Donald W. Rennie Memorial Monograph Series

Great Lakes Monograph No. 4

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes -Lake Ontario Case Study

> great lakes program

> > STATE UNIVERSITY OF NEW YORK AT BUFFALO

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## Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes -Lake Ontario Case Study

**Conference Proceedings** 

February 3-5, 1992

Center for Tomorrow

State University of New York at Buffalo

Sponsored by:

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## In Memoriam

### Donald W. Rennie, M.D. 1925-1992

On December 28, 1992 on a golf course in Myrtle Beach, SC, Don Rennie succumbed to a heart-problem that he had been battling for some time. Losing Don was not only a tremendous loss to his family and to his extended family at the University at Buffalo, but it



was also a loss to anyone who works at protecting and preserving the environment, and the Great Lakes in particular.

Don's love for the environment and the outdoors is exemplified by his passion for golf and sailing. He loved to sail and was very good at it. I think it was this link to the waters of the Great Lakes basin that made him such a strong supporter of Great Lakes research. Beyond his regular duties at the University, Don was a member of the Great Lakes Research Consortium Board of Governors since its inception. He was also a member of the Governing Board of the New York State Sea Grant Institute. These and other activities confirmed Don's commitment to research aimed at understanding and managing the Great Lakes Ecosystem.

I was extremely fortunate to have developed a close working relationship with Don during my brief tenure at UB; as Vice Provost for Research and Graduate Education, he was my immediate supervisor on matters concerning the

Great Lakes Program. I could not have asked for a more supportive administrator, either from a fiscal or a personal perspective. I am very saddened to have lost Don, but I am also very happy to have experienced his wisdom and friendship, even for the brief time we knew each other. In memory of his devotion to improving the Great Lakes Ecosystem and of the tremendous support that he gave to the Great Lakes Program, we proudly dedicate this Great Lakes Program Monograph and all future publications in our Monograph Series to the memory of Donald W. Rennie.

Joseph V. DePinto, Director Great Lakes Program

Reducing Uncertainty in Mass Balance Models in the Great Lakes-Lake Ontario Case Study

### Acknowledgments

There are a number of individuals whose contributions to this monograph and to the workshop which spawned it were instrumental in its success. The workshop was sponsored as part of a cooperative agreement (CR818560) by EPA, ERL-Duluth, Large Lakes and Rivers Research Branch, Grosse IIe, MI. William L. Richardson, Director of LLRS, is the Project Officer.

The workshop was co-organized by the Great Lakes Program at the University at Buffalo and the New York Great Lakes Research Consortium. Joseph V. DePinto, Director of the Great Lakes Program, and Jack Manno, Associate Director of the GLRC, served as co-chairs. Planning and organization was also provided by a Steering Committee comprised of William Richardson, Robert Beltran, Charles Zafonte, Michael Zarrull, Jack Manno and Joe DePinto.

The organizers and Steering Committee would especially like to extend our appreciation to those who contributed time and effort beyond serving as a participant at the workshop. We would like to thank Congressman Henry Nowak for his inspiring welcoming address. We are extremely grateful to Dr. Robert Thomann, whose Keynote Address presented an excellent framework and departure point for workshop discussions. The four workgroup facilitators --William Sonzogni, Melanie Nielson, James Martin, and James Kramer -- deserve special mention for service beyond the call of duty in focusing and synthesizing workgroup deliberations. The lively discussions and extreme willingness on the part of all participants to share their opinions made the facilitators' job that much more difficult. Of course, all other presenters, white paper authors, and panel members rendered incites that were invaluable to the outcome of the workshop.

Lastly, but certainly not least, we would like to thank three individuals who performed yearnan duty in providing logistical support during the workshop and in compiling and editing this proceedings. We gratefully acknowledge Maxine Dakins and Carol Griffin, graduate assistants at SUNY-College of Environmental Science and Forestry who served as technical editors for the Proceedings, and Monica Moshenko, Administrative Secretary of the Great Lakes Program who was responsible for the smooth running of the workshop and was the managing editor of this Proceedings.

We would also like to thank the University Conference and Special Events Office and Food Service Administration for the excellent facilities and food service during the workshop.

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# Table of Contents

Introduction	1
Executive Summary	3
Opening Remarks: Congressman Henry J. Nowak	10
Keynote Address: Robert V. Thomann	13
Management Perspective: Charles Zafonte	37
Managing with Uncertainty: William L. Richardson	44
Charge to Workgroups: Joseph V. DePinto	48
Report of Group 1	51
Report of Group 2	56
Report of Group 3	62
Report of Group 4	68
Closing Panel Discussion	79
Appendix A: White Papers	85
Loadings, Forcing Functions, and Stochastic Variability - Dave Dolan and Tom Young	86
Quantification and Reduction of the Uncertainty in Mass Balance Models by Monte Carlo Analysis of Prior Data - <i>Barry M. Lesht</i>	106
Model and Projection Uncertainty: Methodology Development and Interpretation - <i>Dominic M. DiToro</i>	125
Model Paradigms: A Discussion of Simple and Complex Models - Donald Mackay and Victor J. Bierman	142

Reducing Uncertainty in Mass Balance Models in the Great Lakes-Lake Ontario Case Study

Process Parameterization Uncertainty in Mass Balance Models of Toxics in the Great Lakes: Part 1 - <i>Douglas D. Endicott and John P. Connoliy</i>	166
Process Parameterization Uncertainty in Mass Balance Models of Toxics in the Great Lakes - Part 2 - <i>Douglas D. Endicott and John P. Connolly</i>	211
Organic Contaminants in Lake Ontario, 1968-1991: A Review and a Data Base - <i>Efraim Halton and Natalie Schito</i>	235
The Importance of Large Events - Wilbert Lick	286
Appendix B: Workshop Participants	308
Appendix C: Workshop Participant Roles	312
Appendix D: Post-Conference Survey Results	314

# Introduction

This workshop, held February 3-5, 1992 at the University at Buffalo in Buffalo NY, was sponsored by the U.S. EPA Large Lakes Research Laboratory and was convened by the Great Lakes Program of SUNY Buffalo and the New York Great Lakes Research Consortium of SUNY-ESF. The goal of the workshop was to discuss and develop a set of recommendations for reducing uncertainty in mass balance models of toxics with specific emphasis on application to Lake Ontario.

To virtually eliminate the presence of toxic substances in the Great Lakes, the most appropriate and scientifically defensible targets for toxic load reductions must be selected and the most effective and efficient means to reach those targets must be chosen. In making these decisions, mass balance models that predict the fate of toxic substances, quantify load-to-concentration relationships for key environmental compartments, and determine target load reductions must be used. Since judgements based on these models will have significant legal, regulatory and financial implications, it is essential that the uncertainty associated with mass balance models for toxics in the Great Lakes be reduced to the minimum allowed by the current state of data acquisition, modeling formulation and technology.

This workshop was organized by Dr. Joseph DePinto, Director of the Great Lakes Program, and Jack Manno, Director of the New York Great Lakes Research Consortium, in cooperation with Dr. William Richardson of the EPA's Large Lakes Research Laboratory. A steering committee, recruited by the organizers, helped prepare the agenda and guide the approach to developing recommendations.

The meeting was structured into four working groups to consider sources of modeling uncertainty: loadings and other forcing function data, *in stru* field observations/system response measurements, model paradigms, and process parameterization. A facilitator responsible for leading the discussion and preparing a final report to the entire workshop was designated for each working group.

Prior to the meeting, the organizers arranged for selected participants to prepare White Papers to stimulate preparation for the meeting. The authors were asked to analyze the prospects for reducing uncertainty in the source of modeling error they were addressing, assess the relative value of further reductions in that source of uncertainty when compared with others, and suggest an agenda for discussion by conference participants. These papers served as the starting point for each working group.

The workshop also involved plenary presentations which included an overview of uncertainty in toxics modeling, a management perspective on the applications of mass balance models in the Great Lakes with emphasis on management needs for Lake Ontario, the current methods for quantifying and expressing uncertainty in

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

Great Lakes modeling, the importance of large events, and a management perspective on determining the appropriate levels of complexity, accuracy and cost to fit the application.

These proceedings include transcriptions or summaries of the plenary sessions, the white papers, summaries of the discussions of each working group, and the final recommendations.

Great Lakes Monograph No. 4

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### Executive Summary

A workshop was held on February 3-5, 1992 in Buffalo, New York to focus expert attention on the problem of uncertainty in mass balance models for toxic chemicals in the Great Lakes. In order to focus the discussion, specific emphasis was placed on applications to Lake Ontario. A steering committee was formed whose members included representatvies of U.S. EPA and Environment Canada along with the two institutions that organized the workshop: the Great Lakes Program at the State University of New York at Buffalo and the Great Lakes Research Consortium. Attendance was by invitation of the steering committee and included modeling professionals, university-based aquatic scientists, senior agency personnel responsible for state and federal water quality programs, and others. More than seventy individuals worked over the three day period to derive recommendations for ways to reduce uncertainty and increase confidence in mass balance models and the accuracy of their predictions.

Participants were assigned to one of four work groups. The work groups were defined by the steering committee, and were intended to focus attention on particular ways in which analytical uncertainty and input errors are likely to be introduced into mass balance models. The workgroups were divided as follows:

Group 1 Loadings and other forcing function data, including the influence of stochastic variability

Group 2 *In eltu* field observations/system response measurements for the establishment of initial conditions, boundary conditions, calibration/confirmation data sets, and model post-audit data sets

Group 3 Model paradigms, including model formulation, spatial/temporal resolution, and the effects of process aggregation

Group 4 Process parameterization, including data availability, process experimentation and scaling problems.

The steering committee commissioned white papers to summarize the issues in each of these topic areas. The white papers are printed in the following proceedings. Each work group was asked to review and discuss the white paper prepared for its group, consider the suggestions offered in the papers for reducing uncertainty and offer recommendations from the group. Each group was asked to consider questions of technical feasibility, costs and time needed to implement each of the recommendations. These recommendations were then commented on by a panel made up of management professionals who would be expected to consider their implementation. The intended outcome of the workshop was a set of recommendations to guide decisions about the future direction

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

of mass balance modeling efforts in the Great Lakes: how models should be used and the best way to direct resources toward research most likely to improve the usability of mass balance models for management decisions.

The proceedings following this summary include a more detailed discourse of the discussions in each of the work groups. It also includes the transcripts of the plenary sessions that guided the work group deliberations and a summary of the closing panel comments on the work group recommendations. Presented in the remainder of this Executive Summary are the overall workshop conclusions and recommendations, judged by the organizers to be the consensus of the entire workshop, followed by a listing of the specific recommendations of each of the individual work groups.

To virtually eliminate the impacts of toxic substances in the Great Lakes, the most appropriate and scientifically defensible targets for toxic load reductions must be selected and the most effective and efficient means to reach those targets must be chosen. In making these decisions, mass balance models that predict the fate of toxic substances, quantify load-concentration relationships for key environmental compartments, and determine target load reductions must be used. Since judgements based on these models will have significant legal, regulatory and financial implications, it is essential that the uncertainty associated with mass balance models for toxics in the Great Lakes be reduced to a level commensurate with the management needs. While it was not within the scope of this workshop, we must recognize that the level of confidence needed for a given application must be determined a priori as part of the problem definition. Only then can a problem-specific strategy for reducing uncertainty be devised. Given this caveat, it was the goal of this workshop to identify a list of the most promising modeling improvements possible in the areas of process understanding and parameterization, loading and calibration data sets, and model paradigms. These strategies for reducing model uncertainty could then be selected and implemented on a problem-specific basis as dictated by the particular management needs.

As Dr. Thomann conveyed to the Workshop participants in his Keynote Address, reducing model uncertainty, placed in a positive context, is merely gaining more and more confidence (i.e., a higher degree of certainty) in the ability of our models to explain the variability of a toxic contaminant in physical and biological space and time. Listed below are the areas that we felt the Workshop participants identified as providing the most fruitful avenues of inquiry relative to gaining confidence in model predictions of toxic contaminant behavior in the Great Lakes. These general recommendations are placed into two groupings: 1) those that address the continued development and implementation of a strategy for using mass balance models for managing toxics in the Great Lakes; and 2) those that address needs that are more specific to particular processes or contaminants. Within each grouping the items are <u>not</u> listed in any particular order of priority.

Overall Workshop Conclusions and Recommendations

Great Lakes Monograph No. 4

Model Development and Application Strategies

**1**. The spatial, temporal, and kinetic resolution of a model are what determine its complexity. Much of the unexplained variability in our models is due to *a priori* averaging and lumping that we perform in arder to simplify our modeling frameworks. Development of complex, site-specific toxics mass balance models in the Great Lakes Ecosystem are required if we are to gain a true understanding of sources of uncertainty and to develop approaches for reducing those uncertainties. However, model development and application should proceed along both the simple and complex paths; these paths are complementary and provide an effective process formulation, parameterization and scale dependency testing framework.

2. Since site-specific models are only as good as the data from which they are developed, a good deal of model uncertainty reduction can be achieved by collecting <u>auality</u> data and fully understanding -- and quantifying -- the variability in field data. Also, data collected for a site-specific model application must be directly usable for the application in question. Given limited resources, there is no room for monitoring that has little value as model input or for comparison with model output. To assure these objectives, new field data collection programs should be designed with the full cognizance of the problem definition (including definition of desired accuracy and precision), historical monitoring data and screening model analysis of these data, existing model applications to similar problems, and state-of-the-art statistical techniques.

3. If we are to make advances in reducing model uncertainty, we must focus research effort on developing efficient and unbiased methods for <u>auantifying</u> model error. These methods must account for data variability and attempt to account for model formulation and application errors as well as model parameterization errors.

4. As models become more complex and multimedia in nature, as suggested by the model paradigm work group, it will become necessary to develop better and more efficient modeling support tools. For example, Geographic Information Systems (GIS) linked to a series of toxic chemical loading, fate and transport, and effects models can be invaluable for organizing and analyzing spatial and attribute data, for applying averaging and interpolation schemes that permit higher resolution modeling with sparse data, for restructuring and passing model input/output data between models, for visualizing model output, and many other modeling tasks. We must continue to explore and develop techniques (such as Monte Carlo analysis, maximum likelihood methods, or DiToro's method for apportioning uncertainty between calibration data and model parameterization uncertainty) for model calibration, sensitivity analysis, and error analysis. Finally, expert systems can be used to aid in model formulation and application in an attempt to benefit from previous experiences in a particular modeling domain.

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study Priority Model Formulation and Parameterization Needs

**1.** Accurate representation of sorbent transport and transformation dynamics is <u>crucial</u> to developing accurate toxic mass balance models. Of particular importance are water/sediment exchange process. More effort should be focused on formulating site-specific sorbent dynamics models (including explicit representation of organic carbon sorbent kinetics) and obtaining high resolution (especially in the vertical dimension) calibration and verification data sets.

2. Atmospheric exchange of toxicants, including deposition and phase transfer, represents a major source and sink in the Great Lakes; more research is needed to better quantify the rates and governing conditions for these processes.

**3.** Accurate representation of the food web structure and dynamics is one of the weakest components in an integrated toxics exposure model; definition of the routes of carbon flow in aquatic ecosystems, individual organism metabolism, and toxic chemical assimilation efficiencies are some of the priority data needs.

4. Mercury is a significant problem toxicant in Lake Ontario, yet our understanding of mercury transformations and our ability to obtain accurate field measurements of its various phases are very limited. A comprehensive program to develop an understanding of mercury transport and fate by synthesis of field data and process experimentation in a mass balance modeling framework is strongly recommended.

The remainder of the Executive Summary of this Proceedings presents a summary of the recommendations of each of the four Work Groups. These recommendations are <u>not</u> presented in any particular priority, since the groups did not prioritize their recommendations. However, a feeling for the significance of each recommendation can be obtained by reading the transcripts of the discussions that led to the formulation of these recommendations.

Loadings and other forcing function data, including the influence of stochastic variability

- Loadings estimates are dependent on the quality of the monitoring data provided. It is, therefore, critical that Quality Assurance/Quality Control procedures be carefully established at the beginning of a mass balance modeling project.
- Sampling programs should be designed with the needs of the model in mind. Existing monitoring data and models, as well as state-of-the-art statistical techniques should be used to help design new sampling programs. Spatial and temporal resolution of load estimates must be compatible with the model being used.
- Research is needed into the effect on model uncertainty of using alternative statistical methods for estimating loads, in

Specific Work Group Recommendations

Summary of Recommendations Group particular for samples reported at non-detect.

- State-of-the-art sampling and analysis protocols should be followed whenever possible to minimize censored data.
- Atmospheric inputs are still imprecisely known. More study is needed in this area; in particular, improved estimates of process rates, improved understanding of the correlation between air concentrations on shore and over the open lake, and methods for including short-range transport into loading models.

*In situ* field observations/system response measurements for the establishment of initial conditions, boundary conditions, calibration/confirmation data sets, and model post-audit data sets:

- Additional efforts should be made to analyze the Green Bay experience to help identify the optimal sampling requirements for Lake Ontario.
- Research is needed into methods for quantifying uncertainty, estimating uncertainty from alternative sampling regimes, the possibility of using surrogates that are more easily sampled and measured than toxic organic contaminants.
- Historical sediment data for Lake Ontario and Green Bay should be reviewed to guide future sediment sampling programs.
- Existing data on contaminant levels in Lake Ontario are insufficient for model calibration and additional sampling will be required to obtain toxics concentrations in water, sediment, atmosphere and biota. An optimal water column, sediment and biota sampling program for the data needs of a mass balance model calibration effort for toxics in Lake Ontario should include:
  - five to six lake segments with three to five water column sampling stations and one master station per segment.
  - Sampling of the epilimnion and hypolimnion in each segment, with the master station sampled more frequently with extensive vertical profiling, including two samples in the epilimnion and four in the hypolimnion. In addition to toxics, dissolved and particulate organic carbon, suspended solids, P, N, Si, and CI should be sampled at the master stations
  - sampling under the ice, after spring loading, after stratification, after fall turnover, and during one additional time
  - sampling for a minimum of two years to acccount for variability in weather

one master sampling station in each segment. Sampling should be more frequent and should take place every year, not just for two years. Vertical profiling should be more extensive

volume proportional sampling techniques should be utilized

some data collected during storms to determine the pulse loading associated with big events

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

Summary of Recommendations Group 2

- multiple samples taken during sample collection.
  Preservation of sample is inexpensive compared to the cost of losing a sample.
- sampling grid for sediments that match water column grid, except more intensive
- sampling of blota from various compartments in the food web, with particular concerns with sampling of:
  - seasonal concentrations of toxics in alewife
    - populations
  - different age classes of lake trout
  - mysis and pontopreia
- Because of the characteristics of the contaminants of concern, the needs of the models, and the particular problems in the lake, mass balance models for Lake Ontario should concentrate on PCBs (Total), DDT, Mirex/Photomirex and Plutonium.
- It is essential that measurements of water column and invertebrates concentrations are matched in time. It is less essential to match fish and sediment data.
- Research needs include:
  - Use of plutonium measurements in water and sediment to calibrate sorbent mass balance models.
  - Study photochemistry of mirex and photomirex.
  - Measure the Kow for each chemical to be modeled.
  - Determine how to combine value weighted averaging techniques with maxiumum likelihood estimation for censored data.

**Model paradigms**, including model formulation, spatial/temporal resolution, and the effects of process aggregation

Much of group 3's discussion centered on the comparative advangages of simple models sufficient for whole lake mass balance estimates versus more complex models capable of discriminating between impacts of different inputs, providing information on localized effects, estimating response times to management actions affecting loadings and in general, increasing our understanding of the fate and transport of toxic substances in large lakes (see proceedings for more detail about this debate). Questions about uncertainty for each type of model are significantly different. The group was able to agree on the following general recommendations:

- Continue to use existing models for whole lake issues
- Use simple models to test and refine process descriptions with regard to water/bed exchange processes, air/water exchange processes, biota/water exchange processes, sorption kinetics, food web processes, solids/carbon correlations, and speciation.
- Of the processes described in work group 3's report, water/bed exchange processes are most important. Future research should include increasing the vertical resolution in the bed and developing explicit representations of organic carbon kinetics.

#### Summary of Recommendations Group 3

 Use complex models to add spatial/temporal resolution. In addition these models can be coupled with hydrodynamic/sediment models, can use multiple sediment layers, and can extend into tributaries

Summary of Recommendations Group 4 Process Parameterization including data availability/process experimentation and scaling problems

The members of workgroup 4 each summarized an aspect of the group's deliberations. The following processes were identified as contributing toward model uncertainty. The group identified research needs, sampling methods, or improved process characterization that could reduce the uncertainty associated with each process. The list of processes that follows is not prioritized with respect to importance in reducing model uncertainty.

- Gastro-intestinal uptake and biomagnification of hydrophobic organic chemicals (lack of knowledge about mechanisms is the main source of uncertainty)
- Transformation processes (experimental research is needed to better characterize the processes by which contaminants transform in the environment)
- Physical/chemical properties of contaminants (Kow values and Henry's law constants vary widely. For modeling purposes, guidelines for accepted values are needed)
- Flux across the air-water interface (there is insufficient data to characterize the flux rates at different temperatures for different contaminants)
- Watershed/airshed models (the role of soil processes, and wind driven erosion is undefined)
- Food web structure (uncertainty exists regarding exposure of animals in contact with sediment)
- Impact of large events (data and parameters relevant to large storm and run-off events is needed)
- Measuring mercury (a major field measurements program is needed for methyl mercury)
- Fish mobility (movement patterns need to be better parameterized)
- Resuspension/deposition (contaminant flux due to resuspension/deposition, especially at high stresses, needs improved quantification)
- Sorption processes (sorption phenomena need better characterization, and a basic theory is needed to describe sorption phenomena)
- Carbon Cycle Mass Balance (improved understanding is needed of the dynamics of dissolved organic carbon, phytoplankton-toxicant sorption and effect of phytoplankton growth on carbon content).

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

# Opening Remarks

Congressman Henry J. Nowak

> I am pleased to have the opportunity to welcome everyone here today to the University of Buffalo for this important working conference on mass balance modeling of toxics in the Great Lakes. I can see from the list of participants that this conference will be one of the highlights within the Great Lakes research community this year.

> We are at an important juncture in Great Lakes research. The uncompromising goals of the Great Lakes Water Quality Agreement with Canada has challenged the research community with difficult, yet exciting, problems. In calling for an ecosystem approach that must employ mass balance methods, the Agreement has highlighted the need for improved tools. This approach is required to serve a broad constituency within the Great Lakes Basin that includes every living organism.

> I believe the Great Lakes are the perfect proving ground for such an undertaking. As a unique and identifiable resource, they provide a living laboratory in which to observe cause and effect. With the proper tools, we can come to understand not only the consequence of long term degradation of natural resources, but more importantly we can devise appropriate management schemes for its reclamation and enhancement. I believe ecosystem modeling will play a pivotal role in this effort.

> My challenge as a policy maker is to demonstrate to taxpaying citizens that federal dollars are well spent and provide a positive return on investment. Unfortunately in the environmental area, this has proven an illusive task. While our intuition tells us that pollution is bad... it has been difficult to quantify and demonstrate its damage to our health and economy. While environmental concern continues to gain an increasing share of public attention, they will not have parity with other concerns until we can demonstrate the benefits of our actions to the public at large. It is here that the Great Lakes have provided are remarkable example. It is estimated that over \$12 billion in federal dollars have been spent within the Basin for construction of sewage treatment facilities, an action precipitated in large part by the apparent "death" of Lake Erie in the 1970's. Reaction to the defilement of such a large natural resource created the public support for our first environmental programs, and by all counts, the reclamation of Lake Erie was a remarkable success and perhaps the first example of environmental controls reclaiming a vast natural resource.

> Lake Erie also demonstrated the economic benefits of investment in environmental protection and remediation helping produce a sport fishery in the Great Lakes worth \$4.5 billion per year in economic activity across the Basin. Incidentally, I understand some of the

phosphorus loading models developed in those days were pioneered by individuals here today.

In my mind the Lake Erie example demonstrates how critical mass balance modeling will be to solving our current problems with the persistent toxic chemicals that have permeated the Great Lakes and are found in all forms of life throughout the system. A small body of research and prudent intuition tells us that there may be human health effects associated with PCB's in mothers' milk and their bloodstream that is passed on to their infants. A considerably larger body research confirms both the severe and subtle developmental effects of persistent toxic chemicals on the fish and wildlife population within the Basin. Again, as a policymaker I have to ask myself: Do we know enough at this point to take action? Will we ever have all of the information required to demonstrate absolute cause and effect? And perhaps most importantly, should we wait until then to act? Without the tools to more fully understand the costs of action vs. inaction regarding environmental management these critical policy questions will go unanswered. For this reason, I am excited by the potential of ecosystem modeling on the Great Lakes. If modeling can help us to understand, in a comprehensive fashion, the fate and transport of pollution and its effects, we can then make the best investment of limited federal dollars to protect the health of the ecosystem.

I also believe there is a larger purpose to the work in the Lakes. The vast Great Lakes watershed and its complex environment are mirrored in the institutional arrangements that govern the resource. Two federal governments, eight states, two provinces, and Native Americans provide a unique challenge to policymakers that will provide the model for international environmental agreements on a global level.

In short, if we cannot execute an ecosystem game plan here in the Great Lakes, the challenges of global environmental management may also go unanswered. But I am far from pessimistic. Great Lakes issues have experienced a tremendous renaissance in the past few years. Attention at the federal level has produced new resources across many of the federal agencies committed to meeting the Water Quality Agreement and a greater level of interagency cooperation is also paying off with more coordination and less duplicating of work. This high profile has helped move programs along and build support for the sustained efforts necessary to get results. I can also say with a great deal of pride that by coming to Buffalo to hold this conference, you have come to the right place.

The University of Buffalo's Great Lakes Program under the leadership of **Joe DePinto** has fostered a new center of expertise within the University in the area of environmental modeling. With the confidence and funding from EPA's Environmental Research Lab under the direction of Gil Veith, a critical investment has been made to develop a predictive model for the Buffalo River watershed. Fortunately, UB is one of three Universities within the National Science

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study Foundations' National Center for Geographic Information Analysis, providing an unique opportunity to use existing University resources to develop this powerful model.

I certainly look forward to the results of this conference and its forthcoming applications to the Lake Ontario Lakewide Management Plan. Please be assured that as we move to reauthorize the Clean Water Act this year in Congress, Great Lakes Issues will continue to be a high priority for me.

Thank you again for all of your strong efforts on behalf of our Great Lakes resources.

### Keynote Address

### Uncertainty in Toxics Modeling

Robert V. Thomann Manhattan College

Introduction

I gave a lot of thought on how to approach this subject of uncertainty in toxics modeling and the fact that we will be spending two and a half days looking at various dimensions of this problem. I tried to review what has been done over the years and then decided to turn to the dictionary. The synonyms for uncertainty are: doubt, dubiosity (I), skepticism, suspicion. I checked "dubiosity" and got the word "uncertainty" back again! The definition was a rather negative perspective on uncertainty but that's the way the public thinks about uncertainty and that is probably the way most managers of water quality perceive the notion of uncertainty. In fact, many managers of water quality, when they get to water quality <u>models</u>, seem to think in these terms: suspicious, doubtful, skeptical. Of course to some degree we have to have that healthy skepticism ourselves.

But a look at the flip side of the definition is interesting. The title of this workshop is "Reducing Uncertainty" which is another way of saying we hope to "increase certainty". The dictionary offers a much more comforting kind of definition for "certainty": "assurance"; "conviction"; and "faith strong enough to risk all attack (I)." We ultimately want to provide some kind of assurance or conviction (but not blind "faith") that what we are offering managers with the results of model calculations and field and laboratory observations can be used in the decision making process with some conviction and some assurance.

The basic questions that most managers ask are: "How good are the predictions of the effects of control actions?" "Do you understand the reasons for the observed behavior in toxics concentrations?" "If we carry out some control actions, what assurance do we have that your predictions will, in fact, happen?" "How good is your model?" These are questions that have been asked ever since models were first constructed. These broad questions are very meaningful to those who are ultimately responsible for carrying out programs. So management looks at certainty and uncertainty from a relatively simple point of view. The underlying fear in the notion of uncertainty is that the "wrong" (in some sense) control actions will be promulgated.

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

The Importance of the Problem Context

To a large degree, the significance of uncertainty depends on the problem context. How we perceive uncertainty really depends on what we think are the relevant questions. For example, if we're dealing with a regulatory process on a broad-based generic problem, i.e., across chemicals and across sites, then screening, global, generic steady-state type models of toxics may be appropriate. Order-of-magnitude models of bioaccumulation in a paradiam food chain is an illustration. The significance of uncertainty might also relate to the response time of systems to control actions. In that case, site-specific models may be needed. An example would be estimating whether we can expect a certain mean water quality objective or mean fish chemical concentration be met within the next 10 - 20 years. Finally, uncertainty might also depend on which auestions are being addressed in the permitting waste load allocation process. Chemical allocation models are then necessary and mean and exceedance frequencies, may need to be calculated.

Articulating modeling uncertainty questions must therefore be attempted at specific levels of detail. What is the relative contribution of data variability and model uncertainty to observed chemical variability? What is the confidence interval on a calculated mean chemical concentration? Do we regulate on exceedance of the mean? What are percentile extremes on individual levels? Do we regulate on short term events? Up front articulation of relevant questions is essential because the questions determine the approach that needs to be taken to deal with uncertainty.

