Smallmouth Bass

White Sucker

Yellow Perch

Connecticut River Fish Tissue Contaminant Study (2000)

-Ecological and Human Health Risk Screening

Prepared for Connecticut River Fish Tissue Working Group
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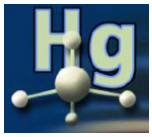
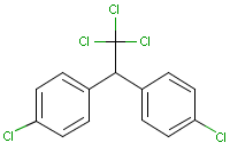


Mercury



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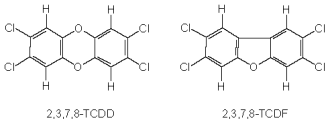
Wednesday, May 31, 2006

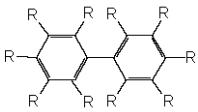
Striped Bass

American Shad

Brown Bullhead



Dioxin and Furan



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[1]Appendix D data validation spreadhseets in Excel and PDF format and all of Appendices E and F are only on the CD version of the report

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Smallmouth Bass - John F. Scarola and N.H. Fish and Game Department
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Brown Bullhead - John F. Scarola and N.H. Fish and Game Department
Striped Bass - Don Flescher (NOAA retired)
American Shad - Don Flescher (NOAA retired)

Dr. Dave Evers, Executive Director of the Biodiversity Research Institute (www.briloon.org) in Gorham, ME, provided Figures 2 and 4 and total mercury in smallmouth bass, yellow perch and white sucker data from BRI reservoir monitoring (Appendix B) in the upper Connecticut River.

Ms. Patti Tyler, currently Regional Science Liaison in EPA Region VIII (Denver, CO), was instrumental in planning this project, preparing the QAPP, overseeing fish processing in the EPA lab, and shipment of fish tissue to external analytical labs.

Members of the Ecology Monitoring Team in the New England Regional Laboratory assisted in fish sample collection and preparation (measuring, filleting, otolith collection, etc.).

Mr. Peter Nolan, recently retired as the Senior Biologist and Ecological Monitoring Team leader, in EPA's Regional Lab, was integrally involved in all steps of planning and implementation of the project and lead EPA's electro-fishing crew.

Ernie Pizzuto lead CTDEP's fish sampling and provided Brook Trout controls from a State fish hatchery.

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NH Fish and Game, CT Fish and Game, and VT Fish and Game Departments were involved in project planning and sample collection.

Dr. Steve Stodola, of the USEPA - New England Regional Laboratory, oversaw this project's protracted, complex data validation process.

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All remaining deficiencies in the report remain the responsibility of the author.

Executive Summary

The Connecticut River Fish Tissue Contaminant Study (2000) was a collaborative federal and state project designed to provide a baseline of tissue contaminant data from several fish species, to better understand the risk to human health from eating Connecticut River fish, and to learn what threat eating these fish poses to other mammals, birds, and fish. The study will also assist future trend analysis and current statistical comparison, allowing ecological and human health risk screening in support of consistent State fish advisories. This was one of the first such studies of fish tissue contamination in the mainstem of a large, multi-state river in the United States.

The project was undertaken at the request of the four Connecticut River watershed states (Connecticut, Massachusetts, New Hampshire and Vermont) and the Connecticut River Joint Commissions for VT and NH, to address limitations in previous state-specific studies, including differing methods of target species selection, fish collection, sample preparation and handling, and laboratory analysis.

Partners in the project included EPA-New England, Connecticut Department of Environmental Protection (CTDEP), Connecticut Fish and Game (CTF&G), Massachusetts Department of Environmental Protection (MADEP), New Hampshire Department of Environmental Services (NHDES), New Hampshire Fish and Game (NHF&G), Vermont Department of Environmental Conservation (VTDEC), Vermont Fish and Game (VTF&G) the New England Interstate Water Pollution Control Commission (NEIWPCC), the US Fish and Wildlife Service (USFWS), and the US Geological Survey (USGS).

The Connecticut River was divided into eight (8) sampling Reaches (segments) for the purposes of this project (Map 1, Table 1). Reach divisions were determined by EPA and state biologists to correspond to major dams and presumably discrete fish populations. The location of individual fish sampling within Reaches was generally not recorded; thus, data analyses were done by species and Reach.

Smallmouth bass, yellow perch and white suckers were collected during 2000[2] from the mainstem of the Connecticut River and composite[3] samples were analyzed for total

---

[2] Project data from a contract laboratory proved highly problematic, requiring protracted data validation by EPA and its contractors. Final data validation for dioxins and furans was ultimately only completed in the fall of 2004. Given the implications of this study for human health and state fish advisories, data quality was considered one of the highest priorities.

[3] Individual fish were separated into fillet and offal. Multiple fish from a Reach were combined into composite fillet and offal samples for lab analysis. Analytical results from fillet and offal composites were added together to estimate whole fish concentrations. One consequence of this approach is that extreme (high or low) values in individual fish tend to be averaged with more moderate values.

mercury, coplanar (dioxin-like) PCBs and organochlorine pesticides, including DDT and its breakdown products[4]. Additionally, in Reach 3, brown bullheads, American shad and striped bass were sampled by the State of Massachusetts. One fillet composite each of smallmouth bass, yellow perch and white sucker fillets from Reaches 1, 4, 5, and 7 (twelve samples in total) was also analyzed for dioxins and furans. This was due to the cost and complexity of current dioxin analytical techniques. State of Connecticut hatchery-raised brook trout were used as a "control" fish species against which to compare wild species' contaminant levels.

Levels of contaminants[5] were compared to EPA and other current human health subsistence and recreational (sport) fisher and ecological risk screening criteria, and also were statistically compared between Reaches and species. Fish weight, length, 'condition' (a measure of health) and age (of selected smallmouth bass) were also assessed and compared with contaminant levels. Screening levels did not consider vulnerable populations, such as women of child-bearing age and young children.

Key Findings

1. Total mercury concentrations in all three species of fish were significantly higher in upstream Reaches than in downstream Reaches. Mercury poses a risk to recreational and subsistence fishers and to fish-eating wildlife.

2. Risk from dioxin-like (coplanar) PCBs was generally lower in upstream Reaches than in downstream Reaches; although this varied by fish species and was different for the humans/mammals, birds or fish that eat them. Dioxin-like PCBs pose a risk to recreational and subsistence fishers and to fish-eating mammals and fish-eating birds.

3. Dioxin toxicity, in the twelve fillet composites analyzed, posed a varying risk to both subsistence and recreational fishers and fish-eating wildlife, even when dioxin-like PCB TEQs (a standardized measure of dioxin toxicity) were not included in the risk calculations. Since risk associated with dioxin is not available for the remainder of the fish samples, these PCB TEQs underestimate human health and ecological risk from consumption of Connecticut River fish.

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[4] Cadmium was sampled in two northern Reaches and non-coplanar PCBs were analyzed in all Reaches. Results are provided in the Appendices.

[5] The current study decided to ***not*** follow the USEPA (2000b) recommendation to assign all non-detects values of half the detection limit. Rather non-detects were given a value of zero. In the case of TEQs, in particular, we believed this could falsely inflate the apparent toxicity. Given our conservative screening assumptions we believe this approach provided both a close approximation of the actual toxicity and was protective of human health and the environment. The detection limits of all analyses are available in Appendices C and D.

4. DDT and related breakdown products from chemical, physical and biological weathering, pose a risk to human subsistence fishers and to fish-eating birds, but not to recreational fishers or fish-eating mammals.

Mercury is mostly deposited in the Connecticut River watershed from the atmosphere. Much of this mercury originates from Midwest power plant and urbanized eastern seaboard emissions. EPA is currently reviewing its 2005 Clean Air Mercury Rule, which with the Clean Air Interstate Rule, may help to reduce these emissions and ultimately the amount of mercury in fish. EPA-New England has worked with all New England states to substantially reduce regional mercury emissions since the late 1990's. Once in the river, mercury bioaccumulates to high levels in the food chain. Saltwater and freshwater fish are the primary source of methylmercury exposure for most people and fish-eating wildlife. Older fish tend to have higher levels of mercury and other contaminants. Higher levels of mercury in the upper 'Reaches' may, in part, be a result of water level manipulations, particularly in reservoirs.

Use and manufacture of PCBs was banned in the U.S. in 1977 after production of over 1.5 billion pounds. DDT use was severely restricted by EPA in 1972 after application of over 1.3 billion pounds during the previous thirty years. Dioxins and PCBs break down very slowly in the environment and bioaccumulate in food chains. Similarly, DDT is very long-lived in the environment in either its original or breakdown forms. There are no known current sources of PCBs or DDT to the Connecticut River so contaminants in the fish result from historical contamination in the watershed. However, dioxins are produced in nature and inadvertently by humans; often through combustion processes such as at waste incinerators. Levels in Connecticut River fish reflect historic and possibly current sources.

Current State Fish Advisories for the Connecticut River

State Departments of Health issue fish advisories based on studies of contaminant risks to "at risk" and other populations[6]. The findings of this report have implications for state fish advisories for the Connecticut River. The entire Connecticut River is covered by state-wide advisories for mercury; however, current state fish advisories for PCBs are variable and site-specific, and there are no advisories for dioxins or organochlorine pesticides, such as DDT. Based on the information from this study, the state health agencies will evaluate existing advisories and consider the need for others, to adequately protect human health. Additional studies to assess the risks from dioxins and other pollutants also need to be considered.

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[6] Connecticut, Massachusetts, New Hampshire and Vermont have slightly differing definitions of "at risk" groups, that generally include children (of varying ages), pregnant women or those who may become pregnant, and nursing mothers.

Mercury: All four states have state-wide advisories for mercury in fish for sensitive "at risk" populations (i.e. women of child-bearing age and young children from 6-12 years of age, depending on the state). Connecticut has a state-wide mercury advisory for all waterbodies and all fish species, except stocked brook trout, for all populations.

PCBs: Massachusetts and Connecticut have PCB advisories for some fish species for all Connecticut River waters in their states. However, Massachusetts and Connecticut provide differing fish consumption advice for sensitive "at risk" and general consumers. New Hampshire and Vermont currently have no PCB advisories for Connecticut River waters.

Dioxin: There are currently no advisories for dioxin for the Connecticut River.

Organochlorine pesticides: There are currently no advisories for organochlorine pesticides, such as DDT, on the Connecticut River.

Chapter Content

Chapter 1 - Introduction summarizes information on the Connecticut River watershed, project history, data validation, natural history of sampled fish species and results of historical contaminant sampling by the four States. Information on Connecticut River sediments is also provided. Statistical and graphical techniques used in subsequent chapters are presented.

