to similar systems (see Section 5.2.3).

The first PCB sediment-water exchange process is pore water diffusive mass transfer between the upper mixed sediment layers and between the top layer and overlying water. This transport process acts on the concentration gradient between dissolved and DOC-bound PCBs in the sediment pore water and in the overlying water. Achman *et al.* (1996) have measured this phenomenon in the Hudson River Estuary and have determined that in this system it is potentially as important as resuspension and subsequent desorption of particle bound PCBs. Because of bioturbation, this process can be 2-3 orders of magnitude greater than molecular diffusion near the sediment-water interface (Portielje and Lijklema, 1999; Thibodeaux, 1996). Deeper than four centimeters (top two layers), the pore water diffusion was set to a value approximately equal to molecular diffusion for compounds of their relative size of dissolved and DOC-bound PCBs. The final HUDTOX calibration values for diffusive mass transfer rates and their seasonal variability, based on an Arrhenius temperature dependence, are presented graphically in Figure 7-6a. This dependence was driven by the same temperature time series developed for the corresponding overlying water column segments (see Figure 7-4) because measurements were not available to specify sediment temperatures on a seasonal basis in the Upper Hudson River.

At the same time as upper sediment mixing processes are enhancing pore water diffusive mass transfer, they are also causing an increased exposure of sediment particulate PCBs to overlying water. This process, which has been formulated in HUDTOX as a sediment-water mass transfer of particulate phase PCBs, is a simplified representation of the very complex and fine-scale dynamics in which sub-surface sediments are transported by mixing processes to the sediment-water interface, desorb PCBs, and then are re-mixed back into deeper sediments without contributing measurable suspended solids to the water column (see Section 5.2.3). An analysis of congener distribution patterns in TIP (Tetra-Tech, Inc. and TAMS, 1998) indicated that PCB sediment-water mass transfer from only pore water sources could not account for observed congener patterns in the water column during low flow conditions and that PCB mass transfer must also be occurring from particulate phase sources. This finding was confirmed during the HUDTOX calibration. Accordingly, values for sediment-water mass transfer rates for PCBs from the particulate phase were determined by calibration to PCB observations after all other sediment-water exchange fluxes were specified. The sediment–water mass transfer rates for particulate PCBs have also been parameterized as seasonally-variable and reach-specific as depicted in Figure 7-6b.

## 7.4. Calibration Results

### 7.4.1. Spring 1994 Solids Results

In keeping with the model calibration strategy discussed above, the first calibration analysis was conducted on short-term solids dynamics using the high frequency data set obtained during the spring of 1994. This data set permitted the testing and refinement of short-term resuspension rate coefficients in response to flows that generated shear stresses in excess of critical shear stresses for both cohesive and non-cohesive sediments. Shown in Figure 7-7 are the calibration results for total suspended solids (TSS) concentration versus time for each sampling station during the study period. The series of plots begins at the upstream boundary at Fort Edward and moves downstream in successive plots. The plots demonstrate that HUDTOX did quite a good job of capturing the river solids dynamics during the course of three major flow events.

Cumulative TSS flux versus time plots (both model generated and data-base estimated) for three important river cross-sections are shown Figure 7-8. The accurate simulation of mainstem flux profiles was another important calibration metric. Again, the model produced quite a good simulation of cumulative river flux profiles during both high and lower flow periods.

It is important to notice the considerably higher suspended solids concentrations (Figure 7-7) and TSS fluxes (Figure 7-8) in the river below Schuylerville; this is largely the result of high tributary solids loadings from Batten Kill, Hoosic River, and the Mohawk River in these lower reaches as discussed in Section 6.4.2. These large tributary solids loadings below the Northumberland Dam have important implications for the response of sediments to PCB loadings from upstream.

**7.4.2. Results for 1991-1997 Calibration Period**

The period from 1991-97 represented the best multiple-year data set for calibrating and testing the behavior of HUDTOX during both high and low flow conditions; therefore, this period was used as the next data set for calibration of TSS and all four PCB state variables. The results of the model application for TSS, using the parameterization described in Section 7.3.1, is presented in Figures 7-9 and 7-10 for all seven years and for 1993, respectively. Note that a logarithmic scale was used for these plots, because of the wide fluctuations in TSS concentrations that occur in the river. Even so, these figures demonstrate that the solids dynamics model is capable of capturing both high-flow event peaks of TSS and low-flow depositional periods. The expansion of 1993 in Figure 7-10 was selected for presentation because this year had the highest flows during the spring runoff period. Measured suspended solids concentrations reached as high as 200 mg/l at Stillwater and 300 mg/l at Waterford, yet HUDTOX was still able to simulate these events.

The success of the model at simulating the cumulative TSS flux at TID, Stillwater, and Waterford (Figure 7-11) suggests that a good closure of the solids mass balance has been attained and, therefore, an accurate estimate of net solids burial rates in these reaches has also been achieved. Again, much higher solids fluxes at Stillwater and higher still at Waterford confirm the importance of tributary TSS loads below TID. Note also in this figure the large, abrupt increases in cumulative solids flux during the spring 1993 runoff period.

