Levels of Bioaccumulative Chemicals of Concern in Air, Water, Sediment and Sentinel Species of the Rochester Embayment of Lake Ontario

Final Report

to

Mr. Donald E. Zelazny
Great Lakes Program Coordinator
NYS Department of Environmental Conservation
270 Michigan Avenue
Buffalo, NY 14203-2999

by

James M. Haynes and Joseph C. Makarewicz
Department of Environmental Science and Biology
State University of New York at Brockport
350 New Campus Drive
Brockport, NY 14420-2973

and

Thomas C. Young
Department of Civil and Environmental Engineering
Clarkson University
Potsdam, NY 13699-5710

October 2004

Table of Contents

Introduction………………………………………………………… 4
Methods……………………………………………………………….. 5
Choice of Bioaccumulative Chemicals of Concern…………….. 5
Choice of Indicator Species….………………………………….. 5
Sample Collection and Processing……………………………… 5
PCB, Mirex and Photomirex Analysis………………………….. 6
Dioxin and Furan Analysis……………………………………… 7
Experimental Design and Statistics……………………………… 7
Chemical Fate and Transport Modeling…………………………. 9
Results……………………………………………………………….. 10
Bass and Turtle………………………………………………….. 10
Air, Water and Sediment………………………………………… 11
Modeling…………………………………………………………. 12
Discussion…………………………………………………………. 13
Temporal and Spatial Differences in Physical Media…………… 14
Differences in Biota Exposed and Not Exposed to
Lake Ontario or its Food Web……………………………..… 14
Which Sentinel Species is the Best Biomonitor?..………………. 15
Does One Chemical Provide as Much Information
as More than One?…………………………………………… 15
Human and Wildlife Health Implications……………………….. 16
Modeling…………………………………………………………. 17
Limitations of the Study………………………………………….. 18
Conclusions………………………………………………………….... 19
Acknowledgments…………………………………………………. 20
Literature Cited……………………………………………………….. 20
Tables………………………………………………………………. 22
1. Total PCB, mirex+photomirex and total dioxin+furan concentrations in the tissues of organisms exposed and not exposed to Lake Ontario water or its food web and in air and sediment of the Rochester Embayment AOC……… 22
2. Two-way ANOVA for total PCB, mirex+photomirex and total dioxin+furan and the ratios of M+P:PCB and D+F: PCB by species and exposure to Lake Ontario water or its food web……………………………………………….. 23
3. Two-way ANOVA for total PCB, mirex+photomirex and the ratio of M+P:PCB by medium, month and exposure to Lake Ontario water or its food web……………………….. 24
4. SEM:mean percent values of mirex+photomirex:total PCB and total dioxin+furan:total PCB ratios in air, sediment and tissues……………………………………………………. 25
5. Estimated risk (human chronic toxicity) of consuming largemouth bass and snapping turtle from portions of the study area exposed and not exposed to Lake Ontario water or its food web……………………………….………………… 26

Figures……………………………………………………………..……. 27
1a. The Rochester Embayment of Lake Ontario………………… 27
1b. The sub-basins of the Rochester Embayment Area of Concern……………………………………………… 28
1c. The Genesee River sub-basin of the Rochester Embayment Area of Concern………………………………… 29
2. Estimated fluxes and compartments of water used to model chemical transport and fate in the lower Genesee River, Irondequoit Creek and Salmon Creek portions of the Rochester Embayment of Lake Ontario……………………... 30
3. Estimated annual PCB loads to Braddock Bay, the lower Genesee River and Irondequoit Bay…………………………. 31
4. Estimated PCB concentrations in water in Braddock Bay, the lower Genesee River and Irondequoit Bay…………. 32
5. Estimated and observed PCB concentrations in sediment in Braddock Bay, the lower Genesee River and Irondequoit Bay……………………………………………… 33
6. Estimated and observed PCB concentrations in largemouth bass in Braddock Bay, the lower Genesee River and Irondequoit Bay……………………………………………… 34
Appendices…………………………………………………………. 35
1. Biological data and concentrations of total PCB and mirex+photomirex for muscle of largemouth bass and snapping turtle exposed and not exposed to Lake Ontario water or its food web………………………………………….. 35
2. Biological data and concentrations of total PCB and mirex+photomirex for eggs of largemouth bass and snapping turtle exposed and not exposed to Lake Ontario water or its food web………………………………………….. 37
3. Biological data and concentrations of total dioxin+furan for selected tissues of largemouth bass and snapping turtle exposed and not exposed to Lake Ontario water or its food web…………………………………………………… 39
4a. Concentrations of total PCB and mirex+photomirex in airsheds located near and far from the Rochester Embayment of Lake Ontario during four months…………….. 43
4b. Concentrations of total PCB and mirex+photomirex in sediment at five locations exposed and not exposed to Lake Ontario water or its food web during four months……… 44

Introduction

In the 1980s, the International Joint Commission (IJC) began the process of creating and implementing remedial action plans (RAPs) in 43 areas of concern (AOCs) throughout the Great Lakes Basin of Canada and the United States. An area identified as an AOC violated one or more of 14 "use impairments" listed by the IJC. For example, "fish and wildlife consumption advisories" due to the presence of bioaccumulative chemicals of concern (BCCs) is a use impairment identified for the Rochester, NY Embayment of Lake Ontario AOC.

The Rochester Embayment AOC (83 km^2) extends several km east and west of the mouth of the Genesee River and includes the 9.7 km reach of the lower Genesee River below an impassable falls (Figure 1a). The Stage I Remedial Action Plan prepared by the Monroe County Department of Health (RAP 1993) accepted the NYS Department of Health fish and wildlife consumption advisory as a use impairment in the Rochester Embayment AOC. However, many of the fishes on the consumption advisory list (e.g., salmon and trout, F. Salmonidae; American eel, *Anguilla rostrata*; common carp, *Cyprinus carpio*; white perch, *Morone americana*) accumulate their body burdens of bioaccumulative chemicals of concern as they move and feed in Lake Ontario beyond the Rochester Embayment. Salmonids, in particular, generally do not reside in the Rochester Embayment AOC or its tributary watersheds except during the last few weeks of their lives when they spawn below impassable barriers. Thus, the current fish consumption use impairment for the Rochester Embayment AOC *appears* to be based on cosmopolitan fish species and lake-wide conditions rather than resident species and local conditions.

The Stage II RAP (RAP 1997) recommended remedial actions, monitoring methods to track the progress of remedial actions, and the development of "delisting criteria" to determine when a use impairment no longer exists. In particular, the need to distinguish local from lake-wide influences of BCCs on the fish consumption advisory was recognized. To accomplish this task, information on the levels of BCCs in air, water and sediment, and in the tissues of *resident* aquatic species, in the AOC was required. Accordingly, our objectives were to:

(1) Determine the extent to which the Rochester Embayment AOC is contributing to the Lake Ontario fish consumption advisory that is due to PCBs, mirex/photomirex and dioxins/furans.

(2) Establish existing concentrations of BCCs in the AOC, and approaches for monitoring progress toward reducing their levels as remediation progresses.

(3) Quantify BCC levels in air, water, sediment and sentinel species in the AOC contributed from sources within and outside of the AOC.

(4) Explore whether one chemical can serve as a surrogate for BCCs generally in the future.

(5) Provide an indication of the levels of BCCs that may be ingested by terrestrial animals, such as mink and humans, that consume fish as part of their diet.

(6) Develop a model that might be used in the future to predict BCC concentrations in biota without having to measure concentrations in all of air, water, sediment and biotic media.

(7) Provide information to help the RAP Toxics Oversight Committee (TOC) prepare "delisting criteria" for the fish and wildlife consumption advisory use impairment.

