PHASE 2 REPORT - REVIEW COPY
FURTHER SITE CHARACTERIZATION AND ANALYSIS
VOLUME 2D - REVISED BASELINE MODELING REPORT
HUDSON RIVER PCBs REASSESSMENT RI/FS

JANUARY 2000

For

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

Volume 2D - Book 3 of 4
Bioaccumulation Models

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

PHASE 2 REPORT - REVIEW COPY
FURTHER SITE CHARACTERIZATION AND ANALYSIS
VOLUME 2D - REVISED BASELINE MODELING REPORT
HUDSON RIVER PCBs REASSESSMENT RI/FS

JANUARY 2000

For

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

Volume 2D - Book 3 of 4
Bioaccumulation Models

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

Table of Contents

PHASE 2 REPORT – REVIEW COPY
FURTHER SITE CHARACTERIZATION AND ANALYSIS
Volume 2D – REVISED BASELINE MODELING REPORT
HUDSON RIVER PCBs REASSESSEMENT RI/FS

BOOK 3 of 4

CONTENTS

Page

PHASE 2 REPORT – REVIEW COPY
FURTHER SITE CHARACTERIZATION AND ANALYSIS
Volume 2D – REVISED BASELINE MODELING REPORT
HUDSON RIVER PCBs REASSESSEMENT RI/FS

BOOK 3 of 4

CONTENTS

PHASE 2 REPORT – REVIEW COPY
FURTHER SITE CHARACTERIZATION AND ANALYSIS
Volume 2D – REVISED BASELINE MODELING REPORT
HUDSON RIVER PCBs REASSESSEMENT RI/FS

BOOK 3 of 4

CONTENTS

Page

PHASE 2 REPORT – REVIEW COPY
FURTHER SITE CHARACTERIZATION AND ANALYSIS
Volume 2D – REVISED BASELINE MODELING REPORT
HUDSON RIVER PCBs REASSESSEMENT RI/FS

BOOK 3 of 4

LIST OF TABLES

BOOK 3 of 4

LIST OF TABLES

PHASE 2 REPORT – REVIEW COPY
FURTHER SITE CHARACTERIZATION AND ANALYSIS
Volume 2D – REVISED BASELINE MODELING REPORT
HUDSON RIVER PCBs REASSESSEMENT RI/FS

BOOK 3 of 4

LIST OF FIGURES

PHASE 2 REPORT – REVIEW COPY
FURTHER SITE CHARACTERIZATION AND ANALYSIS
Volume 2D – REVISED BASELINE MODELING REPORT
HUDSON RIVER PCBs REASSESSEMENT RI/FS

BOOK 3 of 4

LIST OF FIGURES

BOOK 3 of 4

LIST OF FIGURES

<u>**FIGURES**</u>   <u>**TITLES**</u>

1. INTRODUCTION

1.1 Background

The Hudson River watershed encompasses an area of 13,390 square miles, principally in the eastern portion of New York State (Book 2, Figure 1-1). The Hudson River PCB Superfund Site extends from Hudson Falls, New York, to the Battery in New York Harbor (River Mile 0), a stretch of almost 200 river miles. The Upper Hudson refers to the approximately 40-mile stretch of river upstream of Federal Dam at Troy to Hudson Falls (Book 2, Figure 1-2). The Lower Hudson refers to the portion of the river downstream of Federal Dam to the Battery.

For approximately 30 years, two General Electric (GE) facilities, one in Fort Edward and the other in Hudson Falls, used polychlorinated biphenyls (PCBs) to make electrical capacitors. GE discontinued use of PCBs in 1977 when PCBs ceased to be manufactured and sold in the United States. From 1957 through 1975, between 209,000 and 1.3 million pounds of PCBs were discharged from these facilities into the Upper Hudson River. Migration of PCBs downstream was greatly enhanced in 1973 with the removal of Fort Edward Dam and the subsequent release downstream of PCB-contaminated sediments. A region of special concern is the highly-contaminated sediments in Thompson Island Pool (TIP) immediately downstream of the old Fort Edward dam site.

In 1984 the U.S. Environmental Protection Agency (USEPA) completed a Feasibility Study on the site that investigated remedial alternatives and issued a Record of Decision (ROD) later that year. The ROD called for: (1) an interim No Action decision concerning river sediments; (2) in-place capping, containment and monitoring of remnant deposit (formerly impounded) sediments; and, (3) a treatability study to evaluate the effectiveness of the Waterford Treatment Plant in removing PCBs from Hudson River water.

1.2 Purpose of Report

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

Phase 1 - Interim Characterization and Evaluation

Phase 2 - Further Site Characterization and Analysis

Phase 3 - Feasibility Study.

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

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

MCA/TetraTech

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; USEPA, 1998b) and accompanying CD-ROM database re-issued in August 1998 provides the validated data for the Phase 2 investigation. The Data Evaluation and Interpretation Report (USEPA, 1997) presents results and findings of water column sampling, high-resolution sediment coring, geophysical surveying and confirmatory sampling, geostatistical analysis of 1984 sediment data and PCB fate and transport dynamics.

This Revised Baseline Modeling Report is Volume 2D in the Phase 2 series of reports. It includes descriptions of the transport and fate mass balance models, and the fish body burden models that are being used for this PCB Reassessment RI/FS. This report builds upon and supercedes the Baseline Modeling Report, which was released for public comment in May 1999. The revisions in this report incorporate changes based on comments received during the public comment period on the Baseline Modeling Report and on additional analyses.

1.3 Report Format and Organization

Chapter 2 of this report contains background information on the theory of PCB uptake into fish. Chapter 3 contains a description of the specific approaches taken for each of the fish body burden models as well as mathematical descriptions of the individual models. Chapter 4 contains the results from the bivariate BAF analyses. Chapter 5 contains calibration and validation results for the probabilistic empirical model using the hindcasting sediment and water results from the fate and transport models. Chapter 6 contains calibration and validation results for the FISHRAND model (a mechanistic time-varying model incorporating probability distributions and based on a Gobas approach) using the hindcasting sediment and water results from the fate and transport models. Chapter 7 provides predictive results for 1998 – 2067 based on inputs from the fate and transport models for the constant upstream boundary condition, and the zero upstream boundary condition. Chapter 8 contains a discussion of the uncertainties in the modeling analysis as well as a sensitivity analysis. Chapter 9 presents the summary and conclusions for Books 3 and 4 of the Baseline Modeling Report.

The material in this report has been divided into four separate books. Book 1 contains the report text, a list of references, and a glossary of abbreviations and acronyms for the fate and transport modeling. Book 2 contains all tables, figures, plates and appendices for the fate and transport modeling discussed in Book 1. Book 3 contains the report text, a list of references, and a glossary of abbreviations and acronyms for the food chain modeling. Book 4 contains all tables, figures, plates, and appendices for the food chain modeling discussed in Book 3. Within Book 4, Appendix A contains ecological profiles for fish species represented in the fish body burden models and the derivation of feeding preference distributions for the individual fish species.

2. GENERAL BACKGROUND ON PCB UPTAKE

2.1 PCB Compounds

This report examines bioaccumulation of PCBs characterized as Aroclors for the historical datasets and as selected congeners for the Phase 2 dataset. A challenge to developing a modeling framework for PCB bioaccumulation is that PCBs consist of 209 individual congeners, which exhibit varying degrees of bioaccumulation potential, depending on the number and position of chlorine atoms on the molecule. The more highly-chlorinated congeners tend to accumulate in fish tissues. This effect may be a function not of increased uptake, but rather decreased elimination efficiency from the fish.

Studies that have measured PCBs as individual congeners have provided insights into the bioaccumulation processes for watercolumn and sediment-based communities. Several researchers have noted that even though total PCB levels may or may not increase with higher position on the food chain, chlorine content of PCB body burdens tends to increase (Smith et al., 1985; Oliver and Niimi, 1988; Van der Oost et al., 1988; MacDonald et al., 1993). Congener patterns of caged fathead minnows and feral brown bullhead from the area around Thompson Island Pool in the Hudson River were generally similar, sharing 60 percent of their 20 most abundant peaks, but the bullhead had higher concentrations of hexa- and heptachlorobiphenyls (Jones et al., 1989). The fish contained 17 peaks that were not detectable in water samples. It has been noted that when young bluefish enter the Hudson River from offshore, heavier, more chlorinated congeners were accumulated to a greater level than lighter, less chlorinated congeners (LeBlanc and Brownawell, 1994).

A variety of factors control accumulation of PCB congeners (Shaw and Connell, 1984; Jones et al., 1989; Kadlec and Bush, 1994; Ankley et al., 1992; LeBlanc and Brownawell, 1994):

1. Individual PCB congener characteristics, including solubility and partition coefficients, degree of chlorination, and stereochemistry. Shaw and Connell (1984) found that more planar molecules are more strongly absorbed that those with more typical shapes.

2. Characteristics of the fish, including lipid content of gills, blood, and tissue; cardiac output; ventilation volume; gill surface area; epithelium layer of gill; aqueous stagnant layer of gill; ability to biotransform PCBs; and, excretion rates.

3. Environmental factors, including temperature, pH, light, current, suspended particles, and dissolved organic compounds.

2.2 PCB Accumulation Routes

Fish and other aquatic animals are exposed to PCBs through direct contact with water (bioconcentration), and sediment, as well as through dietary sources (bioaccumulation). Due to their hydrophobicity, PCBs tend to accumulate in the lipid portion of organisms. PCBs have also been found to accumulate in predatory fish tissues at higher concentrations than the concentrations in the surrounding water would predict (Thomann and Connolly, 1984), a process

MCA/TetraTech

known as biomagnification. Depending upon the position of an aquatic organism within the aquatic food web, exposure may be intensified through food sources as organisms consume other organisms that have bioaccumulated PCBs in the lipid portion of their tissues. Because of the important role of food as an exposure pathway, the feeding ecology of a fish species is a key aspect in distinguishing between the relative contribution of the water column and sediments to body burdens of PCBs.

2.2.1 Direct Uptake from Water

For fish, direct uptake of PCBs from water occurs primarily across the gills. No significant evidence exists for absorption through the epidermis (Shaw and Connell, 1984).

The significance of direct uptake from water of PCBs has been debated. Based upon laboratory studies, Shaw and Connell (1984) argued that uptake via the gills is the major route for accumulation of PCBs. Some field studies have indicated that water column uptake could account for PCB concentrations observed in biota, if PCB concentrations were normalized for lipid content of the organism (*e.g.*, Clayton et al., 1977).

Other researchers have continued to examine the potential for bioconcentration through the gills to account for PCB concentrations. Caged rainbow trout that were fed clean, commercial food appeared to accumulate PCBs directly from contaminated waters of the St. Lawrence River (Kadlec, 1994; Kadlec and Bush, 1994). Barron (1990) noted that simple evaluations of uptake directly from the water column have assumed that bioconcentration is controlled by the hydrophobicity of the compound, as measured by its octanol-water partition coefficient. He argued that bioconcentration appears to be independent of octanol-water partition coefficients when the coefficient is small or when the molecule to be accumulated is large. He summarized other factors that affect bioconcentration: molecular shape, degree to which the compound is bound to dissolved organic matter, lipid content of the gills, size of the organism, blood flow, variations in enzyme content and activity, and exposure temperature and ionic content.

2.2.2 Uptake via Food

Field studies and modeling efforts have indicated that biomagnification through the food chain is an important component for bioaccumulation. Sloan et al., (1984), for example, suggested that the presence of higher chlorinated Aroclor mixtures in fish of the Lower Hudson River might reflect a food chain component to bioaccumulation. Using existing field data, Thomann (1981, 1989) derived steady-state food chain models, considering uptake of contaminants from both water and food sources through several trophic levels. The models indicated that food assimilation, excretion, and net weight gain were important characteristics that determined bioaccumulation levels. They also demonstrated that for top predators, such as Hudson River striped bass, almost all the observed PCB body burden could be attributed to a food source. In Lake Michigan lake trout, only 2 to 3 percent of the PCB accumulation could be predicted from water column concentrations using an age-dependent model (Thomann and Connolly, 1984), while transfer through the food chain accounted for up to 99 percent of the body burden of PCBs in Lake Michigan lake trout.

MCA/TetraTech

303770

Many researchers have tested, refined, or elaborated upon Thomann's food chain models. One test of the approach examined PCB accumulation in young-of-the-year bluefish which enter the Hudson River Estuary from relatively uncontaminated offshore waters and grow quickly (LeBlanc and Brownawell, 1994). Connolly et al., (1985) considered growth rates, respiration rates, food assimilation efficiency, predator-prey relationships, PCB assimilation efficiency, and bioconcentration factors for PCBs when they applied a model to existing data from the Hudson River system. They predicted PCB levels in Hudson River striped bass, assuming various reductions in concentrations of PCBs in the water column. They also began efforts to incorporate lipid- and non-lipid components of the striped bass into the model. Pizza and O'Connor (1983) conducted laboratory experiments to determine rates of PCB accumulation from the gut and elimination from the body in young-of-the-year striped bass from the Hudson River. An EPA model, Food and Gill Exchange of Toxic Substances, or FGETS, has been used to predict average concentrations of contaminants in the food web over time (*e.g.*, Woolfolk et al., 1994). This model incorporates bioconcentration of contaminants from the water column and biomagnification in the food chain.

Gobas et al., (1993, 1995, 1999) examined the roles of food digestion, food absorption, and rates of gill elimination and metabolic transformation upon bioaccumulation. This model has recently been updated to include exposure from both water and sediment sources, and a pharmacokinetic module. The mechanistic model presented here (FISHRAND) is based on these approaches (1993, 1995, 1999).

As part of this modeling effort, Menzie-Cura & Associates have evaluated a number of fish gut contents from the NYSDEC sampling effort. Similarly, Exponent, Inc. on behalf of General Electric conducted a study on fish gut contents and identified specific invertebrates down to the lowest practical taxonomic level in the diets of fish. This information, together with historical data from the Hudson River power plant studies, have been used to more precisely define food web relationships in the Hudson. The results of this effort are discussed and presented in greater detail in Appendix A.

2.2.3 Uptake from Sediments

Equilibrium partitioning has been suggested to be the major factor controlling bioaccumulation in sediment-based benthic communities. Bierman (1990) used field data from the Great Lakes to determine that for animals at the lower and middle parts of the food chain, including oligochaetes, chironomids, amphipods, sculpin, small smelt, and large smelt, predicted bioconcentration factors based upon equilibrium partitioning coefficients accounted for concentrations of hydrophobic organic compounds. Comparing laboratory and field data, Ankley et al., (1992) confirmed that for oligochaetes, concentrations of PCBs in the sediments could be used to predict concentrations of PCBs in organisms, but that for other species, food or possibly ingestion of contaminated particles could affect concentrations. Ingestion of contaminated food also seemed to be a factor in accumulation of PCBs in a freshwater lake (Van der Oost et al., 1988).

A steady-state food chain model with a benthic invertebrate component was developed to account for both water column and sediment sources of contaminants (Thomann et al., 1992).

This model considered four exposure routes for ingestion of particulate contaminants: sediment organic carbon, overlying plankton, interstitial water, and overlying water. Applying the model to an amphipod-sculpin food web in Lake Ontario (Oliver and Niimi, 1988), Thomann and his co-workers (1992) found that accumulation was based primarily upon a benthic food web rather than upon direct uptake from the water column. They noted however, that including the overlying water and phytoplankton as a food source were necessary to explain the field data. Considering only interstitial water and sediment particles as contaminant sources was not satisfactory.

2.3 Food Web Models from the Literature and their Sensitivity to Input Parameters

All bioaccumulation models use a set of parameters to predict the body burdens of organic contaminants in higher organisms. The uncertainty associated with these parameters contributes to the uncertainty of the risk estimate. Burkhard (1998) compared the sensitivity of the Gobas (1993) and Thomann (1989) model outputs to changes in their input parameters. Sensitivity of the models to changes in input parameters was determined by running each model once with nominal input values, and then changing one input value by 10%, and running the model with the altered input value. A sensitivity index of 1.0 means that a 10% change in the input parameter resulted in a 10% change in the model output. In this case, the model output examined was the bioaccumulation factor, which is equal to the ratio of the lipid-normalized concentration of chemical in fish to the concentration of freely dissolved chemical in water.

For both models, the input parameters with the largest influences were:

- lipid contents of the organisms;

- K_{ow} of the chemical;

- ratio of the concentration of chemical in sediment organic carbon to the concentration in overlying water (Π_{SOCW}); and,

- feeding preferences of the organisms (only for chemicals with log K_{ow} exceeding 6).

The sensitivity index ranged up to about –20 (indicating a decrease in BCF) for the feeding preference of a benthic invertebrate on phytoplankton in the Thomann model. The models were less sensitive to changes in organism weight, temperature (input to Gobas model only) and sediment organic carbon (input to Gobas model only).

The approach described above is limited because it does not take into account uncertainty in input modeling parameters. For example, an input parameter with low sensitivity (i.e. sensitivity index is close to 1) adds considerable uncertainty to estimates of model outputs if the measurement uncertainty distribution of this input parameter is relatively large. Uncertainty associated with the input parameters may result from analytical errors in the measurement of the parameter, sampling that is not representative of the population, or lack of sufficient information about the parameter. Moreover, many input parameters are variable in nature (fish body weight, lipid content, etc.)

The dual influences of variability and uncertainty in the input parameters on model outputs must be considered when evaluating the overall model uncertainty. Monte Carlo simulations should be performed for each input parameter, using a plausible range of values or distribution for each input parameter. Burkhard (1998) compared the ratios of the 90th and the 10th percentiles of the model output derived from the simulations among input parameters. For both models, Π_{SOCW}, K_{ow}, and feeding preferences resulted in the largest range of simulated output values. Table 2-1 summarizes results from Burkhard (1998).

Note, however, that the findings of Burkhard (1998) are based on the analysis of a Great Lakes food web in which benthic organisms are an important food source for higher trophic level organisms. In food webs where the benthic component is less important, the importance of the sediment-related input parameters on the uncertainties associated with predicted model outputs may be different.

The model used by Iannuzzi et al. (1996) is based on a Monte Carlo version of the equations developed by Thomann et al. (1992), and Gobas (1993). They developed probabilistic distributions for several parameters that are typically used in mechanistic bioaccumulation models to predict the uptake of organic contaminants in aquatic food webs. The ranges, central tendencies, and distributions of key parameters of the models were derived from a critical evaluation of the literature on the physiology and ecology of three common estuarine organisms rather than from site-specific experimental data. Distributions of the physical/chemical characteristics (i.e. the octanol-water partition coefficient, K_{ow}) for several congeners of PCBs were also compiled from the literature.

The model used by Iannuzzi et al. (1996) was used to estimate the concentrations of five coplanar PCB congeners in adult mummichog fish, blue crab, and striped bass, using distributions of available data on PCB and total organic carbon (TOC) concentrations that were measured in surface sediments from the Passaic River in northern New Jersey. A model sensitivity analysis was performed to rank input parameters according to their contribution to model predictions.

Results of the sensitivity analysis suggest that the input parameters that most influence the model (not listed in order of importance) are:

- BSAF (biota-sediment accumulation factor) for infaunal organisms;

- lipid content;

- chemical concentrations in sediment;

- total organic carbon (TOC) content of sediments;

- the chemical assimilation efficiency (CAE);

- residence time in the river for striped bass; and,

- log K_{ow}.

In summary, both Burkhard (1998) and Ianuzzi et al. (1996) concluded that the lipid content of the exposed organisms and the K_{ow} of the contaminant influence estimates of tissue concentrations more than other parameters. The ability of organisms to metabolize specific PCB congeners is also an important factor in the quantitative evaluation of uncertainty.

MCA/TetraTech

3. MODELING APPROACH: FISH BODY BURDENS

3.1 Modeling Goals and Objectives

The goal of the bioaccumulation component of the modeling effort is to develop a framework for relating body burdens of PCBs in fish to exposure concentrations in Hudson River water and sediments. This framework is used to understand historical and current relationships as well as to predict fish body burdens for future conditions. Estimates of PCB body burdens in fish are intended to be used in the human health and ecological risk assessments and aid in decision making regarding options for addressing PCB-contaminated sediments in the Upper Hudson River.

The objectives of the body burden modeling effort are based on discussions with the investigators responsible for the human health and ecological risk assessments and with the fate and transport modeling team. Because PCB analytical protocols have varied over time, the framework needs to account for historical as well as current data to the extent possible. Accordingly, the framework is structured to meet the following objectives:

- relate historical body burden data (originally reported as PCB Aroclors, Aroclor totals, and, individual congeners for a limited subset of the historical data) to exposure concentrations in water and sediments;

- relate current and future body burdens (as PCB Aroclors, totals, and individual congeners) to exposure concentrations in water and sediments;

- provide estimates in a form that can be used for human health risk assessments;

- provide estimates in a form that can be used for ecological risk assessments; and,

- provide a set of modeling tools that can be coupled with the output from the PCB fate and transport models to evaluate future management goals and the impact of No Action and/or potential remedial alternatives.

To achieve these objectives, three modeling approaches have been developed to relate PCB exposure concentrations in water and sediment to body burdens. Each of these approaches organizes the data in different ways to provide complementary views of PCB uptake. These approaches are introduced next.

Bivariate BAF Analysis: This analysis uses available time series data to develop statistical relationships between concentrations in water and sediments and those in fish based on observations from the historical New York State Department of Environmental Conservation (NYSDEC) yearly monitoring. This analysis represents an empirical perspective of the statistical relationship between fish body burdens and sediment and water exposures in a tiered approach to food chain modeling.

Empirical Probabilistic Food Chain Model: This model relies on knowledge of feeding relationships to link body burdens to water and/or sediments through a series of empirical transfer coefficients using a combination of the historical NYSDEC data, New York State Department of Health (NYSDOH) data, and the US EPA Phase 2 data. This model provides ground-truth information on observed relationships between food-web compartments.

FISHRAND: Gobas Time-Varying Mechanistic Model: This mechanistic, time-varying model is based on the modeling approach presented in Gobas (1993 and 1995). The model relies on solutions of differential equations to describe the uptake of PCBs over time, and incorporates both sediment and water sources to predict the uptake of PCBs based on prey consumption and food web dynamics.

These approaches complement one another and represent a logical progression in the evaluation of PCB uptake. Both the bivariate analysis and the empirical probabilistic model utilize derived Bioaccumulation Factors (BAFs) and rely on organizing observed data into meaningful relationships, while FISHRAND is mechanistic and based on mass-balance of PCBs rather than direct observations. The agreement between these and the resultant estimates of body burdens provide a check on the three approaches. The bivariate analysis indicates the relative importance of water and sediment pathways from a statistical, data-based point of view irrespective of the underlying biology. The probabilistic bioaccumulation model represents a slight refinement and limited mechanistic consideration by explicit incorporation of feeding preference data and uncertainty and variability information. FISHRAND predicts probability distributions of expected concentrations in fish based on mechanistic mass-balance principles, an understanding of PCB uptake and elimination, and information on the feeding preferences of the fish species of interest.

Selection of fish species for modeling body burdens was based on several criteria including: 1) importance for fishing, 2) abundance, 3) importance in diet of other fish, 4) whether the selected species is representative of particular habitats or trophic levels, and 5) whether the selected species is representative of other fish species. Upon discussion with NYSDEC, USEPA, and NOAA the following species were selected for bioaccumulation modeling:

MCA/TetraTech

Fish Species	Characteristics
Spottail Shiner	Forage Fish, feeds on invertebrates in water column and sediments
Pumpkinseed	Forage Fish, feeds on invertebrates in water column (on aquatic plants) and to a limited degree sediments; popular recreational fish but seldom eaten
Brown Bullhead	Lives in contact with sediment and feeds on a variety of animal life on or in the sediments; can be fished recreationally and is eaten occasionally
Yellow Perch	Inhabits water column and feeds on invertebrates and small fish; popular recreational fish and is commonly eaten
Largemouth Bass	Larger individuals feed primarily on fish but will also eat other vertebrates and invertebrates; popular recreational fish and is commonly eaten
White Perch	Feeds on invertebrates and small fish; lives in the tidal portion of the Hudson; undergoes migrations within the river

Ecological profiles for the selected fish species are provided in Appendix A and are used to discern behavioral and trophic characteristics that could affect accumulation of PCBs.

The Bivariate BAF Analysis uses pumpkinseed, brown bullhead, largemouth bass, white perch, and yellow perch. Sufficient historical data were not available for spottail shiner; however, goldfish were added to the statistical analysis.

In addition to the fish species listed above, the striped bass is included in the evaluation. However, no new models have been developed for this species. A major confounding factor is that the striped bass are a migratory species that are resident in the river for only a portion of the year. As such, it is inappropriate to assume that all PCB exposure occurs within the Hudson River, and under the current modeling framework, this is a key assumption. The modeling program relies upon the work of Thomann to derive estimates for striped bass. It would be desirable to have a model for the shortnose sturgeon, an endangered fish species in the tidal portion of the Hudson. However, data are insufficient to develop a model for this species. It is anticipated that a species-to-species extrapolation will be employed to evaluate the shortnose sturgeon, based on physiological, feeding and habitat selection characteristics.

3.2 Conceptual Basis for Hudson River Bioaccumulation Models

The food chain models developed here share a common conceptual basis including:

1. PCB body burdens in fish are related ultimately to exposure concentrations in water and/or sediments;

2. PCBs in the water column and sediments are not necessarily in equilibrium with each other;

3. Within the water and sediment compartments, an equilibrium or *quasi* -steady-state condition exists at temporal scales on the order of a year and spatial scales on the order of a river segment for the bivariate BAF analysis and the probabilistic empirical model;

MCA/TetraTech

4.   Fish body burdens are in *quasi*-steady-state with the water and/or sediment at time scales on the order of one or more years under both the bivariate BAF analysis and the probabilistic empirical model.

PCB concentrations measured in biota are assumed to be in steady state with PCBs in the environment for the development of bioaccumulation factors (BAFs), and thus can be related by linear coefficients or bioaccumulation factors similar to partitioning coefficients. A steady-state condition is usually considered to hold within a given year; thus the BAF approach represents temporal changes only annually. The simplest approach considers that biota and *all* environmental compartments are in equilibrium with one another, in which case the concentration in any medium can be predicted from the concentration in any other medium. The BAF method is readily modified to address situations in which a disequilibrium exists at steady state between different environmental compartments.

Consider first a completely equilibrated system: Fish may accumulate PCBs through partitioning from the water column, through ingestion of sediment, or through the food chain, while organisms at lower trophic levels may also accumulate PCBs from both water column and sediments. Describing exact accumulation pathways is the task of food web models, but concentrations in any medium or "compartment" in a fully equilibrated system can be predicted from those in any other compartment. As PCBs partition strongly to organic matter and have low solubility, the major environmental reservoir is typically the sediment. "Partitioning" from sediment to biota is conceptually similar to equilibrium partitioning from sediment and pore water as well as from sediment to the water column. Thus, for an equilibrated system, dissolved concentrations in sediment pore water might provide a good index of the bioavailable component. Typically, analytically resolving truly dissolved and DOC-complexed fractions is a very difficult task for pore water samples, but, for lipophilic compounds in sediments with typical organic carbon contents, partition coefficients are such that the mass present in dissolved and DOC-complexed forms is relatively insignificant compared to the total particulate-sorbed mass. This implies that the dissolved portion can be quite well predicted from the sediment-water partition coefficient, regardless of DOC levels. On the other hand, pore water concentrations vary significantly in response to sediment organic carbon fraction (*foc*). Therefore, sediment concentration *normalized to foc* is the best readily available predictor of dissolved concentrations in an equilibrated system (Di Toro et al., 1991). This approach is being used by EPA's Office of Water for establishing sediment quality criteria (USEPA, 1991a).

Of course, PCBs may enter the food chain both through the dissolved phase and ingestion of particulate matter. As Di Toro et al., state, "biological effects (to invertebrates) appear to correlate to the interstitial water concentration. This has been interpreted to mean that exposure is primarily via pore water. However, the data correlate equally well with the organic carbon-normalized sediment concentration. This suggests that the sediment organic carbon is the route of exposure. In fact, neither of these conclusions necessarily follow from these data."

The reason for this surprising conclusion is contained in fugacity, or chemical potential theory, which holds that the biological activity of a contaminant is controlled by its chemical potential (Mackay, 1979). As discussed by Di Toro et al., if pore water and organic carbon phases of the contaminant are in equilibrium then the chemical potentials exhibited by the two

phases are equal. "Hence, so long as the sediment is in equilibrium with the pore water, the route of exposure is immaterial. Equilibrium experiments cannot distinguish between different routes of exposure." Thus, in the simplified equilibrium case, it is necessary to estimate the chemical potential in only one phase. The question then becomes determining which phase is easiest to measure. Where DOC complexing occurs, sediment concentration normalized to foc is clearly the most directly measurable index of chemical potential.

Fish may accumulate PCBs via pathways which arise in the water column as well as from the sediment. The simple equilibrium BAF approach works if sediment and water-column concentrations are in equilibrium with one another, or if all PCB accumulation in fish derives from pathways commencing in the local sediment. On the other hand, if fish accumulate PCBs from both water-column and sediment pathways, *and* water-column concentrations are not in equilibrium with pore water in the same locale, the full-equilibrium assumptions are not valid. In the Hudson and other flowing rivers, it is likely that the upper sediment layer and the water column are generally *not* in equilibrium with one another for hydrophobic toxicants. Further, the upper, bioactive sediment zone is typically not in equilibrium with deeper, buried sediments. However, the sediment-sorbed concentrations and pore-water concentrations within the bioactive zone should be very close to equilibrium, while, in the water column, the dissolved and sorbed fractions should also be close to equilibrium, except during transient events.

The equilibrium partitioning/fugacity arguments set forth by Di Toro et al., (1991) state that the best readily measurable index of chemical potential should be the sediment sorbed fraction normalized to *foc*. This argument applies to both sediments and water column. Both should be compared to the lipid-normalized burden in the organism (Chiou, 1985), as BAF estimates are best expressed on a lipid-normalized basis (USEPA, 1994). BAF factors are expected to vary from species to species with trophic level and foraging preferences. Variability may also reflect differing lipid compositions, with correspondingly different rates of uptake of lipophilic compounds, between fish species (Ewald and Larsson, 1994).

Preliminary analysis suggested that both water and sediment pathways may be important for the accumulation of PCBs in Hudson River fish, and that water column and sediment concentrations are not in equilibrium with one another. USEPA (1991b) Phase 1 RI/FS analyses revealed that summer average water-column concentrations appear to provide a good predictor of average PCB burden in fish species, confirming earlier observations of Brown et al., (1985). This could reflect a dominant role for water-column pathways, or simply an equilibrium between water-column and pore-water PCB concentrations. A role for sediment pathways is suggested by the observation that concentrations in fish in the Thompson Island Pool appear to be elevated above those collected downstream at River Mile 175 by a factor greater that the observed change in water-column concentration. Water-column PCB concentrations in the Upper Hudson below Thompson Island Dam do not appear to be in equilibrium with the upper level of the sediment; for instance, TAMS/Gradient 1993 flow-averaged sampling indicated that total PCB concentrations decline by about 40 percent between Thompson Island Dam and River Mile 156.6 (Waterford), largely representing dilution. The decline in surface sediment concentrations appears to be much more substantial: The GE Sediment Sampling and Analysis Program (O'Brien & Gere, 1993a) revealed a decline of 90 percent in average total PCB concentrations in the top 5 cm of sediment between Thompson Island Pool (River Mile 188.3 to 193) and the reach

from River Mile 155 and River Mile 170. In summary, below Thompson Island Dam the water column is not in equilibrium with *local* sediments. Thus, models for bioaccumulation need to consider both water and sediment pathways, rather than relying on a BAF based on concentrations in a single medium.

Very little information is available on how often contaminants in the environment reach equilibrium among phases. If equilibrium conditions are not reached, time-variant models are more appropriate for predicting contaminant concentrations. The distributions of contaminant concentrations might differ from predicted concentrations if the system is not in equilibrium because there is high temporal variability or because biological processes maintain disequilibrium conditions. Many ecosystem and physical processes are variable over time. The input of a contaminant into an estuary, for example, can occur during episodic events, such as large storms or periodic disposal of dredged sediments.

The FISHRAND model is designed to evaluate the time-varying effects of PCB uptake on predicted PCB fish tissue concentrations based on sediment and water exposure concentrations predicted from fate and transport models as inputs. Both this model and the empirical probabilistic model rely on information regarding feeding preferences of the fish species. To more precisely define food web dynamics in the Hudson River, Menzie-Cura undertook the following analysis.

The invertebrate component in the fish diet can consist of invertebrate species that are themselves exposed to PCBs in surface water, pore water, and through their food. The food items of invertebrate species may, in turn, be exposed to different levels and types of PCBs. Understanding this component of the food web is not simple. Food habits of fish species are described in Appendix A. Invertebrates eaten by Hudson River fish occupy a range of habitats and eat a range of organic materials. The habitat and feeding preference for individual invertebrate species influences the extent to which they are exposed directly and indirectly to PCBs in sediments and in the water column. In our opinion these influences can only be approximated based on available information and there are uncertainties associated with these estimates. A qualitative conceptual framework for considering how invertebrates can be exposed to PCBs in water and sediment is given below. It shows that invertebrate species probably experience a gradient of exposure conditions ranging from predominantly sediment exposure to predominantly surface water exposure. However, we believe that there are many species that will fall between these extremes and which will experience both sediment and water exposures. We have considered this when ascribing feeding preferences for fish that rely on invertebrates for food. However, we acknowledge that there is little quantitative information for determining the extent to which many of invertebrate species – primarily those that live on the surface of sediments - are influenced by sediment and water exposures.