Finally, a comparison of the seven year total solids load through the mainstem transects during both high ($Q > 2$*average flow at a given station) and low ($Q < 2$*average flow) flow conditions is presented in Figure 7-12. A cut-off point between high and low flow conditions of twice the average flow was chosen because it was approximately at this point that the "break" in the TSS concentration versus flow rating curve occurred. This mass load metric demonstrates the capability of the model to accurately capture solids fluxes at both high and low flows. It also demonstrates that about 55 percent of the solids flux over the Thompson Island Dam occurred during low-flow periods. A similar analysis for the entire 21 period from 1977-1997 gave the consistent result that approximately 50 percent of the solids flux at TID occurred during low-flow periods. This result demonstrates that the Hudson River is not a "flashy" system, and, therefore, it does not depend exclusively on high flow events mobilize solids.

The PCB concentration versus time calibration results at mainstem Hudson River stations are presented in Figures 7-13 to 7-15. The model has done a good job of tracking PCB loadings at Fort Edward through the system. It has also demonstrated that it captured the seasonal variability in the system as well as the long term gradual decline in water column PCB levels throughout the model domain.

The fact that the model has done a reasonably good job of simulating the BZ#4 and BZ#52 congener profiles with the same flow, solids, and mass transfer rate parameterization (only chemical-specific parameters have been adjusted) is an excellent check on the scientific validity and internal consistency of our conceptualization and parameterization of how the Upper Hudson River system behaves relative to fate and transport of hydrophobic chemical like PCBs. It is apparent in careful scrutiny of Figure 7-14 that the model tends to overestimate BZ#4 concentrations downstream of TID. This is manifested and even more apparent in Figure 7-16, which is a calibration results plot of the BZ#4/BZ#52 ratios at mainstem stations; the modeled ratios at Stillwater and Waterford tend to be about a factor of two higher than the observed data. Given this result, it is quite possible that the model is underestimating the loss of BZ#4 to the atmosphere by volatilization in these lower reaches below TID. Currently, HUDTOX does not estimate volatilization losses over the TID or any of the other low-head dams in the lower reaches of the river. Future work is planned to investigate the significance of water-air exchanges at dams on PCB dynamics in the Upper Hudson River.

One other observation from Figures 7-14 – 7-16 is that, while the TIP sediments contribute to an increase of both congeners across the pool, the increase is much more pronounced for BZ#4. With the exception of one abnormally large peak in the spring of 1993, the increase in the BZ#4/BZ#52 ratio across the TIP is striking. The ability of HUDTOX to capture this chemical-specific behavior is further evidence of the validity of the model formulation.

Another dataset which can serve as a metric of the ability of HUDTOX to faithfully capture the behavior of the TIP was the time of travel studies conducted by General Electric in June and September, 1997. Essentially, plug-flow monitoring was conducted by allowing a boat to be carried by the current along the length of the TIP while sampling periodically what presumably would be the same control volume of water. The four such surveys (two in June and two in September, 1997) demonstrated the increase in total PCBs that occurred as water flowed over contaminated sediments in the TIP. As shown in Figure 7-17(a-d), HUDTOX, with its various calibrated sediment-water exchange processes, did a reasonable job of capturing the rate of flux of PCBs from sediments to overlying water that obviously occurs in the TIP.

Another way of looking at the importance of the sediment-water exchange processes in the TIP is to compute the load increment across the TIP. Shown in Figure 7-18 is the monthly average total PCB load gain across the pool, both as computed by HUDTOX and estimated from the time series of data at Fort Edward and at the TID from 1991-1997. Aside from the somewhat complicated response of TIP to the Allen Mill gate structure failure in September 1991, the comparison between model and data is very good. HUDTOX was able to capture the increases across the pool that typically occurred in spring and summer months; however, it does not describe the apparent loss of PCB flux across the pool estimated for November and December of several years during the period. The average daily load increment across the TIP (0.5 kg/d) computed by HUDTOX is very close to that estimated from available data (0.43 kg/d).

Finally, the cumulative mass load of PCBs past mainstem stations in the river was another calibration metric during the 1991-1997 period. Shown in Figure 7-19 are the model-computed and data estimated cumulative total PCB mass transport past TID, Stillwater and Waterford.

Note that PCB data for the Stillwater and Waterford stations were only available between April, 1991 and May, 1992. Still, where data were available, model and data cumulative loads compare quite well.

The trends in Figure 7-19 show a continuous increase in the cumulative load at all three stations, with the rate of load increase slowing over time. There are some sharp increases due to major spring flow events during this period, but it is obvious that the increase in cumulative load at other, low-flow times during this period is significant. This observation is more graphically illustrated in Figure 7-20, which indicates that approximately 80 percent of the total PCB transport during this period occurs during low-flow periods when the flow at a given station is less than twice its average flow. This is consistent with the earlier solids load results, and it confirms that the Upper Hudson River is not a very flow-responsive system.

