

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

MAY 1999



For

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

**Volume 2D - Book 3 of 4
Bioaccumulation Models**

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

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ACRONYMS

BAF	Bioaccumulation Factor
BCF	Bioconcentration Factor
BSAF	Benthic Invertebrate: Sediment Accumulation Factor
CD-ROM	Compact Disc - Read Only Memory
cfs	Cubic feet per second
cm	Centimeter
Corp.	Corporation
deg. C	Degree Celsius
DOC	Dissolved Organic Carbon
e.g.	For example
EPA	Environmental Protection Agency
et al.	and others
FA	Flow Average (Phase 2 Water Column Monitoring Program)
FFBAF	Forage Fish: Diet Accumulation Factors
FGET	Food and Gill Exchange of Toxic Substances Model
foc	Fraction organic carbon
fps	Feet per second
g	Gram
GBTOX	Green Bay Mass Balance Model
GE	General Electric
GIS	Geographic Information System
GLI	Great Lake Initiative
HOC	Hydrophobic Organic Chemicals
HUDTOX	Hudson River Mass Balance Model
i.e.	That is
kg	Kilogram
m/s	Meters per second
mg/l	Milligrams per liter
mi ²	Square miles
MT	Metric Ton
MVUE	Minimum Variance Unbiased Estimator
NAPL	Non-aqueous Phase Liquid
ng/m ³	Nanograms per cubic meter
ng/L	Nanograms per liter
NOAA	National Oceanic and Atmospheric Administration
NYSDEC	New York State Department of Environmental Conservation
NYSDOH	New York State Department of Health
NYSDOT	New York State Department of Transportation
PCBs	Polychlorinated Biphenyls
PFBAF	Piscivorous Fish: Diet Accumulation Factors

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ACRONYMS

RI/FS	Remedial Investigation/Feasibility Study
RMA-2V	Thompson Island Pool Hydrodynamic Model
ROD	Record of Decision
RPI	Rensselaer Polytechnic Institute
TSS	Total Suspended Solids
µg/g (ppm)	Micrograms per gram (parts per million)
µg/L	Micrograms per liter
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
WASP4	USEPA, Water Quality Analysis Simulation Program, Version 4
TOC	Total organic carbon
TOXI4	Toxic Chemical Module in WASP4
WASTOX	USEPA toxic chemical modeling framework

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Chapter 1

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 (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 (Figure 1-2). The Upper Hudson refers to the 40-mile stretch of river upstream of Federal Dam at Troy to Hudson Falls. 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 (Figure 1-5), used polychlorinated biphenyls (PCBs) to make electrical capacitors. GE discontinued use of PCBs in 1977 when they 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 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 1976, the New York State Department of Environmental Conservation (NYSDEC) imposed a ban on fishing in the Upper Hudson River due to the potential risk posed by consumption of PCB-contaminated fish. In August 1995, the Upper Hudson was re-opened to fishing for striped bass in the Lower Hudson River. This ban remains in effect.

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.

See Book 2 for figures of the river.

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

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

High- and low-resolution sediment coring;

Geophysical surveying and confirmatory sampling;

Water column sampling (including transects and flow-averaged composites);

Ecological field program.

The Database Report (Volume 2A in the Phase 2 series of reports; TAMS/Gradient, 1995) 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 (TAMS/CADMUS/Gradient, 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 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. The scope of the Preliminary Model Calibration Report was limited to documentation of the conceptual approaches, databases and preliminary calibration results for the fate and transport and bioaccumulation models. The Bivariate and Empirical Probabilistic models were included in the Preliminary Model Calibration Report.

1.3 Report Format and Organization

Section 2 of this report contains background information on the theory of PCB uptake into fish, a general summary of the preliminary modeling results and initial conclusions drawn from this work. Section 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. Section 4 contains the results from the bivariate BAF analyses. Section 5 contains initial calibration and validation results for the probabilistic empirical model using the hindcasting sediment and water results from the fate and transport models. Section 6 contains initial calibration and validation results for FISHRAND (mechanistic time-varying model incorporating distributions and based on a Gobas approach) using the hindcasting sediment and water results from the fate and transport models. Section 7 provides preliminary predictive results for 1998 – 2018 based on inputs from the fate and transport models for the constant upstream boundary condition. Section 8 contains a discussion of the uncertainties in the modeling analysis as well as a sensitivity analysis. Section 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 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 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.

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Chapter 2

2. GENERAL BACKGROUND ON PCB UPTAKE

2.1 PCB Compounds

This report examines bioaccumulation of Aroclors for the historical datasets and 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, each of which exhibit varying degrees of bioaccumulation potential, depending on the degree and substitution of chlorination. 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.

Until recently most environmental studies of PCB contamination measured only complex mixtures or total PCBs. Much of the historical PCB data are reported as Aroclors, mixtures comprised of various congeners, some of which are accumulated more effectively than others. While Aroclors accurately describe commercial PCB mixtures, they may be poor descriptors for PCB mixtures in fish and environmental media. This can pose limitations on model development, as discussed in subsequent sections.

Studies that have measured PCBs as individual congeners have provided insights into the bioaccumulation processes for water column- and sediment-based communities. Several researchers have noted that whether or not total PCB levels increase with position in 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 than those with more regular 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 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 was the major route or 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.

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, 1998) 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, 1998).

As part of this modeling effort, Menzie-Cura & Associates have evaluated a number of fish gut contents from the NYS DEC 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 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.

This model 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.

3. MODELING APPROACH: FISH BODY BURDENS

3.1 Modeling Goals and Objectives

The goal of this 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 for human health and ecological risk assessments and aid in decision making regarding options for addressing PCB-contaminated sediments in the upper Hudson.

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 (NYS DEC) 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 NYS DEC data, New York State Department of Health (NYS DOH) data, and the US EPA Phase II data. This model provides ground-truth information on observed relationships between food-web compartments.

FISHRAND and FISHPATH: Gobas Time-Varying Mechanistic Models: These mechanistic, time-varying models are based on the modeling approach presented in Gobas (1993 and 1995). The models rely on solutions of differential equations to describe the uptake of PCBs over time, and incorporate both sediment and water sources to predict the uptake of PCBs based on prey consumption and food web dynamics. Two models are presented: FISHPATH, a deterministic version, and FISHRAND, a fully probabilistic version.

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 FISHPATH and FISHRAND are 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. FISHPATH describes the mass-balance of PCB uptake and elimination on a deterministic basis, while FISHRAND will predict 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) representative of particular habitats or trophic levels, and 5) representative of other fish species. Upon discussion with NYSDEC, USEPA, and NOAA the following species were selected for bioaccumulation modeling:

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;
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, 1991).

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. TAMS/Gradient (1991) 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 than 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 in average total PCB concentrations in the top 5 cm of sediment of 90 percent 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 and FISHPATH models are 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 these models 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 are 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.

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

		Source of Food		
		Phytoplankton Periphyton	Surface Organic Deposits	Deeper Organic Deposits
General				
Physical	Water column or Phytophilous	Zooplankton Phytophilous invertebrates	Phytophilous invertebrates	
Habitat	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.