In addition to evaluating the questions above in relation to the IJC-defined Rochester Embayment AOC, we also studied three watersheds tributary to Lake Ontario in the AOC: the West, Central and upper Genesee River sub-basins (Figures 1b,c). Levels of BCCs in largemouth bass (*Micropterus salmoides*) and snapping turtle (*Chelydra serpentina*) tissues were examined in animals exposed and not exposed to Lake Ontario water and its food web in Salmon Creek (West sub-basin). Levels of BCCs in air, water and sediment, in and out of the AOC, exposed and not exposed to Lake Ontario water or biota, were compared among the three sub-basins. The resulting comparisons provided the information needed to distinguish between BCC levels associated with the Rochester Embayment AOC and other sources.

Methods

Choice of Bioaccumulative Chemicals of Concern

PCBs, mirex+photomirex and dioxins+furans are responsible for the fish and wildlife consumption use impairment in the Rochester Embayment AOC (RAP 1993). PCBs and dioxins+furans are ubiquitous non-point source pollutants inside and outside of the AOC watershed. To the extent that local remediation programs can reduce sources in the AOC, lower overall levels of these chemicals can be expected in the AOC and its resident biota. Although mirex and photomirex are chemicals of concern in Lake Ontario, there are no known sources in the Rochester Embayment AOC (RAP 1993). Therefore, we used mirex+photomirex as a "control." Because of their low volatility and likely absence above impassable barriers in AOC tributaries (Lewis and Makarwicz 1988), mirex+photomirex should be found only in very low concentrations in air, water, sediment and biotic samples from areas not in contact with Lake Ontario water or its food web.

Choice of Indicator Species

BCCs are found at higher concentrations at higher levels of food webs. To effectively monitor changes in BCC levels as a result of local remedial actions requires sampling of *resident* species high in their food webs. These species are the most likely to suffer adverse health and population effects from exposure to high levels of BCCs, and they are the most likely to be consumed by humans. Snapping turtle and largemouth bass were selected as the sentinel species *to monitor contaminant levels generated from the Rochester Embayment watershed*. Both species are apex predators in aquatic communities that are likely to accumulate BCCs, are most likely to remain resident in local bays, ponds and rivers, and are least likely to enter Lake Ontario.

Sample Collection and Processing

Sampling sites (Figures 1b,c) were chosen to allow testing of specific hypotheses about BCC concentrations in biota and physical media in and out of the Rochester Embayment AOC and exposed and not exposed to Lake Ontario water or its food web. The upper Genesee River near Wellsville and Scio, NY was expected to be an *unpolluted* or *control* area because it was rural, out of the AOC, and not in contact with Lake Ontario. The remaining sampling sites were in the AOC. Upper Salmon Creek ponds and upper Genesee River tributaries were not in contact with Lake Ontario. Lower Irondequoit Creek was in contact with Lake Ontario biota, but not its water, and lower Salmon Creek was in contact with Lake Ontario water and its biota.

In June, August and November 2001 and in March 2002, 24-h air, 1-L water and 1-L sediment samples were collected at convenient locations throughout the AOC and its watershed (Figures 1b,c). Air samples were collected at three sites in the AOC (lower Salmon Creek, lower Irondequoit Creek, lower Genesee River) and at one site out of the AOC (upper Genesee River). Water and sediment samples were collected at a number of sites exposed to Lake Ontario water or its food web (in the lower Salmon Creek and lower Irondequoit Creek subwatersheds) and at a number of unexposed sites (in the upper Genesee River, lower Genesee River and upper Salmon Creek subwatersheds). Sixteen air, 19 sediment and 19 water samples (4 months x 4 or 5 locations each) were collected, and one analysis (total PCBs, mirex+photomirex) was conducted for each sample, for a total of 54 analyses.

Air samples were taken over a 24-hour period with a Graseby high volume air sampler equipped with PUF (polyurethane foam) cartridges to collect vapors from the air. Airflow rates were calibrated with a Model G40 PUF calibration unit. Water was collected just below the surface and, after preservation to pH < 2 with nitric acid (Ultrex grade), samples were analyzed within 30 days. Sediment was collected with an Ekman dredge or stainless steel spoon in pools or back eddies high in organic debris that attracts BCCs. Water and sediment samples were stored at 4^{o}C in pesticide-grade, hexane-rinsed glass containers with Teflon caps.

In the summer of 2001, 30 snapping turtles and 30 largemouth bass were collected, 15 each from portions of the Salmon Creek subwatershed exposed (in wetland embayments of lower Salmon Creek, but six bass were collected in wetland embayments of Sandy Creek; Appendix 1) and not exposed (from ponds in the upper subwatershed because habitat in the upper creek is not suitable for bass and turtles) to Lake Ontario water or its food web. In the summer of 2003, five turtles and three bass were collected in the upper portion of the Salmon Creek subwatershed to balance sample sizes of eggs. Captured animals were examined for tumors and other external abnormalities (re: fish and wildlife deformities use impairment), measured (turtle carapace length, bass total length) and weighed. Tissues (turtle right fore- and hind limbs, eggs and adipose; bass filets and eggs) were removed and placed on ice in the field. In the laboratory tissues were processed and frozen in pesticide-grade, hexane-rinsed glassware with Teflon caps. Turtle egg contents and limb muscle with visible adipose tissue removed, as well as bass filets and eggs, were analyzed for total PCBs and mirex+photomirex, for a total of 82 analyses. A subset of tissues was analyzed for dioxins+furans.

The Salmon Creek subwatershed of the AOC (Figure 1b) was chosen for several reasons. It has ideal slow moving water, marsh and pond habitats for both snapping turtle and largemouth bass in its upper and lower regions. Specimens could be collected safely and easily, in contrast to the large and often dangerous Genesee River subwatershed and the highly suburbanized Irondequoit Creek subwatershed in the eastern portion of the AOC, both of which have good habitat for turtles and bass that is less accessible for sampling. In addition, funding for the project did not permit the larger number of samples needed to study two additional watersheds, and the Salmon Creek watershed was closest to SUNY Brockport.

PCB, Mirex+Photomirex Analysis

Mirex+photomirex and total PCB in air, water, sediment and tissue samples were analyzed with a Hewlett-Packard 5890 gas chromatograph, in splitless mode, equipped with an electron capture detector (ECD) and a DB-5 capillary column. Extraction and cleanups were made with dedicated glassware using pesticide-grade reagents. Skin-off filets (bass) and fore- and hind limbs (turtles), as well as eggs, were extracted and analyzed after homogenization. Extraction procedure and florisil cleanup of tissue generally followed Makarewicz et al. (2003).

Air samples collected on PUF (polyurethane foam) were extracted with hexane (EPA Method TO-4: Determination of organochlorine pesticides and polychlorinated biphenyls in ambient air). Analysis of water samples was by Empore C-18 extraction (EPA Method 525.2: Determination of organic compounds in drinking water by liquid-solid extraction and capillary column gas chromatography/ mass spectrometry). The Water Quality Laboratory at SUNY Brockport is ELAP-certified for water samples, and used GC-ECD (more sensitive than EPA Method 525.2). Sediment samples were air-dried, weighed and extracted in a 1:1 acetone/hexane solution by sonification. Before analysis by GC-ECD, extracts were cleaned by elution through Florisil columns (Plumb 1981).

Mirex+photomirex methodology, detection equipment, quality assurance, extraction techniques, and cross-laboratory comparisons used for fish analysis are reported in Makarewicz et al. (2003). Bass and turtle tissue was extracted overnight (16 ± 4 hrs) in a Soxhletic extractor (a minimum of 200 cycles) with 75-mL of methylene chloride/hexane (20:80 v/v) solvent mixture. The detection limit for each of total PCB and mirex+photomirex was 0.001 ug/g. Confirmatory analysis for total PCBs and mirex/photomirex was with a mass spectrometer (H-P G1800C GCD Plus-Gas Chromatograph Electron Ionization Detector).