### 7.4.3. Results for the 1977-1997 Calibration Period

The hindcast calibration for 1977-1997 was conducted for TSS and Tri+. Tri+ is the only PCB form for which a continuous data set was available for the entire 21-year period. Initial efforts to calibrate the HUDTOX model over the period from 1977 to 1997 were unable to describe the large increase in PCB load between Fort Edward and Schuylerville between 1977 and approximately 1984. This suggests that either the contribution of Tri+ from sediments between Fort Edward and Schuylerville was very large during this period, or the external Tri+ loads are underestimated either at Fort Edward or to the reach between these two locations. Underestimation of Tri+ loads at Fort Edward is a possibility because water column sampling frequency was low and PCB loads were high during this period. A large contribution of Tri+ from the sediments is also a possibility due to unstable conditions resulting from removal of the Fort Edward dam in 1973.

The need for an additional load during this period is evident from examining the cumulative Tri+ load at Schuylerville with and without an additional load at Fort Edward. Illustrated in Figure 7-21 are the data-based estimate of the TID cumulative Tri+ load, along with the HUDTOX predicted cumulative loads for two load estimates at Fort Edward: the data-based load estimate at Fort Edward and a run with an additional load added at Fort Edward that was constrained to meet the cumulative load observed at Schuylerville. Consequently, the actual hindcast calibration for Tri+ focused only on the period 1984 to 1997, not the entire period from 1977 to 1997, due to uncertainty in PCB loads during this earlier period.

Just as a frame of reference, it is worth confirming that the model solids dynamics parameters determined by calibration to spring, 1994 and the 1991-1997 period are also valid for the entire 21-year hindcast period. Figure 7-22 shows quite good agreement between the model-generated and data-derived cumulative TSS loads at mainstem stations over the entire 21-year period. The results suggest that not enough solids are being deposited in the reach from TID to Stillwater, particularly from the mid-80s forward. It is difficult, however, to distinguish whether this minor difference is the result of parameterization of net solids deposition to sediments or due to a slight overestimation of solids loading (see Section 6.4.2 for discussion of solids load calculations) during this period.

Given the 1977-1984 load revision and the calibration of solids dynamics, it is now possible to apply the three PCB calibration metrics to the entire TRI+ hindcast. The concentration versus time profiles at several mainstem stations is shown in Figure 7-23. The richest data for Tri+ were available at Schuylerville, Stillwater, and Waterford; however, a very good Phase 2 data set was available at the TID. This model metric shows a very good comparison between model and data at all mainstem stations. In addition to capturing spatial and seasonal trends in Tri+ for the system, HUDTOX has also been able to accurately simulate the long-term, approximately exponential, decline in water column concentration over the hindcast period. This bodes well for the model's capability to make an accurate estimate of the system response to continued No Action.

Although necessary, water column concentration profiles alone are not sufficient to assure an accurate model forecast. Mass fluxes through the system and accurate sediment trend simulations – the other two metrics described earlier – are also very important. The 21-year cumulative mass load comparisons for Tri+ at mainstem stations with sufficient data are shown in Figure 7-24. This model result is consistent with earlier cumulative mass load calculations for other PCB parameters in that it indicates a gradual decline in the mass transport downriver over time, an obvious result of concentration declines in the water column. Note the much greater slope of these lines (greater mass load carried by the river) during the period from the beginning of this simulation through the mid-1980s. The loading from Fort Edward early in this hindcast period is likely the "declining tail" of the peak loading period to the river, which no doubt occurred prior to 1977.

Comparison with the data-estimated cumulative mainstem load in Figure 7-24 indicates a divergence between model and data that begins in the mid-1980s. The HUDTOX model begins to overestimate cumulative load at Schuylerville and it continues to do so downstream, suggesting that the divergence is occurring upstream of Schuylerville in TIP or just downstream of the TID. It is possible that this divergence is a consequence of not including dechlorination of Tri+ in the model, thus leaving sediment Tri+ concentrations higher than they would be in the presence of even a small rate of decay. This decay process was probably not as important earlier in the hindcast because the load at TID was more strongly controlled by upstream PCB loading at Fort Edward. Later in the hindcast (after the mid-1980s) the mass flux over the TID becomes more dependent on sediment-water mass transfers within TIP.

An important metric for a system whose response time is largely controlled by sediment-water interactions is the ability of the model to accurately simulate sediment concentrations. The results of this metric for the Tri+ hindcast are shown in Figure 7-25. Figure 7-25 shows the long-term simulation of time trends in Tri+ solids-normalized concentrations in surficial (upper mixed layer at 0-4 cm depth) sediments along the entire length of the model domain. In consultation with Menzie-Cura and Associates, Inc., it was judged that a sediment depth of 4 cm was the most appropriate spatial scale for representation of sediment PCB exposures to benthic organisms. Simulations and data estimates are separated into cohesive and non-cohesive areas of the various reaches. Also, much more longitudinal resolution is presented in TIP where data and model output are separated into six sections. Four sediment surveys are available for comparison with model forecasts. The results suggest an outstanding capacity of the HUDTOX model to capture both spatial and temporal trends in surficial sediment concentrations. Again, in a system for which sediment-water interactions are very important, the capacity to reproduce trends in surface sediment concentrations is crucial.

It should be noted that accurate simulation of surface sediment concentrations can be obtained by either "pulling" PCBs up from deeper sediment layers at a higher rate, or by burying PCBs into deeper sediment layers at a higher rate. Future work is planned to further investigate the sensitivity of surficial sediment PCB concentrations to dechlorination and vertical mixing in the sediment bed.