The Sources Of Uncertainty In Toxics Modeling

There are a number of components of uncertainty in the modeling of chemical fate and accumulation. There is inherent variability due to spatial and temporal changes in meteorology, hydrology and food web structure. Measurement and observation errors also are important contributors to overall uncertainty especially for extremely low level chemical concentrations. Model structure itself can be a cause of uncertainty; state variables, inputs, processes, and linkages may or may not be correct. Numerical assignments for inputs and parameters, of course, have considerable potential uncertainty. Other sources of uncertainty are blunders and pre- and post-processing errors of model output. And finally there may be an incomplete understanding of the model which may result in an application of the model for which it was never designed.

From a toxics modeling point of view, I believe that "uncertainty" is really unexplained variability, or unexplained behavior, i.e., variability and behavior that is "left over" or "unexplained" after we've tried to apply as much of what we know at a particular point in time. Large uncertainty in this sense means large confidence limits around a prediction where the range of uncertainty of the prediction may or may not be acceptable. The degree to which variability is explained can therefore be considered a measure of the reduction of uncertainty. Recognizing these sources of doubt, a definition can be offered: "The certainty of a toxics model (or any model) is the degree to which the variability of a chemical in physical or biological space and time is explained by the modeling framework". By "explained", I mean that the engineering/scientific/management community agrees that the model is a valid representation of a set of observations and can be utilized within the given problem context.

### Model and Data Variability

Examples Of Observed Variability Figure 1 is a schematic of the generation of model and data variability. Physical, chemical and biological processes lead to spatial and temporal variability. input load variability further contributes to the total "true" variability of water quality, which, of course, is unknown. There are a variety of sampling constraints that govern the degree to which this real world true variability can be observed. The degree to which sets of observations are meaningful, of course, depends again on the problem context. In addition to sampling constraints, there are modeling constraints that are also a function of problem context. A priori decisions are then made on how to approach the problem: whole lake models, steady state, the state variables themselves, what kind of chemicals will be modeled, and the spatial and temporal grid. Finally, there is a comparison between model calculations and data variability. The degree to which that comparison is "acceptable" is the degree to which uncertainty can be tolerated.

What has been observed about chemical variability? For example, for inputs and parameters what is the chemical response in physio-chemical and biological compartments in terms of temporal and spatial variability? What do the mean, variance, and coefficient of variation look like in some of these processes? What do is known about the probability distribution functions? What is known about response to load reductions?

Figure 2 shows the probability distribution function (pdf) for the PCB load at a station in the upper Hudson River. In general, load probability distribution functions tend toward lognormal behavior which means that significant statistical statements can be made from estimates of two statistical parameters. Suspended solids are an important component of toxics modeling. Figure 3 shows the pdf for the Mississippi River at Jefferson Parish, just to the north of New Orleans. As an example of chemical variability, Figure 4 shows the pdf for chloroform at the same station on the Mississippi River. The top panel shows the time history of chloroform collected at that location, and the bottom panel shows the pdf. As indicated, the pdf is approximately log normal, with a total variability about two orders of magnitude with a coefficient of variation close to unity. This level of variability is common in toxics chemicals. As a final example of physio-chemical behavior, Figure 5 shows the TCDD in surficial sediment in Lake Ontario. The "break" in the pdf may be a result of near shore vs. open lake behavior or varying sediment organic carbon concentrations.

Variability in the biological sector is also quite regular. Figure 6 shows

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study the structure of PCB variability in fish for data collected on the Hudson River and Estuary. It is rather remarkable that across migratory and resident fish that such statistical regularity is observed although it should be recognized that this is a log-log plot. A global coefficient of variation is around 0.6. A model of fish variability exposed to varying chemical concentrations indicates that for a coefficient of variation around 0.6 for chemicals in fish, the global coefficient of variation for the dissolved chemical is about one, similar to observed coefficients of variation. Figure 7 shows a similar behavior for kepone in the James estuary with a coefficient of variation for fish of about 0.6. These data therefore appear to display some considerable statistical regularity which can be exploited to reduce uncertainty.

Figure 8 (from a data compilation on chemical uptake by benthic invertebrates by Thomas Parkerton at Manhattan College) shows the pdf for the Biota Sediment Factor (the ratio of the chemical in the benthic invertebrate on a lipid basis to the chemical in the sediment on organic carbon). The first interesting observation about this figure is that there are 1,770 instances in the literature observed Biota Sediment Factor for deposit feeding invertebrates. The median is approximately two (Indicating a preferential partitioning into lipid over sediment carbon) which had been previously suggested from earlier data analyses. Again, the data show a consistent degree of statistical structure which can be used to make reasonable estimates of variability in the degree to which invertebrates accumulate sediment chemicals.

Intra-species variability is also a source of variability that must be examined. The range of such variability may be large and apparently depends significantly on the exposure history of the individual organisms. Figure 9 shows results from a single collection of 67 fish (Alberta, Canada). The age distribution of the collection is relatively narrow. As shown, the distribution of PCB is about one order of magnitude in range while for BHC, the range is only a factor of two. The difference may reflect varying exposures of the fish to the two chemicals, but in any event the variability within this collection is significant.

The modeling frameworks available to deal with all of this variability are varied and in differing degrees address the overall uncertainty question. The approaches include deterministic models of physio-chemical transport and subsequent chemical accumulation in the food web. Such models are run under both steady state and time variable conditions. Age dependency may also be included in food web models. Monte Carlo simulations can be conducted within these deterministic frameworks to elucidate statistical behavior of outcomes. Parameter uncertainty analyses and models of stochastic behavior are also available. These and other areas will be discussed throughout this workshop and a review is not warranted here. I would like however to indicate the nature of the kind of analyses that can be done to provide a basis for calculating variability and subsequently comparing the results to observed

Model Frameworks and Computed Variability

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Great Lakes Monograph No. 4

#### behavior.

Using a simple whole lake model of the dimensions of Lake Ontario with six 1 cm. sediment layers and following standard physic-chemical partitioning and fate models, the illustrative question that was asked is: "What is the computed chemical variability in a whole lake model due just to load variability?" Figures 10 and 11 show some simulations. A log normally distributed annual load with a coefficient of variation of 50% was inputted into Lake Ontario. Annual water column and sediment response is shown for a 60 year simulation both with and without bioturbation in the sediment. As expected, water column response is considerably more variable than surface sediment and deeper sediment. A number of such simulations were conducted and the coefficient of variation in the water column was calculated to be approximately 50% of the coefficient of variation of the load. From simulations of this type, we can obtain first order insights into partitioning observed variance in chemical concentrations in the water column between load variability ( of which we have some reasonably good knowledge) and other sources of variability.

It is also of interest to note that simulations of the fraction of a chemical in dissolved form for log normal solids and log normal partition coefficient behavior does not result in log normal behavior in the fraction dissolved. This would be expected on statistical grounds. Figure 11 illustrates the point. The range of the fraction dissolved clearly is limited between about 0.6 and unity. The coefficient of variation of the fraction dissolved is quite insensitive to the coefficient of variation of the partition coefficient. These and other results provide the framework for understanding the sources of variability in observed chemical behavior.

Now once we've looked at model frameworks and at observed variability, how unexplained variability is addressed affects the perception of uncertainty and model credibility as illustrated in Figure 12. This Figure picks up where Figure 1 left off. The comparison of model and data variability is the first step as shown in Figure 1, but what is subsequently done with that comparison affects the perception of model credibility. For example, following Figure 12, the model and data may be compared qualitatively as is done in many applications. The comparison is left to speak for itself and the results are generally incorporated into some statements about model performance. Figure 13 shows an example. The quote is the extent of the analysis of model versus data. ( In fact, when I look back at what I've written over the last 35 years, most of what I say after I look at model and data comparisons are permutations of those words.) Such approaches may be useful for initial development and elucidation of processes but are generally not appropriate for detailed management questions.

Returning to Figure 12, attempts may also be made to quantify the unexplained variability resulting from the comparison of model to data. The residual variability may turn out to be acceptable in some

sense and consistent with the question being addressed. (Figure 13 illustrates a level of variability on eight cycle log-log paper that was considered "acceptable" for purposes of demonstrating food chain bioaccumulation.) The model may then be considered suitable for an intended use even though there may still be a considerable amount of residual variability. If the residual variability is unacceptable, then, of course, effort has to be directed towards reducing that variability.

Figures 14-16 illustrate detailed comparisons of model to data variability. The upper Hudson (Figure 14) is a fine time and space scale calculation. It shows a 50-day comparison at Waterford, NY with the original calibration. The probability plot comparison of the model to the data illustrates one way of displaying model and data variability. The same model with a two-day phase shift; is also shown to indicate that very often the exact time variable behavior of the calculation may not be captured. Are we interested mainly in looking at the 95th percentile no matter when it occurs? Is it an uncertainty of timing, or an uncertainty of magnitude? Is the timing of the peak critical, or is it capturing the magnitude of the peak that's important and it really doesn't matter when the peak occurs? The "uncertainty question" clearly has an impact on whether the model is considered suitable for use.

Figure 15 for Saginaw Bay illustrates an additional point. This Saginaw Bay total PCB model was a time variable model with results shown for an inner Bay depositional zone. Model runs A and B represent differing assumptions on parameters including volatilization loss of PCB. For the total PCB, it was concluded that the the cruise mean and individual station mean was captured and the cruise mean variance was captured. But the individual station variance was not captured. A similar result was obtained for the particulate PCB. For the dissolved PCB, the mean is captured, but neither variance component is reproduced by the model. Model performance clearly depends on the model structure, but it also depends on the data averaging that is used. Generally, model performance in terms of unexplained variability is improved as data spatial and temporal averaging is increased.

Figure 16 shows results from a model of cadmium in Foundry Cove on the Hudson estuary. These results are offered as an illustration of model reevaluation and recalibration to improve confidence in the forecasts, in this case, the effect of a load reduction. As can be seen from the plotted data, there was relatively little loss of cadmium over about a 20 year period since the cessation of cadmium loading to the Cove. The question we were asking is why did the surface sediment cadmium concentration remain so high over that period? As shown in Figure 16, the initial model calibration run was not satisfactory and emptied out cadmium from the sediment considerably faster than was observed. Following Figure 12, this result was not acceptable and a reduction in the uncertainty was required. In the final calibration, benthic mixing of the surface sediments (bioturbation) was included which a indicated, provided

Great Lakes Monograph No. 4

-18

a much more satisfactory and credible representation of the data. Now to what degree is the model suitable? There is clearly a substantial amount of individual variability in the surface sediment cadmium data (5 orders of magnitude!) that the model makes no attempt to resolve. If the model is intended to predict changes in surface sediment mean concentrations then perhaps the model is suitable. If however, the intention is to explain the heterogeneity in the sediment (or water column) cadmium then the model is not suitable.

Summary Comments and Thoughts On A Lake Ontario Modeling Strategy

It seems from analysis of data to date that there is a great deal of statistical structure in the physio-chemical and biological chemical behavior. Continual data analysis is essential in order to further elucidate such structures. But data analysis is usually most fruitfully accomplished when a modeling framework is at hand in order to guide the analyses. I don't think present toxics models have fully succeeded in capturing the observed structure in variability; however, the models have provided a first basis for assessing the range of uncertainty and confidence in predictions. But some considerable unexplained variability continues to exist, and whether we need to do anything about that unexplained variability and reduce it depends critically on the kinds of questions that are posed and the management implications of such questions.

One might also ask: "How much of the unexplained variability is due to the relatively crude spatial and temporal scales and relatively crude food web representations of toxics models?" It seems that a considerable portion of the unexplained variability may be due to such crude representations. A classical choice that we might make can be summarized as follows. "Should we average the data and theory a priori and use whole lake models to compare to data?" Or: "Should we minimize a priori averaging and use a much finer spatial and temporal grid and additional state variables, and then average the output for comparisons to data? It seems to me that it is a truism that site-specific models require more detailed spatial, temporal, and state variable resolution to reduce uncertainty. If that is so, then our attempts to reduce uncertainty in the most general sense requires a modeling framework that extends beyond, for example, whole lake models with a single sediment layer. My choice then would be for large complex systems (such as the Great Lakes) that the modeling framework be constructed on as fine a spatial and temporal and state variable level as possible. The calculated output can then be averaged and compiled in a variety of different ways for comparisons to observed data. This implies a great deal of effort in designing appropriate sampling programs to support and be complemented by the more detailed modeling effort.

Finally if we turn attention to Lake Ontario, the subject of this Workshop, it is important to note that Lake Ontario is a specific site. As such there are a variety of site specific questions that may be asked regarding the Lake. For example, what is the near shore to open lake interaction of toxics? To what degree can we forecast the redistribution of chemicals resulting from transient events? Will

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

averaging of a more finely scaled model produce superior results over a whole lake model? I think the days of a Lake Ontario whole lake model with single sediment layer and simple food chain appear to be numbered. Those models have successfully served their original purpose when first constructed almost ten years ago. I think it's time to move on. If we want to reduce uncertainty, I think we have to gradually move away from the "simple models" and provide a framework in anticipation of the more detailed and inevitable management questions of the future. I think the management questions for Lake Ontario would appear to require a model with a much finer grid in time and space and increased realism of food One of the white papers scheduled for this Workshop. webs. addresses this issue of simple versus complex models. I'm coming down on the side of a growing need for more complex and hence more realistic models for Lake Ontario.

I would suggest a spatial scale on the order of 10 by 10 kilometer or about 200 grid points in the horizontal with about 10 layers in the vertical totaling about 2000 grid points total. The temporal time scale is best calculated at the same time scale as an underlying hydrodynamic model which would be an essential element of the overall model. The physio-chemcial model would need to be coupled to a realistic food web model including incorporation of a full carbon balance with phytoplankton-nutrient and zooplankton kinetics. Specific attention should be paid also to the mechanisms in the sediment especially bioturbation.

Modeling frameworks of this type were generally not feasible even a few years ago. But with the increasing availability of super computing capability, the computational aspects while still formidable are not infeasible. As noted earlier, we clearly would also have to design a sampling program consistent with this kind of model detail to address the articulated questions. The absence of such a large data base need not however preclude the beginning construction of such a model since a considerable historical data base already exists that can be used for preliminary modeling efforts. Finally data interpolation schemes can be much better employed to extend existing point data to data surfaces for comparison to detailed spatial model output.

Our quest for reducing uncertainty should of course never degenerate into an objective of being absolutely sure of all of our predictions. Our world requies us to live with some continuing residual level of uncertainty. To ask for complete certainty is to demand the impossible. Now, it is axiomatic that keynote speakers should open with some significant quotation from some wise person. I'd like to close with a quotation from a person who looked at the question of certainty a long time ago and concluded:

"Certurn est quia impossibile est."

(Tertullian, c. 200)

Great Lakes Monograph No. 4



Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

LOAD PROBABILITY DISTRIBUTION FUNCTION

LOAD PROBABILITY DIST. FUNCTIONS TEND TOWARDS LOG NORMAL BEHAVIOR (2 PARAMETER DISTRIBUTION)



Great Lakes Monograph No. 4

FIGURE 2

MISSISSIPPI RIVER @ JEFF. PARISH



Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- **Lake Ontario Case Study** 



Great Lakes Monograph No. 4



Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

STRUCTURE OF PCB VARIABILITY IN FISH

VARIATION OF PCB (1254) IN HUDSON RIVER FISH

1975-1982 COLLECTIONS, RIVER & ESTUARY LOG MEAN STANDARD DEVIATION 1254 PCB (ug/g lipid



Great Lakes Monograph No. 4



### Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study



Great Lakes Monograph No. 4

60

FIGURE


Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

WHAT IS COMPUTED VARIABILITY IN WHOLE AKE MODEL DUE JUST TO LOAD **VARIABILITY?** 



FIGURE 10

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**TIME, YEARS** 

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WIGU EBIOTURBATION

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Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

22222 HOW UNEXPLAINED VARIABILITY IS ADDRESSED AFFECTS PERCEPTION OF UNCERTAINTY AND INTENDED USE OK FOR INITIAL MODEL DEVELOPMENT. SUITABLE FOR UNCERTAINTY **REDUCTION OI** MANAGEMENT QUESTIONS VARIABILITY REQUIRED DETAILED NG FOR MODEL MODEL CREDIBILITY MODEL TO DATA SPEAK MODEL PERFORMANCE "UNACCEPTABLE" NCORPORATE RESULT LET COMPARISON OF "ACCEPTABLE" IN FIGURE 12 **GENERALLY INTO** SOME SENSE VARIABILITY VARIABILITY RESIDUAL FOR ITSELF. RESIDUAL **QUALITATIVELY:** UNEXPLAINED VARIABILITY MODEL VS. QUANTIFY DATA ささささ

Great Lakes Monograph No. 4

A GENERIC FOOD CHAIN BIOACCUMULATION MODEL: QUALITATIVE COMPARISON

CALCULATIONS PROVIDE A REASONABLE REPRESENTATION OF THE "TO ORDER OF MAGNITUDE, THE RESULTS OF THE MODEL OBSERVED DATA..." (THOMANN, 1989)



33

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study



Great Lakes Monograph No.



Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study



Great Lakes Monograph No. 4

# Management Perspective

Applications of Mass Balance Models in the Great Lakes with Emphasis on Management Needs for Lake Ontario

Charles Zafonte, U.S. EPA - Region 2

> There are many different perspectives on what management questions should be asked. The perspective being offered here is that of the EPA and of the Four Parties who signed the declaration of intent for the reduction of toxic chemicals in the Niagara River and who developed a toxics management plan for Lake Ontario. These Four Parties are the two Federal governments, U.S. and Canadian, and two regional governments, New York State and the Province of Ontario. My focus will be on the areas that have significant relevance to the issues being discussed at this conference.

> First, for toxic chemicals in Lake Ontario it is important to note that we're dealing primarily with bioaccumulation problems not with water column problems. For instance, for PCBs in lake trout it looks as though the bioaccumulation factor is on the order of two million and for the herring gull on the order of 25 million.

> The goal of the Lake Ontario toxics management plan is a lake that provides drinking water and fish that are safe for unlimited human consumption and allows natural reproduction within the ecosystem of the most sensitive native species such as bald eagles, ospreys, mink and otters. To achieve this goal four objectives have been established. The first is to achieve a reduction in inputs of toxic chemicals driven by existing and developing programs. The second is to achieve further reductions in inputs driven by special efforts in geographic areas of concern. These areas of concern have remedial action plans (RAPs) developed for them; probably the most significant for Lake Ontario is the Niagara River toxics management plan for the Niagara River RAP area. The third objective is the reason for this conference, i.e., to achieve further reductions in inputs of toxic chemicals driven by lake-wide analyses of pollutant fate. Objective four, zero discharge, has relevance here because preliminary models that have shown in order to reach our most stringent criteria we must have complete elimination of all loadings of certain chemicals to Lake Ontario.

> To go into further detail on objective three, the Four Parties agreed that there are two different ways of doing a lake-wide analysis of the effects of toxic chemicals. The first is a chemical-by-chemical approach and the second is an ecosystem approach. The chemical-by-chemical is more practical, uses existing data, and

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study allows the development of strategies for reducing the concentrations in the lake. However, it does not answer the more basic question of whether or not the ecosystem is healthy. The ecosystem approach for Lake Ontario is being addressed by another group and will not be discussed here, except to say that it is most useful as a check on the effectiveness of the chemical-by chemical approach.

The first step in a chemical-by-chemical approach is the categorization of toxics. This entails examining all chemicals for which ambient data exists, either water column or fish tissue, and comparing the data to the most stringent criteria of the four parties. Each chemical is then categorized as exceeding an enforceable standard; exceeding a more stringent but unenforceable criterion; equal to or less than the most stringent criterion; the current limit of detection is too high to allow complete categorization; or no criterion is currently available. Examples of chemicals falling into the first category, exceeds enforceable standards, are PCBs, dioxin, chlordane, mirex, mercury, iron and aluminum. Iron and aluminum appearing on this list may not be indicative of real problems since the criteria are somewhat questionable and natural sources exist. Examples of chemicals falling into the second category, exceeds a more stringent but unenforceable criterion, are DDT and metabolites, octachlorostyrene, hexachlorobenzene, and dieldrin.

The actions agreed on for chemicals in these first two categories, include constructing a preliminary loadings matrix by December 1989, constructing preliminary models of chemical fate by January 1990, and to establish the preliminary load-reduction targets to meet existing standards by March 1990. The first two actions have been completed but the third action has taken longer than anticipated due to the lack of agreement on a set of ambient criteria. The Great Lakes Water Quality Initiative should provide this set of criteria for the U.S., which will provide a basis for negotiation with Canada. An examination of the loadings matrix for PCBs (Figure 1) shows that the system is dominated by loadings from the Niagara River and upper Great Lakes. Other significant sources of loadings are atmospheric deposition and tributaries in Ontario. Tributaries in New York all tested as non-detectable at the one part per trillion level for the organochlorine toxics of concern and are currently being estimated for purposes of comparison.

There are two basic management questions. The first is, given an ambient standard for a toxic chemical, such as the proposed Great Lakes Water Quality Initiative standard for PCBs of 6.3 ppb, what loading to Lake Ontario would result in this ambient concentration under steady-state conditions? The second is, once the loading to the lake is reduced to this level, how long would it take the system to achieve steady state? Results from simulation models can help to answer these questions.

The Endicott model can help us understand the relationship between PCB load to the lake and concentration of PCBs in lake

trout (Figure 2). Given the 1989 average concentration in lake trout, this model back calculates a steady-state load of 6.3 kg/day. The FDA criterion of 2 ppm in fish tissue corresponds to a steady-state load of 3.9 kg/day so the model indicates the need for a load reduction of about 40% at steady-state conditions to meet the FDA The most stringent criterion, though enforceable standard. unenforceable, is EPA's limit of 2.5 ppb in fish tissue. This criterion is based on a cancer endpoint of one-in-a-million. The model predicts that to achieve this criterion would require a steady-state load of around 0.005 kg/day which corresponds to a 99.9% reduction. The Initiative level is 6.3 ppb in fish tissues corresponding to about 0.01 kg/day, a 99.8% reduction. It is relatively unimportant which criterion, EPA's or the Initiative's, is used since it will require virtual elimination of PCB loadings to Lake Ontario to achieve either. The model result also tells us that the precision of the model prediction is not as important to managers as its accuracy. That is, we need only ensure that the model accurately reflects lake conditions within existing confidence intervals.

Looking at the predicted response to a PCB load cutoff indicates that there will be a fairly quick reduction in the water column and trout and a slower response for sediment (Figure 3). All the curves show that the time frame involved is not one of days or months but of years and even decades. Finally, the relationship between PCB load and PCB concentration in lake trout can be examined for various timelags following a load alteration (Figure 4). Again, this shows that the response to a load change is slow and that, even at twenty years after load cutoff, the steady-state concentration in lake trout will not be achieved where initial loads are less than 1 kg/day.

In closing, here are the questions that EPA feels need to be addressed:

**1.** Recognizing that the preliminary models do not deal with all nine Lake Ontario critical pollutants, what additional work is needed to deal with these chemicals?

2. The preliminary mass balance models indicate that attaining a stringent ambient standard for a bioaccumulative chemical, such as the proposed GLWQInumber for PCBs, would require virtual elimination of all loadings to the lake. This is true even taking into account the uncertainty around the prediction. Since increasing the precision of the load/response prediction is relatively unimportant, what ambient and loading data are needed to ensure that the models accurately reflect the conditions in the lake?

**3.** Since the models indicate that the lake responds over years and decades, would limited U.S. and Canadian monitoring resources be best spent on a low-intensity sampling program, with a commitment for long-term maintenance of the program?



FIGURE -

Great Lakes Monograph No. 4

## LOAD CONCENTRATION RELATIONSHIP: LAKE TROUT PCB (UNCERTAINTY IN PREDICTION IS <u>+</u> FACTOR OF 4)





Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

LAKE ONTARIO MODEL RESPONSE TO PCB LOADING CUTOFF



FIGURE 3

Great Lakes Monograph No. 4



## **FIGURE 4**

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

## Managing with Uncertainty

Determining Appropriate Levels of Complexity, Accuracy, and Cost to Fit the Management Application

William Richardson, U.S. EPA - Large Lakes Research Station

> We are now at a crossroads for modeling, monitoring, and managing toxic substances in the Great Lakes. In the past five years, there have been several meetings to work toward a consensus on the level of monitoring required to proceed with credible mass balance models of toxics in the Great Lakes. Great Lakes managers have recently started to appreciate the role of modeling in aiding the management of toxic substances and the EPA Office of Research and Development is convinced of the need to reduce uncertainty in mass balance models. The problem is that we lack a plan and without a plan there will be a lost opportunity for a coordinated research and monitoring program geared to developing a holistic understanding of chemical behavior in the Great Lakes.

> A research strategy involving U.S. agencies was recently developed for the Great Lakes. This strategy stresses mass balance modeling, from management level models up through complex models, as an important need. Resources to meet this need are being provided; the base EPA research budget for modeling in the Great Lakes has doubled in the last year not including EMAP, atmospheric research, and Congressional add-ons. The question is, what are the priorities for research for mass balance modeling? This meeting should provide input to help set the direction for establishing those research priorities.

> The process of setting research priorities will probably require the organization of some kind of committee structure. Currently, there is an ad hac group developing the next monitoring effort for Lake Ontario but there is no currently active modeling committee for the Lake. This committee structure needs to be organized and revitalized, perhaps building on the Green Bay modeling committee.

Regarding the question of model complexity, if management can make decisions based on a screening or management level model then they should do that. If zero discharge or virtual elimination can be achieved without discussion of costs, benefits, priorities, and relative risk reduction and if managers can have confidence that their goals will be met within a specified period of time then complex model predictions are not needed. Those of us who have

Great Lakes Monograph No. 4

been involved in management activities over the years, however, doubt managers' intuitive abilities to do this. In the end those paying for regulatory efforts, whether they be industry or Congress, will insist on having a high level of scientific credibility and an economically optimal approach backing their decisions. Money for monitoring, research, or clean-up must be spent in the most effective way even if the long term goal remains virtual elimination.

Modelers need to be careful on how they sell management level models, especially since little calibration to field data has been done, and to be careful to describe quantitatively the uncertainty associated with model predictions. Modelers also need to convince management that some basic research is needed to develop a better understanding of the interaction of toxic chemicals with the Great Lakes ecosystem. Without the basic research that was conducted in the late 1970's and early 1980's we could not have the load/response models that we have today. We have good qualitative confidence in our basic modeling paradigms because of the basic research that was done then and we will require more research of this type as a foundation for future modeling efforts.

The process of improving Great Lakes mass balance modeling will consist of several steps. The first step is to have risk assessors and managers determine what water uses, biological species, and geographical areas are at greatest risk and what chemicals are suspected of causing the risk. We need to establish a continuing monitoring and basic research effort like EMAP to run in parallel with mass balance modeling research. Next we need to continue to develop screening level models and to build on existing models and historical databases. Some uncertainties like the impact of large events, the impact of invading species, and interaction with system modifications may need to remain qualitative for now. We need to design a research and monitoring program setting priorities based on the greatest potential for reducing uncertainty and to optimize our sampling designs. Alternative modeling projects should then be proposed to management including the costs required for carrying them out and realistic timetables.

It is important that modelers interact with experimentalists and managers in a continuing dialogue. It is also important that sufficient time is allotted to all steps of a modeling program including data collection, laboratory analysis, and modeling. Managers should apply Total Quality Management concepts to these projects by placing quality first and deadlines second and modelers should insist on having flexible timelines including sufficient time after the data is received to calibrate and validate the models. Finally, we need to incorporate models into decision support systems so that we can integrate our knowledge of loadings, remedial costs, and risk calculations and give this information to field managers so that they can arrive at optimally cost effective decisions.

There is a matrix of possible alternative modeling approaches to take over the next five years (Figure 1). This matrix lays out the

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

	Process Research	W WO Y	Al 1 Masiar Siation AirWatar Watar/Sed Sed Traps No Biological	al 3 Masier Sisilona Il plus Photolysis Plankton Panloning Prad-Prey Relationships	II plus Ecosystam Parameters Chanical Phase Separation/Analysts	Same as IV
	Tribulary	Major Trib and Nagara R. Sampling Monthy Sampling	l plus Weekly Sampling	# plus Walershad Models	li witi Paini sourca Sampliog in Walenthods	Same as IV
	Groundwatar	Engineering Flux Esilmates	Measurement of Mejor equiter - Inputs (no model)	N plus Regional Model	III plus More resolution of models	Same as IV
	Atmospherie	Euleting Shorebesoc Manilaring No Aima Madel	I Plue New Vessel of Buoy Based	lt plue Regional Almo. Model Almo. Sampling Nio Almo Pt. Source	III pius Atmo. Pr. Source Monitoring	Same as IV
els .	Biotopical	BCF and Lake Trout	Lake Trout Pelagic Food Chain	Harring Gua Laka Trout Pelagic and Banthic Food Chain	Coupled Ecorytiam Bioeccumulation Model for Hearing Guil & Lake Trout Food Chain	Same es IV
Alternative Mod	Phene	Dissolved Particulate	Dissolved Biotic and Abiotic solids	i end il plue DOC	LII, 11 plua Truh Dissolved	Same es IV
Possible	Chemicala	PCB4, DDT	l phas Mirax, Dioxins	8 H + H TMP 1A B F Das (pH on)	Same as W plus HQ	Same as W
	No. Cruise	2 in 1 Year	4 in 1 Year	e in 2 Years	10 lh 2 Yean	10 in 2 Years
	No. Station	3 Water	6 Water 30 Sediment 1 Master	6 Mealer 25 Augular 25 Sedimente	5 Masler 50 Rugular 50 Sedment	10 Master 100 Sediment 100 Sediment
	Resolution Ma. of Segments Water Sediment	Read My Lips-No New Model Whole Lake 5	Graham-Rudman Spoolal 14ypo, Epi 3 NausthoraOpen Latia	Tar the Booze H.E. N.S. OW 16: 12 4Déposition Basins	GNP Booster HE.Nu.OW 30, 25 Hamilion Haubor Hamilion Haubor Tromon Haubor Magara Dala Cowago Haubor Bay of Quinta Rochaster Embayment other AOC's	92 Economie Recovery 20 KM Grid 200 50 Prus Harbors Anlegrad Hydrodynamic, Eale, Expound, Foodchain, and Southeni Dynamic, Model (Hasoluijon of Chesapeake Bay Model (Hasoluijon of Chesapeake Bay Model
	Appreximet	81-2 M over 5 Years	e 85-7 M aver 5 Years	H 818-20 M ever 5 Years	V 220-30 M over 5 Years	Duer 5 Years

FIGURE 1

This is a "strawman" which should be vieweed as the the possible product of a workshop on designing a monitoring/research program for Level 2 Modul Duvelopmunt

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Great Lakes Monograph No. 4

approximate budget required to achieve various levels of spatial resolution, toxic chemical coverage, phases, biological resolution, atmospheric detail, groundwater and tributary loadings, and process research. Achieving many portions of this matrix will probably require cooperation among various funding parts of EPA, Environment Canada, and other parties.