Dioxin and Furan Analysis

Due to prohibitive expense, we did not analyze all samples collected for dioxins+furans. Five samples each of turtle and bass muscle tissue and of turtle adipose tissue were collected from animals in the upper (unexposed to Lake Ontario water or its food web) and lower (exposed) portions of the Salmon Creek subwatershed. Turtle adipose tissue was from fat bodies independent of limb muscle. Samples were processed and shipped in accordance with instructions from the contractors: Columbia Analytical Services (CAS) and the US Army Corps of Engineers Waterways Experiment Station (WES). CAS used EPA method 8290 for extractable organics in solid and chemical materials, and is NELAC-certified (E87611, FAC Rule 64E-1 regulations) by the state of Florida. WES used a P-450 liver cell (HepG2) induction assay developed by CAS (1998). The P450 HRGS assay uses human CYP1A1 genes fused to luciferase genes of fireflies, and the modified genes are integrated into human liver cells that are exposed to environmental samples. Dioxins, furans and co-planar PCBs bind to aryl hydrocarbon hydroxylase (AhR) receptors in the liver cells. After lysing, centrifugation and the addition of luciferin, the reaction between luciferase and luciferin produces light in proportion to the amount of dioxin-like contaminants in the sample. Results from CAS and WES analyses are reported as toxic equivalent (TEQ) concentrations.

Experimental Design and Statistics

Separating contaminants generated in the AOC from contaminants transported to it from Lake Ontario (e.g., salmonid migrations; Lewis and Makarewicz 1988) and from those deposited by the atmosphere is difficult. To do so required measuring concentrations in air, water and sediment at four or five locations in and out of the AOC and in the tissues of sentinel species exposed and not exposed to Lake Ontario or its food web. Because of the differing effects remedial actions should have on the concentrations of PCBs, mirex+photomirex and dioxins+furans in air, water, sediment and sentinel species over time and space in the AOC, establishing current levels was necessary to separate lake-wide and atmospheric from watershed (water and sediment) contributions to BCC levels in the AOC now and in the future.

Tissues: Using two-way analysis of variance (Statistix 2001), we tested the null hypothesis that levels of total PCB, mirex+photomirex and total dioxin+furan, and their ratios (M+P:PCB, D+F:PCB), did not differ in turtles and bass from regions of the Salmon Creek subwatershed exposed and not exposed to Lake Ontario or its food web. Because of the connection to Lake Ontario, including availability of migratory species' carcasses and prey fish from the lake, we predicted that levels of BCCs would be higher in the tissues of turtles and bass in the lower, exposed portion than in the upper, unexposed portion of Salmon Creek. Acceptance of the null hypothesis, or rejection of it showing that BCC concentrations are lower in biota not exposed to the lake's water or food web would indicate that the fish consumption use impairment in the AOC is not caused by pollution sources in the AOC. Also, rejection of null hypothesis showing that BCC concentrations are higher or more consistent in one of the two sentinel species would suggest the better species for future monitoring.

Physical Media: Also using two-way analysis of variance (Statistix 2001), we tested the null hypothesis that concentrations of total PCB, mirex+photomirex, and their ratios (M+P:PCB, D+F:PCB), did not differ in air, water and sediment among locations sampled (upper and lower Salmon Creek, upper and lower Genesee River, lower Irondequoit Creek) or among sampling months (June, August, November, March). If airborne PCBs are produced in the AOC, we expected to find a concentration gradient of low to high from the west to east (due to prevailing winds and amount of industry) and from south (near the rural Pennsylvania border) to north (due to population size and amount of industry). For mirex+photomirex, we expected to find a gradient of high to low from Lake Ontario south to the Pennsylvania border. Due to exposure to lake water or its food web, we expected to find higher levels of BCCs in water and sediment in the lower portion of the Salmon Creek and throughout the Irondequoit Creek subwatershed that lacks an impassable barrier to lake biota (see Figures 1b,c).

Acceptance of the null hypotheses for locations, or rejection showing that BCC concentrations in physical media at locations exposed to Lake Ontario or its food web are higher than at unexposed locations, would indicate that the Rochester AOC is not contributing BCCs to the surrounding area. Support of the null hypothesis for sampling months would indicate that time of year for taking future samples for monitoring does not matter. The consensus among local technical experts is that there are no significant sources of BCCs in the AOC and that delisting can proceed expeditiously. If air, water or sediment sources of BCCs exist in one or more subwatersheds of the AOC, testing of the hypotheses above will provide the information needed to begin identifying and remediating those sources. If few differences are found in space and time, future air, water and sediment monitoring for BCCs may be required at only one or a few locations or months, which will save time and money.

Ratios: Ratios of mirex+photomirex:total PCB (M+P:PCB) and of total dioxins+furans:total PCB (D+F:PCB) were calculated for tissues and physical media. Non-zero ratios (i.e., M+P or D+F was detected in a sample) and standard error (SEM):mean ratios were compared to evaluate whether proportions of BCCs were consistent across chemicals, tissues, air, water, sediment, locations and months. If the ratios are consistent within and across these factors, then one BCC likely could serve as a representative of all BCCs in future monitoring.

The critical value for determining whether a treatment was significant was $\alpha = 0.05$. Because of the large number of tests, Tukey's Honest Significant Difference (HSD) test was used to correct α.

Chemical Fate and Transport Modeling

Because modeling is less expensive than sampling and analysis, we explored the possibility that modeling can substitute to a greater or lesser degree for sampling during future BCC monitoring in the AOC. Data on concentrations of total PCB in water, sediment and bass, plus discharge and relevant physiographic data for several streams that are directly or indirectly tributary to the Rochester AOC, were used to create a preliminary model of BCC fate and transport in three subwatersheds of the AOC: Salmon Creek, Irondequoit Creek and the Genesee River. Where possible, these data were augmented by inclusion of estimates of embayment volume and surface area, plus concentrations of total suspended solids and additional discharge data for the systems of concern (USGS Daily Values, USEPA STORET). These data were collated, compiled, and summarized as (1) water- or airborne chemical or hydraulic loads and (2) simple spreadsheet schematic mappings to illustrate flow paths and discharge quantities. Subsequently, this information was used as input to a spreadsheet-based (Microsoft Excel), steady-state, deterministic CMSTR (completely-mixed stirred reactor) model of chemical transport, fate and bioaccumulation.

Modeling of the bioccumulation of BCCs in semi-aquatic snapping turtles is a more complex activity than the resources available, and the model used, for this project could support, so largemouth bass were used in the model. The modeling framework selected to develop preliminary exposure assessments for the project was constructed from well-developed and widely recognized mass balance principles as applied to water bodies. The customary approach to aquatic system modeling involves a mathematical representation of the principle of mass balance, or continuity, as applied to a control volume, point mass, or similar such device. For example, Equation 1 shows the accumulation of a contaminant of concentration, C, to be equal to the net transport flux of the contaminant due to advection and dispersion (N • n) across the boundaries, S, of a control volume, V. Because the contaminant may not be conservative, Equation 1 also shows the effects of contaminant fate process reactions (decay, generation, or transformation) occurring at a net rate, r, over the control volume.

$$\frac{\partial}{\partial t}\left(\int_V C\,dV\right) = -\int_S \left(N \bullet n\right) dA + \int_V r\,dV \qquad (1)$$

When applied to the simple case of a completely mixed reactor with a single inflow and outflow, Equation 1 assumes the familiar form shown as equation 2.

$$V\frac{dC}{dt} = QC_{\text{inflow}} - QC - rV \qquad (2)$$

The analysis presented in this report, in effect, employed several modifications of the steady-state form of Equation 2, shown here as Equation 3:

$$C = \frac{QC_{\text{inflow}} - rV}{Q} \qquad (3)$$

As a generic class, toxic chemical models for aquatic systems typically are intended to describe the environmental fate of substances that are markedly non-conservative (i.e., are environmentally reactive) and partition strongly to solid phases, such as hydrophobic organic compounds and heavy metals (Thomann and Mueller 1987, Chapra 1997). Accordingly, the reaction term in Equation 3 for application to the PCBs in the Rochester Embayment was expanded to include those processes known to affect the bioaccumulation and environmental fate of these compounds, including solid-solution partitioning, volatilization, sedimentation, resuspension, biotransformation, biotic uptake and bioaccumulation. Accordingly, the modifications of Equation 3 used for this work involved adapting the computation to the different physical systems and the environmental media of interest (e.g. water, algae, zooplankton, and fish). In several respects related to the representation of BCC fate process in the model, the model is similar to the much more sophisticated dynamic, mechanistic model known as LOTOX2 (DePinto et al. 1998).