### 7.5. Component Analysis

The results of the HUDTOX calibration presented in the previous section have demonstrated that it has accurately captured the historical behavior of the Upper Hudson River for both solids and PCBs. It is now very instructive to utilize the calibrated model to determine how the interaction of processes included in the model have led to simulation of that behavior. This can most effectively be accomplished by developing model-generated mass balance diagrams that show the relative mass flows by each model processes, many of which cannot be directly measured in the system.

Presented in Figure 7-26 is a HUDTOX-computed TSS mass balance diagram for the period from 1977 to 1997; water column mass balances are shown for four reaches extending from the Thompson Island Pool down to Waterford. Several observations can be made about the river behavior with respect to solids dynamics from inspection of this diagram. First, one can see that tributaries along the length of the river contribute the vast bulk of the solids load carried by this system; the tributary loadings from Batten Kill and Fish Creek (Reach 2) and the Hoosic River (Reach 4) are the most significant tributaries. A second, very significant observation is that the river is net depositional throughout; gross TSS settling exceeds resuspension in all reaches. Given its length, the TIP is relatively efficient at trapping solids in its sediments. Based on this diagram 10.5 percent of incoming solids (upstream+tributary) are trapped in the bottom sediments of the pool. The Schuylerville to Stillwater reach (Reach 3) also traps approximately 10.5 percent of incoming solids but it is more than twice as long as the TIP reach (Reach 1).

A closer analysis of the solids dynamics in the TIP yields information about the relative net burial rates of solids in cohesive versus non-cohesive sediments in the system. Shown in Figure 7-27 are the model-generated average annual solids burial rates along the TIP for the 21-year simulation. It is quite apparent that more net burial occurs in the cohesive sediments than in non-cohesive areas. Annual burial rates in cohesive sediments range from 0.24-0.62 cm/yr along the pool, while burial in non-cohesive areas never exceeds 0.1 cm/yr (very little net deposition). Of course, this is an important consistency check on the model since cohesive sediments would not be cohesive if they were not located in higher deposition areas. Based on these model computations, the cumulative pool-wide average bed elevation change can be determined. Shown in Figure 7-28 is the result of this calculation, which indicates that the average bed elevation change in TIP over the 21-year hindcast period is approximately 4 cm, a very reasonable estimate for a dammed river.

In a similar fashion to what was done with solids, a mass balance diagram for total PCBs has been produced for the period from 1991-1997 (Figure 7-29). This more recent period was selected so as not to be misleading about PCB sediment-water fluxes, which have changed significantly over the 21-year historical period of record. Shown in Figure 7-29 on a reach-specific basis are the seven-year relative mass flows for all five sediment-water exchange processes included in HUDTOX. In the first three reaches the sediments are a net source of PCBs to the water column over this period, with the TIP sediments representing by far the largest net source. This occurs in spite of the fact that all reaches are net sinks for sorbing solids (see Figure 7-26); this type of behavior is not unusual for PCBs when sediment levels are high due to very large historical loadings. In Reach 4 (Stillwater to Waterford), this mass budget indicates the sediments acting as a very small (151 kg) sink of total PCBs. Nonetheless, over the entire upper river from Fort Edward to Waterford there has been a net increase of 1063 kg (a 45 percent increase of the Fort Edward load) in total PCB mass being carried in the river flow. Virtually all of this increase came from releases from the sediment pool.

The cumulative time trend of the sediment-water flux discussed in the above paragraph is shown in Figure 7-30. It shows that on a yearly basis the sediments in the first two reaches were always net sources. Sediments in Reach 3 began the seven year period as a very slight net sink, but by 1993 became a net source. Reach 4 sediments are a very small net sink over the entire seven year period. During certain short-term events, the TIP sediments become a net sink for total PCBs (the Allen Mill gate structure failure in fall, 1991 being the most evident); however, on a yearly time scale TIP sediments were always a net source.

Referring back to Figure 7-29, of the four processes by which PCBs can be transported from sediments to water, the largest sediment to water mass transfer in the TIP is the result of particulate-PCB mass transfer (refer to Section 5.2.3 for discussion of this process). Resuspension and diffusive mass transfer of DOC-bound PCBs are also important in the pool. Downstream of the TID resuspension tends to dominate the sediment to water mass transfer processes.

Focusing on sediment contributions to water column PCBs in the TIP, it is instructive to compare the cumulative HUDTOX-computed net sediment contribution to load gain across the pool (Figure 7-31). One can see that BZ#4 is responsible for almost half of the net sediment release of total PCB between 1991-1997. BZ#52 makes a much smaller contribution, because its total concentration is smaller (see Figure 7-16) in combination with the fact that it is more hydrophobic, hence less mobile, than BZ#4. The negative net contribution of TSS from sediment in the TIP is included in this figure as a reminder that sediments can still be a net source of PCBs at the same time as there is a net deposition of solids.

### Comparison of HUDTOX and Low Resolution Coring Report (LRCR) Results

As part of the Reassessment, TAMS et al. (1998b) conducted an investigation of the change in sediment PCB inventories in TIP 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 TIP 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 sediment areas as opposed to point-to-point comparisons (TAMS and Tetra-Tech, 1999). 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 analysis was that there was no evidence of extensive widespread burial of historically contaminated sediments in TIP.