Chapter 2 - Mercury discusses sources, cycling, biaccumulation, bioconcentration, ecological risks, human health screening, and the current state of the science in the Northeast. Observed levels of total mercury are compared by Reach with ecological and human health screening criteria and statistically between Reaches.

Chapter 3 - Dioxins, Furans, and Dioxin-like (Coplanar) PCBs discusses sources, cycling, ecological and human health screening criteria. Observed levels of dioxins and furans are shown. Coplanar PCBs are compared by Reach with ecological and human health screening criteria by receptor (humans/mammals, birds and fish). Coplanar PCBs are compared statistically between Reaches.

Chapter 4 - Organochlorine Pesticides are graphically compared with human health and eco-risk screening criteria by Reach and statistically between Reaches for DDT and its breakdown products.

Chapter 5 - Weight, Length and Condition are graphically depicted and statistically compared between Reaches and with total mercury.

Chapter 6 - Smallmouth Bass Age, Total Mercury and Coplanar PCB TEQs are graphically depicted and statistically analyzed.

Chapter 7 - Summary, Conclusions and Recommendations summarizes the results from Chapters 2-6 and suggests recommendations to improve similar studies.

Chapter 8 - References, Internet Resources, and Glossary contains a complete bibliography, some internet references, and a glossary of technical terms used in the report.

1.0 Connecticut River Fish Tissue Project - Background

1.1 Connecticut River Watershed

The Connecticut River Joint Commissions of New Hampshire and Vermont (www.crjc.org) describe New England's largest river, "From tiny Fourth Connecticut Lake on the Canadian border, the Connecticut River flows south, linking the states of Vermont and New Hampshire for 255 miles before entering Massachusetts and Connecticut on its way to Long Island Sound. Its watershed covers a full third of New Hampshire and two-fifths of Vermont. With the support of hundreds of valley citizens, New Hampshire designated its longest river into the Rivers Management and Protection Program in 1992. In 1998, President Clinton honored the Connecticut as an American Heritage River, one of fourteen so designated nationwide" (http://www.epa.gov/rivers/98rivers/connecticut.html).

The Connecticut River Watershed Council (CRWC, http://www.ctriver.org/) characterizes the watershed as:

> "...80% forested, 12% agricultural, 3% developed, and 5% wetlands and water. There are 390 towns, villages and cities, which are home to 2.3 million people. The River drops 2,400 feet from its source to the sea, and has a daily average flow of nearly 16,000 cubic feet per second (cfs). The flow has ranged as high as 282,000 cfs and as low as 971 cfs.....The Connecticut has 38 major tributaries, 26 of which drain 100 square miles or more. All told, there are over 20,000 miles of streams in the watershed."

The river has been extensively altered through damming. On the mainstem dams created substantial warm-water habitat where little or none had previously existed (Noon 2003).

EPA-New England (2002) notes the Connecticut River watershed encompasses about 11,260 square miles and the mainstem is approximately 410 miles long. The US Fish and Wildlife Service (FWS) (http://www.fws.gov/r5soc/) has designated the entire 7.2 million acre watershed as the Silvio O. Conte National Fish and Wildlife Refuge with a goal of identifying and protecting it's biodiversity, through cooperative management with the residents.

The FWS has identified numerous Species of Special Emphasis (birds, mammals, fish, reptiles, amphibians, invertebrates and plants in the Connecticut River watershed (http://www.fws.gov/r5soc/sose.htm). Additionally ten federally listed Endangered or Threatened species occur within the watershed, three birds (bald eagle, peregrine falcon, piping plover), a fish (shortnose sturgeon), an insect (puritan tiger beetle), a mussel (dwarf wedge mussel) and four plants (Jesup's milk-vetch, Robbin's cinquefoil,

small whorled pogonia, and northern bulrush)(http://www.fws.gov/r5soc/EndThrSp.htm). The watershed also shelters numerous Species of Special Emphasis (http://www.fws.gov/r5soc/sose.htm).

The CRWC notes “the watershed is home to a rich diversity of species: an estimated 59 species of mammals, 250 species of birds, 22 species of reptiles, 23 species of amphibians, 142 species of fish, at least 1,500 invertebrates, and 3,000 plant species."

The processes of agricultural abandonment, industrialization and urbanization in New England lead to a marked impairment of the river’s water quality. By the 1970's the Connecticut River was referred to as a “landscaped sewer” (USEPA 2000c). Mullaney (2004) provides a comprehensive review of thirty years (1968-1998) of water quality data in the state of Connecticut portion of the river and a historical context for the degradation of the entire river. New England’s rivers were among the most polluted in the nation, prior to the Clean Water Act and other pollution control legislation (Robinson and others 2003).

In 1997 the CRJC produced a six volume Connecticut River Corridor Management Plan (CRJC 1997). Among the recommendations were that fish tissue be sampled to determine the human health and ecological risk. The New England Interstate Water Pollution Control Commission (NEIWPCC), in 1998, published The Health of the Watershed, which identified water quality problems with the river, including toxins, such as PCBs, combined sewer overflows (CSOs), bio-accumulation of contaminants, and nonpoint source pollution. NEIWPCC also noted the presence of public health advisories for PCBs and mercury, on consumption of river fish in all four states.

Historical and ongoing pollution of the Connecticut River has had impacts on fish and wildlife populations and on human health. Coincident with the founding of the USEPA in 1970, the New Hampshire State government issued the first fish consumption advisory (fish advisory) for mercury in Connecticut River fish. As fish contaminant surveys expanded to the other states in the watershed, Federal and State governments issued further fish advisories.

However, previously fish advisories have been characterized by data collected individually by the four affected states within the watershed. Surveys have differed substantially “in methods of target species selection, fish collection, sample preparation and handling, and laboratory analysis”(Tyler, 2000). Furthermore, much of the data are over ten years old.

1.1.1 Project Planning

The Connecticut River Fish Tissue Contaminant Study was designed as a collaborative federal and state project to address these previous deficiencies and “provide comparable data on fish tissue contaminant levels throughout the watershed in support of human health and ecological risk assessments and fish consumption advisories” (Tyler, 2000).

Partners in the project included EPA-New England, Connecticut Department of Environmental Protection (CTDEP), Connecticut Fish and Game (CTF&G), Massachusetts Department of Environmental Protection (MADEP), New Hampshire Department of Environmental Services (NHDES), New Hampshire Fish and Game (NHF&G), Vermont Department of Environmental Conservation (VTDEC), Vermont Fish and Game (VTF&G), the New England Interstate Water Pollution Control Commission (NEIWPCC), US Fish and Wildlife Service (USFWS) and the US Geological Survey (USGS). The University of Connecticut Environmental Research Institute (ERI) (http://www.engr.uconn.edu/eri/) performed analyses for total mercury, chlorinated pesticides and coplanar and non-coplanar polychlorinated biphenyls (PCBs). AXYS Analytical Services, Ltd. (http://www.axysanalytical.com/) performed analyses for dioxins and furans.

On March 8, 2000 a scoping meeting was held at the Lowell, Massachusetts offices of the NEIWPCC (Tyler, 2000). This meeting among the partners established project roles and responsibilities, a project timeline, field sampling protocols and analytical requirements, including issues of laboratory detection levels, analytical methods and other relevant issues. It was agreed that a post-hoc 'debriefing' among all field survey partners would be held to identify problems and strengths of the current approach.

1.1.2 Project Objectives, Sampling Design and Data Validation

As described in the project Quality Assurance Project Plan (QAPP) (Tyler 2000):

> "In the 1998 Report titled "Health of the Watershed - A Report of the Connecticut River Forum" a series of recommendations were provided to improve the collaboration between the four New England states (New Hampshire, Massachusetts, Vermont and Connecticut) and their efforts with respect to water quality monitoring and fish tissue contaminant surveys. At the June 16, 1998 meeting of the Connecticut River Forum, a sub-committee developed the four state comprehensive fish tissue monitoring program for the Connecticut River. The overall objective of the Connecticut River fish study is to perform a watershed wide fish tissue monitoring program which would document current conditions with regard to contaminant concentrations of representative fish from the mainstem of the Connecticut River. The specific objectives of this survey are to serve several purposes:
>
> 1. To establish a baseline of contaminant residues in fish species of different trophic classes for future trend analysis of contaminant uptake by fish in the river. Contaminant residue analyses are to include total

mercury, total PCBs, coplanar PCBs, PCB homologue analyses, dioxins and chlorinated organic pesticides in fish fillet and offal samples.[7]

2. To determine species presence in relation to water quality[8] and ecological health, in addition providing baseline ecological data. The data needs to support decision making based on ecological health and risk.

3. To generate an adequate baseline data set for comparative use to future study efforts.

4. To collect and generate data for use in current and future ecological risk assessment efforts. Data must be of a sufficient quality to support decision making for ecological risks.

5. To produce data that can be utilized for making determinations on risks to human health, based on the consumption of fish in the watershed. Data must be of a quality whereby state public health officials can reliably update fish consumption advisories if deemed appropriate.

To meet these ends, these data will be drawn from various species of fish representing different trophic levels in the different river segments in the Connecticut River watershed. Number of samples collected per species will be such as to provide acceptable sample sizes for adequate representation of the targeted species."