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

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. We have made an effort to represent this uncertainty in the models by expressing feeding preferences as triangular distributions in FISHRAND and as uniform distributions in the empirical probabilistic model. However, our ability to do this is limited by the available knowledge about the system and the species within it. We do not think that this uncertainty can 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 predict accurately 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 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 Section 3.3. 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 depend 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 Section 3.3, 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:

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

in which, for species *i*:

<i>Cf</i>	=	PCB concentration in fish (wet-weight basis)
<i>fl</i>	=	Lipid fraction in fish
<i>Bw</i>	=	Partial BAF relating fish concentration to water-column concentration
<i>Cs_w</i>	=	PCB concentrations on suspended solids
<i>foc_w</i>	=	Organic carbon fraction of suspended solids
<i>Bs</i>	=	Partial BAF relating fish concentration to upper-zone sediment concentration
<i>Cs_s</i>	=	PCB concentration in upper zone sediments (dry-weight basis)
<i>foc_s</i>	=	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 compliment 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.

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 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 derived factors are compared to those in the literature for reasonableness.

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 FISHRAND and FISHPATH, the mechanistic models.

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 water column 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, only the results for total PCBs, expressed as $\Sigma\text{Tri}+$, will be discussed. 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 (TAMS/Gradient, PMCR, 1996). Results presented here are for total PCBs, expressed as ΣTri^+ .
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 earlier sections. 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.

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 river segments used to assess exposure to fish are the same as those used in the HUDTOX fate and transport model. 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.

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. Fate and transport modeling segments 10 through 29 in the TIP are averaged, and 37 through 41 for Stillwater.

Predictions are provided at four river reaches: 189 (TIP), 168 (Stillwater), 157, and 154 (just above the Federal Dam).

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:

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

where,

$BSAF$ = biota - sediment accumulation factor

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

$C_{sediment}$ = mean PCB concentration in sediments as $\mu\text{g/g}$ 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 considering total PCBs. The Data Evaluation and Interpretation Report (TAMS/CADMUS/Gradient, 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 total water using a BAF approach between water and fish:

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

where,

$PWBAF$ = The bioaccumulation factor between water column invertebrates and total 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:

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

where,

- $FFBAF$ = forage fish bioaccumulation factor
- C_{ff} = concentration in individual forage fish (μg per g lipid)
- C_{diet} = weighted average of diet concentration (μg 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 include largemouth bass, white perch and yellow perch. These species also feed upon invertebrates, which can represent from 10% of the diet in adult largemouth bass to 85% of the diet in the case of yellow perch. The piscivorous fish bioaccumulation factor (BAF) is defined as:

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

where,

- BAF = piscivorous fish bioaccumulation factor relative to diet
- C_{fish} = concentration in piscivorous fish (μg per g lipid)

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

In the case of yellow perch, the weighted average in the diet is expressed as 15 percent forage fish, 20 percent benthic invertebrates and 65 percent water column invertebrates. The largemouth bass diet is 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 benthic invertebrate lipid-normalized concentrations as well as sediment TOC-normalized concentrations.

The BSAF for brown bullhead is defined as:

$$BSAF = \frac{C_{BB}}{C_{sed}} \quad (3-6)$$

where,

$BSAF$ = brown bullhead bioaccumulation factor

C_{BB} = concentration in brown bullhead (μg per g lipid)

C_{sed} = concentration in the sediment (μg per g carbon).

The dietary bioaccumulation factor is defined as:

$$BAF = \frac{C_{fish}}{C_{invert}} \quad (3-7)$$

where,

BAF = brown bullhead bioaccumulation factor

C_{fish} = concentration in brown bullhead (μg per g lipid)

C_{invert} = concentration in benthic invertebrate (μg per g lipid).

3.5 FISHPATH and FISHRAND Mechanistic Modeling Framework

3.5.1 Rationale and Limitations

FISHPATH and FISHRAND incorporate time-varying information on water and sediment concentrations to mechanistically describe the uptake of PCBs into fish tissues. The models are based on the peer-reviewed time-varying Gobas model (Gobas, 1993; Gobas et al.,

1995; 1999). FISHPATH is a deterministic model programmed in Stella™ while FISHRAND is designed to incorporate probability distributions and is programmed in Fortran-90 and Delphi-3.

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 section is presented in section 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 the same proportions as in the probabilistic model.

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:

$$\frac{dC_f}{dt} = k_1 * C_{wd} = k_d * C_{diet} - (k_2 + k_e + k_m + k_g) * C_{fish} \quad (3-8)$$

where:

- k_1 = gill uptake rate (L/Kg/d)
- C_{wd} = truly dissolved concentration in water
- 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} = concentration in fish

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 based on:

- K_{ow} of the compound,
- weight of the fish (V_f , in kg) ,
- rate of chemical transport in the aqueous phase of the gill (Q_w , in units of L/day),
- rate of chemical transport in the lipid phase of the gill (Q_L , in units of L/day).

$$k_1 = \frac{1}{\frac{V_f}{Q_w} + \frac{V_f}{Q_L} * K_{ow}} \quad (3-9)$$

where:

k_1 = gill uptake rate (d^{-1})

Q_w = transport rate in the aqueous phase

Q_L = transport rate in the lipid phase

V_f = fish weight in kg (described by a distribution in FISHRAND)

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

$$Q_w = 88.3 * V_f^{0.6} \quad (3-10)$$

$$Q_L = \frac{Q_w}{100} \quad (3-11)$$

The gill elimination rate is then given by:

$$k_2 = \frac{k_1}{L_f * K_{ow}} \quad (3-12)$$

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:

$$K_d = \frac{E_d * F_d}{V_f} \quad (3-13)$$

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:

$$E_d = \frac{1}{5.3e-8 * K_{ow} + 2.3} \quad (3-14)$$

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

$$F_d = 0.022 * V_f^{0.85} * e^{0.06T} \quad (3-15)$$

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:

$$k_e = 0.02 * k_d \quad (3-16)$$

k_e = fecal egestion rate (d^{-1})

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

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 ($T > 10^\circ\text{C}$), the growth rate constant, k_g , is given by:

$$k_g = 0.01 * V_f^{-0.2} \quad (3-17)$$

For temperatures less than or equal to 10°C ($T \leq 10^\circ\text{C}$), the growth rate constant, k_g , is given by:

$$k_g = 0.002 * V_f^{-0.2} \quad (3-18)$$

3.5.3 Spatial Scale for Model Application

The model takes as starting concentrations the predicted sediment and water concentrations from the fate and transport model. Concentrations are averaged across individual sampling grids to represent the integrating effects of fish foraging and habitat strategies. In the Thompson Island Pool, 29 segments are averaged for water and 5 segments (both cohesive and noncohesive) for sediments. 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 (except for white perch, which tend to range throughout the river, including main channel areas). Water column concentrations are also area-weighted, under the assumption that fish will spend preferentially more time in near-shore areas but are likely to be found throughout the range.

3.5.4 Temporal Scales for Estimating Exposure to Fish

The model uses dissolved water concentrations averaged on a monthly basis, 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. Consequently, the mechanistic models use monthly average dissolved water concentrations as inputs.

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:

$$E[x] = \exp^{\ln(x) - \sigma^2 / 2} \quad (3-19)$$

And the variance as:

$$V[x] = (E[x])^2 + e^{\ln \sigma^2 - 1} \quad (3-20)$$

3.5.5 Application Framework

Two versions of this model have been developed. The first, FISHPATH, was developed using Stella™, a dynamic simulation software package. This version of FISHPATH provides time-varying, but deterministic, results. This model was first developed based on the Gobas published version (1993). The model was run in steady-state mode using the Lake Ontario data presented in Gobas (1993) to demonstrate and verify model functionality and reliability. The model was then coded in Fortran-90 with user interface developed in Delphi-3 and again run in a steady-state, deterministic manner to demonstrate and verify concordance with the Stella version and with the Gobas (1993) published results. The Fortran version, however, has the ability to incorporate probabilistic information and is referred to as FISHRAND.