MCA/TetraTech

Conceptual Framework for Considering The Influence
Of Sediment and Water as Exposure Media
For Invertebrates in the Diet of Fish

		Source of Food		
General Physical Habitat		Phytoplankton Periphyton	Surface Organic Deposits	Deeper Organic Deposits
	Water column or Phytophilous	Zooplankton Phytophilous invertebrates	Phytophilous invertebrates	
	At sediment surface	Meroplankton, Epibenthic invertebrates living in littoral zone	Epibenthic invertebrates	
	Below sediment surface		Infaunal invertebrates	Infaunal invertebrates

The simplified conceptual framework indicates how habitat location and food type could influence the relative degree of influence of water and sediment on PCB exposure for invertebrates. The increasing influence of sediments is illustrated qualitatively with an increasing gray scale. Habitat affects the availability of different food types as well as the water exposures experienced by invertebrates. For example, infaunal invertebrates are exposed primarily to pore water while zooplankton are exposed primarily to surface water. Epibenthic invertebrates may be exposed to some mix of pore water and surface water.

Examples of invertebrate species that may occupy the matrix of physical habitat and food type are given below.

		Source of Food		
General Physical Habitat		Phytoplankton Periphyton	Surface Organic Deposits	Deeper Organic Deposits
	Water column or Phytophilous	*Bosmina* (Cladocera); Copepods, Gastropods	*Dicrotendipes spp.* (Chironomidae)	
	At sediment surface	*Gammarus spp.* (Amphipoda), Ostracods	Gastropods, *Caecidotea* (Isopoda)	
	Below sediment surface		*Chironomus* (Chironomidae)	*Limnodrilus spp.* (Oligochaetea)

MCA/TetraTech

As the conceptual framework suggests, PCB exposure for invertebrate species can be complex, involving aspects of their feeding and physical ecology. Some species occur in a variety of habitat types. Examples include the amphipod *Gammarus* and the chironomid insect larvae of the genera *Polypedilum* and *Dicrotendipes*. Some invertebrates – planktonic rotifers, copepods, and cladocerans – are carried with water masses and experience exposures associated with "parcels" of water that are transported downstream. Other invertebrates live on the surface of plants and experience water exposures that vary over time as water passes a particular location. Still others are meroplanktonic (*Chaoborus, Gammarus*) and may be carried with the currents diurnally, the remainder of the time spent in the sediments. Therefore, while we simplify the characterization of food webs for modeling purposes, it should be evident that the system is complex and that representations of relationships between water, sediment, invertebrates, and fish should be viewed as uncertain estimates. This uncertainty is represented in the models through the expression of feeding preferences as distributions in FISHRAND and through distributions of transfer coefficients as derived in the empirical probabilistic model. However, our ability to represent this uncertainty is limited by the available knowledge about the system and the species within it. This uncertainty cannot be easily reduced.

3.3 Bivariate BAF Analysis for Fish Body Burdens

3.3.1 Rationale and Limitations for Bivariate BAF Analysis

The Bivariate BAF Analysis provides an empirical summary of historical data on fish body burden in the Hudson River. The analysis relies on the available time series of environmental and fish concentration data in the Upper Hudson to relate observed PCB concentrations in fish to PCB levels in the water and sediment. If water and sediment concentrations are not in equilibrium, a single BAF is not adequate; instead bioaccumulation is controlled by the simultaneous effects of both water and sediment concentrations. Thus, a statistical model with two independent variables (water and sediment concentrations) is appropriate.

The development of statistical relationships is enhanced by the availability of extensive historical monitoring data that enable comparison of PCB levels in fish and the environment over time. The nature of these data, which consist primarily of Aroclor-equivalent quantitations in the fish and total PCB estimates by packed-column gas chromatography in the water column, however, constrains the statistical approach. Although more recent studies by TAMS/Gradient, NOAA, and GE provide congener-specific PCB measurements in all media, these data are limited in that they (1) are available only for the 1990s, (2) represent only a small number of individual samples for a given fish species, and (3) do not provide a time-series perspective on the relationship between fish body burdens and environmental concentrations.

Statistical relationships do not, of course, prove physical causality. Statistical models that capture historic conditions are not guaranteed to accurately predict future conditions, particularly if the characteristics of the PCB source change over time. For this reason, the Bivariate BAF Analysis has not been used to predict future concentration trends. The Bivariate BAF Analysis, however, is an important first step for the development of more complex, food web models, for which the database is limited. By summarizing historical relationships between fish body

MCA/TetraTech

burdens and environmental concentrations, the Bivariate BAF Analysis provides important constraints on the form and parameterization of the food web bioaccumulation model.

3.3.2 Theory for Bivariate BAF Analysis of PCB Bioaccumulation

The general theoretical framework for deriving Bivariate Statistical Models was introduced in Chapter 3.2. The fact that the water and sediment compartments are not in equilibrium with each other, but are approximately internally equilibrated, suggests that bivariate BAFs that relate body burden to *both* sediment and water-column chemical potential could account for bioaccumulation pathways from both water and sediment. Correlating fish body burdens to both water and sediment removes the difficulty of disequilibrium between the sediment and water compartments.

The Bivariate BAF Analysis is essentially a 'black box' approach wherein the details of exposure pathways and physiological processes are not specified but the net effect is captured. The actual PCB concentration found in a given fish depends on the cumulative effects of dietary/food chain accumulation, plus direct accumulation from the water (and perhaps sediment), all balanced by species-specific rates of depuration or metabolism. Net accumulation in a fish species thus depends on all lower trophic levels. There are, however, only two main external forcing functions, water and sediment PCB concentrations, which enable a 'black box' model to be developed through statistical analyses with water and sediment concentrations as input and fish burden as output.

For steady-state concentrations in the environment, the net result of the unspecified processes contained within the 'black box' is functionally equivalent to a steady-state food web model. For instance, the simplified steady-state food web model of Thomann et al., (1992) for Lake Ontario, which avoids the need for a detailed study of population dynamics through steady-state assumptions, is externally forced by water and sediment concentrations alone. It is thus equivalent to a bivariate BAF relating fish body burden to water and sediment concentrations, where the food web interactions determine the values of the two BAF factors. Therefore, a bivariate regression relating average PCB body burden in a given species (by location and year) to concentrations in local water and sediment provides a useful tool for assessing bioaccumulation of PCBs by fish, and for providing a statistical perspective on the more sophisticated, biologically-based food chain models.

As discussed in Chapter 3.2, fugacity theory indicates that chemical potential is best estimated by the sorbed fraction in both sediments and water column, normalized to *foc*. This suggests a regression analysis to predict fish PCB burdens from environmental concentrations through species-specific relationships should take the following form:

$$\frac{Cf_i}{fl_i} = \left[Bw_i \cdot \frac{Cs_w}{foc_w} \right] + \left[Bs_i \cdot \frac{Cs_s}{foc_s} \right] \tag{3-1}$$

in which, for species i:

Cf	=	PCB concentration in fish (wet-weight basis)
fl	=	Lipid fraction in fish
Bw	=	Partial BAF relating fish concentration to water-column concentration
Cs_W	=	PCB concentrations on suspended solids
foc_W	=	Organic carbon fraction of suspended solids
Bs	=	Partial BAF relating fish concentration to upper-zone sediment concentration
Cs_S	=	PCB concentration in upper zone sediments (dry-weight basis)
foc_S	=	Organic carbon fraction of the sediments.

While this formulation is theoretically optimal, foc_W is not available in the historic database for the Hudson River; as a result, Bw must be expressed on a whole-water basis as a matter of practical necessity.

3.4 Probabilistic Bioaccumulation Food Chain Model

3.4.1 Rationale and Limitations

The Probabilistic Food Chain Models are developed to predict distributions of PCB body burdens within the selected fish species. These models complement the Bivariate BAF Analyses that predict single population statistics such as the average values of PCBs. The conceptual approach is presented in Figure 3-1. The Probabilistic Models have been developed to provide:

1. information on the fractions of the fish populations that are at or above particular PCB levels; and

2. an empirical framework for constructing biologically-based food chain relationships that explicitly incorporate variability and uncertainty inherent in the underlying data.

PCB body burdens in Hudson River fish vary among individuals within a species for any given reach of the river. This intra-species variability in concentrations can be described as a distribution. The characteristics or shapes of these distributions can be important for evaluating human health and ecological risks. For example, two distributions may have the same average value but may differ in spread, one having values distributed closely around the average, the other including much higher as well as much lower values. The distribution with a greater fraction of high values may pose a greater risk than the tighter distribution. Probabilistic models that predict the characteristics of distributions provide risk assessors with the information needed for making these evaluations. Probabilistic models also provide a tool for quantifying the uncertainties associated with estimating body burdens of PCBs.

MCA/TetraTech

303785

The distribution of concentrations of PCBs within a species reflects a number of factors that are also variable. These include the composition of PCBs, spatial and temporal exposure field of PCBs in water and sediments, the uptake and depuration rates of PCBs within and among trophic levels, and the feeding behavior, lipid content, and history of the fish. Many of these factors are unknown or poorly known for the selected Hudson River species. The approach taken in building the Probabilistic Food Chain Models is to combine information from available measurements for the river with knowledge concerning the ecology of fish species and the trophic relationships among fish and invertebrates.

The models presume *quasi* steady-state conditions for which mean seasonal exposure concentrations in water and surface sediments change slowly relative to the species uptake and depuration kinetics. The models are constructed by identifying the major pathways linking individual fish species with sediment and water components. These pathways include direct exposure as well as trophic relationships. Within the models, each major pathway is represented by a distribution of transfer or bioaccumulation factors. Using information on species' ecology, statistical distributions for PCB transfer or bioaccumulation factors are developed among media and biological components. These factors are derived from measurements of PCB concentrations in various compartments and do not require assumptions about kinetic processes, although it is assumed that fish will be in a quasi steady-state with the environment. The transfer and bioaccumulation factors reflect the sum of the underlying processes and are specific to Hudson River fish and environmental conditions.

The models are designed to identify the relative contributions of PCBs in Hudson River sediments and water to body burdens of the six selected fish species. Because exposure to PCBs may occur via water column and sediments, it is important to distinguish between these two media. Food is expected to be the primary route of exposure for fish but direct uptake from water may also be important depending on the specific chemical. In developing the models, the role of direct water uptake versus food was examined, and quantitatively evaluated using the mechanistic FISHRAND model.

Because of the important role of food as an exposure pathway, what and where a fish eats are viewed as key aspects of distinguishing between the relative contribution of the water column and sediments to a species' body burden of PCBs. Some species feed predominantly on benthic invertebrates, others on pelagic invertebrates, and still others on forage fish. Some species, such as the largemouth bass, feed on all three components to varying degrees. As discussed earlier, identification of the specific life histories of the invertebrates that fish tend to consume plays an important role in identifying predominant exposure pathways.

3.4.2 Model Structure

The conceptual framework for the probabilistic PCB food chain models is illustrated in Figure 3-1. A separate model is developed for each fish species reflecting the particular species biology and available information on PCB BAFs. These models can be developed for individual congeners, homologue groups, Aroclors, or total PCBs. In this report, the results for ΣTri+ PCBs (the sum of tri- through decachlorinated biphenyls) are discussed. ΣTri+ is a good representation

MCA/TetraTech

of total PCBs in biota. The models are designed to evaluate *quasi* steady-state conditions on an annual basis. The features of the models include:

1. Two groups of invertebrates are described: a) invertebrates that live within sediments and feed primarily on sedimentary material (primarily deposit feeders), and b) invertebrates that feed primarily on organic particulate matter transported in the water column (zooplankton, many epiphytic invertebrates, and some filter feeding invertebrates).

2. Invertebrates in group "a" are presumed to reflect localized sediment concentrations and to be in steady state with the sediments as described by lipid and organic carbon normalized BAFs.

3. Invertebrates in group "b" are presumed to reflect PCB concentrations associated with whole water column concentrations. These invertebrates are presumed to be exposed to PCBs associated with organic particulate material in the form of detritus or algae as well as through direction partitioning of the dissolved phase. In the Hudson, it is presumed that both forms of organic material will be important in the diets of invertebrates. The invertebrates that feed in this manner are presumed to be in steady state with temporally averaged whole water column concentrations of PCBs as described by whole water BAFs.

4. In most cases, the models are designed to estimate body burdens in adult fish. These larger fish are the ones important for human health risk assessment. In addition, because the primary population-level risk of PCBs to fish is reproductive impairment, body burdens in adults can be used in the ecological evaluation. Because young fish of some species (e.g., pumpkinseed sunfish) are important as forage fish, body burdens are estimated for these juveniles. Fish fall into one of several types depending on their foraging strategies. The species-specific models incorporate such information and recognize the variability that exists among and within species.

5. The lipid normalized BAF factors between invertebrates and fish, and fish and fish are represented by distributions derived from Phase 1 and 2 studies carried out in the Hudson and from the literature. Values have been derived for the calibration congeners, Aroclors, and total PCBs (USEPA, 1996). Results presented here are for ΣTri+. ΣTri+ PCBs represent total PCBs in biota samples.

6. The food chain models are designed to take as input the water and sediment concentrations predicted by the fate and transport models described in Books 1 and 2. The key input parameter for sediments is the PCB concentration normalized to sediment organic carbon. The key input parameter for the water column is total concentration of PCBs in the water (including both particulate and dissolved). Since feeding occurs primarily in the warmer months, the probabilistic model has been developed using summer averages. The fate and transport model results are averaged to provide summer water concentrations and annual sediment concentrations.

MCA/TetraTech

Based on the above, the following media and biological compartments are identified: 1) water, 2) sediment, 3) water invertebrates, 4) sediment invertebrates, 5) forage fish, and 6) the individual fish species.

The food chain models are currently implemented as a Monte Carlo spreadsheet model. For the Monte Carlo spreadsheet model, the relationships among compartments and the distributions for BAFs are incorporated into an Excel™ spreadsheet with a Crystal Ball™ software add-in. Excel™ is a standard spreadsheet and provides the basic computational framework. Crystal Ball™ software permits the input data to be represented as distributions rather than single point values; the software also enables Monte Carlo analyses to be performed. The species-specific Excel™/Crystal Ball™ spreadsheet incorporates uncertainties in exposure concentrations, food chain transfers, foraging behavior, and lipid content. Monte Carlo operations yield cumulative distributions of body burdens on a lipid normalized and whole fish basis for each species. Key variables in the probabilistic model are represented by a distribution of values rather than a single point estimate (such as a mean or upper-bound value). Monte Carlo simulation is a method of sampling from these distributions within a computational framework. Generally, the greater the number of simulations, the lower the standard error associated with the mean. In developing the probabilistic model, Monte Carlo simulations were run a minimum of 10,000 trials.

The distributions are representative of variability in the data as described in subsequent sections. The distributions can also represent uncertainty, for example, by providing a range of feeding proportions rather than single values. In this case, both variability and uncertainty are represented in the distributions. For example, observed variability in the relationship between sediment concentrations and benthic invertebrates is attributable to both true population heterogeneity (variability) as well as measurement error (uncertainty). It is operationally difficult to truly separate these two sources. Consequently, the model can be viewed as predicting population profiles of PCB concentrations rather than the uncertainty associated with predictions for any given percentile of variability.

3.4.3 Spatial Scale for Model Application

The probabilistic food chain model used the river segmentation developed for the fate and transport models together with available fish data to assess PCB exposure from the water-column and sediment.. For most fish species, these model segments are expected to encompass the exposure zones for fish that may be caught in a particular segment of the river. The primary zone of exposure for most fish species is presumed to be the summer foraging areas. Fish are expected to obtain most of their PCB body burden via food. Profiles for the species (Appendix A) indicate most of the feeding occurs during the warmer periods of the year. On a relative basis, little feeding occurs in the winter. Therefore, the summer foraging areas are where most of the fish species' exposure occurs. Because most of the selected fish species exhibit limited spatial movements during the summer, foraging areas and exposure zones can be highly localized. A notable exception is the white perch, a semi-anadromous species that migrates over larger stretches of the river. White perch are found primarily below the Federal Dam in the Lower Hudson River.

MCA/TetraTech

The HUDTOX model provides daily estimates of sediment and water concentrations for segments in the upper river (see Books 1 and 2). For water concentrations, there are both spatial and temporal gradients in concentration that are appropriately averaged to provide estimates representative of how fish integrate exposures. Fish exposures will vary around this mean value. Calibration results for fish body burdens are presented for two river miles: 189 (Thompson Island Pool), and 168 (Stillwater). These locations represent the bulk of fish concentration data for the upper river.

The model covers three river reaches: 189 (TIP), 168 (Stillwater), and 154 (Waterford to just above the Federal Dam). Each of these encompass a roughly 5 mile interval of exposure.

3.4.4 Temporal Scales for Estimating Exposure to Fish

Exposure concentrations for water are estimated as summer averages (May through September). This averaging period is coincident with the time that fish are at their summer foraging areas. Sediment concentrations show very little variation on an annual basis, thus sediment concentrations are averaged annually.

3.4.5 Characterizing Model Compartments

3.4.5.1 Sediment to Benthic Invertebrate Compartment

This compartment of the model relates the concentrations of PCB in benthic invertebrates to sediment concentrations of PCB. It assumes that the PCB levels in the invertebrates are related directly to levels in the surrounding sediments. This relationship is represented by an empirically-derived biota sediment accumulation factor (BSAF) that reflects the combination of passive and/or active bioaccumulation mechanisms occurring in the sediments. PCB uptake into benthic invertebrates appears to be the result of partitioning between the organic carbon of the sediments and the lipid of the invertebrate species (Bierman, 1990). This relationship is a simple ratio:

$$BSAF = \frac{C_{benthic}}{C_{sediment}} \qquad (3\text{-}2)$$

where,

$BSAF$ =   biota - sediment accumulation factor

$C_{benthic}$ =   the concentration of PCB in an individual organism as $\mu g/g$ lipid

$C_{sediment}$ =   mean PCB concentration in sediments as $\mu g/g$ organic carbon

3.4.5.2 Water Column: Water Column Invertebrate Compartment

Individual PCB congeners can be strongly associated with either the truly dissolved phase in the water column or the particulate phase. These differences average out to some extent when evaluating a mixture of PCBs. The Data Evaluation and Interpretation Report (USEPA, 1998) provides estimated partition coefficients for a number of key congeners. These data show the fraction of PCB concentrations associated with the particulate phase increases with increasing chlorination. For the lighter chlorinated congeners, bioaccumulation is driven primarily by direct uptake from the dissolved phase in the water. For the higher chlorinated congeners, consumption of particulate matter represents the route of greatest bioaccumulation.

Combining both the dissolved and particulate concentrations in a whole water concentration, we considered the role of whole water using a BAF approach between water and fish:

$$PWBAF = C_{invert}/C_{water} \qquad (3\text{-}3)$$

where,

$PWBAF =$ The bioaccumulation factor between water column invertebrates and $\Sigma Tri+$ water PCB concentrations

$C_{invert} =$ mg PCB per Kg lipid in invertebrate tissue

$C_{water} =$ mg PCB per L water

3.4.5.3 Forage Fish Compartment

Several of the fish species selected for modeling consume other, smaller forage fish of which there are numerous species in the Hudson. Rather than quantify PCB concentrations in individual forage fish species, the model assumes that piscivorous fish will consume any species less than 10 cm. This assumption is supported by forage fish abundance data for the Hudson River from the literature as well as piscivorous fish gut analyses (MPI, 1984). A composite forage fish compartment has been developed that reflects the composition of forage fish in the Hudson and the feeding habits of these fish. The details of how the forage fish compartment was derived are presented in Appendix A. The analysis indicated that Hudson River forage fish are composed of species that feed to varying degrees on invertebrates in the water column and in the sediments. When the relative abundance and feeding behavior of the species are taken into account, the composite forage fish diet is comprised of approximately 67% water column invertebrates and 33% sediment invertebrates. All piscivorous fish that feed on Hudson River forage fish are assumed to be preying on species that - on average - feed on water column and sediment invertebrates in these percentages.

The forage fish bioaccumulation factor (FFBAF) is defined as:

$$FFBAF = \frac{C_{ff}}{C_{diet}}$$ (3-4)

where,

$FFBAF$ =   forage fish bioaccumulation factor

C_{ff} =   concentration in individual forage fish (μg ΣTri+ per g lipid)

C_{diet} =   weighted average of diet concentration (μg ΣTri+ per g lipid – species-specific benthic and water column invertebrate fractions)

3.4.5.4 Piscivorous Fish Compartments

Adult piscivorous fish eat a combination of forage fish and invertebrates. Since forage fish concentrations are derived primarily from water column invertebrate concentrations, it is assumed that direct ingestion of water column invertebrates by piscivorous fish is encompassed in this step. In the model, therefore, piscivorous fish PCB body burdens are quantitatively related (in varying degrees, depending on the fish species) to the benthic invertebrate and forage fish boxes.

The piscivorous fish under consideration in this model is the largemouth bass. The piscivorous fish bioaccumulation factor (BAF) is defined as:

$$BAF = \frac{C_{fish}}{C_{diet}}$$ (3-5)

where,

BAF =   piscivorous fish bioaccumulation factor relative to diet

C_{fish} =   concentration in piscivorous fish (μg ΣTri+ per g lipid)

C_{diet} =   weighted average of diet concentration (μg ΣTri+ per g lipid).

The largemouth bass diet consists of 90 percent forage fish and 10 percent benthic invertebrates.

3.4.5.5 Demersal Fish

The final category of fish to be considered are the demersal or bottom-feeding fish. The best species to consider for this compartment is the brown bullhead, which feeds primarily from sediment sources, although it is properly considered an omnivorous fish. Brown bullhead lipid-normalized concentrations were compared to sediment TOC-normalized concentrations.

The BSAF for brown bullhead is defined as:

$$BSAF = \frac{C_{BB}}{C_{sed}}$$

(3-6)

where,

$BSAF$	=	brown bullhead bioaccumulation factor
C_{BB}	=	concentration in brown bullhead (μg ΣTri+ per g lipid)
C_{sed}	=	concentration in the sediment (μg ΣTri+ per g carbon).

3.5 FISHRAND Mechanistic Modeling Framework

3.5.1 Rationale and Limitations

FISHRAND incorporates time-varying information on water and sediment concentrations to mechanistically describe the uptake of PCBs into fish tissue. The model is based on the peer-reviewed time-varying Gobas model (Gobas, 1993; Gobas et al., 1995; 1999). FISHRAND is designed to incorporate probability distributions and is programmed in Fortran-90 with a Microsoft Excel™ graphical user interface.

Figure 3-2 shows the conceptual model for the Hudson River food web. The numbers show in the Figure 3-2 represent the mean dietary percentage from particular compartments for each species. Development of the distributions for each of the parameters described in this chapter is presented in Chapter 6.

3.5.2 Model Structure

The model consists of a series of compartments as in the empirical probabilistic model. Pelagic invertebrates are assumed to be in equilibrium with truly dissolved water column concentrations, and benthic invertebrates are assumed to be in equilibrium with sediment concentrations. Forage fish feed on these two compartments in accordance with their species-specific foraging strategies. Piscivorous fish consume some amount from each compartment in similar proportions as in the empirical probabilistic model, although in this model distributions are used to reflect feeding preferences.

Biota can gain PCBs via uptake from the water column or through consumption of contaminated prey (both sediment and water based), and lose PCBs via fecal excretion or respiration.

The general form of the differential equation describing the change in concentration of PCBs in biota with respect to time is given by:

$$\frac{dC_f}{dt} = k_1 * C_{wd} + k_d * C_{diet} - (k_2 + k_e + k_m + k_g) * C_{fish}$$

(3-7)

MCA/TetraTech

303792

where:

k_1 = gill uptake rate (L/Kg/d)
C_{wd} = truly dissolved ΣTri+ PCB concentration in water (ng/L)
k_d = dietary uptake rate (d^{-1})
C_{diet} = concentration in the diet (g/g)
k_2 = gill elimination rate (d^{-1})
k_e = fecal egestion rate (d^{-1})
k_m = metabolic rate (d^{-1}) (assumed to be zero)
k_g = growth rate (d^{-1}) (takes the place of explicit age-class consideration)
C_{fish} = ΣTri+ PCB concentration in fish (μg ΣTri+ per g)

3.5.2.1 Rate Constants

Direct Uptake from Water

The rate at which fish take up chemicals from water depends upon the gill ventilation rate and the rate of diffusion of the chemical across the gills. The Gobas (1993) model uses experimental data to derive uptake rates given by:

$$k_1 = \frac{1}{V_f/Q_w + V_f/Q_L * K_{ow}}$$

(3-8)

where:

k_1 = gill uptake rate (d^{-1})
K_{ow} = octanol/water partition coefficient
Q_w = transport rate in the aqueous phase (L/day)
Q_l = transport rate in the lipid phase (L/day)
V_f= fish weight in kg (described by a distribution in FISHRAND)

The transport rates in the aqueous and lipid phases are given by:

$$Q_w = 88.3 * V_f{}^{0.6}$$

(3-9)

$$Q_l = \frac{Q_w}{100}$$

(3-10)

26   MCA/TetraTech

The gill elimination rate is then given by:

$$k_2 = \frac{k_1}{L_f * K_{ow}}$$

(3-11)

Uptake from Consumption of Prey Items

The rate at which fish take up chemicals from food depends upon the food ingestion rate, the rate of diffusion of the chemical across the intestinal wall, and the fecal egestion rate. The Gobas model (1993) assumes that the efficiency with which chemicals are taken up from food is related to the transport of chemical across aqueous and lipid phases of the gut:

$$K_d = \frac{E_d * F_d}{V_f}$$

(3-12)

where:
k_d = dietary uptake rate constant (d^{-1})
E_d = uptake efficiency (unitless)
F_d = food ingestion rate (kg food/day)
V_f = fish weight (kg)

The uptake efficiency, E_d, is given by:

$$E_d = \frac{1}{5.3e - 8 * K_{ow} + 2.3}$$

(3-13)

And the food ingestion rate, F_d, in [kg food/day], is given by:

$$F_d = 0.022 * V_f^{0.85} * e^{0.06T}$$

(3-14)

where:
F_d = food ingestion rate (kg food/day)
V_f = fish weight (kg) (described by a distribution in FISHRAND)
T = monthly mean water temperature (deg C)

Fecal egestion rate constant

The fecal egestion rate is given by:

$$k_e = 0.2 * k_d$$

(3-15)

k_e = fecal egestion rate (d^{-1})
k_d = dietary uptake rate constant (d^{-1})

MCA/TetraTech

303794

Growth rate constant

The growth rate constant presented in the original Gobas model is given by the following equations.

For temperatures greater than 10°C (T>10°C), the growth rate constant, k_g, is given by:

$$kg = 0.01 * V_f^{-0.2} \qquad (3\text{-}16)$$

For temperatures less than or equal to 10°C (T≤10°C), the growth rate constant, k_g, is given by:

$$kg = 0.002 * V_f^{-0.2} \qquad (3\text{-}17)$$

3.5.3 Spatial Scale for Model Application

The initial concentrations are the predicted sediment and water concentrations from the fate and transport model. The average concentrations across individual sampling grids represent the integrating effects of fish foraging and habitat strategies. In the Thompson Island Pool (river mile 189), the nearshore segments just above the Thompson Island Dam and the corresponding cohesive and noncohesive sediment segments were used to estimate sediment-based exposures. Sediment concentrations represent a weighted average of cohesive and non-cohesive sediments based on area and an assumption that fish, on average, spend 75% of their time over cohesive sediments (the exception may be the white perch, which tend to range throughout the river, including main channel areas).

The water-column PCB concentrations were adjusted based on flow and upstream concentration at Fort Edward to better reflect nearshore exposure concentrations. Within the TIP, strong lateral gradients in PCB concentrations in water have been reported by GE during low flow conditions, with higher concentrations in the nearshore area. Based on theoretical considerations and an analysis of the available nearshore and center channel data collected by GE, it was determined that lateral gradients in concentration are likely to be significant only at lower flows, approximately less than 4,000 cfs at Fort Edward. Under conditions of flow less than 4,000 cfs and upstream concentrations of total PCB greater than 15 ng/l, the average ratio of TID-West to center channel concentrations is 1.14, while for flow less than 4,000 cfs and upstream concentrations less than 15 ng/l the average ratio is 1.45. Both ratios are significantly different from unity. At upstream flows greater than 4,000 cfs, the ratio is not significantly different from 1.0 and no correction is required.

3.5.4 Temporal Scales for Estimating Exposure to Fish

FISHRAND uses mean monthly dissolved water concentrations, and annual average sediment concentrations. Sediment concentrations show significant spatial heterogeneity, but little variation over time. Very little is gained by specifying monthly average sediment concentrations versus annual averages. Dissolved water concentrations, by contrast, show significant temporal variability.

MCA/TetraTech

The expected value for spatially and temporally averaged exposures is obtained under the assumption that concentrations follow a lognormal distribution. Under this assumption, the expected value is given as:

$$E[x] = e^{\ln(x) + \sigma^2/2} \qquad (3\text{-}18)$$

And the variance as:

$$V[x] = (E[x])^2 + e^{\ln \sigma^2 - 1} \qquad (3\text{-}19)$$

3.5.5 Application Framework

The FISHRAND model was coded in Fortran-90 with a user interface developed in Microsoft Excel™. It is implemented as a Microsoft Excel add-in program and can be run interactively. To demonstrate model functionality, the model was run in a steady-state, deterministic manner to demonstrate and verify concordance with the Gobas (1993) published results.

- *Level 1:* Using generic model parameters derived from monitoring data and model constants obtained from the literature without site-specific calibration.

- *Level 2:* Calibration of the model and parameters using available site-specific data.

The generic model application (Level 1) can be used to show general validity of the modeling approach. The generic model should capture major bioaccumulation processes in different ecosystems and across sites. General consistency of the generic model predictions with observed experimental data for a number of different sites can be used to judge model validity.

This report presents the site-specific application of FISHRAND (Level 2). Often calibration is done by simple model fitting to the observed data without consideration of associated uncertainties. For non-linear models such as FISHRAND this approach may lead to unreliable predictions. Our approach to FISHRAND calibration incorporates robust statistical methods applicable to non-linear models. A sensitivity analysis relying on elasticities is used to select several of the most important parameters for calibration. Likelihood profiles are used to select ranges of variation for these parameters and to assign corrected prior distributions for these parameters. Finally, parameter distribution updating using Bayesian Monte Carlo techniques are used to incorporate the full range of experimental data to derive posterior distributions for the model parameters with which future predictions are to be made.

3.5.5.1 Initial Validation: Comparison with Gobas (1993) Lake Ontario Data for the Steady-State Case

As an intermediate step in the FISHRAND development, a deterministic version of the FISHRAND model, FISHPATH, was developed and run in a steady-state, deterministic manner to demonstrate and verify concordance with the Gobas (1993) published results.

MCA/TetraTech

303796

The steady-state solution is given by:

$$C_{fish} = \frac{k_1 * C_{wd} + k_d * C_{diet}}{k_2 + k_e + k_m + k_g}$$

(3-20)

Figure 3-3 shows the comparison between FISHRAND, and published data from Gobas (1993). Note that the figures also include a comparison to a deterministic version of the model, called FISHPATH, that was used during the development of FISHRAND. EPA has since discontinued the use of FISHPATH. Pages 1 and 2 of this figure present the variables used in the model. Page 3 describes bioavailability in the water column and bioaccumulation in phytoplankton and zooplankton. This page also shows the predicted results from the Gobas model as published ("Predicted" in the table), observed results from field observations, and the results from FISHRAND run in steady-state (final column). The final box shows the result from FISHPATH. Page 3 shows that FISHRAND and the original Gobas predictions show good agreement.

Page 4 of Figure 3-3 shows the comparison for benthic invertebrates. FISHRAND and the Gobas model as published show identical predictions. Pages 5 and 6 present the equations used for fish uptake , while page 7 presents the final comparisons between the Gobas model as published (1993), field observations, and FISHRAND. FISHRAND predicts virtually identically to published Gobas results, indicating that the model is performing as published.

3.5.5.2 Initial Validation: Comparison with Gobas (1995) Lake Ontario Data for the Time-Varying Case

Figure 3-4 shows the comparison between FISHPATH, FISHRAND, and published data from Gobas (1995). FISHRAND and FISHPATH were run using inputs specified in Gobas (1995) and compared to results published in that article. Model results showed concordance with the published data, indicating that the models were correctly coded and ready to be modified for use in the Hudson River modeling application.

3.5.5.3 Calibration Approach: Sensitivity Analysis

Calibration focused on a few parameters that are (i) considered highly uncertain, and (ii) important for model performance. To determine the most important parameters, a sensitivity analysis was conducted using the approximate analytical solution to the Gobas model for small time intervals t:

$$C_f(t) = \frac{a_1 + a_2}{a_3} * [1 - \exp(-a_3 * t)] + C_f(0) * \exp(-a_3 * t)$$

(3-21)

MCA/TetraTech

where

$$a_1 = k_1 * C_{wd}$$
$$a_2 = k_d * C_d$$
$$a_3 = (k_2 + k_e + k_M + k_g)$$

In particular, (3-21) provides the steady state Gobas' solution when $t \to \infty$ and the initial condition when $t \to 0$.

The rate coefficients in the Gobas model are functions of 11 constants:

C_1: the constant equal to 88.3 in equation (3-9);

C_2: the power constant equal to 0.6 in equation (3-9);

C_3: the constant equal to 100 in equation (3-10);

C_4: the constant equal to $5.3*10^{-8}$ in equation (3-13);

C_5: the constant equal to 2.3 in equation (3-13);

C_6: the constant equal to 0.022 in equation (3-14);

C_7: 0.85 in the same equation (3-14);

C_8: the constant 0.06 in equation (3-14);

C_9: 0.2 factor in equation (3-15);

C_{10}: 0.01 constant in equation (3-16);

C_{11}: the 0.2 power in the last equation for T > 25°C) (3-16).