The Connecticut River was divided into eight (8) sampling Reaches for the purposes of this project (Map 1; Table 1). Reach divisions were determined by EPA and State biologists to correspond to major dams and presumably fairly discrete fish populations. The location of individual fish sampling within Reaches was generally not recorded. Thus data analyses are by species and Reach. Natural history information of sampled fish species is provided in Table 3. Field sampling focused on smallmouth bass, yellow perch, and white suckers in Reaches 1-7. These three species are among those recommended by EPA's 1993 Fish Contaminant Workgroup. EPA (2000a) notes,

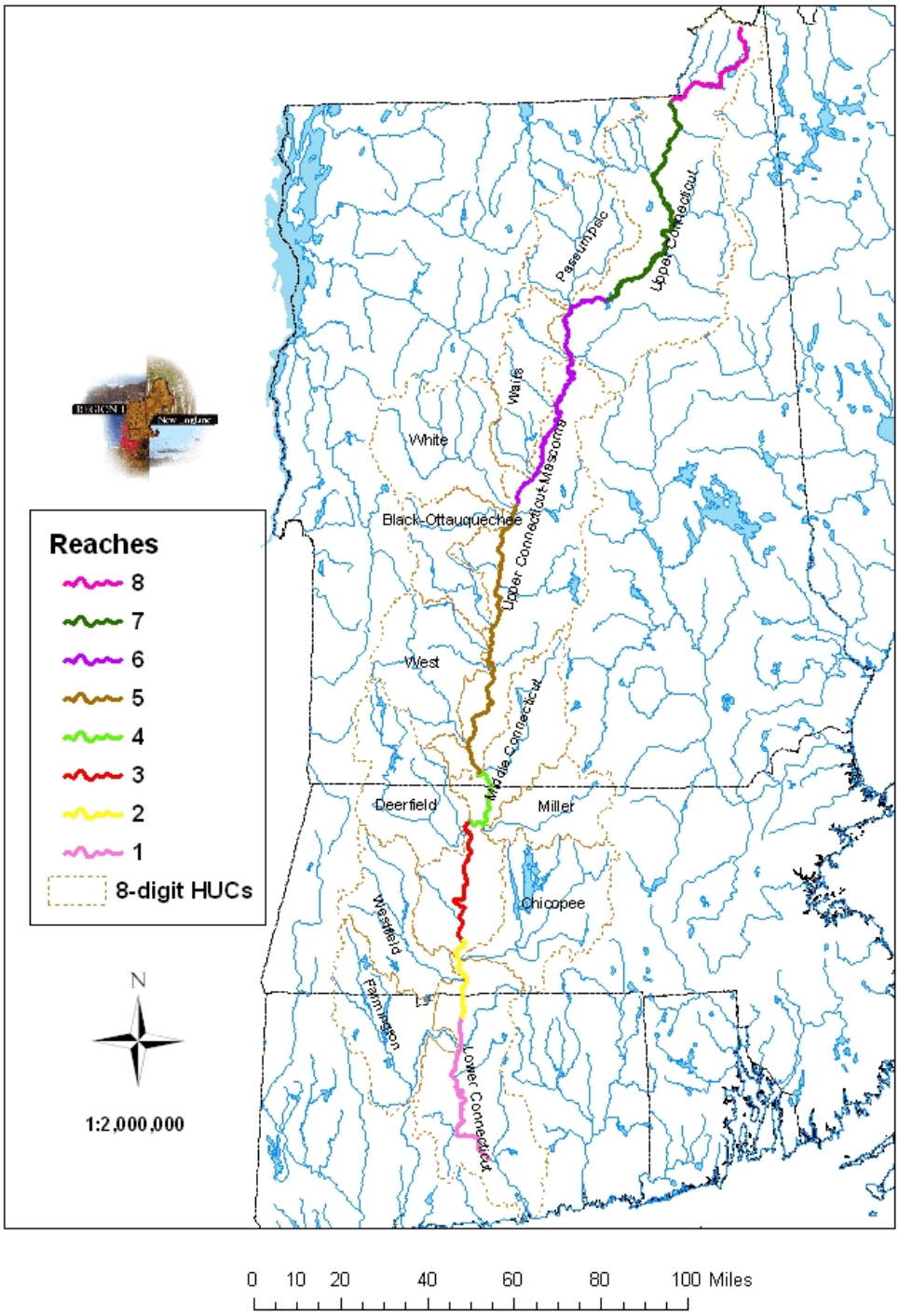
"Use of two distinct ecological groups of finfish (i.e., bottom-feeders and predators) as target species in freshwater systems is recommended. This

---

[7] Individual fish were separated into fillet and offal. Multiple fish from a Reach were combined into composite fillet and offal samples for lab analysis. Analytical results from fillet and offal composites were added together to estimate whole fish concentrations. One consequence of this approach is that extreme (high or low) values in individual fish tend to be averaged with more moderate values.

[8] No water quality parameters were monitored concurrently with fish collection. See recommendations in Chapter 7.

Connecticut River Fish Tissue Sampling Reaches



Map 1. Connecticut River Fish Tissue Sampling Reaches

Table 1. Connecticut River Fish Tissue Sampling Reaches

Reach	~Latitude[9] - Top	~Longitude - Top	~Length (miles)	~% of Mainstem	Description
0	41.48 N	72.50 W	22	5	Clearly tidal area[10] of CT River (not sampled)
1	41.95 N	72.61 W	49	12	Haddam, CT to Enfield, CT
2	42.21 N	72.60 W	20	5	Enfield, CT to Holyoke Dam, MA
3	42.61 N	72.55 W	36	8	Holyoke Dam, MA to Turners Falls Dam, MA
4	42.77 N	72.51 W	21	5	Above Turners Falls dam, MA to Vernon dam, VT
5	43.67 N	72.30 W	77	18	Above Vernon dam, VT to Wilder dam
6	44.34 N	71.87 W	74	18	Above Wilder dam in Lebanon/Hanover, NH to Moore dam
7	45.00 N	71.53 W	88	21	Above Moore dam Littleton, NH to Canaan, VT dam
8	45.23 N	71.20 W	36	9	Above Canaan, VT dam in West Stewartstown/Clarksville, NH
Total Mainstem Length			**423**	**100.0**	

permits monitoring of a wide variety of habitats, feeding strategies, and physiological factors that might result in differences in bioaccumulation of contaminants. Bottom-feeding species may accumulate high contaminant concentrations from direct physical contact with contaminated sediment and/or by consuming benthic invertebrates and epibenthic organisms that live in contaminated sediment. Predator species are also good indicators of persistent pollutants (e.g., mercury or DDT and its metabolites) that may be biomagnified through several trophic levels of the food web."

Sampling difficulties in Reach 8 lead to only two white sucker composites. Reach 8, unlike the other Reaches, is primarily a cold water fishery making it difficult to sample

[9] Latitude and longitude refer to the approximate top-most point in the Reach. These locations may be viewed from the air using Google Earth™ (http://earth.google.com/).

[10] Although tidal effects in the Connecticut River extend at least to Hartford (Donlon pers. comm. 2006).

comparable species. In Reach 3, additionally, brown bullheads, American shad, and striped bass were opportunistically sampled by the State of Massachusetts. State of Connecticut fish hatchery raised brook trout were used as a “clean control" fish species against which to compare contaminant levels in the wild fish species. These fish were only exposed to contaminants in their food, atmospheric deposition and water while being grown in tanks. It was thought that they would therefore reflect the lowest attainable contaminant levels.

Sampled fish were transported either alive or, more typically, on ice to the EPA Regional lab in Lexington, MA.[11] Fish were typically frozen in the lab and thawed prior to lab processing. In a few instances fish were processed on receipt, without being frozen. Individual fish were weighed and their total length measured and recorded from snout to end of the tail (caudal) fin. Fish were filleted and composited (offal and fillet separately). In some instances otiliths and or scales were recovered and archived for aging. Bile was also collected for some individuals allowing possible further analysis, such as for estrogenic effects (Adolfsson-Erici 2005). Obvious external abnormalities (i.e. deformities, lesion, tumours) were recorded on an ad-hoc basis as these can be an indications of chemical exposure.[12] The EPA SOPs (Standard Operating Procedures) used in fish collection and processing may be found in Appendix D.

Map 1 provides an approximate delineation of the Reaches used in sampling and analyzing Connecticut River fish in the current study. Below Reach 1 (~22 miles; ~5% of mainstem) the Connecticut River becomes tidal, excluding this area from the study. Other Reach divisions were drawn at major dams following discussion among the study participants. Reach 8 (~36 miles; ~9% of mainstem) only yielded a small sample of white suckers, allowing a very poor characterization of this more pristine stretch of the Connecticut. Reaches 1-7 encompassed ~364 miles (~86%) of the mainstem of the Connecticut River.

1.1.3 Data Validation of the CT River Fish Data

According to the Quality Assurance Project Plan (QAPP) (Tyler 2000), a third party data validation was required for this project. This validation work was coordinated by Dr. Steve Stodola of the Quality Assurance Unit of the USEPA New England Regional Lab. The validation was performed with contractor support provided under the ESAT (Environmental Services Assistance Team) contract.

Appendix D provides the data validation (DV) reports and the validated data for each contaminant. Additional supporting information from the extensive data validation may be obtained by contacting this report's author.

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[11] The former location of the EPA Regional lab until September, 2001.

[12] See Appendix F - CT River Fish Data Spreadsheets.

Data Validation is the first step in assessing the quality of a particular set of data. It is defined as a standardized review process for judging the analytical quality and usefulness of a discrete set of chemical data. It is standardized in the sense that it uses specific evaluation procedures which are described in our Region I Data Validation Functional Guidelines (USEPA 1996). Its main focus is to identify any problems that the laboratory may have had in analyzing the samples, such as poor surrogate recovery. Data validation can also help identify some sampling problems, such as holding time violations, which are usually documented in the data package.

Data validation can be viewed as a decision making process during which established quality control criteria are applied to the data . These quality control procedures and criteria are typically agreed upon in the planning phase of the project and incorporated by the laboratory into their analytical method as the samples are being processed. Unfortunately in this project, this was not done and the data validation proved much more complex and problematic[13].

During the data validation decision making process, individual sample results are either accepted, rejected or qualified. Data which meet all the validation QC (Quality Control) criteria are accepted as unqualified and can be used as reported. Data which are rejected (R) for not meeting one or more validation criteria cannot be used at all. For these situations an “R” would be reported on the Data Summary Table for that particular analyte in that particular sample. Some data will inevitably fall into the range between the acceptable the limit and totally unacceptable limit. These data are qualified as estimated (J) to indicate that one or more validation criteria were not met. The numeric value report by the laboratory is recorded on the Data Summary Table followed by a “J.” Estimated data may or may not be usable depending on the intended use of the data. In general, the estimated (J) data can be used after examining the reason for the data qualification and the use to which the data will be put.

So in summary, the data validation process transforms analytical laboratory results and some sampling input into useful information. The end product of data validation then is information of known analytical quality. The purpose of data validation is to assess and summarize the quality of the laboratory’s analytical data for the end user, for example site manager, risk assessor, hydrogeologist, statistician, etc. who then decides on the usability of the data.

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[13] Project data from a contract laboratory proved highly problematic, requiring protracted data validation by EPA and its contractors. The eventual cost for contractor support for data validation was over $30,000, not including EPA staff time. Final data validation for dioxins and furans was ultimately only completed in the fall of 2004. Given the implications of this study for human health and state fish advisories, data quality was considered one of the highest priorities.

1.1.4 Data Validation Tiers

EPA Region 1 (EPA-New England) has three tiers of data validation:

- **Tier I** – data package is checked for completeness and any Performance Evaluation (PE) samples are checked for accuracy;

- **Tier II** – quality control results are checked against criteria; reported results are qualified as either acceptable, estimated (J) or rejected (R) data;

- **Tier III** – in-depth examination of raw data for technical and analytical errors; preferred level of validation for human health and ecological risk assessment.

In a Tier I validation, the data package is checked for completeness. Did the laboratory supply all the documentation that they were required to under their contract? During a Tier I validation the Performance Evaluation samples, if present, are evaluated to assess any potential usability issues. A Tier I data validation report would consist of the documentation of any missing information that could not be retrieved from the laboratory, a discussion of the PE sample results, and a summary of the laboratory results (unqualified).