We also need to understand what can be expected of these various approaches. The screening level models that exist now are only good within two orders of magnitude, include many scientific caveats because of a lack of calibration data, are not to be used for numerical target load establishment but only to set program direction, and have little scientific credibility. By little scientific credibility I mean that the results can be successfully challenged by scientists working for other involved parties. As we increase the amount of funding, and therefore resolution, we should get an increase in certainty. At the first level on the matrix the models have less uncertainty but are still not to be used for numerical target load establishment and their scientific credibility still remain slow. The second level may involve uncertainties on the order to 2 to 5 times the estimate, may allow broader questions to be answered, have more scientific credibility, and may be used to set numerical target loads at least for some chemicals. The third level may have uncertainties on the order of a factor of 1 to 2, may be able to begin to address watershed issues but cannot set target loads within a watershed, and should have moderate scientific credibility. The fourth level would allow us to begin to understand mercury, the load/response relationships, and the inter-relationships between nutrients and toxics. In addition it would allow us to establish loads within the watershed and has moderate scientific credibility. Finally, the last level should have an accuracy to within about 20%, can be used to address nearshore and harbor issues, will improve understanding of long term sediment transport and resuspension, help to estimate the impact of major events, and has considerable scientific credibility.

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

# Charge to Workgroups

Joseph V. DePinto Great Lakes Program University at Buffalo

> There are two basic premises that have come out of the plenary session papers; the first is that models are not done in a data vacuum. A diagram developed by Paul Roberts at Stanford points out that there are many interactions between modeling computation and analysis and data gathering and evaluation (Figure 1). Data are used, whether they come from laboratory experimentation, process experimentation, or field observation, to help understand the system, develop the modeling framework, and parameterize the model. Additionally, the model helps to direct the data needs so that the model and data gathering components are coupled in both directions; the entire process can be thought of as hypothesis formulation and testing.

> The second basic premise is that all models are uncertain; there is no model that has no errors and nouncertainty associated with it. Analytical uncertainty can be broken down into stochastic variability, input error, and model error. Input error can be further reduced to measurement, parameter, and aggregation errors and model error split into formulation and use components. In developing the workgroups for this workshop, this paradigm for model uncertainty was used and the work divided into the following four areas.

Group 1

 Loadings and other forcing function data, including the influence of stochastic variability

Group 2

 In stu field observations/system response measurements for the establishment of initial conditions, boundary conditions, calibration/confirmation data sets, and model post-audit data sets

#### Group 3

 Model paradigms, including model formulation, spatial/temporal resolution, and the effects of process aggregation



Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- **Lake Ontario Case Study** 

Group 4

Process parameteriztion, including data availability, process experimentation and scaling problems.

The charge to the workgroups includes several components. First, review and discuss the white papers. The floor will then be open for comments from the group participants regarding sources of uncertainty and prospects for improving model accuracy. The group should then discuss the proposed recommendations for achieving reductions in model uncertainty and come to group consensus. There commendations should be prioritized in terms of technical feasibility, cost-effectiveness, and time-to-implementation and, finally, the group should prepare a report on the group deliberations and recommendations.

## Report of Group 1

### Loadings and Other Forcing Functions

Group 1 was charged with discussing reducing uncertainty in mass balance models of toxics as it relates to loadings and other forcing function data, including the influence of stochastic variability. Over the last twenty years mathematical models have been extremely useful in guiding science and management in the Great Lakes. Continued development of models, both simple and complex models, is essential; however, one of the greatest contributors to uncertainty in lake model results are the loadings of toxics which are usually key forcing functions in the models.

White Paper

Dave Dolan and Tom Young gave a presentation based on their White Paper, "Loadings, Forcing Functions, and Stochastic Variability." The authors assumed that loadings are usually the forcing functions or independent variables in most models. They defined uncertainty as the value or reliability of information. Uncertainty reduction takes place through either improved data collection or data handling procedures.

The authors discussed two approaches to assessing loading uncertainty, first order analysis and Monte Carlo simulations. First order analysis or variance propagation is the simpler of the two methods and is based on the Taylor series expansion about the mean of an uncertain input such as a load. Monte Carlo simulations are more accurate than first order analysis and they have the added advantage of producing a probability density function to describe the error rather than just estimating the mean and variance. Since the Monte Carlo simulations are computationally intensive, first order analysis is usually used to estimate uncertainty in simple models.

The authors discussed uncertainties in three types of loads: tributaries, point sources, and nonpoint sources (runoff, atmospheric, combined sewer overflows). Tributaries have received more attention than other sources because they are often the largest source of contaminant loading. They recommended using optimization techniques to select the number and frequency for sampling toxic contaminants. On the other hand, they suggest that conventional physical and chemical parameters such as pH and suspended solids not be optimized since they are inexpensive to collect and test. The Balanced Incomplete Block Design (BIBD) can also be used to estimate the total load of a contaminant with fewer samples than conventional sampling techniques require. Data handling improvements suggested were the use of better load estimation methods and use of the generalized load estimation procedure for censored data.

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study Point sources generally have less uncertainty associated with them than nonpoint sources, however, temporal variability in loading due to variability in concentration or discharge is a significant source of uncertainty. Optimization techniques can be used to obtain a more efficient sampling design. They indicated that atmospheric deposition was the most important source of variability for nonpoint sources of toxics.

Dolan and Young recommended the use of first order uncertainty analysis for mass balance models and the use of optimization procedures to identify the main sources of uncertainty. Historical data should be looked at prior to sampling design and state-of-the-art methods should be used to process and analyze data.

## Discussion

Following a discussion of general caveats to keep in mind regarding modeling in Lake Ontario, the group focused their discussion into four areas: Monitoring/Laboratory Techniques, Sources of Toxics, Censored Data/Uncertainty Analysis, and Sampling Design.

The group identified three important caveats for modelling in Lake Ontario. First, the purpose of the model must be clearly defined to best target ways to reduce loading uncertainty. Second, reducing uncertainty depends on the chemical being studied (there is no one best way to reduce uncertainty). Third, careful planning, which takes a significant amount of time and effort, needs to be done up-front in any kind of modeling effort. While obvious, this is often overlooked and data collection frequently begins before planning is completed.

### Monitoring/Laboratory Techniques

The group discussed several monitoring and laboratory techniques designed to reduce uncertainty including Quality Assurance/Quality Control procedures (QA/QC), automated sampling, site specific monitoring during extreme events, state-of-the-art methods to estimate loads, and the use of surrogates to obtain information about toxics.

The assumption underlying all modelling efforts is that the analytical work in labs has sufficient quality assurance and quality control. The group discussed the difficulties that arise when labs following the same procedures produce differences in contaminant levels of up to two orders of magnitude. Quality Assurance/Quality Control procedures need to be carefully established at the beginning of loadings studies to ensure data (toxics and conventional) comparability and to reduce uncertainty in the loadings estimates. The group also recommended assigning one person the responsibility of coordinating QA/QC efforts, particularly for large studies.

Automated sampling of suspended particulate matter is

Great Lakes Monograph No. 4

encouraged as it often can be used to synthesize missing or limited data or to establish transport variability. Automated daily monitoring of particulate matter can be used as a surrogate method to estimate toxic chemical loadings between events, especially for tributaries.

For some toxic substances most of the load comes from specific locations, therefore these areas should receive more attention in the future. Estimating loads from these sources during extreme events such as large storms is very important because extreme event loading may overwhelm all other sources of toxics. Simulation modeling to estimate loading during extreme events is useful, but without sampling during extreme events models can not be calibrated.

When calculating loads, especially tributary loads, state-of-the-art calculation methods should be used. Examples of these methods include the ratio estimator method for estimating annual loading and regression estimators for estimating loading on a shorter time scale.

Other more easily used parameters can be used to establish the pattern of behavior for toxic chemicals (e.g., particulate organic carbon, remote sensing derived parameters); however, the uncertainty generated by using the surrogates needs to be established. Surrogates should not be substituted for routine monitoring of toxics but should be used to fill in the gaps in toxics data.

Sources of Toxics

The group discussed the uncertainty associated with the sources of taxics to Lake Ontario including sewage treatment plants, chemical spills, hazardous waste sites, atmospheric inputs, and unmonitored areas. Additional monitoring of discharges of taxics from sewage treatment plants, especially for Canadian plants, is needed. Taxic chemical spills represents a special category of loading that should be considered in mass balance models of Lake Ontario. Groundwater contaminated by leachate from hazardous waste disposal sites represents a potentially continuous long term source of taxics. Methods of predicting or directly measuring these contributions should be explored, particularly where the source is a significant one.

Discussion of atmospheric inputs of toxics yielded three areas of concern. First, atmospheric inputs (wet fail, dry fail, and vapor exchange) are still imprecisely known but may be very important sources for some toxics. More study is needed in this area, with particular emphasis on improving estimates of process rates. Second, research is still needed to establish the correlation between atmospheric conditions at shore based stations and conditions over the lake proper. Current methods of extrapolating loading from shore based monitoring stations to the lake proper may be inadequate. Third, short range, urban transport of atmospheric inputs particularly in terms of metals, needs to be incorporated into loading models.

Contaminant contributions to Lake Ontario from ungauged and unmonitored areas (e.g. downstream from monitoring stations in urban regions) are difficult to measure. These loading sources should be estimated using existing prediction technologies, but further research is needed to develop better prediction methods.

### Censored Data/Uncertainty Analysis

Whenever possible, uncertainty of load estimates should be calculated using techniques such as first order error analysis and/or Monte Carlo simulations. More research is needed on the effect of using various estimating techniques on reducing uncertainty.

Discussions about censored data centered around the issue of estimating censored data, sampling protocols to minimize censored data, and interpretation of censored data. Data is said to be censored if a nondetect is reported. Statisticians claim the information is not all there whenever a nondetect is recorded. First, censored data should be estimated using accepted statistical techniques such as those used in The Green Bay Mass Balance Study The statistical techniques to be used should be (GBMBS). established before the study begins and should be followed consistently throughout the study. Second, to minimize censored data, state-of-the-art sampling and analysis protocols should be used such as large volume samples for PCB's in water and clean room techniques for metals. Third, chemists and biologists have an important role to play in improving the interpretation of censored data. Their knowledge of the contaminant and its properties should be used in conjunction with statistical techniques to determine if the recorded level should be recorded as zero or a non-detect. For example, a non-detect for a pesticide may in fact indicate a zero concentration because the pesticide degrades. Chemists would expect the parent material to be absent, i.e., zero.

#### Sampling Design

The group discussed the use of general sampling design considerations, the use of simulation modeling to obtain load estimates, and the use of existing data and models to design monitoring programs. Monitoring for some substances may be site or event specific. To reduce uncertainty, this fact must be considered when designing monitoring programs. The spatial and temporal resolution of load estimates must be compatible with the models to be used. The group also thought that the data organizing power of GIS should be explored for Lake Ontario mass balance models.

Simulation modeling should be used as an aid in estimating loads

that are difficult to measure, such as extreme events, rural nonpoint sources, groundwater inputs, and combined sewer overflows. Existing monitoring data and models should be used to help design new monitoring programs. Historical data should be used to construct Balanced incomplete Block Designs (BIBD) to identify significant sources of contaminants. Optimization methods should also be employed to increase sampling efficiency and cost effectiveness of monitoring efforts.

### Recommendations

The group prioritized their recommendations to reduce uncertainty in loadings. In priority order, the group recommended:

- Quality Assurance/Quality Control procedures need to be carefully established at the beginning of a study to reduce uncertainty in the loadings estimates.
- Existing monitoring data and models should be used to help design new monitoring programs.
- State-of-the-art statistical techniques should be used to design sampling programs.
- Censored data should be estimated using accepted statistical techniques.
- The spatial and temporal resolution of load estimates must be compatible with the model being used.
- Atmospheric inputs are still imprecisely known but they may be very important sources for some toxics. More study is needed in this area; in particular, improved estimates of process rates are needed.
- State-of-the-art sampling and analysis protocols should be followed whenever possible to minimize censored data.

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

# Report of Group 2

## In Situ Field Observations/System Response Measurements

Introduction

This workgroup was charged with the task of developing recommendations for quantifying and reducing uncertainty as it relates to in situ field observations/system response measurements. Specifically the group addressed in situ field measurements for biota, water, and sediment as a way of defining initial conditions, boundary conditions, calibration and confirmation data sets, and model post-audit data sets. The model post-audit suggests monitoring and surveillance requirements, as well as research requirements to reduce uncertainty in modelling.

The group tried to answer the question, "Where are the loads originating and how will controls of separate components reduce fish contaminant levels below the action level specified in the Lake Ontario Toxic Management Plan?" The outcome of the discussion is a set of recommendation related to reducing uncertainty of in situ data. Twenty scientists participated in the discussion. A summary of the discussion of this working group and its recommendations follows.

White Papers

The workgroup began with presentations by the three white paper authors. Barry Lesht discussed his white paper, "Quantification and Reduction of the Uncertainty in Mass Balance Models by Monte Carlo Analysis of Prior Data". He suggested that the Green Bay mass balance study be used to help identify the number of sampling stations needed to reasonably estimate the total mass of a contaminant in Lake Ontario with a specified accuracy. He recommended that researchers look at the data that currently exists to see if it can be used for modelling. Dr. Lesht also thought basic research was needed on methods to quantify uncertainty.

Efraim Halfon presented a summary of his white paper, "Organic Contaminants in Lake Ontarlo, 1968-1991: A Review and a Data Base." In his paper he reviewed 500 papers which addressed the food web and concentrations of toxic contaminants in Lake Ontario. Dr. Halfon said that although there is a substantial amount of information on toxics available, we have very little information on the food chain. Contaminant modelling has emphasized the chemistry of toxics and has not looked at the transfer of energy and contaminants throughout the food chain to the top fish predators. He was also concerned about the long time lag between research and publication of modelling results. Finally, he recommended more coordination and planning on data collection.

Dominic Dilloro discussed his white paper: "Model and Projection

**Uncertainty:** Methodology Development and Interpretation." He discussed classical statistical theory (maximum likelihood estimate) and nonclassical theory (generalized inverse estimate) as they apply to determining the level of uncertainty in models. He suggested that the maximum likelihood classifier can serve as the lower bound and the generalized inverse estimate can serve as the upper bound in estimating the true parameter uncertainty. He was critical of the use of whole lake simple models because they treat all loads as identical regardless of the flow rate or concentration of contaminants. Dr. Difforo thought that very large storms can have a major impact on modelling results, but they are not adequately accounted for in any of the simple models.

Discussion

Following a discussion of issues raised in the white paper, participants were asked to discuss the ways to reduce uncertainty for *in situ* modelling. One of the topics the group addressed was the level of sophistication needed in toxics modelling for Lake Ontario, that is, do you want edible fish or a healthy ecosystem? The group decided that if achieving edible fish was a step in the right direction to obtaining a healthy ecosystem and that achieving a healthy ecosystem would require more complex models.

The group frequently addressed what had been learned from the Green Bay study. They thought the Lake Ontario exercise should not be as extensive as the Green Bay model in terms of the number of chemicals monitored or the density of sampling stations. The final topic the group discussed was the use of uncalibrated model results by decision makers. Uncalibrated models have a lot of uncertainty in them, thus the focus of the group should be to obtain the data needed to calibrate current models for Lake Ontario.

**Surveillance Monitoring** The group looked at two types of *in situ* data needed to reduce uncertainty in Lake Ontario modelling. First, contaminant loadings from tributaries, atmosphere deposition, point sources, and nonpoint sources are needed. Most of the loadings originate in the atmosphere or from tributaries. Although there are 13 tributaries, the group thought that only the main tributaries, Niagara River and the Oswego River, should be monitored.

The second type of data needed is the concentration of contaminant in the water column, sediment, and biota. The group limited their discussion of which chemicals to address to those listed in the Lake Ontario Toxics Management Plan. The analysis of which chemicals to recommend for monitoring involved several considerations; the participants thought that the overriding criteria to be used was to maximize the amount of information that can be obtained from the broadest range of chemicals at the least cost. The suite of chemicals to be sampled should include a wide range of physical and chemical properties taking into account ambient water, sediment, and biotic components, and the chemicals must be consistently and easily detectable. The group also thought it was

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study important that state of the art Quality Assurance and Quality Control techniques be used with the selected chemicals.

Contaminants were divided into two main groups, those that were not recommended to be studied (Table 1) and those that were recommended for study (Table 2).

### Table 1 Contaminants to Avoid Studying in Lake Ontario

#### **Trace Metals**

Aluminum Iron Mercury

Organics

Chlordane Dieldrin Dioxin Hexachlorobenzene Octachlorostyrene 2378-TCDD

The chemicals listed in Table 1 were not recommended because they were not in the Lake Ontario Toxics Management Plan, the levels may not be high enough to be a problem, or the analytical work associated with measuring the chemical is difficult or expensive. Mercury, a concern of expressed by other workgroups, was not recommended because of the effort that would be required in terms of sampling and sample analysis, different models would have to be used, and the models would have to be fine tuned to deal with mercury.

#### Table 2

### Contaminants Recommended for Study in Lake Ontario

#### DDT PCBs (Total)

#### Mirex/Photomirex Plutonium

The chemicals listed in Table 2 were recommended for study in Lake Ontario. DDT was recommended for study because it is found in high concentration and is relatively easy to measure. Mirex and photomirex were recommended because they are contaminants unique to Lake Ontario. Further, they originated from a known source (Niagara and Oswego Rivers) and their loadings are approximately known. Dr. Hassett has analyzed the ratio of mirex to photomirex in sediments and has found it to be constant throughout the lake at 0.13 suggesting that photomirex can be used as a tracer for other contaminants. The mirex/photomirex ratio could be used as a check on the accuracy of mass balance models.

Great Lakes Monograph No. 4

Although PCBs are expensive to test, they are readily measurable in all media and their chemical properties cover the entire range of hydrophobic compounds making them applicable as a surrogate for other chemicals once the models are validated. PCBs should be measured by selecting one congener from each homologue. The PCB congeners can then be correlated to obtain total PCBs.

Plutonium was recommended because it is easy to measure in water and sediment, loading stopped 20 years ago, and the magnitude of loading is known. Although plutonium is not a human health concern, plutonium modelling would enable modelers to predict the fate of other toxics if loadings were eliminated.

## Monitoring Required to Reduce Uncertainty

There is data available on the level of contaminants in water and fish tissue for Lake Ontario, however, the group thought the data was insufficient for model calibration. They recommended additional data needs for the water column, sediment, and biota.

Water column

The group discussed the number of samples needed from the water column. According to statistical theory, the accuracy of the mean is improved by a factor of 1/square root n, where n is the number of sampling stations. Thus, 100 stations are not 100 times better than one station, they are only 10 times better. This discussion influenced the number of segments, number of sampling stations in each segment, and the frequency of testing. Several recommendations were made by the group regarding water column testing.

- The Green Bay study should be examined to help decide the number and location of sampling stations.
- Lake Ontario should be regionalized into five or six segments.
- Each segment should have at least three but preferably five sampling stations.
- Each segment should include epilimnion and hypolimnion sampling.
- Sampling should be done under the ice, after spring loading, after stratification, after fall turnover, and during one additional time.
- Sampling should continue for a minimum of two years to account for variability in weather.

One master sampling station should be established in each segment. Sampling should be more frequent and should take place every year, not just for two years. Vertical profiling should be more extensive including two samples in the epilimnion and four in the hypolimnion. In addition to toxics, dissolved and particulate organic carbon, suspended solids, P, N, SI, and CI should be sampled at the master stations.

- Volume proportional sampling is necessary.
- Data collection should take place during storms to determine the pulse loading associated with big events.
- Multiple samples should be taken during sample collection.
  Preservation of sample is inexpensive compared to the cost of losing a sample.
- Post audit analysis should occur by resampling the stations in five or ten years.

#### Sediment

Historical data on Lake Ontario and Green Bay should both be reviewed to determine the sampling intensity needed for sediment. In general, the entire lake needs to be sampled, not just the deposition zones. Further, the sampling grid should match the water column sampling grid except that it should be more extensive.

#### Biota

Contaminant levels should be determined at various levels in the food chain. Information should be collected on alewife, smelt, scalpin, lake trout, chinook salmon, and the invertebrates *misis* and *pontoporela*. The top priority should be alewife because it comprises 90% of the weight in the lake and is what most people eat. Sampling of alewifes should emphasize seasonal variation in contaminants. Lake trout change dramatically during their life cycle in terms of what they eat, thus different age classes should be sampled. *Misis* and *pontoporeia* are important to sample because they contribute the bulk of the energy in the food chain. Sampling frequency and location decisions can be addressed by looking at Lake Ontario historical data and the results from Green Bay.

Summary of Recommendations

- More coordination of research and monitoring efforts is needed to avoid duplication of efforts.
- Current data should be studied to see where the gaps are in the data, to estimate uncertainty, or to explore the possibility of monitoring surrogates instead of toxics.
- Concentrate efforts on collecting data on PCBs, DDT, Mirex, and Photomirex.
- The lake should be regionalized into five to six segments with three to five sampling stations per segment. Sampling plans, including time and space components, should be set.

up for measuring toxics concentrations in water, sediment, and biota.

- ⇒ Use data from monitoring data to validate and verify existing models.
- Sampling seasonal concentrations of toxics in alewife populations should be a top priority.
- It is essential that measurements of water column and invertebrates concentrations are matched in time. It is less essential to match fish and sediment data.

#### Research needs include:

- Use plutonium measurements in water and sediment to calibrate models.
- Study photochemistry of mirex and photomirex.
- $\Rightarrow$  Measure the Kow for each chemical to be modeled.
- Continued research is needed to improve analytical techniques.
- Determine how to combine value weighted averaging techniques with maximum likelihood estimation for censored data.

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

# Report of Group 3

## Model Paradigms

### Introduction

This workgroup was chartered with the task of discussing reducing uncertainty in mass balance models of toxics in the Great Lakes as the uncertainty relates to issues of model paradigms including model formulation, spatial and temporal resolution, and the effects of process aggregation. The outcome of the discussion is a set of recommendations on the most effective ways to reduce the uncertainty arising from these sources. Twenty scientists representing both the U.S. and Canada from a broad range of academia, regulatory agencies, and industry participated in the discussion.

The group identified two major goals it wished to achieve. The first goal was to identify research needs for reducing uncertainty arising from issues of model paradigms. The second was to discuss needs for monitoring and surveillance in Lake Ontario to insure accurate and useful modeling results.

A summary of the discussion of this working group and of its recommendations follows.

White Paper

The workgroup began with a presentation by Donald Mackay of the University of Toronto and Victor Bierman of Limno-Tech, Inc., authors of the white paper "Model Paradigms: A Discussion of Simple and Complexi Model". Don Mackay made the points that there will be a range of management questions and often these questions are not very well articulated since managers vary in sophistication and understanding of what models can and cannot do. The modeler has a duty not only to produce the model but to try and anticipate some of the questions, there will probably have to be a range of management questions, there will probably have to be a range of models from the simplest credible model to very complex, multi-segment, high-resolution, hydrodynamic models.

The simplest credible model is one that contains air, one mixed water column, and one mixed sediment layer. In Lake Ontario there is a mass of PCBs in water, a mass in sediment and, in the course of a year, there will be a mass which will evaporate. The rate constants for these mass transfers exist and it is the challenge for the modeler to try to estimate them as closely as possible. The simple model, if the rate constants are well estimated, will give an accurate representation of what is going on in the Lake. Dr. Mackay also made the point that modelers must convey to the user the uncertainties involved in the model outputs. There are a number of types of uncertainty; there is uncertainty in the parameter estimates, there are parameters which vary over time, and there is the uncertainty which arises from questions about the structure of the model. Propogation of error through the model can give an estimate of the uncertainty in the results which arises from the parameter estimates but cannot estimate the uncertainty arising from incorrect or inadequate model structure. Research to help define mechanisms for incorporation into models must continue.

Victor Bierman began by saying that the recommendations most likely to be acted on are those perceived by managers to have the highest probability for reducing uncertainty in answering management questions. Two principal management questions are: if external loadings are changed what will be the new state of the system, and, how long will it take the system to reach its new state? These questions can be used as a litmus test against which recommendations can be compared to test for utility. In addition to these, another issue is the reconciliation of open lake or whole lake questions to those involving near shore areas since near shore areas are likely to be of interest to managers and questions involving them may require more complex models.

An important question for Lake Ontario modeling is the relative need for steady-state versus time variable models. Clearly, time variable models are needed to answer the second management question; how long will it take to reach steady state? Another need is to dynamically couple the water column and sediment layer together in the model since it can be shown that the water column responds much more quickly to a change in load than does the sediment. Overall, Dr. Bierman stated that there are three reasons to use time variable, coupled water column-sediment models. First, the toxic chemical concentrations in sediments respond at different rates than the toxic chemical concentrations in the water column. Second, sediments can act as toxic chemical sources or toxic chemical sinks, depending on the dynamic state of the system and finally, in-lake toxic chemical concentrations are not proportional to external loadings under non-steady-state conditions.

Models may also require additional spatial and process complexity in the surface sediments since there is a large range of uncertainty in sediment response times for a reasonable range of values for assumed mixed layer sediment depth. Also, there are significant differences in resuspension potential between near-shore and open-water zones in large lakes and, in Lake Ontario, the open-water depositional zone represents approximately one-half of the total lake area.

Finally, additional complexity may be needed to represent the transformation and fate of organic carbon sorbents since unequal fractions of particulate organic carbon between the water column

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study and sediment will cause unequal dissolved phase toxic chemical concentrations, even at steady state. Also, a given loading condition for a particular chemical may satisfy a water quality criterion but not necessarily a sediment quality criterion and toxic chemicals released within the sediment bed, if they are not buried into deeper sediment layers, will recycle back to the water column over a long period of time. In addition, toxic chemicals released in the nepheloid layer and/or at the sediment-water interface may "short circuit" slower sediment recycling processes and be recycled quickly back to the water column.

## Simple versus complex models

After a brief discussion of issues raised in the white paper, participants in the group were each given a chance to voice their opinions on critical sources of uncertainty and areas of needed research and to suggest recommendations for the group to consider. A stimulating discussion of the need, or lack of need, for additional model complexity ensued and the pros and cons of both simple and complex models were identified. In an attempt to grapple with the model complexity issue, a set of important management questions were identified and the appropriateness of each type of model for answering each question was discussed.

Simple models are defined here as whole lake models whether they be steady-state or dynamic. Some advantages of simple models include that they are immediately applicable; educational; cheap; more friendly; may be sufficient for whole lake estimates; may have less data requirements; provide insights and understanding; and mistakes or blunders are easier to detect. Some disadvantages are that they can't discriminate between impacts of different inputs; don't discriminate between on and off shore effects or provide information on localized effects; their parameterization is difficult; and there is uncertainty in estimating response times to changes in loadings.

Complex models are defined as models with increased spatial, temporal, and/or kinetic resolution when compared to simple models. The advantages of complex models include increased spatial resolution in the results, for example, near and far shore processes can be studied separately; fewer implicit assumptions and more formalization of the assumptions; less aggregation; more direct comparisons to data; can be used to aid in the formulation of and increase the credibility of simple models; allow the analysis of the relative significance of various processes; and they may be able to reduce the need for calibration if they are more mechanistic, Some disadvantages of complex models are that it may be more difficult to synthesize and interpret the results; there are more degrees of freedom; it is difficult to do optimization and some methods for uncertainty analysis; blunders are more likely; scenarios are more difficult to simulate; and we currently have an incomplete understanding of some critical processes.

The usefulness and appropriateness of simple or complex models depends on the specific application. To assess the appropriate level
of complexity for mass balance models of toxics in Lake Ontario, six management questions were identified and the ability of both simple and complex models to answer these questions were estimated. The results of this analysis are shown in Table 1.