Results

Mirex, photomirex, dioxins and furans were not found in all samples and their concentrations were low. Therefore, mirex+photomirex and dioxins+furans was computed for each sample to increase sample size (vs. analyzing each chemical separately) and to improve statistical power. In the results and discussion below, “exposed” = in contact with Lake Ontario water or its food web and “unexposed” = not in contact.

Bass and Turtle Analyses

PCBs were found in the muscle tissue (n=60) and eggs (n=23) of all largemouth bass and snapping turtles sampled from portions of the Salmon Creek subwatershed exposed and not exposed to Lake Ontario water or its food web. In exposed samples, mirex+photomirex was detected in 11/15 bass filets, 2/15 turtle limbs, 5/6 sets of bass eggs, and 5/5 sets of turtle eggs. In unexposed samples, mirex+photomirex was detected in 1/15 bass filets, 0/15 turtle limbs, 2/6 sets of bass eggs, and 1/6 sets of turtle eggs (Appendices 1,2). In exposed samples, dioxins+furans were detected in 3/5 bass filets, 5/5 turtle limbs and 5/5 turtle adipose samples. In unexposed samples dioxin+furan was detected in 5/5 filets, 2/5 limbs and 4/5 adipose samples (Appendix 3).

For total PCB in bass filets, concentrations of ranged from 0.005 to 0.290 µg/g in exposed samples and from 0.009 to 0.103 µg/g in unexposed samples. In turtle limbs, concentrations ranged from 0.003 to 0.064 and from 0.006 to 0.018 ug/g in exposed and unexposed samples, respectively (Table 1, Appendix 1). In bass eggs, total PCB concentrations ranged from 0.025 to 0.309 ug/g in exposed samples and from 0.035 to 0.287 ug/g in unexposed samples. In turtle eggs, concentrations ranged from 0.109 to 0.469 ug/g and from 0.024 to 0.268 ug/g in exposed and unexposed samples, respectively (Table 1, Appendix 2).

For mirex+photomirex in bass filets, concentrations ranged from non-detectable to 0.006 ug/g in exposed samples and from non-detectable to 0.002 ug/g in unexposed samples. In turtle limbs, concentrations ranged from non-detectable to 0.006 in exposed samples; no mirex+photomirex was detected in unexposed turtle limbs (Table 1, Appendix 1). In bass eggs, mirex+photomirex concentrations ranged from non-detectable to 0.028 ug/g in exposed samples and from non-detectable to 0.017 ug/g in unexposed samples. In turtle eggs, concentrations ranged from 0.009 to 0.047 ug/g in exposed samples, but no unexposed turtle eggs had a detectable concentration of mirex+photomirex (Table 1, Appendix 2).

For total dioxins+furans in bass filets, concentrations ranged from non-detectable to 0.005 ng-TEQ/Kg dry weight in exposed samples and from 0.001 to 0.008 ng-TEQ/Kg dry weight in unexposed samples. In turtle limbs concentrations ranged from non-detectable to 0.003 and from 0.001 to 0.002 ng-TEQ/Kg dry weight in exposed and unexposed samples, respectively. In turtle adipose tissue, concentrations of total dioxin/furan ranged from 6.611 to 34.707 ng-TEQ/Kg dry weight in exposed samples and from non-detectable to 0.325 ng-TEQ/Kg dry weight in unexposed samples (Table 1, Appendix 3).

Total PCB and mirex+photomirex concentrations were higher ($P = 0.019$, $P = 0.001$, respectively) in exposed than in unexposed muscle samples, and also in exposed egg samples for mirex+photomirex ($P < 0.001$). There was no difference between exposed and unexposed samples in the concentrations of total PCB in eggs ($P = 0.267$) or of total dioxins+furans in muscle tissue ($P = 0.644$). Total PCB ($P = 0.002$) and mirex+photomirex ($P = 0.001$) concentrations were higher in bass than in turtle muscle, but there was no difference in total dioxins+furans in muscle between species ($P = 0.275$). The concentration of mirex+photomirex was higher ($P = 0.038$) in turtle than in bass eggs, but there was no difference in the concentration of total PCB ($P = 0.403$). The concentration of total dioxins+ furans was higher ($P = 0.001$) in the adipose tissue of exposed than in unexposed turtles (Table 2).

The ratio of mirex+photomirex to total PCB (M+P:PCB) was higher ($P < 0.001$) in exposed than in unexposed muscle samples, but the ratio did not differ between bass and turtles ($P = 0.616$). There was no difference in the total dioxins+furans to total PCB ratio (D+F:PCB) in muscle by location ($P = 0.429$) or by species ($P = 0.732$). For eggs, there also was no was no difference in the M+P:PCB ratio between locations ($P = 0.470$) or between species ($P = 0.213$). Except for mirex+photomirex in muscle and eggs, there were no interactions between BCC concentrations or their ratios (Table 2); interactions for mirex+photomirex resulted from the large number of non-detectable concentrations across locations and species (especially for unexposed turtles).

We attempted to compare the results of total dioxin+furan TEQs determined analytically with P450 enzyme induction liver cell assays designed to detect total dioxin+furan-like BCCs, including co-planar PCBs. At the low concentrations found in bass and turtle muscle (analyses in 2001) and in turtle adipose tissue (analyses in 2003), the cell assay was not sensitive enough. Bass filets from the exposed and unexposed portions of the Salmon Creek subwatershed (n=5 each) and turtle limbs from the unexposed sampling sites (n=5) all had concentrations below detection limits (Table 1, Appendix 3). The two exposed turtles with dioxin+furan-like BCCs detected by the cell assay in muscle (n=5) and in adipose (n=5) tissue were the same individuals. As determined by the cell assay, concentrations of total dioxin+furan-like BCCs in exposed samples of turtle muscle and adipose averaged 0.002 and 2.183 ng-TEQ/Kg dry weight, respectively (Table 1, Appendix 3). Cell assay:analytical ratios for turtle muscle and adipose were 596 and 0.269, respectively. These results are so inconsistent, and the samples sizes are so small, that no conclusion can be drawn. Finally, the cell assay did not respond to mirex or photomirex standards, indicating that they do not have properties like dioxins, furans or co-planar PCB congeners.

Air, Water and Sediment Analyses

Air, water and sediment samples were collected at five locations (but not in the upper Salmon Creek subwatershed for air) (Figure 1b): upper and lower Genesee River and upper Salmon Creek (none exposed to Lake Ontario water or its food web), and lower Irondequoit Creek and lower Salmon Creek (both exposed to Lake Ontario water or its food web), and in four months (March, June, August, November). The upper Genesee River location was out of the Rochester metropolitan area near the Pennsylvania border (Figure 1c). PCBs were found in all air (n=16) and sediment (n=19) samples, but in no water samples. Mirex+photomirex was found in 14/16 air samples and in 10/19 sediment samples, but in no water samples. Because of small sample sizes, there were not enough degrees of freedom to measure interaction effects between locations (n=5) and months (n=4). Dioxins and furans were not analyzed in air, water or sediment samples.