3.5.5.1 Comparison with Gobas (1993) Lake Ontario Data: The Steady-State Case

The steady-state solution is given by:

$$C_{fish} = \frac{k_1 * C_{wd} + k_d * C_{diet}}{k_2 + k_e + k_m + k_g} \quad (3-21)$$

Figure 3-3 shows the comparison between FISHPATH, FISHRAND, and published data from Gobas (1993). 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, FISHPATH, 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 and FISHPATH. FISHRAND and FISHPATH predict virtually identically to published Gobas results, indicating that the models are performing as published.

3.5.5.2 Comparison with Gobas (1995) Lake Ontario Data: 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.

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 (TAMS/Gradient, 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. Data and methods used for development of the BAFs 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 the lower environmental concentrations in this reach are accounted for), 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 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/carp (*Cyprinus carpio*), 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. Pumpkinseed occupy a lower trophic level: they 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 are 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 Section 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. 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 or 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 report primarily 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 through 1990, 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 have been 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 section 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+ 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 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?” Analysis, in which the performance of historical Aroclor quantitation methods is evaluated in terms of PCB congeners based on a theoretical analysis.

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 $\Sigma\text{Tri-}$). 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 $\Sigma\text{Tri+}$, as described in the Baseline Modeling Report. Because fish tend not to accumulate significant amounts of mono- and dichlorobiphenyls, translations of historical quantitations to either total PCBs or $\Sigma\text{Tri+}$ are expected to be similar.

4.1.1.6 Theoretical “What if?” Analysis

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):

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

$$[Aroclor] = \left(\sum_{j=1}^m area_j \right) \cdot RF_s \quad (4-1)$$

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:

$$\sum_{j=1}^m area_j = \sum_{i=1}^n \frac{[congener_i]}{RF_{ci}} \quad (4-2)$$

where,

- n = number of congeners associated with selected packed column peaks,
- $[congener_i]$ = 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.

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

$$\sum_{j=1}^m \text{area}_j \approx \frac{\sum_{i=1}^n [\text{congener}_i]}{RF_p} \quad (4-3)$$

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:

$$RF_p = [\text{Aroclor}_{\text{std}}] \cdot \frac{\sum_{j=1}^m \text{wt \% peak}_j}{\sum_{j=1}^m \text{area}_j} = [\text{Aroclor}_{\text{std}}] \cdot \frac{\sum_{i=1}^n \text{wt \% congener}_i}{\sum_{k=1}^n \text{area}_k}$$

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

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

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:

$$[\text{Aroclor}] \approx \frac{\sum_{i=1}^n [\text{congener}_i]}{\sum_{j=1}^m \text{wt \% peak}_j} \quad (4-5)$$

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 (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.

The congener data ΣTri^+ may be regressed against Hazleton reported results for total PCBs 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.

$$\Sigma\text{Tri}^+ = -200.7 + 0.8720 \times 1977 \text{ Sum (1016-1254)} \quad R^2 = 99.4\%$$

(862.7) (97.2) (0.0065)

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

(881.6) (98.7) (0.0093)

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

(961.8) (108.4) (0.0109)

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

(1762) (198.4) (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 significantly different from the theoretical relationship obtained between sum of congeners and the Hazleton 1992 method using the "what if?" analysis presented in 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 which 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 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 which 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 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 slightly 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 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.

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	$0.8642 \cdot (\text{Aro 1016} + \text{Aro 1254})$	WI, RAL
1979-1982	$1.2210 \cdot (\text{Aro 1016} + \text{Aro 1254})$	RAL, HAZ
1983-1990	$1.3070 \cdot (\text{Aro 1016} + \text{Aro 1254})$	HAZ, RAL
1990-1993	$1.4157 \cdot (\text{Aro 1016} + \text{Aro 1254}/60)$	HC
1992-1997	$0.8754 \cdot (\text{Aro 1248} + \text{Aro 1254} + \text{Aro 1260})$	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 (TAMS/Gradient 1996) and earlier by Brown et al. (1985), a good predictor of annual average fish PCB body burden 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 sparsity 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 (TAMS/Gradient 1991). For the Phase 2 analysis, USGS data have been obtained through the end of Water Year 1995. Significant 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 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 Aidentified 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 Aby 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, 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. 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^+ .

The interpretation of USGS capillary column analyses is less clear at present (although QEA is currently engaged in examining original chromatograms and sample analysis reports). During the period 1988 to Sept. 1991 USGS continued the approach of selecting a single or mixed Aroclor standard for quantitation. In contrast to earlier years, however, only Aroclors 1242, 1248 and 1254 are reported as identified Aroclors; Aroclor 1221, 1232 and 1016 standards were not used. From October 1991 on, USGS consistently reported quantitations against Aroclor 1242 and 1254 standards, presumably based on a specified rule for peak separation. Because Aroclor 1242 was the lightest Aroclor standard used, it is suspected, pending further investigation, that USGS data for this period should also approximate ΣTri^+ .

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; however, during 1994-1996 GE did not sample below Thompson Island Dam, so USGS data are used. For the Thompson Island Pool, 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 Schuylerville. USGS Fort Miller data, commencing in 1987, are assumed representative of the Thompson Island Pool for 1987-1990. For 1991 on, GE Thompson Island Dam-West data are used for the Thompson Island Pool, with application of a bias correction factor. This bias correction factor (discussed in the Baseline Modeling Report) is necessary to make these nearshore concentration measurements approximate center-channel concentrations, consistent with estimation from downstream USGS data in earlier years.

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. Except for 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 0.56.

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 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 Σ Tri+ 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 Σ Tri+ for the Hudson River between Fort Edward and Federal Dam, with separate estimates for cohesive and non-cohesive sediments. We assumed that cohesive (fine-grained) sediment concentrations are most relevant to fish exposure pathways from sediment independent of water column concentrations. Two different approaches were used to process sediment data (Table 4-8). Method 1 uses an arithmetic weighted average of model predictions of cohesive and non-cohesive sediment concentrations, based on the relative area in each sediment type for a reach and the assumption that fish show a preference for organic sediments, spending 75% of their time in such sediments. These results have been normalized to organic carbon (OC) concentrations. A similar approach was used for the probabilistic bioaccumulation model (section 5) and FISHRAND (section 6); however, for the bivariate BAF analysis weighted model predictions are used directly, without any attempt to derive corrected moment estimates from a log-normal distribution assumption. Method 2 uses model predictions of dry-weight sediment concentrations from the cohesive sediment area only. These estimates are reported in Table 4-8 as base-10 logarithms, as they were used in a log-log regression model, as described below.

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 TAMS/Gradient 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 $\Sigma\text{Tri}+$ in dated layers of this core appear to be less than concentrations in cohesive sediment above Federal Dam near Waterford 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 near Waterford, diluted by incremental flow from the Mohawk. Sediment concentrations at this station were therefore extended for 1993-1997 based on relationship to concentrations in cohesive sediment near Waterford. For Method 1, the average ratio between Group 3 sediment and Core 11 concentrations was used to extend the record. For Method 2, post-1992 concentration estimates are based on simple 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 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 (TAMS/Gradient 1996), all analyses presented here are in terms of Σ Tri+ 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 (Section 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 groups described above and across all groups based on (1) a standard BAF approach with regression to water-column concentration only, and (2) bivariate BAF regression on water column and sediment concentrations. Results were generally consistent among groups, implying that cross-sectional models across groups are appropriate.