### Table 1

# Ability of Models to Answer Management Questions (Y=Yes, N=No, P=Partial)

Question		Simple	Complex	
Whe	en will lake water be safe for unlimited co	nsumption on a		
A)	Whole lake basis?	Р	Y	
B)	Local basis?	N	Y	
Whe	en will fish be safe for unlimited consumpt	ion on a		
A)	Whole lake basis?	P	Y	
B)	Local basis?	N	Y	
Pro	tection of most sensitive species on a			
A)	Whole lake basis?	P	Y	
B)	Local basis?	N	Ŷ	
Per	forming waste load allocations on a			
A)	Whole lake basis?	Р	Y	
B)	Local basis?	N	Y	
[de	ntification of remedial options	P	Y	
Planning of field/monitoring studies		<b>Y</b>	Y	

Model-to-Data and Model-to-Model Comparisons

A useful definition of model uncertainty is that it is a measure of how well model output compares to some independent source of information. This information source can be observations gathered in the laboratory or in the field or it can be another model which has been independently constructed. Model-to-data comparisons and model-to-model comparisons are both useful and provide different types of information about sources of model uncertainty.

Model-to-data comparisons are fairly common and form the basis of

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

most model calibration, validation and post-audit studies. These types of comparisons allow an empirical assessment of uncertainty to be performed and provide information about the appropriateness of loading estimates and parameter values. In addition, model-to-data comparisons help in the identification and improvement of knowledge of process descriptions. Examples include the identification of critical process descriptions in eutrophication models and the incorporation of sediment/food chain processes in toxic models. Problems with model-to-data comparisons include the need to match the time and space scale of the model to that of the data and, when whole-lake models are used, the averaging in the data can be problematic. Finer time and space scales may be required to allow more direct comparison.

Model-to-model comparisons are useful for several reasons. These types of comparisons also allow uncertainty to be empirically estimated and help to estimate of the effect of model assumptions, structure and completeness. Three types of model-to-model comparisons could be performed: round robin studies of models of essentially the same complexity, round robin studies involving models of varying complexity and resolution, and studies involving comparison of contemporary models with historical models to assess the effectiveness of changes in modeling approaches.

# Recommended Approach

The group developed a recommended strategy for future research on and development of mass balance models of toxics in Lake Ontario. First, there should be the continued use of existing models for whole lake issues and for addressing other appropriate management questions. At the same time, two parallel efforts should be launched which will complement each other, result in the development of more sophisticated models, and provide feedback to each other to assess the effectiveness of this approach.

The first path involves the further development of the simple, or whole-lake, models. The recommended approach is to use simple models to test and refine process descriptions. The first process description to be examined would be water/bed exchange processes including increased vertical resolution in the bed and an explicit representation of organic carbon kinetics. The simple models would also be used to study the air/water exchange process, sorption kinetics, biota/water exchange, more sophisticated food web processes, solids/carbon correlations, and speciation including hydrophilic organics and metals.

The parallel path involves the construction of models with increased spatial, temporal, and kinetic resolution, the complex model. These models would be used to take existing kinetics and add spatial/temporal resolution, couple with hydrodynamic/sediment models, use multiple sediment layers, and extend into tributaries. These models could be used to address either whole lake or local management questions by allowing averaging over the relevant portion of the lake. Additionally, these models can produce results which are directly comparable to data on the same time and space scale and allow the importance of large events to be addressed.

# Additional Recommendations

Several additional points were discussed by the group for consideration as recommendations. First, there was an overall consensus on the need for improved coordination and communication between agencies and organizations involved in modeling activities. Open lines of communication, discussion of successes and failures, and a sharing of resources are necessary to leverage limited resources effectively. Along those lines is a need for increased peer review of modeling studies. This type of review would encourage communication, facilitate the incorporation of improved mechanisms into new models, and raise the overall level of the activities of the modeling profession.

Another recommendation discussed was the need to coordinate and link groundwater, atmospheric and watershed models with water quality models. While important, it was recognized that this will be a difficult task to accomplish and may be some way off though research is beginning on linking Geographic Information System (GIS) based watershed models with water quality models. There was a general consensus on the need to continue the collection of field and laboratory data with respect to processes described under simple model. A final suggestion was to add some complexity levels (coupling hydrodynamic and sediment transport) to the existing Green Bay model and compare the results with those obtained from the existing framework.

Summary Of Recommendations

- Continue to use existing models for whole lake issues
- Use simple models to test and refine process descriptions with regard to water/bed exchange processes, air/water exchange processes, biota/water exchange processes, sorption kinetics, food web processes, solids/carbon correlations, and speciation.
- Of the process descriptions listed above, water/bed exchange processes are most important. Future research should include increasing the vertical resolution in the bed and developing explicit representations of organic carbon kinetics.
- Use complex models to add spatial/temporal resolution. in addition these models can be coupled with hydrodynamic/sediment models, can use multiple sediment layers, and can extend into tributaries.

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

# **Report of Group 4**

## Process Parameterization

Introduction

This workgroup was charged with the task of discussing reducing uncertainty in mass balance models of toxics in the Great Lakes as the uncertainty relates to issues of process parameterization including data availability, process experimentation, and scaling problems. The outcome of the discussion was a set of recommendations on the most effective ways to reduce the uncertainty arising from these sources. Thirteen scientists from both the U.S. and Canada and from a broad range of academia, regulatory agencies, and industry participated in the discussion.

A summary of the discussion of this working group and of its recommendations follows.

White Papers

The workgroup began with presentations by the white paper authors. John Connolly of Manhattan College and Doug Endicott of the United States Environmental Protection Agency presented their white papers "Process Parameterization Uncertainty in Mass Balance Models of Toxics in the Great Lakes, Parts 1 and 2". Ephram Halfon of the Canada Center for Inland Waters presented his white paper "Organic Contaminants in Lake Ontario, 1968-1991: A Review and a Data Base."

The following are summaries, by topic, prepared by the participants of this workgroup.

# GASTRO-INTESTINAL UPTAKE AND BIOMAGNIFICATION OF HYDROPHOBIC ORGANIC CHEMICALS

Frank Gobas

To reduce uncertainties in estimates of dietary uptake kinetics and biomagnification, it is important to standardize experimental procedures for measuring and reporting dietary uptake efficiencies and to determine relationships between intestinal uptake and magnification and Kow, food digestability, and the "availability" of chemicals in food.

A large part of the uncertainty in food-chain accumulation models is due to the fact that the intestinal uptake and magnification of organic chemicals is a rather complex and largely unexplored function of: the properties of the chemical (e.g. Kow); the properties of the food-phase related to the release rate or bioavailability of the

Great Lakes Monograph No. 4

chemical in the food; the digestibility of the food; and the physiology related to food-uptake (e.g. benthic invertebrates and fish have different food-uptake mechanisms).

Another source of uncertainty is introduced in the form of error in experimental measurements of dietary uptake efficiencies. Reduction in the uncertainty can be achieved by:

(1) Developing "standard" procedures or protocols for measuring and reporting values for dietary uptake efficiencies. Modelers should then only use the "good" values and forget the bad ones;

(2) Determine the relationships between intestinal uptake/dietary uptake efficiency, and the properties of the chemical, in particular Kow valves;

(3) Determine the relationship between food digestability and the dietary uptake efficiency of the chemical;

(4) Determine the extent of food digestability in the appropriate biological organisms (e.g. fish, benthic species, birds);

(5) Determine the availability of chemical uptake from the various foods.

Since a lack of knowledge regarding mechanisms is the main source of uncertainty, laboratory experiments followed up by field testing is likely to be the most successful way to reduce uncertainty.

## TRANSFORMATIONS

Deborah Swackhamer

Omission of these processes can lead to substantial uncertainty in model predictions, dependent upon the chemical or group of chemicals under consideration, the management questions being addressed by the model, and the complexity of the model framework. The specific process considered here include: microbial degradation, formation, photolysis, hydrolysis, and chemical speciation/dissociation.

The parameters leading to uncertainty in modeling these processes are the rate coefficients as a function of given conditions (e.g. temperature, substrate, water chemistry, biology) and accurate chemical concentrations in the reactant phase. For example, models applied to mercury fate would need accurate rate constants and chemical concentrations for methylation rates; models applied to mirex fate need accurate photolysis rates. For stable compounds such as PCBs, these processes (and thus their uncertainty) will be less important. The importance of these processes is also dependent on the models' time scale; over long periods of time (decades) photolysis or biodegradation may be more important for PCBs than shorter time periods. If the models are to be used for evaluating remediation measures, these processes

may be more important to consider, e.g. these processes may contribute more to contaminant fate in dredged, disturbed areas than in ambient, undisturbed areas.

Experimental research is needed to better characterize the parameters mentioned above. Development of better analytical methods is needed to more accurately measure the chemical species most influenced by these processes, such as: mercury species in water; metal complexes, etc. Laboratory experiments are needed to determine the process rate constants under controlled, varying conditions. These would need to be verified with field measurements as much as possible. Some of this could be incorporated into routine monitoring efforts, such as the chemical species concentrations, and degradation product ratios (e.g. mirex/photomirex; DDT/DDE).

# PHYSICAL/CHEMICAL PROPERTIES OF CONTAMINENTS

Michael Zarrull

The reported physical/chemical properties such as Kow values and Henry's law constants for many contaminants of interest vary widely. Recent measurements of some compounds (especially those with very high Kow's) show differences from literature values by several orders of magnitude.

Since much of the behavior of a compound to be modeled is inferred from its "known" physical/chemical properties, a high degree of confidence must be associated with these values. Often, the temperature dependence relationship of physical/chemical properties over environmentally significant ranges is missing (e.g. Kow at 20 degrees Celsius vs. at 0 to 25 degrees Celsius). A review is needed of available literature and a record of the range of reported values. This review, including a list of priority compounds to be modeled, will provide the basis to direct the specific measurements to be made.

For the use of models, a protocol or guideline of acceptable values is required. Additionally, laboratory/field measurements of physical and chemical properties over a given range of environmentally significant conditions is required. A new suite of values would thus improve model certainty considerably.

A timeline for creation of such a new model would include: literature review of conflicts (less than one year); generation of protocol for use in existing models (less than two years); and, time to re-measure the physical and chemical properties for Great Lake compounds (either less than five years for short list (less than 25 compounds) or less than ten years for long list (100-200 compounds)). The total time range to change the present conditions would therefore be between two and ten years.

# CALCULATING NET FLUX OF VOLATILE TOXIC POLLUTANTS ACROSS THE AIR/WATER INTERFACE OF LAKE ONTARIO

Terry Clark

**Statement of Problem:** Insufficient concurrent air and water concentration data exist to characterize seasonal gradients within the lower air marine layer as well as the air/water interface, both of which determine the direction and rate of flux. Flux includes air/water diffusive exchange as well as deposition; these components should be resolved.

**Initiative:** Collect concurrently, hourly air and water samples and air/water properties near the air/water interface on relatively calm, ice-free days during each of the four seasons. (Hopefully this could be extended to higher-wind conditions at a site in the middle of Lake Ontario.)

Focus Chemicals: Volatile toxic pollutants for which analytical detection limits and uncertainties are suitably low.

**Parameters:** Dissolved water concentrations and at two levels in the marine layer (e.g., 1m and 5m) hourly mean air concentrations, temperature, and 3 - dimensional wind velocities.

Work Plan/Schedule: During each of the four seasons do two things. For three weeks use an instrumented vessel on Lake Ontario sampling for as many days as possible (relatively calm days only). Within 8 months of the end of each seasonal cycle: analyze air/water samples, QA data, calculate net flux for each sampling event, and characterize seasonal net flux.

# WATERSHED MODELS FOR PCB'S AND OTHER TOXIC SUBSTANCES IN THE LAKE ONTARIO BASIN

William Snodgrass

**Problem Area** 

To understand the response of Lake Ontario to control efforts, we must be able to model the changes in airshed concentrations of PCB's.

Uncertainty

The major uncertainty is the factors that control PCB presence in

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

watershed, their sorption and possible transformation in soils (agricultural areas, urban areas, forested areas) and their release into the atmosphere by wind driven erosion of soils and volatilization from soil systems.

Recommendations

First we should develop a basin monitoring network to define PCB deposition and air concentrations of PCB's and other priority organics. After that we should develop a diagnostic mass balance model for the watersheds of the Great Lakes, the airshed of the Great Lakes, and each of the Great Lake water bodies to: define the relative importance of fluxes; the possible long-term trends that might be expected; and to develop necessary field/laboratory measurements to access watershed processes and various control efforts (vertical elimination, etc.).

Importance

This would be used to provide managers with a perspective on response times in Lake Ontario PCB concentrations when communicating the results of mass balance modelling to environmental managers.

Logistics / Schedule

A diagnostic model could be defined within one year and parallel to full measurements. The measurement program would require 3-5 years of data to reasonably provide baseline data for amassing model uncertainty and probably 3 years to provide experimental and field insight into watershed release processes.

#### FOOD WEB STRUCTURE

John Connolly

The computed hydrophobic contaminant concentrations in top predator fish are largely dependent on the number of trophic levels in the food web and the association of the components of the food web with the water column and sediment environments. Of particular importance is the pathway of contaminant movement between sediments and the top predator fish. Considerable uncertainty exists with regard to the exposure regime of animals in contact with sediment. The water they take in for respiration and the particles they ingest may be characteristic of the overlying water, the sediment or the benthic boundary layer.

Analysis of stomach contents of animals feeding on the benthos is needed to quantify the components of the food web.

Determinations of stable carbon and nitrogen isotopes in sediment and water column particulates, benthic animals and denersal fish should be made to define the routes of carbon flow, and thus the routes of contaminant transport to the fish. Current knowledge is wholly inadequate to define the benthic component of the food web. This modeling component is only important for hydrophobic, and possibly super-hydrophobic contaminants. In addition, seasonal variations in food web structure need to be determined and the recommended field experiments should be conducted over several years so that inter-annual variability can be assessed.

## LARGE EVENTS

Wilbert Lick

Large events such as major storms on lakes and large run-offs in rivers, despite their infrequent occurrence, are responsible for most of the sediment and contaminant transport in lakes and rivers. In addition, the flux of contaminants form the bottom sediments to the overlying water due to resuspension/deposition of sediments is generally larger than the fluxes due to bioturbation and diffusion. The fluxes of sediments and contaminants change continuously in magnitude and direction. There is no steady state. Because of this, an average state is difficult to define and may not be meaningful. For these reasons, it is the large, time-dependent event that must be considered in the modeling and prediction of the transport and fate of sediments and contaminants.

More specifically, data and parameters relevant to large storm and run-off events are needed. In particular, data are needed on the resuspension of sediments at high shear stresses, the deposition of sediments during strong currents, the variation of the resuspension properties of sediments with depth and not just near the sediment/water interface. Also data are needed on weather conditions, floods, changes in bathymetry, and sediment and contaminant concentrations during large storms and run-offs. This requires field instrumentation capable of surviving large events and able to measure and record during these events. Because of difficulties in making measurements during large events, laboratory experiments must be devised which can extend the present ranges of parameters to those values which are realistic during large storms and run-offs.

#### MERCURY

#### William Snodgrass

A major field measurements program is required for mercury, particularly methyl mercury to provide the data base for constructing the model. The logistics/schedule should involve a 3-5 year effort to provide data input for a parallel model applicator

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

effort. Shipboard support is required. Laboratory based measurements (where possible) are needed to define process rate constants as a function of specific environmental conditions.

Initiate a chemical measurements program on Lake Ontario for methyl mercury particularly in the following waste masses: water column profiles; atmospheric deposition; and major land-based sources such as the Niagara River. This program should determine the observed levels, if there is a biogeochemically influenced profile of the water column, and provide insight into the relative potential role between land based inputs and *in situ* formation. Other mercury species should be measured as well, but priority given to methyl mercury.

#### FISH MOBILITY

John Connolly

Fish move between three types of habitats: one suitable for reproduction; one suitable for feeding; and one suitable as a refuge in periods of unfavorable abiotic or biotic conditions. The timing and extent of movement varies between individual fish and as a function of age and sex. Quantitative relationships between movement and various biotic and abiotic factors do not exist. Since contaminant models rely on limited data from tagging studies and anecdotal information to define a single deterministic movement pattern, the error in the defined pattern may be substantial.

Field measurements of fish location and movement and biotic and abiotic conditions such as temperature, light intensity, age, sex and prey densities are necessary so that a productive framework may be developed and the natural variability within a population may be assessed. Movement over the full annual cycle needs to be determined and within-population variability needs to be quantified. A minimum of two years of field study are necessary to determine the reproducibility of the relationships between movement and the various abiotic and biotic factors.

### RESUSPENSION/DEPOSITION Wilbert Lick

The flux of contaminants from the bottom sediments to the overlying water is primarily due to resuspension/deposition, bioturbation and diffusion and is modified by chemical sorption as well as other reactions. The flux due to resuspension/deposition is generally larger, sometimes by as much as several orders of magnitude, than the fluxes due to bioturbation and diffusion. Despite this, the containment flux due to resuspension/deposition has not been adequately quantified, especially at higher stresses.

In order to determine this contaminant flux accurately, research is

needed on sediment resuspension and deposition at high flows, the rate of sorption of hydrophobic chemicals by the sediments and the effects of this sorption and other reactions on the contaminant flux during sediment suspension/deposition. Especially important at low stresses is the dynamics of the nepholoid layer and the parameters on which this dynamics depends.

Although sediment resuspensions at low shear stresses (due to wave action and currents) is beginning to be understood, resuspension at high shear stresses is not well understood or quantified. A few experiments on the deposition of sediments and the incorporation of sediments and contaminants into the bottom sediments, in the presence of currents, have been done and show the significant effects that currents have on the deposition and subsequent consolidation of the bed. These results are not sufficient for understanding or quantifying this process, and they need to be extended.

A nepholoid layer is often present just above the sediment-water interface in low to moderate currents in rivers and lakes. The occurrence of this layer, its properties, dynamics, and effect on the contaminant flux need to be understood and quantified. In order to quantify the contaminant flux during resuspension/deposition, sorption rates, equilibrium partitioning, and the parameters on which this sorption depends must be understood and accurately determined.

## SORPTION PROCESSES William Snodgrass

Sorption processes are a major area of concern in mass balance modelling because particle fluxes are the dominant transport mechanism for a variety of substances and/or because particulate forms of the contaminants are the largest reservoir of contaminants found in areas such as sediments. The sorption phenomena of concern includes the following examples: partitioning of hydrophobic chemicals onto particles or into aggregates of particles; the calculation of precipitation by algal induced blooms and sorption/competition of organics and metals is important; and precipitation of metals such as mercury, lead, calcium and others as sulfides in sediments.

Sorption of Hydrophobic Organic Chemicals

The major area of uncertainty is that sorption theory based upon Kow (local equilibrium or kinetics) data does not work for superhydrophobic compounds (Kow 710) partitioning into algae and a variety of other characteristics identified in the workshop. Another example of identified uncertainty is the apparent need for a variety of data sets to calibrate the mass balance models with "apparent partner coefficients" which are a couple of orders of

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

magnitude above values predicted by the local equilibrium assumptions.

Recommendations

Initiate laboratory based experiments which define sorption and desorption kinetics, reversible, binding sites, and irreversible sorption site as a function of a variety of particle characteristics, including solid type, nature of organic carbon, free of aggregation of particles, etc. Previous experimental data should be repeated using proper experimental protocols which have recently been defined. Additionally, we need to develop a basic theory to describe sorption phenomena. The final recommendation is to gather field and laboratory data to asses the bioavailability of organic compounds in food to organisms from particulate forms and as a function of the labile characteristics of organic carbon (e.g., algal remain, bacterial remains; condensed macro molecules of organocarbon in sediments.

#### Lab/field

 The initial focus of this work is with laboratory based measurements and modelling and theory development.

#### Work Plan Schedule

 The general schedule requires an interactive approach with 2-4 years being required for laboratory work with field samples to obtain suspended solids and sediments for conformation measurements.

#### Completed

This laboratory work will be straightforward, but require careful attention to experiment protocol. Major innovation and creativity may be needed to design the appropriate experiments.

Carbon Cycle Mass Balance

Contemporary scientific evidence and mass balance models recognize that the fate of hydrophobic chemicals that bioaccumulate are closely linked to the content and fate of organic carbon in the environment. The distribution of these chemicals between phases (particulate or dissolved) is a function of the characteristics of the chemical as well as the content of organic carbon in the phases. In fact, scientists have begun to normalize toxic chemical data for a common frame of reference as the mass of chemical per mass of organic carbon.

Based on these observations, toxic chemical models have begun to characterize organic carbon in the aquatic systems via either implicit methods (e.g. percent organic carbon, lipid content, etc.) or explicit modeling (e.g. Green Bay Mass Balance Model Framework). The effort to model toxic chemicals sorbed to carbon has exposed areas of model uncertainty which can be addressed in future efforts. These areas of uncertainty are in two areas; the first is the uncertainty regarding the mass balance of organic carbon in aquatic systems, including production and transformation processes such as carbon to chlorophyll ratios; transformation of particulate organic carbon to dissolved organic carbon and detritus; and specification of when, where, and how the carbon gets transported to the sediment - water interface. The second area is the uncertainty regarding the fate of sorbed toxicant on biotic compartments of organic carbon (i.e., POC) when the cell dies and undergoes lysis.

Recommendations to lessen these uncertainties in future efforts include research on the dynamics of DOC (experimental and field); *in situ* studies of the sediment/water interface that include fine scale measurements of organic carbon; laboratory experiments using C14 labeled PCB or other toxicants that better define phytoplankton-toxicant "sorption" or release; and more extensive efforts to model phytoplankton growth in terms of carbon content.

# Summary Of Recommendations

- Physical chemical properties: Literature review and laboratory/field measurements of Kow values and of Henry's Law constants.
- Air-water interface: Develop a research program to measure concentrations of volatile toxic pollutants at the air/water interface and characterize the seasonal net flux.
- Sorption processes: Develop a basic theory to describe sorption phenomena and initiate laboratory experiments to define sorption and desorption kinetics.
- Transformation: Develop better analytical methods and determine process rate constants in laboratory and field.
- Large Events: Consider the large, time-dependent event in modeling; collect data relevant to large storm and run-off events.
- Resuspension/Deposition: Research sediment resuspension and deposition at high flows.
- Dietary Uptake in Fish: Develop standard procedures for measuring dietary uptake efficiency and determine the relationship between dietary uptake efficiency, food

digestability and Kow.

- Food web structure: Quantify the components of the food web through stomach content analysis, define the routes of carbon flow, determine seasonal variation in food web structure.
- Mercury: Develop a field measurements program for methyl mercury.

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# Closing Panel Discussion and Responses to Recommendations

Brett Kaull, Congressman Henry Nowak's Office

Donald O'Connor, Manhaitan College

William Richardson, U.S. EPA - Large Lakes Research Station

Wayne Willford, U.S. EPA - Great Lakes National Program Office

Charles Zafonte, U.S. EPA - Region 2

Michael Zarruli, Canada Center for Inland Waters

#### William Richardson:

- The results from this conference should be used to plan future modeling research.
- It's good to see scientists and decision makers talking and working together toward consensus.
- There is a need to carry on with the Green Bay data set and the work that is going on there.
- We need to coordinate our data gathering and other efforts so that we can leverage our resources better.
- We need a vision and a mission to come out of this workshop. This will help convince management and get future funding.
- We need to be cautious about not overselling models. We should do follow-up research to check model results.
- Mercury is an important problem. We must initiate research

#### on it soon.

#### Wayne Willford:

- Models are built to respond to management needs but these needs change over time. We need to be able to anticipate future needs so that there can be a response when new questions arise.
- Decisions will be made and regulatory actions will be taken whether models are used or not. Modelers shouldn't be afraid to have their models used.
- Uncertainty about loadings is a major issue. We need a good loadings matrix; this matrix would be useful to management whether models are used or not.
- It would be a strategic error to ignore a management identified problem like mercury just because it is a difficult problem to deal with. Instead we should present proposals for the research needed to respond to this problem.
- How can we move models from data consumers to predictors so that we can lower our data collection needs?
   Models should allow us to be more proactive rather than requiring research which is retrospective in nature.
- We should move steadily from the simple to the complex.
   However, we should not be hesitant to use models as we progress since decisions will be made with or without them.
- Future research needs should focus on improving understanding rather than on an improving a mass balance. Additionally, sensitivity analysis should be used to identify priorities for research.

#### Brett Kauli:

- Policy makers need models as a tool to help them use tax dollars wisely.
- The Great Lakes is a good place for a case study since it is an important resource and involves two countries and many states and provinces.
- Models may help to make the connection for why money should be spent on regulation and remediation. They bring environmental benefits into the policy decision making process.
- To get federal support behind a project there must be a tool to show that investment in the environment will pay a dividend. Models help decision makers develop informed intuition.
- There is a need for coordination since coordination leads to a decreased need for resources without sacrificing quality.

#### Michael Zarrull:

- There is a need for a framework for process research.
- Along with reducing uncertainty in mass balance models, it is also important to think about reducing uncertainty in the research manager's future budgets.
- Money is an important consideration. We must use our resources as effectively as possible.

#### **Donald O'Connor:**

We should be planning to construct one complex "mother

of all models" whose primary purpose would be scientific understanding. This model could give birth to simpler, more specific models designed to answer key management questions.

- Modeling is a relatively young field; it started in 1926 and only really got going in the 1950's. Because of this, and the need to use models now, we lack the leisure to develop the discipline slowly.
- Progressing in complexity down two parallel paths as suggested by Group 3 is a good idea. (Complex and Simple models)
- We must relate what we do to real problems and then demonstrate the application of models to these problems.
   We must be more articulate about the application of our models. We must both maintain the integrity of science and answer the questions that are being posed to us.

#### **Charles Zafonte:**

- This conference represents significant progress on reducing uncertainty.
- There is a need for both simple and complex models. We need to continue to learn from the simple models, verify them with data, and gain consensus on what we've learned.
- Research proposals should be written on the issues that arose as important in this conference, for example uncertainty surrounding the sediment/water interface.
- We should make coordination a priority. We need to get people who are working on similar projects communicating

with each other.

- Mercury is a real environmental problem in Lake Ontario and we need to find out what is going on. Research proposals for developing a Level 1 mercury model should be prepared.
- It was suggested that we monitor three chlorinated organics. We need to ensure that the other five are dealt with also.
- Funding is a major issue. The continued pressure on funding is the most important issue for decision makers.

Several questions to the panel were posed by the conference participants. John Toil brought up the point that researchers are conservative on the use of models of unpredictable systems because they are worried about scientific credibility and policy makers are conservative because they're worried about policy credibility. A solution is that scientists and regulators could begin with what type of answers and level of uncertainty they're both comfortable with and then work backward to generate a set of feasible research and policy objectives. In addition, modelers need to be more sophisticated in presenting uncertainty and managers need to be more sophisticated in framing questions.

Paul Rogers suggested that, for the Green Bay modeling project, models that were thought to be state-of-the-art at the beginning of the project should be compared to the current models. This would give a good indication of what was gained for the money spent. Wayne Willford responded that it was just a pilot project to learn what to do and how to do it. Donald O'Connor said we've at least gained knowledge and decreased uncertainty and Bill Richardson said such a study would be a good idea but keep in mind that the modeling costs are small compared to the data collection costs.

Charles Hall pointed out that sophisticated computer graphics can help to bridge the gap between scientists and decision makers. Bill Richardson responded that this is currently being pursued and that a supercomputer is being installed in Green Bay with sophisticated visualization capabilities.

Elfron Halfon pointed out that five models have been developed for Lake Ontario and we don't have consensus on their credibility so how can we develop just one model? Donald O'Connor responded that we should stress the unity of what we know and get consensus on scientific beliefs and then get these beliefs into the models. In addition, we need to establish a repository of modeling history so that we will have a perspective as we advance.



# Appendix A: White Papers

# Loadings, Forcing Functions, and Stochastic Variability

Dave Dolan International Joint Commission

Tom Young Clarkson University

## Introduction

In this paper, model forcing functions (especially loadings) are discussed. Important issues are identified and the possibilities for reducing their uncertainty are presented. At this point, a couple of definitions would be useful:

- Forcing Function An independent variable in a model formulation. By independent it is meant that the variable is not affected by changes in the model. Thus, forcing functions can appear on the right hand sides of differential equations, but not the left. Some forcing functions, such as loading, can often be controlled and thus are of management interest, others, such as weather, are basically uncontrolled.
- Uncertainty An indication of the value or reliability of information. In this paper, the indicator used is the standard deviation of the model estimate of an output variable.

Reductions in uncertainty occur in a variety of ways. It is assumed that, whenever possible, state-of-the-art methods for data handling will be used, so that this area will not add to uncertainty. Further, it is assumed that new data will be collected in an effort to reduce uncertainty and that, because of budget constraints, it is desired to optimize this effort in some way.

Loads of Concern Contaminant loads frequently are handled in models of toxic chemical fate and transport as if they were independent variables, or forcing functions, that drive the response of the modeled system. However, the loading of toxic chemicals and other substances of interest are not truly independent variables; rather, they respond to numerous external forces, true forcing functions, in achieving their observed states. The coupling between loads, forcing functions, and chemical fate is partly deterministic and partly stochastic. Here, the emphasis will be on identifying the uncertain element in the linkages between loads and forcing functions. Toxic chemical loads of concern to this discussion will be identified as belonging to one of

## Great Lakes Monograph No. 4

three categories. These include:

- tributary inflows,
- direct point sources (industrial and municipal inputs), and
- direct non-point sources (rural and urban runoff, in-place pollutants, groundwater, and atmospheric inputs).

Loads in each of these categories possess attributes that vary in a manner that makes load quantitation difficult without encountering substantial uncertainty. On the other hand, several issues related to uncertainty are common to most protocols for estimating loads and forcing functions. An important issue common to any load or forcing function estimate is selection of appropriate time and space scales for aggregating information. This consideration is important because it can determine the accuracy with which uncertainty in the estimates may be known for given actual variability in the quantities of interest. An in-depth discussion of the issue of time and space scales appears in a companion paper.