As there are six individual fish species, there are 66 additional variables are considered as unknown in addition to the environmental variables (e.g., fish weight, diet, etc.). It is not mathematically feasible to obtain best estimates of all 66 variables.

The sensitivity analysis focuses on the relationship between predicted fish body burden and these 11 constants. After obtaining the partial derivatives, elasticities were estimated. Elasticities interpret the effect of a percentage change in the independent variable on the dependent variable. The elasticity for a parameter is calculated at the point of the means of each of the independent variables as:

$$E_j = \frac{\frac{\partial Y}{\overline{Y}}}{\frac{\partial X}{\overline{X}}} \qquad (3-22)$$

where:

Y = ΣTri+ PCB concentration in fish; and,

X = each of the constants $C_1 - C_{11}$ above, as well as the user-specified parameters.

The analytical expressions for the elasticities were obtained using the Maple software package. The expressions of the derivatives were coded in FORTRAN and the elasticities were calculated simultaneously with the calculations of the concentrations themselves. Elasticities averaged over time and environmental parameters were considered in selecting the parameters to evaluate using likelihood profile methods and then for updating in the Bayesian Monte Carlo procedure.

3.5.5.4 Calibration Approach: Likelihood Profiling

Likelihood Profiling is a powerful technique to determine confidence limits for model parameters. Likelihood profiling was implemented in a simplified FISHRAND model (fish diets were not randomized, and the simulation scheme was modified to eliminate random fluctuations of the calculated concentrations for a fixed value of the model parameter selected for the profiling) to derive corrected prior distributions. Bayesian updating (see chapter 3.5.5.5) was then used to derive posterior parameter distributions in the complete FISHRAND model. Likelihood profiling is used before formal Bayesian updating for three reasons: a) To obtain best estimates and probability for the parameters for which empirical distributions were unavailable (e.g., Gobas model constants such as growth rate, assimilation efficiency etc.); b) To reduce uncertainty and assign narrower distributions for the parameters for which empirical measurements resulted in very broad and/or highly uncertain distributions (both methods are based on the same likelihood function, so if the likelihood function has a higher value in the profiling, it will correspondingly have a larger probability following Bayesian updating); and c) to minimize the intensive computation required by the Bayesian updating calibration technique (both methods are based on the same likelihood function). Often the empirically derived prior distributions do not adequately reflect values in the tails, and this method allows for a better representation of the full distribution.

The idea of extending likelihood profiling to compute parameter distributions has been suggested by Bates and Watts (1988) but it was only recently that appropriate computational methods have been developed (Quinn et al., 1999).

The likelihood function reflects consistency between experimental and modeled data, The following form of likelihood function is used in our calculation assuming lognormal distributions of measured body burdens:

$$L\langle y_m | y(x) \rangle = \frac{1}{y_m} \frac{1}{\sqrt{2\pi}\sigma_{ym}} \exp{-\frac{1}{2\sigma_{ym}^2}(\ln(y_m) - \ln(y(x)))^2} \quad . \tag{3-23}$$

where:

y_m = measured concentration in fish,

y = calculated concentration from the model,

σ_{ym} = measured standard deviation for fish concentration, and,

x = vector of model parameters.

Equation 3-23 provides the likelihood function for one measurement. The method uses the product of likelihood functions for all available measurements.

The likelihood function 3-23 depends on model parameters. The values of x for which likelihood function is maximized are called the maximum likelihood estimates (MLE) for the model parameters. The likelihood ratio is defined as the ratio of the likelihood function for specified values of x and the likelihood function for the MLE of x.

$$LR(x) = \frac{L\langle y_m | y(x) \rangle}{L\langle y_m | y(x_{MLE}) \rangle}$$ (3.24)

The statistical inference about parameter values is based on the fact that -2Ln(LR) is asymptotically distributed as χ^2 (r) where χ^2 is the chi-squared distribution and r is the number of degrees of freedom equal to the dimension of vector of parameters x.

The likelihood ratio Ln(LR) is plotted as a function of only one model parameter x in small increments from its maximum likelihood estimate. For each fixed value of the selected parameter x in equation 3.24, the likelihood function in the numerator is maximized with respect to all other model parameters. This maximum is calculated using numerical simplex methods. The tables of chi-square distributions with one degree of freedom are used to build confidence intervals for the parameter. These intervals were used to approximate either normal, lognormal, or triangular parameter distributions.

The likelihood profile can be utilized only for a simplified model. Therefore Bayesian updating is used for calibration of the complete model.

3.5.5.5 Calibration Approach: Formal Bayesian Updating Procedure

FISHRAND implements a "multi-dimensional" Monte Carlo approach in which all model parameters are categorized as uncertain or variable. Variable parameters are those reflecting population heterogeneity, while uncertain parameters reflect lack of knowledge. This Bayesian approach reduces uncertainties in our knowledge about the simulation of uptake of PCBs, and improves our knowledge about natural variability in the system. The user can assign "uncertainty" and "variability" attributes to all model parameters interactively. The general scheme of random sampling implemented in FISHRAND is presented in Figure 3-5.

The FISHRAND model incorporates distributions instead of point estimates for model parameters. The calibration approach takes advantage of this feature by incorporating Bayes Rule. The procedure is as follows. Using the distributions specified in Level 1 (generic model

MCA/TetraTech

303800

constants together with site-specific distributions of lipid content, sediment and water concentrations generated from the HUDTOX model, fish weight, K_{ow}, and dietary preferences), the model generates distributions of fish body burdens for each species, location, and year. These simulated values are compared to available NYSDEC monitoring data. The model output and the observation are reconciled using Bayes rule to determine a posterior mass function for the model output, that is, the distribution that leads to a best fit between model output and observations. The algorithm proceeds as follows:

1. Define a prior density $p(x_j)$ on all model parameters $(x_j \in \bar{x})$ (obtained from site-specific data for lipid, weight, TOC, etc.)
2. Sample from this distribution n times using a Monte Carlo scheme and generate sample inputs $x_{i,j}(i=1,n)$ for each $(x_j \in \bar{x})$
3. Run the model for each set of input samples to determine the sampled output $y_{i,o}(i=1,n)$ for model output of interest $y_o(y_o \in \bar{y})$.
4. Evaluate the likelihood function $L\langle y_m | y_{i,o}\rangle$ for each sample $y_{i,o}$ of model output y_o using the error structure of the observed data/measurement.
5. Reconcile the model output and observation using Bayes Rule—obtain posterior mass function for inputs and outputs.

Figure 3-6 provides a schematic of the Bayesian updating procedure. Using Monte Carlo simulation, a representative sample $x_{i,j}(i=1,n)$ for each input x_j is generated from the initially specified (prior) distribution $p(x_j)$. A probability mass function $p(x_{i,j}) = \dfrac{1}{n}$ is associated with the ith sample $x_{i,j}(i=1,n)$ for each input x_j. The model is then run iteratively n times for each vector of sampled inputs. This results in n sample values, $y_{i,o}(i=1,n)$ for model output y_o each with probability mass function equal to $\dfrac{1}{n}$. If the log-error (ε) on y_m is normally distributed (assuming a lognormal distribution for ΣTri+ PCB concentration in fish) with a mean of zero and standard deviation σ_{ym}, then the likelihood function $L\langle y_m | y_{i,o}\rangle$ is expressed as:

$$L\langle y_m | y_{i,o}\rangle = \frac{1}{y_m}\frac{1}{\sqrt{2\pi}\sigma_{ym}}\exp-\frac{1}{2\sigma_{ym}^2}\left(\ln(y_m)-\ln(y_{i,o})\right)^2 \qquad (3\text{-}25)$$

The posterior mass function for each sample $y_{i,o}$ is determined from Bayes rule as:

$$P\langle y_{i,o} \mid y_m \rangle = \frac{p(y_{i,o}) * L\langle y_m \mid y_{i,o} \rangle}{\sum\limits_{i=1}^{n} p(y_{i,o}) * L\langle y_m \mid y_{i,o} \rangle} \qquad (3\text{-}26)$$

Since $p(y_{i,o}) = \dfrac{1}{n}$, equation (3-26) readily reduces to

$$P\langle y_{i,o} \mid y_m \rangle = \frac{L\langle y_m \mid y_{i,o} \rangle}{\sum\limits_{j=1}^{M} L\langle y_m \mid y_{i,o} \rangle} \qquad \cdot \qquad (3\text{-}27)$$

It is critical to recognize that for each simulated replication, the same posterior probability mass function is associated with inputs *and* outputs. Hence, the posterior probability mass function for input samples $x_{i,j}$ is also given by:

$$P\langle x_{i,j} \mid y_m \rangle = \frac{L\langle y_m \mid y_{i,o} \rangle}{\sum\limits_{j=1}^{M} L\langle y_m \mid y_{i,o} \rangle} \qquad \cdot \qquad (3\text{-}28)$$

The sample values $x_{i,j}$ and the associated posterior probability mass functions $P\langle x_{i,j} \mid y_m \rangle$ characterize the posterior density function for model input x_j.

Systematic and unrecognized errors between models and experimental data were found to result in false precision in Bayesian updating, *i.e.* posterior parameter distributions are estimated to be narrow while in fact they are much broader (Small and Fischbeck, 1999). This false precision does not significantly affect central estimates for the parameter distribution. One way to address this issue is to implement Markov Chain Monte-Carlo sampling (MCMC). Given the complexity of the FISHRAND model, implementation of MCMC would result in significant computational difficulties. Therefore we implemented multiple regression analysis in which parameter variance as derived from the likelihood profiling and Bayesian updating is matched with experimentally-observed data by means of the least squares method (variance correction procedure).

The FISHRAND calibration focused on optimizing wet weight concentrations. This was done for three reasons. First, the model predicts a wet weight concentration in fish, and provides lipid normalized results by dividing the predicted wet weight concentration by a percent lipid.

MCA/TetraTech

303802

Second, the lipid content of any given fish is difficult to predict from first principles alone. Finally, potential target levels in fish are typically described as wet weight concentrations.

Optimizing the model for wet weight concentrations provides a more sound basis upon which to make future predictions. In addition to predicting fish responses to changes in sediment and water concentrations, it is also necessary to predict lipid content. Although it is possible to obtain close to perfect agreement between model predictions and observed body burdens by inputting the observed lipid concentrations for each year for which measurements are available, this approach limits the ability of the model with respect to forecasts of fish tissue PCB concentrations. The FISHRAND model predicts wet weight concentrations by relying on a distribution of lipid values in each fish species that is representative of the observed variability in lipid content. This provides a more robust basis upon which to make predictions.

3.5.6 FISHRAND Model Validation

To validate the model, several approaches were followed.

First, the calibrated model for one river mile was run for another river mile and predicted body burdens compared to measured body burdens at this location. Satisfactory agreement for both river miles implies model validity across locations in the Hudson River.

A second approach involves model calibration using only part of the available dataset and comparison of model predictability of the remaining portion of the dataset. A good concordance of the model prediction with observed data implies model validity within the timeframe of available measurements and therefore model usability for the future predictions.

Finally, model predictions for the policy-relevant endpoints (such as concentrations at some point in the future) can be compared for the model calibrated using all available experimental data and then only a portion of the data. Closeness of the model predictions shows robustness of the model.

MCA/TetraTech

4. BIVARIATE BAF ANALYSIS OF FISH BODY BURDENS

4.1 Data Used for Development of Bivariate BAF Analyses

Equation (3-1) presents an idealized formulation for developing bivariate BAFs. Actual implementation is constrained by data availability. Among other issues, quantitation methods used for fish are not directly equivalent to those used for water, and quantitation methods have changed over time. Establishing the spatial/temporal history of sediment concentrations also presents difficulties.

Initial attempts to develop bivariate BAFs for the Hudson River were presented in the PMCR (EPA, 1996), using data through 1992. Since that time, additional fish, water column, and sediment data have become available, running through 1997. Additional evidence has also been developed on the proper interpretation of historical Aroclor PCB quantitations. Finally, the approach used for bivariate BAFs has been refined based on comments generated in EPA's Peer Review of the PMCR and initial draft of the BMR. Data and methods used for development of the bivariate BAF analysis are described below.

4.1.1 Fish Data

4.1.1.1 Locations and Species Analyzed

Statistical development of a bivariate BAF requires a sufficiently large range of data (over differing environmental conditions in space and/or time) to distinguish accumulation originating from water column and sediment pathways. As in the PMCR, the bivariate BAF analysis is based on NYSDEC fish data from the Upper Hudson River below Fort Edward coupled with NYSDEC data from the uppermost part of the Lower Hudson River (above River Mile 142). Samples collected between River Mile 142 and 153 are from the freshwater portion of the Lower Hudson. The species collected in this area are largely the same as those collected in the Upper Hudson, and PCBs in this reach are derived primarily from the Upper Hudson. It is therefore appropriate to include samples between River Mile 142 and 153 (if adjustment is made for the lower exposure concentrations expected in this reach), thus providing a larger database for analysis. Samples collected further downstream within the freshwater portions of the Hudson were not included due to lack of contemporaneous measurements or estimates of water column and sediment concentrations.

The longest-running and most extensive sample data in the Upper Hudson come from NYSDEC collections at River Miles 168-176 (near Stillwater) and at River Miles 142 and 152 (below Federal Dam). A good representation over time is also available for River Miles 189-190 (lower Thompson Island Pool), and smaller amounts of data are available at River Mile 160 (Waterford, above Federal Dam). The species for which the most data are available are pumpkinseed (*Lepomis gibbosus*), largemouth bass (*Micropterus salmoides*), and brown bullhead (*Ictalurus nebulosus*). Lesser, but still extensive, data are available for goldfish (*Carassius auratus*), white perch (*Morone americana*), and yellow perch (*Perca flavescens*).

These species represent a range of trophic levels, habitat preference, and foraging behavior: Largemouth bass are piscivorous, with adults occupying the top of the aquatic food chain. Yellow perch represent an intermediate trophic level, foraging on invertebrates and small fish. Unlike largemouth bass, yellow perch are migratory within the river. Adult white perch are benthic predators, with older white perch becoming increasing piscivorous, and utilize both shallow areas and the main channel bottom. The species is semi-anadromous, with spawning occurring in the upper reaches of the Lower Hudson River and winter movement down river. They are also found in the lower two lock pools of the Upper Hudson River. Pumpkinseed occupy a lower trophic level, feed primarily on invertebrates, and are an important food source for larger fish. Goldfish also occupy a lower trophic level, feed primarily on invertebrates in the water column, and consume detrital algae. Brown bullhead are omnivorous bottom feeders, with diet including offal, waste, small fish, mollusks, invertebrates, and plants. Feeding preferences may vary with the age and size of the individual. Thus, a range of trophic positions and forage preferences is available for analysis in the historic data. Appendix A provides more detailed information on the foraging strategies of each of these species (except goldfish).

Data summaries for the NYSDEC fish analyses through 1988 were provided in the Phase 1 report, while the PMCR provided a summary through the 1992 sampling, with a total of 10,311 fish analyses available, of which 3,412 were collected between River Miles 142 and 194. Additional data are now available for 1993 through 1997, including 994 NYSDEC samples collected between River Miles 142 and 194, and some corrections have been made to the database supplied by NYSDEC. Analyses presented in this chapter are based on a release of the NYSDEC database provided on November 17, 1998, which contains some minor additions and updates subsequent to the release of TAMS/Gradient Database Release 4.1.

4.1.1.2 Lipid Normalization

As described in Chapter 3, PCBs accumulate primarily in fish lipid tissue, and it is appropriate to normalize fish body burdens to concentration on a lipid basis. This helps remove variability in concentrations due to variability in individual lipid content. Nearly all the NYSDEC fish analyses report percent lipid, so lipid-normalized concentrations are readily calculated. It should be noted, however, that extraction and determination of lipid content is also subject to uncertainty. This does not, however, present a major problem. Laboratory analyses for PCBs are based on a lipid extract; thus the lipid-normalized concentration should be consistent (except for round-off error) as long as the extraction procedures used for PCB and lipid analysis are consistent, even though results are reported on a wet-weight basis. Error in lipid determination primarily introduces error into reported wet-weight concentrations, which are not used in the BAF analysis.

4.1.1.3 Season, Age, and Sex

PCB body burdens in fish may vary in accordance with seasonal growth and spawning cycles. These bioenergetic factors are not included in the simple BAF approach; however, their importance as potential confounding factors should be recognized. To help minimize these

effects, only data from summer collections (May to September) were used. Within this time period, collections for individual species have tended to be even more focused. Most summer samples are in the May-June period for brown bullhead (95%), goldfish (100%), largemouth bass (97%), white perch (100%), and yellow perch (100%). Pumpkinseed samples are predominantly from August-September (90%). The empirical models, which result, will be specific to these collection times.

Age of individuals also affects PCB body burden, as various PCB congeners tend to bioaccumulate over time, feeding preference often shifts to higher trophic levels with increasing size, and growth dilution effects change with age. Sex differences in PCB concentrations have also been noted in the Hudson and elsewhere, perhaps due in part to loss of PCBs from females when eggs are expelled (see Sloan et al. 1995). Within the historical database, age is usually not given, and weight and length are uncertain surrogates. Sex determination is also missing for many samples. Therefore, the BAF analysis has not accounted for age and sex effects, although these undoubtedly contribute to the variability among individual samples.

4.1.1.4 Laboratories and Methods for PCB Analysis

An important conclusion of the PMCR (see also Butcher et al., 1997) is that valid interpretation of historical trends in PCB concentrations cannot be made without consideration of the changes in analytical methods which have occurred over time. That is, a comparison is valid only when there is consistency in what is being measured. The most dramatic change in analytical methods is that between the Phase 2 TAMS/Gradient data, using state-of-the-art, capillary-column, PCB congener analyses, and older analyses based on packed-column quantitation of Aroclor equivalents. The historical fish analyses in the NYSDEC database primarily consist of packed-column Aroclor quantitations. Because an Aroclor is a complex mixture of many individual congeners, interpretation of the historic Aroclor data raises difficult technical issues. In addition, Aroclor quantitation methods have changed over time, and these changes have significant implications for the interpretation of historical trends in the data and the development of valid statistical relationships.

Shifts in laboratories may also influence results. A summary of samples between River Miles 142 and 193 by laboratory and year is provided in Table 4-1. As will be seen from this table, a majority of the Upper Hudson samples from 1977 on were analyzed by the same contract laboratory (referred to for convenience as "Hazleton"), although this laboratory has undergone a number of changes in name and/or ownership (see also Sloan et al., 1985). The major exceptions are samples from 1991 to 1992, analyzed by NYSDEC's Hale Creek Field Station ("Hale Creek"). As described below, it has been possible to develop analyses of what was actually measured (in terms of PCB congeners) by the various Aroclor quantitation methods used by Hazleton and Hale Creek. This has not been possible for the six laboratories represented in the "Other" category. Therefore, the analysis has been restricted to Hazleton and Hale Creek results, 1977 to 1997.

Aroclor standards used by these two laboratories for quantitation, and NYSDEC conventions for estimating total PCBs from Aroclor data, are summarized in Table 4-2.

Quantitations by Hazleton for 1977 through 1990 are consistently based on analysis against Aroclor 1016 and Aroclor 1254 standards on packed column GC; an Aroclor 1221 standard was used on most Hazleton analyses through early 1993, but not thereafter. Reported detection limits range from 0.01 to 1.0 ppm wet weight for each Aroclor, with detection limits for most samples at 0.1 ppm, and the vast majority of samples collected between River Miles 142 and 193 were reported with values above quantitation limits for both Aroclor 1016 and Aroclor 1254. Total PCB concentrations in fish through 1990 were calculated by NYSDEC as the sum of Aroclor 1016 plus Aroclor 1254, because (1) 68 percent of the total Aroclor 1221 results, and 55 percent of those between River Mile 142 and 196 are reported as nondetects (versus less than 1 percent nondetects for Aroclor 1016 and Aroclor 1254 in this portion of the river); (2) Aroclor 1221 quantitations are not available for later data; and (3) when Aroclor 1221 is detected, substantial double-counting may occur between quantitations to Aroclor 1016 and Aroclor 1221 standards.

Hazleton analyses through 1990 are discussed in detail in the PMCR and in Butcher et al. (1997). These analyses against Aroclor standards on an OV-1 stationary phase were based on only a few packed-column peaks, and are sensitive to the quantitation method used, which has changed over time. Estimating an Aroclor concentration from a few peaks can introduce significant error in estimates if the environmental distribution of PCB congeners differs from that of the unaltered Aroclor standard. After commencing in 1977, quantitation peaks were changed in 1979 and in 1983; the 1983 quantitation scheme was used consistently through 1990 (see Sloan and Jock, 1990; Armstrong and Sloan, 1988). Hazleton analyses from 1992 on substituted an Aroclor 1248 or 1242 standard for Aroclor 1016, and added Aroclor 1260. Quantitation peaks for the 1992 to present Aroclor 1248 method were tentatively identified from area reports and sample calculation sheets provided by EnChem, successor to Hazleton, coupled with interpretation of sample chromatograms to identify peaks identified on absolute retention time (RT) in terms of retention time relative to p,p'-DDE (RRT), as used by Webb and McCall (1973) and others. Packed-column GC peaks and associated congeners are summarized in Table 4-3.

For 1991-1993, the database contains many fish analyses for Aroclors performed using capillary column GC at NYSDEC's Hale Creek field station. The analytical approach is documented in "Analytical and Laboratory Procedures at Hale Creek Field Station", which contains the method documentation for "OC1.103. Organochlorine Residues", dated 9/27/1990. The Hale Creek analyses were performed on a Perkin-Elmer Sigma 115 with SPB-1 methyl silicone bonded phase capillary column. The Control inputs attached to this method appear to show that Aroclor 1016 was analyzed via 7 capillary column peaks (with retention times relative to p,p'-DDE ranging from 0.73 to 0.87), and Aroclor 1254-1260 (combined) by 14 peaks (with retention times relative to p,p'-DDE ranging from 0.96 to 1.31). A specific identification of congeners associated with these SPB-1 peaks has not been made.

4.1.1.5 Standardization of PCB Analytical Results

The "Hazleton" and Hale Creek results in the NYSDEC database include Aroclor quantitations by five different sets of methods/quantitation peaks. As demonstrated in Butcher et al. (1997), these shifts in quantitation can introduce spurious apparent changes in reported Aroclor and total PCB concentrations in fish. For instance, the change in quantitation peaks

between 1977 and 1979 is estimated to result in an apparent decline in Aroclor 1016 concentration of approximately 40 percent, regardless of actual environmental trends.

It is thus essential to establish a consistent quantitation basis, or "translation" procedure, to develop an empirical analysis of trends in fish concentrations and correlations between fish body burdens and environmental concentrations. Development of translations for historical data has relied on a weight of evidence approach. Three separate lines of evidence have been pursued:

- Split Sample Analyses, in which one sample is split and analyzed by different methods. This is the most direct approach, but is available for only a limited number of methods and samples.

- Interlaboratory Comparisons, designed to evaluate contract laboratory performance. The interlaboratory comparisons are similar to split samples, in that they provide direct comparison between methods, but do not provide detailed documentation on methods used.

- Theoretical "What If?" Analyses, in which the performance of historical Aroclor quantitation methods is evaluated in terms of PCB congeners, based on interpretation of congener data "as if" analyzed by the historical methods.

The baseline or reference condition for the development of translation procedures is taken as the sum of PCB congeners as quantitated by Aquatec for the TAMS/Gradient Phase 2 sampling. Translations have been developed for two targets: total PCBs (i.e., sum of quantitated congeners, consisting of 90 target and 36 non-target congeners and representing more than 90 percent of the total concentration of Aroclors 1016, 1242, and 1254, as described in the DEIR, Appendix A), and the sum of trichloro- through decachlorobiphenyls (denoted ΣTri+). The latter target was selected for the BAF analysis because most of the historical monitoring of PCB concentrations in water and sediment is most readily interpreted in terms of ΣTri+, as described in Volume 1, Chapter 2.6 of this report. Because fish tend not to accumulate significant amounts of mono- and dichlorobiphenyls, translations of historical quantitations to either total PCBs or ΣTri+ are expected to be similar.

4.1.1.6 Theoretical "What If?" Analyses

The theoretical analysis is presented first, because it can be developed for all the "Hazleton" methods and provides some insights for interpreting the limited data available from split samples and interlaboratory comparisons.

An interpretation of what was actually measured in historical packed-column analyses can be made by converting the TAMS/Gradient Phase 2 fish congener data to equivalent Aroclor measurements *as if* analyzed by NYSDEC methods. According to Sloan *et al.* (1984):

MCA/TetraTech

Quantitation was done by comparing several peak heights or areas to those produced by the respective Aroclors. The principal peaks used for quantitation include a single one for Aroclor 1221 representing a monochlorobiphenyl; two for Aroclor 1016 reflecting mixtures of trichlorobiphenyl; and three peaks for Aroclor 1254 primarily composed of tetra-, penta- and hexachlorobiphenyl congeners.

While the NYSDEC method employs several peaks for Aroclor quantitation, these are evaluated via a single composite response factor. Given selection of m packed-column peaks for quantitation, the reported Aroclor value is obtained as

$$[\text{Aroclor}] = \left(\sum_{j=1}^{m} \text{area}_j \right) \cdot \text{RF}_s \qquad (4\text{-}1)$$

where

area_j = the area associated with packed-column peak j, and

RF_s = a composite or net response factor defined as the concentration of standard Aroclor injected divided by the sum of the peak areas of the selected packed-column peaks.

The area within the selected packed-column peak is related to the sum of the concentrations of individual PCB congeners associated with those peaks by congener peak response factors:

$$\sum_{j=1}^{m} \text{area}_j = \sum_{i=1}^{n} \frac{[\text{congener}_i]}{\text{RF}_{ci}} \qquad (4\text{-}2)$$

where

n = number of congeners associated with selected packed column peaks,

$[\text{congener}_i]$ = concentration of an individual PCB congener i associated with the selected packed column peaks, and

RF_{ci} = the response factor for congener i, defined as the concentration of congener i in the Aroclor standard divided by the peak area contributed by this congener.

If the congener response factors within the individual peaks are relatively consistent, this may also be approximated as

$$\sum_{j=1}^{m} area_j \approx \frac{\sum_{i=1}^{n} [congener_i]}{RF_p} \qquad (4\text{-}3)$$

where

RF_p = area-weighted mean response factor for the selected packed column peaks or their constituent congeners in a capillary column analysis. RF_p is defined as the concentration of the Aroclor standard times the weight percent of PCB congeners contained in the selected peaks divided by the peak area, or:

$$RF_p = [Aroclor_{std}] \cdot \frac{\sum_{j=1}^{m} wt\,\% \, peak_j}{\sum_{j=1}^{m} area_j} = [Aroclor_{std}] \cdot \frac{\sum_{i=1}^{n} wt\,\% \, congener_i}{\sum_{k=1}^{n} area_k}$$

Substituting Equation (4-3) into Equation (4-1) yields

$$[Aroclor] \approx \sum_{i=1}^{n} [congener_i] \cdot \frac{RF_s}{RF_p} \qquad (4\text{-}4)$$

Because the ratio of the response factors on the right-hand side of this equation is equivalent to the inverse of the weight percent of total PCBs contained in the selected packed column peaks, this simplifies to:

$$[Aroclor] \approx \frac{\sum_{i=1}^{n} [congener_i]}{\sum_{j=1}^{m} wt\,\% \, peak_j} \qquad (4\text{-}5)$$

where the denominator represents the total weight percent of the Aroclor contained in the congeners making up the packed column peaks used for quantitation. The relationship is only approximate, because the response factors of individual congeners are not equal. Calibrated response factors for the congeners that are (1) included within peaks used for quantitation of a specific Aroclor and (2) regularly detected in Hudson River biota were, however, found to vary over a small range, and, in most cases, estimated response factors relative to BZ #52 for these congeners are within 15% of unity. Thus, the simple approximation of Equation (4-5) is judged to provide an adequate basis for comparing historical packed-column GC analyses with more recent capillary column results.

As indicated by Equation (4-5), translating between congener data and historical Aroclor quantitations also requires the total weight percent of the quantitated peaks in the Aroclor standards. These values were obtained by summing the weight percentages of congeners

associated with packed column peaks in Aroclor standards (see Table 4-3) as developed from analyses of Aroclor standards in the Phase 2 laboratory effort. The weight percentages are given in Table 4-4. It should be noted that weight percentages reported for individual congeners in Aroclor standards vary considerably (e.g., Albro and Parker, 1979; Schulz et al., 1989; Draper et al., 1989 for Aroclor 1016). Some of this variability is likely due to batch differences in Aroclor standards, and some to analytical methods. For purposes of this study, it is most important to use consistent results for Aroclor standards analyzed by the same methods and laboratory as the reference biological data.

Estimates of ΣTri+ obtained from the Phase 2 congener data may be regressed against total PCB estimates by Aroclor quantitation "as if" calculated by Hazleton methods to yield a translator. Regression results are summarized below and in Figure 4-1. Standard errors for the dependent variable estimates and for each coefficient are shown in parentheses below the equation.

$$\Sigma\text{Tri+} = -200.7 + 0.08720 \times 1977 \text{ Sum } (1016+1254) \qquad R^2 = 99.4\%$$
$$(862.7) \quad (97.2) \quad (0.0065)$$

$$\Sigma\text{Tri+} = -62.5 + 1.224 \times 1979 \text{ Sum } (1016+1254) \qquad R^2 = 99.3\%$$
$$(881.6) \quad (98.7) \quad (0.0093)$$

$$\Sigma\text{Tri+} = -216.5 + 1.320 \times 1983 \text{ Sum } (1016+1254) \qquad R^2 = 99.2\%$$
$$(961.8) \quad (108.4) \quad (0.0109)$$

$$\Sigma\text{Tri+} = -111.0 + 0.8798 \times 1992 \text{ Sum } (1248+1254+1260) \quad R^2 = 97.3\%$$
$$(1762) \quad (198.4) \quad (0.0135)$$

4.1.1.7 Split Sample Comparisons

The NYSDEC database (11/17/98 update) contains a limited number of fish samples analyzed for PCBs by multiple laboratories. Most relevant for the "Hazleton" analyses are splits of 1995 samples from the Hudson analyzed by both Hazleton (using the 1992 method) and NOAA (using capillary column GC analysis comparable to the Aquatec results). There are two other series of splits between Hazleton and Hale Creek (1987 Smith Pond, 1996 Queensberry area), but for these samples Hazleton reports against Aroclor 1016 and 1254/60 standards. Hazleton thus apparently used a version of the Hale Creek method, and not their own "1992" method for these analyses. There are also 1993 split samples between Aquatec and Hale Creek for pumpkinseed in the Upper Hudson. These samples may be matched on tag number to identify true split samples.

The 1995 Hazleton-NOAA splits consist of 20 largemouth bass (collected between river miles 113 and 189) and 35 striped bass (collected between river miles 27 and 152) quantified for 107 target congeners. In 54 out of the 55 samples the total calculated by Hazleton was greater than the total calculated by NOAA (the one exception is the most highly contaminated sample). The slope of a regression of the NOAA results against the Hazleton results is 0.87, and is not

MCA/TetraTech

303812

significantly different from the theoretical relationship obtained between sum of congeners and the Hazleton 1992 method using the *"What if?"* analysis presented above. The split samples thus appear to confirm the theoretical analysis.

The 1993 Hale Creek-Aquatec splits consist of 15 pumpkinseed samples, including three highly contaminated specimens from Griffin Island. For 13 of the 15 samples, the total reported by Aquatec using capillary column GC is higher than the Hale Creek Aroclor sum. The two exceptions are very lightly contaminated specimens. The slope of a regression of the Aquatec results against the Hale Creek results is 1.46, with an R^2 of 94%. This result is consistent with an interpretation that Hale Creek analyses are approximately equivalent to Hazleton analyses by the 1983 method.

The results of 1997 split samples between EnChem (successor to Hazleton) and GE's contractor NEA (identified to peak/congener basis by capillary column GC) are not yet ready to be released or reported in detail, but results of 56 samples were made available for preliminary inspection by NYSDEC. The theoretical *"What if?"* analysis suggested that the 1992-1997 Hazleton/EnChem Aroclor method should result in substantially higher results than the 1983 Hazleton method, and should yield a slight overprediction of the sum of congeners, with a slope of about 0.90 for congener sum versus Hazleton Aroclor sum. The provisional data suggest that this is indeed the case, as the EnChem Aroclor sum appears to be consistently higher than the NEA sum of congeners. The average ratio between NEA and EnChem results is approximately equal to the theoretical slope of 0.90. Regression analysis suggests that the over-prediction could be even greater. However, it should be noted that the NEA congener analysis is not necessarily fully equivalent to the Aquatec congener analysis that serves as a baseline for our comparison. Thus, the provisional 1997 data also appear to confirm the theoretical analysis.

4.1.1.8 Interlaboratory Comparisons

NYSDEC has conducted several rounds of interlaboratory comparison for contract laboratory evaluation. Results for 1989, 1992, and 1995 comparisons were provided by NYSDEC. For the 1989 study, eight laboratories participated, analyzing four samples. These samples are not identified, but three of the four appear to have had significant PCB contamination. The 1992 study included twelve laboratories and analysis of five samples (two Lake Ontario coho salmon, clean largemouth bass composite, Hudson River striped bass, and great horned owl tissue). The 1995 study involved four laboratories and three samples. One of the samples was a composite of previously analyzed fish with no detectable PCBs. Samples 2 and 3 were splits of the same sample, which was a composite of striped bass fillets collected from New York City Harbor with less than 1 ppm PCBs. Hazleton and Hale Creek participated in each of these interlaboratory comparisons. The quantitations were to Aroclor standards of the individual laboratory's choosing, and separate reference analyses for PCB congeners by capillary column were not included.