A direct comparison of results from the HUDTOX model with results from the LRCR is not possible due to the different assumptions in these two approaches. The LRCR analysis included only cohesive sediment areas that were historically known to be more contaminated than average TIP sediments, whereas the HUDTOX model included both cohesive and non-cohesive sediment areas over the full range of sediment inventories found in TIP. The LRCR analysis did not account for Tri+ mass loss that would be transported downstream of TIP or redeposited in TIP 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 TIP, and redeposition in TIP.

An approximate comparison of results suggests consistency among the HUDTOX, DEIR and LRCR analyses. A components analysis of the Tri+ hindcasting calibration indicated that 2,000 kg of Tri+ was lost from the TIP sediment inventory between 1984 and 1994. Most of this loss was due to Tri+ mass flux across TID and a small portion was due to volatilization. If the Tri+ inventory in 1984 is taken to be approximately 14,500 kg (TAMS et al., 1997), then this mass loss out of the pool correspond to approximately 14 percent. This value is within the range of the 4 to 59 percent estimate of mass loss from historical hotspots in the LRCR analysis. As an independent check on both of these approaches, the annual rate of net export of Tri+ from TIP was estimated to range between 0.36 and 0.82 kg/day over the period April 1991 to October 1995 (TAMS et al., 1997). Assuming a value of 0.60 kg/day, the net export of Tri+ from TIP sediments between 1984 and 1994 would be 2,190 kg which corresponds to a mass loss of 15 percent of the 1984 inventory. Because of its focus on hotspots, the LRCR is not able to distinguish between loss from TIP and redistribution to less contaminated areas within the pool. When coupled with the LRCR findings, HUDTOX and the DEIR suggest that there has also been a significant amount of redistribution of Tri+ mass within TIP 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 LRCR analysis. Results in Figure 7-28 indicate that the increase in sediment bed elevation in TIP between 1984 and 1994 computed by the HUDTOX model is approximately 1.6 cm. This is a poolwide result and it should be understood that there are differences between cohesive and non-cohesive sediment areas within TIP (Figure 7-27). 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, on a poolwide basis a net sedimentation rate of 1.6 cm over 10 years is small compared to the surface layer depth of 23 cm (9 in) in the LRCR sediment cores. Considering the differences in spatial and temporal scales of the two approaches, it can be concluded that the HUDTOX model and the LRCR are in qualitative agreement with respect to the question of widespread burial of historically contaminated sediments in TIP.

### 7.6. Conclusions

The above presentation of the calibration of HUDTOX has demonstrated that the model has been successful at representing the hydraulics, solids, and PCB dynamics of the Upper Hudson River over a long historic time period. This period of record was characterized by a significant transition from an early phase of high upstream PCB loads through a long declining phase to present-day conditions where upstream PCB loads are now very small (at or near current detection limit). The fact that HUDTOX has been able to successfully simulate this decadal-scale transition indicates that it is a reasonable, scientifically credible representation of the water, solids and PCB dynamics in the Upper Hudson River. The HUDTOX calibration also demonstrates that the model is internally consistent with the major trends and magnitudes of the best available data during this period.

With regard to the Upper Hudson River recovery, the controlling processes today and in the future are system hydraulics, external solids loads, sediment-water fluxes, water-air fluxes, and PCB fate in the sediments. It has been determined that this system is currently in the tail of a long PCB washout curve controlled largely by the rate at which PCBs are depurating from the upper mixed sediment layer. The surficial sediment depuration rate is crucial to the estimation of the river's recovery time under a continued No Action scenario. The surficial sediment depuration takes place by a combination of sediment to water feedback flux (resuspension and other mass transfer processes discussed above) and burial to deep sediments by net accumulation of "clean" solids from the watershed. Over the 21-year simulation period, external control of the depuration rate has shifted from upstream PCB loading to loading of "clean" solids from the watershed. Therefore, simulation of the river's recovery trajectory depends on an accurate representation of the processes controlling sediment-water interactions of PCBs and dynamics of solids in the system. The above HUDTOX calibration and diagnostic analysis has served to demonstrate that these important processes are well-characterized and well-parameterized by the calibrated HUDTOX model.

That is not to say that there are no unresolved scientific issues. There does not yet exist a complete understanding of all the physical, chemical, and biological processes that control PCB dynamics in the Upper Hudson River. PCB partitioning (particularly in sediments), non-flow-dependent sediment-water PCB fluxes (both dissolved and particulate), and sediment dechlorination and biodegradation are examples of processes for which a complete understanding is lacking. Nevertheless, the success of this model calibration confirms that HUDTOX is a credible and useful model for providing information on the principal Reassessment questions. In its present form, HUDTOX is a valid tool for providing information on system responses to continued No Action, impacts of a 100-year peak flow event, and for comparing responses among different remedial alternatives. Model forecasts for continued No Action and No Action with a superimposed 100-year peak flow event are presented in Chapter 8.