A second issue of common concern is that of observation uncertainty such that the uncertainty may be attributed to the physical and chemical methods used for data collection (e.g., sampling schedule, field and laboratory methods for sampling, handling, preservation, storage, and analytical quantitation). Such methodological uncertainties may be systematic or random and provide the target for quality assurance and control programs (QA/QC). In the design of a monitoring program, however, the need to randomize is not always recognized. Nevertheless, the need to randomize at some stage of monitoring is always present. Otherwise, the analysis of results by statistical models cannot be without an unknowable amount of bias. accomplished Uncertainties due to sampling and analysis methodologies will be addressed to a limited degree in this paper, but a detailed discussion is outside of the scope of this paper. One special area of data uncertainty that frequently arises in estimating loads of toxic chemicals for mass balance models is the issue of non-detect observations. Dealing with non-detect data will be examined in this paper in the context of estimating contaminant loads and doing so to minimize uncertainty.

A third common issue involving uncertainty arises over the approach to be used for data analysis, or the statistical estimation method to be employed. To a large extent, such concerns parallel those that emanate from uncertainties over model specification, including process parameterization. This is appropriate, because the statistical analysis applied to yield a loading estimate or time series must be faithful to an underlying mathematical (i.e., statistical) model. This aspect of uncertainty also will be given detailed treatment in this discussion.

# Tradeoffs

As has been alluded to above, the feasibility of obtaining perfect load estimates is reduced by a number of difficult issues: scientific, logistic, economic and natural. It is important to not only divide these issues into ones that can be controlled and those that can't, but also into those that represent tradeoffs or compromises and those that don't.

Tradeoffs occur when there is a task to perform within a fixed budget (either dollars or manpower or both). In the context of load estimation, they involve questions such as: how many tributaries and sources can be sampled? how many samples per source can be taken?, etc. These are mainly economic and logistic considerations. Scientific issues in load estimation tend not to be as subject to tradeoffs because the usual approach is to apply state-of-the-art science without advancing to unproven areas.

# Assessment of Loading Uncertainty

As is true in the larger context of model uncertainty analysis, the evaluation of load estimation uncertainty is, itself, a procedure that may incur considerable error. Except in simple models, it is presently not possible to objectively and uniquely assess uncertainty due to model (statistical) formulation, dependent and independent variables, and parameters. Most effort in uncertainty analysis has been put toward evaluating uncertainty due to errors in parameters and independent variables or forcing functions.

Two fundamentally different approaches to the assessment of parameter uncertainty have been developed: Monte Carlo simulation and first order analysis (variance propagation). The approach taken with the former method involves assigning probability density functions to each uncertain model parameter or variable, and then "sampling" the distributions at random for calculation of a model result. This procedure is repeated a large number of times, and the distribution of model results may be analyzed statistically to ascertain the combined effects of all the uncertain parameters on the overall uncertainty exhibited by the model.

The term, first order analysis, is apt because the approach is based on using the first order terms of a Taylor series expansion about the mean of each uncertain parameter or input variable. For a single equation, multi-parameter model (e.g., Y=f(X), where X is the vector of uncertain parameters), the expression for the estimated uncertainty of the model result (V(Y), variance of outcome, Y), due to parameter uncertainty, is given by Equation 1.

$$V(Y) = \sum_{i=1}^{n} \left(\frac{\partial f}{\partial X_{i}}\right)^{2} V(X_{i}) + 2 \sum_{i=1}^{n} \sum_{j=1}^{i-1} \left(\frac{\partial f}{\partial X_{i}}\right) \left(\frac{\partial f}{\partial X_{j}}\right) COV(X_{i}, X_{j})$$
(1)

If the uncertain parameters are uncorrelated, then Equation 1 simplifies to the first term on the right and the total prediction uncertainty is due to the sum of the individual contributions by each uncertain parameter.

Monte Carlo simulation has two main advantages over first order analysis. First, Monte Carlo simulation does not lose exactness of model representation, as first order analysis does due to truncation of the Taylor series expansion. Thus, within the limits of the deterministic model and parameter distributions, Monte Carlo simulation is complete. Second, the results of Monte Carlo simulation provide a complete probability density function estimate to describe parameter error, rather than only an estimate of the mean and variance. The Monte Carlo procedure, however, is computationally intensive. Consequently, first order analysis may be favored for its convenience on simple models. Uncertainty analysis for complex models (dynamic, multi-state, multi-parameter, detailed spatial resolution) may require more computation for Monte Carlo simulation than can be justified. Statistically efficient methods of directing the sampling required for the simulations (e.g., the latin hypercube design) can greatly reduce the computational requirements.

First order analysis provides a reasonably uncomplicated approach to assessing uncertainty that may be adapted for use with models of high complexity. Because of its wide utility, it will be used here to demonstrate a procedure for ranking the uncertainty in lake water concentration for a contaminant of concern that is associated with uncertainty in each of the loading categories discussed previously. To do this, of course, a model must be specified that relates concentration and loads. Given in Equation 2 for the purposes of illustration is a mass balance equation for a lake of volume, V, an outflow rate of Q, a contaminant of concern with water column concentration, C, and which receives loads of the contaminant from tributaries (2Wtrib,i), direct point sources (2WPTS,i), external direct non-point sources ( $\Sigma W_{NPS, i}$ ), atmospheric sources ( $W_{ATM}$ ), and which loses mass due to the net of sedimentation, resuspension, diffusion, and bioturbation over the sediment with surface area A<sub>s</sub>,  $(J_{SED}A_s),$ bv evaporation/volatilization over the water surface with area A, (JEVAPA), and which reacts within the water column by a first order process with rate law -KC.

$$V \frac{dC}{dt} = \sum_{i} W_{TRIB, i} + \sum_{j} W_{PTS, j} + \sum_{k} W_{NPS}$$

$$+ W_{ATH} - J_{SED} A_{s} - J_{EVAP} A - QC - kCV$$
(2)

which has the steady-state solution:

$$C = \frac{\sum_{i} W_{TRIB, i} + \sum_{j} W_{PTS, j} + \sum_{k} W_{NPS} + W_{ATM} - J_{SED}A_{s} - J_{EVAP}A}{(Q + kV)}$$
(3)

$$\frac{\partial C}{\partial W_{m}} = \frac{1}{Q + KV}$$
(4)

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

The partial derivatives in Equation 1 ( $\partial$  f/, $\partial$ XI) are sensitivity coefficients; they indicate the rate of change in the dependent or predicted variable with respect to the uncertain parameters. By analogy, the steady-state concentration of contaminant in Equation 3 may be taken to be the dependent variable and the loads may be taken to represent uncertain parameters, giving Equation 4. Here, the objective is projecting the uncertainty in loads onto made about the steady-state contaminant predictions concentration. Because of the simplicity of this model, the sensitivity of the lake water concentration at steady-state to each of the loads is identical, as shown in Equation 4 (Wm is an arbitrary loading term from Equation 2 or 3).

The contributions of the loads to the uncertainty of the concentration prediction, however, are not identical. Rather, they depend on their individual variances. If the loads are assumed to be independent of each other to permit simple extension of the illustration (seasonality alone suggests that this is not a particularly good assumption), then individual load contributions to the uncertainty of concentration is given by Equation 5, while the total uncertainty *due to loading* is given by Equation 6.

$$S_{c}^{2}]_{W} = \frac{S_{W^{2}}}{(Q+kV)^{2}}$$
(5)

$$S_{c_{y}}^{2} = \left(\frac{1}{(Q+kV)^{2}}\right) \sum_{m=1}^{n} S_{w_{m}}^{2}$$
 (6)

Further demonstration of the first order uncertainty of lake concentration to loading may be pursued using the illustrative (default) data on contaminant loadings from D. Mackay's steady-state model (PROGRAM NOTL) for Lake Ontario; also other attributes of Lake Ontario required for Equation 3 were taken from the Mackay model (V=1.67x10<sup>2</sup> m<sup>3</sup>, V/Q=6.5 y, k=6.07x10<sup>7</sup> y<sup>-1</sup>). The loads of toxic chemical range from 100 to 200 kg y<sup>-1</sup>. The analysis is shown in Table I. To perform the analysis, coefficients of variation were required for the load estimates. The values used are given in Table I and are hypothetical; they are suggestive of the relative ranking of the uncertainty with which each load may be known.

To put the concentration uncertainty estimates into context, Equation 3 may be calculated for the volume, discharge, and chemical decay attributes noted parenthetically above. To do this with the minimal information given, it will be assumed that the net interaction with sediment and atmosphere is zero. As indicated in Table I, the given loadings total 700 kg y<sup>-1</sup>. This would yield a steady-state concentration estimate of 2.7 ng L<sup>-1</sup> by Equation 3. Because the partial uncertainties hypothesized for the loadings total 2.0 ng L<sup>-1</sup>, the steady-state concentration estimate has an overall coefficient of variation of 74 percent. The relative ranking of the partial uncertainties closely tracks the assumed coefficients of variation. This underscores the importance to uncertainty analysis of knowing the properties of the underlying error structure as well as

Great Lakes Monograph No. 4

#### possible.

in the example presented in Table I, the direct point sources have been split into municipal and industrial. In general, this split is desirable because these sources represent different management options (pretreatment programs vs. direct effluent controls). Sufficient information currently exists to make this division of the point source load.

In the case of the tributary load, a split has been made into the Niagara River and "all others." This was done because the Niagara load is comparatively well known due to the program of the Niagara River Toxics Committee. The differences in coefficients of variation reflect this situation.

First-Order Analysis of Concentration Estimate Uncertainty Attributable to Loading Uncertainty for Lake Ontario Using Illustrative Data

Source of Uncertainty	Lond Magnitude (kg/y)	Assumed Load Coefficient of Variation (%)	Load Standard Deviation (ng y*)	Partial Uncertainty in Concentration Estimate Due to Load Uncertainty (ng L <sup>-1</sup> )
Municipal Point Sources	100	25	25x1012	0.1
Industrial Point Sources	120	25	30x 1012	0.1
Direct Non-Point Sources	130	·. 100	130x10 <sup>42</sup>	0.5
All Other Influent Tributaries	150	200	300x10 <sup>12</sup>	1.2
Niagara River	200	20	40x 10 <sup>12</sup>	0.2
TOTAL	700	•	-	2.0

For non-point sources, no such division is possible given existing knowledge, although it would be desirable because of the implications for control options.

When a model formulation is agreed on for Lake Ontario, the above analysis should be repeated using current data. The partial uncertainties should be estimated and ranked and then the sampling efforts should be concentrated on the highest sources of uncertainty. In this type of analysis, the importance of historical data analysis is made clear. Another point that should be made is that methods of load estimation based on extrapolation and typical concentrations (among other procedures) that are used in lieu of real data should continue to be developed, since improving their effectiveness will improve the utility of the uncertainty analysis.

Major Sources Of Loading Uncertainty The average load, L [M T<sup>-1</sup>], delivered to a receiving water during some specific time interval,  $\Delta t$  [T], through an interface of area, A [L<sup>-</sup>], for a contaminant that is carried by water flowing at an instantaneous velocity, v, [L T<sup>-1</sup>], and concentration, C [M L<sup>-3</sup>], may be represented by Equation 7 when contaminant transport occurs by purely advective processes. If contaminant transport occurs by purely diffusive or dispersive processes along the instantaneous concentration gradient normal to the interface, dC/dz [M L<sup>-4</sup>], with a transport coefficient,  $D_z$  [L<sup>-2</sup> T<sup>-1</sup>], then Equation 8 may be used to represent the average load to the receiving water.

$$L = \frac{1}{\Delta t} \int_{At} \int_{A} v(A,\tau) C(A,\tau) \, dA \, d\tau \tag{7}$$

$$L = -\frac{1}{\Delta t} \int_{\Delta t} \int_{A} D_{z}(A,\tau) \frac{dC(A,\tau)}{dz} dA d\tau \qquad (8)$$

Equations 7 and 8 are one-dimensional, idealized, deterministic simplifications of the complex, stochastic situation that exists and determines loads during contaminant transport. If it were possible to monitor continuously in time and space and with absolute accuracy all boundaries of a receiving water body, then one could compute loads without uncertainty, at least in theory. Even if monitoring with that intensity were technologically feasible, however, it would be impractical. Nevertheless, these equations can serve to illustrate the major sources of uncertainty that affect estimates of toxic chemical loading and other forcing functions of interest for Great Lakes modeling. In particular, any condition or change in conditions that alters any of the variables in Equations 7 and 8 will affect, in turn, the resulting estimate of load. By corollary, uncertainty in the variables of Equations 7 and 8 will propagate through the relationship to affect the load estimate. Any quantity, therefore, that produces uncertainty in flow velocities, concentrations, dispersion or diffusion coefficients, or concentration gradients can lead to uncertainty in contaminant loading estimates. The role of sampling design in reducing uncertainty is examined below; after a survey of the major sources of uncertainty associated with the loads in each of the categories identified earlier.

# **Tributary Mouth Loadings**

Contaminant loading estimates for rivers that enter the Great Lakes derive uncertainty from a combination of several sources. Because tributary inputs constitute the largest single load for many contaminants, considerable attention has been given to tributary load estimation and uncertainty. Exhaustive coverage of tributary load uncertainty will not be given here, however, the main contributory elements will be examined. The discussion will focus on uncertainty associated with estimating loads of contaminants that partition strongly to the solid phase. This will be done for two reasons. First, many anthropogenic organic contaminants that are of concern to mass balance modelers of toxic chemicals are surface active due to hydrophobicity or polyvalency and, therefore, may be predominantly associated with transported solids. This phase partitioning is a complex phenomenon involving thermodynamic and kinetic constraints that result from chemical and physical characteristics of the solid and liquid phases, and the contaminant(s) of concern. Some of the more important factors include pH, particulate and dissolved organic carbon levels, solid phase levels of hydrous metal oxides, sorbent and sorbate concentrations and kinetics of adsorption and desorption. The second reason for focusing this discussion on particulate matter is the fact that particulate matter, and associated contaminants, generally are subject to greater spatial and temporal heterogeneity than contaminants in the dissolved phase. Consequently, the uncertainty of total tributary loads will be heavily influenced by the uncertainty of particulate loads of such contaminants. Moreover, reductions in particle-associated tributary loading uncertainty by

improved sample design will yield more certain soluble phase loadings, too.

Sediment and sediment-associated pollutants that reach the mouth of a tributary originate largely from non-point sources in the watershed and result from of a complex interplay of numerous forces. Of special importance are (1) climate, in general, and the nature, amount, and intensity of precipitation, in particular; (2) orientation, degree, and length of slopes; (3) geology and soil types; (4) land use; (5) condition and density of the channel system; (6) particle settling velocity; and (7) streamflow regime. In addition, the finest resolution of sediment load variability, and that of associated contaminants, for a receiving water generally will depend on the coarsest resolution of either meteorologic events, receiving water events, or channel geometry and geology. Fluvial loading uncertainty, therefore, will depend in large measure on the variability of these physical factors. This dependence, of course, is in addition to the influence of physicochemical factors specific to the contaminant of interest, such as, solubility, volatility, partitioning, and temperature dependencies, plus the biochemical influences of uptake and decay.

I he interplay of gravitational and viscous forces on particulate matter in water results in fluvial systems having a selective transport capacity for particle-bound pollutants. Thus, as fluid forces vary in time and space, so too does the movement of particulate contaminants. In general, therefore, the total loading of particle-bound contaminants is related to discharge in a non-linear manner that consists of a watershed-determined movement of fine particles superimposed on a discharge-dependent and spatially varying flux of coarse sediments. The consequence of selective transport for loading uncertainty arises immediately as a requirement to design sampling protocols that address concentration and velocity variability over a sample transect.

Cross-sectional variability in particulate contaminant concentration also is a problem consisting of two components, because fine and coarse particulate matter behave differently. Fine matter (coarse silt and smaller) may be considered to be uniformly distributed vertically and horizontally at an appropriate distance downstream from a source of sediment, so long as flows are sufficiently turbulent. This criterion is not well defined but will depend on characteristics of the particles, the fluid, and the site of concern (discharge, cross-sectional area, channel width and depth). Coarse sediment (fine sand and greater), on the other hand, shows a strong dependence on the hydraulic character of the system. In particular, the transport of sand-size particles depends on bedform (depth and dune forms) and flow regime (development of turbulence). The combined effect of these components is relatively low variability across the cross-section if the amount of fine sediment is high relative to sand.

Temporal variability, of course, adds an additional dimension of uncertainty to the fluvial load problem. Concentrations of suspended matter and associated pollutants at a stream

cross-section during a hydrologic event often shows a time-dependence that reflects the character of the hydrograph, generally increasing and then decreasing during the event, due to erosion, scour and deposition. The peak concentration, however, often does not coincide with the peak of flow and may lead or lag the flow peak. Most frequently the concentration peak leads the hydrograph somewhat; however, for suspended matter the actual pattern realized by a given drainage system depends on the size of the watershed, location of the causative event, and antecedent streamflow. Time of year exerts significant influence on the solids levels found in most systems. For fine suspended matter, this influence is a result of the dependence of concentration on rate of supply, which in turn depends on erodability, land use patterns, precipitation, intensity, and pattern, antecedent soil moisture, and spring freeze-thaw cycles. Seasonal variability in coarse suspended matter concentrations depends mainly on the streamflow conditions that are realized in the systems of interest.

Three additional sources of uncertainty in tributary mouth loading estimates will be discussed: seiching, near upstream point sources, and gauge to confluence distance. Seiching is a condition that gives rise to periodic reversals of flow at the tributary-lake confluence and leads to an especially difficult load estimation problem. The problem can be so severe that loads of conservative as well as non-conservative contaminants cannot be estimated by projection from a near upstream monitoring point without unreasonably high uncertainty. The main factors prohibiting extrapolation of the upstream estimate are transport time phase error and physical phenomena dependent on the particle size distribution of the solid phase matter, sedimentation, resuspension, and delivery to the receiving water.

Consideration must be given to uncertainty attributable to upstream point sources that are proximate to the confluence of concern. The uncertainty such sources contribute to the load estimate is that due to inadequate mixing over the cross-section and the resulting transverse gradients. Combined sewer overflows, which often occur in near-mouth reaches, also give rise to uncharacteristic flow-concentration responses during wet weather, and their influence may contribute uncertainty in the fluvial load estimate.

Commonly, an existing gauging site may not be the most desirable location for sample collection, or the toxic chemical observations of interest may be pre-existing and from a site that is a substantial distance upstream from the confluence. Uncertainty in "extrapolating" the upstream measurements over the unmonitored portion of the tributary give rise to uncertainty in the tributary load estimate.

# Data Collection

Since, using the illustrative example in Table I, the largest source of loading uncertainty was the "all other influent tributaries," the

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

following discussion will concentrate on ways to reduce the uncertainty for tributary loads. Some of the recommendations discussed below will be applicable to other sources of uncertainty; others will be added where appropriate.

Economic and logistical considerations can be optimized for given fixed dollars and resources (sampling crews, lab capacity, etc.). However, it is recommended that certain sampling <u>not</u> be optimized for and in fact be designed for built-in redundancy when possible. In general, physical and chemical variables that are relatively inexpensive to obtain but critical to load estimation and subsequent modeling efforts (such as flow, temperature, pH, chloride, suspended solids and other conventionals) should not be subject to optimization. Ideally, existing jurisdictional programs for these parameters should continue or even be strengthened during the study. In addition, sampling for toxic contaminants should also include these important parameters to both provide a redundant measure (for safety purposes) and a way of relating these measurements to more routine ones made historically.

The sampling that should be optimized is for the toxic contaminants themselves. Due to the cost per sample of many of these chemicals, as well as limited lab capacity, field equipment and expertise, the tradeoffs really occur at this level of sampling. The compromise will come down to accuracy load estimate vs. cost of sampling. As a hypothetical example, suppose one wishes to sample 95% of the tributary flow to Lake Ontario (suspended solids load could also be used here) on a monthly basis for a suite of organic and metal contaminants. The list of tributaries to be sampled is:

> Oswego Trent Genesee Moir Salmon Credit

Twelve Mile Creek Black Welland Buffalo Napanee

Fortunately, the largest tributary, the Niagara, is well sampled by an existing program at a weekly frequency. However, this list will require new efforts. The cost would be:

#### # tributaries x 12 x cost per sample -

If this is within the budget, then no optimization is necessary. However, assuming it is too expensive and no additional funds are available, the tradeoff occurs in number of samples (less tributaries or less months). Alternatively, if a certain maximum uncertainty is allowed, then a program could be designed to achieve this at minimum cost. See Lesht (1991) for a more detailed treatment.

An alternative approach to this type of optimization is the Balanced Incomplete Block Design proposed by El-Shaarawi and Williams (1989) for Niagara River point sources. Briefly, it allows the estimation of the total load of a contaminant, the individual loads of larger tributaries and standard errors of the loads with substantially less samples needed than conventional designs. Again, assuming a fixed number of samples allocated to the effort, it should be possible to estimate the total tributary load, the relative contribution of at least four of the major tributaries and provide the equivalent of at least three replications at better than half the cost of a conventional design. This is a type of tradeoff also, but it occurs without giving up the primary objective, which is an accurate total load. This approach may not be appropriate for all scales of modeling but it should be considered because of the substantial savings it offers.

## Data Handling Improvements

Improvements to reduce uncertainty in load and forcing function estimation in the area of data handling should not be subject to tradeoffs. The best available methods should be used so that no information that is collected is unused or partially used. In past projects this has occurred in two areas: load estimation methods and censored data handling.

Considerable effort has been devoted to demonstrating that load estimation methods that ignore the correlation between measured variables are unacceptable. Besides the fact that they do not use all available information, they introduce significant biases into load estimates. Ratio and regression estimates are two methods that do consider the correlation between variables and these should be used whenever possible.

One problem that inhibits the use of these methods is that of data censoring. This practice should be avoided whenever possible in the laboratory, but in many cases it is unavoidable. Similarly, if data are to be censored, they should have one detection limit reported. Again, sometimes this is impossible. Therefore, a generalized load estimation procedure is being developed for use with censored data that will maximize the information that can be obtained from partially censored loading data sets (up to 80% censoring). This involves a maximum likelihood estimate for statistical parameters that describe loading. This procedure will solve the problem of "minimum and maximum" load estimates that was caused by partial censoring of loadings data in the Green Bay study. The procedure is an extension of work by El-Shaarawi and Dolan and will be available in early 1992.

## Point Sources

Quantitation of contaminant point source loadings to the Great Lakes may be done with greater certainty than non-point source loadings, because the technical and logistical aspects of sampling are less complicated for point sources. The simplicity of point source load estimation results from ignoring the spatial component of variability during monitoring, a convenience permitted by the point character of the source (the interfacial area, A, in Equations 7 or 8 is negligible). The degree of simplification this affords is such that a continuous record of an instantaneous load is possible for some contaminants (e.g., oxygen deficit). Of course, the extent to which the point source model is inappropriate for the monitoring data will lead to uncertainty in estimates based on it.

Most important to the overall uncertainty of most point source load estimation questions is the uncertainty associated with temporal variability of the load, whether due to variability in concentration or discharge or both. Temporal variability becomes a problem whenever a continuous record of the contaminant load is not available for the point source of interest. This is, of course, generally the case for Great Lakes contaminants, even though permitted dischargers are required to monitor their effluents routinely. As will be discussed later, proper sampling design can significantly reduce the influence of temporal variability on the uncertainty of point source load estimates.

The temporal variability in point source loads may possess a considerable level of determinism, or structure, that can be exploited to improve load estimate accuracy. Such structure that may be present will depend on the nature of the point source. <u>Municipal</u> wastewater effluents, for example, may show periodicity over 8 to 12 and 24 hour cycles for some contaminants, weekly cycles for others, and seasonal or annual cycles for still others. <u>Industrial</u> point sources, on the other hand, tend to show less temporal structure, though they do reflect manufacturing or other production cycles. In general, variability in point sources is associated with community size, meteorologic and geographic factors, mixtures of influent sources (industrial/sanitary), and design flow rate of the facility of concern.

## Data Collection Improvements

The location, design flow and industrial category of all point sources in the basin are known. This information should be used in optimizing the sampling design for point sources. A GIS would be most useful in identifying accurately the direct point sources.

The same optimization considerations discussed under tributaries are relevant with point sources. However, the practicality of mixing effluents to achieve the *Balanced Incomplete Block Design* is dubious, especially from a legal and analytical chemistry viewpoint. The question of utilizing effluent self-monitoring data is unresolved. Some self-monitoring data will probably be used, but toxic contaminant data obtained this way will usually be subject to less stringent quality assurance procedures.

### Data Handling Improvements

In general, load estimation with point sources is easier, given adequate data. Ratio and/or regression estimations are probably not necessary, and a simple summation of the products of flow and concentration should be adequate. The same type of considerations for censored data apply to point sources.

## Non-Point Sources

The major phenomena that produce uncertainty in non-point source load estimates for use in toxic chemical mass balance models consist of "true" forcing functions in the sense that they are truly independent variables that govern both the deterministic elements of the quantities represented in Equations 7 and 8 and the stochastic elements that are only implied by the previous discussion.

Direct non-point loads from rural runoff derive uncertainty from numerous sources, but it is possible to generalize these by stating that rural runoff is mainly associated with (1) random hydrologic events that have their roots in meteorologic or climatic phenomena, (2) sediment movement that accompanies runoff, and (3) partitioning of the chemical of interest between water and sediment. The forcing functions that govern uncertainty in rural runoff load estimates, therefore, relate mainly to these three phenomena. Physical forcing functions that affect rural runoff include meteorologic and climatic variables such as temperature, wind speed and direction, precipitation quantity, intensity, and form; terrestrial attributes such as distribution and size of source areas, soil type and erodability, land use and management practices, slope, aspect, depression storage, and antecedent moisture conditions. Chemical forcing functions that lead to uncertainties in rural runoff load estimation include the phase partitioning behavior of the contaminants of interest and the rate, timing, and mode of environmental release of the contaminant in the source area, Biological variables that influence the degree of certainty with which rural runoff loads may be determined include seasonal and ecological succession, evapotranspiration, migration, and distribution of ground cover.

In a general way, <u>urban runoff</u> loading of contaminants depends on the same factors as those cited above for rural runoff loads. Urban runoff loads normally differ substantially, however, in that they generally reflect much higher rates of runoff compared to rural ones. This is due to the generally greater imperviousness of surfaces that intercept precipitation. Further, urban runoff normally is collected for routing to ultimate disposal. Under circumstances that are favorable to surface receiving waters, such routing is through separate storm sewers and settling basins followed by application to infiltration beds to recharge groundwater. Under less favorable circumstances, the

routing is through combined sewers (runoff and sanitary wastewater) that may be allowed to overflow during runoff events that exceed the volumetric design capacity of wastewater treatment facilities. Urban runoff loads also differ from rural ones in that urban loads depend on population density and street cleaning effort. Empirical models (e.g. STORMS - US Army Corps of Engineers) are available to aid in estimating urban runoff loads, however, monitoring is required for any quantitative assessment of estimate uncertainty, which may be large.

Dissolved phase contaminants predominate in <u>aroundwater</u> and are transported into (and out of) the receiving waterbody by advection, dispersion, and diffusion at the sediment-water interface. Contaminant loads from infiltration of contaminated groundwater are difficult to quantify directly and frequently are estimated by mass balance closure; consequently, they are often notably uncertain. Among the numerous determinants of groundwater contaminant transport are included aquifer thickness, hydraulic gradient, proximity of recharge and contaminant source areas, and such contaminant attributes as partitioning behavior, susceptibility to decay, and concentration gradients. When groundwater loading of contaminants is estimated directly, then each of the parameters named above can contribute uncertainty to the result.

Contaminated sediments, or in-place pollutants, may enter the overlying water in the dissolved or particulate phase. Mechanisms that lead to the introduction of in-place pollutants into the water column include bioturbation, the net result of scour, resuspension and sedimentation; diffusion, and advection (via groundwater). At least in principle, each of these mechanisms may be quantified, but each is determined by parameters that are difficult to measure directly, that vary spatially and temporally, and that generally possess high uncertainty. The determinants of in-place contaminant loading rates are numerous. Some of the more significant ones include temperature, and contaminant-specific diffusion and dispersion coefficients, hydraulic gradient and conductivity, viscosity (water and surficial sediment slurry), porosity and bulk density of sediments, thickness of active sediment layer and sediment cohesiveness, velocity of overlying water and boundary shear stress; state of water column stratification (thermal) and internal current structure; burrowing invertebrate population type, density, activity level; migration of biota and seasonal succession; chemical-specific characteristics, such as partitioning behavior, volatility, solubility; sediment particle fraction of organic carbon; concentrations of contaminants in water, pore water, and sediment particles; and, antecedent conditions.

Direct <u>atmospheric deposition</u> of contaminants consists of two spatially and temporally variable processes which are subject to significant uncertainty: dry and wet deposition (scavenging). Dry deposition fluxes consists of the air-to-water interfacial transport of contaminants bound to particulate matter, in the gas phase, or dissolved in water vapor. The physical processes that lead to dry deposition of particulate matter at the water surface are size
dependent and include aravitational settling for large particles (>5 Brownian motion for fine particles (<0.3 m), and m), interception/impaction for intermediate size particles. In addition to the transport rate dependence on particle size, the phase distribution of atmospheric contaminants also depends on particle size, and smaller particles normally contain higher amounts of contaminants per unit of weight or volume. Gas phase contaminants also may be deposited after transport to the water surface. Wet deposition of contaminants occurs as a result of the tendency of precipitation to cleanse the atmosphere by scavenging particulate matter and absorbing gases. Transport of wet deposition occurs largely by gravity, though the transport processes that permit scavenging and absorption processes are more diverse. The principal factors causing uncertainty in estimating atmospheric loads of contaminants include the meteorologic factors involved in atmospheric transport (i.e. wind speed and direction, temperature, precipitation kind and amount), attributes of the contaminants of interest (concentration gradients, partitioning behavior), and the receptor area.