For a Tier II validation, the results of the QC checks and the PE sample results are assessed against the particular DV criteria and then applied to qualify the data set. This results in the proper qualifiers being applied to the data. A Tier I validation is required to be done before the Tier II validation is performed. So the product of the Tier II validation would be a full DV report discussing the results of the QC checks and a Data Summary Table with the proper qualification applied along with worksheets and backup documentation.

A Tier III data validation includes: the Tier I Completeness Evidence Audit; the Tier II assessment of the QC check results; and an in-depth review of the data to verify the accuracy of the lab results. During Tier III the chromatograms, the spectra and instrument out-put are examined in detail. The data set is checked for calculation and transcription errors. Issues of proper compound identification are examined. The product would be a full DV Report with all these items discussed and documented.

1.1.5 Summary of the Data Validation

Table 2 summarizes the data validation findings for this study.

1.1.5.1 Mercury

The mercury results from forty-six fish samples were carried through a Tier III data validation as representative of the whole group used in the study. The samples had been analyzed by ERI in Connecticut. A Standard Reference material tissue sample was analyzed in duplicate in conjunction with the samples. Recoveries of 94% and 84% were acceptable.

Preservation and holding time criteria were met. Duplicate precision and lab fortified blank recovery met acceptance criteria. There was low level blank contamination typical of this type of analysis. One matrix spike recovery was slightly below the lower acceptance limit resulting in the estimation (J) of five other samples in this group.

Forty-one mercury results were reported as acceptable. They ranged from 0.17 to 0.74ppm (mg/kg) (ppm) with a laboratory reporting limit of 0.008 ppm. The laboratory did achieve the Project Quantitation Limit of 0.04 ppm.

The laboratory performed extra QC measures not required by the QAPP. They analyzed post digestion spike and post digestion dilution samples. The QC results for all these samples were within acceptable limits.

Overall the quality of the mercury data was quite acceptable for this project.

Table 2. CT River Fish Tissue Data Validation Summary

Contaminant	Data Validation Tier (I, II, or III)	Description
Mercury	Modified Tier III	A modified Tier III data validation was performed on the results from 46 fish tissue sample analyses, selected as representative of the whole data set. A separate Performance Evaluation (PE) sample was found acceptable. The reported results were determined to be usable for the project data quality objectives. See the data validation (DV) report in Appendix D-1 for details.

Dioxins & Furans	Modified Tier II	A modified Tier II validation was performed on the data from all 12 fish samples analyzed for dioxins/ furans by AXYS Analytical Services. A tissue PE sample was not available. However, other PE samples analyzed in the same time period were acceptable. Other minor quality problems did not impact the usability of the data for project objectives. See the DV report in Appendix D-2 for details.
Coplanar PCB Congeners	Modified Tier II	A modified Tier II validation was performed on the results from 15 fish samples analyzed by ERI. Validation identified several quality problems which resulted in the estimation (J) of all of the data. The results are usable for screening purposes only. See the DV report in Appendix D-3 for details.
Chlorinated Pesticides/ Non-Coplanar PCBs[14]	Tier III	A Tier III validation was performed on the results from 44 fish samples analyzed by ERI. One tissue Standard Reference Material (SRM) was evaluated. A small percentage of the data was rejected (R) and cannot be used due to low matrix spike recoveries. The remaining results were estimated (J) due to other quality problems. However, these were not serious enough to prevent the use of the estimated data for the project objectives. See the DV report in Appendix D-4 for details.

1.1.5.2 Dioxin and Furans

ERI subcontracted out 12 fish tissue samples to AXYS Analytical Services for dioxin/furan analysis. AXYS is a very reliable laboratory that has a solid track record with EPA. These samples were carried through a Tier II data validation. These were the only samples analyzed for dioxins and furans.

The following QC checks were performed and found to be acceptable: sample preservation and holding times, initial and continuing calibrations, peak resolution, instrument sensitivity, matrix spike and duplicate recovery, and internal standard recoveries.

The laboratory analyzed a Standard Reference Material for this project, but the data was lost due to a computer failure. Fortunately, the lab had PE samples which had been analyzed during the same time frame as the fish samples.

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[14]Non-coplanar PCBs are not considered further in this report as toxicity is much less than for the dioxin-like (coplanar) PCBs. Historically total PCBs were summed in analyses, which provided no indication of the toxicity of the mixture. However, the complete validated data set for non-coplanar ("non-dioxin-like") PCBs is available in Appendix D-4.

Low levels of dioxin/furans were found and ranged from 0.11 to 3.8 ppt (ng/kg) with a reporting limit of 0.10 ppt. The laboratory did achieve the Project Quantitation Limit of 1.0 ppt.

Even though some of the results were close to the detection limit we believe that the lab's analytical method provided reliable results.

1.1.5.3 Coplanar PCB Congeners

The data for 15 fish tissue samples analyzed for the 12 coplanar PCBs was available for review from ERI. These results were carried through a Tier II data validation.

The following QC checks were performed and found to be within acceptable limits: preservation and holding times, initial and continuing calibration, chromatographic resolution check, and blank runs.

Eleven samples had acceptable surrogate recoveries; four of the samples had slightly high surrogate recoveries and were estimated. The laboratory did not have a Standard Reference Material sample or a matrix spike for this set of samples. As a consequence all the results are estimated. But given the acceptable values for the other QC parameters, it was decided that these estimated results could be used for screening level comparisons in the Study.

The results ranged from 0.39 to 43 ppb (ng/g or ug/kg) well above the ~ 0.35 ppb detection limit reported by the laboratory. The laboratory did achieve the Project Quantitation Limit of 2 ppb.

1.1.5.4 Chlorinated Pesticides and Non-Coplanar PCBs

The data from 44 fish tissue samples analyzed for chlorinated pesticides was available for review from ERI. A Tier III data validation was carried out on the data.

The following QC parameters were checked and found to be acceptable: sample preservation and holding time, blank analyses, surrogate recoveries, and analyte identification. Several of the other QC parameters were found to have exceedances. For these instance the qualification actions recommended by the DV functional guideline were applied to the results.

The chlorinated pesticide results ranged from a low of 0.24 ppb (ng/g or ug/kg) for gamma-BHC to a high of 93 ppb for p,p'-DDE. Indeed p,p'-DDE was the major contaminant, having been found in all the samples. The reported detection limits for the chlorinated pesticides averaged around 0.6 ppb. The laboratory did achieve the Project Quantitation Limit of 2 ppb.

Validation resulted in the estimation (J) of all the PCB results. The results ranged from a high of 92 ppb for PCB 153 down to values near the detection limit, e.g., 0.37 (ng/g or ug/kg) for PCB 195. Significant hits were noted for PCB 118, PCB 153, PCB 138, and PCB 187 in many of the samples. The detection limits for the PCBs averaged 0.6 ppb. The laboratory did achieve the Project Quantitation Limit of 2 ppb.

Even though some of the chlorinated pesticide data in this set had to be rejected due to the QC exceedances, the positive results for p,p'-DDE and p,p'-DDT across all the samples will have a significant impact and should not be ignored. However, the over all quality of this data set was the lowest of the four that were considered.

1.1.6 Correct TEF Values for Dioxin/Furan and Coplanar PCB DV Memos

In the original DV memos for dioxin/furans (8/20/2002) and Coplanar PCBs (12/26/2003), the TEF (Toxicity Equivalent Factor) values for fish were used rather than the correct ones for humans and mammals. This error was not carried over into the calculations performed in the body of this report. Data Summary Tables with the correct TEF values are included in Appendix D-3.

Table 3. Natural History of Sampled Species. Adapted from www.Fishbase.org (2002; 2005; 2006) and other sources, as noted.

Common Name	Species Name	Natural History
Smallmouth Bass (Reaches 1-7)	*Micropterus dolomieu*	Introduced species. Demersal (frequenting bottom habitats); freshwater. Inhabits shallow rocky areas of lakes, clear and gravel-bottom runs and flowing pools of rivers, cool flowing streams and reservoirs fed by such streams. Young feed on plankton and immature aquatic insects while adults take in crayfish, fishes, and aquatic and terrestrial insects. Sometimes cannibalistic. Trophic level of adults 3.2±0.4(S.E.)[15]. Preyed upon by fishes and turtles. Preyed on by smallmouth bass, yellow perch, catfish, sunfish, and suckers (Scott and Crossman 1973; Yamamoto and Tagawa 2000; Billard 1997). Smallmouth bass were first reported in Massachusetts in 1850. They were stocked in many of Massachusetts' reservoirs, lakes, and streams, particularly in the middle of the last century, and can be considered locally common. The majority of Massachusetts records are from the western and southeastern portion of the state (Hartel and others 1996). Smallmouth bass were introduced to New Hampshire in 1867 when flooding of Cold Spring Trout Ponds by a Charlestown, NH fish culture business, transplanted Lake Champlain fish into the Connecticut River (Noon 2003).

[15]The trophic level (troph) of fish is an inferred value based on their diet composition, and the trophic level of prey organisms. "The troph of a given group of fish (individuals, population, species) is then estimated from

$$\text{Troph} = 1 + \text{mean troph of the food items}$$

where the mean is weighted by the contribution of the different food items.

Following a convention established in the 1960s by the International Biological Program, we attribute primary producers and detritus (including associated bacteria) a definitional troph of 1 (Mathews 1993)." (Froese and Pauly 2000).

Common Name	Species Name	Natural History
White Sucker (Reaches 1-8)	*Catostomus commersoni*	Native species. Demersal (frequenting bottom habitats). Inhabits a wide range of habitats, from rocky pools and riffles of headwaters to large lakes. Usually occurs in small, clear, cool creeks and small to medium rivers. May be found at a depth greater than 45 m (Scott and Crossman 1973). Moves to shallower water near sunrise and sunset to feed. Fry (1.2 cm in length) feed on plankton and other small invertebrates; bottom feeding commences upon reaching a length of 1.6-1.8 cm. Preyed upon by birds, fishes, lamprey, and mammals. One 1990 study from the Juniata River, Pennsylvania found them feeding entirely on zoobenthos (Johnson and Dropkin 1995) Trophic level of adults 2.8±0.3(S.E.). Preyed on by chain pickerel, and small and largemouth bass (Scott and Crossman 1973). In Massachusetts, white suckers are found in virtually every drainage system with the exception of the islands of Martha's Vineyard and Nantucket and several of the smaller mainland coastal streams. This species is abundant in many locations (Hartel and others, 1996).