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. In all species, except perhaps goldfish, there appears to be a positive correlation between fish body burden and both water and sediment concentrations. However, the strength of the relationships vary by species. For instance, brown bullhead have a stronger linear relationship to sediment, while pumpkinseed have a stronger linear relationship to water concentrations. In all cases, the variance or spread of the distribution increases with concentration. This condition of scale-dependent variability (heteroscedasticity) can present problems for regression analysis and suggests use of a log-log transformation (see Figure 4-4 for pumpkinseed). A log-log transformation results in a stabilization of variance; however, the transformation implies that the relationship of fish body burden to water and sediment concentration is non-linear (multiplicative rather than additive model) and that BAFs are also scale-dependent, rather than constant.

Two sets of regressions are presented. The first set uses arithmetic average concentrations in fish and water, coupled with Method 1 estimates for sediment. The second set uses log-log-regressions, with sediment estimates given by Method 2 (see Table 4-8). For each set, regressions were conducted against water concentration only (standard univariate BAF approach), 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 (R^2 ranging from 26 to 72 percent); however, the coefficient on water column concentration is in all cases statistically significant at the 95 percent confidence level.

Table 4-10 shows a bivariate regression on arithmetic average water concentrations and Method 1 sediment concentrations. The bivariate approach increases R^2 for all species, with all but goldfish having adjusted multivariate R^2 values greater than 67 percent. Large improvement, however, is seen only for brown bullhead and largemouth bass, species which presumably have a larger sediment-originated food chain pathway of PCB bioaccumulation.

Better statistical results are obtained with a log-log transformation to remove heteroscedasticity. Table 4-10 displays the results of a univariate log-log BAF analysis of fish lipid concentration against water concentration. The explanatory power of water-only models is again relatively low, with R^2 values ranging from 38 to 77 percent. Much of the unexplained variability is due to differences among sample location groups, with the regression line for Group 1 (Thompson Island Pool) generally lying parallel to, but above the regression line for downstream groups (see, for instance, Figure 4-4). This suggests that differences in sediment concentrations among locations may increase explanatory power.

Table 4-11 displays the results of the log-log bivariate BAF analysis. Including sediment concentration as an independent variable brings all R^2 estimates above 74%, with a large increase for brown bullhead, goldfish, and largemouth bass. A large increase in predictive ability for these species occurs because the coefficient on sediment is large, presumably reflecting a significant sediment food chain contribution to body burden. For pumpkinseed and white and yellow perch the coefficient on sediment concentration is smaller, and a correspondingly smaller increase in R^2 occurs.

Figures 4-5 through 4-7 show observed versus predicted average concentrations from the log-log bivariate BAF model for brown bullhead, largemouth bass, and pumpkinseed. In each case a strong positive correlation is evident, although there is also clearly variability which is unexplained by the simple BAF model.

4.3 Discussion of Bivariate BAF Results

4.3.1 Comparison to Published BAF Values

For comparison to published BAF results, Tables 4-9 through 4-12 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. For the log-log models, the BAF is scale-dependent, and values reported in the tables are based on typical Upper Hudson concentrations of 100 ng/l and surface sediment concentrations of 10 mg/kg ΣTri^+ .

The calculated \log_{10} BAFs for the univariate arithmetic model range from 6.28 for pumpkinseed to 6.66 for largemouth bass on a L/kg basis. Estimates are slightly lower for the bivariate arithmetic model. These univariate BAFs, relating lipid-normalized body burden in fish to total PCB concentrations in water, are sometimes denoted as BAF_1^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_1^{fd} . The two forms of the univariate BAF can be related as

$$BAF_1^{tc} = \frac{BAF_1^t}{f_d} \quad (4-6)$$

where f_d is the freely dissolved fraction of the chemical. Under average conditions in the Upper Hudson, the freely dissolved fraction of Tri+ is estimated, based on analysis of three-phase partitioning in the DEIR for representative congeners, to be about 50 percent for Σ Tri+ PCBs. Using Equation (4-6), base-10 logarithms of BAF_1^{fd} s would thus be equal to the calculated BAF_1^t s plus about 0.3 log units.

U.S. EPA (1994) summarizes estimated BAF_1^{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_1^{fd} of 6.51 for alewives. Similar to pumpkinseed, this species feeds on invertebrates that accumulate PCBs from the water column (assumed alewife diet of 60 percent zooplankton and 40 percent *Diporeia* sp.) The Gobas model estimate compares well to the estimate of 6.21 to 6.28 + 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 6.44 to 6.66 + 0.3.

4.3.2 Fit of Bivariate Models to Observations

A bivariate BAF approach, including both water and sediment as independent variables, improves on the ability of a simple univariate BAF approach to fit observations of fish body burdens of Σ Tri+ PCBs. Section 4.2 presents the bivariate model in two forms: as an arithmetic and as a log-log regression. The log-log model has advantages in terms of both predictive ability and residual error structure. A disadvantage is that the log-log model introduces a non-linearity into the BAF relationships. This non-linearity is not large, however, in the range of concentrations observed in the Hudson River. For example, Figure 4-8 compares the arithmetic and log-log univariate (water-only) models for pumpkinseed, showing the close similarity between the regression lines. (The univariate rather than the better-performing bivariate model is shown here for clarity of display in two dimensions).

While the overall model fit is good, many individual data points are not accurately predicted by the bivariate model. 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 4-9 through 4-11. 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 4-9), both models do a reasonable job of capturing trends in concentration in Group 2 (although underestimating observations for 1992 and 1997), while in Group 4 the arithmetic model provides a closer fit to observations. Both models underpredict concentrations in brown bullhead in Group 4 from 1993 on, probably reflecting an error in sediment concentrations which are based on high resolution core data through 1992, but estimated thereafter.

For pumpkinseed (Figure 4-10), model fit is quite close in Group 4. This species is less sensitive to sediment concentrations than brown bullhead (as described in Section 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, the model does not match the strong drop in PCB body burdens in the most recent, 1997 samples.

Finally, for largemouth bass (Figure 4-11), 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.

Variability in observations which 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 mis-represent 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 which should minimize the regression coefficient. The major source of unrepresented variability is likely to be uncertainty in the estimates of water column exposure concentrations. This would explain why model fit is better for brown bullhead, which depends strongly on sediment concentrations, than for pumpkinseed, which is most strongly driven by water column concentrations. In addition, errors in model fit appear to increase upstream, with the highest error variance for estimates within the Thompson Island Pool, particularly for observations prior to 1991. Water column concentrations in the Thompson Island Pool are expected to be more variable than those downstream, as this is near the source area; further, water column concentration estimates prior

to the start of GE sampling in 1991 are based on downstream USGS measurements and should be regarded as highly uncertain.

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, nor 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 Sections 5 and 6.

4.3.3 Relative Importance of Sediment and Water Pathways

As discussed in Section 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 which 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.