No clear trend among laboratories is evident in the 1989 comparisons. Comparison of Hazleton results is difficult, however, because Hazleton used Aroclor 1248, 1254, and 1260 standards, while Hale Creek results, using Aroclor 1016 and 1254/60 standards, predate their

MCA/TetraTech

1990 methods documentation. Hazleton results were lower than Hale Creek on the two more contaminated samples (total PCB concentration of about 10 ppm), and higher than Hale Creek on the two lightly contaminated samples (less than 1 ppm). Comparison is also hampered by not knowing which (if any) samples are Hudson River fish. Samples that represent congener/Aroclor mixtures significantly different from those found in the Hudson River would likely provide different results on a comparison of Hazleton and other methods.

In the 1992 interlaboratory comparisons, Hazleton Environmental Services (HES) used Aroclor 1242, 1254, and 1260 standards, which approach differs from the methods used by Hazleton for Upper Hudson River fish samples in the 1990s. 1992 Hale Creek analyses were apparently done using their capillary column method OC1.103, as discussed above. Hazleton and Hale Creek were in relatively close agreement for four of the five samples, including all the fish samples. The major discrepancy is in the analysis of the owl tissue, for which Hazleton reported 4.5 ppm total PCBs, versus 1.5 for Hale Creek. One reason for the discrepancy is that Hazleton quantitated this sample as Aroclor 1260 only. Hazleton's "1992" method for Aroclor 1260 uses only three peaks, which represent the more chlorinated end of the 1260 spectrum, accounting for only about 8 percent of the total mass of Aroclor 1260. Scaling up to total PCBs from a few peaks at one end of the spectrum is likely to result in significant potential for mis-estimation. In all the fish samples, Hazleton's results were somewhat less than those reported by Hale Creek, with an average difference of -13%. The discrepancy is greatest (-21%) for the Hudson River striped bass sample.

In the 1995 interlaboratory comparisons, Hazleton used their standard "1992" approach of quantitating to Aroclor 1248, 1254 and 1260 standards. For the two contaminated 1995 samples, results from Hazleton were approximately 1.4 times those from Hale Creek. The report transmitting the 1995 results (memorandum from Larry Skinner to Robert Bauer, January 17, 1996, *Comparison Study of Contract Labs for Total PCB and % Lipids)* states: "All laboratories were in the acceptance limits of ±3 standard deviations of the mean, with laboratory 2 [Hazleton] being consistently higher than the rest." The ratio of Hazleton to Hale Creek in 1995 is consistent with predictions from the theoretical analysis of 'Hazleton' methods, assuming that Hale Creek results are similar to Hazleton 1983 method results."

4.1.1.9 Translation Methods

The available evidence suggests that the "*What if?*" analyses provide a reasonable basis for translating "Hazleton" Aroclor results to a basis consistent with congener analyses. Approximate translation of the Hale Creek Aroclor data can be based on the analyses of split samples described above.

Regression relationships between Aroclor sum and congener total can be performed with or without a constant. In most cases, it was found that the constant was not significantly different from zero. In addition, a zero-intercept regression is attractive because (1) samples detected as near-clean by packed column are best interpreted as likely to be near-clean on capillary column analysis as well, and (2) a zero-intercept regression will prevent prediction of any negative concentrations on transformation. Therefore, zero-intercept results are presented below.

MCA/TetraTech

Resulting zero-intercept translation methods for the state variable ΣTri+ are presented below. Applicable laboratory codes from the database are also indicated. Note that the proposed translation factors are only applicable to the laboratories for which they were developed.

Time Period	Equation	Applicable Laboratory Codes
1977-1978	$0.8642 \cdot (Aro\ 1016 + Aro\ 1254)$	WI, RAL
1979-1982	$1.2210 \cdot (Aro\ 1016 + Aro\ 1254)$	RAL, HAZ
1983-1990	$1.3070 \cdot (Aro\ 1016 + Aro\ 1254)$	HAZ, RAL, HES
1990-1993	$1.4157 \cdot (Aro\ 1016 + Aro\ 1254/60)$	HC
1992-1997	$0.8754 \cdot (Aro\ 1248 + Aro\ 1254 + Aro\ 1260)$	HAZ, HES, EC

The annual averages of ΣTri+ PCB concentrations (as mg/kg-lipid) for summer-collected fish samples, arranged by species and a "group" designating location, are shown in Table 4-5. The original NYSDEC data, contained in the TAMS/Gradient database, have been corrected to a consistent ΣTri+ basis using the relationships described above.

4.1.2 Water Column Data

As noted in the PMCR (USEPA, 1996) and earlier by Brown et al. (1985), a good predictor of annual average PCB body burden in many fish species appears to be the summer average water column concentration. Therefore, the BAF analyses use summer averages of water column data, based on observations for May through September for consistency with the averaging period used for fish. For fish collected in May or June this means that the water column average includes samples from after the time of fish collection. Given the relative sparseness of water column observations, however, it appears likely that including all water column data for May through September will provide a better statistical estimate of concentrations in a given season than restricting the estimate to May-June observations only.

For most of the period of fish sampling, the only data available on water-column concentrations are the USGS monitoring. These data commence in 1977 for most locations in the Upper Hudson, with 6 to 58 samples per station per year. Sampling locations and methodology were described in detail in the Phase I Report (USEPA, 1991b). For the Phase 2 analysis, USGS data have been obtained through the end of Water Year 1997. Significant

MCA/TetraTech

corrections and updates to the USGS data have occurred since the release of the PMCR, and are reflected in Database Release 4.1.

There are three major sources available for the USGS water column PCB data: WATSTORE, USGS/Albany NWIS database, and printed USGS Water Resources Data, New York. For some years there are significant discrepancies between these data sources, requiring a retrospective reconciliation. Data used in the PMCR were obtained primarily from WATSTORE, but WATSTORE is a secondary source, which is periodically updated from the USGS/New York NWIS electronic database system. Where discrepancies exist, WATSTORE is less reliable than the other two sources. We noted major differences between these sources for the period prior to October 1986, primarily related to (1) failure to reflect actual PCB detection limit of 0.01 µg/l for many observations, which was lower than the default detection limit of 0.1 µg/l expected by WATSTORE for the relevant parameter codes, and (2) failure to report identified Aroclors shown in the printed reports. Almost all USGS PCB data from the Hudson from October 1983 on was quantitated at an 0.01 µg /l detection limit, but WATSTORE generally does not show this until 10/86. In addition, a significant fraction of the data prior to October 1983 was also quantitated at the 0.01 µg /l detection limit.

USGS PCB data were revised using both NWIS and the printed Water Resources Data. For October 1983 through September 1986, data at the lower detection limit of 0.01 µg/l are primarily given only in the printed data, which is also the source for Aroclor identification. For 1978-1982, the printed data show total PCBs at a detection limit of 0.1 µg/l and do not report identified Aroclors; however, NWIS for these years shows that *some* samples were quantitated at the 0.01 µg/l level and does show Aroclors.

USGS analyses prior to 1986 were obtained using packed-column GC; those from 1988 on used a capillary column methodology (personal communication from Ken Pearsall, USGS/Troy, to Jonathan Butcher, Tetra Tech, based on letter received from Brooke Connor in USGS Denver laboratory). It was previously believed that all analyses prior to November 1987 used packed column GC; however, QEA has obtained original chromatograms and sample analysis sheets indicating use of a capillary column method as early as fall of 1986 (personal communication from Jim Rhea, QEA, to Jonathan Butcher, Tetra Tech, 10/30/1998).

The USGS packed column methodology is described in general in Wershaw *et al.* (1983). A clearer description of exactly what was done is given in Schroeder and Barnes (1983). The analysis was a two-step procedure: (1) Determine an appropriate Aroclor standard, based on requirements that at least 60 percent of the peaks in the standard are present in the sample and "both relative peak ratios and column detention time must match." If a single Aroclor standard cannot be found which matches these criteria, use a standard containing a mixture of two or more Aroclors. (2) Calculate concentrations by dividing the area of a sample's identified PCB peaks by the area of all peaks for an Aroclor standard, then multiplying this ratio by the concentration of the Aroclor standard.

Step 2 indicates that this is not a Webb and McCall (1973) procedure with peak-by-peak quantitation. Instead, the observed peaks in a sample are scaled-up to estimate a complete Aroclor concentration. No compensation is made for differing response factors, only the sum of

peak areas is used. It is not certain exactly which packed-column peaks were observed by USGS, although it appears likely that the mono- and dichlorobiphenyls were not represented. The first peak used is thought to be either RRT .21 or RRT .28. For quantitations against an Aroclor 1221 or 1232 standard (where there is substantial unobserved concentration in peaks below RRT .21) this approach is equivalent to assuming that the early-eluting (unobserved) congeners in the sample are present in the same fraction as in the Aroclor standard. In reality, concentrations of these congeners (*e.g.*, BZ#4) are likely to be higher in the environment due to dechlorination. In addition, USGS used a dual column method, and always selected the lower of the two values obtained. Finally, no corrections were made for incomplete extraction. Extraction efficiency, it is estimated, probably exceeds 80 percent in nearly all samples.

Because of these factors, and the fact that the original chromatograms are not available, it is difficult to predict exactly what was measured in USGS packed column analyses. For GE, NEA conducted split sample experiments to compare the USGS packed column method (based on the description in Schroeder and Barnes) to capillary column analyses, using individual or mixed standards composed of Aroclor 1242, 1254, and 1221 (O'Brien & Gere, 1993). Updated results of these analyses are contained in TAMS/Gradient Database Release 4.1 (1998). Regression analysis of the split samples reveals that a linear relationship exists between USGS-method total PCBs and capillary column ΣTri+, with an intercept not significantly different from zero and a slope not significantly different from one. Thus, the USGS packed-column data can be used as a direct measure of ΣTri+.

USGS capillary column methods (in use after September 1986) are capable of detecting responses to a wider range of PCB congeners; however, quantitations were still reported based on composite response factors derived from manufactured Aroclor standards. This technique results in potential biases in calculating either total PCBs or ΣTri+, because the relative weight percentages of congeners in the environment generally differs from those found in the Aroclor standards. QEA (Rhea and Werth, 1999) investigated the potential biases in this method by reanalyzing the original chromatograms from USGS 1987 samples from the Hudson River. This reanalysis indicated that USGS capillary column quantitations for Aroclor 1242 provide an approximately unbiased estimated of ΣTri+, while the sum of Aroclor 1242 and Aroclor 1254 (as used in earlier versions of this report) over-estimates ΣTri+. Based on the results of this study, the following conventions were applied to the USGS capillary column data:

1. When USGS capillary column direct quantitation for Aroclor 1242 is available, use this number as an estimate of ΣTri+.

2. When capillary column direct quantitation for Aroclor 1248 is present, but quantitation for Aroclor 1242 is not, use Aroclor 1248 as an estimate of ΣTri+.

3. When USGS capillary column data reports only total PCBs, not Aroclors, estimate ΣTri+ as 75 percent of the reported total PCB concentration.

Most of the historical USGS results are available only as whole water quantitations. Few USGS samples distinguish dissolved and particulate PCB fractions, and almost no organic carbon data were collected. Therefore, the preferred formulation of normalizing the particulate

fraction corrected to an organic carbon basis cannot be employed. Instead, all regressions were based on whole water, unfiltered PCBs. The BAFs for fish concentrations are thus relative to whole water rather than organic carbon-normalized particulate PCBs.

Starting in 1991, capillary-column determinations of PCBs in the water column are available on a homologue and congener basis from GE. These high-resolution data are presumed more accurate than USGS results, and may be used to directly estimate ΣTri+. The same may be done with TAMS/Gradient Phase 2 water column results from 1993.

Summer average water column concentrations were estimated at four locations, corresponding to reaches with available fish sampling. Assignment of sources for water column concentrations is shown in Table 4-6. For the period from 1991 on, capillary column PCB analysis by EPA and GE is used where available. 1993 concentrations below Thompson Island Dam are estimated from TAMS/Gradient Phase 2 monitoring. Flow-averaged samples are available at Waterford, while instantaneous transect samples are used at Stillwater and Green Island. During 1994-1996 neither EPA nor GE sampled below Thompson Island Dam, so USGS data are used.

For 1991 on, GE Thompson Island Dam-West (TID-West) data are used to represent water column concentrations in the lower Thompson Island Pool. Within the TIP, GE has reported strong lateral gradients in PCB concentrations in water during low flow conditions, with higher concentrations in the nearshore area. Nearshore concentrations are, however, theorized to be the more relevant measure of exposure concentrations for fish and their food webs, which are believed to rely to a much greater extent on the nearshore habitat than the channel habitat. Thus, no bias correction factor is applied to the TID-West observations for use in the BAF analysis.

For the Thompson Island Pool prior to 1991, direct measurements are not available and upstream USGS data at Rt. 197, Fort Edward is judged of limited value for determining exposure concentrations, due to the gain in PCB concentrations within the pool. Therefore, Thompson Island Pool concentrations are estimated from downstream measurements, scaled by a drainage ratio where appropriate. Prior to 1987, scaled USGS Stillwater data have been used in preference to Schuylerville data to estimate Thompson Island Pool concentrations because averages at the two stations are generally similar, but greater sampling density is available at Stillwater. USGS Fort Miller data, commencing in 1987, are assumed representative of outflow from the Thompson Island Pool for 1987-1990.

Use of downstream data to estimate TIP concentrations prior to 1991 introduces a potential inconsistency, as the downstream results will be more similar to center channel than nearshore concentrations in the TIP when a lateral concentration gradient exists. Therefore, a correction is applied to these data to approximate TIP nearshore concentrations. An analysis of ΣTri+ in 53 GE samples pairing TID-West observations to observations in the center channel or immediately below Thompson Island Dam from Sept. 18, 1996 through September 15, 1998 suggests that a consistent bias in nearshore samples is only present when flow at Fort Edward is less than about 4,000 cfs (so that lateral mixing is reduced). The relative bias is also smaller when upstream concentrations at Fort Edward are higher, which increases center channel concentrations. Under conditions of flow less than 4,000 cfs and upstream concentrations of

MCA/TetraTech

total PCB greater than 15 ng/l, the average ratio of TID-West to center channel concentrations is 1.14, while for flow less than 4,000 cfs and upstream concentrations less than 15 ng/l the average ratio is 1.45. Both ratios are significantly different from unity. At upstream flows greater than 4,000 cfs, the ratio is not significantly different from 1.0 and no correction is required. Because USGS sampling does not reliably track a parcel of water from Fort Edward to downstream stations, and detection limits were often high, the upstream concentration criterion is difficult to apply. Therefore, the estimated correction factor of 1.14 was used to correct all downstream-inferred concentrations with flow at Fort Edward less than 4,000 cfs to approximate TIP nearshore conditions prior to averaging.

For years other than 1993, direct water column monitoring results are not available below Federal Dam (except for a limited number of early USGS data, all non-detects). Concentrations in this reach are therefore estimated by drainage area scaling from Waterford or other upstream stations. This scaling is equivalent to assuming that incremental flow from the Mohawk River contributes insignificant PCB concentration. Summer average concentrations used for BAF estimation are summarized in Table 4-7 and Figure 4-2.

4.1.3 Sediment Data

The second forcing function for the bivariate BAFs is sediment concentration. Fish may accumulate PCBs from the sediment directly through the consumption of benthic organisms or direct ingestion in the case of deposit feeders, or indirectly through the consumption of other organisms which consume benthos. Surface sediment concentrations are anticipated to be correlated to water column concentrations; however, full equilibrium with the water column is likely to exist only at the interface, and not through the entire bioactive depth. In depositional areas, sediment concentrations will resemble water column concentrations, but with a "memory" integrating across several years. Further, because most of the movement of sediment occurs during spring floods, sediment concentrations should be more closely tied to spring high flow concentrations than to summer low flow concentrations. Thus, sediment concentration data provides a separate, semi-independent exposure data series to the bivariate BAF. The Pearson correlation coefficient between average water column and sediment concentrations used in this analysis is 0.32.

Areally-averaged annual observations of sediment concentrations for reaches in which fish collections occurred do not exist. Indeed, the sediment database covers only a few points in time, including the 1976/78 NYSDEC survey of the Upper Hudson, the 1984 NYSDEC survey of the Thompson Island Pool, the 1991 GE survey of the Upper Hudson, and targeted sampling of hotspot locations in the 1994 EPA Low Resolution Sediment Coring program. As with the fish data, there are significant analytical differences between these sampling campaigns. Finally, sediment concentrations in the Hudson are known to exhibit a high degree of spatial heterogeneity, so that inference from small samples may not be representative of a reach-average exposure concentration.

Because of these limitations, observed sediment data are not used directly in the Bivariate BAF analysis. Instead, predicted sediment concentrations, averaged over 0 to 4 cm depth, from the HUDTOX model were used. For the HUDTOX hindcast run, all the available sediment data

were processed to provide a consistent estimate of ΣTri+ PCBs and the model was calibrated to provide a reasonable fit to available observations in time and space. The HUDTOX predictions thus provide a best-estimate, process-based interpolation of the available sediment data. HUDTOX results are a smoothed estimate of observed data in space and time, which helps minimize the effects of sparse data and analytical uncertainty on BAF estimates which depend on spatially averaged exposure concentrations.

The calibrated HUDTOX model provides reach-by-reach estimates of ΣTri+ for the Hudson River between Fort Edward and Federal Dam, with separate estimates for cohesive and non-cohesive sediments. It is assumed that cohesive (fine-grained) sediment concentrations are most relevant to fish exposure pathways from sediment independent of water column concentrations. Accordingly, organic-carbon normalized concentrations of ΣTri+ in cohesive sediment are used for all reaches in which the model includes a cohesive sediment segment. For the reach immediately above Federal Dam, the model does not include a cohesive sediment segment; organic-carbon normalized concentrations of ΣTri+ in non-cohesive sediment were used for this reach. The model provides logarithmic predictions of concentration by reach, which are converted to arithmetic estimates of sediment exposure concentration as

$$arithmetic\ mean = \exp\left(\mu_x + \sigma^2_x / 2\right) \qquad (4\text{-}6)$$

where μ_x is the average logarithm of concentration in the reach, and σ_x is the standard deviation of the logarithms of concentration in the reach. The estimated sediment ΣTri+ concentrations used in the BAF analysis are summarized in Table 4-8.

For the area from River Mile 142 to 153, below Federal Dam, no HUDTOX model predictions of sediment concentration are available. This reach has also not been covered by NYSDEC sediment surveys. For this reach, sediment concentration trends over time were estimated based on analysis of TAMS/Gradient High Resolution Core 11, from the Albany Turning Basin at River Mile 143.5. This location accumulated steady sediment deposition following dredging in 1971 (see USEPA, 1997). In dated cores with steady deposition rates, a core layer provides an indication of the PCB content of sediment deposited from the water column at the core location in a given year. As there are no significant local sources of PCBs in this reach, surface cohesive sediment concentrations in this reach are assumed to be equal to the concentration in the corresponding dated core layer. Core 11 was collected in August 1992. Prior to about 1984, concentrations of ΣTri+ in dated layers of this core appear to be less than concentrations in cohesive sediment above Federal Dam, after accounting for flow dilution from the Mohawk. This early period likely represents residual effects of mass movement of highly contaminated organic sediment downstream to Waterford following removal of the Fort Edward Dam. After 1984, concentrations in Core 11 appear to follow a trend similar to concentrations in cohesive sediment above Federal Dam, diluted by incremental flow from the Mohawk. Sediment concentrations at this station were therefore extended for 1993-1997 based on average flow dilution by the Mohawk (factor of 0.585).

4.1.4 Functional Grouping of Sample Locations for Analysis

Four functional groupings of available data were formed for the purposes of analysis. These represent the major fish sampling locations and associated environmental data. The groups are:

Group 1: River Mile 188 to 193, the lower Thompson Island Pool from Griffin Island to Thompson Island Dam.

Group 2: River Mile 168 to 176, the NYSDEC fish collection station near Stillwater. Prior to 1997, samples are from River Mile 168.

Group 3: River Mile 155 to 157, Waterford area above Federal Dam (limited NYSDEC sample collection only). Most of these samples are from River Mile 157, several miles above the confluence with the Mohawk River.

Group 4: River Mile 142 to 152, the upper part of the Lower Hudson, below Federal Dam. These stations are influenced by dilution from the Mohawk River. Most samples are from River Mile 142 (Albany Turning Basin) and River Mile 152 (Green Island).

4.2 Results of Bivariate BAF Analysis

For a given location and year, the PCB analyses of individual samples for a given species exhibit a high degree of variability, reflecting individual characteristics (e.g., age, weight, condition, and life history) and intra-year environmental effects that cannot be addressed in the simple regression approach described here. In contrast, the central tendency or mean of species-location-year observations shows much less variability. Analysis of means used a weighted regression, with weights given as the inverse of the standard error of the mean (Theil, 1971), giving relatively less weight to smaller or less consistent samples. As expected, models on means have much stronger predictive ability than models on individual observations. As the intention of the bivariate BAF analysis is to provide initial information on the central tendency of fish body burden response, models on the means are reported here.

In contrast to the PMCR (USEPA, 1996), all analyses presented here are in terms of ΣTri+ PCBs. Quantitations of individual Aroclors potentially provide information on bioaccumulation of lighter versus heavier Aroclors, as presented in the PMCR. However, the changes in quantitation methods for fish (Chapter 4.1.1) make it difficult to draw inferences regarding individual Aroclor quantitations over time.

Regression models were created by species for the four individual sample location groups described above and across all groups based on (1) a standard BAF approach with univariate regression on water-column concentration only, (2) univariate regression on sediment concentration only, and (3) bivariate BAF regression on water column and sediment concentrations. Results were generally consistent among location groups, implying that cross-sectional models across groups are appropriate, so these are reported here. Results vary strongly between species, as expected.

303821

For a given species, plots of mean fish body burden versus water column concentration show a general positive correlation, but with variability which appears to increase with water column concentration. Figure 4-3 displays scatterplot matrices for lipid-normalized fish concentration versus water and organic carbon-normalized sediment concentrations for all six fish species under consideration. The scatterplots include a 68.3 percent bivariate confidence ellipse about the sample means, which helps visualize the strength of correlation. In all species, except perhaps goldfish, there appears to be a strong positive correlation between fish body burden and both water and/or sediment concentrations. However, the strength of the relationships varies by species. For instance, brown bullhead have a stronger linear relationship to sediment, while pumpkinseed have a stronger linear relationship to water concentrations. For each species, regressions were conducted against water concentration only (standard univariate BAF approach), against sediment concentration only, and against water and sediment concentrations simultaneously (bivariate BAF approach). Table 4-9 shows results of regression analysis of arithmetic average fish concentrations versus water concentrations. The percentage of total variability explained by the regressions is fairly low (adjusted multiple R^2, which adjusts the standard R^2 estimate of the percent of variability explained by the regression downward to account for model improvement due solely to adding an extra variable, ranging from 34 to 71 percent); however, the coefficient on water column concentration is in all cases statistically significant at the 95 percent confidence level. Models for all species except goldfish include all NYSDEC fish data selected in Chapter 4.1.1. For goldfish, regression diagnostics suggested that arithmetic average lipid-normalized concentrations for 1977 and 1978 at Stillwater (Group 2) were high outliers. In each of these years, the average is strongly influenced by one extremely high value, which raises the average about 50 percent. These samples might represent inaccurate quantitations of either PCB or lipid content. The averages for these two years were recalculated with the high outlier value eliminated before calculating the regression models shown in Tables 4-9 through 4-11.

Figure 4-4 shows a plot of ΣTri+ lipid concentration in pumpkinseed versus summer average water concentration, with labels indicating location group. A strong positive correlation is evident, although the quality of fit is degraded by a few samples, particularly one from Group 1 that combines a high fish tissue concentration and low estimated water column concentration. This may reflect a poor estimate of the water column exposure concentration in this year. The scatterplot does not reveal strong evidence for scale-dependent variance (heteroscedasticity).

Table 4-10 presents the complementary regressions against sediment only. Although there is an increase in adjusted multiple R^2 for brown bullhead, the quality of the fits generally remain weak.

Table 4-11 shows a bivariate regression on arithmetic average water concentrations and organic-carbon normalized sediment concentrations. The bivariate approach increases the adjusted multiple R^2, relative to regression on water column concentrations alone, for all species except white perch, with species other than goldfish and white perch having adjusted multiple R^2 values greater than 70 percent. Large improvements relative to the water-only models, however, are seen only for brown bullhead, goldfish, and largemouth bass; species that presumably have a significant sediment-originated food chain pathway of PCB bioaccumulation.

MCA/TetraTech

303822

Figures 4-5 through 4-7 show observed versus predicted average concentrations from the bivariate BAF model for brown bullhead, largemouth bass, and pumpkinseed. In each case a strong positive, and approximately linear, correlation is evident, although there is also clearly variability which is unexplained by the simple BAF model. Significant outliers are labeled in the plots. For largemouth bass, the 1977 and 1978 observations from Group 2 are much higher than predicted. This could perhaps reflect carry-over body burden from years prior to 1977 in this relatively long-lived species. For pumpkinseed, the major under-prediction is for Group 1 in 1989. This suggests that water column exposure in 1989 may have been higher than is estimated from sparse USGS samples below Thompson Island Dam in this year

4.3 Discussion of Bivariate BAF Results

4.3.1 Comparison to Published BAF Values

For comparison to published BAF results, Tables 4-9 and 4-11 contain estimates of a univariate $\log_{10}$ BAF for total PCBs in units of liters of water per kg of fish lipid. The BAF may be obtained directly from the coefficient on water concentration (with appropriate units correction) from the arithmetic univariate model. A BAF estimate may also be obtained from the coefficient on water in the bivariate model, but the result may not be fully comparable to a univariate BAF.

The calculated $\log_{10}$ BAFs for the univariate models range from 6.21 for goldfish to 6.62 for largemouth bass on a L/kg basis. Estimates are somewhat lower for the bivariate models. The univariate BAFs, relating lipid-normalized body burden in fish to total PCB concentrations in water, are sometimes denoted as BAF_l^t (U.S. EPA, 1994). BAFs are also frequently reported on the basis of the freely-dissolved fraction of a chemical in the water column, BAF_l^{fd}. The two forms of the univariate BAF can be related as

$$BAF_l^{fd} = \frac{BAF_l^t}{f_d} \tag{4-7}$$

where f_d is the freely dissolved fraction of the chemical. Under average conditions in the Upper Hudson, the freely dissolved fraction of $\Sigma Tri+$ is estimated, based on analysis of three-phase partitioning in the DEIR for representative congeners, to be about 50 percent for $\Sigma Tri+$ PCBs. Using Equation (4-7), base-10 logarithms of BAF_l^{fd}s would thus be equal to the calculated BAF_l^ts plus about 0.3 log units.

U.S. EPA (1994) summarizes estimated BAF_l^{fd}s for PCB congeners by trophic level based on the food-web/fugacity model of Gobas (1993) for conditions in Lake Ontario. Results calculated here compare favorably to results presented by U.S. EPA (1994) for BZ #28 and BZ #31. These congeners are both included in the quantitation scheme used by NYSDEC for Aroclor 1016, and constitute about 14 percent of the total weight of raw Aroclor 1242. For BZ#28 and BZ#31, the Gobas model predicts a BAF_l^{fd} of 6.51 for alewives. Similar to

MCA/TetraTech

303823

pumpkinseed, this species feeds on invertebrates that accumulate PCBs from the water column (assumed alewife diet of 60 percent zooplankton and 40 percent *Diporeia* spp.) The Gobas model estimate compares well to the estimate of 6.23 to 6.27 + 0.3 presented here for pumpkinseed BAF_1^{fd}. The Gobas model prediction for BZ#28 and BZ#31 in piscivorous fish is 6.68, which compares well with the Hudson River largemouth bass estimate of BAF_1^{fd} of 6.47 to 6.62 + 0.3.

4.3.2   Fit of Bivariate Models to Observations

A bivariate BAF approach, including both water and sediment as independent variables, generally improves on the ability of a simple univariate BAF approach to fit observations of fish body burdens of ΣTri+ PCBs. While the overall model fit is reasonable, the bivariate model does not accurately predict a number of the individual data points. Performance of the model can best be visualized by examining long runs of data at specific locations. The most extensive fish time-series data are for brown bullhead, pumpkinseed, and largemouth bass in Group 2 (River Miles 168-176), and for pumpkinseed and brown bullhead in Group 4 (River Miles 142-152). Observations and model predictions for these series are shown in Figures 4-8 through 4-10. In examining these figures, it should be recalled that individual observations have been weighted by the inverse of their standard error. Thus, some apparent outliers represent small sample sizes with high uncertainty.

For brown bullhead (Figure 4-8), the model does a reasonable job of capturing trends in concentration in Group 2 (although underestimating a number of observations), while in Group 4 the model provides a closer fit to most observations. The model underpredicts concentrations in brown bullhead in Group 4 from 1993 on, perhaps reflecting an error in sediment concentrations, which are based on high resolution core data through 1992, but estimated thereafter.

For pumpkinseed (Figure 4-9), model fit is quite close in Group 4, with the exception of a few early years. This species is less sensitive to sediment concentrations than brown bullhead (as described in Chapter 4.3.3), and predictions are apparently unaffected by estimated sediment concentrations after 1992. In Group 2, the general trend in PCB body burden is captured, but some individual observations lie well off the regression line. For instance, high body burdens in 1989 and 1992 are not captured by the model. This is a period in which the upstream Bakers Falls source was active, and exposure concentrations may have been higher than captured in limited water column monitoring.

Finally, for largemouth bass (Figure 4-10), the model does an adequate job of capturing trends over time, except that average body burdens in small samples in the earliest years are under-estimated.

Observations for all three species are also available since the mid-1980's in Thompson Island Pool. Within the TIP, water and sediment concentrations are better characterized by frequent sampling than downstream; however, proximity to the upstream and TIP sediment sources also likely increases intra-year and spatial variability of exposure concentrations. Examination of model performance against TIP samples is thus a good indicator of model

MCA/TetraTech

303824

robustness. Results for the three species are compared in Figure 4-11. From this figure it will be noted that (1) the bivariate BAF model represents the general trend in concentration in each species, and (2) the model does a good job of replicating the relative difference in lipid-based concentrations *between* species. For pumpkinseed, the fit is close except for the 1989 observation noted previously. Brown bullhead and largemouth bass were not sampled in 1989, but are under-estimated by the model in 1990, suggesting that the available downstream USGS data may under-estimate water column exposure in the TIP in this period. For brown bullhead, observations start higher and end lower than the model predictions. One potential cause could be HUDTOX misrepresentation of the rate of decline of surface sediment concentrations. This would also impact the largemouth bass predictions, as both species exhibit substantial correlation between body burden and sediment concentrations. Largemouth bass display the greatest discrepancies between predictions and observations. In part, this may reflect the fact that adult largemouth bass concentrations are likely to integrate over several years of exposure.

In sum, variability in observations that is unexplained by the bivariate BAF may have a number of sources. These can generally be divided into data uncertainty and model uncertainty. Data uncertainty addresses the fact that exposure concentrations in water and sediment are not precisely known. Water column concentrations are in many cases estimated from only a few samples, and the estimates have considerable uncertainty relative to actual summer average concentrations. Sediment concentrations are derived from the output of the HUDTOX model, which has been calibrated to sediment observations at a limited number of points in time. As with water, sediment concentration estimates may misrepresent actual exposure concentrations in a given year. Data uncertainty has two effects: it may cause individual observations to be mis-estimated, and it may bias the regression coefficients. Use of the full data set, including observations over 21 years at multiple sample locations, provides a robust model that should minimize biases in the regression coefficients. The major source of unrepresented variability is likely to be uncertainty in the estimates of water column exposure concentrations.

The second component of unexplained variation, model uncertainty, reflects the fact that the simple bivariate BAF model does not provide a complete representation of the factors controlling PCB bioaccumulation in fish. Most notably, the BAF model does not take into account age, weight, size-related foraging strategies, and sex of individuals, all of which may be important to PCB bioaccumulation and could result in systematic differences between individual samples. The simple BAF approach also does not take into account the differences in PCB congener patterns present in water, sediment, and biota, or differences in congener patterns among locations. Unlike data uncertainty, model uncertainty can be addressed through use of more sophisticated models, such as those presented in Chapters 5 and 6.

4.3.3 Relative Importance of Sediment and Water Pathways

As discussed in Chapter 3, PCBs may enter the food chain from environmental concentrations in either water or sediment. The relative importance of these two environmental sources will depend on food preferences and behavior of a given species, among other factors. The bivariate model gives a qualitative indication of the importance of water versus sediment that is useful in developing more complex bioaccumulation models. The two sources cannot be

fully separated by statistical analysis, however, as water and sediment concentrations are correlated, as are coefficient estimates in the bivariate model.

Three methods can be used to make statements about the apparent relative importance of the independent variables in a multiple regression model: partial correlation coefficients, normalized beta coefficients, and elasticities (Pindyck and Rubinfeld, 1981). Note that the measures of relative importance are not direct measures of whether PCBs in fish derive ultimately from water or sediment-mediated pathways, as exposure concentrations at the sediment-water interface will tend toward equilibrium between the two media. Instead, these measures will tend to distinguish the relative importance of contributions from near-surface sediments that are not in direct contact with the water column.