No photomirex was detected in air samples. Mean total PCB and mirex concentrations ranged from 0.79 to 1.21 and from 0.02 to 0.03 ng/m^3, respectively, at the four sampling locations (Table 1). There were no differences in total PCB ($P = 0.431$) and mirex concentrations ($P = 0.699$), or in M:PCB ratios ($P = 0.898$), among the four sampling locations (Table 3). Among sampling months, the concentrations of total PCB and mirex ranged from 0.55 to 1.32 and from 0.01 to 0.06 ng/m^3, respectively (Table 1). The total PCB concentration was lower ($P = 0.037$) in March than in August (Table 3). Mirex concentrations varied in a more complex way across months, but concentrations in March were lower ($P = 0.004$) than in November and August. There were no differences in M:PCB ratios across months ($P = 0.258$). Raw data is in Appendix 4a.

For reasons explained in the discussion, no PCBs or mirex+photomirex were detected in water samples. Values for similar systems in western New York were used for modeling.

In sediment, mean total PCB and mirex+photomirex concentrations ranged from 0.046 to 0.590 and from non-detectable to 0.010 ug/g, respectively. There was no difference in total PCB concentration ($P = 0.205$), or in M+P:PCB ratios ($P = 0.259$), among the five sampling locations, but the level of mirex+photomirex in lower Salmon Creek sediments (most directly in contact with Lake Ontario water or its food web) was higher ($P = 0.003$) than at the other four locations (Table 3). One sample, particularly high in PCBs (1.541 ug/g), was collected in lower Salmon Creek near the Braddock Bay Inn on Manitou Road in Greece, NY. Another sample (0.509 ug/g PCB) collected at Black Creek Park in Churchville, NY resulted in the relatively high value for lower Genesee River sediments. Among months, there were no differences in total PCB ($P = 0.555$) or in mirex+photomirex concentrations ($P = 0.734$), but the M+P:PCB ratio was lower in March ($P = 0.042$) than in August (Table 3). Raw data is in Appendix 4b.

Modeling

Figure 2 illustrates flow paths and discharge quantities of major streams in the AOC subwatersheds studied: Salmon Creek, Genesee River and Irondequoit Creek. It also shows volumes of the receiving water bodies: Braddock Bay, lower Genesee River and Irondequoit Bay, respectively. Estimated loadings of PCBs to the three watersheds are shown in Figure 3 (mirex+photomirex data was too sparse to permit modeling). Concentrations representing environmental exposure (water and sediment) and bioaccumulation (bass tissue), are shown in Figures 4-6. These data were cast to facilitate comparisons between measured values (mid-point of observed ranges) and for high and low model-based predictions for each contaminant, medium, and system of interest. The results, taken as a whole, indicate:

(1) The model generally under-predicted water-phase concentrations for the contaminants (Figure 4), indicating possible targets for calibration of the model, given sufficient analytical data in the future. Such targets could include adjustments to sedimentation and resuspension dynamics, partition coefficients, or suspended solids and sediment characteristics;

(2) The model generally predicted sediment-phase concentrations with good accuracy – if not high precision (Figure 5). This indicated little need to consider adjusting partition coefficients during calibration, but strengthened support for possible improvements by adjusting sediment dynamics and characteristics; and

(3) The model appeared to overestimate fish tissue concentrations, though observations of contaminant levels in fish tissue were too few to provide much support for this result. Adjustment of bioconcentration factors might be appropriate if more data becomes available.

Discussion

The snapping turtle has been used as an indicator of spatial and temporal trends in ecosystem health and localized contaminant bioaccumulation (cf. Pagano et al. 1999). In a small sample of turtle eggs, Pagano et al. (1999) found an average of 1.1 and 1.5 ug/g of total PCB and 0.02 and 0.04 ug/g of mirex in animals from Sodus Bay and from Rice Creek, respectively (both sites are similar to lower Salmon Creek in contact with Lake Ontario or its food web). Their PCB values were higher, by roughly a factor of five, than the concentrations of total PCB in exposed samples (0.260 ug/g), but our mirex+photomirex values (LSC: 0.030 ug/g) were identical to theirs (Table 1, Appendix 2). Therefore, given the geographic differences, the results of two studies are in fairly good agreement.

Concentrations of dioxin+furan congeners found in turtle adipose tissue collected in upper and lower Salmon Creek were compared with those found in 2-year old brown trout (*Salmo trutta*) and coho salmon (*Oncorhynchus kisutch*) collected from Lake Ontario in the Rochester Embayment (Skinner 1999). More congeners were found in turtles exposed to Lake Ontario or its food web (lower Salmon Creek), and fewer congeners were found in unexposed turtles (upper Salmon Creek), than in the salmon and trout. This result is logical: exposure to Lake Ontario should result in more congeners and higher concentrations in biota exposed to the lake's water or its contaminated food web.

Concentrations of total PCB in bass and turtle muscle tissue collected in the upper and lower Salmon Creek locations were compared with those found in bluegill (*Lepomis macrochirus*) and pumpkinseed (*L. gibbosus*) collected in Presque Isle Bay, Lake Erie, also an AOC, from July through September, 2001 (G. Andrasso, Chemistry Dept., Gannon University, pers. comm.). Combined samples of 10 fish each produced these results for total PCB: 0.297 and 0.283 ug/g for 80-130 mm TL and 0.316 and 0.562 ug/g for 130 and 160 mm TL pumpkinseed and bluegill, respectively. These values, for fish feeding one or two trophic levels below largemouth bass and snapping turtle, are an order of magnitude higher than levels found in bass and turtle muscle in and out of contact with Lake Ontario and its food web in the Rochester Embayment (Table 1). It appears that bass and turtles exposed to portions of the Rochester Embayment AOC exposed to Lake Ontario water or its food web are less contaminated with PCBs than centrarchids in the Erie, PA AOC.

Concentrations of total PCB and mirex+photomirex in our air samples were compared with air samples collected at four sites on Lake Ontario (Point Petrie, Canada; two near Oswego, NY; Potsdam, NY) and Lake Erie (Sturgeon Point, Canada; Stockton, NY) (IADN 1999, Chiarenzelli et al. 2001). Concentrations at the other locations were similar to those we found, and followed the same seasonal trends (lower in colder months, Table 3).

This project addressed key questions, the answers to which provide the information needed to determine whether or not the fish and wildlife consumption use impairment can be delisted for the Rochester Embayment Area of Concern. Below we address those questions.

Are spatial (subwatershed) or there temporal (seasonal) differences in BCC concentrations in air, water or sediment in the AOC? How do BCC concentrations in air, water and sediment in the Rochester metropolitan area (AOC) compare with levels in a putatively "unpolluted" area in the upper Genesee River subwatershed?

Except for a higher concentration of mirex+photomirex in sediments collected from lower Salmon Creek, the sampling location most directly exposed to Lake Ontario water and its food web, no differences in total PCB and mirex+photomirex concentrations, or their ratios, were found in air and sediment samples collected at four locations in the Rochester Embayment region (two exposed and two not exposed to Lake Ontario water or its food web) and one putatively "pristine" location on the Genesee River some 90 mi south of the Rochester Embayment AOC (Figures 1 b,c; Table 3). Consequently, the evidence suggests that air and sediment in the Rochester Embayment AOC, except for the sampling location in most immediate contact with Lake Ontario, are no more contaminated with BCCs than inland areas. These results support delisting of the fish and wildlife consumption use impairment.