Common Name	Species Name	Natural History
Yellow Perch (Reaches 1-7)	*Perca flavescens*	Native species. Benthopelagic; freshwater; brackish; depth range to 56 m. Inhabits lakes, ponds, pools of creeks, and rivers. Also found in brackish water and in salt lakes. Most commonly found in clear water near vegetation; tends to shoal near the shore during spring (Frimodt 1995). Feed continually during the day with peak feeding at sunrise and sunset. Inactive at night in shallow water. Winter in deep water. Primarily zooplankton feeders, commencing with immature copepods and rotifers, including cladocerans as they grow larger (Smithwood pers. comm. 2005). Yellow perch are very cannibalistic when young perch are abundant. Trophic level of juveniles and adults 3.7±0.6(S.E.). Preyed upon by fishes and birds (Scott and Crossman 1973). Primarily a shoaling (schooling) species. Spawns between February and July in the northern hemisphere and between August and October in the southern hemisphere. In North America yellow perch are widely distributed and common (Collette and others 1977). Historically yellow perch were present in New Hampshire's southern waters, but they were introduced to more northern waters (Noon 2003).

Common Name	Species Name	Natural History
American Shad (Reach 3)	*Alosa sapidissima*	Native species. Spend most of its life at sea, returning to freshwater streams to breed. Newly hatched larvae are found in rivers during the summer; by autumn they enter the sea and remain there until maturity. Feed on plankton, mainly copepods and mysids, occasionally on small fishes. Feeding ceases during upstream spawning migration and resumes during the downstream post-spawning migration. Shad historically occupied the Connecticut River only as far up as Bellows Falls (Noon 2003). In Massachusetts, the American shad historically entered virtually all coastal streams. Damming, dredging, pollution, and other alterations of Massachusetts waters, caused large declines in the mid-1800s. Shad were eliminated from the Massachusetts portions of the Connecticut, Blackstone, and Charles rivers and the Merrimack suffered declines. Since the mid-1950's, with new or improved fishways and fish-lifts, shad numbers have increased dramatically, especially in the Connecticut and Merrimack rivers (Hartel and others 1996).
Brown Bullhead (Reach 3)	*Ameiurus nebulosus*	Native species. Occurs in pools and sluggish runs over soft substrates in creeks and small to large rivers. Also found in impoundments, lakes, and ponds. Rarely enters brackish waters. A nocturnal feeder that feeds mollusks, insects, leeches, crayfish and plankton, worms, algae, plant material, fishes and has been reported to feed on eggs of least cisco, herring and lake trout. Juveniles (3-6 cm) feed mostly on chironomid larvae, cladocerans, ostracods, amphipods, bugs and mayflies. Can tolerate high carbon dioxide and low oxygen concentrations and temperatures up to 31.6 °C although experiments show upper lethal temp. to be 37.5°C; resistant to domestic and industrial pollution. Has been observed to bury itself in mud to escape adverse environmental conditions. Preyed on by chain pickerel. Brown bullheads are common to abundant and found in every major drainage in Massachusetts, but are generally absent from hillstream systems (Hartel and others 1996)

Common Name	Species Name	Natural History
Striped Bass (Reach 3)	*Morone saxatilis*	Native species. Inhabits coastal waters and are commonly found in bays but may enter rivers in the spring to spawn. Some populations are landlocked (Robins and Ray 1986). Larvae feed on zooplankton; juveniles take in small shrimps and other crustaceans, annelid worms, and insects; adults feed on a wide variety of fishes and invertebrates, mainly crustaceans. Feeding ceases shortly before spawning. Prey on nekton, finfish and bony fish. Historically, striped bass were very abundant and probably entered most of Massachusetts' larger rivers before environmental changes associated with dams and pollution. With the improvements in many of Massachusetts' fishways during the last decade, non-reproducing stripers are now migrating the length of the Connecticut and Merrimack rivers into New Hampshire. Striped bass typically undergo natural population fluctuations that have been documented since before the turn of the 20th century. The changes in abundance have now been linked to peak years of successful reproduction followed by years of less successful reproduction. In recent years these natural fluctuations have been compounded by man-induced changes that effect water quality and thus reproductive and larval success (Hartel and others 1996).

1.2 Historical Fish Contaminant Data

1.2.1 State of Connecticut

In Connecticut and bordering portions of Massachusetts surveys of fish tissue contamination in the Connecticut River have been conducted since at least 1976. From 1976 to 1984 the US Fish and Wildlife Service (USFWS) National Contaminants Biomonitoring Program collected approximately eight whole body samples by species of white catfish (*Ameiurus catus*) , yellow perch (*Perca flavescens*), and white perch (*Morone americana*) from a site in Glastonbury, CT (Reach 1 in the current study). These samples were analyzed for pesticides, poly-chlorinated biphenyls (PCBs) and heavy metals.

In 1985 the USFWS, CT Department of Environmental Protection (CTDEP) and the Massacusetts Department of Environmental Quality Engineering (MADEQE) (now the MADEP) surveyed two sites in Massachusetts and three sites in Connecticut. Thirteen whole body composite samples were collected by species of white sucker (*Catostomus commersoni*), channel catfish (*Ictalurus punctatus)* yellow perch, and largemouth bass (*Micropterus salmoides*). They were analyzed for organo-chlorine pesticides, PCBs, polynuclear aromatic hydrocarbons (PAHs) and heavy metals.

In 1988-89 CTDEP surveyed the river from the Massachusetts state line to Lyme, CT (Reaches 2 to 0) collecting 90 samples (eighteen individual fish each) of carp (*Cyprinus carpio carpio*), channel catfish, large and smallmouth bass, and white perch. Fillets were analyzed for total PCBs with mean concentration and range by species (ppm) of: carp (2.43; 0.31-10.49), channel catfish (0.85; 0.20-2.60), largemouth bass (0.14; 0.01-0.47), smallmouth bass (0.49; 0.04-1.76) and white perch (0.20; 0.01-0.96).

In 1989 the USFWS and CTDEP surveyed from Haddam to Lyme, CT (Reach 0 in the current study) for white perch, yellow perch, black crappie (*Pomoxis nigromaculatus),* smallmouth bass (*Micropterus dolomieu*) and largemouth bass. Whole body and fillet composite samples were analyzed by species for organo-chlorine pesticides, a hydro-carbon scan, total PBCs, PAHs, and heavy metals.

A subsequent survey in 1990 by CTDEP in Lyme, CT (Reach 0 in the current study) of 18 large specimens of carp were also analyzed for total PCBs (Total PCBs) in their fillets. Total PCB concentrations ranged from 0.018-2.830 ppm with a mean concentration of 1.08 ppm.

In 1991 and 1992 CTDEP continued surveys in Haddam and Lyme, CT (Reach 0 in the current study) collecting 43 specimens of large and smallmouth bass and white perch, analyzing fillets for heavy metals, including total mercury. Total Hg was found in seventeen largemouth bass scaled fillets at a mean concentration of 0.20 mg/kg (ppm) with a range from 0.09-0.29 ppm. Six smallmouth bass scaled fillets had total Hg mean

concentrations of 0.19 mg/kg (ppm), with a range of 0.09-0.30 ppm. In twenty white perch total Hg concentrations averaged 0.23 and ranged from 0.08-0.39 ppm.

In 1995 the University of Connecticut Environmental Research Institute (ERI) analyzed fillets from 28 specimens of largemouth bass caught by CTDEP from the Massachusetts state line to E. Haddam, CT (Reach 2-0 in the current study) for total mercury (Total Hg).

The Connecticut Department of Public Health (CTDPH) currently has fish advisories only for common carp and catfish on the entire length of the Connecticut River based only on PCBs. A state-wide advisory is in effect for mercury in fish for sensitive "at risk" populations[16]. Connecticut has a state-wide mercury advisory for all waterbodies and all fish species, except stocked brook trout, for all populations. Additional information on Connecticut's fish advisories may be found by calling the CTDPH (860-509-7742) and at: (http://www.dph.state.ct.us/BRS/EOHA/webfsh.htm).

Further information on the above studies may be obtained by connecting Mr. Ernie Pizzuto of the CTDEP at 860-424-3715 or ernest.pizzuto@po.state.ct.us.

1.2.2 State of Massachusetts

In Massachusetts at least two historic surveys of fish tissue contamination in the CT River were conducted in the late 1980's (Maietta, 1988), in response to findings of elevated PCB levels during a 1987 survey for channel catfish and white catfish (*I. catus*) (Maietta, 1989). In 1987 ten channel catfish were collected below and above the Holyoke Dam (Reaches 2 and 3 in the current study) and above the Turner's Falls Dam (Reach 4 in the current study), since the dams are barriers to fish migration. Skin-off fillets were analyzed for heavy metals, including total mercury (total Hg) and PCBs. Aluminum (Al), chromium (Cr), manganese (Mn), nickel (Ni) and lead (Pb) were found at or below unspecified detection limits in most fish. A ten year old catfish had the highest levels of Al, iron (Fe), Ni, and zinc (Zn) of all fish analyzed. Total Hg, the metal of greatest human health concern was observed at levels ranging from 0.07 to 0.88 ppm with an overall mean value of 0.41 ppm. Total Hg levels were significantly correlated with fish age ($r = 0.630$; $p = 0.001$) for all stations combined. This effect was not detectable at separate stations.

In 1988 (Maietta, 1989) relatively small samples of several species were sampled: Connecticut River (mile 80.0) (Reach 2 in the current study) yielded five American shad (*Alosa sapidissima*), a single white catfish, two channel catfish, three walleye (*Stitzostedion vitreum*), two smallmouth bass, one largemouth bass, one white perch,

[16] CT, MA, NH and VT have slightly differing definitions of "at risk" groups, that generally include children (of varying ages), pregnant women or those who may become pregnant, and nursing mothers.

two white suckers, one American eel (*Anguilla rostrata*) and one rock bass (*Ambloplites rupestris*). Connecticut River (mile 93.0) (Reach 2 in the current study) yielded an unspecified number of carp, channel catfish, white suckers, largemouth bass, white perch, yellow perch, rock bass, American eel, and black crappie. At mile 125.4 (Reach 3 in the current study) one white sucker, one chain pickerel (*Esox niger*), one white perch, one American eel, and one smallmouth were sampled. This last small sample was supplemented by fishing below the Vernon VT dam (mile 136.5) (Reach 4 in the current study) collecting six white suckers, four walleyes, two smallmouth bass, one yellow perch, and one American eel. Skin-off fillets were analyzed individually or as composites for metals, PCB Arochlors (complex mixtures of PCB congeners) and organic pesticides. Most species were also aged using scale impressions. Total Hg concentrations averaged 0.24 mg/kg (ppm) and ranged from 0.02-0.65 ppm, well below fish advisory levels at that time. Aroclor 1254 was present in 30 of 47 samples. Aroclors 1260 and 1242 were found in 18 and 7 of the 47 samples, respectively. These three Arochlors were summed to estimate total PCBs.[17] Connecticut River mile 136.5 and mile 125.4 (Reach 4 in the current study) were considered the same segment and had a mean total PCB level of 0.30 mg/kg (ppm). Connecticut River (mile 93.0) (Reach 3) fish had a mean total PCB concentration of 0.40 mg/kg (ppm).