A partial correlation coefficient is a measure of the correlation of one independent variable with the dependent variable when other independent variables are held constant. The square of the partial correlation coefficient may be interpreted as the percentage of variance in the dependent variable which is accounted for by the part of the independent variable in question which is uncorrelated with the other independent variable(s) (Pindyck and Rubinfeld, 1981).

Normalized beta coefficients are the coefficients obtained from a linear regression in which each variable is normalized by subtracting its mean and dividing by its standard deviation. For two independent variables, X_1 and X_2, the normalized regression model has the following form:

$$\frac{Y_i - \overline{Y}}{s_y} = \beta_1^* \frac{X_{1i} - \overline{X_1}}{s_{x1}} + \beta_2^* \frac{X_{2i} - \overline{X_2}}{s_{x2}} + \varepsilon_i \qquad (4\text{-}8)$$

where the s values indicate standard deviations and an overbar indicates the mean value. The normalization corrects for scale differences among the independent and dependent variables. A normalized beta coefficient of 0.7 can be interpreted to mean that a 1 standard deviation change in the independent variable will lead to an 0.7 standard deviation change in the dependent variable.

Elasticities interpret the effect of a percentage change in the independent variable on the dependent variable, and also represent a normalization of the regression. The elasticity for a coefficient j is calculated at the point of the means of each of the independent variables as

$$E_j = \beta_j \frac{\overline{X_j}}{\overline{Y}} \approx \frac{\partial Y}{\overline{Y}} \bigg/ \frac{\partial X}{\overline{X}} \qquad (4\text{-}9)$$

Estimated percent contributions, normalized beta coefficients and elasticities for the bivariate arithmetic model are given in Table 4-12. For pumpkinseed, which forage primarily in the water column, and for white and yellow perch, water column concentrations appear to be the most important variable in determining body burden of ΣTri+ PCBs. In contrast, brown bullhead, resident fish which forage on the bottom, are more sensitive to sediment

concentrations. At the highest trophic level, lipid-based concentrations in largemouth bass, which are primarily piscivorous, are correlated with about equal strength to water and sediment exposure fields.

4.4 Summary

A bivariate BAF analysis, relating lipid-based ΣTri+ PCB concentrations in fish to PCB concentrations in both the water column and sediment, provides good explanatory power in predicting annual mean body burden in six fish species throughout the Upper Hudson River, based on analysis of NYSDEC monitoring data for 1975 through 1997. Water-column and sediment PCB concentrations are clearly not in complete equilibrium in most of the Upper Hudson, and inclusion of sediment concentration as an independent variable results in a significant increase in explanatory power for most species.

The increase in explanatory power provided by the bivariate approach is greatest for those species that have a larger sediment-derived component of food-chain pathways. PCBs in brown bullhead appear to be most strongly determined by sediment concentrations, while PCBs in pumpkinseed and white and yellow perch are more strongly related to water column concentrations. Largemouth bass tissue concentrations are correlated with both sediment and water exposure concentrations.

The BAF analysis summarizes the historic data on PCB concentrations in fish, water, and sediment. It is not intended to be a quantitative tool for prediction of future fish body burdens, as the coefficients which have been derived are potentially biased by uncertainty in exposure concentration data, and the simple BAF representation makes no attempt to account for causal relationships between exposure and body burden. While the BAF approach appears adequate to estimate annual average concentrations, it does not represent individual and within-year variability expected to result from age and variations in foraging with size, nor seasonal patterns related to temperature and the spawning cycle. The bivariate BAF analysis does, however, provide an important foundation for more sophisticated analyses, as presented in Chapters 5 and 6 of this report.

MCA/TetraTech

THIS PAGE INTENTIONALLY LEFT BLANK

MCA/TetraTech

5. CALIBRATION OF PROBABILISTIC BIOACCUMULATION FOOD CHAIN MODEL

The components of the food chain model and general model structure are described in Chapter 3.5. The model takes as exposure concentrations the summer-averaged whole $\Sigma Tri+$ water concentration for PCBs and the annual average sediment concentration for PCBs normalized to fraction organic carbon. As discussed in Chapter 3.5, these exposure concentrations are converted to body burdens of PCBs through a number of bioaccumulation factors (BAFs) that link media and food chain components. These BAF values and the uncertainty or variability around them are derived from the available data for the Hudson and from data for other systems. The derivation of the BAFs is presented in the Preliminary Model Calibration Report (1996). Analyses presented here are based on Release 4.1b of the TAMS/Gradient database. The original NYSDEC data, contained in the TAMS/Gradient database, have been corrected to a consistent $\Sigma Tri+$ basis using the relationships described in Chapter 4.1.1.9.

Each compartment in the model is briefly described. The relationship between each of the compartments is described by a distribution of accumulation factors for total PCBs expressed as $\Sigma Tri+$ based on field data. These BAFs relate the body burden of one compartment to the expected dietary exposure of that compartment. The dietary exposure is assumed to implicitly incorporate actual exposures from all sources (*i.e.*, direct water uptake). Distributions presented in the Preliminary Model Calibration Report (USEPA, 1996) report are derived for the calibration congeners (BZ#4, BZ#28, BZ#52, BZ#101+90, and BZ#138), Aroclors 1016 and 1254, and for $\Sigma Tri+$ PCBs to describe the range of expected bioaccumulation factors between two compartments.

5.1 Overview of Data Used to Derive BAFs

5.1.1 Benthic Invertebrates

The EPA team collected 20 (including background) colocated benthic invertebrate and sediment samples during the Phase 2 field collection program. Five sediment samples and three to five benthic invertebrate samples were taken at each location. Benthic invertebrates were identified to the taxonomic group level for PCB analyses. PCB results were provided for individual congeners, homologue sums, total PCBs, and Aroclor equivalents. In addition, percent lipid data are also provided. These data were used to characterize the relationship between sediment PCB concentrations and resulting benthic invertebrate body burdens.

5.1.2 Water Column Invertebrates

Phase 2 activities did not include data collection related to water column invertebrates. The data on water column invertebrates is obtained from the NYSDOH studies done as part of the Hudson River PCB Reclamation Demonstration Project (Simpson et al., 1986). NYSDOH conducted long-and short-term biomonitoring studies from 1976 to 1985 using caddisfly larvae, multiplate samples, and chironomid larvae. NYSDOH placed artificial substrate samplers (multiplates) along 17 sites for five weeks in the Hudson river from Hudson Falls to Nyack, New

York (Novak et al., 1988). Samplers remained in place for five weeks during July through September collecting a composite of sediment, algae, plankton and various macroinvertebrates. After collection, the samplers were analyzed for Aroclors 1016 and 1254. Total PCB values are obtained by summing the individual values for Aroclors 1016 and 1254. Percent lipid values are also provided. These data, combined with information from the Phase 2 dataset, provide an indication of the relationship between water column invertebrates and water column sources.

The short-term biomonitoring study conducted by NYSDOH involved the chironomid larvae, *Chironomus tentans*. Twenty-five laboratory-raised chironomid larvae in nylon mesh packets were placed, in groups of ten, in steel mesh baskets at four Hudson River locations (one at Bakers Falls, two at Thompson Island Pool, and one at Fish Creek). One set of packets was exposed to the sediment at a collection site on the eastern shore of Thompson Island Pool. The remainder were placed in the water column. These short-term data are available for selected congeners and provide some information related to the time-frame and magnitude of the short-term relationship between water column invertebrates and water column sources.

5.1.3 Fish

The EPA team collected fish data from the same 20 benthic invertebrate and sediment locations. Between three to five of the selected fish species were collected at each location (i.e., not all species were collected from all locations. For further detail, refer to the TAMS/Gradient SAP/QAPP, 1992). Data are provided for individual congeners, homologue sums, total PCBs, and Aroclor equivalents. Percent lipid, length and weights of individual fish as well as composited samples are also provided.

NYSDEC has been collecting fish data for over 30 species in the Upper Hudson since 1975. From 1975 to 1988, fish data were collected every year. In 1988, fish sampling frequency changed from yearly to every other year. The bulk of the sampling (75 percent) has been conducted for largemouth bass, brown bullhead, and pumpkinseed.

For the NYSDEC samples, chemical analyses for Aroclors 1016, 1254 and in some years, 1221 and 1242, are provided in the database as well as weight, length, percent lipid, and, for some years, sex and age. Generally, 30 fish were collected for each species at several locations.

5.1.4 Literature Values

There are studies from the literature which provide additional information on the relationship between sediment, benthic invertebrates, water and water column invertebrates. (e.g. Whittle et al., 1983; Bierman, 1990; Bierman, 1994; Wood *et al.*, 1987; Larsson, 1984; Lake et al., 1990; Oliver, 1987; Oliver & Niimi, 1988; Thomann, 1981; van der Oost et al., 1988; Thomann, 1989; Thomann & Connolly, 1984; Bush *et al.*, 1994; Thomann et al., 1992; Harkey *et al.*, 1994; Endicott *et al.*, 1994; and others). These studies are primarily useful for comparative purposes, as they refer to systems that may experience conditions unlike those in the Hudson River.

5.2 Benthic Invertebrate:Sediment Accumulation Factors (BSAF)

Distributions of BSAFs between sediment concentrations and benthic invertebrate concentrations were derived by:

1. Evaluating the sediment data to determine which river miles display significant heterogeneity and variability in concentrations;

2. Calculating the BSAF by dividing a measured individual benthic invertebrate concentration by the mean sediment concentration at a sampling location; and,

3. Using the final distribution representative of the relationship between benthic invertebrates and sediment within the overall model to predict the historical fish data in a validation exercise.

5.2.1 Sediment Concentrations

An assessment of the range of sediment concentrations by river mile and congener provides information on the variability inherent in these data. Figure 5-1 shows mean TOC-normalized sediment concentrations (μg/g) and associated 95% confidence intervals for the upper and lower portions of the Hudson River. This figure shows that sediment concentrations, even normalized, show significant spatial variability.

5.2.2 Approach

BSAF for benthic invertebrates were calculated from the Phase 2 dataset using colocated sediment and benthic samples. The sampling rationale will be presented as part of the ecological risk assessment (work in progress). PCB concentration and lipid data were available for Amphipods, Bivalves, Chironomid, Gastropods, Isopods, Odonata, Oligochaetes, Unsorted Total (everything in a sample), Sorted Total (unidentified remaining after sorting), and Epibenthic species.

The ideal data pairs to calculate BSAF are individually collected samples of sediment and benthic invertebrates. In the absence of this ideal condition, we used individual benthic invertebrate samples and mean sediment concentrations for a given co-located sampling location. However, in the areas that display highly variable PCB concentrations in sediments, it may be that the mean does not adequately represent the exposure level for benthic invertebrates. The heterogeneity in sediment concentrations over small spatial scales contributes to higher variability in the BSAF calculated from data collected in these areas. Thompson Island Pool is an area in which such variability in calculated BSAF occurs. Matching individual invertebrate concentrations to the mean sediment exposure in this area results in more variable ratios. Also, the ratios for Thompson Island Pool are higher in magnitude than for the upper river generally and significantly higher than the lower river.

Species identified as epibenthic showed BSAF that were not significantly different from species identified as benthic based on t-tests. In addition, the sampling program did not specifically sample for epibenthic species and were only identified as such as a function of

sampling rather than species identification. The BSAF calculated for each river mile were combined to represent the range of accumulation factors in the river generally. The implications for the food chain model are that this distribution of BSAF represent the range among the prey species of fish feeding off the bottom. This is a reasonable approximation if the fish feed on benthic invertebrates indiscriminately such that the probability of preying on a particular species is proportional to that species' abundance.

For those sampling locations at which there were enough data to run normality tests, it was determined that the benthic invertebrate data follow a lognormal distribution. This was verified by log-transforming benthic invertebrate PCB concentrations and running standard normality tests. The final BSAF distribution is characterized by a geometric mean and geometric standard deviation. The variability in the sediment and benthic invertebrate concentrations has a significant impact on calculated BSAF, because widely divergent individual benthic invertebrate concentrations are normalized to one sediment concentration considered to be indicative of exposures.

The BSAF by river mile charts were developed using the data for the combined benthic species as reported in database release 4.1 and shown in Figure 5-2. The charts for BSAF by river mile and the BSAF by species show the mean BSAF and the associated 95% confidence interval. These plots provide information on the variability of BSAF by river mile, and the species that contribute most to the observed variability. Those species showing the highest variability also have the lowest number of samples, indicating the sensitivity of statistical analyses to artifacts of undersampling.

5.2.3 Calculations of BSAF Values for Benthic Invertebrates

Figure 5-2 shows the BSAF for ΣTri+ PCBs (all species combined) by river mile. Typically, the calculated BSAF values are around one, with the exception of river mile 189, which is at approximately 3. Error bars for river mile 100 are very wide, with an upper bound comparable to the error bar for river mile 189.

Figure 5-2 also shows the BSAF ΣTri+ PCBs (all river miles combined) by species. The BSAF for chironomids, about 2, is higher and has wider error bars than the other river miles. However, this is based on only three samples. The BSAF for sorted and unsorted totals, which represent the diversity of species found at any given location, show a mean of approximately one with narrow error bars. Odonata and bivalves show the lowest BSAF.

Differences in BSAF values by location and/or species may be attributable to:

- True sediment exposure concentrations may be higher or lower than those estimated (the BSAF procedure involves dividing an individual measured invertebrate concentration by an average sediment concentration from the same sampling location. For the highly variable sediment concentrations, there are both high and low individual sediment values in the average. Thus, it may be that the true sediment concentration corresponding to the individual measured invertebrate concentration is higher or lower than the average.)

MCA/TetraTech

- Exposure for certain species may be derived from water column sources, particularly for those invertebrates which are surface scramblers and more like invertebrates that might be found on the vegetation.

The model was run by applying the distribution derived above to each mean sediment concentration by river mile. The 10th, 25th, 50th, 75th, 90th percentiles and maximum were calculated. These percentiles were compared to the output from the frequency analysis on the benthic invertebrate data using the SPSS™ software package. After log-transforming the results, the observed benthic invertebrate concentrations were plotted against the percentiles predicted from the model. The results of this exercise were presented in the Preliminary Model Calibration Report (EPA, 1996). Figure 5-3 presents the cumulative distribution for BSAF estimated for ΣTri+ PCBs.

The modeled ΣTri+ PCB distributions in benthic invertebrates compared favorably to the observed distributions of ΣTri+ PCB concentrations as presented in the PMCR (EPA, 1996). The BSAF model for benthic invertebrates captures the observed variability in the underlying data. In areas where the sediment concentrations display heterogeneity (such as Thompson Island Pool), the model accurately captures maximum observed concentrations.

5.3 Water Column Invertebrate:Water Accumulation Factors (BAFs)

5.3.1 Approach

Water column invertebrates are defined as those that receive most of their exposure to PCBs via the water column. As defined, this group includes zooplankton as well as invertebrates living on substrates such as plants or rock surfaces but are not in direct contact with the sediments. The approach presented in the Preliminary Model Calibration Report (1996) was based on relating body burdens in water column invertebrates (on a lipid-normalized basis) to water concentrations (normalized to particulate organic carbon). This was done for the following reasons:

1.   It is assumed that PCBs in the particulate phase in the water column and PCBs in the dissolved phase in the water column are in quasi steady-state over time scales of months during the Summer as discussed in Chapter 8. Thus by establishing relationships between invertebrates and a particular phase (particulate organic carbon in this case), overall accumulation from the water column will be taken into account.

2.   The relationship to PCBs normalized to particulate organic carbon was selected because, while water column invertebrates will accumulate PCBs directly from the dissolved phase, the higher chlorinated congeners are predominantly associated with the particulate phase which form the food base for the invertebrates. Partition coefficients derived in the Data Evaluation and Interpretation Report (USEPA, 1998) show that as much as 60 percent of PCBs in the water column are associated with the particulate phase for tetra- and higher chlorinated congeners.

This report presents an alternative approach which also relates water concentrations to observed water-column macroinvertebrate concentrations using a BAF approach, but rather than incorporating the POC-normalized water column concentration, this approach relies on a whole water concentration (*i.e.*, uptake from both the dissolved and particulate phases). This alternative approach was explored because the historical data only measured PCBs in whole water. In the PMCR (EPA, 1996), assumptions were made about the relationship of total suspended solids (measured by the USGS) and total water concentrations based on observed relationships from the Phase 2 dataset. To estimate particulate organic carbon from a whole water concentration, it was necessary to assume a fraction organic carbon of the total suspended sediments. The BAF approach presented here was chosen to avoid making these assumptions.

These BAF derivations rely upon historical data from the New York State Department of Health studies for the Hudson River PCB Reclamation Demonstration Project (Simpson *et al.*, 1986). NYSDOH conducted long- and short-term biomonitoring studies from 1976 to 1985 using caddisfly larvae, multiplate samples and chironomid larvae.

NYSDOH placed artificial substrate samplers (multiplates) along 17 sites for five weeks in the Hudson river from Hudson Falls to Nyack, New York (Novak *et al.*, 1988). Samplers remained in place for five weeks during July through September collecting a composite of sediment, algae, plankton and various macroinvertebrates. After collection, the samplers were analyzed for Aroclors 1016 and 1254. Invertebrates collected on the samplers included: Chironomidae, Oligochaetes, Trichoptera, Ephemeroptera, Amphipoda and Elimidae. Chironomid larvae and pupae were the most abundant invertebrate component from Fort Edward to Saugerties. In addition, caddisfly larvae were hand-picked from rocks at five designated sites: Hudson Falls, Fort Edward, Fort Miller, Stillwater and Waterford.

The short-term biomonitoring study conducted by NYSDOH involved the chironomid larvae, *Chironomus tentans*. Twenty-five laboratory-raised chironomid larvae in nylon mesh packets were placed, in groups of ten, in steel mesh baskets at four Hudson River locations (one at Bakers Falls, two at Thompson Island Pool, and one at Fish Creek). One set of packets was exposed to the sediment at a collection site on the eastern shore of the Thompson Island Pool. The remainder were placed in the water column.

The study found that the congener pattern of PCBs in *C. tentans* differed substantially from that in the water. Specifically, the whole water column concentrations were dominated by 2 or 3-dichlorinated congeners, contributing nearly 50% of the total concentration. The *C. tentans* samples were characterized by a greater number of congeners, with each congener contributing a much lesser proportion to the overall total (i.e., no single congener contributed greater than 10% to the total body burden), and higher chlorinated congeners dominated. For the 26 congeners evaluated, most congeners reached 90% equilibrium in under eight days. The September results showed even higher *C. tentans* concentrations corresponding to lower water concentrations. However, the September results are considered suspect in the article due to suspected analytical error.

The chironomid species (*C. tentans*) were raised in the laboratory and only experienced water-based exposures in this study. They were, however, allowed to come into contact with

detrital matter and the like in the water column. *C. tentans* is primarily a filter feeder or surface deposit feeder (Swindoll and Applehans; 1987; Wood et al., 1987).

The NYSDOH multiplate samples represent the only Hudson River specific information available on the potential relationships between water column invertebrates and water column concentrations. The short-term studies address uptake of specific congeners, but cannot be used in this analysis, as they reflect uptake responses on the order of 48-96 hours, rather than quasi-steady state conditions.

In this approach, total water column concentrations are related to macroinvertebrates by:

$$BAF_{water} = C_{invert}/C_{water} \qquad (5-1)$$

where,

BAF_{water} = The bioaccumulation factor between water column invertebrates and particulate bound PCB in mg/Kg / mg/L

C_{invert} = mg PCB per Kg lipid in invertebrate tissue

C_{water} = mg PCB per L total water

5.3.2 Calculation of BAF_{water} for Water Column Invertebrates

Figure 5-4 presents the results of BAF calculations for water column invertebrates. Values shown are the mean with 95% confidence intervals. The mean log-transformed BAF is approximately 6.1. The bottom portion of Figure 5-4 shows the cumulative distribution function for whole water to water column invertebrates.

5.4 Forage Fish:Diet Accumulation Factors (FFBAFs)

As a group, forage fish are expected to have a diet that varies depending on the data available for that given river mile. Individual forage fish will vary from this percentage. For example, spottail shiners are expected to feed evenly on water column and benthic invertebrates, while pumpkinseed favor water column food sources. An appropriate weighted mean was used in the model depending on the specific species caught at a sampling location in order to develop the accumulation factors. The approach used to develop FFBAF for forage fish is described below.

5.4.1 Approach

Forage fish consume both water column and benthic invertebrates. As a result, their dietary exposure to PCBs is represented as a weighted average of the PCB concentration in the diet. Distributions in the FFBAF are derived from measured concentrations of PCBs in forage fish at a river mile divided by the estimated concentrations in their diet. Measured benthic invertebrate concentrations were used to estimate the benthic component combined with water column invertebrate concentrations estimated from the water column BAF discussed previously.

FFBAF values were derived by:

1. Evaluating the available data for forage fish <10 cm for each river mile. The dietary concentration was estimated based on life history and foraging information (see Appendix A).

2. Plotting concentrations to identify a) which species contribute most to data variability and b) which river miles show the greatest uncertainty and variability in observed concentrations.

3. Estimating the expected PCB concentrations in water column invertebrates for total PCBs using the distribution described earlier in this chapter and combining these estimates with measured benthic invertebrate concentrations.

4. Deriving a river-wide distribution of FFBAF by taking the ratio of a measured individual forage fish concentration to the arithmetic mean dietary concentration. The mean diet is represented by the weighted average of the benthic invertebrate (measured) and water column invertebrate (estimated) compartments.

The method provides a basis for deriving FFBAF values for forage fish as a group as well as for the selected fish species, spottail shiner and adult pumpkinseed sunfish. The Phase 2 data were not adequate for estimating FFBAF values specifically for small pumpkinseed sunfish that may be eaten by other fish species. Other approaches for pumpkinseed are discussed in subsequent chapters.

5.4.2 Forage Fish Body Burdens Used to Derive FFBAF Values

Bar charts were developed to show lipid-normalized concentrations in forage fish by river mile. Mean concentrations and 95% confidence intervals are shown for the upper and lower Hudson River for ΣTri+ PCBs in Figure 5-5.

In general, concentrations show far less variability in the lower river than in the upper river. As a trend, concentrations decline relatively steadily from river mile 169.5 down to 88.9. At river mile 58.7, a slight increase is seen. Within the upper river, concentrations are highest at river mile 189.5. River mile 191.5 shows lower concentrations than river miles 194.1 or 189.5, probably as a result of the specific location chosen for sampling. However, these data show that PCB body burdens in forage fish are highly variable in the Thompson Island Pool area and areas close to sources of PCBs. Forage fish body burdens may also reflect the sediment type of the habitat (i.e. fine-grain sediments tend to accumulate higher levels of PCBs).

Table 5-1 shows the coefficient of variation for the forage fish from the EPA/NOAA Phase 2 dataset sorted in order of increasing coefficient of variation for wet weight and lipid normalized PCB results. The numbers in parentheses refer to the number of samples in each calculation. This table shows that the wet weight coefficient of variation is attributable to absolute differences in PCB concentration while the lipid-normalized values are attributable to lipid content.

Figure 5-5 shows that mean concentrations are similar for river miles 189.5 and 194.1, are significantly higher at these locations than elsewhere in the river. This figure shows that forage fish ΣTri+ PCB concentrations at most of the river miles ranged from just above 0 to about 300 μg/g. River miles 189.5, 191.5, and 194.5 show significantly higher concentrations than at other locations in the river. Concentrations are highest at 189.5, lower but still much higher than river-wide averages at 191.5, and then increasing again at 194.1 to nearly the level at 189.5.

5.4.3 Calculation of FFBAF Values for Forage Fish

The body burden data provide important information on the expected variability in forage fish concentrations. The data show that the greatest variability in fish concentrations exists within the Thompson Island Pool and areas closest to the source of PCBs. This is also the area showing greatest sediment concentration heterogeneity, and an analysis of the water column data show that water column concentrations vary significantly depending on the time of year. Fish in this area experience transient exposures and integrate both "hot spots" and less contaminated area exposures.

The forage fish model was run for ΣTri+ PCBs to evaluate the goodness-of-fit between observed and modeled fish body burdens. As described in Appendix A, the expected contribution of benthic and water column invertebrates was estimated based on the forage fish data available for each river mile. For example, there are a number of river miles for which forage fish concentrations are represented by spottail shiners. Data show that spottail shiners consume relatively equal amounts of benthic and water column invertebrates. Other river miles have a number of forage fish species represented, and accordingly a weighted mean was used to estimate an overall feeding preference by river mile.

The model calculated 10th, 25th, 50th, 75th, and 90th percentiles and the maximum. Percentiles were calculated from the observed forage fish body burden distribution at each river mile using the SPSS™ software package. The modeled concentrations of PCBs in forage fish follow a lognormal distribution, characterized by long right tails. After log-transforming the fish concentration percentiles (both observed and modeled), the observed percentiles were plotted against the model-generated percentiles. These results were presented in the Preliminary Model Calibration Report (EPA, 1996). The lower portion of Figure 5-5 shows the cumulative distribution function for ΣTri+ PCB forage fish:diet accumulation factor.

5.5 Piscivorous Fish:Diet Accumulation Factors (PFBAF): Largemouth Bass

The Phase 2 dataset imposes limitations on these analyses. In the TAMS/Gradient Phase 2 dataset, there were no data available for largemouth bass of the correct size (all samples were for largemouth bass less than 16 cm). Largemouth bass do not become piscivorous until at least 20 cm. At the small sizes of the largemouth bass in the Phase 2 dataset, the largemouth bass display feeding patterns equivalent to a typical forage fish, such as pumpkinseed. Therefore, analysis for largemouth bass has to rely on the data from the Phase I NYSDEC dataset. In the absence of suitable Phase 2 data, an analysis was made relating largemouth bass lipid-normalized

concentrations to pumpkinseed lipid-normalized concentrations for measurements reported as Aroclors 1016 and 1254 (representative of ΣTri+, which, in turn, is representative of total PCBs).

5.5.1 Largemouth Bass to Pumpkinseed BAF for ΣTri+ PCBs

Figure 5-6 shows the ratio of largemouth bass greater than 25 cm to pumpkinseed less than 10 cm for ΣTri+ PCBs by river mile and year. The lower portion of this figure shows the cumulative distribution function for largemouth bass to pumpkinseed ratios. The largemouth bass samples were collected in the spring, and the pumpkinseed samples in the fall. The following spring individual largemouth bass concentrations were divided by the arithmetic mean pumpkinseed concentration for the previous fall.

These BAF values implicitly incorporate seasonal variation. Insofar as these ratios are consistently constructed (that is, always a spring-caught piscivorous fish over the forage fish average from the previous fall), their application is valid. However, these ratios may not only capture trophic level differences, but seasonal differences as well.

5.6 Demersal Fish: Brown Bullhead:Sediment Accumulation Factors

Data are available for brown bullhead from the NYSDEC dataset for river miles 189 and 168 for intermittent years since 1977. The approach taken to develop brown bullhead:sediment accumulation factors was to divide individual observed brown bullhead lipid-normalized ΣTri+ body burdens by the average TOC-normalized ΣTri+ annualized sediment concentrations predicted by the HUDTOX model for each reach. These BSAF were developed for 1977 – 1990, and then the resulting distributions used to predict 1991 – 1996 concentrations for each reach to validate the distributions.

Table 5-2 and Figure 5-7 provide the parameters of the final distributions developed for brown bullhead BSAF. Distributions are presented separately for river mile 189, river mile 168, and combined. Statistical tests (t-test assuming equal and unequal variance) were significant at $p < 0.005$ between the two locations, suggesting that given the available data, the relationship between sediment and brown bullhead concentrations is different between the two locations. The mean accumulation factors derived for each location are below one, but higher at river mile 189 than at river mile 168. Several factors could account for this difference:

- Inconsistencies or incorrect averaging of the HUDTOX sediment concentrations do not accurately reflect true exposure concentrations to the brown bullhead; and,

- The BSAF do not account for water-column based exposures (across the gill, diet, etc.) that may be occurring.

5.7 Validation of Probabilistic Model Using Fate and Transport Model Output as Input

Table 5-2 presents the final distributions used in the empirical probabilistic model. Full details on distribution development were presented in the Preliminary Model Calibration Report (1996). The sediment and water concentrations used to generate pumpkinseed and largemouth

bass concentrations were obtained from the hindcasting results from the fate and transport model (see Books 1 and 2). Figure 5-8 shows the TOC-normalized sediment concentrations and whole water summer concentrations used in the empirical probabilistic model.

The model was run for river miles 168 (Stillwater), 189 (TIP), and 155 (Waterford-Federal Dam region). Figure 5-9 presents the results of the calibration for largemouth bass and pumpkinseed. Wet weight results were calculated by multiplying the lipid-normalized results by the average observed lipid for that location and species (across all years).

5.8 Discussion of Results

Table 5-3 presents the relative percent difference estimated between predicted and observed body burdens on a lipid-normalized basis. Corresponding wet weight concentrations are obtained by multiplying the lipid-normalized results by an appropriate value for lipid. Wet weight results for largmeouth bass at river mile 189 show fairly good agreement with the data, although the median predicted body burden tends to be underpredicted for recent years. The model appears to underpredict on a lipid-normalized basis. For pumpkinseed at river mile 189, both wet weight and lipid-normalized concentrations show roughly the same relationship to the data. The model performs better at river mile 168. For this location, both wet weight and lipid normalized results show good agreement with the data for largemouth bass and pumpkinseed. At river mile 155, data were only available for the largemouth bass. At this location, the model performs well, particularly as there is little fluctuation in the mean observed PCB content of largemouth bass from year to year.

Figure 5-10 presents the results for brown bullhead, and Figure 5-11 presents the results for the pumpkinseed. Brown bullhead shows good agreement between lipid normalized predictions and observed data for river mile 189, but significantly overpredicts at river mile 168. However, applying an average lipid percent (1.2) results in wet weight predictions that show good agreement at both river miles 189 and 168. Pumpkinseed concentrations are fairly well captured, although significant increases and/or decreases are not as well captured.

The predicted 95th percentile typically captures maximum observed concentrations, suggesting that predicted 95th percentile concentrations are protective of the population at this level.

As an empirical model, this model represents quasi-steady state conditions. To the extent that the BAF relationships constructed between compartments represent a variety of conditions in the river, these will be represented in the output. The model is not designed to predict short-term fluctuations in concentrations, or short-term responses in the system.

THIS PAGE INTENTIONALLY LEFT BLANK

MCA/TetraTech

6. FISHRAND: TIME-VARYING MECHANISTIC MODEL BASED ON A GOBAS APPROACH

6.1 Overview of Calibration Procedure

The calibration procedure began by estimating the elasticity of user-specified parameters and model constants to determine the sensitivity of model results on input assumptions. The next step was to evaluate the literature and site-specific information to obtain best estimates of central tendency values and distributions for the input parameters in the FISHRAND model. Prior to implementing the formal Bayesian updating calibration procedure, these empirical distributions were refined using likelihood profiling techniques in the simplified FISHRAND model. The full FISHRAND model was then formally calibrated starting with the prior distributions obtained through the likelihood profiling method and applying the Bayesian updating procedure to obtain posterior estimates of distributions. Both the sets of model results are compared to data for the state variable ΣTri+ PCB in fish tissue on a wet weight and lipid normalized basis.

The model was calibrated first for Stillwater (river mile 168) and then applied to the other two locations. For river mile 154, the calibrated model for river mile 168 was run without further calibration or adjustment in the distributions. The calibration was refined for river mile 189 as compared to 168 since environmental parameters (e.g. TOC) differ between these two locations.

6.2 Sensitivity Analysis to Determine Parameters for Updating in Calibration

The FISHRAND calibration procedure focused on optimizing wet weight concentrations. This was done for a number of reasons. First, the model is designed to predict a wet weight concentration in fish, and lipid normalized results are calculated by dividing the predicted wet weight concentration by the percent lipid. Second, the lipid content of any given fish is difficult to predict from first principles alone, and lipid content is a highly significant parameter in predicting body burdens (see Chapter 8). Finally, potential target levels in fish are typically described on a wet weight basis.

To determine the most important parameters, a sensitivity analysis was conducted using the analytical solution to the Gobas model. The sensitivity analysis focuses on the relationship between predicted fish body burden and the 11 constants plus environmental parameters described in chapter 3. After obtaining the partial derivatives, elasticities were estimated. Elasticities interpret the effect of a percentage change in the independent variable on the dependent variable based on equation 3-22. The results of this exercise are shown in the following table:

Parameter	Sign of derivative	Comment
C_4	-	Uptake efficiency
C_d related parameters	+	K_{ow}, plankton lipid concentrations
C_6	+	Food ingestion rate
C_{10}	-	Growth rate
L	+	Percent lipid in fish
TOC	+-	Total organic carbon
V_f	+-	Fish weight

The model was found to be insensitive to the other parameters. In addition to sensitivity to parameters, correlation between variables was also evaluated in the selection of calibration parameters. For example, K_{ow} affects uptake efficiency, PCB partitioning at the base of the food web, and excretion rate. Thus, rather than select all three parameters, only K_{ow} was selected. The final parameters selected for calibration include: TOC, K_{ow}, growth rate coefficient, and percent lipid in fish.

The model was calibrated first for Stillwater (river mile 168) and then applied to the other two locations. For river mile 154, the calibrated model for river mile 168 was used without further calibration. Since experimental data show that TOC is significantly different at river mile 189 as compared to the remainder of the river, a different distribution was used for this river mile. Percent lipid is also different for river mile 189. Each of the model inputs is discussed next.