For future biomonitoring, it is clear that March is a poor month for sampling, especially for air (Table 2). The summer months consistently yielded higher concentrations of total PCB and mirex+photomirex in air samples, undoubtedly due to higher volatilization rates of BCCs from soils and water bodies into the air when temperatures are warmer. Similarly, more BCCs would enter water due to wet and dry deposition from air during the warm summer months. BCC levels in sediments did not show a seasonal effect, probably because BCCs bind tightly to the organic fraction of sediments and have low volatilization rates. However, sample sizes for air and sediment sampling were small (n = 3 to 4), so strong conclusions regarding the lack of differences among locations and months can not be drawn at this time, especially because two "hot" samples strongly influenced mean sediment concentrations at the unexposed Genesee River and the exposed Salmon Creek locations (Appendix 4b).

Do the two sentinel species exposed and not exposed to Lake Ontario or its food web have different BCC concentrations?

The concentration of total PCB and mirex+photomirex in muscle was higher in bass and turtles exposed to Lake Ontario or its food web than in unexposed animals, and mirex+photomirex in eggs also was higher in exposed than in unexposed samples (Table 2). There was no difference in total dioxins+furans in muscle tissue or in total PCB in eggs between exposed and unexposed samples, but total dioxins+furans in turtle adipose was much higher in exposed than in unexposed samples (Table 2). Except for total PCB in eggs and total dioxin+furan in muscle, BCC concentrations were higher in biota exposed to Lake Ontario or its food web. In no case was the BCC concentration higher in animals not exposed to Lake Ontario or its food web. These data support the hypothesis that the fish and wildlife consumption use impairment in the Rochester Embayment AOC is due to contact with Lake Ontario, not sources within the AOC, and that the use impairment can be delisted.

Which sentinel species, largemouth bass or snapping turtle, provides the most useful information for biomonitoring? Which tissue (muscle, egg or adipose) is most suitable for biomonitoring purposes?

In muscle tissue, total PCB and mirex+photomirex concentrations were higher in bass than in turtles (Table 2), but there was no difference between the species in total dioxin+furan concentrations. In eggs, the concentration of total PCB did not differ between bass and turtles, but the concentration of mirex+photomirex was higher in turtles (Table 2). The differences described above may be due to differences on lipid content between species, but percent lipid was not determined in the analyses. These data suggest that while either species is a suitable sentinel, largemouth bass may be the better choice if muscle tissue is analyzed and snapping turtle may be better if eggs are analyzed. However, handling of bass in the field and preparing their tissues for extraction is much simpler than for turtles, so sampling of bass muscle tissue and eggs may be sufficient for future biomonitoring needs.

As expected, eggs and adipose (both high in lipids) had higher BCC concentrations than muscle (Table 2). Eggs and adipose are advantageous for biomonitoring because higher concentrations of BCCs are easier to detect analytically. They are disadvantageous for biomonitoring because lipids make extraction and cleanup more difficult, and, in the case of eggs, greater sampling effort is required to collect a sufficient sample size because only half of organisms sampled are female.

Although we did not measure total PCB and mirex+photomirex in turtle adipose, the strong presence of total dioxin/furan in adipose, and a previous study by Pagano et al. (1999) on PCBs in turtle eggs, suggests that turtle eggs are an excellent candidate tissue for future biomonitoring. Another advantage of turtle eggs is that skilled observers can collect them from nests during the spring mating season without sacrificing females. Disadvantages of using turtle eggs for future monitoring are that they are available for only a few weeks in May-June and that they do not comprise a large portion of human or wildlife diets.

Snapping turtles and largemouth bass are both plentiful in the AOC, and neither is difficult to collect with nets or, in the case of bass, by electrofishing. Turtle adipose tissue gave by far the strongest signal of differences between animals exposed and not exposed to Lake Ontario water or its food web (concentrations of total dioxins+furans were 165 times higher in exposed turtles), so overall the snapping turtle (either eggs or adipose) is likely the better sentinel species for future biomonitoring of worst-case conditions. Alternatively, largemouth bass muscle is much more likely to be consumed by humans and wildlife.

Does measuring one BCC provide just as much information on remedial progress as measuring more than one BCC?

We approached this question in two ways. First, we examined the ratios of mirex+photomirex (M+P:PCB) and of total dioxins+furans (D+F:PCB) to total PCB. If ratios are similar across chemicals, physical media, locations, months, species and tissues, it would be reasonable to conclude that measuring one BCC during future monitoring would provide information similar to measuring all. In the analyses for tissues and physical media, 10/12 ratios were not significantly different. The M+P:PCB ratios for muscle samples from exposed and unexposed organisms in Salmon Creek and for sediments among months (not related to the PCB sediment ‘hot spot” in lower Salmon Creek; Table 3, Appendix 4) were significantly different from other ratios (Tables 2 and 3).

Second, we examined ratios of the standard error of means to means (SEM:Mean) for tissues and physical media across sampling locations and months. For tissues, these ratios were quite stable (Table 4), ranging from 20 to 35% (excluding a 62% outlier), and the differences were not significant (Chi-square = 5.98, $P = 0.817$). There were no differences in SEM:Mean ratios among the five sampling locations ($P = 0.758$) or among months ($P = 0.378$). Combined across locations and months, the SEM:Mean ratios for sediment and air did not differ ($P = 0.118$ and 0.145, respectively), but sample sizes were small (Table 4).

Overall, our results support the hypothesis that one organochlorine BCC might serve as a surrogate for all. Since PCBs had the highest concentrations in all media at all locations in all months, they are probably the best candidate for future monitoring of a single BCC. However, none of the total PCB concentrations found in this study exceeded U.S. Food and Drug Administration (FDA) standards for human consumption, whereas total dioxin+furan concentrations in the adipose tissue of turtles exposed to Lake Ontario and its food web exceeded standards for human and wildlife consumption (see below). Therefore, while expensive, monitoring of dioxin+furan levels in turtles exposed to the Lake Ontario food web probably should continue.

What are the health implications for organisms that consume bass and turtles?

Recommended human consumption limits for PCBs, mirex and dioxins/furans evolve as more experimental and epidemiological data are collected. According to USEPA (2000), a typical mixture of PCBs may become chronically toxic (i.e., reproductive, developmental, or other effects) at ingestion rates higher than 0.02 ug/Kg-d and carcinogenic at rates higher than 2.0 mg/Kg-d. Mirex is listed as a probable human carcinogen, and may become chronically toxic at ingestion rates higher than 0.2 ug/Kg-d (USEPA 2000). Dioxins/furans are considered carcinogenic when ingestion rates exceed $1.56 * 10^{-5}$ mg/Kg-d, but despite great concern in the scientific and medical communities about the chronic adverse effects of dioxins and furans at very low levels, USEPA (2000) does not list chronic toxicity values for them. Generally consistent with USEPA guidelines for carcinogenicity, the US Food and Drug Administration has set action level concentrations in tissues consumed by humans of 2.0 mg/Kg (= 2.0 ug/g) for total PCB and 0.1 mg/Kg (= 0.1 ug/g) for mirex and its derivatives (e.g., photomirex). Exposure guidelines generally assume ingestion by a 70-Kg adult.

Other organizations also have made recommendations concerning human health and exposure to the BCCs addressed in this report. The Great Lakes Sport Fish Advisory Task Force suggested that consumption of Great Lakes fish resulting in BCC exposure below 0.05 ug/Kg-d would provide an adequate human "health protection value," and further suggested that protecting for PCBs would also protect for other BCCs and any synergistic effects (GLSFATF 1993). The World Health Organization (WHO) recommends that dioxin+furan levels in food consumed by humans not exceed 10 ng-TEQ/Kg (Skinner 1999). Finally, Newell et al. (1987) proposed that concentrations of dioxin+furan in the food of wildlife less than 2.3 ng-TEQ/Kg would not cause chronic toxicity.