In 2001 the Massachusetts Department of Public Health issued a new statewide fish consumption advisory in response to growing information and concerns about mercury contamination. MDPH advised pregnant women, women of childbearing age who might become pregnant, nursing mothers and children under 12 years of age to refrain from eating certain marine fish and expanded its previously issued (1994) statewide fish consumption advisory which cautioned pregnant women to avoid eating fish from all freshwater bodies due to concerns about mercury contamination, to include women of childbearing age who might become pregnant, nursing mothers and children under 12 years of age. MDPH also included advice on healthy eating habits to maximize nutritional benefits while minimizing risks . In addition, MDPH issues waterbody-specific advisories. In the early 1990s MDPH issued updated fish consumption advice for the Connecticut River, based on PCBs, advising sensitive populations not to consume any fish from the river. It also advises the general public against eating channel catfish, white catfish, American eel or yellow perch. This advisory covers all towns from Northfield to Longmeadow (i.e. Agawam, Chicopee, Deerfield, Easthampton, Gill, Greenfield, Hadley, Hatfield, Holyoke, Longmeadow, Northampton, Northfield, Montague, Springfield, South Hadley, Sunderland, Whatley, and West Springfield). Information on Massachusetts fish consumption advisories may be obtained from the MDPH Center for Environmental Health, Environmental Toxicology Program at 617-624-5757 or at http://db.state.ma.us/dph/fishadvisory/.

Further information on all of the above studies may be obtained by connecting Mr. Robert Maietta of the MADEP at 508-767-2793 or robert.maietta@state.ma.us.

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[17] This method is now known to significantly underestimate total PCBs in environmental samples.

1.2.3 State of New Hampshire

The State of New Hampshire first monitored their fish for total Hg in 1970, collecting and analyzing over 1,000 samples from 10% of the State's waterbodies. Fish from the Connecticut River at Moore Reservoir (Reach 7 in the current study), Bellows Pool and Hinsdale (Reach 5 in the current study) had elevated levels of total mercury. Typically elevated levels were observed in smallmouth bass, perch and pickerel. A post-hoc summary of this data, by the author, for species in the current study is shown in Table 4.

In 1989 the USFWS and the New Hampshire Division of Public Health Services conducted a comprehensive assessment of metal and organic contaminants in Connecticut River fish at five locations (Isaza and Dreisig, 1989). Smallmouth bass, yellow and white perch, walleye, white suckers and chain pickerel were sampled. Skin off fillets and offal were composited and analyzed for cadmium, chromium, lead, mercury, DDT and Homologs, PCBs and PAHs. Table 5 depicts mean levels of total mercury observed in fillet and offal samples. Concentrations of contaminants approximated those observed in other New England river fish. PCBs and cadmium exceeded levels considered safe for wildlife. PCB levels did not exceed the FDA action level of 2 ppm and thus did not warrant an advisory, at that time.

Table 4. Summary of Observed Total Mercury Data in Selected Species from the Connecticut River 1970 NH Fish Survey (Data from Houghton, 1971)

SPECIES (# of fish in sample)	Mean Total Hg (ppm)	Minimum Total Hg (ppm)	Maximum Total Hg (ppm)
Yellow Perch (16 fish)	0.31	0.02	0.8
Sucker (8 fish)	0.33	0.08	0.6
Smallmouth Bass (11 fish)	0.49	0.13	1.3

Table 5. Summary of Mean Total Mercury in Fillet and Offal in Selected Species from the Connecticut River 1989 Fish Survey (Data from Isaza and Dreisig, 1989)

SPECIES	Fillet (*u*g/g - ppm, wet weight)	Offal (*u*g/g - ppm, wet weight)
Yellow Perch	0.16	0.90
White Perch	0.16	0.11
Smallmouth Bass	0.13	0.05

In 1994 New Hampshire and Vermont prepared a joint report on the Connecticut River's water quality (NHDES and VTDEC 1994). However, no new sampling of fish tissue was

conducted as part of this report. They recommended that "additional and ongoing fish tissue analysis is needed."

Also in 1994 the New Hampshire Division of Public Health Services published an addendum report on mercury in fish in inland waters (Dreisig and Dupee 1994). Dreisig and Dupee (1994) did not sample the Connecticut River, but their report, together with a 1996 addendum did increase the recommended consumption limit of fish by women of reproductive age and young children, based on mercury contamination and EPA's revised reference dose. However, all fish sampled in this study were considered to pose a health risk to "heavy fish consumers", analogous to the subsistence fisher category in USEPA (2000b).

In August, 1996 and October, 1998 New Hampshire sampled fifteen smallmouth bass from Moore Reservoir (Reach 7 in the current study) for mercury. Mean mercury in skin off fillets was 0.93 ppm, with a range from 0.4 to 1.63 ppm. Three yellow perch sampled from this reservoir in August, 1996 had a mean mercury in skin off fillets of 1.2 ppm, ranging from 1.09 ppm to 1.27 ppm.

In October, 1998 in Comerford Reservoir (Reach 6 in the current study) ten smallmouth bass were sampled for mercury in skin off fillets. Mean mercury was 0.82 ppm with a range from 0.46 ppm to 1.22 ppm. Seven yellow perch sampled in 1996 and 1998 contained a mean mercury level in skin off fillets of 0.99 ppm with a range from 0.62 ppm to 1.35 ppm.

In McIndoes Reservoir (Reach 6) fifteen smallmouth bass were sampled in October 1998 for mercury in skin off fillets. Mean mercury was 0.65 ppm, ranging from 0.22 ppm to 1.33 ppm. Six yellow perch sampled in 1996 and 1998 had mean mercury in skin off fillets of 0.23 ppm, with a range of 0.14 ppm to 0.39 ppm[18].

New Hampshire rescinded an advisory for total PCBs in all species of fish along a ~260 mile long stretch of the Connecticut River on September 1, 2001. The rescinded advisory had been established in 1992. A state-wide advisory is in effect for mercury in fish. 'At risk' and other populations are advised to limit consumption of NH freshwater fish. In addition to the state-wide advisory, Comerford (Reach 6) and Moore Reservoirs (Reach 7) currently have specific advisories recommending 'at risk' populations avoid consuming any fish and all others to limit consumption.

Further information may be obtained by contacting Ms. Pamela Schnepper (Pschnepper@des.state.nh.us) 603-271-3994, Toxicologist at NHDES. Information on current NH fish advisories:http://www.wildlife.state.nh.us/Fishing/fish_consumption.htm.

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[18]Results of sampling of smallmouth bass, yellow perch, and white suckers in the Comerford, Moore and McIndoes Reservoirs, by the Biodiversity Research Institute, in 2000-2003 is compared with data from Reaches 6 and 7 in Appendix B.

1.2.4 State of Vermont

The State of Vermont has done very limited sampling in the mainstem of the Connecticut River, as most of these are not Vermont state waters. Ewald and Mulligan (2003) chronicle the complex, interesting history of the boundary dispute. Mulligan (pers. comm. 2005) notes, " the boundary was reaffirmed in 1934 as the ordinary low water mark on the west bank. The boundary is identified with markers. In some places, dam construction has inundated the state line, so much of Moore and Comerford reservoirs[19], for example, are Vermont waters."

In 1970 the Vermont Department of Fish and Game had edible portions from individual fish analyzed for mercury from the Connecticut River near Windsor, VT (Reach 5 in the current study). Three smallmouth bass were sampled with 0.2, 0.3 and 0.4 ppm of Hg. Additionally three yellow perch were sampled with 0.3, "trace", and 1.1 ppm of Hg (VTANR-DEC, 1990).

In December 1975 and January 1976 fish were sampled for PCB Arochlor 1254 from the Vernon Pool, either from the bottom of Reach 5 or top of Reach 4 in the current study. Fifteen yellow perch were found to have an average value of 0.54 ppm. However, seven white suckers and sixteen smallmouth bass had only a "trace" level (VTANR-DEC, 1990).

The Vermont Department of Health currently has fish advisories for mercury in all fish in all state waters. "At risk" populations are cautioned to not consume any fish from Comerford Reservoir (Reach 6) and Moore Reservoir (Reach 7). Other fishers are advised to limit meals. In McIndoes Reservoir (Reach 6) Vermont advises limiting consumption of all fish. Specific fish advisories in effect for Vermont waters may be found at: (http://www.state.vt.us/health/fish.htm). Ms. Razelle Hoffman-Contois (Rhoffma@vdh.state.vt.us) (802-863-7558) may be contacted for additional information on Vermont's fish advisories. The public may also call 1-800-439-8550.

1.2.5 USGS NAWQA Basin Study

In 1992-1993 the USGS analyzed organochlorine contaminants in white sucker composites from five sites in the mainstem of the Connecticut River, as part of the National Water-Quality Assessment Program (NAWQA) (Coles 1996; 1998; 1999). The size of Connecticut River white suckers sampled by the USGS were highly comparable to those in the current study.

[19] McIndoes Reservoir is also jointly claimed by Vermont and New Hampshire.

Coles (1998) observed that,

> "The Connecticut River mainstem sites...whose drainage-basin population densities increase progressively to about 10-fold, showed a downsream trend of increasing total DDT concentrations from 0 (nd) to 260 ug/kg at... (Longmeadow, MA) (highest in the CT River basin sites)."

Observed levels of DDT homologs were consistent with the historic pattern of DDT use. Total DDT was not correlated with agricultural land use. However, there was a significant difference between low, medium and high density population basins and total DDT. Higher population basins had higher total DDT concentrations in whole white suckers (Coles 1998).

Total chlordane was also related to drainage basin population density, consistent with extensive use in urban areas prior to being banned. Total chlordane also was not correlated with agricultural land use. Nonachlor was the most abundant and recalcitrant form observed by Coles (1998; 1999).

Coles (1996) analyzed length-age relations and total PCB content of mature white sucker composites. He found the Connecticut River fish were smaller at a given age than those from Canadian lakes. White suckers displayed a linear growth rate following maturity, but growth rate varied widely among sites. Young fish are known to grow faster and female white suckers grow faster than males (Scott and Crossman 1973). Coles (1996) found age of fish had no effect on the lipid fraction and did not appear to relate to total PCB content.