Two methods which can be used to make statements about the relative importance of the independent variables in a multiple regression model are normalized beta coefficients and elasticities (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:

$$\frac{Y_i - \bar{Y}}{s_y} = \beta_1 \frac{X_{1i} - \bar{X}_1}{s_{x1}} + \beta_2 \frac{X_{2i} - \bar{X}_2}{s_{x2}} + \varepsilon_i \quad (4-7)$$

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

$$E_j = \beta_j \frac{\bar{X}_j}{\bar{Y}} \approx \frac{\frac{\partial Y}{\partial X_j}}{\frac{\bar{Y}}{\bar{X}_j}} \quad (4-8)$$

Normalized beta coefficients and elasticities for the bivariate arithmetic model are given in Table 4-13. For pumpkinseed, which forage primarily in the water column, and for white and yellow perch, which migrate small distances, water column concentrations appear to be the most important variable in determining body burden of $\Sigma\text{Tri}+$ PCBs. In contrast, brown bullhead, resident fish which forage on the bottom, are more sensitive to sediment concentrations. At the highest trophic level, largemouth bass, which are primarily piscivorous, appear to respond about equally to water and sediment pathways, suggesting that the bass integrate food web contributions from both water column and sediment/detrital feeders.

4.4 Summary

A bivariate BAF analysis, relating lipid-based $\Sigma\text{Tri}+$ 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.

The increase in explanatory power provided by the bivariate approach is greatest for those species which 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, occupying the highest trophic level in the water column, appear to integrate both sediment and water pathways.

The BAF analysis summarizes the historic data on PCB concentrations in fish, water, and sediment. It is not intended to be a predictive tool, 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 sections 5 and 6.

Chapter 5

5. CALIBRATION OF PROBABILISTIC BIOACCUMULATION FOOD CHAIN MODEL

The components of the food chain model and general model structure are described in Section 3.5. The model takes as exposure concentrations the summer-averaged total ($\Sigma\text{Tri}+$) water concentration for PCBs and the annual average sediment concentration for PCBs normalized to fraction organic carbon. As discussed in Section 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 4.1 of the TAMS/Gradient database. Results presented here are draft and subject to change based on ongoing model refinement.

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 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 (TAMS/Gradient, 1996) report are derived for the calibration congeners, Aroclors 1016 and 1254, and for total 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 striped bass, largemouth bass, brown bullhead, pumpkinseed, American shad, and American eel.

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 ($\mu\text{g/g}$) 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 (Chernoff, 1995, personal communication) 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 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. 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 Σ Tri+ PCBs (all species combined) by river mile. The mean BSAF for river miles 100, 189 and 189.5 are higher and have wider error bars than the other river miles. The BSAF for river mile 189 is about 6; the BSAF for river miles 100 and 189.5 are about 3. The BSAF for the other river miles are about 1, with very narrow error bars.

Figure 5-2 also shows the BSAF Σ Tri+ PCBs (all river miles combined) by species. The BSAF for chironomids, about 4, is higher and has wider error bars than the other river miles. The BSAF for Isopods, about 3, also has wide error bars. BSAF for the remaining river miles range between 0 and 2, with narrower error bars.

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 (LTI et al., 1996). Figure 5-3 presents the cumulative distribution for BSAF estimated for Σ Tri+ PCBs.

The modeled $\Sigma\text{Tri}+$ PCB distributions in benthic invertebrates compared favorably to the observed distributions of $\Sigma\text{Tri}+$ PCB concentrations as presented in the PMCR (LTI et al., 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 Section 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 (TAMS/Tetra Tech/Gradient, 1998 - pending publication) 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 total water concentration (*i.e.*, uptake from both the dissolved and particulate phases). This alternative approach was explored because the historical data only measured total PCBs. In the PMCR (LTI et al., 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 II 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.

This study showed that the PCB congener pattern in the chironomid tissue differed significantly from the congener pattern observed in the water (Novak, 1988; TAMS/Gradient, 1991). Other studies have also found this to be the case (Kadlec and Bush, 1994). Water column invertebrates respond on the order of days to changes in water column concentrations of PCBs. Novak (1984) found that chironomids exposed to the water column show concentrations 10^5 times higher than water concentrations within 96 hours. The data show that concentrations in water column invertebrates represent the first important link in the biomagnification of PCBs along the aquatic food chain.

Other studies have shown that kinetic processes are significant even before this stage of the food web (Skoglund *et al.*, 1996). In a model developed for the Great Lakes, Skoglund found that phytoplankton accumulate more PCB than would be predicted by equilibrium partitioning alone. Under low growth conditions, the kinetic model and the equilibrium model results were similar. However, during periods of intense growth, the equilibrium model did not fit the observed data as well as the kinetic model.

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:

$$\text{BAF}_{\text{water}} = C_{\text{invert}}/C_{\text{water}} \quad (5-1)$$

where,

$\text{BAF}_{\text{water}}$ = 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 $\text{BAF}_{\text{water}}$ 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 section 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 section 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 sections.

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 total 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 relatively steadily decline 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).

Figure 5-5 shows that mean concentrations are similar for river miles 189.5 and 194.1, and significantly higher at these locations than elsewhere in the river. This figure shows that forage fish total PCB concentrations at most of the river miles ranged from just above 0 to about 300 $\mu\text{g/g}$. 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 total 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 (LTI et al., 1996). The lower portion of Figure 5-5 shows the cumulative distribution function for total 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 Total PCBs

Figure 5-6 shows the ratio of largemouth bass greater than 25 cm to pumpkinseed less than 10 cm for total 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.

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

Table 5-1 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 5-7 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) and 189 (TIP) as these are the two locations with the most fish data. Figure 5-8 shows the results of the calibration on lipid-normalized basis for each of the river miles, Figure 5-9 presents the results on a wet-weight basis assuming the same percent lipid as FISHRAND and FISHPATH (average of all lipids across river miles or 0.15 for largemouth bass). Wet weight concentrations were not estimated for pumpkinseed.

5.7 Discussion of Results

On a lipid-normalized basis, average concentrations predicted by the model show excellent agreement with observed averages. Similarly, the predicted 90th percentile concentrations predicted by the model show good agreement with maximum observed concentrations, except for particular years showing temporary increases in body burdens. The inability of the model to capture 1991 and 1992 observed concentrations for largemouth bass is related to two factors: the first is that the model is an empirical model. 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. The second is that the predictions in fish will mirror concentrations in sediment and water. The largemouth bass, as a top piscivore and large fish, integrates both sediment and water exposure sources but to some extent mirrors water. Consequently, these concentrations are sensitive to the specified water concentrations. While 1992 shows a transient increase in whole water concentrations (see Figure 5-7), it is not high enough to be reflected in fish concentrations.

The assumption of percent lipid plays an important role in estimating wet weight concentrations from the predicted lipid-normalized concentrations. On a lipid-normalized basis, model predictions and observed data show excellent agreement. The agreement is less robust when evaluated on a wet weight basis. This may be attributable to uncertainties in lipid quantitation, as well as year-to-year changes and fluctuations in lipid composition in the fish population of interest.

Largemouth bass percent lipid values, evaluated over all years and sampling locations, show significant variability, although for most years the lipid fractions are between one and three. The lipid content of a fish can make a tremendous difference in predicted concentrations. To represent the potential population of largemouth bass, we chose to use the median lipid value for the upper river as a whole, under the assumption that a fish in one location could equally well have been found at a different location. Under this assumption, predicted wet weight

concentrations show less of a good fit with the historical data than using the observed lipid content from year-to-year. However, for future predictions, unless a mechanistic explanation could be hypothesized, there is very little basis upon which to vary lipid content from year-to-year. Consequently, we prefer to use a median lipid content to translate lipid-normalized results to wet weight results.

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6. FISHPATH AND FISHRAND: TIME-VARYING MECHANISTIC MODELS BASED ON A GOBAS APPROACH

6.1 Model Input Data

Both the historical NYS DEC and US EPA Phase II datasets were used in the development and validation of the FISHPATH and FISHRAND models. 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 NYS DEC 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.