# Data Collection

Of the non-point sources discussed above, the most important is probably atmospheric deposition. Fortunately, this source also has the best prospects for data collection improvements because of current research and monitoring programs on air toxics. Urban and rural non-point sources are less important because only direct sources need to be estimated; indirect sources are covered by tributary monitoring. At the scale of Lake Ontario, it is doubtful that new samples of urban and rural runoff will be taken, unless these sources are much larger than anticipated. The importance of groundwater on a lakewide basis is unclear. Sampling should occur in the most susceptable areas and a judgement made whether further sampling is warranted. In-place pollutants may not be considered as external forcing functions, depending on the model formulation. It is probably that the level of modeling used on Lake Ontario will include contaminated sediments.

# Data Handling Improvements

Once again, censored data are an issue for non-point sources, especially for atmospheric deposition monitoring. Load estimation methods will have to be worked out that allow use of partially censored data. Also, the estimation procedures for runoff and groundwater need to be researched thoroughly.

# Unresolved Issues and Conclusions

Due to the optimization of sampling resources that will undoubtedly occur, there will be some sources that are unmonitored or inadequately monitored. In the latter case, it may be that the desired sample size was not achieved, the required quality control was not practiced or a method involving extrapolation over a wide range was used. The decision that needs to be made is whether to use this information, and if it is to be used, how to incorporate it into the forcing functions and still minimize uncertainty.

In conclusion, there are several opportunities for reducing uncertainty in forcing function estimation. Many involve "up front" planning and analysis and require historical or typical data to use in this effort. Others involve using the best available methods for processing and analyzing data once it is collected.

It is recommended that the first-order uncertainty analysis discussed in this paper be conducted with the model formulation to be used in the actual mass-balance effort. Some type of optimization should then be done to reduce the target sources of uncertainty. This effort should use real data wherever possible. For data collection not subject to optimization, it is recommended that redundancy be built into the sampling effort. References

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Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study 103

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Overview

The general objective of this workshop is to investigate and discuss methods by which uncertainties in mass balance models for toxics in the Great Lakes may be reduced. As described by the workshop prospectus, this paper is focused on problems of reducing (and quantifying) uncertainty as they relate to "*in situ* field observations/system response measurements for the establishment of initial conditions, boundary conditions, calibration/confirmation data sets, and model post-audit data sets." I have taken this description to refer not only to the evaluation of uncertainty in the field observations themselves, but also to the uncertainty associated the analyses of *in situ* observations as they interact in the overall modeling process. Thus, I will be concerned here with quantification and reduction of uncertainty both (1) as they may be applied to descriptions of the system that is being modeled and (2) as they may be associated with model simulations.

The relationship between environmental models (of which mass balance models are a major subset) and field data is a particularly close one. Field data are needed at almost every stage of model development. *In situ* observations are often critical for identification and calibration of model parameters and are required for verification of model performance. The questions I address relate both to ways of estimating the uncertainty in representation of the field data themselves and to methods by which the uncertainty associated with model forecasts may be described. I show that opportunities for quantifying and reducing uncertainty occur both in the design of sampling programs for collecting field data, and in the process of identifying the model parameters that appear to be most critical for success of a model. A common feature of both

Great Lakes Monograph No. 4

applications is the use of prior data and Monte Carlo methods. I note that although these methods may involve intense computation, the computational requirements are not particularly excessive and are suitable for operational analysis. After a brief introductory discussion touching on my general goals and approach, I present the methods, describe some case studies, and explore some potential applications to a mass balance study of Lake Ontario.

Introduction

What do we mean by model "uncertainty?" In the context of this workshop we are concerned with models that are to be used for regulatory and management purposes. Quoting from the workshop prospectus, the models are intended "... to understand and predict exposure pathways ... to quantify load/concentration relationships ... to determine target load reductions." Therefore, in a qualitative sense, the uncertainty that concerns us refers to the difference between the estimated future value of some system property calculated by the numerical model and the "true" value of that property. If we are to make the results of environmental models valuable for management, we must determine whether the predictions obtained from the models are meaningful and useful (Beck 1987). One way to do this is to quantify the confidence we have in the model estimates, that is, to calculate some metric of the difference between what the model predicts and what actually occurs in nature (as best as we can estimate) and provide that metric to management along with the prediction. We should keep in mind that attempts to reduce the uncertainty associated with mass balance models will, to a certain extent, depend on the nature of the uncertainty metric being considered.

How an uncertainty metric is best calculated or expressed (or used, for that matter) is the subject of some debate (O'Neill and Gardner 1979; Scavia et al. 1981; Beck 1987; Haness et al. 1991) and will depend on the particular application. We should recognize from the outset that in all respects (both data and model) we are dealing with imperfect representations of the system of interest and, furthermore, that the system is invariably influenced by stochastic processes. Imperfect models (of different sorts) are used both to describe the field data and to produce the predictions. Because both types of models are necessarily imperfect idealizations and are, at least in structure, generally deterministic, Monte Carlo methods provide a convenient way of accounting both for the stochastic aspects of the system and for the unavoidable uncertainty in model parameter estimation, especially when the models are nonlinear. The Monte Carlo methods discussed below do not require any a priorl assumption about the statistical properties of the component errors and are offered as alternatives (complements) to more traditional methods of first-order error propagation and parametric statistics.

I have structured this paper as follows. I first discuss the use of Monte Carlo methods to quantify the uncertainty associated with field measurements of limnological variables. The variables I consider

107

here are those measured in units of mass concentrations in water. This is typical of many of the state variables incorporated in mass balance models of toxics. Although the nature of the appropriate field measurement will depend on the model structure, in most cases it will be necessary to estimate the total mass of a contaminant within some spatial segment of the system being modeled. The Monte Carlo approach is intended for the situation in which the methods of classical parametric statistics are not applicable. This is usually the case in limnological studies, where samples are seldom true replicates (Hurlebert 1984) and are often correlated in space and/or time (Reckhow and Chapra 1983). Under these circumstances, a traditional parametric model (e.g., an analysis of variance model) may be inappropriate. Originally used to evaluate the size of candidate sampling networks for the Green Bay Mass Balance Study (Lesht 1988b), recent experiments (Lesht 1991a) suggest that it may be possible to extend the method to design (or at least determine the key features of) optimized sampling networks of different sizes. This extension would be useful for estimating the relative advantage of reducing the sampling uncertainty by increasing the number of samples collected in terms of the added costs of sampling and analysis. [See Lesht (1991b) for a similar application to tributaries.]

In the second part of the discussion I describe the use of regionalized sensitivity analysis (Spear and Hornberger 1980; Fedra et al. 1981; Hornberger and Spear 1981) to identify a set of model parameters and initial conditions that produce simulations agreeing in some objective sense with a set of criteria determined from field observations. The regionalized sensitivity analysis method has been used to determine which model parameters in a simple Great Lakes total phosphorus model were most critical for producing an acceptable simulation (Lesht et al. 1991). When an acceptable set of parameter vectors is identified, it is a simple matter to use the vectors (again in Monte Carlo mode) to estimate the uncertainty of future model projections (expressed as a probability distribution, if desired) in combination with explicit consideration of the uncertainty associated with loadings and other forcing variables. This type of information may also be used within the context of management decisions, by making it possible to assess the uncertainty associated with particular control actions (Fontaine and Lesht 1987). Finally, I suggest that these approaches be used for future studies in Lake Ontario.

Uncertainty Associated with Limnological Sampling Networks

The first and most obvious reason for investigating the uncertainty associated with limnological sampling networks is to provide some assessment of the confidence with which we report a descriptive statistic (e.g., mean concentration) determined by the sampling. This assessment will be required if the descriptive statistic is to be used for model calibration and verification. The second reason is to determine, if possible, the functional relationship between the uncertainty associated with descriptive estimates and the properties of the sampling scheme (*l.e.*, the number of sampling locations). Such a relationship is useful for the initial design of a sampling program and is necessary if we want to evaluate proposed changes in the sampling program in terms of the expected changes in the

#### estimated uncertainty.

Background

The types of models that we are considering here can best be evaluated in terms of the correspondence of the model predictions (output) to some measures of the modeled system (field data). For mass balance models, one type of appropriate comparison is with an estimate of the total state variable mass, estimated by multiplying the average variable concentration by the system volume. Because the average in situ concentration usually is estimated from discrete samples collected during limnological surveys, it is important to be able to quantify the uncertainty associated with estimates made from point measurements. If the sampled variable is spatially homogeneous, then this uncertainty may easily be determined by using the results of parametric statistics. The expected uncertainty then may be reduced a known amount by increasing the number of samples. The problem is more difficult, however, when we are sampling variables that may not be spatially homogeneous (i.e., their expected value depends on location), as is usually the case for limnological variables. Under this circumstance, the simple sample average may be biased by the relationship between the sample locations and the underlying spatial distribution of the variable, which is, necessarily, unknown.

One way to compensate for spatial heterogeneity is to conduct a form of stratified sampling in which the estimation of simple statistics is restricted to data collected in regions of the lake that are thought, usually on the basis of an analysis of historical data (*e.g.*, Kwiatkowski 1978; Kwiatkowski 1980), to be homogeneous. In terms of modeling, however, this procedure requires separate calculation of the state variables within each region and additional modeling or specification of region-specific forcing functions as well as any inter-regional transport and exchange. Furthermore, the assumption of homogeneity may be difficult to verify after the sampling is conducted. An alternative approach is to use a spatial interpolation model to estimate the value of the variable in each cell of a gridded representation of the lake or segment. The estimates may then be summed to produce an estimate of the overall mean value. When the estimates are weighted by the relative volumes of the cells in the grid the resulting value is often referred to as a volume-weighted mean.

To calculate the uncertainty associated with the simple mean of a homogeneous process is a simple matter, but in most cases no simple measure of the uncertainty is associated with the volume-weighted mean. The volume-weighted mean is obviously a function of the interpolated estimates, which, in turn, depend on the original sample data. If the configuration of a sampling network is changed, the spatial interpolation and hence the volume-weighted mean will change. The magnitude of the change will depend on the relationship between the modified sampling network and the spatial structure of the sampled variable. Our problem then is to find a way of expressing the uncertainty in the estimated

volume-weighted mean as a function of the properties (e.g., size) of the sampling network.

Calculation of a Volume-Weighted Mean The key to calculation of a volume-weighted mean is the horizontal spatial interpolation of the sampled data. This interpolation is usually expressed as

$$z^{\bullet}(x_{o}) = \sum_{j=1}^{N} w_{o,j} z_{j} , \qquad (1)$$

in which  $z^*$  is the estimated value at unsampled location  $x_0$ , the  $z_j$  values are the sampled data (j = 1, 2, ..., N), and the  $w_{0,j}$  values are weights appropriate for the positions  $x_0$  and  $x_j$ . Many methods are available for calculating the interpolation weights  $w_{0,j}$ . In one simple case, that embodied in VWA, the computer code developed by the U.S. Environmental Protection Agency's Large Lakes Research Station (Yui 1978), the weights are functions of the distance between the two locations. Specifically,

$$w_{o,j} = D_{o,j}^{-\alpha} / \sum_{i=1}^{N} D_{o,i}^{-\alpha} , \qquad (2)$$

where  $D_{i,j}$  is the Euclidean distance between points *i* and *j*, and is a parameter that controls the amount of influence of distant observations on the estimated value at a point. A lower value of a indicates a stronger influence of distant observations. In practice, the selection of a value for a will depend on many factors and may be done empirically. One appropriate selection method is cross-validation, in which the value of a is optimized to minimize the difference between the data values at the observed points and the estimates interpolated at those same points from the other observations. Analysis of the overall cross-validation error as a function of a may be used to estimate the spatial heterogeneity of the sampled data (Lesht 1988a) and can serve as a screening tool prior to the application of spatial analysis.

The volume-weighted mean is calculated by weighting the cell estimates by the cell volume and summing over the total number of cells. This summation may be written

$$Z = \sum_{i=1}^{Q} v_i z_i^* \quad , \tag{3}$$

where Z is the volume-weighted mean value,  $z_i$  is the estimated value in cell *i*, and Q is the number of cells in the region of integration. The weight,  $v_i$ , is the ratio of the cell volume to the total region volume.

Estimating the Uncertainty as a Function of Network Size

# Case Study -- Green Bay Whole-Bay Model

Of course, uncertainty is associated with the spatial interpolation model, and if we choose to use a volume-weighted mean to represent some property of the lake, we are faced with the problem of quantifying that uncertainty. One way to do this is to examine the differences in volume-weighted means that result from spatial interpolations made by using different sets of sample data. The basic idea is that the uncertainty associated with sampling a spatially inhomogeneous variable may be estimated empirically by repeated, extensive, random resampling of a reference data set. If the reference data set is comprehensive (that is, if it adequately resolves the major scales of spatial variation), the method will provide a good estimate of the uncertainty associated with using networks of fewer stations. The degree to which the reference network resolves the major scales of spatial variation may be determined as part of this analysis in conjunction with the screening analysis described above. An initial data set is required for the purposes of exploration or design, but the analysis may be used with data of current interest to evaluate smaller networks and to estimate an upper bound on the uncertainty of the full network.

The Green Bay Mass Balance Study was intended to be the prototype of mass balance studies in the Great Lakes. Early in the project the planners asked the question "How many stations do we need to sample to be reasonably sure that we can estimate the total mass of a contaminant in Green Bay with a specified accuracy?" The question was asked for two reasons. First, because the data were to be used for calibration and verification of models, it was important to provide some estimate of the uncertainty associated with the field data. Second, given the costs of sampling and chemical analysis, there was some desire to optimize the sampling. The optimization decision required some estimate of the trade off between the number of sampling stations occupied and the estimated uncertainty in the mean concentrations.

I approached this problem empirically by using the Monte Carlo method outlined above. Beginning with a reference data set (Conley 1983) consisting of turbidity data (used as a surrogate for suspended particle concentration) collected at 31 stations during 5 cruises, I repeatedly subsampled the data and then calculated the volume-weighted mean turbidity from the (randomly selected) test networks. Approximately 14,000 different networks of varying sizes were tested. Figure 1 shows how the distribution of volume-weighted average turbidity estimates depended on the number of stations used in the spatial interpolation. I was able to estimate the probability of obtaining a volume-weighted mean

value that was within a fixed percentage of the "true" value (defined by the full network) as a function of the number of sample locations by successively applying the resampling procedure to test networks ranging in size from 1 station to 31 stations (Fig. 2). The curves shown in Fig. 2 provided the Green Bay Mass Balance Study planners with a way to evaluate the benefits of reducing the uncertainty associated with incomplete sampling of a spatially distributed variable in terms of the cost required for additional sample locations.

# Problems and Limitations

The Green Bay Mass Balance Study was concerned with a number of toxic contaminants, especially polychlorinated biphenyls (PCBs). Unfortunately, no prior sampling for these contaminants had been conducted with sufficient detail to provide a useful reference data set. The most complete previous sampling of Green Bay available to us was Conley's (1983) work. Because the substances of interest are strongly associated with particles, I used a variable (turbidity) that is related to suspended material as a surrogate for the nonexistent measurements of toxics. Although I expect that the major features of the analysis would be similar, it is not at all certain that the results shown in Fig. 2 would be the same for another variable.

The uncertainty treated in this example is that due solely to the incomplete sampling of a spatially distributed variable. It is implicitly assumed that the sample values themselves are exact. Turbidity can be measured with fairly high accuracy, and the sample values used in the case described above for Green Bay were actually water column averages. The averaging tended to reduce the effects of other sources of error, such as that associated with collection and chemical analyses. Simulation studies of spatial sampling in the presence of uncorrelated noise show that, as may be expected, adding noise is equivalent to reducing the number of stations in the sampling network (Lesht 1988a). The effect varies with the signal-to-noise ratio, but fairly dense sampling networks (1 station per 200 km<sup>2</sup>) seem to be able to resolve spatial signals if they are at least four times the level of the noise. It may be possible to use cross-validation to estimate the signal-to-noise ratio, but this idea has not been tested. Although the smoothing inherent in spatial interpolation tends to reduce the effects of random fluctuations in the data, the uncertainty estimates obtained probably are somewhat low when analytical noise is present (but not large enough to overwhelm the spatial signal).

Without replicate sampling, it is impossible to estimate the uncertainty associated with the reference network. This is a consequence of the classic sampling problem. All of the information we have about the system comes from the reference network. If the reference network is large enough to be itself divided (to produce "replicate" reference networks), empirical estimates of the uncertainty associated with smaller "reference" networks can be made. Because this was not possible in Green Bay, the estimated uncertainty must be considered relative to that inherent in the original

#### sampling.

One attraction of the inverse distance-weighting spatial interpolation algorithm used in VWA is that it is very easy to incorporate into Monte Carlo codes. Other, perhaps more sophisticated spatial interpolators (e.g., Kriging), that could be used instead would be much less efficient computationally. Although it is generally agreed that Kriging is more accurate than other spatial interpolation methods, to my knowledge, Kriging has not been used in production volume-weighting codes. In cases where the sampling locations are fairly evenly distributed (unclustered), the advantage of Kriging over inverse distance methods is very slight.

This method of spatial analysis is not applicable to all types of variables that might be used in a mass balance model for toxics (e.g., contaminant concentrations in fish). Uncertainties in variables that cannot be expected to have spatial structure but are still sampled must be estimated by other techniques.

# Extension – Determining the Properties of Optimal Sampling Networks

The analysis described above was aimed at determining the relationship between the uncertainty of an estimate and the size of a randomly configured sampling network. Selecting the stations carefully would probably reduce the uncertainty associated with a network of a particular size. Because a very large number of "candidate" networks could be selected from a reference network. however, the way to do this objectively is not immediately clear. In the case of Green Bay, I explored several possible methods of selecting efficient subsets of the original reference network. I found that two statistical approaches (successive elimination of the stations with the highest average spatial covariance and successive elimination of the stations closest to the center of a cluster formed in a five-dimensional space based on the turbidity values for each cruise) were generally unsatisfactory. Experiments with an empirical quantification of the relative success of each station during the Monte Carlo runs were more successful and led to identification of a 22-station network that would have a greater than 80% chance of producing a whole-bay estimate within 10% of the "true" value. Tests with data from cruises not included in the Monte Carlo runs confirmed that the 22-station network met the specified uncertainty criterion for all cruises.

In more recent work (Lesht 1991a) I have experimented with using the combinatorial optimization method of simulated annealing (Kirkpatrick et al. 1983) to try to determine the general features of an "optimal" sampling network. The basic idea is that the uncertainty associated with field measurements of a spatially distributed variable can be reduced by using a sampling network configured to minimize the errors associated with the spatial interpolation. If the features (e.g., station density, non-isotropy) of optimal networks can be identified and generalized, then these features could be incorporated into the design of new sampling networks that should

provide estimates with reduced (relative to randomly configured networks) uncertainty. My preliminary results indicate that the approach is feasible and that the simulated annealing algorithm efficiently finds a "near-optimal" network configuration.

Regionalized Sensitivity Analysis of Mass Balance Models

According to O'Neili and Gardner (1979), the three major sources of uncertainty in environmental models are (1) the uncertainty associated with the model structure (i.e., that uncertainty resulting from attempting to describe a complicated system with a limited model), (2) the uncertainty associated with assigning values to model parameters (whether the parameter values are determined by laboratory or field experiment or by "tuning" the output of the model to match field observations), and (3) the uncertainty associated with natural variability in the system's forcing variables (e.g., meteorological or loading variability). The first source of uncertainty, which refers to the structural uncertainty of the model, is perhaps the most serious (in terms of the difficulty of evaluating it and its effects on long-term predictions) and can perhaps be addressed only by considering a wide suite of alternative models. Given alternative models, however, each will be affected by the other two sources of uncertainty. We may ask how we can use our knowledge of the uncertainty associated with in situ observations to help estimate and reduce the uncertainty associated with model predictions. In this section, I describe a method that uses in situ descriptions to quantify the combined prediction uncertainty due to imprecise parameter definition and stochastic forcing. The method also ranks the parameters that are most important in terms of producing successful simulations so that efforts can be directed toward reducing their uncertainty.

# Background

In many environmental models, final parameter values are determined by "tuning" the model output to a set of field data. This method produces a single parameter set that is then used for model simulations. The parameters themselves are widely recognized to be uncertain, and the effect of this uncertainty on model predictions is often estimated by direct sensitivity or differential methods. These methods (e.g., first-order sensitivity analysis) may be inaccurate or difficult to apply, especially when the models are nonlinear or the parameter uncertainties are large.

Only recently (Dilloro and Parkerton, personal communication) have methods been developed that incorporate some estimate of the uncertainty in the field observations into the differential method of estimating the uncertainty of the prediction. Limnological data are generally sparse, however, and it is often difficult to apply strict statistical criteria to either calibration or validation. As an alternative, it is instructive to use Monte Carlo methods to identify a set of "acceptable" parameter vectors rather than attempting to determine a single "best" parameter vector by using some optimization technique. This set of parameter vectors, when used to simulate some test data set, produces an "acceptable" simulation as defined by some objective set of criteria. In terms of forecasts, when an acceptable set of parameter vectors has been determined, each member of that set is considered to produce an equally valid forecast in terms of the uncertainty associated with the data used to define the acceptance criteria. This approach, known as regionalized sensitivity analysis (RSA), was first used by Spear and Hornberger (1980) and has been described in some detail by Fedra et al. (1981), by Hornberger and Spear (1981), and by Hornberger and Cosby (1985). Recently, Lesht et al. (1991) used this method to examine a simple mass balance model of phosphorus in the Great Lakes.

#### Method

Assume that a time-dependent environmental model may be represented by the set of differential equations

# $dx(t)/dt = f\{x, u, x_0; t\}(4)$

where x(t) is a vector of state variables; u is a vector of forcing variables; is a vector of (say) n model parameters, here assumed constant with time;  $x_0$  is a vector of initial conditions; and t is time. In this notation, the structure of the model is embodied in the (possibly nonlinear) vector function f. Given a set of forcing variables and initial conditions, the function *I* is a mapping from the domain of all possible parameter vectors () to a range of all possible state variable solutions (x). We may define an additional set of vector functions g that relate the state variables (x) to some set of (say) m environmental measurements (y), (e.g., in situ field observations). The functions g may include simple direct mappings of the state variables, or they may be more complicated functions of the state variables. The in situ field observations are clearly necessary for evaluating the model performance; we must have some idea of how the natural system is behaving before we can determine whether the model produces a reasonable representation of the system.

In RSA we use in situ observations (perhaps in combination with other information) to define a set of criteria that describes the behavior of the modeled system. We then use Monte Carlo methods to randomly choose parameters values (and possibly initial conditions) from some feasible domain () and use those parameters to produce model predictions (x mapped via functions g to y). If the model predictions satisfy the criteria defining the system behavior, then the randomly selected parameter vector is classified as acceptable. Parameter vectors resulting in simulations that do not satisfy the behavior criteria are classified as unacceptable. If the problem is fairly well constrained in terms of the behavior criteria, the acceptable and unacceptable parameter vectors will separate in regions of parameter space. Once determined, the set of acceptable parameter vectors may then be used (perhaps in conjunction with stochastic forcing variables) to generate a population of future behaviors. The uncertainty of the model

predictions is described by the statistical distribution of the future behaviors. Furthermore, and perhaps of more immediate interest, comparison of the statistical distributions of the acceptable and unacceptable parameter vectors makes it possible to identify the elements of the parameter vector (that is the individual parameters) that are most important for producing acceptable simulations. If effort (e.g., additional field work or experimentation) is to be expended in reducing the uncertainty associated with any parameter, RSA provides a way to prioritize those expenditures. Finally, Hornberger and Spear (1981) propose that the method could be used to examine management alternatives as well.

# Case Study - Great Lakes Total Phosphorus Model

Although our work was exploratory, we had two goals in mind when we (Lesht et al. 1991) applied RSA to a simple model (Chapra 1977) of Great Lakes total phosphorus. We were interested in (1) using the model to check the internal consistency of over a decade of phosphorus loading estimates and *in situ* observations of total phosphorus concentrations and (2) identifying the model parameters that were most important for producing an acceptable simulation. Our motivation for answering the first question was to see if the RSA method could be used to determine the levels of uncertainty that could be tolerated in the loading estimates for a given level of uncertainty in the field observations and model parameters. The second question was motivated by our curiosity about which parameters had the greatest effect on the simulations and could benefit most from further study.

Our application of RSA was relatively straightforward. We defined the system behavior in terms of the annual average total phosphorus concentration measured in each of the major basins of the Great Lakes from 1980 to 1986. Eleven basins were modeled, but, because of limited field observations, only seven basins were used in the analysis. The acceptance criteria we used were based on an arbitrary "confidence interval" around the observed mean values. We added a stochastic element to the acceptance criteria by accepting a simulation if it was within the confidence intervals 80% of the time (I.e., if the simulation matched 35 of the 43 observations defining the behavior of the system). The model was run to simulate the period 1974 to 1986 by using phosphorus loading estimates made by the International Joint Commission as the forcing variable. Parameter values and initial conditions were selected randomly from rectangular distributions centered on the calibration values presented by Chapra and Sonzogni (1979). Two thousand model runs were made; these were split almost evenly between acceptable (1019) and unacceptable (981) simulations.

Examination of the cumulative frequency distribution functions of the parameters in the two sets of simulations (e.g., Fig. 3) showed that 9 of the 40 model parameters were important (as determined by the Kolmogorov-Smirnov statistic) for producing an acceptable

simulation. Of these 9, 6 parameters represented the apparent loss of phosphorus from the water column to the sediments, 2 were the advective flows into and out of the western basin of Lake Erie, and the last was the initial condition assumed for Lake Superior. Interestingly, one of the observations we used to define the system behavior (total phosphorus concentration in western Lake Erie 1982) was missed by all 2,000 simulations. We interpreted this to be a datum that was not representative of the annual average conditions we intended to simulate with the model. It also could be interpreted as an example of structural inadequacy of the model. The high concentrations observed in 1982 probably were related to the unusual frequency of spring storms that resuspended much of the total phosphorus contained in the sediments of the shallow western basin. The model, based on constant parameters, was unable to simulate this "anomalous" condition.

We have not yet used our results to examine the relationship between uncertainty in loading estimates and the field observations. The basic idea would be to assign different levels of uncertainty to the loading estimates and use the set of acceptable parameter vectors to simulate a population of predictions that could be compared with the field data. By definition, the acceptable parameter vectors will all satisfy the behavior criteria when the model is forced with the original loading estimates. The purpose of the exercise would be to determine how much we could perturb the loading estimates before some percentage of the previously acceptable simulations became unacceptable. This would be yet another way to assess the relative value of attempting to further reduce different sources of uncertainty. Similarly, if independent estimates of the loading uncertainty were available, it would be possible to couple them with stochastic simulations made by using the acceptable parameter vectors to estimate a target accuracy for the field observations.

# Problems and Limitations

One attraction of RSA is that it allows us to develop a set of parameter vectors that result in acceptable simulations. The utility of producing such a parameter set obviously depends on the discriminating power of the behavior-defining classification scheme. In the case of the Great Lakes total phosphorus model, acceptable simulations were based on only one basic description of the system, the confidence limits of the observed annual average total phosphorus concentrations. This description seemed to provide adequate discriminating power (because half of the simulations were rejected as unacceptable) and was suited to the model, but more complicated models will require much more elaborate descriptions of the system.

We assumed that the loading estimates forcing the model were exact. Although it is possible to accommodate stochastic loading functions, the effect of the accommodations on the identification of critical parameters is not clear. For a given set of behavior defining criteria, the number of acceptable simulations would probably be reduced and more model runs would be required to produce a sufficient simulations for parameter discrimination.

Our analysis showed that important information about parameter differences can be determined from a univariate analysis of the parameter distributions. More complicated models would be expected to have multivariate relationships among parameters. These relationships may not be evident from the univariate analysis alone. The existing methods for determining these relationships are somewhat cumbersome. Thus, simulating the multivariate relationships for future projections may be problematic.

Possible Applications of Monte Carlo Methods in Reducing the Uncertainty of Mass Balance Models of Toxics in Lake Ontario

The basic theme of this paper is that much can be learned from information that has already been collected; indeed, this information is critical for designing any new sampling program. Lake Ontario is unique among the Great Lakes in the amount of sampling that has been done and should provide a very rich data set for the modeling initiative. Not only will these data be useful for quantifying the uncertainty associated with analyses of field data, but they also will be useful for assessing the uncertainty associated with all phases of the modeling process. In terms of specific applications to Lake Ontario, I suggest the following applications:

- Conduct a spatial analysis of survey data to assess the relative importance of the uncertainty associated with spatial heterogeneity. Several different variables should be analyzed, including whatever data are available for toxics. If spatial heterogeneity is found to be important, then use Monte Carlo methods to determine the expected uncertainty associated with sampling networks of different sizes. If new sampling is required, use Monte Carlo methods to optimize the network design. Examine alternative ways of expressing descriptions of the system to be modeled (e.g., volume-weighted means, frequency distributions).
- Perform regionalized sensitivity analysis on candidate models. Use alternative definitions of the system's behavior to check the sensitivity of the identification of critical parameters. Determine the appropriate prediction limits (*l.e.*, time scales for each model) and conduct RSA on an ensemble of independent data sets by using the candidate

models or derivatives. Compare identification of critical parameters as a check on the stability of the uncertainty in model structure. If additional sampling is contemplated, use the RSA results to identify the parameters that are significant for understanding the modeled system and design the sampling program to limit the values of the variables that are critical for identification of the significant parameters (*l.e.*, define tighter constraints).