# Chapter 8

# 8. MASS BALANCE MODEL FORECAST SIMULATIONS

## 8.1. Introduction

In 1984 USEPA issued an interim decision of No Action concerning sediments contaminated with PCBs in the Upper Hudson River. This Reassessment is being conducted to provide technical information for reassessment of that No Action decision. As a first step in providing that information, the calibrated HUDTOX mass balance model was used to conduct forecast simulations designed to estimate long-term system responses to continued No Action and impacts due to a 100-year peak flow. The forecast simulations extend 21 years into the future from January 1, 1998. Results of these forecast simulations include PCB concentrations in the water column and sediments. These PCB exposure concentrations will be used as inputs to the ongoing ecological and human health investigations in the Reassessment.

## 8.2. No Action

Before conducting forecast simulations with any mass balance model, model inputs must be specified. In essence, model inputs themselves must be predicted before the model can be used to make predictions. It is not possible to make absolute predictions of river flows, solids loads, PCB loads or other model inputs. Consequently, it is not possible to use a mass balance model to make absolute predictions of the future. Results from forecast simulations can provide useful information on trends and approximate magnitudes of system responses to continued No Action under a specified set of assumptions. Mass balance models are most useful for comparing responses among different remedial alternatives and between remedial alternatives and continued No Action.

### 8.2.1. Approach

Forecast simulations were conducted for total PCBs because total PCB concentrations are required for the ecological and human health investigations in the Reassessment. The HUDTOX model was run for a 21-year forecast simulation period beginning on January 1, 1998 and extending through 2018. The initial water column and sediment PCB concentrations for forecast simulations were the same as the final PCB concentrations computed by the HUDTOX model in the 1991-1997 calibration simulation. The reason for selecting a 21-year simulation period was strictly operational. The most simple and direct approach for specifying the required model inputs was to re-use model inputs for the 1977 to 1997 hindcasting application and project them forward in time. Longer-term forecast simulations are planned as part of future work. With the exception of upstream PCB concentration at Fort Edward, all flows, solids loads and other external forcing functions in the forecast simulations were the same as those used for the 1977-1997 hindcasting application. In addition, all internal model parameters in the forecast simulations were the same as those determined in the calibration applications. The forecast simulations used the same model input file as the 1977-1997 hindcasting application with the exception of initial conditions for PCB water and sediment concentrations, and PCB loads at Fort Edward.

While water column PCB concentrations measured at Fort Edward show a declining trend through 1997, it is impossible to predict whether these concentrations will continue to decline, remain constant or increase in the future. A complicating factor is that stochastic pulse loads have occurred during the historical period. To conduct the forecast simulations, two different assumptions were made for upstream PCB concentrations at Fort Edward: first, water column PCB concentrations were held constant at a value equal to the observed annual average PCB concentration for 1997 (9.9 ng/l); and second, water column PCB concentrations were held constant at zero. Note that 9.9 ng/l is below the detection limit (11 ng/l) because many non-detects occurred in 1997 and these were assigned a value of one-half the detection limit. This approach to the forecast simulations constituted a single factor experiment in which upstream PCB load at Fort Edward was the only variable. It assumes that there will be no future load increases from any sources upstream of Fort Edward. In particular, it assumes no PCB releases from the GE Hudson Falls site other than those that might have existed during 1997 and no large releases such as occurred with the partial failure of the Allen Mill gate structure in 1991. In future work, other scenarios for continued No Action will be designed and additional forecast simulations will be conducted as part of the Feasibility Study.

It should be noted that after preparation of the Baseline Modeling Report, data became available for solids and PCBs from a high flow event that occurred in the Upper Hudson River in January, 1998 (O'Brien & Gere, 1999). The instantaneous peak flow during this event reached 35,300 cfs at Fort Edward, a flow that exceeded the maximum recorded USGS daily average flow for the entire 1977 to 1997 hindcast simulation period. A flood event with a peak flow of similar magnitude (35,200 cfs) was recorded during May of 1983. Both of these events represented a recurrence interval of approximately once in 15 years.

Results for the January 1998 event indicated that water column PCB concentrations were substantially higher than those observed during 1997. High PCB concentrations were observed between Hudson Falls and Fort Edward, in TIP and down to Schuylerville. These results appear to indicate that there are PCB sources above Rogers Island that can be activated by high river flows. Future work is planned to investigate the significance of these sources and their potential implications regarding assumptions about upstream boundary PCB loadings during model forecast simulations.

### 8.2.2. Results

Results are expressed in terms of PCB concentrations and mass fluxes in the water column at Thompson Island Dam and Waterford, and PCB concentrations in surficial sediments (0-4 cm) in Thompson Island Pool and in downstream reaches between Northumberland Dam and Waterford. In consultation with Menzie-Cura and Associates, Inc., it was judged that a sediment depth of 4 cm was the most appropriate spatial scale for representation of sediment PCB exposures to benthic organisms. PCB concentrations are presented at daily average and summer average (June through September) time scales.

Water column PCB concentrations appear to decline for both constant and zero upstream boundary cases (Figure 8-1); however, it is difficult to discern relative trends on the log scale in this figure. Results for summer average PCB concentrations (Figure 8-2) are more indicative of long-term response trends because much of the variability due to high flow events is removed and results can be compared on a linear scale. Summer average PCB concentrations decline at both locations and there is separation between results for the constant and zero upstream boundary cases. The rate of decline appears to be greater at TID than at Waterford. Annual PCB fluxes show trends similar to those for summer average PCB concentrations in the water column (Figure 8-3).