6.1.1 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}) (Σ Tri+); and,
- Total organic carbon in sediment (inside TIP versus outside TIP).

6.1.1.1 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. The probabilistic empirical model uses TOC-normalized sediment concentrations and whole water concentrations, while FISHRAND and FISHPATH use truly dissolved water concentrations and dry weight sediment concentrations ($\mu\text{g PCB} / \text{g solid}$).

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.

Initial concentrations are not available for each of the FISHRAND compartments in 1977 for all river miles. Since the model requires initial PCB concentrations to be specified and these were all set to zero, the model requires several years to reach a quasi-equilibrium state in which PCB concentrations (in fish, in particular) are not sensitive to initial concentrations. Therefore, all modeling results are considered robust beginning in the early 1980's.

6.1.1.2 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. Monthly temperatures are characterized by distributions that are the same for each location.

Actual monthly averages were used for the periods for which there were measurements available. For time periods for which there were no measurements, the following approach was taken: temperature was regressed day of the month for each month, and then the monthly average was obtained as the square of the area under the regression line, divided by the number of days in that month.

Additional averaging was made over all years of observations to obtain "annually averaged monthly average" model for temperature (in which average temperatures for a fixed month in different years are equal). This model was applied to the actual monthly average temperature measured to obtain residuals from the annually averaged model. The residuals are well described by a normal distribution with a mean of zero and a standard deviation of 2.21. Thus in time periods for which there were no measurements (1977-1990, and 1998-2018), FISHRAND uses a normal distribution of the temperature with the mean equal to the annually averaged monthly average described above (dependent on month number only) and a standard deviation of 2.21 (not dependent on time).

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. The approach taken was to adjust the distribution upward 20% in the sensitivity analysis to evaluate the potential effect of temporary increases in temperature during the summer months.

6.1.1.3 Total Organic Carbon in Sediment

The distribution for total organic carbon content is shown in Table 6-1. Based on 1993 data, mean TOC does differ significantly within the Thompsons Island Pool as compared to other upper Hudson locations outside the pool. Consequently, two distributions were used in this analysis. Section 8.0, Uncertainty Analysis, discusses the sensitivity of the model to TOC assumptions.

6.1.1.4 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 Σ Tri- PCB mixture. Several approaches for characterizing K_{ow} were evaluated. Individual PCB congeners contained in the Σ Tri+ 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, 1995).

6.1.2 Species-Specific Data

Data from the historical NYS DEC fish monitoring results, US EPA Phase II 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
- Dietary composition of fish diet

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.

6.1.2.1 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 NYS DEC largemouth bass data (no exclusions as all fish were greater than 25 cm) and none of the EPA Phase II data (fish were all very small). The Phase II data was also not suitable for pumpkinseed, which were all very large fish (larger than the largemouth bass). For yellow perch, the historical NYS DEC dataset showed a lipid distribution that was very low when compared to the literature (Great Lakes technical support documents) and to the Phase II dataset. Thus, only Phase II yellow perch lipid data were used in developing a lipid content distribution. White perch and brown bullhead lipid were obtained from the historical NYS DEC dataset. 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.

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, 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. If there were clear differences, an effort was made to discern the origin of the 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.

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. The yellow perch distribution based on the NYS DEC data was significantly lower than a) values from the literature, and b) the measured lipid from the EPA Phase II program. As initial model calibration runs showed yellow perch concentrations were significantly overpredicted, the Phase II data only were used to derive the lipid distribution. Subsequent model calibration results for yellow perch were then within the range of observed data.

Lipid content represents an important parameter in all the bioaccumulation models. Further analysis on lipid content is currently being carried out and a more detailed rationale will be provided.

Lipid Content for Benthic and Water Column Invertebrates

The US EPA Phase II 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 the literature.

Literature values were used to construct a phytoplankton distribution (Gobas, 1993). Only the spottail shiner consumes a small amount of phytoplankton.

6.1.2.2 Fish Weight

Figure 6-3 present the cumulative distribution functions for fish weight for each of the fish species. As described previously, an effort was made to determine if there were observable relationships between weight and lipid content which should be accounted for in the model structure. The same data were used to develop both the lipid content and weight distributions.

6.1.2.3 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 Section 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.

6.2 Results of the Calibration Exercise

Using the predicted hindcasting for sediment and water from the fate and transport models, Figure 6-4 shows the results of the calibration for each of the fish species for both lipid-normalized and wet weight concentrations. In general, the model is better at capturing lipid-normalized concentrations versus wet weight concentrations. Table 6-2 presents the relative percent difference between the mean FISHRAND predicted concentration and the observed concentrations for lipid-normalized and wet weight results across all species and locations. The lowest upstream modeling location (river mile 154, just above the Federal Dam) is compared to monitoring results from river mile 152, just below the Federal Dam. Thus, these results may not be directly comparable.

The model predicts a monthly fish body burden, which can be further averaged to represent a seasonal or annual concentration. To evaluate whether the model was capturing observed seasonal differences, results from river mile 154 were compared to the NOAA 1995 dataset for river mile 152. These results are shown in Figure 6-5. Again, these two locations may not be directly comparable. The model shows that concentrations tend to increase in the late summer, when feeding is maximized. This is also the time that lipid content is likely to be highest; thus, lipid-normalized concentrations would be at their lowest. FISHRAND does not currently adjust the lipid distribution seasonally insofar as lipid increases and decreases throughout the year will balance each other out. A t-test using the NOAA 1995 dataset of lipid content between spring and fall was highly insignificant in the case of white perch and highly significant in the case of yellow perch.

Historical data for spottail shiner and benthic invertebrates is only available for 1993. The mean benthic invertebrate concentration within the TIP was 13.9 ppm wet weight, as compared to 14.0 predicted by FISHRAND.

7. INITIAL BIOACCUMULATION MODEL PREDICTIONS

This section describes the initial modeling results from the probabilistic empirical model as well as FISHRAND. Sediment and water concentration inputs are taken from the fate and transport model (Books 1 and 2). These results may be modified in response to additional refinements in the transport and fate modeling results. Two modeling predictions were provided from the fate and transport modelers: a zero upstream boundary condition (cessation of the source at Ft. Edward) and a constant upstream boundary condition (assuming a small but constant upstream source). A comparison of these two results shows that they are very close. Thus, only the constant upstream boundary condition was evaluated.

7.1 Probabilistic Empirical Model

The model takes TOC-normalized annual average sediment concentrations and summer-averaged whole water concentrations as inputs. Based on the distributional relationships between compartments presented in Section 5, predictions were made for the zero and constant upstream boundary conditions for pumpkinseed and largemouth bass.

7.1.1 Sediment and Water Concentration Inputs

Figure 7-1 shows the sediment and water concentrations used for the zero upstream boundary condition, while Figure 7-2 presents the sediment and water concentrations predicted from the fate and transport model under the constant upstream boundary condition. These figures show that sediment concentrations decline exponentially between 1998 and 2018 under both scenarios and also show very similar concentrations. Whole water concentrations show significant variability over time.