A standard meal of fish, for the purpose of calculating exposure rates, is assumed to be 227 g (0.5 lb) of skinned, properly trimmed (lateral red muscle and dorsal and ventral fatty tissue removed), and properly cooked (by a method that removes oils from the tissue consumed) flesh. Estimated consumption rates of wild-caught fish by various demographic groups were presented in GLSFATF (1993): reasonable worst case, 180 g/d; 90^{th} percentile recreational angler, 140 g/d; 95^{th} percentile Superfund default subsistence angler, 130 g/d; FDA 50^{th} percentile subsistence angler, 70 g/d; 50^{th}

percentile recreational angler, 30 g/d; average Great Lakes recreational angler, 13 g/d; and average per capita fish consumption in the US, 6 g/d. From these data, concentrations of BCCs in a set of samples, and recommended, risk-based consumption limits (fish meals/month) can be calculated (USEPA 2000). For the samples collected in this study, those calculations follow (Table 5).

For the maximum total PCB concentrations detected in our samples of bass filet and turtle limb muscle, the associated USEPA (2000) recommendation is to eat no more than 0.5-2 meals per month from animals exposed to Lake Ontario water or its food web. For the same tissues from samples with maximum concentrations not exposed to Lake Ontario water or its food web, the associated USEPA recommendation is eating no more than 1-8 meals per month. For bass eggs eaten by humans, the USEPA recommendation is no more than 0.5 meals/month from exposed and unexposed fish. For maximum mirex+photomirex concentrations detected in our samples of bass and turtle muscle and eggs, the USEPA guidelines suggest that 16 or more meals a month would result in exposures below chronic toxicity thresholds. For maximum dioxin+furan concentrations detected in our samples of bass filet and turtle limb muscle, WHO (Skinner 1998) and DEC (Newell et al. 1987) criteria suggest a relatively low risk of chronic toxicity to humans or wildlife (>16 meals/month).

Adipose tissue from exposed turtles had total dioxin+furan concentrations in the range of DEC and WHO chronic toxicity criteria for wildlife (none to 1.53 meals per month) and humans (1.27-6.66 meals per month). Of particular concern is that the dioxin+furan congeners found most often in our samples, and in the highest concentrations, were 2,3,7,8-TCDD and 2,3,7,8-TCDF (TEF = 1) and 2,3,4,7,8-PCDF (TEF = 0.5), the most dangerous congeners to humans and wildlife. Therefore, consumption of turtle adipose tissue from animals exposed to Lake Ontario and its food web presents substantial risks to the health of humans (e.g., turtle soup) and wildlife (e.g., scavengers).

Modeling

No formal process was implemented with the goal of calibrating the model with the data. That would involve minimizing prediction error with respect to a subset of uncertain model parameters (e.g., partition coefficients among physical media and bioconcentration factors). It is evident from the work to date that the accuracy of the model would benefit from calibration; that is, predictions could be improved by systematically adjusting parameters over a constrained range of values to align the predicted values more closely with the observed data. It should be noted, however, that the amount of data, and especially its spatial and temporal resolution, limits expectations on the accuracy that can actually be achieved without further sampling. Nevertheless, the accuracy achieved by the model, as illustrated in Figures 4-6, suggests that it could have a useful role, without further calibration, for semi-quantitative forecasting of the effects of future load reductions in the watersheds or airsheds, as well as on environmental exposure concentrations and bioaccumulation in these systems. More specifically, the results shown in Figures 4-6 indicate the comparatively simple modeling approach used here predicted concentrations of the appropriate order of magnitude when applied to the Rochester Embayment region. This result suggests that the modeling approach may be used with a measure of confidence to predict accurately (1) the direction of trend in response to management decisions that affect loads, and (2) the approximate magnitude of change in contaminant level to be expected. Furthermore, the predicted outcomes by the model include responses observable in the water column, in the sediments, and in the tissues of fish in the affected region.

Limitations of the Study

In the original proposal, bass and turtles were to be sampled from Salmon Creek above and below an impassable barrier about 10 km south of Lake Ontario. Two problems prevented this approach. 1) While the barrier may be impassable for bass, it certainly is passed by salmonids during fall spawning runs and, as stated in the proposal, turtles could simply walk around it. Bass and turtles from lower Salmon Creek were collected about 2 km south of Lake Ontario, far from the barrier, so it is very unlikely that they had traveled there from the upper Salmon Creek portion of the subwatershed. Thus, we are confident that samples from lower Salmon Creek represented organisms exposed for their entire lives to Lake Ontario water and its biota. 2) Bass and turtles do not live in upper Salmon Creek because the habitat (small, swift stream with rocky substrate) is not suitable for them. Therefore, we collected samples in several ponds near upper Salmon Creek and its tributaries, reasoning that the ponds represented AOC conditions not in contact with Lake Ontario.

In the time between proposing and conducting this project, PCB contamination was discovered in Brockport Creek, a tributary of upper Salmon Creek. Therefore, it was possible that all of Salmon Creek is contaminated with PCBs and by sampling in ponds not connected to the creek we underestimated contamination levels in the upper subwatershed. However, sediment analyses conducted in relation to removal of contaminated sediments at the Brockport site indicate that PCB levels in Salmon Creek sediments are the same as background concentrations 2 km downstream from the remediation site (K. Cloyd, NYSDEC, Avon, NY, personal communication). Accordingly, we believe that our comparison of BCC concentrations in biota exposed and not exposed to Lake Ontario water or its biota is valid. A definitive test of this conclusion would be to conduct a similar study on the Genesee River in the AOC. A series of three large waterfalls in the City of Rochester are truly impassable barriers.

A reviewer of an earlier draft of this report (L.X. Skinner, NYSDEC Bureau of Environmental Protection, Albany) noted that levels of total PCB we originally reported in water (21-182 ng/L) were consistent with values reported for the most contaminated waters in New York, an unlikely result for the areas we sampled. This suspicion was confirmed by reviewing our analytical data and Litton (1996, 1997a,b). Litton reported total PCB concentrations (aqueous and dissolved/suspended solid fractions combined) of approximately 2-15 ng/L in western New York streams with no known sources of persistent organic chemical pollution and of approximately 30-200 ng/L in streams with suspected sources of pollution. In Lake Ontario, the concentration of total PCB was 110-120 pg/L (Litton and Donlon 1998). After rechecking all aspects of our analyses we found that the original chromatograms for PCBs in water were very “dirty”. For this project we purchased certified, pesticide-free glassware, which we did not wash before collecting samples. Therefore, in the summer of 2004, we collected a new 1-L water sample from each of our five sites with the same glassware and lids cleaned in our lab. The subsequent analyses produced “clean” chromatograms and total PCB was below our detection limit of 1 ng/L. We do not believe this problem affected sediments collected in the same jars because only a few grams from the middle of the 1-L sample, not exposed to the surface of the jar or lid, were used for analysis. For the modeling results presented above, we used typical values from Litton (1996, 1997a,b) for potentially “contaminated” and “uncontaminated” streams in western New York.