Coles (1998) compared results from several previous Connecticut River fish tissue studies (Table 6). Coles (1998) concluded there was a trend of increasing levels of organochlorine contaminants downstream in the basin. Coles (1998) concluded total DDTs and total PCBs had not declined, but total chlordane had decreased since earlier studies.

Table 6. Summary of Total DDT, Chlordane and PCBs in Whole Fish Composites from the Connecticut River (Adapted from Coles 1999). -- analysis not performed; Reaches of current study shown in brackets

Site	Year	Spp	DDT (Total)	Chlordane (Total)	PCBs (Total)	Reference
near Lancaster, NH **(Reach 7)**	1994	WS	16	nd	nd	Coles (1999)
at Hanover, NH **(Reach 6)**	1986	SMB	80	--	380	Isaza and Dreisig, 1989
at W. Lebanon, NH **(Reach 5)**	1986	SMB	21	--	300	Isaza and Dreisig, 1989

at Claremont, N.H. **(Reach 5)**	1986	SMB	40	--	260	Isaza and Dreisig, 1989
at South Charleston, NH **(Reach 5)**	1993	WS	80	14	690	Coles (1999)
at Brattleboro, VT **(Reach 5)**	1986	SMB	80	--	580	Isaza and Dreisig, 1989
N. of MA-NH Border **(Reach 4)**	1986	SMB	100	--	800	Isaza and Dreisig, 1989
at Montague City, MA **(Reach 3)**	1993	WS	140	14	820	Coles (1999)
at Holyoke, MA **(Reach 2 or 3)**	1985	WS	210	70	1,060	USFWS, 1986
at Chicopee, MA **(Reach 2)**	1985	WS	200	160	1,640	USFWS, 1986
near Longmeadow, MA **(Reach 2)**	1993	WS	260	63	1,400	Coles (1999)
at Enfield, CT **(Reach 2)**	1985	WS	160	120	880	USFWS, 1986
near Portland, CT **(Reach 1)**	1993	WS	160	64	940	Coles (1999)
above Middletown, CT **(Reach 1)**	1985	WS	140	120	1,160	USFWS, 1986
at Haddam, CT **(Reach 1)**	1985	WS	160	150	1,580	USFWS, 1986

1.2.6 Connecticut River Reservoir Sampling

The Biodiversity Research Institute of Gorham, ME provided data collected in 2000-2003 on mercury in whole and filleted smallmouth bass, yellow perch, and white suckers from impoundments in Reach 6 (McIndoe Falls Reservoir; Comerford Reservoir) and Reach 7 (Moore Reservoir). This data is compared to that found in the current study in Appendix C.

1.2.7 National Study of Chemical Residues in Fish

This USEPA (1992a; 1992b) study collected white suckers at 32 sites and smallmouth bass at 26 sites from a total of 388 sites. 314 of these sites were selected because of known point and non-point source problems, 39 were USGS National Stream Quality Accounting Network (NASQAN) sites, and 35 were selected as ambient sites. Many sites were selected because of known or suspected high dioxin levels.

Table 7. Mean Contaminant Levels found in Smallmouth Bass Fillets and Whole White Suckers in the National Study of Chemical Residues in Fish (USEPA 1992a; 1992b)

Contaminant (ppb)	Smallmouth Bass Fillets	Whole White Suckers
Mercury (ppm)	0.34	0.11
Total PCBs	496.22	1,697.81
alpha-BHC	0.36	3.31
gamma-BHC	0.15	1.66
Dieldrin	2.34	22.75
Endrin	ND	0.24
Heptachlor Epoxide	0.07	1.09
Mirex	1.99	4.35
Oxychlordane	0.54	3.10
Total Chlordane	4.01	18.43
DDE	33.63	78.39
Total Nonachlor	7.82	20.83
Hexachlorobenzene	0.36	3.62
Dioxin Congeners		
2,3,7,8-TCDD[20]	7.20E-04	8.08E-03
1,2,3,7,8-PentaCDD	ND	2.05E-03
1,2,3,4,7,8-HexaCDD	ND	1.03E-03
1,2,3,6,7,8-HexaCDD	7.90E-04	1.96E-03
1,2,3,7,8,9-HexaCDD	ND	8.80E-04
1,2,3,4,6,7,8-HeptaCDD	6.70E-04	3.72E-03
OctaCDD	NA	NA

[20]Chlorinated dibenzo-p-dioxins (CDDs) [dioxins] and chlorinated dibenzofurans (CDFs) [furans].

Contaminant (ppb)	Smallmouth Bass Fillets	Whole White Suckers
Furan Congeners		
2,3,7,8-TetraCDF	1.93E-03	2.29E-02
1,2,3,7,8-PentaCDF	ND	1.10E-03
2,3,4,7,8-PentaCDF	5.10E-04	2.64E-03
1,2,3,4,7,8-HexaCDF	1.28E-03	2.21E-03
1,2,3,6,7,8-HexaCDF	1.23E-03	1.29E-03
1,2,3,7,8,9-HexaCDF	ND	1.06E-03
2,3,4,6,7,8-HexaCDF	ND	1.09E-03
1,2,3,4,6,7,8-HeptaCDF	6.90E-04	1.23E-03
1,2,3,4,7,8,9-HeptaCDF	ND	1.13E-03
OctaCDF	NA	NA
Dioxin/Furan Human/Mammalian TEQ[21]	1.51E-03 (0.0015)	1.51E-02 (0.0151)
Dioxin/Furan Fish TEQ	1.34E-03 (0.0013)	1.38E-02 (0.0138)
Dioxin/Furan Bird TEQ	3.43E-03 (0.0034)	3.65E-02 (0.0365)

NA - not analyzed
ND - not detected
Whole white suckers had approximately an order of magnitude greater TEQs than smallmouth bass fillets.

1.3 Contaminants in Connecticut River Sediment

Breault and Harris (1997) have noted that,

> "The chemistry of streambed sediment influences the biotic quality of a stream as aquatic organisms ingest particulate matter and accumulate trace elements and organic compounds (Forstner and Wittmann, 1979; Luoma, 1983). The accumulation of trace elements and organic compounds in aquatic organisms can cause various physiological problems and even death of the organisms. Subsequent ingestion of

[21] TEQ toxicity is based on WHO consensus TEFs for humans/mammals, birds and fish (Van den Berg and others 1998) (see Chapter 3);

aquatic organisms transfers the accumulated contaminants upward through the food chain."

The National Water-Quality Assessment (NAWQA) for the Connecticut River basin sampled sediment from 25 sites, 5 of which were in the mainstem of the river, most others in proximal tributaries (Breault and Harris, 1997). Breault and Harris (1997) observed that "although some streambed sediments in the CT River basin had high trace-element concentrations, many were among the lowest observed...For example, mercury concentrations were highest—about 15 times the average crustal abundance—in streambed sediment at site 28 on the Hockanum River near East Hartford, Connecticut, however, mercury concentrations generally were lowest in the Connecticut River Basin compared to the other basins in the study" (i.e. Housatonic and Thames river basins).

EPA has supported two recent assessments of sediment quality in the Connecticut River. Nolan and Bridges (1999), of EPA's Regional Lab, sampled ten stations in 1998 along a 225 mile distance of the mainstem of the Connecticut, including the entire Vermont and New Hampshire boundary (Map 2[22]). Sites were selected to be downstream of major tributaries and/or populated areas and considered potential "hot spots". Mercury and PCBs were not found at any stations above the laboratory reporting limits. DDT Homologs were only found at low concentrations at Stations UTCR-3 and UTCR-8.

In 2000 EPA's Superfund program surveyed 100 sediment sites in the middle and upper Connecticut River for 159 potential contaminants (Map 2). The results of this much more substantial survey were presented to the interested communities in public forums. Figure 1 displays the 'low level'[23] mercury results from that survey as a cumulative distribution function. Table 8 summarizes descriptive statistics for low level mercury observed in EPA's 2000 Connecticut River study. Although maximum concentrations were similar to those observed by Breault and Harris (1997), generally much lower values were observed. It is not believed that Connecticut River sediments are a significant source of mercury in fish.

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[22]Map 2 delineates the 8-digit NHD HUC 'watersheds' of the Connecticut River. However, nationally, at all mapping scales, only about 45% or less of hydrologic unit codes (HUCs) are true watersheds, in which the boundary delineates the surface and subsurface drainage of a geographic area to a particular receiving point on a stream, typically a stream confluence (Omernik 2003). It is not possible to delineate a continuous coverage of 'true' watersheds across an entire region, inevitably areas have to be included in the cataloguing units that are not hydrologically contained within the boundary (Omernik 2005; pers. comm.). HUCs and most ostensible 'watershed' coverages are delineated with such continuous coverages.

[23]Low level refers to the analytical method, not the observed concentrations.

Table 8. Observed Concentration of Mercury in Streambed Sediment Samples from EPA's 2000 Superfund Study of the Connecticut River

Trace Element	Minimum Conc. (ppm)	Lower Quartile (ppm)	Median (ppm)	Upper Quartile (ppm)	Maximum Conc. (ppm)
Mercury	0.0004	0.008	0.016	0.037	0.93

The current EPA point-of-contact for this study (Savitski 2001) is Ms. Nancy Smith (Smith.nancya@epa.gov) or 617-918-1436. Lori Siegel, Ecological Risk Assessor at NHDES. 603-271-0699 (lsiegel@des.state.nh.us) is currently completing a risk assessment of both EPA sediment data sets.