# Unresolved Issues and Questions for the Workshop

The following unresolved issues and questions should be addressed by the workshop:

- In my opinion, the most important unresolved issue involving model uncertainty is a very general one. Despite recent attention, methods of estimating model uncertainty are still rather poorly developed. Especially in the case of complex environmental models, we should be very careful that having the ability to provide some metric of uncertainty with our models, does not tempt us to believe that these metrics allow us to quantify the likely difference between the model predictions and what will actually occur in nature. The potential danger involved with specifying a quantitative measure of uncertainty is that those who make management decisions may act on them as if they are fact. We must find a way to make it clear what the uncertainty estimates really mean in the context of using the models for regulatory purposes.
- The previous comment notwithstanding, I think that it also is important to consider how we express uncertainty in our model predictions. The metric(s) we provide should be related to the anticipated use(s) of the model. In the regulatory environment this consideration puts the burden on the modeler to understand how the model is expected to be used.
- Methods must be explored to deal with structural uncertainty. We can all cite many examples of models, developed under one set of assumptions, that failed miserably when unmodeled processes affected the modeled systems. In many cases our uncertainty analysis will implicitly include structural inadequacy with the uncertainty in parameter values.
- We must carefully consider the relationship between the state variables of the model and the measured characteristics of the system. How well do we understand

the functional mapping between the model state variables and our field observations? Comparing the model results to field observations is of little use if the two represent different things.

Summary and Concluding Thoughts I have discussed two sources of uncertainty in this paper. The first is the uncertainty resulting from incomplete sampling of a spatially heterogeneous variable. With the procedure used in the Green Bay Mass Balance Study, this uncertainty can be quantified and its dependence on the size of the sampling network can be determined. Given a description of the uncertainty associated with field observations, the spatial uncertainty can be reduced by objectively designing any future sampling network.

The second source of uncertainty I considered is that inherent in modeling a stochastic system. The model structure, the model parameter values, and the input forcing functions all are uncertain. The combined effects of these uncertainties, however, can be assessed in relationship to the uncertainty associated with the field observations. Efforts to reduce uncertainty can be prioritized by using Monte Carlo methods to assess the relative value (in terms of the model predictions) of reducing particular sources.

In his review of uncertainty in water quality models, Beck (1987) said, "The way in which a model is derived from, or evaluated by reference to the *in situ* field data must clearly influence both its ability to predict future behavior and the confidence to be attached to that prediction." It is must be understood that, because our view of nature is limited, the "true" behavior of the system can never be determined exactly. Our goal then must be to provide some objective evaluation of our ability to represent that behavior. Because it explicitly includes the stochastic nature of the system, Monte Carlo analyses are attractive ways of providing the required evaluation.

# Acknowlegments

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Fig. 3. Comparison of cumulative distribution functions of the normalized (mean equal to zero and variance equal to one) model parameter representing the apparent settling velocity in central Lake Erie, for acceptable simulations (solid line) and unacceptable simulations (dotted line).



Fig. 2. Percent of estimates falling within specified ranges of the "true" value as a function of network size for data from Conley's (1983) Cruise 3.



Fig. 1. Histograms of volume-weighted average turbidity estimates made by using data from Conley's (1983) Cruise 3 for three network sizes. The total number of estimates in each histogram is 500. The solid vertical lines show the "true" value obtained from the full network.

Great Lakes Monograph No. 4

 $\overline{122}$ 

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Great Lakes Monograph No. 4

124

Model and Projection Uncertainty: Methodology Development and Interpretation

A White Paper Prepared for the Workshop: Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes: Lake Ontario Case Study.

by

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# I. Introduction

The subject of this workshop is: Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes: Lake Ontario Case Study. In this white paper we present a methodology for estimating the uncertainty to be associated with (1) the calibration data and (2) the model. The model uncertainty is used to establish the uncertainty of (3) the model parameters and (4) the model projections. This methodology is intended to answer the questions: "How good is the model?", and "How good are the projections?"

The methodology is based on an analysis of the residuals: the difference between the observed concentrations and model calculations. The initial problem is to apportion the uncertainty between data uncertainty - which are due to differences between the true data mean and the sample mean used in the calibration - and other sources of variations, which we call model uncertainty or model error. Once this is done, the parameter uncertainty is estimated by requiring that all the model uncertainty be accounted for by parameter uncertainty. We compare this result to the result obtained from applying the Maximum Likelihood method of estimation. Finally, the uncertainty of the parameters can be used to assess the uncertainty of the model projections using, for example, Monte Carlo methods, or from the first order analysis presented below.

#### **II. Framework - The Classical Case**

It is important to realize that classical model uncertainty analysis is based on a probabilistic model that makes certain explicit assumptions. Consider a simple linear model of concentrations versus time:

$$c(t_i) = f(\bar{\Theta}, t_i) + \epsilon_i$$
$$= \theta_1 + \theta_2 t_i + \epsilon_i \qquad ($$

where:

#### $c_1 = Observed concentration at t_i$

1)

 $f(\vec{\theta}, t_i) =$ Model concentration at  $t_i$ 

 $\vec{\theta} = \text{Model parameter vector: } \vec{\theta} = \begin{bmatrix} \theta_1 \\ \theta_2 \end{bmatrix}$ 

 $\epsilon_i = \text{Random fluctuations about the true mean}$ 

It is explicitly assumed that the model:  $f(\bar{\theta}, t_i) = \theta_1 + \theta_2 t_i$  represents the *true* mean of the random process and that  $\epsilon_i$  represents random fluctuations about the mean. These random fluctuations are assumed to be due to phenomena that are not included in the model. The only problem is to estimate the parameters of the model,  $\theta_1$  and  $\theta_2$ , and their uncertainties.

The random fluctuations,  $\epsilon_i$ , are thought of as real, and since they are not captured by the model, they are referred to as model error. However, this nomenclature should not be taken to mean that the model is actually in error since it is assumed that the model represents the true mean of the random process. It is simply that the model in incomplete; it cannot compute the fluctuations,  $\epsilon_i$ . To this extent only are the fluctuations are considered to be model errors.

For these linear models, a full statistical theory of estimation and uncertainty exists [Liebelt, 1967, Searle, 1971]. The statistical theory is known as (multiple) linear regression. The assumptions of regression analysis are:

- 1) t, is known exactly.
- 2)  $\epsilon_r = N(0, \sigma_e^2)$ . That is, the random variations are normally distributed with unknown variance  $\sigma_e^2$ .
- 3) The model is correct. The underlying relationship between  $c(t_i)$  and  $t_i$  is exactly a straight line.

It is interesting to note that even for this simple model, the assumptions are somewhat restrictive. There are many cases for which  $t_i$  are quantities that are measured with less precision than time and, therefore, are not known exactly. Also the structure of the random component of the model may be more complicated - for example the variance may depend on  $t_i$ .

But the most restrictive of the assumptions is that the model is *exactly* a straight line. Of course, if it were known that the model was deficient in some way, i.e. not a straight line but somewhat curved, then presumably that would have been included in the model in the first place. Hence, although the assumption that the model is a true representation of the mean seems an unrealistic assumption, it appears to be inescapable since, presumably, every effort has been made to make the model as realistic as possible.

For a straight line model, the following are available:

1) Optimal estimates,  $\hat{\theta}_1$ ,  $\hat{\theta}_1$  and  $\hat{\sigma}_{\epsilon}^2$  are available for the parameters:  $\theta_1$ ,  $\theta_2$  and  $\sigma_{\epsilon}^2$ .

2) Parameter uncertainty covariance,  $\Sigma_{\theta}$  for  $\hat{\theta}_1$ ,  $\hat{\theta}_2$  where:

 $\Sigma_{\bullet} = E\left\langle \begin{bmatrix} (\hat{\theta}_1 - \theta_1)^2 & (\hat{\theta}_1 - \theta_1)(\hat{\theta}_2 - \theta_2) \\ (\hat{\theta}_2 - \theta_2)(\hat{\theta}_1 - \theta_1) & (\hat{\theta}_2 - \theta_2)^2 \end{bmatrix} \right\rangle$ 

E () denotes the expectation, i.e. the probabilistic average of the quantity in brackets.

3)

Confidence limits for projections:  $c_{5x}$ ,  $\overline{c}$ ,  $c_{95x}$ 

Our objective is to find an analogous methodology that is applicable and workable for mass balance models.

# III. Methodology

Mass balance models compute concentrations of various constituents in various model segments at various times. Consider the vector of concentrations of these constituents, ordered by type and model segment. As a concrete example, consider a simple model of Lake Ontario with a water column (w) and a sediment (s) layer. The dissolved (d) and particulate (p) concentrations of two PCB homologs (#1) and (#2) are being considered together in the model. Then, the concentration vector can be defined as:

$$\vec{c}(t_i) = \begin{bmatrix} c(t_i)_{1,d,w} \\ c(t_i)_{1,p,w} \\ c(t_i)_{1,d,s} \\ c(t_i)_{1,d,s} \\ c(t_i)_{2,d,w} \\ c(t_i)_{2,p,w} \\ c(t_i)_{2,d,s} \\ c(t_i)_{2,p,s} \end{bmatrix}$$

(2)

where homolog number, dissolved or particulate, water column or sediment are denoted by the subscripts. In general, let:

 $\overline{c}_i = \overline{c}(t_i) = \text{Observed mean concentration vector at } t_i$ 

 $\vec{f}(\vec{\theta}, t_i) =$ Model concentration vector at  $t_i$ 

# $\vec{\Theta}$ = Model parameter vector

The relationship between the observed mean concentrations and the model results is:

$$\vec{c}_i = \vec{f}(\vec{\theta}, t_i) + \vec{\epsilon}_i \tag{3}$$

where  $\bar{\epsilon}_i$  are the residuals: the differences between the observed mean concentrations and model computations.

The residual errors are assumed to arise from two distinct sources. The first source arises because the observed mean concentrations are not the true means since they are based on a finite number of measured concentrations. The second source are random fluctuation that are associated with all the phenomena that are not explicitly included in the model. This second source is termed the random model error. Thus:

$$\vec{\epsilon}_i = \vec{\xi}_i + \vec{\zeta}_i \tag{4}$$

where:

 $\overline{\xi}_i$  = uncertainty of the mean concentration

 $\vec{\xi}_i$  = random model error

Therefore the statistical model that includes these two sources of fluctuations is:

$$\vec{c}_i = \vec{f}(\vec{\theta}, t_i) + \vec{\xi}_i + \vec{\xi}_i \tag{5}$$

It is used in the uncertainty analysis below.

#### A. Parameter Estimation - Maximum Likelihood

A complete statistical methodology would include methods for computing the optimal estimates of the parameters,  $\overline{\theta}$ , such that some criteria that measures goodness of fit is minimized. Such a formulation is available within the context of maximum likelihood estimation [Schweppe, 1973; Sorenson, 1980]. If we ignore for the moment the distinction between data uncertainty and model error, then the relevant equation is:

$$\vec{c}_i = \vec{f}(\vec{\theta}, t_i) + \vec{\epsilon}_i \tag{6}$$

If we assume that:

$$\vec{\epsilon}_i = N(0, \Sigma_{\epsilon}) \tag{7}$$

that is, that the random fluctuations are normally distributed with zero mean and unknown covariance,  $\Sigma_{s}$ , then it turns out that a full theory is available. The optimal estimate for the residual covariance matrix is:

$$\Sigma_{\epsilon} = \frac{1}{N} \sum_{i=1}^{N} \vec{\epsilon}_{i} \vec{\epsilon}_{i}^{\mathsf{T}} = \frac{1}{N} \sum_{i=1}^{N} (\vec{c}_{i} - \vec{f}(\vec{\theta}, t_{i})) (\vec{c}_{i} - \vec{f}(\vec{\theta}, t_{i}))^{\mathsf{T}}$$
(8)

which is simply the average of the residual variances and covariances. The optimal parameter estimate,  $\hat{\theta}$ , is found from the condition:

$$\hat{\theta} = \min |\Sigma_{\epsilon}| \tag{9}$$

where  $\Sigma_{\epsilon}$  is the covariance of the residuals, given by eq.(8), and  $|\Sigma_{\epsilon}|$  is the determinant of  $\Sigma_{\epsilon}$ . In order to compute these maximum likelihood estimates it is necessary to find the parameter vector that minimizes the determinant of the residual covariance matrix. Note that the method automatically accounts for the proper weighting to be given to each of the concentrations in the vector,  $\overline{c}$ . This result is quite interesting and, for certain problems, it may well be a feasible method for generating optimal parameter estimates.

The parameter uncertainty covariance is also known for N large:

$$\Sigma_{\theta} = \left(\sum_{i=1}^{N} \mathbf{J}_{i}^{\mathsf{T}} \Sigma_{\epsilon}^{-1} \mathbf{J}_{i}\right)^{-1} \qquad N \to \infty$$
(10)

where:

$$\mathbf{J}_{i} = \frac{\partial \vec{f}(\vec{\theta}, t_{i})}{\partial \vec{\theta}} \tag{11}$$

the Jacobian of the model solution. Note that computing the Jacobian of the solution requires only that the model be run an additional time for each parameter in  $\overline{\Theta}$ . The Jacobian can be computed by a simple difference approximation to eq.(11).

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

131

In fact, we had proposed to use this parameter uncertainty covariance for any calibrated model even if the parameter estimates were not computed using the maximum likelihood equations given above, although no justification was given for this suggestion other than it appeared to be an expedient choice since it was a known solution [Di Toro and van Straten 1979; van Straten, 1983].

There are arguments to be made for not using optimal estimation methods. Calibration is not just minimizing residual errors. It is necessary to balance the goodness of fit with other more subjective criteria, for example, the physically realistic range of the parameters, other independent estimates of the parameters, and the degree to which these parameters values are judged to be reliable. In practise, it has been found that unless the problem is well constrained and only a few parameters are to be estimated, the optimal methods are temperamental and can produce strange results. The numerical minimization problem in eq.(9) is not trivial. Local minima abound in the surface defined by the equation:  $|\Sigma_{e}|$  in multidimensional parameter space.

Thus, instead of insisting on optimal parameter estimation, we accept the hand calibration as the "optimal" parameter estimates. The parameter uncertainty methodology discussed below is designed to accommodate this view of parameter estimation.

#### **B.** Estimating Model and Data Uncertainty

The first step in computing parameter uncertainty is to isolate the model error. That is, it is necessary to estimate the magnitudes of the model error and data mean uncertainty from the residuals. This is done as follows.

For certain times and model segments, there are a number of measurements that are combined to estimate the mean value of the data in that segment. Let the index *j* denote this replication. Hence the statistical model becomes:

$$\vec{c}_{i,j} = \vec{f}(\vec{\theta}, t_i) + \vec{\xi}_i + \vec{\xi}_{i,j}$$
(12)

where:

# $\vec{c}_{i,j} = \vec{c}(t_i)$ for replication $j = 1, ..., n_i$

# $\overline{\xi}_i$ is the model error at time $t_i$

 $\xi_{i,j}$  is the random fluctuation about the data mean at time  $t_i$  and replication j.

The problem is to estimate the model uncertainty covariance:

$$\Sigma_{t} = E \left\langle \vec{\xi}_{i} \vec{\xi}_{i}^{T} \right\rangle$$
(13)

and the data uncertainty covariance.

$$\Sigma_{\xi} = E\left(\vec{\xi}_{i,j}\vec{\xi}_{i,j}^{T}\right) \tag{14}$$

from the residuals. It turns out that the problem can be solved using the vector version of the One-Way Random Unbalanced Analysis of Variance Model (ANOVA) [Searle, 1971]. This can be seen if eq.(12) is written in terms of the residuals which more closely resembles the standard form for ANOVA models:

$$\vec{\epsilon}_{i,j} = \mu + \vec{\xi}_i + \vec{\xi}_{i,j} \tag{15}$$

where  $\mu$  is the mean of the residuals;  $\vec{\xi}_i$  contributes the variance due to model uncertainty; and

 $\bar{\xi}_{i,j}$  contributes the variance due to data replication. The ANOVA methods estimate the magnitude of these variances. The matrix ANOVA methods are analogous except that they estimate the covariances.

#### C. Estimating Parameter Uncertainty

The fundamental idea is to compute the parameter uncertainty covariance that accounts for the observed model error covariance. That is: given the magnitude of the model error covariance:  $\Sigma_{\xi}$ , how large must the parameter uncertainty covariance,  $\Sigma_{\theta}$ , be in order to account for all the model error covariance.

Note that we assume that this is the proper way to compute the parameter uncertainty covariance. In effect, this method of estimating parameter uncertainty assumes that all the model fluctuations are actually *caused* by fluctuations of the parameters. Thus the model produces the mean concentrations, and the parameter uncertainties produce the random component. We will compare the result of this point of view with the maximum likelihood results below.

In order relate model uncertainty to parameter uncertainty, it is necessary to have the relationship between a parameter variation:  $\overline{\delta\theta}$ , and the resulting model variation. Let  $\overline{\xi}$ , be the model fluctuation due to the parameter fluctuation  $\overline{\delta\theta}$ :

$$\vec{\xi}_i = \vec{c}_i - \vec{f} \left( \vec{\theta} + \vec{\delta \theta}, t_i \right)$$
(16)

Expand the model in a Taylor series and retain only the first order terms:

$$\vec{f}(\vec{\theta} + \vec{\delta\theta}, t_i) \approx \vec{f}(\vec{\theta}, t_i) + \mathbf{J}_i \vec{\delta\theta}$$
(17)

where:

$$\mathbf{J}_{i} = \frac{\partial \overline{f}(\vec{\Theta}, t_{i})}{\partial \vec{\Theta}} \tag{18}$$

is the Jacobian of the model solution with respect to parameter variations. Then:

$$\vec{\xi}_i = -\mathbf{J}_i \overline{\delta \theta} \tag{19}$$

The the covariance of  $\overline{\xi}_i$  is found as follows:

$$\Sigma_{t}(i) = E\left\{\overline{\xi}_{i}\overline{\xi}_{i}^{\mathsf{T}}\right\}$$
$$= E\left\{J_{i}\overline{\delta\theta}\overline{\delta\theta}^{\mathsf{T}}J_{i}^{\mathsf{T}}\right\}$$
$$= J_{i}\Sigma_{\theta}J_{i}^{\mathsf{T}}$$
(20)

where:

$$\Sigma_{\theta} = E\left\{\overline{\delta\theta}\overline{\delta\theta}^{\mathsf{T}}\right\}$$
(21)

Great Lakes Monograph No. 4

The problem is to solve for the parameter uncertainty covariance,  $\Sigma_{\bullet}$ , given the model uncertainty covariances,  $\Sigma_{\bullet}(i)$ , at times,  $t_{i}$ .

1. Estimating  $\Sigma_{\theta}$  - The Constant Case

The equation that relates  $\Sigma_0$  to  $\Sigma_1(i)$  is:

$$\Sigma_{t}(i) = J_{i}\Sigma_{\theta}J_{i}^{\mathsf{T}}$$
(22)

Consider, first the case where there is no time variation in the problem so that  $\Sigma_{\xi}(i) = \Sigma_{\xi}$ . Then the relationship between model uncertainty covariance and parameter uncertainty

covariance is:

$$\Sigma_r = J \Sigma_{\mu} J^{T}$$
(23)

This equation can be solved for  $\Sigma_{\theta}$  if an matrix inverse exists for the Jacobian matrix, J. Let the inverse of J be denoted by J<sup>-</sup>. Then, the solution to eq.(23) is:

$$\Sigma_{\theta} = J^{T} \Sigma_{\xi} J^{T}$$
 (24)

In fact, Generalized Inverses do exit [Pringle and Rayner, 1971]. For example,

$$\mathbf{J}^{-} = (\mathbf{J}^{\mathsf{T}} \mathbf{J})^{-1} \mathbf{J}^{\mathsf{T}}$$
(25)

if the inverse of  $J^T J$  exits. We use this Generalized Inverse to solve for  $\Sigma_{\phi}$  and call it the

Generalized Inverse Estimator (GIE) of the parameter uncertainty covariance. In fact, it satisfies the condition:

$$\Sigma_{\theta} = \min_{\Sigma_{\theta}} ||\Sigma_{\xi} - J\Sigma_{\theta}J^{T}||$$
(26)

where the matrix norm ||A|| of any matrix A is defined as:

$$||A|| = \sum_{i,j} a_{i,j}^{2}$$
(27)

Thus, the GIE is the matrix which is the element-by-element least squares solution of the matrix equation that requires the parameter uncertainty to account for as much of model uncertainty as possible. Further it can be shown from the properties of the Generalized Inverse [Pringle and Rayner, 1971] that the GIE given by eq.(24) is equivalent to:

$$\Sigma_{\theta} = \left(J^{\mathsf{T}}\Sigma_{\xi}^{-1}J\right)^{-1} \tag{28}$$

2. Estimating  $\Sigma_{\theta}$  - The General Case

For the case where model variations occur at the various times,  $t_i$ , it seems reasonable to require that the parameter uncertainty account for the average observed model uncertainty. Thus we require that:

$$\Sigma_{\xi} = \frac{1}{N} \sum_{i=1}^{N} (\mathbf{J}_{i} \Sigma_{\theta} \mathbf{J}_{i}^{\mathsf{T}})$$
(29)

It can be shown that the GIE for this case is:

$$\Sigma_{\mathbf{g}} = \left(\frac{1}{N} \sum_{i=1}^{N} \mathbf{J}_{i}^{\mathsf{T}} \Sigma_{\xi}^{-1} \mathbf{J}_{i}\right)^{-1}$$
(30)

This is essentially a time averaged version of eq.(28) before the final matrix inversion.

# 3. Relationship Between GIE and MLE Parameter Uncertainty Covariances

We have presented two different estimates of the parameter uncertainty covariance. The first is derived from applying the principle of Maximum Likelihood and assuming that the calibrated parameters are optimal. The result is:

$$\Sigma_{\theta}^{\mathsf{MLE}} = \left(\sum_{i=1}^{N} \mathbf{J}_{i}^{\mathsf{T}} \Sigma_{\xi}^{-1} \mathbf{J}_{i}\right)^{-1}$$
(31)
where we use the model uncertainty covariance,  $\Sigma_{\xi}$ , rather than the residual uncertainty

covariance,  $\Sigma_{\epsilon}$ , so that only model error causes parameter uncertainty. The second estimate follows from the principle of maximizing the parameter uncertainty using the Generalized Inverse.

$$\Sigma_{\theta}^{\mathsf{GIE}} = \left(\frac{1}{N}\sum_{i=1}^{N} \mathbf{J}_{i}^{\mathsf{T}} \boldsymbol{\Sigma}_{\xi}^{-1} \mathbf{J}_{i}\right)^{-1}$$
(32)

These two estimates are related as follows:

$$\Sigma_{\theta}^{\mathsf{GIE}} = \left(\frac{1}{N}\sum_{i=1}^{N} \mathbf{J}_{i}^{\mathsf{T}} \Sigma_{\xi}^{-1} \mathbf{J}_{i}\right)^{-1}$$
$$= N \left(\sum_{i=1}^{N} \mathbf{J}_{i}^{\mathsf{T}} \Sigma_{\xi}^{-1} \mathbf{J}_{i}\right)^{-1}$$
$$= N \Sigma_{\theta}^{\mathsf{MLE}}$$
(33)

so that

$$\Sigma_{\theta}^{MLE} = \frac{1}{N} \Sigma_{\theta}^{GIE}$$
(34)

What is striking and unexpected is that there is any relationship at all between two such dissimilar approaches to the problem. They differ only by the  $\frac{1}{N}$  factor.

It can be shown that the maximum likelihood estimate is optimal in the sense that no better parameter estimates can be made within the assumptions of the method [Sorenson, 1980]. The GIE provides the most pessimistic estimate of parameter uncertainty. All the model uncertainty translates to parameter uncertainty and additional calibration data does not necessarily decrease parameter uncertainty. Hence, one would expect that the true parameter uncertainty covariance for a hand calibrated model to be bracketed by these two estimates:

$$\Sigma_{\theta}^{\text{MLE}} = \frac{1}{N} \Sigma_{\theta}^{\text{CIE}} \le \Sigma_{\theta}^{\text{TRUE}} \le \Sigma_{\theta}^{\text{CIE}}$$
(35)

A simple illustration may help clarify the situation.

#### 4. Illustrative Example

The difference between the two parameter uncertainty covariance estimates can be understood by examining the simplest model, a single constant scalar.

$$\vec{f}(\vec{\theta}, t_i) = \theta_1 \tag{36}$$

For this model, the statistical problem is to estimate the mean,  $\theta_1$ , of the concentrations. The Jacobian for the model is:

$$\mathbf{J}_{i} = \frac{\partial \vec{f}(\vec{\Theta}, t_{i})}{\partial \vec{\Theta}} = 1 \tag{37}$$

The MLE for the parameter uncertainty for  $\theta_1$  is:

$$\Sigma_{9}^{MLE} = \left(\sum_{i=1}^{N} J_{i}^{T} \Sigma_{\xi}^{-1} J_{i}\right)^{-1}$$
$$= \left(N \Sigma_{\xi}^{-1}\right)^{-1}$$
$$= \frac{\sigma_{\xi}^{2}}{N}$$
(38)

where  $\Sigma_{\xi} = [\sigma_{\xi}^2]$  is the 1 × 1 covariance matrix. The diagonal element is the variance of the model uncertainty. In this case  $\sigma_{\xi}^2$  is the variance of the observed concentrations. The result is the well known formula for the variance of the sample mean.

By contrast the GIE is:

$$\Sigma_{\theta}^{\text{CIE}} = \sigma_{\xi}^{2} \tag{39}$$

This is not unexpected since the model is the parameter itself:  $\vec{f}(\vec{\theta}, t_i) = \theta_1$ , and therefore the parameter uncertainty should be equal to the model uncertainty.

This simple case suggests the following interpretation. The ML method assumes that the model is true. The presence of the random fluctuations,  $\xi_i$ , prevent the estimation of the true values of the parameters,  $\overline{\Theta}$ . When a ML estimate of  $\overline{\Theta}$  is made,  $\overline{\Theta}_{MLE}$ , that estimate can differ from the true parameter vector,  $\overline{\Theta}$ . The covariance of this variation is:

$$E\left(\left(\vec{\theta}_{\mathsf{MLE}} - \vec{\theta}\right)\left(\vec{\theta}_{\mathsf{MLE}} - \vec{\theta}\right)^{\mathsf{T}}\right) = \Sigma_{\theta}^{\mathsf{MLE}}$$

$$\tag{40}$$

i.e. the parameter uncertainty covariance. As more and more data are added to the estimate, the parameter uncertainty covariance decreases as  $\frac{1}{N}$ . The reason is that the random fluctuations,  $\vec{\xi}_i$ , can be more effectively averaged out and their presence are less of a hindrance to finding the true parameters.

By contrast, the GI estimator does not assume a set of true parameters for which an optimal estimate has been made. It simply assigns the parameters as much of the model uncertainty covariance as is possible. Adding more data to the calibration may not reduce the parameter uncertainty covariance at all ( no  $\frac{1}{N}$  behavior). This appears to be a rather pessimistic estimate of the actual parameter uncertainty covariance. In any case, it is a simple matter to use both estimates (they differ only by the leading  $\frac{1}{N}$ ), and examine the effect on the magnitude of the model projection uncertainty.

#### **D.** Projection Uncertainty

The second principal reason for evaluating model uncertainty is to calculate the uncertainty of projections made using the model. The procedure is to run the model to evaluate a remedial alternative:

$$\vec{c}_i^{\mathsf{P}} = \vec{f}^{\mathsf{P}}(\vec{\Theta}, t_i) \tag{41}$$

where the superscript P indicates that this is a projection. In order to evaluate the uncertainty of the projection, the relationship between a parameter variation  $\overline{\delta \theta}$ , and a concentration variation  $\overline{\delta c}_{1}^{P}$  is required:

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

$$\overline{\delta c}_{i}^{P} = \overline{f}^{P} (\overline{\theta} + \overline{\delta \theta}, t_{i}) - \overline{f}^{P} (\overline{\theta}, t_{i}) \approx J_{i}^{P} \overline{\delta \theta}$$

$$\tag{42}$$

to first order in  $\overline{\delta\theta}$ . The model uncertainty covariance for this magnitude of parameter variation

$$\Sigma_{c,i}^{P} = E\left\{\overline{\delta c_{i}}^{P} \overline{\delta c_{i}}^{PT}\right\}$$
$$= J_{i}^{P} \Sigma_{a}^{CIE} J_{i}^{PT}$$
(43)

Note that the parameter uncertainty covariance,  $\Sigma_{\varphi}^{GIE}$ , plays a dominant role in determining the magnitude of model uncertainty. Also note that the  $\frac{1}{N}$  term, would be included if the ML estimate, were intended to be used.