Surficial sediment PCB concentrations decline for both constant and zero upstream boundary cases (Figure 8-4). In absolute terms, declines in concentrations are greater in Thompson Island Pool than in downstream reaches (Northumberland Dam to Waterford). In sharp contrast to results for water column PCB concentrations (Figure 8-2), there appears to be no difference between constant and zero upstream PCB boundary cases in any portion of the river during the entire 21-year forecast.

### 8.3. 100-Year Peak Flow

There is concern 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. As mentioned above, 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, 1993).

#### 8.3.1. Approach

The HUDTOX model was run for a 21-year forecast simulation with a peak flow corresponding to the peak flow in a 100-year flood imposed in spring of the first year. This peak flow was imposed on the forecast simulation for continued No Action with zero PCB concentration at Fort Edward. 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 experiment in which the only differences between continued No Action and the 100-year peak flow would be due to changes in flow-dependent sediment resuspension. This design was also 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 8-5 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. Daily flows at Fort Edward were scaled up by a factor of 1.972 from March 13 through March 29. The 1977 peak spring flow in the time series was scaled up from 24,000 cfs to a value of 47,330 cfs on March 15. The duration, rise and fall of the 100-year flow in this modified hydrograph was generally consistent with other observed peak flows in the 21-year historical period. The value of 24,000 cfs for the first spring peak in 1977 was close to the historical average spring peak flow of 21,339 cfs at Fort Edward. This modified hydrograph represents a 100-year peak flow but does not necessarily represent the duration, rise and recession characteristics of a 100-year flood event.

### 8.3.2. Results

Differences in water column PCB concentrations between the base No Action case and imposition of a 100-year peak flow are relatively small and of short duration (Figure 8-6). Forecasted PCB concentrations are actually lower for during the 100-year peak flow due to dilution, and then remain lower due to deposition by increased external loadings of less-contaminated sediments due to the event. Results are shown only at TID because this location is immediately downstream of the most contaminated sediments in the Upper Hudson River. Imposition of a 100-year peak flow on the base No Action case causes an increase of approximately 59 kg in cumulative total PCB flux across TID (Figure 8-7). Most of this flux increase occurs over a very short period of time during the peak flow event.

## 8.4. Discussion

A very significant result is that surficial sediment PCB concentrations are not controlled by upstream PCB loads, at least for the loading range between the constant and zero upstream boundary cases in these forecast simulations. Another significant result is that water column PCB concentrations are influenced by upstream PCB loadings (Figure 8-2), and the relative degree of influence increases with time over the 21-year forecast as PCB concentrations in the surficial sediments decline (Figure 8-4).

These responses suggest that sediment PCB concentrations are controlled primarily by sediment-water flux and exchange between surface and deep sediments. They also suggest that water column PCB concentrations are controlled by a combination of sediment-water exchange and upstream loading. For the constant upstream boundary assumptions in these forecasting simulations, the rate of decline of PCB concentrations in the water column is controlled by the rate of decline of PCB concentrations in the surficial sediments. For example, the apparent first-order decay rate for summer average water column PCB concentrations at TID (Figure 8-2) is 0.073/yr. The corresponding decay rate for PCB concentrations in the surficial sediments of TIP is 0.069/yr. This suggests that although a constant upstream PCB load contributes to PCB concentration in the water column, the response trajectory of the water column PCB concentration is controlled by sediment-water fluxes.

Another conclusion that can be drawn from the above results is that the water column and sediments of the Upper Hudson River have not reached steady-state with the present upstream PCB loads. For example, results in Figure 8-2 indicate that even after 21 years with constant upstream boundary concentrations, water column PCB concentrations still continue to decline and have not yet dropped below the 1997 upstream boundary concentration.

Results of the forecast simulation for the 100-year peak flow indicated that this event causes a relatively minor and short-lived perturbation to the long-term response trajectory for continued No Action. Although not shown, forecasted summer average PCB concentrations in the water column with and without the 100-year peak flow are virtually indistinguishable one year after the event. The estimated additional PCB flux of approximately 59 kg over Thompson Island Dam for this event is a small fraction of the total sediment PCB inventory in TIP. The size of this inventory in 1984 (in terms of Tri+) was estimated at 14,500 kg (TAMS et al., 1997).

Results from this baseline modeling effort are necessary but not sufficient to guide a decision on continued No Action versus remedial scenarios. Information on PCB exposure concentrations will provide input to the ecological and human health investigations in the Reassessment. Remediation decisions will ultimately be based on the desired ecological and human health endpoints, and the desired schedule for attaining these endpoints.

THIS PAGE LEFT BLANK INTENTIONALLY

## 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.

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., DePinto, J.V., Young, T.C., Rodgers, P.W., Martin, S.C., and Raghunathan ,R.. 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.

Borah, Deva K. 1989. "Scour Depth Prediction Under Armoring Conditions". *Journal Hydraulic Engineering* 115(10), p. 1421.