7.1.2 Predicted Largemouth Bass Body Burdens under Zero Upstream Boundary Conditions

Figure 7-3 shows the empirical probabilistic model lipid-normalized predictions for largemouth bass at river miles 189 and 168, while Figure 7-4 presents the same results on a wet weight basis. Under the assumptions presented here, largemouth bass only barely achieve 2 ppm on an average basis for river mile 189 by the end of the modeling period. For river mile 168, largemouth bass achieve 2 ppm wet weight PCB concentration on an average basis by 2010. Average wet weight concentrations hover above and below 2 ppm for several years. The upper-bound concentrations (represented by the 90th or 95th percentiles) do not achieve 2 ppm by the end of the modeling period for these river miles.

At river mile 157, 2 ppm is predicted for 2005 on a mean basis, and as soon as 2003 for river mile 154. The 90th percentile predicted concentration for river mile 157 achieves 2 ppm by 2011, and 2017 for the 95th percentile. In the calibration, the 90th percentile concentrations typically occurred at or above the maximum observed concentration, except for 1991 and 1992 for largemouth bass at river mile 168. Thus, it is likely that in the absence of predicted short term fluxes or spikes in water column concentrations, the 90th percentile predicted concentration will be protective of the population at this level. The predicted 90th percentile concentration

achieves 2 ppm by 2007, and the 95th percentile predicted concentration achieves 2 ppm by 2008 for river mile 154.

7.1.3 Predicted Largemouth Bass Body Burdens under Constant Upstream Boundary Conditions

Figure 7-6 shows the empirical probabilistic model lipid-normalized predictions for largemouth bass at river miles 189 and 168, while Figure 7-7 presents the same results on a wet weight basis. Under the assumptions presented here, largemouth bass only barely achieve 2 ppm on an average basis for river mile 189 by the end of the modeling period. For river mile 168, largemouth bass achieve 2 ppm wet weight PCB concentration on an average basis by 2010. Average wet weight concentrations hover above and below 2 ppm for several years. The upper-bound concentrations (represented by the 90th or 95th percentiles) do not achieve 2 ppm by the end of the modeling period.

7.2 FISHRAND Results

This model uses truly 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 constant upstream boundary condition. As discussed next, the fate and transport modeling results for the zero and constant upstream boundary conditions were similar enough that only the constant upstream boundary condition was modeled using FISHRAND.

7.2.1 Sediment and Water Concentration Inputs

Figure 7-9 shows the sediment and water concentrations used for the zero upstream boundary condition, while Figure 7-10 presents the starting sediment and water concentrations predicted from the fate and transport model under the constant upstream boundary condition. These figures show that sediment concentrations decline exponentially between 1998 and 2018 under both scenarios and also show very similar concentrations. Dissolved water concentrations show significant variability over time. Monthly average concentrations are used in FISHRAND for water and annual average sediment concentrations.

7.2.2 Predicted PCB Concentrations in Fish under Constant Upstream Boundary Conditions

Figures 7-11 through 7-18 present the results of the predictive modeling for river miles 189, 168, 157 and 154. The odd-numbered plots are lipid-normalized, the even-numbered plots show the wet weight results. The mean predicted concentration is depicted by a square line, while the 95th percentile is depicted by the triangular line.

Table 7-1 presents a range of years that particular target levels that have been used in other contexts will be achieved. These target levels should not be viewed as endorsement of particular goals, but rather merely provide perspective on the range and trend of predicted

concentrations. The selected target levels include: the FDA Action Level of 2 ppm wet weight, and several ranges of values designed for the protection of human consumption of fish from the Great Lakes Uniform Sportfish Advisory Task Force. None of the fish for any of the locations achieve concentrations less than 0.5 ppm within the modeling period (up to 2018). Generally, there are approximately ten years between the mean and 95th percentile in achieving any particular target level, suggesting that ten years is an appropriate interval for capturing the observed range in population concentrations.

The best estimate is the center of the ranges shown in Table 7-1. A final quantitative uncertainty is currently underway, but initial results suggest that based on the relative percent difference between predicted and observed, as well as an initial evaluation of parameter uncertainty, the error bounds on the mean estimate of time to achieve any given target is approximately plus or minus three years.

Concentrations in largemouth bass in the TIP achieve 2 ppm on a mean basis several years before river mile 168. As shown in Figures 7-9 and 7-10, predicted dissolved water concentrations are typically higher at river mile 168 than in the TIP. Consequently, those fish who derive much of their body burden from water column sources (such as the largemouth bass), will reflect this exposure through higher body burdens. The brown bullhead, by contrast, exposed to higher sediment concentrations within the TIP and primarily a bottom feeder, does not achieve 2 ppm within the modeling period in the TIP, but does so at river mile 168.

7.3 Discussion of Results

The empirical probabilistic model results show increasing spread in the concentrations at higher percentiles. That is, the difference between the 90th and 95th percentiles is greater than the difference between the median and the average, for example. This is an attribute of lognormal distributions.

Results of a sensitivity analysis conducted for FISHRAND are presented in section 8. This analysis shows that lipid content is an important variable in predicting fish body burdens.

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 decision makers 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. Any probabilistic analyses that might be planned for the human health and/or ecological risk assessments will benefit from these results.

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 0.2 ppm wet weight, or 2.0 ppm wet weight), these results can be explicitly predicted. For example, under current assumptions and based on the results of the fate and transport modeling, both FISHRAND and the empirical probabilistic model predict that concentrations in largemouth bass will achieve 2 ppm at Waterford within the prediction period under the constant upstream boundary condition.

FISHRAND modeling results suggest that PCB concentrations in largemouth bass decline more quickly within the TIP than at river mile 168. As discussed above, this is partially attributable to the higher predicted dissolved water concentrations at river mile 168 as compared to 189 from the fate and transport models. This higher dissolved water concentration will be reflected in the organisms with proportionally greater direct exposure to water column sources. As discussed in the sensitivity analysis portion of section 8, the percent lipid distributions for individual fish species and for water column invertebrates play an important role in the model.

Chapter 8

8. DISCUSSION OF UNCERTAINTY

This section 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 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 most important of these have been selected for explicit modeling, based on professional judgment, prior experience and existing models. See Book 1 for a further discussion of uncertainties in the fate and transport models.

A qualitative analysis of the uncertainties in the models suggests that uncertainties in fish body burdens is approximately a factor of two. That is, given adjustments in parameters and changes in sediment and water exposure concentrations from modifications to the fate and transport models, resulting fish body burdens will not change by more than a factor of two. However, a factor of two correspondingly increases the 95th percentile, such that the interval of years within which a particular target level might be achieved grows larger (i.e., from 10 years to 20 years).

8.1.2 Model Uncertainties in the Bioaccumulation Models

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

8.1.2.1 Probabilistic Empirical Model and Bivariate Statistical 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 and FISHPATH

FISHRAND and FISHPATH are 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 and FISHPATH do not explicitly consider benthic feeding strategies but rather rely 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 II database average one, exactly what equilibrium partitioning would predict. The species categorized as benthic versus epibenthic from the Phase II 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.

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. The model has to be validated in different settings before attempting to use it for regulatory decisions. Therefore, FISHRAND model does not directly account for these processes and uses as the prototype an earlier version of Gobas model that was tested and applied for several sites and in different environmental settings (Morrison et al., 1997, Buckhard, 1998).

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. This is a powerful tool to analyze uncertainties in model predictions. 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.

8.2.2 Lipid Content

Lipid content of organisms play 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. The model, too, 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.

Based on the results of NOAA's mussel method detection limit (MDL) study (see TAMS/Gradient, February 1993 for details), the percent lipid determination for benthic invertebrates was considered to be 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.