6.3 Model Input Data: User Specified Parameters

Both the historical NYSDEC and EPA Phase 2 datasets were used in the development and validation of the FISHRAND model. Distributions of species-specific fish weight, lipid content (expressed as a percentage), organic carbon content of sediment (expressed as a percentage), and feeding range preferences for the individual fish species were developed for use in FISHRAND. Sediment and truly dissolved water concentrations from the 21-year hindcasting of the fate and transport model were used to generate fish body burdens to compare to the historically observed NYSDEC data set. Further distributions incorporated include a distribution for K_{ow} and for starting sediment and water concentrations as predicted by the fate and transport models. Analyses presented here are based on Release 4.1b of the TAMS/Gradient database. The original NYSDEC data, contained in the TAMS/Gradient database, have been corrected to a consistent ΣTri+ basis using the relationships described in Chapter 4.1.1.9.

There are two kinds of model parameters:

- Non species-specific parameters that apply either to the location being modeled or the form of PCB being modeled, and,

- Species-specific parameters (e.g., lipid content, weight, etc.).

Table 6-1 provides the empirical distributions derived for each of the user-specified input parameters based on site-specific data, except for sediment and water concentrations. These are provided in Figure 6-1.

6.3.1 Non Species-Specific Parameters

A number of environmental parameters specific to either the location or form of PCBs being modeled were described by distributions, including:

- Annual sediment concentrations (location specific);

- Monthly water concentrations (location specific);

- Monthly temperature (location specific);

- Log octanol-water partition coefficient (K_{ow}) (ΣTri+); and,

- Total organic carbon in sediment (TOC).

Prior distributions for K_{ow} and TOC were obtained using the likelihood profiling method. Sediment and water distributions were obtained directly from HUDTOX and were not adjusted in any way. Temperature was obtained empirically and not adjusted.

6.3.1.1 Sediment and Water Concentrations

The sediment and water concentrations used in calibrating and validating the FISHRAND model were generated from the fate and transport model (Books 1 and 2). Figure 6-1 presents the dry weight sediment concentrations and dissolved water concentrations predicted by the hindcasting calibration for ΣTri+. The probabilistic empirical model uses TOC-normalized sediment concentrations and whole water concentrations, while FISHRAND relies on freely dissolved water concentrations and dry weight sediment concentrations (μg PCB / g solid).

The model requires monthly dissolved water column concentrations and annual sediment concentrations (sediment concentrations vary only slightly within a given year, allowing for the use of an annual concentration). HUDTOX generates daily water column and sediment concentrations for the hindcasting period and every other day for the prediction period. These results are averaged by month for water and by year for sediment, characterized by a mean and standard deviation (equations 3-19 and 3-20). Sediment concentrations represent an area-

weighted average of cohesive and non-cohesive sediments and assume that fish preferentially spend 75% of their time in cohesive sediment areas.

Water column concentrations were weighted toward nearshore areas in the TIP and averaged across the river for downstream locations. Lateral gradients are of most importance in the lower TIP and less important downstream because (1) downstream dams have generally smaller, narrower pools plus higher flows, so lateral mixing should be better, (2) the lateral gradient in the TIP is only strong when flows are low AND the upstream concentration at Ft. Edward is less than 15 ng/L on a ΣTri+ basis. (Water downstream of the TIP is almost always in excess of 15 ng/L ΣTri+); (3) the density of hot spots and surface sediment concentrations are generally lower downstream, thus the lateral gradient should be less; (4) lateral gradients in the TIP are likely enhanced by shallow macrophyte beds, and there are fewer of these in the downstream pools. Lateral gradients are enhanced by shallow macrophyte beds due to (1) structure decreasing flow and making the flow field more heterogeneous; (2) increased sediment trapping and deposition; and (3) enhanced and more varied biological activity.

6.3.1.2 Temperature

Growth rate is modeled as a temperature dependent relationship, thus, monthly average temperature is required for FISHRAND. Temperature data for all upper Hudson river locations was compiled from the General Electric and EPA datasets. Together, these datasets provided nearly 2,200 datapoints over the course of several years. Temperature data were grouped by month and year of collection and river mile and statistically evaluated across locations. The mode of the distribution for any location is the same as the average value used in the HUDTOX model for that segment.

During the summer months, when temperatures are highest and fish are consuming the most dietary items, some fish species are likely to spend proportionally more of their time in shallower, nearshore areas which may not have been captured in the monitoring program. However, temperature is also required by the HUDTOX model to estimate partitioning behavior, and to use a very different temperature from that used in HUDTOX (and shown by the data) would result in an inconsistency between the two models. A sensitivity analysis in which the temperature was adjusted upward by 20% for the summer months was conducted for the FISHRAND model, and the resulting body burdens changed by less than 5%. Consequently, the same observed temperatures as were used in HUDTOX were also used in FISHRAND.

6.3.1.3 Total Organic Carbon in Sediment

TOC is most important in the estimation of ΣTri+ PCB concentrations in benthic invertebrates (the FISHRAND equation takes the same form as equation 3-6), which are consumed by upper trophic level fish. From a calibration perspective, it does not matter whether benthic lipid or TOC is selected as a calibration parameter as the net effect is the same. Benthic invertebrate data are only available for one year (1993), thus data for lipid in invertebrates are only available for that year.

MCA/TetraTech

TOC was selected as a calibration parameter because:

- It has an analagous relationship in the sediment-based pathway as K_{ow} does in the water-based pathway;

- The sensitivity analysis showed that K_{ow} and TOC are dependent in the model (which may be a reflection of indirect dependence due to model structure and data imperfection); and,

- There are more data available for TOC than benthic lipid (although note that TOC as reflected in fish diet as compared to composition in bottom sediment may be different).

Mathematically, TOC in the FISHRAND model is in the form of 1/TOC, thus, small values of TOC will lead to large changes in results while 1/TOC approaches a constant value for larger values of TOC.

6.3.1.4 Log Octanol-Water Partition Coefficient (K_{ow})

The K_{ow} used in this analysis is representative of the distribution of K_{ow}s that might be expected in the ΣTri+ PCB mixture. Several approaches for characterizing K_{ow} were evaluated. Individual PCB congeners contained in the ΣTri+ mixture will be taken up by fish to varying degrees as expressed by the K_{ow}. One approach was to evaluate an average congener profile in water and fish in the upper Hudson and weight the K_{ow} values according to the weighting of that particular congener in the mixture. This approach proved infeasible, however, and another approach was taken.

In the approach taken, K_{ow} is described by a triangular distribution according to the cumulative distribution of K_{ow}s in the mixture. This distribution ranges from 5.12 to 8.3 with a mode of 6.6. Individual K_{ow} values were obtained from the Great Lakes Initiative Technical Support Document for the Procedure to Determine Bioaccumulation Factors (EPA, 1994).

6.3.2 Species-Specific Data

Data from the historical NYSDEC fish monitoring results, EPA Phase 2 data and the NYS DOH macroinvertebrate data collection effort were used to develop species-specific distributions for:

- Lipid content for fish, benthic invertebrates, water column invertebrates, and phytoplankton;

- Fish weight; and,

- Dietary composition of the fish diet.

MCA/TetraTech

303847

These distributions represent typical values found in the population of interest based on observed data. Using distributions for particular parameters instead of point estimates in effect follows a population over time in which fish enter and leave the compartment in equal rates. Triangular distributions were derived for the dietary composition for each fish species based on the proportion of the diet represented by benthic invertebrates, water column invertebrates, phytoplankton, and/or forage fish based on the indicator species gut contents analysis presented in Appendix A. Table 6-1 presents a summary of the distributions used in this analysis.

6.3.2.1 Lipid Content

Lipid Content for Fish

Figure 6-2 presents the cumulative distribution functions for lipid content in each of the fish species. Lipid data were combined across years and locations based on a series of analyses described next. Only those lipid data were used for the fish of appropriate size (*i.e.*, only largemouth bass > 25 cm; pumpkinseed < 10 cm; white perch > 17 cm; yellow perch > 15 cm). This resulted in keeping all of the historical NYSDEC largemouth bass data (no exclusions as all fish were greater than 25 cm) and none of the USEPAEPA Phase 2 data (fish were all very small). The Phase 2 data was also not suitable for pumpkinseed, which were all very large fish (larger than the largemouth bass). White perch, yellow perch, and brown bullhead lipid were obtained from the historical NYSDEC dataset and the Phase 2 USEPA. None of the data points were excluded for brown bullhead and approximately 100 small fish were excluded for white perch.

Individual percent lipid measurements were regressed against both weight and length for each species and location to determine if there was a correlation between lipid content and either weight or length which should be accounted for in the model. In a few cases, this analysis showed a weak correlation but overall there was no relationship between lipid and weight or length. Thus, the model assumes no correlation between the two but rather samples randomly from the assigned lipid distribution for each species. Figure 6-3 shows the combined results of weight-lipid relationships for each of the species, although the analysis was originally conducted for each individual location, year, and species.

Lipid content in fish will depend on a number of factors, including temperature, prey availability, and foraging success. Year-to-year differences in lipid content are difficult to predict from first principles, so the ideal situation is one in which species-specific lipid distributions can be developed irrespective of location or time. The first step in developing species-specific lipid distributions was to statistically evaluate lipid data across years and locations to determine if there were clear differences. Comparisons of means (using the Bonferroni correction to account for multiple comparisons) was carried out to determine significant differences.

There was no pattern to differences in lipid content within a species by location or year. Typically, differences were observed across years and locations, for example, between river mile 168 in 1993 and river mile 189 in 1995. There were no observable consistent differences such

as, for example, 1995 lipid content was lower at all locations, or river mile 189 was consistently lower than 168. As there were no observable patterns to differences in lipid, and no clear basis upon which to predict a lipid distribution for any given year, lipid data across all years and locations were combined within a species. Figure 6-4 shows the results of the mean lipid content for each fish species by year for each location.

All derived lipid distributions were compared to the literature (EPA, 1994 and 1995) to determine whether they were within the range observed for these species in other systems. These values all proved consistent.

Lipid Content for Benthic and Water Column Invertebrates

The US EPA Phase 2 data were used to develop a lipid distribution for benthic invertebrates presented in Table 6-1. The NYS DOH dataset was used to develop a lipid distribution for water column invertebrates from the multiplate sampling effort. These distributions were compared to literature values. The water column invertebrate lipid distribution was used as an updating parameter in the Bayesian procedure.

Literature values were used to construct a percent lipid distribution in phytoplankton (Gobas, 1993). Note, however, that only the spottail shiner consumes a small amount of phytoplankton (5% or less of the diet).

6.3.2.2 Fish Weight

Figure 6-5 presents the cumulative distribution functions for fish weight for each of the fish species. As described previously, no observable relationships between weight and lipid content were discovered which should be accounted for in the model structure. The same data were used to develop both the lipid content and weight distributions.

6.3.2.3 Dietary Composition

Dietary composition is based on the results of the analysis presented in Appendix A for each individual fish species and summarized in Table 6-1. As noted in Chapter 3, it is very difficult to quantitatively describe feeding preferences based on snapshots of information. Further, despite the extensive gut content analyses that have been conducted by Menzie-Cura and Associates, Inc. and Exponent, Inc., soft-bodied organisms that may have been consumed typically will have been digested, thus, it is virtually impossible to specifically identify all the prey organisms in the diet of fish. The results presented in Table 6-1 represent professional judgment and a careful analysis of all the available data.

PCB concentrations in the diet are described as a "random walk" in monthly time intervals in which it is assumed that fish and prey meet randomly from month to month. The concentration in the fish diet assumes that distributions are fixed on monthly intervals, but

concentrations in the diet can change from month to month while still relying on the same feeding preference distribution for each species.

6.4 Calibration Results

Tables 6-2 and 6-3 provide the empirical, prior, and posterior distributions obtained from the calibration procedure. Following the sensitivity analysis described in chapters 3 and 6.1, likelihood profiling methods were used to determine the best prior distributions for the Bayesian updating procedure. The posterior distributions were obtained by applying the Bayesian Monte Carlo updating procedure described in chapter 3.5.5.5.

Figures 6-6 through 6-9 present the results of the calibration procedure. Two sets of results are presented: the first set of results rely on the "generic" model constants as described in the literature by Gobas (1993 and 1995) together with the "prior" site-specific and species-specific distributions as described previously. These are the results of the FISHRAND model prior to updating any of the distributions. The next set of results incorporates a formal calibration procedure in which the prior distributions are updated based on a comparison of the model output to observed data.

As described previously, the calibration procedure emphasizes a close fit between predicted and observed body burdens on a wet weight basis, sometimes at the expense of lipid-normalized results. Since the model is very sensitive to lipid concentrations, it is possible to obtain nearly perfect agreement between predicted and observed data by incorporating observed lipid concentrations. Direct incorporation of these observed temporal changes in lipid concentrations is not useful for forecast purposes (there is no basis upon which to predict future lipids), and the approach taken here was to describe lipid content as an empirical distribution based on the available data (as described above).

Using the predicted hindcasting for sediment and water from the fate and transport models, Figure 6-6 shows the results of the comparison between the initial model runs prior to updating and the updated model runs for largemouth bass, Figure 6-7 for brown bullhead, Figure 6-8 for yellow and white perch, and Figure 6-9 for pumpkinseed. The calibration procedure focused on the subset of parameters that most influence predicted fish concentrations. The sensitivity analysis described previously was used to determine which model constants have the most influence on predicted body burdens. This figure shows a comparison of the predicted 50th percentile (median) as compared to the median from the data. The bars represent the 95% confidence interval on the median from the NYSDEC data.

The model predicts a monthly fish body burden, which can be further averaged to represent a seasonal or annual concentration. The results shown in Figures 6-6 through 6-9 are results obtained for the same month during which the samples were taken (e.g., typically May – June samples). Table 6-4 presents the relative percent difference between predicted and observed using the monthly results. Slightly different results are obtained when comparing the annualized output with observed concentrations. Observed concentrations are more likely to represent a seasonal concentration rather than an annualized concentration as demonstrated by limited same

year seasonal data available for white perch and yellow perch from below Federal Dam collected during 1995 by NOAA.

As mentioned previously, the calibration focused on optimizing results on a wet weight basis. The updating procedure significantly improved wet weight fits while often changing lipid normalized results only slightly or not at all. The most significant differences occurred for largemouth bass at 189 and 168. Figure 6-6 shows that prior to updating, lipid normalized concentrations were very close, but wet weight concentrations showed a positive high bias. This high bias was eliminated through the updating procedure. Wet weight concentrations typically fall within the error bars of the data following updating, and lipid normalized concentrations show roughly the same relationship to the data after updating as prior to updating.

Table 6-4 provides a summary of the relative percent difference between modeled and observed. The values in this table were calculated on a median basis by taking the observed concentration minus the predicted concentration and dividing by the observed concentration. On a wet weight basis for river mile 189, largemouth bass results (first page) show that the highest difference is 100% in 1991 and the next highest relative percent difference is 48% in 1985. Typically, the model predicts within 16% or less, and Figure 6-6 shows that the predicted model results are within the error bars for the observed median. In general, the model captures the trends in the data, decreasing in 1991 although not as much as the data suggest. However, in absolute concentrations, the difference between predicted and observed in 1991 is approximately 1 ppm.

For brown bullhead at river mile 189, the model shows excellent agreement on both a wet weight and lipid normalized basis for all years. Predicted brown bullhead body burdens follow the trend in the data, and are within the error bars of the median for all years except 1991. Relative percent differences (shown in Table 6-4) are within 12% or less for seven of the nine years for which data are available, and within 38% - 41% for the remaining two years.

Data are available for yellow perch at river mile 189 for three years as shown in Figure 6-8. On a wet weight basis, the model predicts within the error bars of the median for all three years, and overpredicts the median by 1% - 32% as shown in Table 6-4.

Predicted pumpkinseed concentrations at river mile 189 follow the trend in the data for both wet weight and lipid normalized results as shown in Figure 6-9. Predicted concentrations are within the error bars on the median for all but two years, and fall within 22% or less for five of seven years for which data are available, and within 53 – 60% for the remaining two years.

For river mile 168, again largemouth bass concentrations typically capture the trend but overpredict from 1989 – 1991 and underpredict slightly for 1992. This may reflect an inaccurate representation of the true exposure concentrations, or changes in the food web structure during those years (i.e., largemouth bass diet shifted significantly from the specified distributions. In general, however, the model predicts wet weight body burdens at river mile 168 that are within the error bars, except for a few years.

Observed brown bullhead concentrations at river mile 168 are much more variable than at river mile 189. At river mile 168, brown bullhead concentrations do not appear to follow predicted sediment concentrations as smoothly as at river mile 189. The model generally captures trends at this location, but overpredicts during the late 1970's, and underpredicts in 1990 and 1992. Of the sixteen years for which comparisons are available, the relative percent difference between predicted and observed is less than 12% for ten of these years, within 30 – 35% for five of the years, and within 56% for one year (1977).

Results for yellow perch at river mile 168 are shown in Figure 6-8. The model predicts within the error bars on the median on a wet weight basis for all years except 1980 and 1992. The absolute difference in concentration is within 2 ppm for 1992. Relative percent differences shown in Table 6-4 are within 60% for all years.

Pumpkinseed concentrations follow the trend in the data for river mile 168 as shown in Figure 6-9. Error bounds on the observed medians are very tight for this location. On an absolute basis, predicted pumpkinseed median concentrations fall within less than 1 ppm of observed medians, and within 35% or less expressed as a relative percent difference, shown in Table 6-4.

The calibrated model for river mile 168 was run without any further updating for river mile 155 in a quasi-validation exercise. Figure 6-6 presents the results for largemouth bass. On a wet weight basis, of the eight years, the model predicts within 10% for four years, within 50% for three years, and within 100% for one year. These values (except for 1991 – 100%) are within the error bars of the median and in absolute concentrations within 1 ppm of the observed median. There is only one year of data available for yellow perch, and for this one year the predicted median was within 38% of the observed median, and within the error bars on the median.

Typically, calibration results are within a factor of two or less of the median and fall within the error bars of the median.

Figures 6-10 through 6-12 show quantile-quantile plots for river miles 189, 168, and 155, respectively. These plots provide a measure of the goodness of fit of the variability of predicted fish body burdens as compared to the observed variability in fish body burdens.

6.5 Model Validation: Calibration Using Partial Dataset

To validate the model, several approaches were followed. First, the calibrated model for river mile 168 was run for river mile 155 and predicted body burdens compared to measured body burdens at this location. Figure 6-6 presents the results for largemouth bass. On a wet weight basis, of the eight years, the model predicts within 10% for four years, within 50% for three years, and within 100% for one year. These values (except for 1991 – 100%) are within the error bars of the median and in absolute concentrations within 1 ppm of the observed median. There is only one year of data available for yellow perch, and for this one year the predicted median was within 38% of the observed median, and within the error bars on the median.

MCA/TetraTech

A second approach involved recalibrating the model using only pre-1990 data, then running the model for 1991 – 2067 and comparing the results. A number of comparisons were evaluated:

- Comparison of previously obtained posterior distributions with posterior distributions obtained using pre-1990 data only;

- Comparison of predicted versus observed body burdens for 1991 – 1996 (these data were not used in the pre-1990 calibration); and,

- Comparison of predicted results for 1998 – 2067 from full calibration to pre-1990 only calibration results.

The results showed that the posterior distributions obtained from the pre-1990 only calibration are close to the results obtained from the full calibration. Most importantly, the relative proportion of change between K_{ow} and TOC remained the same although the absolute values changed somewhat. These results are shown in Table 6-5.

The relative percent differences using pre-1990 only data are within 30% of the values obtained using the full dataset. Forecast results are also similar. Table 6-6 shows the ppm wet weight difference between the annualized forecast results obtained for largemouth bass, brown bullhead, and yellow perch using the posterior distributions from the pre-1990 only data as compared to the full dataset. Largemouth bass concentrations are 0.2 ppm higher in the long term than predicted using the full dataset, while brown bullhead and yellow perch show a difference of less than 0.08 ppm wet weight.

6.6 Relative Contribution of Sediment and Water Pathways

The relative contribution of the different pathways were evaluated several different ways. Using the results from FISHRAND directly, the following contribution of direct water uptake across the gill versus diet was determined:

Species	← River Mile →			
	168 -154	189	168 -154	189
	Direct Water Uptake		Diet	
Spottail shiner	15%	15%	85%	85%
Pumpkinseed	13%	12%	87%	88%
Yellow Perch	6%	6%	94%	94%
White Perch	3%	4%	97%	96%
Brown Bullhead	2%	5%	98%	95%
Largemouth Bass	4%	4%	96%	96%

The second approach was to run the model in steady-state mode to obtain average estimates of wet weight fish body burdens and regress the predicted fish concentrations against sediment (dry weight ppm) and whole water (ng/L) concentrations. Although the FISHRAND

model is nonlinear in specific parameters, the best fit between sediment, water, and fish was linear. From these results, it is possible to obtain percent contribution of sediment and water to the overall variance, normalized beta coefficients, and elasticities. These results are presented in Table 6-7. These results can be compared to the results from the bivariate statistical model, although note that the bivariate model regresses lipid-normalized fish body burdens against whole water and TOC normalized sediment concentrations, which is not directly comparable to the FISHRAND approach, which regresses wet weight fish body burdens against dry weight sediment and dissolved water concentrations.

This table shows that predicted fish body burdens are more sensitive to changes in sediment than they are to changes in the dissolved water concentrations, given the assumptions inherent in the regression. These results should be interpreted as indicative of the relative role of sediment versus water rather than a strictly quantitative absolute relationship. The FISHRAND model is designed to provide information on the ultimate origin of PCBs (water or sediment) as it is a food web model - although this is to some extent predefined by model assumptions. The Bivariate BAF model cannot do this: instead, the Bivariate BAF model assesses the correlation of fish concentration with the part of the sediment time series that is not correlated with water concentrations. This might be taken to reference deeper (i.e., non-interface) sediment pathways. However, the Bivariate BAF model combines observed water with modeled sediment concentrations. This means that the water component also has attributed to it all the parts of the exposure time series which were not captured by HUDTOX (but are reflected in the observed summer water concentrations).

MCA/TetraTech

7. BIOACCUMULATION MODEL FORECASTS

This chapter describes the initial modeling results from the FISHRAND model. Sediment and water concentration inputs are taken from the fate and transport model (Books 1 and 2). Three modeling forecasts were provided from the HUDTOX model: a zero upstream boundary condition (cessation of the source at Ft. Edward), a 10 ng/L constant upstream boundary condition (assuming a small but constant upstream source at 10 ng/L), and a 30 ng/L constant upstream boundary condition (assuming a larger but still constant upstream source at 30 ng/L).

The FISHRAND model requires freely dissolved water concentrations averaged monthly and annual average sediment concentrations as inputs. The model mechanistically describes PCB uptake over time and results are presented here for largemouth bass, yellow perch, pumpkinseed, brown bullhead and white perch under the three scenarios. All uptake parameters are described by distributions which reflect the variability in fish responses to changes in sediment and water concentrations. The sediment and water concentrations themselves are also described as distributions from the daily HUDTOX output.

It is difficult to quantify the uncertainty in every single model parameter. Because lipid content, fish weight, and other important variables in the model reflect population heterogeneity more than they reflect uncertainty, these were described as variable. Approximate uncertainty is estimated by applying the maximum under and overpredictions from the relative percent differences presented in Table 6-4 from the hindcast calibration.

7.1 Sediment and Water Concentration Inputs

Figure 7-1 shows the sediment and water concentrations used for the zero upstream boundary condition; Figure 7-2 presents the exposure sediment and water concentrations predicted from the fate and transport model under the 10 ng/L upstream boundary condition; and Figure 7-3 provides the predicted exposure concentrations under the 30 ng/L upstream boundary condition. These figures show that sediment concentrations decline exponentially between 1998 and 2067 under all scenarios.

7.2 Predicted PCB Concentrations in Fish under Zero Upstream Boundary Condition

Figure 7-4 presents the results of predicted fish body burdens on a wet weight basis for largemouth bass predicted median concentrations under the three upstream boundary conditions. Figure 7-5 shows the same results for brown bullhead, and Figure 7-6 shows these results for yellow perch and white perch. For all species, concentrations decline roughly exponentially and approach different asymptotes depending on the species and upstream boundary condition. The median and 95th percentile asymptotes approached by each species are found in Table 7-1. The values in parentheses are approximate uncertainty bounds on the predicted values based on the maximum difference between predicted and observed from the hindcast calibration. Table 7-2 provides a comparison of example target levels (note that target levels will be determined during the feasibility study. The values shown in Table 7-2 are to provide a benchmark for when order-

of-magnitude concentrations will be achieved) based on the 10 ng/L upstream boundary condition.

Figure 7-4 shows that concentrations in largemouth bass at river mile 189 decline roughly exponentially. The lowest achieved concentration is approximately 0.05 ppm wet weight, with a margin of error of approximately 0.03 ppm on either side on a median basis. This is interpreted as 50% of fish are expected to show concentrations above this value and below this value. Figure 7-7 shows the results for the 25th, 50th and 95th percentiles for each of the locations. The 95th percentile concentration is interpreted as the expected body burden for 95% of the population. That is, 95% of the population would be expected to experience the shown concentration or less. For 95% of the population at river mile 189, the lowest concentration achieved is roughly 0.1 on an annualized basis. At river mile 168, largemouth bass concentrations decline to approximately 0.005 to 0.06 ppm on a median basis (best estimate of 0.02), and at river mile 154, concentrations are predicted to decline to approximately 0.007 to 0.02 ppm.

Brown bullhead concentrations at river mile 189 are predicted to be somewhat higher than predicted largemouth bass concentrations. By the end of the forecast period, the forecast median is approximately 0.1 ppm, and the 95th percentile is predicted to fall at approximately 0.1 to 0.24 ppm. For river mile 168, predicted brown bullhead median concentrations achieve 0.01 to 0.04 ppm, and 0.005 to 0.02 ppm at river mile 154. The corresponding 95th percentile values are 0.015 to 0.06 ppm and 0.01 to 0.04 ppm, for river miles 168 and 154, respectively. The 25th, 50th, and 95th percentiles predicted under the zero upstream boundary condition are presented in Figure 7-8.

Yellow perch concentrations at river mile 189 are predicted to fall to 0.03 to 0.06 ppm on a median basis, and to 0.05 to 0.11 ppm on a 95th percentile basis. Predicted concentrations fall to 0.005 to 0.02 ppm on a median basis at river mile 168, while the 95th percentile is expected to reach 0.01 to 0.04 ppm. At river mile 154, median concentrations fall to approximately 0.004 ppm, and the 95th percentile to 0.005 to 0.008 ppm. Median concentrations for all three boundary conditions are shown in Figure 7-6, and the percentile concentrations under the zero upstream boundary condition in Figure 7-9.

White perch concentrations are predicted to fall to 0.005 – 0.02 ppm on a median basis at river mile 154, and to approximately 0.01 – 0.04 ppm on a 95th percentile basis.

7.3 Predicted PCB Concentrations in Fish under the 10 ng/L Upstream Boundary Condition

Figure 7-4 presents the results of predicted fish body burdens on a wet weight basis for largemouth bass predicted median concentrations under the three upstream boundary conditions. Figure 7-5 shows the same results for brown bullhead, and Figure 7-6 shows these results for yellow perch and white perch. For all species, concentrations decline roughly exponentially and approach different asymptotes depending on the species and upstream boundary condition. The median and 95th percentile asymptotes approached by each species are found in Table 7-1. The values in parentheses are approximate uncertainty bounds on the predicted values based on the

MCA/TetraTech

maximum difference between predicted and observed from the hindcast calibration. Table 7-2 provides a comparison of example target levels (note that target levels will be determined during the feasibility study. The values shown in Table 7-2 are to provide a benchmark for when order-of-magnitude concentrations will be achieved) based on the 10 ng/L upstream boundary condition.

Figure 7-4 shows that concentrations in largemouth bass at river mile 189 decline roughly exponentially. The lowest achieved concentration is approximately 1.5 ppm wet weight, with a margin of error of approximately 0.8 ppm on either side on a median basis. This is interpreted as 50% of fish are expected to show concentrations above this value and below this value. Figure 7-10 shows the results for the 25th, 50th and 95th percentiles for each of the locations. The 95th percentile concentration is interpreted as the expected body burden for 95% of the population. That is, 95% of the population would be expected to experience the shown concentration or less. For 95% of the population at river mile 189, the lowest concentration achieved is roughly 3.4 on an annualized basis. At river mile 168, largemouth bass concentrations decline to approximately 0.08 to 0.9 ppm on a median basis (best estimate of 0.3), and at river mile 154, concentrations are predicted to decline to approximately 0.07 to 0.2 ppm.

Brown bullhead concentrations at river mile 189 are predicted to be somewhat higher than predicted largemouth bass concentrations. By the end of the forecast period, the forecast median is approximately 0.7 ppm, and the 95th percentile is predicted to fall at approximately 0.6 to 1.3 ppm. For river mile 168, predicted brown bullhead median concentrations achieve 0.3 to 1.2 ppm, and 0.1 to 0.4 ppm at river mile 154. The corresponding 95th percentile values are 0.5 to 1.8 ppm and 0.015 to 0.06 ppm, for river miles 168 and 154, respectively (Figure 7-11).

Yellow perch concentrations at river mile 189 are predicted to fall to 0.7 to 1.5 ppm on a median basis, and to 1.8 to 3.9 ppm on a 95th percentile basis. Predicted concentrations fall to 0.1 to 0.4 ppm on a median basis at river mile 168, while the 95th percentile is expected to reach 0.015 to 0.06 ppm. At river mile 154, median concentrations fall to approximately 0.1 ppm, and the 95th percentile to 0.15 to 0.4 ppm. Median concentrations for all three boundary conditions are shown in Figure 7-6, and the percentile concentrations under the 10 ng/L upstream boundary condition in Figure 7-12.

White perch concentrations are predicted to fall to 0.1 – 0.4 ppm on a median basis at river mile 154, and to approximately 0.2 – 0.8 ppm on a 95th percentile basis.

7.4 Predicted PCB Concentrations in Fish under the 30 ng/L Upstream Boundary Condition

Figure 7-4 presents the results of predicted fish body burdens on a wet weight basis for largemouth bass predicted median concentrations under the three upstream boundary conditions. Figure 7-5 shows the same results for brown bullhead, and Figure 7-6 shows these results for yellow perch and white perch. For all species, concentrations decline roughly exponentially and approach different asymptotes depending on the species and upstream boundary condition. The median and 95th percentile asymptotes approached by each species are found in Table 7-1. The

MCA/TetraTech

303858

values in parentheses are approximate uncertainty bounds on the predicted values based on the maximum difference between predicted and observed from the hindcast calibration.

Figure 7-4 shows that concentrations in largemouth bass at river mile 189 decline roughly exponentially. The lowest achieved concentration is approximately 3.5 ppm wet weight, with a margin of error of approximately 1.8 ppm on either side on a median basis. This is interpreted as 50% of fish are expected to show concentrations above this value and below this value. Figure 7-13 shows the results for the 25th, 50th and 95th percentiles for each of the locations. The 95th percentile concentration is interpreted as the expected body burden for 95% of the population. That is, 95% of the population would be expected to experience the shown concentration or less. For 95% of the population at river mile 189, the lowest concentration achieved is roughly 8.1 on an annualized basis. At river mile 168, largemouth bass concentrations decline to approximately 0.3 to 3.0 ppm on a median basis (best estimate of 1.0), and at river mile 154, concentrations are predicted to decline to approximately 0.3 to 0.08 ppm.

Brown bullhead concentrations at river mile 189 are predicted to be somewhat lower than predicted largemouth bass concentrations. By the end of the forecast period, the forecast median is approximately 1.8 ppm (1.0 – 2.2 error bounds), and the 95th percentile is predicted to fall at approximately 1.4 to 3.1 ppm (best estimate of 2.6 ppm). For river mile 168, predicted brown bullhead median concentrations achieve 0.8 to 3.0 ppm, and 0.3 to 1.2 ppm at river mile 154. The corresponding 95th percentile values are 1.4 to 5.2 ppm and 0.5 to 1.8 ppm, for river miles 168 and 154, respectively. The 25th, 50th, and 95th predicted percentiles are shown in Figure 7-14.

Yellow perch concentrations at river mile 189 are predicted to fall to 1.9 to 4.2 ppm on a median basis, and to 3.1 to 6.7 ppm on a 95th percentile basis. Predicted concentrations fall to 0.4 to 1.4 ppm on a median basis at river mile 168, while the 95th percentile is expected to reach 0.8 to 3.0 ppm. At river mile 154, median concentrations fall to approximately 0.3 ppm, and the 95th percentile to 0.4 to 0.7 ppm. Median concentrations for all three boundary conditions are shown in Figure 7-6, and the percentile concentrations under the 30 ng/L upstream boundary condition in Figure 7-15.

White perch concentrations are predicted to fall to 0.3 – 1.2 ppm on a median basis at river mile 154, and to approximately 0.6 – 2.4 ppm on a 95th percentile basis.

7.5 Discussion of Results

The models were designed to predict the observed variability in fish tissue measurements taken since 1977. Some of the variability that has been observed over time is attributable to uncertainty, but this is likely to be small relative to the actual population heterogeneity in the environment. The parameter-specific distributions developed here were designed to capture variability rather than uncertainty. It can be argued that the dietary composition distributions, for example, represent uncertainty, but in fact they were derived based on observations of what fish have consumed in the environment. Similarly the lipid distribution, which contains measurement error, is primarily a distribution reflecting the differences in lipid content among individual fish.

Presenting predicted fish body burdens probabilistically provides important information for decisionmakers and for other aspects of the analysis. The ecological and human health risk assessments require predicted body burdens to evaluate the potential risk from PCB exposure under specific conditions. These results characterize exposure concentrations in fish as distributions rather than single point estimates.