Brown, Jr., J.F., R.E. Wagner and D.L. Bedard. 1984. "PCB Transformations in Upper Hudson Sediments." *Northeastern Environmental Science*. 3:184-189.

Brownawell, B. 1986. *The role of Colloidal Oreganic 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 Tofflemire, T.J. 1983. "Uptake of Airborne Poolychloriniated Biphenyls in Foliage." *Science.* 216: 520-522.

Butcher, J.B. 1993. "Flood frequency analysis, Fort Edward at Roger's Island Gage" Hudson River. Memorandum on Revised Log Pearson Flood Frequency Analysis.

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. 1960. *Open-Channel Flow*. McGraw-Hill. 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 Robbins, J.A. 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.

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 Reserach* 17(4): 479-494.

Gailani, J., W. Lick, C.K. Ziegler, and D. Endicott. 1996. "Development and calibration of a gine-grained sediment transport model for the Buffalo River." *Journal of Great Lakes Research* 22(3):765-778.

Hoff, R.M., W.M.J. Strachan, C.W. Sweet, *et al.* 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. Tofflemir. 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.

Karickhoff, S.W., Brown, D.S., and Scott, T.A. 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 Kennedy, J. F. 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.

Limno-Tech, Inc., Menzie Cura and Associates, Inc., and The CADMUS Group, Inc. 1996. "Preliminary Model Calibration Report." Phase 2 Report. Further Site Characterization and Analysis Volume 2B. Hudson River PCBs Reassessment RI/FS. USEPA Region II. October 1996.

Lin, Hsin-Chi J., and Richards, David R. (1993). "Numerical Model Investigation of Saugus River and Tributaries, Massachusetts, Flood Dam age Reduction." *Technical Report HL-93-5*, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Little, W. C., and Mayer, P. G. 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 Armstrong, D.E. 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, William H., Jr., Letter, Joseph V., Jr., Stewart, J. Phillip, Brogdon, N. James, Jr., Anthony, Thomas W. (1984). "Columbia River Hybrid Modeling System." *Journal of Hydraulic Engineering* 110(3), 300-311.

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., Wasserman, W., and Kutner, M. H. 1985. *Applied Linear Statistical Models*, 2nd Ed., Richard D. Irwin, Inc.

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. "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. 1993b. "Hudosn 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. 1999. "1998 High Flow Monitoring Program, Hudson River Project." *General Electric Company, Corporate Environmental Programs*. Albany, New York.

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.

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, 1998. "Sediment Bed Mapping Study of the Upper Hudson River from Northumberland Dam to Troy Dam." Prepared for the General Electric Company. Final Report.

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 Eisenreich. S.J. 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.

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.

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. 1996. *SYSTAT® Version 6.0 for Windows® Statistics*. 444 North Michigan Avenue, Chicago, IL 60611 U.S.A.

TAMS Consultants, Inc. and Gradient Corporation, 1998a. "Database for the Hudson River PCBs Reassessment RI/FS, Phase 2 Report Further Site Characterization and Analysis Database Report" Volume 2A, Release 4.1b.

TAMS Consultants, Inc. and Gradient Corporation. 1991. "Phase I Report - Review Copy. Interim Characterization and Evaluation" Volume 1. *Hudson River PCBs Reassessment RI/FS*. August 1991.

TAMS Consultants, Inc. and Gradient Corporation. 1992. "Final Phase 2 Work Plan and Sampling Plan." *Hudson River PCBs Reassessment RI/FS*. September 1992.

TAMS Consultants, Inc. and Gradient Corporation. 1995. "Further Site Characterization and Analysis Database Report." Phase 2 Report - Review Copy. *Hudson River PCBs Reassessment RI/FS*. October 1995.

TAMS Consultants, Inc., and Tetra Tech, 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 U.S. Environmental Protection Agency, Region II and U.S. Army Corps of Engineers, Kansas City District. February 1999.

TAMS Consultants, Inc., and Tetra Tech, 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 U.S. Environmental Protection Agency, Region II and U.S. Army Corps of Engineers, Kansas City District. February 1999.

TAMS Consultants, Inc., Gradient Corporation and Tetra Tech, Inc. 1998b. "Further Site Characterization and Analysis" Volume 2C-A – Low Resolution Sediment Coring Report, *Hudson River PCBs Reassessment RI/FS.* July 1998.

TAMS Consultants, Inc., The Cadmus Group, Inc. and Gradient Corporation. 1997. "Further Site Characterization and Analysis" Volume 2C - Data Evaluation and Interpretation Report. *Hudson River PCBs Reassessment RI/FS.* February, 1997.

Tetra Tech, Inc. and TAMS Consultants, Inc. 1998. "Review and Commentary on General Electric/Quantitative Environmental Analysis, LLC Thompson Island Pool Sediment PCB Sources, Final Report", Book 3, Section 1. In TAMS/Limno-Tech/Tetra Tech/Menzie-Cura. 1998. *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.*

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 Mueller, J.A., 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.

Tsivoglou, E.E. and J.R. Wallace. 1972. *Characterization of Stream Rearation Capacity* EPA-R3-72-012. U.S. Environmental Protection Agency, Washington, D.C.

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.

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 van Gelder, A. 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.

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.