Conclusions

1. Largemouth bass and snapping turtles exposed to Lake Ontario water or its food web generally have higher concentrations of total PCB and mirex+photomirex in their muscle tissue and eggs than animals not exposed to Lake Ontario.
2. Total dioxin+furan concentrations in bass and turtle muscle do not differ between locations exposed and not exposed to Lake Ontario water and its food web, but concentrations in turtle adipose tissue are much higher in exposed than in non-exposed animals.
3. Total PCB and mirex+photomirex concentrations are higher in bass muscle than in turtle muscle, and mirex+photomirex concentrations in bass eggs are higher than in turtle eggs, but there are no differences between the two species in concentrations of total PCB in eggs and of total dioxin+furan in muscle.
4. In relation to USEPA criteria for human health, maximum concentrations of total PCB detected in bass filets and eggs and turtle limb muscle, in areas of the Salmon Creek watershed exposed and not exposed to Lake Ontario water or its food web, were in a range associated with chronic toxicity problems, but minimum concentrations were not. Mirex+ photomirex concentrations were below the range associated with chronic toxicity, as were total dioxin+furan concentrations except in turtle adipose tissue (WHO and DEC criteria). Consumption of turtle adipose tissue presents a substantial risk, especially for scavengers or subsistence humans who consume meals prepared with adipose tissue.
5. Largemouth bass muscle and eggs or snapping turtle eggs are good candidate tissues for future biomonitoring. BCC concentrations were higher in bass than in turtle muscle, and eggs of both species had detectable levels of total PCB and mirex+photomirex that are below regulatory agency standards for human and wildlife health. However, turtle adipose tissue had dioxin+furan levels much higher than regulatory standards, so biomonitoring of this tissue alone would provide excellent information on when all tissues that could be consumed by humans and wildlife fall below regulatory action limits.
6. Although sample sizes were small, there is no evidence to suggest that the Rochester Embayment portion of the AOC has more polluted air or sediment than a putatively "pristine" area about 150 km south of the AOC near the Pennsylvania border. Only sediment samples from lower Salmon Creek, in direct contact with Lake Ontario water or its food web, had a significantly higher concentration of a BCC (mirex+photomirex) than was found at other locations; however, one of three samples also had a high PCB concentration (1.5 ug/g).
7. Concentrations of BCCs in air were generally higher in warm (August) than in cold (March) months; therefore, future monitoring of BCC levels in physical media should take place in the summer in order to measure the highest annual concentrations of BCCs.
8. Reasonably stable mirex+photomirex:total PCB, total dioxin+furan:total PCB, and standard error:mean ratios across species (bass, turtle) and tissues (muscle, egg, adipose), locations (exposed and not exposed to Lake Ontario water or its food web), months (spring, summer, fall) and media (air, sediment) suggest that monitoring of one BCC in the future to assess changes in overall BCC levels is a possibility. Total PCB is the best candidate BCC for physical media and would work for tissues, but see conclusion #5 above about dioxins+ furans. Despite the attraction of using one BCC as a surrogate for all in future monitoring, their differing modes of toxic action may preclude this simplified approach.

9. The P450 enzyme-induction liver cell assay was not sensitive enough to detect the low levels of dioxin-like BCCs found in the tissues of bass and turtles exposed to Lake Ontario water or its food web, so standard analytical procedures will be required for future biomonitoring.
10. Preliminary mass balance, fate and transport modeling shows reasonable agreement between measured BCC concentrations and model predictions, warranting further efforts to refine the model and, within limits, to substitute modeling for sampling to monitor remediation progress in the future.
11. **The data provided here suggest that the fish and wildlife consumption use impairment for the Rochester Embayment AOC is nearing a time of delisting for locations not in contact with Lake Ontario water or its food web. However, before delisting can occur, a similar study must be conducted and similar results must be found for sentinel biota in the Genesee River and Irondequoit Creek portions of the AOC.**

Acknowledgments

This project was supported by the New York Great Lakes Protection Fund and Columbia Analytical Services. Nicholas Parnell collected biological and physical samples, and was assisted by Ryan Walter, Benjamin DiSalvo, Sara and Jeffrey Wellman, Matthew Lochner, Randall Rhyne, Christopher Tolar and Christopher Haynes. Ted Lewis and Hilary Richardson analyzed tissues and physical media for total PCB, mirex and photomirex. Jane Freemyer, Columbia Analytical Services, Houston, TX coordinated dioxin and furan analyses. Laura Inouye, USACOE, Waterways Experiment Station, Vicksburg, MS coordinated cell assays. Carole Beal, Dana Harris (Wellsville, NY Water Treatment Plant), Lawrence Huff, Gary Neuderfer, Margaret Peet, Kenneth Podgers, Frank Rock and Robert Sodoma allowed us to collect samples on their properties. Lawrence Skinner and Gary Neuderfer, NYSDEC toxicologists, critically reviewed an earlier version of this report.

Literature Cited

CAS (Columbia Analytical Services). 1998. P450 HRGS Overview. Houston, TX.

Chiarenzelli, J., and 10 coauthors. 2001. Enhanced airborne polychlorinated biphenyl (PCB) concentrations and chlorination downwind of Lake Ontario. Env. Sci. Technol. 35:3280-3286.

Chapra, S.C. 1997. *Surface Water-Quality Modeling*. McGraw-Hill: New York.

DePinto, J.V., S. Liu, T. C. Young, and W. Booty. 1998. Development of LOTOX2: Solids and PCB calibration, and management application. Great Lakes Research Review 4(1):15-21.

GLSFATF. 1993. Protocol for a Uniform Great Lakes Sport Fish Consumption Advisory. Great Lakes Sport Fish Advisory Task Force. Wisconsin Dept. of Health and Social Services: Madison.

IADN. 1999. Total PCB and mirex summary results. International Atmospheric Deposition Network. http://www.msc.ec.gc.ca/iadn/results/1998.

Lewis, T.W., and J.C. Makarewicz. 1988. The exchange of mirex between Lake Ontario and its tributaries. J. Great Lakes Res. 14:388-393.

Litton, S. 1996. Trackdown of Chemical Contaminants to the Niagara River from Buffalo, Tonawanda and North Tonawanda. NYSDEC Division of Water. Albany, NY.

Litton, S. 1997a. Follow-Up Contaminant Trackdown Investigations of Niagara River and Lake Ontario Basin, 1995-1996. NYSDEC Division of Water. Albany, NY.

Litton, S. 1997b. Enhanced Toxics Monitoring from Final Chlorinated Wastewater Effluents and Surface Waters Using the Trace Organics Platform Sampler (TOPS). NYSDEC Division of Water. Albany, NY.

Litton, S., and J. Donlon. 1998. Enhanced Toxics Sampling for Trace Organic Chemicals in Lake Ontario. NYSDEC Division of Water. Albany, NY.

Makarewicz, J.C., E. Damaske, T.W. Lewis and M. Merner. 2003. Trend analysis reveals a recent reduction in mirex concentrations in coho (*Oncorhychus kisutch*) and chinook (*O. tshawytscha*) salmon from Lake Ontario. Environ. Sci. Technol. 37:1521-1527.

Newell, A.J., D.W. Johnson, and L.K. Allen. 1987. Niagara River Biota Contamination Project: Fish Flesh Criteria for Piscivorous Wildlife. Tech. Rept. 87-3. Division of Fish and Wildlife, NYSDEC. Albany, NY.

Pagano, J.J., P.A. Rosenbaum, R.N. Roberts, G.M. Sumner and L.V. Williamson. 1999. Assessment of maternal contaminant burden by analysis of snapping turtle eggs. J. Great Lakes Res. 25(4):950-961.

Plumb, R.H. 1981. Procedure for handling and chemical analysis of sediment and water samples. EPA/CE-81-1.

RAP. 1993. Stage I Remedial Action Plan for the Rochester Embayment of Lake Ontario. Monroe County Department of Health. Rochester, NY.

RAP. 1997. Stage II Remedial Action Plan for the Rochester Embayment of Lake Ontario. Monroe County Department of Health. Rochester, NY.

Skinner, L.C. 1999. Dioxins and furans in Lake Ontario salmonids. NYSDEC. Albany, NY.

Statistix. 2001. Statistix 7. Analytical Software. Tallahassee, FL.

Thomann, RV., and Mueller, J.A. 1987. *Principles of Surface Water Quality Modeling and Control*. Harper and Row: New York.

USEPA. 2000. Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories. Vol. 2: Risk Assessment and Fish Consumption Limits (3rd ed.). EPA 823-B-00-008. Office of Water. U.S. Environmental Protection Agency. Washington, DC.

USEPA STORET. 2003. US Environmental Protection Agency stream discharge data. http://www.earthinfo.com/databases/st.htm.

USGS Daily Values. 2003. US Geological Survey stream discharge data. http://earthinfo.com/databases/dv.htm.