The modeling results can be used directly in the context of specific numerical target levels. It is straightforward to obtain specific modeling results, that is, if risk managers determine a particular percentile of population should achieve a target level (say, the 75th or 90th need to achieve 0.1 ppm wet weight, or 2.0 ppm wet weight), these results can be explicitly predicted. Variability in the population response to sediment and water concentrations are reflected in the individual fractiles. Uncertainty for any given fractile based on the uncertainty in sediment and water concentrations can also be modeled.

Figures 7-4 through 7-6 present the FISHRAND forecast results on a median basis for the three upstream boundary conditions. These figures show the effect the difference in the upstream boundary condition has on the asymptotic concentration that predicted fish body burdens approach. Figures 7-7 through 7-9 provide the 25th, 50th, and 95th percentiles for largemouth bass, brown bullhead, and white and yellow and perch, respectively, for each of the upstream boundary conditions.

THIS PAGE INTENTIONALLY LEFT BLANK

8. DISCUSSION OF UNCERTAINTY

This chapter provides a discussion of uncertainties in the bioaccumulation model approach and assumptions. These uncertainties can be broadly categorized as model uncertainty and parameter uncertainty. Model uncertainty is the error associated with how well a model approximates the true relationships between environmental components. For example, these would include terms representing functional aspects of the environment that were not included in the analysis. Model error includes: inappropriate selection or aggregation of variables, incorrect functional forms, and incorrect boundaries. Parameter uncertainty refers to the uncertainty in estimating specific values of parameters and forcing functions in the models (e.g., sediment and water concentrations, etc.) as well as inherent variability (e.g., lipid content, fish weight). Most modeling parameters will exhibit both variability and uncertainty. Variability, which typically cannot be reduced but can be better characterized by collecting additional data, represents known variations in parameters based on observed heterogeneity in the environment. True uncertainty in parameter estimates could be reduced by collecting more data.

8.1 Model Uncertainty

8.1.1 Model and Parameter Uncertainties in the Fate and Transport Models

Since the bioaccumulation models rely on the sediment and water concentrations from the fate and transport models, it is important to identify potential sources of uncertainty in these models to be able to understand the effect on predicted fish body burdens. By necessity, the fate and transport models are not able to capture every single mechanism contributing to transport processes. The uncertainty associated with water and sediment concentrations resulting from potential changes in most sensitive parameters have been selected for explicit modeling, based on professional judgment, prior experience and existing models. See Book 1 Chapter 7.5 for a further discussion of uncertainties in the fate and transport models.

8.1.1.1 Sediment and Water Averaging

To forecast future Tri+ body burdens in fish, the same 75% cohesive and 25% noncohesive averaging was conducted to maintain consistency with the hindcast calibration. There is uncertainty in these estimates. The true exposure concentration that fish experience relative to sediment is unknown.

8.1.2 Model Uncertainties in the Bioaccumulation Models

The bioaccumulation models contain a number of simplifications in uptake processes. In addition, the two statistical approaches presented here contain inherent limitations as compared to the mechanistic approach. These two aspects of model uncertainty in the bioaccumulation models are discussed next.

8.1.2.1 Probabilistic Empirical Model and Bivariate BAF Model

These two models use observed data to construct relationships between compartments. One limitation of these kinds of statistical approaches lies in their predictive power. Models of this sort cannot reliably be used in terms of prediction as they do not necessarily capture the mechanistic basis for responses to changes in the system. They can be used to extrapolate beyond the range of observed data to evaluate trends based on current conditions, but they cannot be used to evaluate changes in the system and expected responses to those changes.

8.1.2.2 FISHRAND

FISHRAND is based on the modeling approach developed by Gobas (1993). This approach has been used in the Great Lakes as well as in a number of other modeling contexts. Further refinements on the original model have been presented in the literature (Gobas et al., 1995; Morrison et al., 1997). These later approaches involve the following modifications:

- Explicit consideration of benthic invertebrate feeding preferences (e.g., burrowers versus epibenthic species etc.) resulting in a biomagnification mechanism rather than the equilibrium partitioning (BSAF) approach taken here;

- An age-class model for each year of a fish's life rather than the growth dilution approach presented here; and,

- An explicit pharmacokinetic model to consider the role of metabolism.

Benthic feeding: FISHRAND does not explicitly consider benthic feeding strategies but rather relies on the original equilibrium partitioning approach for several reasons. First, distributions are used in FISHRAND for a) sediment concentrations, b) total organic carbon in sediment, and c) benthic invertebrate percent lipid. The sediment concentration distributions are described as lognormal, while the TOC and lipid distributions are described as triangular. Given these distributional shapes and the nature of the relationship between sediment concentrations and invertebrate concentrations, the use of these distributions in the BSAF equation adequately describe the observed variability in benthic invertebrate concentrations as compared to empirical data. This observed variability may be attributable to biomagnification but insofar as the model adequately describes observed data and the equilibrium partitioning equation has been widely used and accepted, it was decided to take this approach for FISHRAND.

As shown in Figure 5-2, observed biota:sediment accumulation factors from the EPA Phase 2 database average one, exactly what equilibrium partitioning would predict. The species categorized as benthic versus epibenthic from the Phase 2 dataset did not show statistically significant different BSAFs (t-tests).

Age-Class Modeling: The body weight, lipid content and dietary preferences change significantly over the lifespan of individual fish and the latest Gobas model is developed for

individual generations of age classes of organisms (Gobas et al., 1995). In this study, we have categorized fish into species-specific age classes. For example, in the case of largemouth bass, yellow perch, white perch and brown bullhead, the adults in the population are of primary concern. It is the adult fish in the population that will be consumed by humans and some ecological receptors. Forage fish (pumpkinseed and spottail shiner) serve as primary prey base for the larger fish (that are piscivorous) and also other ecological receptors (such as mink and kingfisher, as examples). Juvenile fish of all species are assumed to have feeding habits more similar to the forage fish. Two classes of forage fish are considered: one that obtains its predominant food source from the water column (pumpkinseed) and the other equally from water and sediment (spottail shiner). These two categories are representative of the kinds of feeding strategies forage fish and juvenile fish will utilize.

These discreet fish populations are represented by distributions for fish weight and lipid concentrations. Each individual fish in the population is assumed to grow, i.e. to increase its individual volume and weight. Such volume increase can lead to decrease in concentration in this fish if uptake is too slow to compensate for the reduction in chemical mass per volume. The volume of the population is assumed to be equilibrated by the processes of fish death and reaching the minimal size to be included in the population.

The approach taken in this report was chosen to maximize the utility of the existing database and to minimize the number of assumptions required for modeling. Virtually all the data available for the Hudson River are for fish falling within a particular grouping of age-classes. Within these age-classes, feeding preferences are consistent and key parameters (e.g., weight, lipid, etc.) are represented by distributions. This approach minimized the number of assumption that had to be made since there are not enough site-specific data available to support explicit age-class considerations for the larval and juvenile largemouth bass, brown bullhead, yellow perch, and white perch.

Pharmacokinetics: The metabolism of PCBs likely plays an important role in the ability of fish to retain PCBs (Niimi, 1997; Gobas, 1999). Experimental data suggest that PCBs can biomagnify in the food chain due to pharmacokinetic processes in fish (Gobas, 1999, Connolly, 1988, Gobas, 1993). Specifically, food digestion and absorption in gastrointestinal tract is hypothesized to increase PCB fugacity. Even though these processes have been recently incorporated in the fish bioaccumulation model by Gobas (Gobas et al., 1999) we believe that the experimental database and theoretical foundation of this model have to be developed further to provide better estimates for the required parameters and associated uncertainties. In addition, it would be best if the Gobas et al., 1999 model were validated for a number of sites before using it for regulatory decisions. Therefore, the FISHRAND model does not directly account for these processes and uses as the prototype an earlier version of the Gobas model that was tested and applied for several sites and in different environmental settings (Morrison et al., 1997, Buckhard, 1998).

Table 6-2 shows that the relative percent difference between predicted and observed for FISHRAND is typically within 25-40%, and significantly less than that for many individual years, species, and locations.

8.2 Parameter Uncertainty

All of the parameters used in FISHRAND have some uncertainty associated with them. For example, even though there is an extensive database of percent lipid for specific fish species across locations and times, there is laboratory uncertainty associated with these measurements. The full extent of that uncertainty is not known. Fish feeding preferences are highly uncertain. Stomach content analyses provide only limited information as the soft-bodied organisms are the first to be digested and cannot typically be observed, even if a fish is caught immediately after consuming such organisms. Biomass data, which are required to translate numbers of organisms observed in the stomach contents to meaningful percent mass or volume estimates, are often unavailable. Further it is typically not known whether a fish will selectively feed on particular organisms or whether the fish is strictly an opportunistic feeder, in which case feeding will in large measure depend on the biomass of prey items in the environment.

8.2.1 Sensitivity Analysis

Our literature review and experimental data collected for the Hudson River has shown that: 1) river ecosystem characteristics vary significantly from one location to another depending on flow rate, depth, sediment structure, etc.; and 2) certain parameters in the model (such as feeding preferences) are only imprecisely known. Moreover, most of the measurements are not easily related to the FISHRAND generic input parameters because, by their own nature, experimental measurements are taken at a specific time and space while the FISHRAND model parameters are, in contrast, values corresponding to averages over time, space and species.

The effect of variation of all input parameters on all model outputs were evaluated in a sensitivity analysis using the Monte Carlo methodology. In this method, combinations of values for the input parameters are generated randomly. Each parameter appears with the frequency suggested by its probability distribution. For each combination of input parameters, the output of the model is recorded. The combination of all possible outputs generated in this manner is used to construct the distribution of model outputs, which reflect the influence of the undetermined parameters on the output values.

The partial rank and Spearman rank regression techniques (Morgan and Henrion, 1990) are used as a formal method to find the most important parameters for the model performance. If the Spearman or partial rank regression coefficient (PRRC or SRRC) is close to 1 or -1 for a specific input model parameter, this parameter significantly influences model output. Table 8-1 shows that the correlation coefficients estimated for the percent lipid in water column invertebrates are above 0.5 for most species and location for the lipid normalized results. The percent lipid in fish is strongly negatively correlated with PCB body burden expressed on a lipid-normalized basis. This is because increases in lipid increase the PCB storage capacity of the fish, reducing the apparent concentration. As expected, the percent lipid in fish is positively associated for the wet weight results, but less so. This confirms that particularly on a lipid-normalized basis, the percent lipid distribution is very important. K_{ow} and benthic percent lipid are also important for some species on a wet weight basis. Feeding preferences are only weakly correlated with body burdens in terms of sensitivity to this parameter. Tables 8-2 through 8-4

MCA/TetraTech

present the correlation coefficients for weight and lipid normalized results, expressed as partial rank correlation coefficients, and Spearman rank correlation coefficients.

As described in Chapters 3 and 6, sensitivity to model constants was evaluated by approximating an analytical solution and then taking partial derivatives of all the model constants with respect to fish concentration. Derivatives of the model constants were evaluated across the full ranges of all parameters to determine the sign and magnitude of each of the derivatives. The assimilation efficiency and growth rate were determined to be the most important parameters in terms of effect on predicted fish concentration. This procedure was described in the approach to calibration in Chapters 3 and 6.

8.2.1.1 *Lipid Content*

Lipid content of organisms plays an important role in the model. Uncertainty in the interpretation of observed data is attributable to differences in laboratory determination of lipid content of fish tissue. PCBs are lipophilic, stored primarily in fatty tissue, and it is generally agreed that lipid normalization (*i.e.*, expressing PCB body burden on a lipid basis) provides a more consistent basis for evaluating bioaccumulation than wet-weight PCB concentrations. Lipid-normalized PCB body burden is calculated as the reported wet-weight PCB concentration divided by the lipid concentration. FISHRAND first estimates a wet-weight concentration and then lipid-normalizes these results. Unfortunately, any imprecision in the determination of lipid concentration will also result in imprecision in the calculation of lipid-normalized PCB body burden. Further, the propagation of uncertainty will be non-linear, as the lipid-normalized concentration involves division by the lipid content. Therefore, estimation of the uncertainty in lipid-based PCB concentrations must also include an analysis of the uncertainty in determination of lipid concentration. Inter-laboratory comparisons conducted by NYSDEC in September 1992 showed an average variability between laboratories of ten percent in determining lipid content of biological specimens, with results from some pairs of laboratories showing a consistent relative bias.

Information on the precision of lipid determinations in Hudson River fish data is provided by three sets of interlaboratory comparisons performed for NYSDEC in 1989, 1992, and 1995. The 1989 comparisons involved 4 samples and 8 laboratories, the 1992 comparisons involved 5 samples and 12 laboratories, and the 1995 comparisons involved 3 samples and 4 laboratories. The two laboratories responsible for the majority of NYSDEC fish analyses (Hazleton and successors, and Hale Creek) participated in each of the interlaboratory comparisons.

Over the 12 samples, standard deviations between laboratories on percent lipid determinations ranged from 0.052 to 0.52. The standard deviation is scale dependent, however, and it is more informative to examine the coefficient of variation (standard deviation divided by the mean). Coefficients of variation on percent lipid ranged from 0.023 to 0.38, with an average of 0.099, indicating a relatively high degree of precision in lipid determinations.

Results reported by Hazleton appear to show consistent deviations relative to the mean across all laboratories. For the 1989 results, all Hazleton lipid determinations were less than the mean, with the discrepancy ranging from –0.75 to –3.88 standard deviation units on the

percentage value, with an average of –2.55 standard deviations. For both 1992 and 1995, all Hazleton results were greater than the interlaboratory mean, with an average discrepancy of 4.47 standard deviations. The discrepancies appear relatively large because the standard errors are small.

The interlaboratory mean depends on the characteristics of the laboratories that participated in a given year. When Hazleton is compared to Hale Creek, however, the same pattern emerges: Hazleton results are consistently lower than Hale Creek in 1989, and consistently higher in 1992 and 1995. The Hale Creek lipid determinations do not show any consistent bias with time relative to the interlaboratory mean. Across all samples, the discrepancies for Hale Creek versus the mean range from –1.0 to +0.99 standard deviation units, with an average of –0.29 standard deviations.

Hazleton results are compared to the interlaboratory means in Figure 8-1. While the discrepancies are sometimes large in terms of standard deviation units, the average absolute difference between Hazleton and the interlaboratory mean is only 0.65 percentage points.

Based on the results of NOAA's mussel method detection limit (MDL) study (see USEPA, February 1993a for details), the percent lipid determination for benthic invertebrates was considered as estimated. Therefore, the percent lipid of benthic invertebrates was based on the mean of all invertebrates analyzed in the Phase 2 study. The variability seen in the percent lipid composition was associated with the small sample mass associated with some of the samples (1 gram wet weight). The confidence of percent lipids was higher for fish samples, which had more material available for analysis.

8.2.1.2 K_{ow}

The optimal posterior distribution for K_{ow} was determined through the Bayesian calibration procedure. However, there is uncertainty as to whether this optimized distribution represents the true distribution in the future. It is likely that the congener composition of the PCB mixture in the environment may change over time, and there is uncertainty as to whether the optimized distribution obtained through calibration to historical data remains valid for future forecasts. However, the for which the Kow distribution was optimized represent data obtained over a 21-year period, and for the most part, direct source contributions (as opposed to sediment or in-river PCB contributions) have declined. There is greater confidence having used data over a longer time period than simply one or two years.

The optimized K_{ow} distribution is quite different between river miles 189 and 168 (the same distribution was used at 154 as 168). This suggests that the congener distribution may differ between river miles (as has been suggested by other analyses, e.g., USEPA, 1999b; NOAA, 1998). Also, the river behaves quite differently between the Thompson Island Pool (river mile 189) and the remainder of the river.

MCA/TetraTech

303868

9. SUMMARY AND CONCLUSIONS

Three food chain models were developed to describe the uptake of PCBs, expressed as $\Sigma Tri+$, which is representative of total PCBs in fish tissues. These models are:

Bivariate BAF Analysis

The Bivariate BAF Analysis relates measured PCB levels in water and sediments (two variables, or "bivariate") to measured PCB levels in fish. This analysis was applied to the Upper Hudson River and to a segment of the Lower Hudson River near Albany. The Bivariate BAF Analysis was developed using the historical PCB Aroclor database. Results presented in this report build upon the earlier analysis presented in the Preliminary Model Calibration Report (1996).

Empirical Probabilistic Food Chain Model

The Empirical Probabilistic Food Chain Model is contructed by linking fish body burdens to PCB exposure concentrations in water and sediments. The model combines information from available PCB exposure measurements with knowledge about the ecology of different fish species and the relationships among larger fish, smaller fish, and invertebrates in the water column and sediments. The Probabilistic Model was developed using both historical and 1993 field data, and was applied to the Upper Hudson River down the Federal Dam at Troy. In contrast to the Bivariate BAF Analysis, which provides average body burden estimates, the Probabilistic Model provides information on the expected range of uncertainty and variability around these average estimates.

Mechanistic Time-Varying Model (FISHRAND) Based on Gobas (1993)

The FISHRAND model is based on 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 (EPA, 1995). This probabilistic model was programmed in Fortran-90 using the LSODE (the Livermore Solver for Ordinary Differential Equations (Radhakrishnan and Hindmarsh, 1993)) and incorporating a Microsoft Excel™ graphical user interface.

Food Web Biology

As part of the development of the food web models, species-specific profiles (i.e., descriptions of feeding behavior, habitat preferences, range and movement) were developed for yellow perch, largemouth bass, pumpkinseed sunfish, brown bullhead, white perch, spottail shiner, shortnose sturgeon and striped bass. These profiles include: information on species-specific characteristics influencing bioaccumulation potential of PCBs; as well as the details of specific gut analyses conducted by Menzie-Cura & Associates, Inc., Exponent, Inc.; and information in the literature from the Hudson River power plant studies. These profiles helped develop dietary composition distributions for each of the fish species.

Target Levels for Fish Body Burdens

Appropriate fish body burden target levels for the protection of ecological receptors and human health have not yet been established for the Hudson River PCBs Site Reassessment. To provide perspective on the range of concentrations predicted for each fish species, four different values have been selected. These values do not represent particular target levels and should not be interpreted as potential target levels for this site. These values were selected strictly for comparative purposes. The concentrations selected represent a range of concentrations and orders of magnitude.

9.1 Summary of Food Web Models

- The Bivariate BAF Analysis represents PCBs in terms of the sum of trichloro- through decachlorbiphenyls (denoted ΣTri+). Historical Aroclor quantitation schemes are not consistent with one another, but can be translated to a consistent estimate of ΣTri+. Information on mono- and dichlorobiphenyl concentrations is not available in most of the historical PCB monitoring data. The Probabilistic Bioaccumulation Food Chain Model and FISHRAND also represent ΣTri+ (approximately equivalent to total PCBs in fish tissue).

- The Bivariate BAF Analysis for fish body burden in a given species is based on the historical dataset of Aroclor measurements, with corrections for changing quantitation methods. It is designed to provide a statistical perspective on the empirical relationships between water, sediment, and fish body burdens. The statistical model relies on a bivariate regression approach which relates fish body burdens to concentrations in both water and sediment. This allows for the possibility that water and sediment concentrations are not in equilibrium, as is frequently observed in the Upper Hudson River.

- The Probabilistic Bioaccumulation Food Chain Model consists of the following biotic compartments: (a) benthic invertebrates; (b) water column invertebrates; (c) forage fish; (d) piscivorous fish; and (e) demersal fish. PCB concentrations are expressed as lipid-normalized in biota, total organic carbon normalized in sediments and whole water in the water column. Relationships among compartments are expressed as bioaccumulation factors between the concentration in a given compartment and the expected dietary exposure for that compartment. The dietary exposure is based on a weighted concentration in the diet.

- Statistical distributions of bioaccumulation factors have been derived for:
    - sediments to benthic invertebrates;
    - whole water PCB concentrations to water column invertebrates;
    - expected dietary concentrations to composite forage fish; and
    - pumpkinseed to largemouth bass.

- FISHRAND was developed based on Gobas (1993) and compared to published modeling results for Lake Ontario to verify model functionality. This model was then modified for the Hudson River by eliminating Lake Ontario species and including Hudson River species along with site-specific and fish specific parameters.

- Species-specific profiles are presented for yellow perch (*Perca flavescens*), largemouth bass (*Micropterus salmoides*), pumpkinseed (*Lepomis gibbosus*), brown bullhead (*Ictalurus nebulosus*), white perch (*Morone americana*), spottail shiner (*Notropis hudsonius*), shortnose sturgeon (*Acipenser brevirostrum*) and striped bass (*Morone saxatilis*). These profiles describe foraging strategies, home-ranges, habitat preferences and information on reproduction for each of these species.

- The foraging strategies of the invertebrate prey base for the fish species is viewed as a key component to evaluating relative sediment versus water influences on fish body burdens. An analysis is presented here that uses an indicator species approach based on identified macroinvertebrates from the gut contents of Hudson River fish in order to differentiate sediment versus water exposure pathways via the food chain.

- FISHRAND predicts expected body burdens in fish on a population-level basis. The model assumes a cycling of the population in which older fish are replaced by younger fish within a particular size range. For this modeling application, the age-class of interest includes the adult of the species for piscivorous, semi-piscivorous and omnivorous fish while for the forage fish the age-class of interest is the young-of-year (or yearlings).

- The FISHRAND model calibration procedure focused on achieving wet weight concentrations rather than lipid normalized concentrations. This is because the model predicts a wet weight concentration and the method provides for more robust predictions within the decisionmaking context for this site.

- Both the probabilistic and mechanistic models were run using predicted hindcasting water and sediment concentration results from the fate and transport models as inputs in a validation exercise. The models were used to predict observed fish concentrations (from NYSDEC) for the period 1977 – 1997 for several locations above the Federal Dam at Troy.

- The FISHRAND model was run for 70-year forecasts (1998 – 2067) using sediment and water concentrations from the HUDTOX model. Three scenarios were run, assuming: a) a zero upstream boundary condition, and b) a 10 ng/L constant upstream boundary condition, and c) a 30 ng/L constant upstream boundary condition (see Books 1 and 2).

9.2 Principal Report Findings

The following conclusions have been drawn based on the work presented in this Revised Baseline Modeling Report:

- The Bivariate BAF Analysis for fish body burdens explains about 80 percent of the observed variability in summer average concentrations of tri- through deca-chlorinated PCBs in fish from the freshwater portion of the Hudson River. Much of the remaining,

MCA/TetraTech

303872

unexplained variability is due to uncertainty in historic water column concentrations. The BAF analysis suggests a need to consider both the water column and local sediments as sources for bioaccumulation of PCBs in Upper Hudson River fish. The relative importance of water and sediment sources determined in the Bivariate BAF Analysis is consistent with species feeding behavior: for species that feed in the water column, the water column pathway tends to dominate, while for bottom-feeders, the sediment pathway tends to be dominant. Fish-eating species at higher levels in the food chain appear to accumulate PCBs from both water column and sediment pathways.

- Using the hindcast calibration results from the fate and transport models, the probabilistic empirical model reasonably captures observed historical PCB concentrations in fish. Comparisons are available for largemouth bass, brown bullhead, and pumpkinseed at river miles 168 and 189, and for largemouth bass at river mile 154.

- Using the hindcast calibration results from the fate and transport models, the FISHRAND model captures observed historical PCB concentrations in fish to within a factor of two for most locations and species, and typically significantly better than that. Largemouth bass concentrations are captured within a factor of 1.3 for 1990 – 1997. Comparisons are available for largemouth bass, pumpkinseed, yellow perch and brown bullhead at river miles 189, 168, and 154. White perch comparisons are available at river mile 154.

- Predictions from the probabilistic empirical model for largemouth bass compare favorably to the results for FISHRAND on a median basis. On a 95th percentile basis, the probabilistic model typically predicts approximately a factor of two higher than the FISHRAND model.

- Within year variability predicted by the FISHRAND model is approximately a factor of two. Month to month comparisons of model output to data (that is, comparing model results for the month corresponding to the month of sample collection) showed the lowest relative percent difference. However, comparisons to data for annualized FISHRAND predictions are similar although individual relative percent differences are slightly larger as the annualized results average out this seasonal variation.

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

- At the end of the 70-year forecast period, the lowest achieved concentration for largemouth bass at river mile 189 under the zero upstream boundary condition is approximately 0.1 ppm wet weight, with an error of approximately a factor of two on either side on a median basis. This asymptote is approached in roughly 2039 and median predicted concentrations remain approximately at that level from then on. For 95% of the

population at river mile 189, the lowest concentration achieved is roughly 0.3 on an annualized basis, again in approximately 2039. At river mile 168, largemouth bass concentrations decline to approximately 0.005 to 0.06 ppm on a median basis (best estimate 0.02 ppm), and at river mile 154, concentrations are predicted to decline to approximately 0.007 to 0.02 ppm (best estimate 0.01). These values all occur at roughly 2039.

- Under the zero upstream boundary condition, brown bullhead concentrations at river mile 189 are predicted to be somewhat higher than predicted largemouth bass concentrations. By the end of the forecast period, the median is predicted to be approximately 0.1 ppm, and the 95th percentile is predicted to fall at approximately 0.1 to 0.24 ppm. These values are first achieved in approximately 2039. Concentrations increase briefly from 2048 – 2052 (to slightly above 0.4 ppm), and then decrease again by 2059. For river mile 168, predicted brown bullhead median concentrations achieve 0.01 to 0.04 ppm, and 0.005 to 0.02 ppm at river mile 154. The corresponding 95th percentile values are 0.015 to 0.06 ppm and 0.01 to 0.04 ppm, for river miles 168 and 154, respectively.

- Under the zero upstream boundary condition, yellow perch concentrations at river mile 189 are predicted to fall to 0.03 to 0.06 ppm on a median basis, and to 0.05 to 0.11 ppm on a 95th percentile basis. Predicted concentrations fall to 0.005 to 0.02 ppm on a median basis at river mile 168, while the 95th percentile is expected to reach 0.01 to 0.04 ppm. At river mile 154, median concentrations fall to approximately 0.004 ppm, and the 95th percentile to 0.005 to 0.008 ppm..

- Under the zero upstream boundary condition, white perch concentrations are predicted to fall to 0.005 – 0.02 ppm on a median basis at river mile 154, and to approximately 0.01 to 0.04 ppm on a 95th percentile basis.

- At the end of the 70-year forecast period, the lowest achieved concentration for largemouth bass at river mile 189 under the 10 ng/L upstream boundary condition is approximately 1.5 ppm wet weight, with an error of approximately a factor of 1.4 on either side on a median basis. For 95% of the population at river mile 189, the lowest concentration achieved is roughly 3.4 on an annualized basis. At river mile 168, largemouth bass concentrations decline to approximately 0.08 to 0.9 ppm on a median basis (best estimate of 0.3 ppm), and at river mile 154, concentrations are predicted to decline to approximately 0.07 to 0.2 ppm (best estimate of 0.1).

- Under the 10 ng/L upstream boundary condition, brown bullhead concentrations at river mile 189 are predicted to be somewhat higher than predicted largemouth bass concentrations at river miles 168 and 154, and somewhat lower at river mile 189. By the end of the forecast period, the median is predicted to be approximately 0.7 ppm, and the 95th percentile is predicted to fall at approximately 0.6 to 1.3 ppm. For river mile 168, predicted brown bullhead median concentrations achieve 0.3 to 1.2 ppm, and 0.1 to 0.4 ppm at river mile 154. The corresponding 95th percentile values are 0.5 to 1.8 ppm (best estimate of 0.9 ppm) and 0.15 to 0.6 ppm (best estimate of0.3), for river miles 168 and 154, respectively.

- Under the 10 ng/L upstream boundary condition, yellow perch concentrations at river mile 189 are predicted to fall to 0.7 to 1.5 ppm on a median basis (best estimate of 1.4 ppm), and to 1.8 to 3.9 ppm (best estimate of 3.5) on a 95th percentile basis. Predicted concentrations fall to 0.1 to 0.4 ppm on a median basis at river mile 168, while the 95th percentile is expected to reach 0.15 to 0.6 ppm. At river mile 154, median concentrations fall to approximately 0.1 ppm, and the 95th percentile to 0.2 ppm.

- Under the 10 ng/L upstream boundary condition, white perch concentrations are predicted to fall to 0.1 – 0.4 ppm on a median basis at river mile 154, and to approximately 0.4 ppm on a 95th percentile basis.

- At the end of the 70-year forecast period, the lowest achieved concentration for largemouth bass at river mile 189 under the 30 ng/L upstream boundary condition is approximately 3.5 ppm wet weight, with an error of approximately a factor of 1.4 on either side on a median basis. For 95% of the population at river mile 189, the lowest concentration achieved is roughly 8.4 on an annualized basis. At river mile 168, largemouth bass concentrations decline to approximately 0.3 to 3.0 ppm on a median basis (best estimate of 1.0 ppm), and at river mile 154, concentrations are predicted to decline to approximately 0.3 to 0.8 ppm (best estimate of 0.4).

- Under the 30 ng/L upstream boundary condition, brown bullhead concentrations at river mile 189 are predicted to be somewhat higher than predicted largemouth bass concentrations at river miles 168 and 154, and somewhat lower at river mile 189. By the end of the forecast period, the median is predicted to be approximately 1.8 ppm, and the 95th percentile is predicted to fall at approximately 1.4 to 3.1 ppm at river mile 189. For river mile 168, predicted brown bullhead median concentrations achieve 0.8 to 3.0 ppm, and 0.3 to 1.2 ppm at river mile 154. The corresponding 95th percentile values are 1.4 to 5.2 ppm (best estimate of 2.6 ppm) and 0.5 to 1.8 ppm (best estimate of 0.9), for river miles 168 and 154, respectively.

- Under the 30 ng/L upstream boundary condition, yellow perch concentrations at river mile 189 are predicted to fall to 1.9 to 4.2 ppm on a median basis (best estimate of 3.8 ppm), and to 3.1 to 6.7 ppm (best estimate of 6.1) on a 95th percentile basis. Predicted concentrations fall to 0.4 to 1.4 ppm on a median basis at river mile 168, while the 95th percentile is expected to reach 0.8 to 3.0 ppm. At river mile 154, median concentrations fall to approximately 0.3 ppm, and the 95th percentile to 0.5 ppm.

- Under the 30 ng/L upstream boundary condition, white perch concentrations are predicted to fall to 0.3 – 1.2 ppm on a median basis at river mile 154, and to approximately 0.6 ppm on a 95th percentile basis.

- The results of the FISHRAND model show that between 4 and 15% of the ΣTri+ PCB uptake in fish is attributable to direct water uptake, and the remainder to dietary sources. The forage fish (pumpkinseed and spottail shiner) are at the high end of this range; the remaining fish at the low end. It is difficult to analytically separate water and sediment sources in the dietary pathway, so the relative influence of water and sediment was evaluated using a steady-state solution to the dynamic model. Sediment (mg/kg dry

weight) and dissolved water (ng/L) were regressed against predicted fish concentration (mg/kg wet weight) to evaluate the effect of changes in sediment and water concentrations on predicted fish body burdens. This analysis showed that brown bullhead are most sensitive to changes in sediment concentration and not very sensitive to changes in water concentration; largemouth bass are more sensitive to sediment concentrations than to water concentrations but water plays a larger role than for brown bullhead; yellow perch are driven primarily by the water; white perch show greater sensitivity to sediment; and pumpkinseed and spottail shiner are more sensitive to small changes in water concentration.

THIS PAGE INTENTIONALLY LEFT BLANK

MCA/TetraTech

References

REFERENCES

Albro, P.W. and C.E. Parker. 1979. Comparison of the compositions of Aroclor 1242 and Aroclor 1016. *Journal of Chromatography*, 169: 161-166.

Armstrong, R.W. and R.J. Sloan. 1988. PCB Patterns in Hudson River Fish: 1. Resident Freshwater Species. Pp. 304-324 in C.L. Smith, Ed., *Fisheries Research in the Hudson River*. State University of New York Press, Albany, NY.

Anderson, R.C. and D. Brazo. 1978. Abundance, feeding habits and degree of segregation of the spottail shiner (*Notropis hudsonius*) and longnose dace (*Rhinichthys cataractae*) in a Lake Michigan surge zone near Ludington, Michigan. *Mich. Acad.* 10(3):337-346.

Ankley, G.T., P.M. Cook, A.R. Carlson, D.J. Call, J.A. Swenson, H.F. Corcoran, and R. A Hoke. 1992. Bioaccumulation of PCBs from sediments by oligochaetes and fishes: comparison of laboratory and field studies. *Can. J. Fish. Aquat. Sci.* 49:2080-2085.

Barron, M. 1990. Bioconcentration. *Environ. Sci. Technol.* 24:1612-1618.

Bates, D. and D. Watts. 1988. Nonlinear Regression Analysis and its Applications. New York: John Wiley & Sons.

Bath, D.W. and J.M. O'Connor. 1982. The biology of the white perch (*Morone Americana*) in the Hudson River estuary. *Fish Bull. U.S.* 80:599-610.

Beebe, C. A., and I.R. Savidge. 1988. Historical perspective on fish species composition and distribution in the Hudson River estuary. *American Fisheries Society Monograph.* 4:25-36.

Bierman, V. J. Jr., et al. 1992. Development and Validation of an Integrated Exposure Model for Toxic Chemicals in Green Bay, Lake Michigan. U.S. EPA Cooperative Agrement CR-814885.

Bierman, V.J., Jr. 1990. Equilibrium partitioning and biomagnification of organic chemicals in benthic animals. *Environ. Sci. Technol.* 24:1407-1412.