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9. SUMMARY AND CONCLUSIONS

Three food chain models were developed to describe the uptake of PCBs, expressed as ΣTri^+ , which is representative of total PCBs in fish tissues. These models include:

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 constructed 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 Models (FISHPATH and FISHRAND) Based on Gobas (1993)

As a result of the peer review process conducted for the Preliminary Model Calibration Report, it was determined that a time-varying, mechanistic model should be included in the suite of models being used to evaluate the potential for PCB uptake into fish tissue. Consequently, two additional mechanistic models were developed to describe the uptake, absorption, and elimination of PCBs in fish over time. These models are 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). Two versions of the model were developed for the sake of quality assurance and convenience:

- FISHPATH: a deterministic version programmed in Stella-4™ Software
- FISHRAND: a probabilistic version programmed in Fortran-90 and Delphi-3 using the LSODE (the Livermore Solver for Ordinary Differential Equations (Radhakrishnan and Hindmarsh, 1993))

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.

Applicable and Relevant and Appropriate Requirement (ARAR)

Appropriate target levels for fish body burdens have not yet been established. Several target levels used in other contexts are presented in this report to provide perspective on predicted fish concentrations. These include the 2 ppm wet weight United States Food and Drug Administration (FDA) Action Level, and the Great Lakes Uniform Sportfish Advisory Task Force PCB concentrations in fish for human consumption. These are as follows:

- Greater than 1.9 ppm wet weight – no fish consumption is recommended
- 1.1 – 1.9 ppm wet weight: 6 meals per year
- 0.1 – 1.0 ppm wet weight: 1 meal/month

These values should not be construed as endorsement of particular target levels, but rather are designed to provide perspective on predicted fish body burdens relative to environmentally-protective concentrations that have been developed for other purposes.

9.1 Summary of Food Web Models

- The Bivariate BAF Analysis represents PCBs in terms of the sum of trichloro- through decachlorobiphenyls (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 and FISHPATH also represent ΣTri^- (equivalent to total PCBs).
- 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; (e) demersal fish; and (f) omnivorous fish. PCB concentrations are expressed as lipid-normalized in biota, total organic carbon normalized in sediments and fraction organic carbon normalized in the particulate phase 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.
- FISHPATH and FISHRAND were developed based on Gobas (1993) and compared to published modeling results for Lake Ontario to verify model functionality. These models were then modified for the Hudson River by eliminating Lake Ontario species and including Hudson River species: largemouth bass, spottail shiner, pumpkinseed, yellow perch, white perch, and brown bullhead. FISHPATH is the deterministic version, while FISHRAND incorporates frequency distributions for most of the 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.
- Using the hindcasting results from the fate and transport models, both the probabilistic empirical model and FISHRAND/FISHPATH accurately capture observed historical PCB concentrations in fish. Comparisons are available for largemouth bass and pumpkinseed at river miles 168 and 189 for the empirical probabilistic model, while comparisons are available for largemouth bass, pumpkinseed, yellow perch and brown bullhead for FISHRAND.

- The probabilistic empirical model predicts particular percentiles (50th or median, average, 75th, 90th, and 95th are presented here). FISHRAND also has the ability to predict particular percentiles but only the median (50th) and 95th are presented here.
- FISHRAND captures largemouth bass lipid-normalized and wet weight concentrations within the Thompson Island Pool to within a factor of 1.5, lipid-normalized concentrations at river mile 168 to within a factor of 1.2, and wet weight concentrations at river mile 168 to within a factor of two. In general, wet weight concentrations for all species and locations are within approximately a factor of two of observed concentrations, although there are exceptions. Lipid-normalized results are generally within a factor of 1.5, again, with some exceptions. Comparisons to observed data for the lowest upstream location (154) show less good agreement with observed data as the observations were collected from below the Federal Dam and FISHRAND models just above the dam.
- Individual congeners will also be modeled but these results are not presented here.

9.2 Principal Report Findings

This report does not present definitive answers to the principal Reassessment questions since this will require the completion of all of the Phase 2 and Phase 3 reports. However, a number of conclusions have been drawn based on the work presented here, including:

- 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, 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.
- The Probabilistic Bioaccumulation Food Chain Model captures the historical New York State Department of Environmental Conservation (NYS DEC) mean observed fish concentrations using the fate and transport sediment and water concentrations as inputs. The model predicted that 90th percentiles typically occur at maximum observed concentrations, suggesting that the model is protective of fish populations at this level.
- FISHPATH (deterministic Gobas mechanistic time-varying model) and FISHRAND (probabilistic Gobas mechanistic time-varying model) accurately reproduce both steady-state and dynamic published results for Lake Ontario, indicating the models are functional as originally intended. These models were developed in response to the peer

review comments which specified the development of a mechanistic model to be included in the suite of models used to evaluate PCB uptake in fish from the Hudson River.

- 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, we are interested in the adult of the species for piscivorous, semi-piscivorous and omnivorous fish while for the forage fish we are interested in the young-of-year (or yearlings).
- 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 NYS DEC) for the period 1977 – 1996 for several locations above the Federal Dam at Troy. The fate and transport models assumed a) a constant upstream boundary condition, and b) a zero upstream boundary condition (see Books 1 and 2). As these results were very similar, only the constant upstream boundary condition was run for FISHRAND.
- Predictions from the probabilistic empirical model for largemouth bass compare favorably to the results for FISHRAND. The probabilistic empirical model provides a useful check on the FISHRAND results.
- Forecasts for the FISHRAND model suggest that largemouth bass will achieve 2.0 ppm on an average wet weight basis between 2008 and 2014, with the best estimate of 2011 for river mile 189 (within the Thompson Island Pool), and between 2011 and 2019 (best estimate 2015) for river mile 168 (Stillwater) under constant upstream boundary conditions. Largemouth bass average values will not achieve target levels of 1.1 ppm or 0.2 ppm within the 21-year forecast period at these locations. In addition, the 95th percentile value will not achieve any of the target levels in the forecast period. Note that the target levels are for comparison purposes only, and that appropriate levels will be determined in the Feasibility Study.
- Forecasts suggest that for river mile 189, average values for yellow perch will achieve 2.0 ppm between 2007 and 2014 (best estimate 2010), and 1.1 ppm between 2015 and 2021. 95th percentile values would not reach any of the targets within the forecast period. Average yellow perch values will achieve 2.0 ppm between 2008 and 2014 (best estimate 2011) for river mile 168, but the lower target values and the 95th percentile values will be not reached within the forecast period.
- For brown bullhead, the average fish body burden is forecasted to reach 2.0 ppm between 2014 and 2020 (best estimate 2017) at river mile 168. Within the 21-year forecast period, no other target levels will be achieved for average brown bullhead at river mile 168, and none of the target levels are achieved at river mile 189.

- At river miles 157 and 154, forecasts for all species modeled achieved the FDA action level of 2 ppm by 2021, even at the 95th percentile value.
- For all locations and species modeled, predicted average body burdens did not fall below 0.5 ppm within the 21-year forecast period.
- The sensitivity analysis showed that the percent lipid distribution in individual fish species is the most important parameter in FISHRAND, followed by K_{ow} and percent lipid in prey items. Based on the ability of the model to capture historical observed concentrations by a factor of 2, the uncertainty bounds on the time to achieve particular target levels is estimated to be plus or minus three years.
- Additional modeling work is currently underway. This additional effort includes modeling specific individual congeners for several locations to document the ability of the model to capture the biomagnification dynamics. The modeling analysis will also be updated to reflect revisions to the fate and transport model results.

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