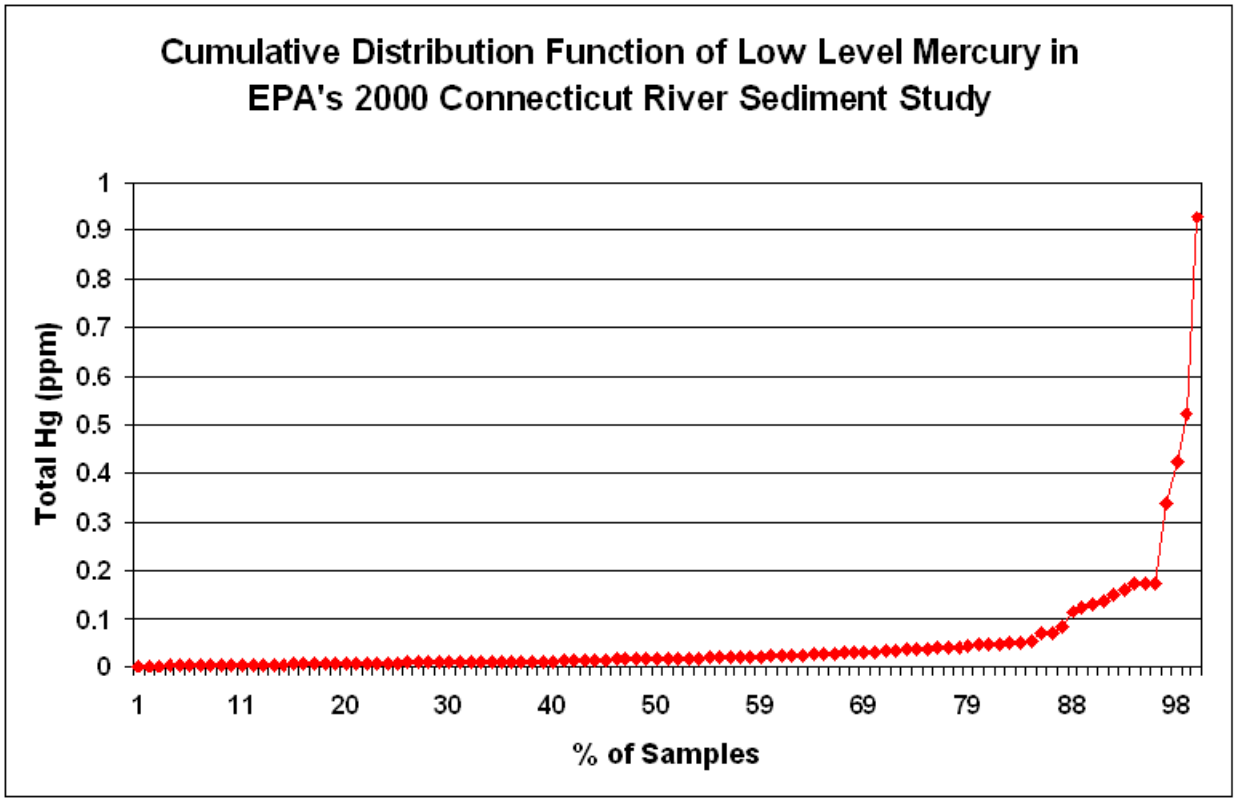
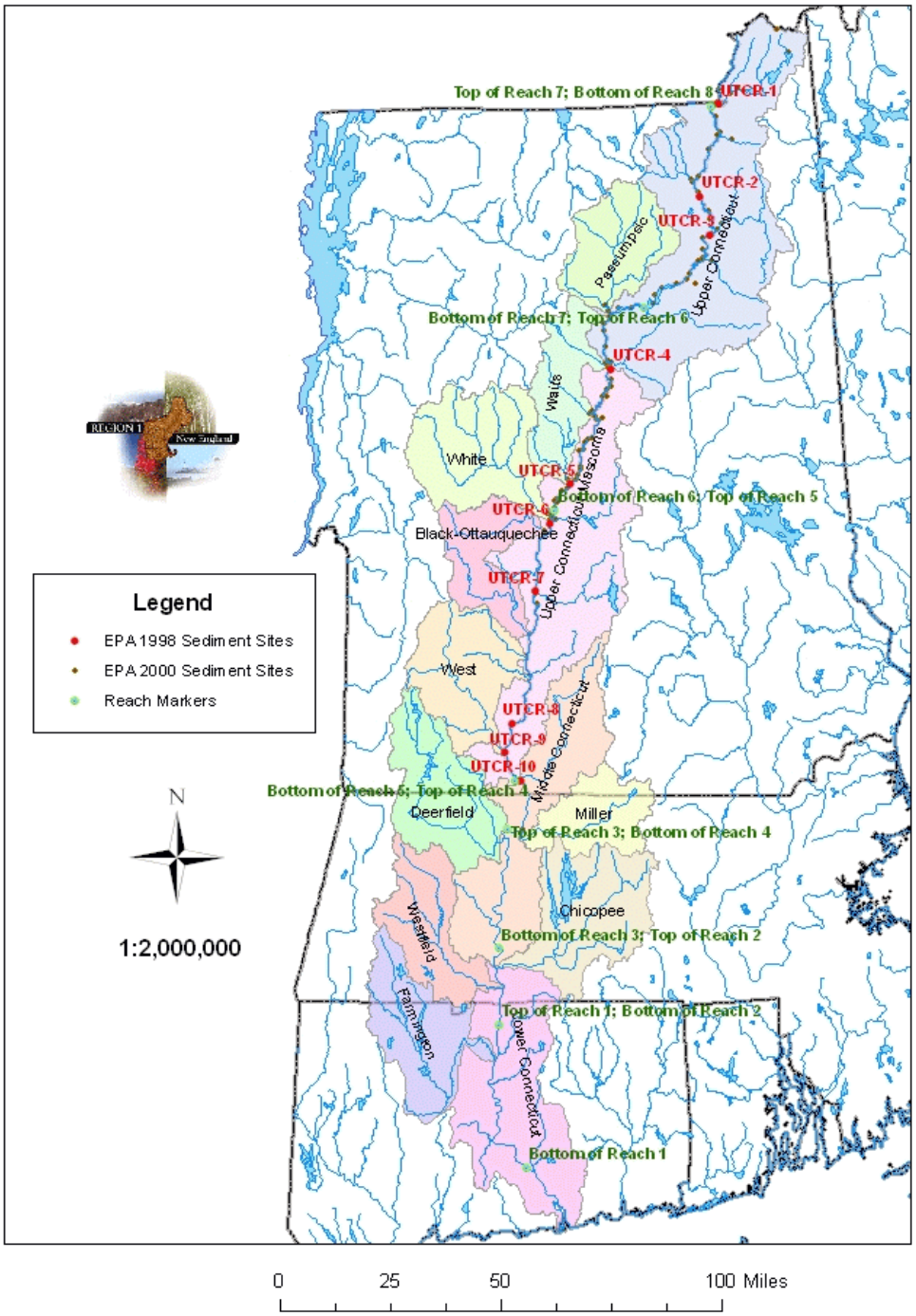


Figure 1. CDF of Low Level Mercury in EPA's 2000 Connecticut River Sediment Study

Connecticut River (8-digit HUC) 'Watersheds' - EPA 1998 and 2000 Sediment Sampling Sites



Map 2. Connecticut River (8-digit NHD HUC) 'Watersheds' - EPA 1998 and 2000 Sediment Sampling Sites

1.4 Contaminants in Fish

The contaminants in the current study are Persistent Bioaccumulative and Toxic (PBTs) Pollutants and/or Persistent Organic Pollutants (POPs). EPA (2002) notes that POPs adversely affect humans and wildlife, are readily transported by wind and water, are globally distributed, persist for long time periods and can bioaccumulate through food chains.

USEPA (2002) concludes,

> "PBTs..can build up in the food chain to levels that are harmful to human and ecosystem health. They are associated with a range of adverse human health effects, including effects on the nervous system, reproductive and developmental problems, cancer, and genetic impacts"
>
> "The (human) populations at risk, especially to PBTs such as mercury, dioxins, and Polychlorinated Biphenyls (PCBs), are children and the developing fetus."

As Breault and Harris (1997) note, many of the contaminants found in stream and river sediments are resistant to biological, chemical or physical breakdown processes, including chlordane, DDT and PCBs. Many of the contaminants found in streams and rivers, such as the Connecticut, are present as a result of human activities. Breault and Harris (1997) conclude,

> "[As] many biological systems are not well adapted to the effects of these constituents, they may be toxic or in some way harmful to aquatic organisms at very low concentrations...Once in streams or streambed sediments, trace elements and organic compounds can be absorbed or be ingested by aquatic organisms. If benthic organisms become contaminated, they can act as a source of contaminants to fish. Many of the hydrophobic and lipophilic contaminants are readily stored in the fatty tissue of fish, where they tend to bioaccumulate, and commonly are not readily metabolized. Fish biomagnify these compounds both through uptake from food and directly from water passing over their gills. Fish-eating mammals and birds consume the contaminated fish, and continue to pass contaminants up the food chain. This accumulation of streambed sediment contaminants in fish tissues increases the likelihood that these contaminants will be detected; thus, tissue analysis can be used to provide information about the occurrence and distribution of stream associated contaminants at otherwise undetectable concentrations"

The current study confirms this as contaminants were observed in fish tissue at levels considerably higher than were typically found in sediment.

1.5 Data Analysis Methods

Chapters 2 through 6 analyze contaminants (mercury, coplanar PCBS/dioxins, organo-chlorine pesticides, morphometric (weight and length) data, and smallmouth bass age. Observed levels of contaminants were compared to EPA or other published human health and ecological screening levels[24].

Analysis of Variance (ANOVA) was used to statistically compare differences between species and Reaches. EPA statistician, Dr. James Heltshe (pers. comm. 2005), advocated use of parametric, rather than non-parametric tests, in all statistical analyses of CT River fish data, given it's indeterminate (multivariate) distribution, the small sample size, and lower power of non-parametric tests. An Analysis of Covariance of total mercury by species and Reach, with length as the covariate, was also undertaken, yielding results highly similar to those of the factorial and one-way ANOVAs. However, in some samples fish size appears to be confounded with total mercury. Thus only the results from the ANOVA are shown. Statistical analyses were performed in STATISTICA versions 5 through 7.1 (StatSoft 2005).

Morphometric data were used to assess fish "condition" (i.e. health) and are compared between Reaches using ANOVA. Smallmouth bass age is compared graphically with contaminant levels. Parametric and non-parametric correlation and linear regression are also used where appropriate.[25]

Empirical Cumulative Distribution Functions (CDFs)[26] were generated for total mercury in whole and filleted fish by species, over all Reaches, for coplanar PCB human/ mammalian, fish, and bird TEQs in whole and filleted fish by species, and for total DDT Homologs in whole and filleted fish by species.

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[24]The current study constitutes a human health and ecological risk screening and not a full risk assessment. Ecological risk assessment is a "...process that evaluates the likelihood that adverse ecological effects may occur or are occurring as a result of exposure to one or more stressors"(USEPA 1998). Human health risk assessment, for example, to mercury includes hazard identification and dose-response assessments and assessment of exposure covered in Volumes 4 and 5 of EPA's Mercury Study Report to Congress (USEPA 1997b; 1997c).

[25]One reviewer recommended comparing this study's results with watershed/HUC land use/cover data, but this proved to beyond the scope of the current report. Additional exploration of this data set using such ancillary data may reveal additional explanatory factors and relationships.

[26]"A CDF indicates, across the full range of values, the proportion of samples at or below a given value. CDFs are a useful descriptive tool in determining whether most of the values are very low, with a few high values or whether values cover a broader range" (USEPA 2001e:11). CDFs in this report only display observed values from a small sample of fish species in each Reach and thus are not indicative of the entire population of fish within a Reach.