Bierman. V.J., Jr. 1994. Partitioning of organic chemicals in sediments: Estimation of interstitial concentrations using organism body burdens. Chapter 9 in: *Transport and Transformation of Contaminants Near the Sediment-Water Interface*. (Ed. J.V. DePinto, W. Lick and J.F. Paul) CRC Press, pp. 153-175.

Biscayne, P.E. and C.R. Olsen. 1976. Suspended particulate concentrations and compositions in the New York bight; proceedings of the symposium, special symposia Vol. 2, Middle Atlantic Continental Shelf and the New York Bight. *American Soc. of Limnology and Oceanography;* pp. 124-137.

Bopp, R.F. and H.J. Simpson, 1984. Persistent chlorinated hydrocarbon contaminants in the New York Harbor complex, 1st year final report for Contract HUD 1183-A38, by Lamont-Doherty Geological Observatory of Columbia Univ., submitted to Hudson River Foundation; 6 pp. + extensive tables, figures, app.

Bopp, R.F. 1979. *The geochemistry of polychlorinated biphenyls in the Hudson River*. Ph.D. Dissertation, Columbia University. *Univ. Micro. Intern*. 8008704, 191 pp.

Boreman, J. 1981. Life histories of seven fish species that inhabit the Hudson River Estuary. *National Marine Fisheries Service*, Woods Hole Laboratory, No. 81-34, October.

Brown, M.P., M.B. Werner, R.J. Sloan, and K.W. Simpson. 1985. Polychlorinated biphenyls in the Hudson River, recent trends in the distribution of PCBs in water, sediment and fish. *Environmental Science and Technology* 19(8):656-661.

Buckley, J. and B. Kynard. 1981. Spawning and rearing of shortnose sturgeon from the Connecticut River. *Prog. Fish-Cult*. 43:74-76.

Burkhard, L.P. (1998). Comparison of two models for predicting bioaccumulation of hydrophobic organic chemicals in a Great Lakes food web. *Environ. Toxicol. Chem*. 17: 383-393.

Burmistrov, D., Linkov, I. (1999). "Reducing Uncertainty in The Radionuclide Transport Modeling for the Techa River Using Bayesian Updating." In: *"Proceedings of the IUR Workshop 1-5 June 1998"* E. Van den Strict, ed. IUR, 1999 (in press)

Bush, B., S. Dzurica, L. Wood, and E.C. Madrigal. 1994. Sampling the Hudson River Estuary for PCBs using multiplate artificial substrate samplers and congener-specific gas chromatography in 1991. *Environmental Toxicology and Chemistry* 13(8):1259-1272.

Butcher, J.B., T.D. Gauthier, and E.A. Garvey. 1997. Use of historical PCB Aroclor measurements: Hudson River fish data. *Environmental Toxicology and Chemistry*, 16(8): 1618-1623.

Carlson, D.M. 1986. Fish and their habitats in the Upper Hudson Estuary. Region 4 Fisheries, Stamford, New York. November.

Carlson, D.M. 1992. Importance of wintering refugia to the largemouth bass fishery in the Hudson River Estuary. *Journal of Freshwater Ecology* 7:173-180.

Chabot, F. and E. J. Maly. 1986. Variation in diet of yellow perch (*Perca flavescens*) in a Quebec reservoir. *Hydrobiologia* 137:117-124.

Chiou, C.T. 1985. Partition coefficients of organic compounds in lipid-water systems and correlations with fish bioconcentration. *Environ. Sci. Technol*. 19:57-62.

Clayton, J.R., S.P. Pavlou, and N.F. Brietner. 1977. Polychlorinated biphenyls in coastal marine zooplankton: bioaccumulation by equilibrium partitioning. *Environ. Sci. Technol.* 11:676

Cole, J.J., N.F. Caraco and B.L. Peierls. 1992. Can phytoplankton maintain a positive carbon balance in a turbid, freshwater, tidal estuary?. *Limnology and Oceanography* 37(8):1608-1617.
Connolly, J.P. and R. Tonelli, 1985. Modelling Kepone in the striped bass food chain of the James River estuary. *Estuarine, Coastal and Shelf Science* 20:349-366.

Connolly, J.P., R.P. Winfield, and J.R. Blasland. NO DATE. Application of a food chain model of PCB accumulation to the striped bass of the Hudson Estuary. Report to the Hudson River Foundation. 35 pp.

Crance, J.H. 1986. Habitat suitability index models and instream flow suitability curves: shortnose sturgeon. *U.S. Fish Wildl. Serv. Biol. Rep.* 82(10.129) 31 pp.

Di Toro, D.M., C.S. Zarba, D.J. Hansen, W.J. Berry, R.C. Swartz, C.E. Cowan, S.P. Pavlou, H.E. Allen, N.A. Thomas, and P.R. Paquin. 1991. Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. *Environmental Toxicology and Chemistry* 10(12):1541-1583.

DiToro, D.M. 19085. A particle interaction model of reversible organic chemical sorption. *Chemosphere* 14(10):1503-1138.

Domermuth, R.B. and R.J. Reed. 1980. Food of juvenile American shad (*Alosa sapidissima*), juvenile blueback herring (*Alosa aestevalis*) and pumpkinseed (*Lepomis gibbosus*) in the Connecticut River below Holyoke Dam, Massachusetts. *Estuaries* 3:65-68.

Dovel, W.L. 1992. Movements of immature striped bass in the Hudson Estuary. In *Estuarine Research in the 1980s: The Hudson River Environmental Society Seventh Symposium on Hudson River Ecology* (Ed: C.L. Smith) State University of New York Press, pp. 276-300.

Dovel, W.L., A.W. Pekovitch, and T.J. Bergren. 1992. Biology of the shortnose sturgeon (*Acipenser brevirostrum* Lesueur, 1818) in the Hudson River Estuary, New York. In *Estuarine Research in the 1980s: The Hudson River Environmental Society Seventh Symposium on Hudson River Ecology* (Ed: C.L. Smith) State University of New York Press, pp. 187-216.

Draper, W.M., D. Wijekoon, and R.D. Stephens. 1989. Speciation and quantitation of Aroclors in hazardous wastes based on PCB congener data. Chemosphere, 22: 147-163.

Endicott, D., R. Kreis, D. Griesmer, and L. Mackelburg. 1994. PCB partitioning and bioaccumulation in Green Bay, Lake Michigan. Presented as a poster at the *15th Annual Meeting of the Society of Environmental Toxicology and Chemistry*, October 30 - November 3, 1994. Denver, Colorado.

303881

Exponent, Inc. 1998. Data documentation and interpretation report: Submerged aquatic vegetation and fish community analysis. Prepared for General Electric Company, Albany, NY, April.

Exponent, Inc. 1998. Volume 1: Data report – macroinvertebrate communities and diets of selected fish species in the upper Hudson River. Fall and Spring. Prepared for General Electric Company, Albany, NY. May and September.

Ewald, G., and P. Larsson. 1994. Partitioning of ^{14}C-labelled 2,2',4,4'-tetrachlorobiphenyl between water and fish lipids. *Environmental Toxicology and Chemistry* 13(10):1577-1580.

Feldman, R.S. 1992. *PCB accumulation in Hudson River pumpkinseed sunfish and bullhead: influences of invertebrate prey.* Ph.D. Dissertation, State University of New York.

Fish, P.A. and J. Savitz. 1983. Variations in home ranges of largemouth bass, yellow perch, bluegills, and pumpkinseeds in an Illinois lake. *Trans. Am. Fish. Soc.* 112:147-153.

Gauthier, T.D. 1994. Aroclor Translation Procedures. Internal memorandum, July 7, 1994. Gradient Corporation, Cambridge, MA.

General Electric. 1993a. Data Summary Report, Hudson River Project Sampling and Analysis Program, 1991 Hydrographic Survey of the Upper Hudson River. Prepared by O'Brien and Gere Engineers, Inc., Syracuse, NY. Prepared for General Electric Company, Corporate Environmental Programs, Albany, NY.

General Electric. 1993b. Data Summary Report, Hudson River Project Sampling and Analysis Program, 1991 Sediment Sampling and Analysis Program. Prepared by O'Brien and Gere Engineers, Inc., Syracuse, NY. Prepared for General Electric Company, Corporate Environmental Programs, Albany, NY.

Geoghegan, P., M.T. Mattson, and R.G. Keppel. 1992. Distribution of the shortnose sturgeon in the Hudson River Estuary, 1984-1988. In *Estuarine Research in the 1980s: The Hudson River Environmental Society Seventh Symposium on Hudson River Ecology* (Ed: C.L. Smith) State University of New York Press, pp. 217-227.

Gerking, S.D. 1958. The restricted movement of fish populations. *Biol. Rev.* 34:221-242.

Gilbert, C.R. 1989. Species profiles: life histories and environmental requirements of coastal fishes and invertebrates: Atlantic and shortnose sturgeons. *U.S. Fish Wildl. Serv. Biol. Rep.* 82(11.122). U.S. Army Corps of Engineers. TR EL-82-4. 28 pp.

Gladden, J.B., F.R. Cantelmo, J.M. Croom and R. Shapot. 1988. Evaluation of the Hudson River ecosystem in relation to the dynamics of fish populations. *American Fisheries Society Monograph* 4:37-52.

Gobas, F.A.P.C., J.B. Wilcockson, R.W. Russell, and G.D. Haffner. 1999. Mechanism of biomagnification in fish under laboratory and field conditions. *Environ. Sci. Technol.* 33:133-141.

Gobas, F.A.P.C., M.N. Z'Graggen and X. Zhang. 1995. Time response of the Lake Ontario ecosystem to virtual elimination of PCBs. *Env. Science Technol.* 29(8):2038-2046.

Gobas, F.A.P.C. 1993. A model for predicting the bioaccumulation of hydrophobic organic chemicals in aquatic food-webs: Application to Lake Ontario. *Ecological Modelling* 69:1-17.

Gobas, F.A.P.C., X. Zhang, and R. Wells. 1993. Gastrointestinal magnification: the mechanism of biomagnification and food chain accumulation of organic chemicals. *Environ. Sci. Technol.* 27:2855-2863.

Gobas, F.A.P.C., D.C.G. Muir, and D. Mackay. 1988. Dynamics of dietary bioaccumulation and fecal elimination of hydrophobic organic chemicals in fish. *Chemosphere* 17:943-962.

Gunn, J.M., S.U. Quadri and D.C. Mortimer. 1977. Filamentous algae as a food source for the brown bullhead (*Ictalurus nebulosus*). *J. Fish Res. Board Can.* 34:396-401.

Harkey, G.A., M.J. Lydy, J. Kukkonen, and P.G. Landrum. 1994. Feeding selectivity and assimilation of PAH and PCB in *Diporeia* spp. *Environmental Toxicology and Chemistry* 13(9):1445-1455.

Hasler, A.D. and W.J. Wisby. 1958. The return of displaced largemouth bass and green sunfish to a 'home' area. *Ecology* 39:289-293.

Hjorth, D.A. 1988. Feeding selectivity of larval striped bass and white perch in the Hudson River Estuary. In *Fisheries Research in the Hudson River* (Ed: C.L. Smith) State University of New York Press, Albany, pp. 134-147.

Hydroscience, Inc. 1975. Development of a steady state water quality model for New York Harbor. Volume I, for ISC; 302 pp.

Hydroscience, Inc. 1978a. Estimation of PCB reduction by remedial action on the Hudson River ecosystem. For NYS DEC; 107 pp.

Hydroscience, Inc. 1987b. Seasonal steady state modeling. NYC 208 Task Report, Task 314 for Hazen & Sawyer Engineers, and NYC DWR; 697 pp.

Iannuzzi, T.J., Harrington, N.W., Shear, N.M., Curry, C.L., Carlson-Lynch, H., Henning, M.H., Su, S.H., and Rabbe, D.E. (1996). "Distributions of key exposure factors controlling the uptake of xenobiotic chemicals in an estuarine food web." *Environ. Toxicol. Chem.* 15: 1979-1992.

Johnson, J.H. 1983. Summer diet of juvenile fish in the St. Lawrence River. *New York Fish and Game Journal* 30(1).

Jones, P.A., R.J. Sloan, and M.P. Brown. 1989. PCB congeners to monitor with caged juvenile fish in the Upper Hudson River. *Environ. Toxicol. Chem.* 8:793-803.

MCA/Tetra Tech

303883

Kadlec, M.J. 1994. *Bioconcentration of Congener Specific Polychlorinated Biphenyl (PCB) in Rainbow Trout (*Oncorynchus mykiss*) Exposed to the Water Column of the St. Lawrence River.* M.S. Thesis, State University of New York at Albany.

Kadlec, M.J. and B. Bush. 1994. Bioconcentration of congener specific polychlorinated biphenyl (PCB) in rainbow trout (*Oncorynchus mykiss*) exposed to the water column of the General Motors superfund site, Massena, N.Y. Presented at the *Superfund XIV Conference, Hazardous Materials Research Institute,* Washington, DC.

Klauda, R.J., J.B. McLaren, R.E. Schmitt and W.P. Dey. 1988. Life history of white perch in the Hudson River estuary. *American Fisheries Society Monograph* 4:69-88. Also in *Science, Law and Hudson River Power Plants: A Case Study in Environmental Impact Assessment.*

Kramer, R.H. and L.L. Smith, Jr. 1960. Utilization of nests of largemouth bass, Micropterus salmoides, by golden shiners, Notemigonus crysoleucas. *Copeia* (1):73-74.

Lake, J.L, N.I. Rubinstein, H. Lee II, C.A. Lake, J. Heltsche and S. Pavignano. 1990. Equilibrium partitioning and bioaccumulation of sediment-associated contaminants by infaunal organisms. *Environ. Tox. Chem.* 9:1095-1106.

Larsson, P. 1984. Transport of PCBs from aquatic to terrestrial environments by emerging chironomids. *Environmental Pollution (Series A),* 34:283-289.

Lawler, Matusky & Skelly Engineers. 1992. 1990 Year Class Report of the Hudson River Estuary Monitoring Program. Report to *Consolidated Edison Company* of New York, Inc.

Lawler, Matusky & Skelly Engineers. 1974. 1973 Hudson River aquatic ecology studies at Roseton and Danskammer Point. Volume III: Fish. Prepared for Central Hudson Gas & Electric Corporation, October.

LeBlanc, L. and B. Brownawell. 1994. Tests of biaccumulation models for PCBS: a study of young-of-the-year bluefish in the Hudson River Estuary. Report to the *1993 Polgar Fellowship Program.* pp. VII-1 - VII-42.

Linkov, I., Burmistrov, D. Kandlikar, M. and schell, W.R. (1999). "Reducing Uncertainty In The Radionuclide Transport Modeling for Chernobyl Forests Using Bayesian Updating." In: *"Contaminated Forests: Recent Developments In Risk Identification and Future Perspectives,"* Linkov, I., Schell, W.R., eds. Kluewer, Amsterdam (in press)

Lutz, C.H. and V.A. McFarland. 1994. PCB accumulation factors indicate steady-state bioaccumulation in impounded black bullheads, *Ameiurus melas.* Presented at SETAC. November 9, 1994.

MacDonald, C.R., C.D. Metcalfe, G.C. Balch and T.L. Metcalfe. 1993. Distribution of PCB congeners in seven lake systems: interactions between sediment and food-web transport. *Environ. Toxicol. Chem.* 12:1991-2003.

Mackay, D. 1979. Finding fugacity feasible. *Environ. Sci. Technol.* 13:1218.

Makarewicz, J.C. 1983. Champlain canal fisheries survey: New York state barge canal. Report to Malcolm-Pirnie, Inc.

Makarewicz, J.C. 1987. Hudson River fisheries study. Report to *Halfmoon Electric Project for Interpower* of New York, Inc.

Mansueti, R.J. 1957. *Movements, reproduction and mortality of the white perch in the Patuxent River estuary, Maryland.* Diss. for D.SC. Johns Hopkins Univ.

McBride, N.D. 1985. Distribution and relative abundance of fish in the Lower Mohawk River. *New York State Department of Environmental Conservation.* Stony Brook, New York.

McFadden, J.T. Texas Instruments Incorporated and Lawler, Matusky & Skelly Engineers. 1978. Influence of the proposed Cornwall pumped storage project and steam electric generating plants on the Hudson River Estuary with emphasis on striped bass and other fish populations. Revised. Report to *Consolidated Edison Company* of New York, Inc.

McLaren, J.B., J.C. Cooper, T.B. Hoff and V. Lander. 1981. Movements of Hudson River striped bass. *Trans. Am. Fish. Soc.* 110:158-167.

Menzie, C.A. 1980. The chironomid (*Insecta:Diptera*) and other fauna of *a Myrophyllum spicatum* L. plant bed in the lower Hudson River. *Estuaries*, 3(1):38-54.

Merritt, R.W. and K.W. Cummins. 1978. *An Introduction to the Aquatic Insects of North America.* (Iowa: Kendall/Hunt Publishing Company).

Mesing, C.L. and A.M. Wicker. 1986. Home range, spawning migrations, and homing of radio-tagged Florida largemouth bass in two central Florida lakes. *Trans. Am. Fish. Soc.* 115:286-295.

Morgan, M.G., and M. Henrion. 1990. *Uncertainty: A guide to dealing with uncertainty in quantitative risk and policy analysis.* (Cambridge, UK: Cambridge University Press).

Morrison, H., F.A.P.C. Gobas, R. Lazar, D.M. Whittle, and G.D. Haffner. 1997. Development and verification of a benthic/pelagic food web bioaccumulation model for PCB congeners in western Lake Erie. *Environ. Sci. Technol.* 31:3267-3273.

MPI. 1984. New York State barge canal environmental report maintenance dredging program, 1985-1995. Report to *New York State Department of Transportation.*

Nack, S. and W. Cook. 1986. Characterization of spawning and nursery habitats of largemouth bass (*Micropterus salmoides*) in the Stockport component of the Hudson River National Estuarine Research Reserve. In *Polgar Fellowship Reports of the Hudson River National Estuarine Research*

Reserve Program (Eds: E.A. Blair and J.C. Cooper) New York State Department of Environmental Conservation, The Hudson River Foundation, and The U.S. Department of Commerce.

National Oceanic and Atmospheric Administration (NOAA). 1984. Emergency striped bass study, Study V: biotic factors affecting juvenile striped bass survival in the Hudson Estuary. U.S. Department of Commerce. National *Marine Fisheries Service*. September.

Niimi, A.J. 1997. Evaluation of PCBs and PCDD/Fs retention by aquatic organisms. *The Science of the Total Environment* 192(2):123-150.

Novak, M.A., A.A. Reilly, B. Bush and L. Shane. 1990. In situ determination of PCB congener-specific first order absorption/desorption rate constants using chironomus tentans larvae (insecta: diptera: chironomidae). *Wat. Res.* 24(3):321-327.

Novak, M.A., A.A. Reilly, and S.J. Jackling. 1988. Long-term monitoring of polychlorinated biphenyls in the Hudson River (New York) using caddisfly larvae and other macroinvertebrates. *Arch. Environ. Contam. Toxicol.* 17:699-710.

NUS. April 1984. Volume 1, Feasibility Study, Hudson River PCBs Site, New York, EPA Contract No. 68-01-6699. Table 4-2, pp 4-13.

O'Brien & Gere. 1993. Data Summary Report, Hudson River Project, 1991-1992 Sampling and Analysis Program, Temporal Water Column Monitoring Program. Report to General Electric Company, Corporate Environmental Programs. O'Brien & Gere Engineers, Inc., Syracuse, NY.

O'Brien & Gere Engineers, Inc. 1993. 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'Connor, D.J. 1985. Modeling Frameworks. Toxic Substances Notes, Manhattan College Summer Institute in Water Pollution Control, Manhattan College, Bronx, New York.

Oliver, B.G. 1987. Biouptake of chlorinated hydrocarbons from laboratory-spiked and field sediments by oligochaete worms. *Environ. Sci. Technol.* 21:785-790.

Oliver, B.G., and A. J. Niimi. 1988. Trophodynamic analysis of polychlorinated biphenyl congeners and other chlorinated hydrocarbons in the Lake Ontario ecosystem. *Environ. Sci. Tech.* 22:388-397.

Piavis, P.G. 1991. Yellow perch. Habitat requirements for Chesapeake Bay living resources. *Chesapeake Research Consortium, Inc.* Solomons, Maryland. 2nd Edition. pp 14-15.

Pindyck, R.S. and D.L. Rubinfeld. 1981. Econometric Models and Economic Forecasts. McGraw-Hill Book Company, New York.

Pizza, J.C. and J.M. O'Connor. 1983. PCB dynamics in Hudson River striped bass. II. Accumulation from dietary sources. *Aquatic Toxicology* 3:313-327.

Quinn, S.L, D.W. Bacon and T.J. Harris. 1999. Assessing the precision of model predictions and other functions of model parameters. *The Canadian Journal of Chemical Engineering* 77:723-737, August.

Raney, E.C. 1952. The life history of the striped bass, *Roccus saxatilis* (Walbaum). *Bull. Bingham Oceanog. Coll.* 14:5-110.

Raney, E.C. 1967. Some catfishes of New York. *Conservationist* 21(6):20-25.

Raney, E.C. and D.A. Webster. 1940. The food and growth of the young common bullhead, *Americurus nebulosus* (LeSueur) in Cayuga Lake, New York. *Trans. Am. Fish. Soc.* 69:205-209.

Rhea, J. and M. Werth. 1999. Technical Memorandum Re: Phase 2 Evaluation of Analytical Biases in the USGS Water Column Database. Memorandum to John Haggard, GE Corporate Environmental Programs, March 22, 19899. Quantitative Environmental Analysis, LLC, Montvale, NJ.

Sadzikowski and Wallace. 1976. A comparison of food habits of size classes of three sunfishes (*Lepomis macrochirus* [Rafinesque], *L. gibbosus* [Linnaeus] and *L. cyanellus* [Rafinesque]). *Am. Midl. Nat.* 95:220-225.

Schaefer, R.H. 1970. Feeding habits of striped bass from the surface waters of Long Island, NY. *NY Fish and Game Journal*, 17:1-17.

Schroeder, R.A. and C.R. Barnes. 1983. Trends in Polychlorinated Biphenyl Concentration in Hudson River Water Five Years after Elimination of Point Sources. Water-Resources Investigations Report 83-4206. USGS, Albany, NY.

Schulz, D.E., G. Petrick, and J.C. Duinker. 1989. Complete characterization of polychlorinated biphenyl congeners in commercial Aroclor and Clophen mixtures by multidimensional gas chromatography-electron capture detection. Environmental Science and Technology, 23: 852-859.

Scott, W.B. and E.J. Crossman. 1973. *Freshwater Fishes of Canada.* Bulletin 184. Fisheries Board of Canada, Ottawa.

Setzler, E.M., W.R. Boynton, K.V. Wood, H.H. Zion, L. Lubbers, N.K. Mountford, P. Frere, L. Tucker, and J.A. Mihursky. 1980. Synopsis of biological data on striped bass, *Morone saxatilis* (Walbaum). NOAA Technical Report NMFS Circular 433, FAO Synopsis No. 121, U.S. Dept. of Commerce, Rockville, MD. 69 pp.

Setzler-Hamilton, E.M. 1991. White perch. Habitat requirements for Chesapeake Bay living resources. *Chesapeake Research Consortium, Inc.* Solomons, Maryland. 2nd Edition. pp 12-20.

303887

Shaw, G.R. and D.W. Connell. 1984. Factors controlling bioaccumulation of PCBs. In *PCBs and the Environment Volume 1* National Technical Information Service, pp. 501-516.

Shoemaker, H.H. 1952. Fish home areas of Lake Myosotis, New York. *Copeia* 2:83-87.

Simpson, K.W. and R.W. Bode. 1980. *Common Larvae of Chironomidae (Diptera) from New York State Steams and Rivers*. Bulletin No. 439, New York State Museum, The University of the State of New York

Sloan, R., M. Brown, R. Brandt, and C. Barnes. 1985. Hudson River PCB relationships between resident fish, water and sediment. *Northeastern Environmental Science* 3:137-151.

Sloan, R.J., B. Young, and K. Hattala. 1995. PCB Paradigms for Striped Bass in New York State. Technical Report 95-1 (BEP). New York State Department of Environmental Conservation, Albany, NY.

Small, M. and Fischbeck. 1999. False prediction in Bayesian updating with incomplete models. *Human and Ecological Risk Assessment* 5(2):291-304.

Smith, V.E., J.M. Spurr, J.C. Filkins, and J.J. Jones. 1985. Organocholorine contaminants of wintering ducks foraging on Detroit River sediments. *J. Great Lakes Res.* 11:231-246.

Smith. S. 1987. Trophic status of the spottail shiner, *(Notropis hudsonius)* in Tivoli North Bay's Hudson River fresh tidal marsh. Polgar Fellowship Reports of the *Hudson River National Estuarine Research Reserve Program.*

Steinberg, L.J., Reckhow, K.H., and R.L. Wolpert. 1997. Characterization of parameters in mechanistic models: a case study of a PCB fate and transport model. *Ecological Modelling* 97(1-2):35-46, April.

Steinberg, L.J., Reckhow, K.H., and R.L. Wolpert. 1996. Bayesian model for fate and transport of polychlorinated biphenyl in upper Hudson River. *Journal of Environmental Engineering* 122(5):341-349.

Swindoll, C.M., and Applehans, F.M. 1987. Factors influencing the accumulation of sediment-sorbed hexachlorobiphenyl by midge larvae. *Bull. Environ. Contam. Toxicol.* 39:1055-1062.

Texas Instruments. 1976. Hudson River ecological study in the area of Indian Point. *Thermal effects report.* Dallas, Texas.

Texas Instruments. 1980. 1978 year class report for the multiplant impact study: Hudson River Estuary. Report to *Consolidated Edison Company of New York, Inc.*, September.

Theil, H. 1971. Principles of Econometrics. John Wiley & Sons, New York.

MCA/Tetra Tech

Thomann, R.V. 1981. Equilibrium model of fate of microcontaminants in diverse aquatic food chains. *Can. J. Fish. Aquat. Sci.* 38:280-296.

Thomann, R.V. 1989. Bioaccumulation model of organic chemical distribution in aquatic food chains. *Environ. Sci. Technol.* 23:699-707.

Thomann, R.V. and J.P. Connolly. 1984. Model of PCB in Lake Michigan lake trout food chain. *Environ. Sci. Technol.* 18:65-71.

Thomann, R.V., Mueller, J.A., Winfield, R.P. and Huang, C.R. (1991). Model of fate and accumulation of PCB homologues in Hudson Estuary. *Journal of Environmental Engineering,* Vol. 117, No.2.

Thomann, R.V. 1989. Bioaccumulation model of organic chemical distribution in aquatic food chains. Accepted for publication, *Environ. Sci. Technol.*

Thomann, R.V., J.P. Connolly, and T.F. Parkerton. 1992. An equilibrium model of organic chemical accumulation in aquatic food webs with sediment interaction. *Environmental Toxicology and Chemistry* 11:615-629.

Thomann, R.V., Mueller, J.A., Winfield, R.P., and Huang, C.R. (1989). Mathematical model of the long-term behavior of PCBs in the Hudson River estuary. *The Hudson River Foundation,* New York, NY.

Thomas, W. A. and McAnally, W.H., 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.

Thurston, Kerry A., 1998. "Database Transmittal 10/13/98 (0612.246)." E-mail from Kerry A. Thurston, O'Brien & Gere Engineers, Inc. to John Haggard, General Electric, regarding GE database update as of October 12, 1998.

United States Environmental Protection Agency (USEPA). 1991a. Proposed technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. August 1991. Office of Science and Technology, Health and Ecological Criteria Division, Washington, DC.

United States Environmental Protection Agency (USEPA). 1991b. Phase 1 Report - Review Copy Interim Characterization and Evaluation, Hudson River PCB Reassessment RI/FS. USEPA Work Assignment No. 013-2N84. Prepared by TAMS Consultants, Inc. and Gradient Corporation. August, 1991

United States Environmental Protection Agency (USEPA). 1992. Final Phase 2 Work Plan and Sampling Plan, Hudson River PCB Reassessment RI/FS. USEPA Region II, New York. Prepared by TAMS/Gradient. September, 1992.

United States Environmental Protection Agency (USEPA). 1993a. Phase 2B Sampling and Analysis/Quality Assurance Project Plan, Volume 2 Benthic Invertebrate and Sediment Grab Sampling, Hudson River PCB Reassessment RI/FS, February 18, 1993. USEPA, Region II, New York. Prepared by TAMS/Gradient. February, 1993.

United States Environmental Protection Agency (USEPA). 1993b. Great Lakes water quality initiative technical support document for the procedure to determine bioaccumulation factors. Office of Water. EPA-822-R-93-009, August.

United States Environmental Protection Agency (USEPA). 1994. Great Lakes Water Quality Initiative Technical Support Document for the Procedure to Determine Bioaccumulation Factors. EPA-822-R-94-002. Office of Water, Office of Science and Technology, U.S. Environmental Protection Agency, Washington, DC.

United States Environmental Protection Agency (USEPA). 1995. Great Lakes Water Quality Initiative Technical Support Document for the Procedure to Determine Bioaccumulation Factors. EPA-820-B-95-005. Office of Water, Office of Science and Technology, U.S. Environmental Protection Agency, Washington, DC.

United States Environmental Protection Agency (USEPA). 1996. Phase 2 Report, Further Site Characterization and Analysis, Volume 2B - Preliminary Model Calibration Report, Hudson River PCBs Reassessment RI/FS. Prepared for U.S. Environmental Protection Agency, Region 2, New York, NY, by Limno Tech, Inc., Menzie-Cura & Associates, Inc., and the Cadmus Group, Inc.

United States Environmental Protection Agency (USEPA). 1997. Phase 2 Report, Further Site Characterization and Analysis, Volume 2C - Data Evaluation and Interpretation Report, Hudson River PCBs Reassessment RI/FS. Prepared for USEPA, Region II, New York. Prepared by TAMS et al. February, 1997.

United States Environmental Protection Agency (USEPA). 1998a. Phase 2 Report- Further Site Characterization and Analysis. Volume 2C-A Low Resolution Sediment Coring Report. Addendum to the Data Evaluation and Interpretation Report, Hudson River PCBs Reassessment RI/FS. USEPA, Region II, New York. Prepared by TAMS/Gradient/Tetra Tech. July, 1998.

United States Environmental Protection Agency (USEPA). 1998b. Database for the Hudson River PCBs Reassessment RI/FS. Release 4.1b (Compact Disk). Prepared for USEPA, Region II and the US Army Corps of Engineers, Kansas City District. Prepared by TAMS Consultants, Inc. August, 1998.

United States Environmental Protection Agency (USEPA). 1999a. Phase 2 Report - Further Site Characterization and Analysis, Volume 2D - Baseline Modeling Report Hudson River PCBs Reassessment RI/FS. Prepared for USEPA Region 2 and US Army Corps of Engineers, Kansas City District. Prepared by Limno-Tech, Inc. (LTI), Menzie-Cura & Associates, Inc. (MCA), and Tetra-Tech, Inc. May, 1999.

United States Environmental Protection Agency (USEPA). 1999b. Phase 2 Report - Further Site Characterization and Analysis, Volume 2E - Baseline Ecological Risk Assessment Hudson River PCBs Reassessment RI/FS. Prepared for USEPA, Region 2 and the US Army Corps of Engineers, Kansas City District. Prepared by TAMS/MCA. August, 1999.

Van der Oost, R., H. Heida, and A. Oppenhuizen. 1988. Polychlorinated biphenyl congeners in sediments, plankton, molluscs, crustaceans, and eel in a freshwater lake: Implications of using reference chemicals and indicator organisms in bioaccumulation studies. *Arch. Environ. Contam. Toxicol.* 17:721-729.

Velleux, M. and D. Endicott. 1994. Development of a mass balance model for estimating PCB export from the lower Fox River to Green Bay. *Journal of Great Lakes Research*, Vol. 20, No. 2.

Waldman, J.R. 1988a. 1986 Hudson River striped bass tag recovery program. *The Hudson River Foundation*, New York, NY 48 pp + Append.

Waldman, J.R. 1988b. Private Communication

Webb, R.G. and A.G. McCall. 1973. Quantitative PCB standards for electron capture gas chromatography. Journal of Chromatographic Science, 11: 366-373.

Wells, A.W., J.A. Matousek, and J.B. Hutchinson. 1992. In *Estuarine Research in the 1980s: The Hudson River Environmental Society Seventh Symposium on Hudson River Ecology* (Ed: C.L. Smith) State University of New York Press, pp. 242-264.

Wershaw, R.L., M.J. Fishman, R.R. Grabbe, and L.E. Lowe, ed.s. 1983. Methods for the Determination of Organic Substances in Water and Fluvial Sediments. USGS Techniques of Water-Resources Investigations, Book 5, Laboratory Analysis, Chapter A3. Open-File Report 82-1004. USGS, Denver, CO.

Whittle, D.M. and J.D. Fitzsimmons. 1983. The influence of the Niagara River on contaminant burdens of Lake Ontario biota. *J. Great Lakes Res.* 9(2):295-302.

Wood, L.W. G.Y. Rhee, B. Bush and E. Barnard. 1987. Sediment desorption of PCB congeners and their bio-uptake by dipteran larvae. *Water Res.* 21:875-884

Woolfolk, M., M. Barta, and G. Drendel. 1994. Modeling the accumulation of PCBs in largemouth bass from Lake Hartwell, South Carolina. Presented at *SETAC*.

Young. 1988. A report on striped bass in New York marine water. *NYS Marine Fisheries*, Stony Brook, NY.

THIS PAGE INTENTIONALLY LEFT BALNK

MCA/Tetra Tech