The diagonal elements of  $\sum_{c,i}^{p}$ , diag[ $\sum_{c,i}^{p}$ ] are the prediction error variances for time  $t_i$ . Hence the approximate 95% confidence limits are:

$$c_i^{\mathsf{P}} = \frac{1.96}{\sqrt{N}} \sqrt{\operatorname{diag}[\Sigma_{e,i}^{\mathsf{P}}]}$$
(44)

where the  $\frac{1}{\sqrt{N}}$  term is included for the ML estimate of parameter uncertainty. For the GI

estimate, set N = 1. Therefore, in practice, the ambiguity between an MLE and GIE interpretation is  $\frac{1}{\sqrt{N}}$ . For example, if N = 10, then  $\frac{1}{\sqrt{N}} = 0.32$  and the confidence limits would be ~ 32% narrower using MLE versus GIE. It is a matter of judgement whether or not to include the  $\frac{1}{\sqrt{N}}$  since it depends on whether one thinks the parameter estimates are optimal in the sense of Maximum Likelihood, or that the parameter fluctuations are the cause of the model error fluctuations and should be reflected in the parameter uncertainty.

#### E. Status of Applications

is:

We have tested the ANOVA method for discriminating between data and model uncertainty using artificial data sets and indeed the method can estimate the two covariance matrices if

sufficient data are available [Di Toro, D.M. and Parkerton, T.F. 1991]. Some difficulties occur is the data sets are small. The GIE methodology has been tested to see if in fact it can recover the parameter uncertainty covariance for the case where the model errors are generated by fluctuating parameters. For large data sets, the method is quite reliable. We are in the process of testing the method using more realistic mass balance and food chain models and actual data sets. Preiiminary results indicate that there may be some practical limitations imposed by small data sets [D: Toro, D.M. and Parkerton, T.F. 1992]

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# Model Paradigms: A Discussion Of Simple And Complex Models

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#### Introduction

This paper discusses model paradigms and explores the issue of determining model complexity. As we discuss later there are situations in which simple models are adequate, but other situations require more complex models, which of course are more faithful to reality. A key issue which must be addressed by modelers is then the "optimal" level of complexity. This is a matter of judgement and is the essence of the "art of modeling." A convincing argument can be made that the modeler should select a level of complexity appropriate to the question being addressed. We therefore discuss in some detail the purposes of, or incentives for, models.

Perhaps to add a touch of class to these proceedings, we should bear in mind the Principle of Parsimony stated by William of Occam 650 years ago, and referred to as "Occam's Razor".

"Essentia non sunt multiplicanda praeter necessitatem"

which can be translated as "What can be done with fewer (assumptions) is done in vain with more" or colloquially in this context, "Don't make models of toxic chemicals in the Great Lakes any more complicated than is absolutely necessary".

There are two primary incentives for developing models of contaminant behavior: to assist rational management, and to further the science of contaminant behavior. Essentially, a mass balance model brings together information from a variety of sources to synthesize a statement of mass balance, for example, where the contaminant has accumulated, its concentrations, its sources, its rates of transport and transformation and how fast contaminant inventories are changing. Because lakes are complex systems with variations in space and time, we can never hope to establish exact mass balances, only approximations. In many respects, assembling a lake mass balance is like trying to follow the progress of a ball game, but

Incentives for Models only part of the field is visible, and then only for part of the time. We have some items of information (usually concentrations at a specific time and place, with error) and the task is to deduce all the missing items (usually masses and fluxes). In some cases, we may be quite successful, and in others the information is so fragmentary that any mass balance is highly speculative.

The key point is that if an approximate mass balance can be established, it represents a very powerful assembly of data whose value greatly exceeds the sum of the parts. From the management perspective, it enables various remedial strategies to be tested and justified - it exposes possible futures. From the scientific viewpoint, it represents attainment of the goal of understanding the entire system's dynamics as distinct from having piecemeal information about its parts.

Errors and Credibilitv

- Because the model results are merely estimates, it is critically important that the model documentation conveys information about:
  - How accurate the results are perceived to be, i.e. errorlimits. Often, these will be judgements of error magnitude because there is no "truth" for comparison, nor may there even be other estimates from independent sources.
  - What assumptions and simplifications are inherent in thecalculation, so that the reader can form an opinion about the model's credibility.

Here there are two limiting situations. A very simple model must contain sweeping assumptions which are easily understood but which are so sweeping that the model lacks credibility. A very complex model must contain numerous parameters and equations and mathematical operations. Are the parameter values correct? Are the equations correct? Have the operations been done correctly? The time required to check all these factors can be considerable. Most "managers" lack the time or skill to perform these checks, thus they must rely on other parties to verify the model's structure and contents. A complex model will require many days of intensive study, thus verification will be expensive. Usually, it is not done. The model thus may lack credibility because it is too difficult to verify. It is not peer reviewed.

One solution is to have several modeling teams address the same problem and compare the results. This is similar in concept to the analytical chemist's "round robin". Comparisons between models may contain the same error, however, the comparison should reveal gross discrepancies.

Perhaps one conclusion is that models must be designed with a level of complexity appropriate not only to the environmental situation being addressed, but also to the proposed application, whether it be scientific or

managerial. The manager must be comfortable with the model and must be willing to devote adequate resources for verification. Purchasing a model is not like purchasing a car. The car's performance is predictable from past experience. The model is "one of a kind", a custom effort of unknown quality.

# Designing Models

Most water quality models are compartmental in nature, i.e. they divide the system into a number of compartments which are (usually) fixed in space, have defined volumes, areas, flows and homogeneous composition and temperatures. A mass balance can then be written around each phase envelope. The first problem is to decide on the number of compartments or segments. This decision should be based on composition or chemical concentration differences. In most lake models, the first segmentation is into air, water column and bottom sediments, three compartments with usually quite different chemical compositions. It may be appropriate to discriminate between chemical dispersed in different states within each compartment, i.e. into subcompartments. Examples are:

- Air: Gaseous, aerosol associated
- Water: Dissolved, sarbed to filterable particles; sorbed to non-filterable matter or dissolved in biota ranging from bacteria to fish.
- Sediment: Similar to water.

Two simplifications can often be made. First, if the fraction of chemical in a compartment or subcompartment is negligible and if that chemical therein experiences no unique or important transport or transformations, then the compartment can be ignored. But this raises a problem. It is possible, that for one chemical, a subcompartment is negligible, but for another it is not. For example, aerosol associated benzene is negligible but aerosol associated pyrene, is not. If the model is to be applied to numerous chemicals, it seems that we must include all possible relevant subcompartments.

Second, if thermodynamic equilibrium exists between chemical in these compartments, then an equilibrium relationship can be introduced (usually a partition coefficient) to relate concentrations, thus one variable can be eliminated. Alternatively, a total concentration can be defined from which the individual phase concentrations can be deduced.

For example, if the phases have defined volumes V1 and V2, variable concentrations C1 and C2, and a fixed partition coefficient K12 which is C1/C2, then if C1 is defined, C2 can be calculated as C1/K12, and the amounts C1V1 and C2V2, can be deduced. Alternatively, a total concentration, CT can be defined as (C1V1 + C2V2)/(V1 + V2) and the individual concentrations are then:

C1 = CT/(v1 + v2/K12) C2 = CT/(v1K12 + v2)

# where v1 and v2 are the volume fractions V1/(V1 + V2) and V2/(V1 + V2)

This equilibrium or constant concentration ratio assumption is very useful because it reduces the number of variables. It should be invoked whenever it can be justified. Failure to invoke it necessitates introducing another variable and probably a need to estimate the rates of transfer between the subcompartments, possibly as rate constants.

Perhaps most difficult in this context is the treatment of the non-filterable or colloidal or DOC fraction in the water column or the sediment. Rarely are data available on the fraction of the chemical present in this form, indeed it may be misleading to regard it as a discrete compartment because there may be a continuum of sorbed material from dissolved carbohydrates and proteins through fulvic acids, to humic acids, to humin and large particles.

A second spatial segmentation is possible for each compartment, for example the water column can be divided horizontally or vertically, or both. The sediment can be treated as one of more layers, and different depositional regimes can be defined horizontally. Perhaps the decision to segment should be on the basis of observed concentration differences and the desire to reproduce these differences in the model. It is tempting to segment on a hydrodynamic basis, identifying discrete volumes of water which may be separated by a narrows. Every new segmentation should be questioned and included only when needed. The modeller should adopt the strategy of aggregating whenever possible and strive to reduce the number of segments. This is the Principle of Parsimony pronounced by William of Occam, 650 years ago and stated earlier.

Another difficulty arises when the compartments vary in volume with time, for example an epilimnion-hypolimnion combination.

Most perplexing is the issue of segmentation in the bottom sediments. Should there be separate treatment of a nepheloid layer? Is one surface layer adequate? If not, how many layers are needed? Introducing each layer necessitates defining inter-layer transport parameters which may be poorly quantified. Yet, for strongly sorbing chemicals, the measurable sediment chronology contains a wealth of information which can only be exploited for the purposes of future prediction by a multilayer model. Perhaps there is a need for a number of models of varying complexity. Perhaps it is impossible to predict in advance which model or level of complexity is optimal until the model is run and sensitivities are tested. This iteration towards the optimum can be done from both sides, simple and complex.

We can start with a simple model and increase its complexity in the light of experience. Or we can start with a complex model and trim it down. It is likely that the former approach is easiest. Regardless of the approach, the modeller should keep an open mind and retain the flexibility to change the model structure in the light of experience.

### Documentation

It is difficult to follow the calculations in a new model, thus the modeller has a duty to document the model parameters, equations and operations, preferably in tables which can be consulted for complete information. This should include all chemical parameters (e.g. vapour pressure, solubility), all reactivity rate parameters (e.g. halflines), all environmental parameters (e.g. volumes, areas, rainfall rates), all rate equations used (e.g. for volatilization), and all mathematical data (e.g. integration, time steps). For all parameters and variables the units should be clearly defined. A specimen calculation should also be included.

## Simplicity vs Complexity

When preparing for the Workshop the authors of this contribution decided to present differing viewpoints, i.e. to be advocates for simplicity or complexity. One of us (D.M.) presented the case for simplicity, and the other (V.J.B.) the case for complexity. The following sections summarize some of the key points made on both sides, and include some ideas presented by the workshop participants.

The Case For Simple Models (D. Mackay)

> To examine the role of management as the sponsor of models let us consider PCB's in Lake Ontario. We can envisage three separate modelling efforts: A, B and C in order of increasing complexity and cost. The models give the following hypothetical results:

#### Model A

1990 Water: 1.0 mg/L +/- 0.5 mg/L. (whole Lake, annual average) Sediment: 200 mg/g +/- 150 mg/g Fish: 0.8 ug/g +/- 0.5 ug/g

1991 similar, but approximately 5% lower etc.

1992 similar, but approximately 9% lower

\*\* 3 years with 5 data points each year = 15 points

#### Model B

1990 Water Segment 1: 1.5 mg/L +/- 0.4 mg/L (annual average) Water Segment 2: 1.0 mg/L +/- 0.4 mg/L Water Segment 3: 0.8 mg/L +/- 0.3 mg/L plus two other segments Sediment: 3 segments with similar data Fish: 5 segments, 2 trophic levels, similar data

1991 similar to 1990 but approximately 5% lower

\*\* 3 years data with 18 data points each year = 54 points

#### Model C

1990 Water Segment 1, Month 1: 1.8 mg/L +/- 0.3 mg/L

Month 2: 1.7 mg/L +/- 0.3 mg/L etc. for 12 months

Water Segment 2, Month 1: 1.5 mg/L +/- 0.2 mg/L etc. for 12 months plus 3 other water segments Sediment: 3 segments for 12 months Fish and benthos: 5 trophic levels in 5 segments for 12 months

1991similar, but 5% lower etc.

\*\* 3 years with 396 points each year = 1188 points

We can now ask these management questions:

**1**. Will the results of the models be viewed with any difference in credibility? Will the stated uncertainties be believed?

2. If the errors or uncertainties are accepted, will make any difference to the final managerial decisions?

It is possible that the answer to both questions is "NO". This is not to suggest that we be deliberately sloppy, but we should adopt the strategy of developing the simplest respectable model, present the results honestly, have the model thoroughly peer reviewed, then ask the "managers" if they wish to buy more certainty. We can even give them a quotation!

From a scientific perspective, perhaps we should always strive to improve models by developing better equations, more accurate parameters and more ingenious ways of manipulating the equations and presenting the results. We hope that enlightened funding agencies will see the fundamental merit in studying and quantifying contaminant behavior in Lakes because it is always valuable to know more, rather than less, about the system.

# An Example of a Simple Model

The Model Described Briefly Here Was Developed as a result of the Barrie UC Workshop and the Niagara-on-the-Lake Workshop in June 1991. The "proceedings" are being finalized in early 1992. The material given here is essentially an advance excerpt from that "proceedings".

It has inevitable similarities to other models including the Endicott Model, the Fink Model developed for the National Wildlife

Federation and Mackay's Fugacity Model. The model is written in "rate constant" format with all process rates (kg/year of chemical) being expressed as a product of a rate constant (years-1), and the amount of chemical in the compartment (kg). It is believed that this makes the model much easier to understand, especially by "managers".

The model accepts as input a set of key parameters listed in Table 1 which is actually a printout of the program. These are the usual model quantities.

These data are sufficient to deduce the steady-state chemical mass balance as depicted in Figure 1 and on the computer output.

The water column is treated as a single well mixed compartment, as is the sediment which has a fixed depth. The processes included are:

- ⇒ chemical discharge
- chemical inflow
- deposition from the atmosphere
- evaporation
- ⇒ outflow
- transformation in water
- transformation in sediment
- water to sediment transport
- sediment to water transport
- sediment burial

An option can be included to include the rates of change of water and sediment concentrations (and hence amounts) which are used in a pseudo-unsteady-state calculation as described later.

The working equations relating these quantities to a series of rate constants are conventional in nature.

Steady-State Mass

The steady-state mass balances for water and sediment are then:

Balance

E + MSkS = MW(k1 + k2 + k3 + k4)

MWk4 = MS(k5 + k6 + k7)

where E is total loading rate from all sources including the atmosphere (kg/year) and MW and MS are the masses of chemical in the water and sediment respectively, from which the "forwards" result becomes:

MS = MWk4/(k5 + k6 + k7)

MW = E/[k1 + k2 + k3 + k4(k6 + k7)/(k5 + k6 + k7)]

All process rates and concentrations can be deduced. A food chain model can also be included which consists of six organism

Great Lakes Monograph No. 4

#### MASS BALANCE CALCULATION OF THE FATE OF PCB in LAKE ONTARIO

Forwards, loading to concentration calculation

#### Input quantities

Total concentration in air ng/m3	5.50E-01
Chemical concn in rain (if input) ng/L	0.00E+00
Tributary loadings kg/year	0.00E+00
Other loadings kg/year	1.00E+03

#### Key parameters: \* indicates deduced quantity

Water area (m2)	1.95E+10
Sediment area (m2)	1.17E+10
Water volume (m3) *	1.67E+12
Sediment volume (m3) *	1.17E+08
Suspended solids mass (kg) *	6.68E+09
Suspended solids concn in water (m	g/L)   4.00000
Solids concn in bottom sediment (m	g/L)*   160000.0
Porosity of bottom sediment	0.080000
Sediment solids mass (kg) *	1.87E+10
Sediment solids density (kg/m3)	2000.00
Sediment organic carbon content (g	/g) 0.020000
Mean water depth (m)	85.641
Mean active sediment depth (m)	0.01000
Water residence time (years)	6.500
Frn on depositing particles in wat	er •   0.500000
Fraction dissolved in water column	* 0.500000
Fraction on particles in sedmt	0.999958
Fraction dissolved in sediment	0.000042
Fraction sorbed in atmosphere	0.050000
Fraction gaseous in atmosphere *	0.950000
Volatilization MTC: air side (m/h	1.00000
Volatilization MTC: water side (m/	h)   0.010000
Air-water partition coefficient	5.00E-03
Log octanol-water partition coeffi	cient   6.60E+00
Octanol-water partition coefficien	t • 3.98E+06
Overall water side MTC (m/h) *	3.33E-03
Sediment-water diffusion MTC	1.00E-04
Transformation half life in water	(h) 5.00E+05
Transformation half life in sedime	it (h) 5.00E+05
Transformtn rate const in water (h	-1) *   1.39E-06
Transformtn rate const in sedmt (h	-1) *   1.39E-06
Deposition rate g/m2.day	0.73000
Resuspension rate g/m2.day	0.22000
Burial rate g/m2.day	1.00000
Fraction particles deposited per y	ear *   0.777811
Fraction sediment deposited per ye	er *   0.277552
Mass particles deposited per year	(kg) * 5.20E+09
Fraction sediment resuspended per	year * 0.050188
Mass sediment resuspnded per year	(kg) * 9.40E+08
Fraction sediment buried per year	• 0.228125
Mass sediment buried per year (kg)	• 4.27E+09
Rate of water concentration change	e yr-1   0.00000
Rate of sedmt concentration change	yr-1   0.00000
Scavenging ratio of aerosols Q	100000.
Dry deposition velocity (m/h)	7.200

TABLE 1 ILLUSTRATION OF A SIMPLE MODEL

Rate constants (years-1)

k1 evaporation from water	1.70E-01
k2 outflow from the lake	1.54E-01
k3 transformation in water	1.21E-02
k4 water to sediment transport	3.92E-01
k5 sediment to water transport	5.39E-02
kó transformation in sediment	1.21E-02
k7 burial from sediment	2.28E-01
Total rate constant from water	7.28E-01
Total rate constant from sediment	2.94E-01
Water to sediment deposition	3.89E-01
Water to sediment diffusion	3.07E-03
Sediment to water resuspension	5.02E-02
Sediment to water diffusion	3.67E-03
Water inventory change Iw	0.00E+00
Sediment inventory change is	0.00E+00

MASS BALANCE SUMMARY FROM RATE CONSTANT CALCULATIONS

Total mass in water (kg)	1740.40
Total mass in sediment (kg)	2319.51
Total mass in system (kg)	4059.91
1	
Total loadings	1142.86
Tributary loadings kg/year	0.00
Emissions to water except atm and tribs	1000.00
Municipal point sources kg/year	0.00
Industrial point sources kg/year	0.00
Non-point sources kg/year	0.00
Loadings from areas of concern kg/year	0.00
Deposition from atmosphere	142.86
Rain dissolution	1.81
Wet deposition of particles	47.73
Total wet deposition	49.54
Dry deposition	33.82
Absorption	59.50
k1 evaporation rate from water (kg/year)	296.70
k2 outflow rate from the lake	267.75
k3 transformation rate in water	21.13
k4 water to sediment transport rate	682.19
k5 sediment to water transport rate	124.91
kó transformation rate in sediment	28.16
k7 burial rate from sediment	529.12
Total rate of removal from water	1267.78
Total rate of removal from sediment	682.19
Water to sediment deposition rate	676.85
Water to sediment diffusion rate	0.00
Sediment to water resuspension rate	116.41
Sediment to water diffusion rate	8.51
Water inventory change	0.00
Sediment inventory change	0.00
Water concentration ng/L or ug/m3	1.042
Sediment concentration ng/g	123,900

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#### TABLE 1 ILLUSTRATION OF A SIMPLE MODEL (Continued)

Great Lakes Monograph No. 4

150

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FOOD CHAIN RESULTS

FOOD CHAIN RESULTS					TABLE 1			
					ILLUSTRATIO	N OF A SIMPLE	MODE	(Continued)
Log Kow			0.0					(contended)
Kow		-	3981070					
Sediment OC content	t		.02					
Temperature deg C	-	1	8					
water concentration	n (total) r	ng/L	1.042154					
water concentration	n (dissolve	ed) ng/l	.5210772					
Sediment solids co	ncentration	n ng/g	123.9004					
Sediment organic C	concn ng	g/g 0C	6195.022					
ORGANISM	Zoopinktn	Benthos	Sculpin	Alewife	Smelt	Lake trout		
CONCN ng/kg	1.04E+05	7.55E+05	1.43E+06	8.85E+05	1.20E+06	3.11E+06		
CONCN ug/g	1.04E-01	7.55E-01	1.43E+00	8.85E-01	1.20E+00	3.11E+00		
CONCN ng/g lipid	2.07E+03	1.51E+04	1.78E+04	1.26E+04	3.00E+04	1.95E+04		
BIOMAGNIE FACTOR	1.00E+00	7.28E+00	8.60E+00	6.09E+00	1.45E+01	9.38E+00		
VOLUME (L)	0.00E+00	0.00E+00	5.40E-03	3.20E-02	1.60E-02	2.50E+00		
LIPID CONTENT	5.00E-02	5.00E-02	8.00E-02	7.00E-02	4.00E-02	1.60E-01	,	
k1 (water uptake)	0.00E+00	0.00E+00	7.13E+02	3.50E+02	4.62E+02	6.12E+01		
Kd (food uptake)	0.00E+00	0.00E+00	3.10E-02	2.37E-02	2.63E-02	1.23E-02		
k2 (water loss)	0.00E+00	0.00E+00	2.24E-03	1.26E-03	2.90E-03	9.61E-05		
ke (egestn loss)	0.00E+00	0.00E+00	6.20E-03	4.75E-03	5.27E-03	2.47E-03		
km (metabolism)	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00		
kg (growth)	0.00E+00	0.00E+00	5.68E-03	3.98E-03	4.57E-03	1.67E-03		
food concn (aver)	0.00E+00	0.00E+00	6.38E+05	3.64E+05	5.71E+05	1.06E+06		
FOOD PREFERENCES		Food	d organisms	5				
Consumer	Zooplakta	Benthos	Sculpin	Alewife	Smelt	Lake trout		
Sculpin	0.180	0.820	0.000	0.000	0.000	0.000		
Alewife	0.600	0.400	0.000	0.000	0.000	0.000		
Smelt	0.540	0.210	0.250	0.000	0.000	0.000		
Lake trout	0.000	0.000	0.100	0.500	0.400	0.000		

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study



Great Lakes Monograph No. 4

classes with plankton (at equilibrium with water) at the base of the water food chain and benthos (at equilibrium with sediment) at the base of a benthic food chain. The other four organisms form a food web with defined food preferences.

### Discussion

This model, or one similar to it, is regarded as the simplest possible credible model. To eliminate a compartment or a process would greatly weaken the model's applicability and for some chemicals at least it would remove any hope of achieving reasonable estimates of fate. A strong case can be made that this should be a starting point for models, a first-attempt which can be improved upon in the light of experience.

A worrisome consideration emerges when more complexity is introduced. It is entirely possible that the paradigm on which even this simple model is based is wrong. Let us explore just two possibilities.

Perhaps the well-mixed-water in contact with well-mixed-sediment concept is wrong. There may be a nepheloid layer, tens of centimeters deep, above the sediment in which there is active organic carbon conversion and contaminant release. When a hydrophobic contaminant does settle on the bottom, it may essentially remain there with virtually no release or diffusive mixing. Sorption may be essentially irreversible. If this is the case, dividing up the sediment into multiple layers is pointless. If the water column is to be meaningfully segmented vertically it may involve layers 10 cm deep above the sediment. It is thus essential that we better understand these phenomena (which are so difficult to investigate). A more complex model with the same basic misrepresentation merely adds a greater number of fundamentally erroneous parameters.

Perhaps the two-film evaporation equations cease to apply at very low concentrations. There have been no actual measurements of fluxes of hydrophobic chemicals at typical lake concentrations. If, for some reason, surface microlayers become significant retarding factors at low concentrations, the expression for evaporation may be wrong. An erroneous equation may be easier to detect with a simple model in which there are fewer adjustable parameters.

The key conclusion is that we must be absolutely sure that the basic physics and chemistry are understood so that the equations are fundamentally correct. Complex models tend to obscure such fundamental inadequacies. They merely compute more mistakes!

A final issue relates to the scale of the model. It is certainly true that a simple Lake Ontario model can not treat locally high shoreline or near-shore contamination. It could not include Hamilton Harbour or the Bay of Quinte. A more complex spatially resolved model could treat these areas. Perhaps each "Area of Concern" or region of high local contamination should be treated as a source to the simple whole lake model. The mass balance envelope would then be drawn to exclude such areas, but would accept contaminant input

from them. By judicious selection of the phase envelope it may be possible to treat 95% or more of Lake Ontario with a simple model, then apply other, separate simple models to "Areas of Concern" or near-shore regions.

Is there not a case for developing a family of simple models which operate separately, at different scales and which "feed" from each other? This approach would perhaps satisfy proponents of simplicity and complexity.

The Case For More Complexity (VJ. Bierman)

I agree with the philosophy that models of toxic chemicals in the Great Lakes should not be made any more complicated than absolutely necessary. The case for additional model complexity should be driven by two principal, generic management questions:

1. If external loadings are changed, what will be the new state of the system?

2. If external loadings are changed, how long will it take the system to reach its new state?

A corollary to the first question is: given an in-lake target state, what change in external loading (if any) is required to produce this state?

Additional model complexity must have the potential to reduce uncertainties in answering one or both of these questions. While advances in scientific understanding should be a principal goal in model development, a reality is that most model development and applications research in the Great Lakes is supported by mission-oriented agencies. Consequently, sponsors/managers can not be expected to pay for additional model complexity unless there is some reasonable expectation that uncertainties will be reduced in answering critical management questions. I believe that strong cases can be made for additional model complexity in several key areas that bear directly on such critical questions.

Figure 2 contains a simple conceptual model for toxic chemicals. It is similar to the model proposed in Figure 1. There are three principal compartments: air, water and sediment. The state variables are particulate and dissolved phase toxic chemical concentrations in the water column and sediment compartments. Sorbed chemicals are normalized to particulate organic carbon, as opposed to suspended/bedded solids. Within a compartment phase concentrations are related by a simple equilibrium equation. The usual process mechanisms are included: settling, resuspension, deep burial, air-water and sediment-water transfers, decay, photolysis, etc.

The principal purpose for introducing this simple model is to emphasize the importance of organic carbon as the principal controlling sorbent volume for hydrophobic, organic chemicals. It is not possible to understand or predict the behavior of these

# A Proposed Conceptual Model

Great Lakes Monograph No. 4

chemicals in the Great Lakes without understanding the dynamics and fate of organic carbon. This model will be used below for several Lake Ontario examples.

# Idealized Load-Response Relationships

Load-response relationships in coupled water-sediment systems such as the Great Lakes can have complex ramifications for addressing critical management questions. These complexities were discussed in considerable detail for Lake Ontario during an UC-sponsored modeling workshop (February 18-19, 1987) that involved comparisons among three different toxic chemical models. The principal points to be made here are the following:

**1.** Toxic chemical concentrations in the sediments respond at different rates than toxic chemical concentrations in the water column.

2. Sediments can act as toxic chemical sources or toxic chemical sinks, depending on the dynamic state of the system.

**3.** In-lake toxic chemical concentrations are not proportional to external loadings under non-steady-state conditions.

These points support the case that toxic chemical models for the Great Lakes must be time variable. Steady-state models alone are not sufficient. Furthermore, these time variable models must include both water column and sediment compartments, and explicit representation of settling, resuspension, deep burial and sediment-water diffusion.

For the idealized example in Figure 3, total toxic chemical concentrations in the water column and sediment are zero at t = 0. At t = 0 a constant external loading is imposed. Water concentrations quickly approach near-equilibrium values (approximately 90% in 2-3 years) while sediment concentrations show a much slower approach (90% after 20 years). During this temporal period the sediments are a sink for toxic chemicais. At t = 20 years external loading is step-reduced to zero. Water concentrations show a two-component response: a fast initial decrease followed by a much slower decrease toward eventual eauilibrium. It is critical to note that this decreasing water column concentration trajectory is not the inverse of the increasing trajectory. Sediment concentrations follow an exponentially decreasing trajectory with a relatively small time constant. During this recession period the sediments are a source for toxic chemicals because "sediment bleeding" controls the long-term response trajectory of water column toxic chemical concentration.

I his example can be made more concrete by considering some of the management implications of sediment quality criteria (SQC) now being developed by the U.S. Environmental Protection Agency. The SQC can be used to prevent future sediment contamination or to remediate present



FIGURE 2

· · · · ·

sediment contamination. Lack of a unique loading-sediment response relationship can confound implementation of the appropriate management strategy, as depicted in Figure 4. Under the application of a constant external load that is less than the total maximum daily load (TMDL), sediment concentrations will depend on the dynamic state of the system, however, they will remain less than the indicated SQC. Prevention is the proper management strategy in this case. Under the application of a constant external load that is greater than the TMDL, sediment concentrations could be less than or greater than the SQC, depending on when they are measured. Consequently, in order to implement the proper management strategy, the dynamic state of the system must be known. Finally, if the system is in equilibrium with an external load that is greater than the TMDL, remediation is required and a steady-state analysis might suggest the indicated loading reduction to meet the TMDL. However, even if this reduction is implemented instantaneously, sediment concentrations could remain in violation of the SQC for a considerable period of time before reaching equilibrium.

From these idealized examples it can be seen that for a given external loading, in-lake concentrations for both water column and sediment compartments depend on the dynamic state of the system. That is, for a given external loading, there does not necessarily exist a unique set of water column and sediment response concentrations. This behavior has direct bearing on both of the above principal management questions. To understand and predict the behavior of such a system, time variable mass balance models must be used, in conjunction with long time-series data for loadings and in-lake concentrations.

# Sectiment Response Times

Having established that sediment dynamics can confound load-response relationships, attention should be directed to factors controlling sediment response times and their associated uncertainties. The principal point is that there is a large range of uncertainty in sediment response times for a reasonable range of values for assumed mixed layer sediment depth. This point supports the case that toxic chemical models for the Great Lakes must incorporate additional complexity in the surface sediments.

As a simple example, the conceptual model in Figure 2 was used to estimate 90% response times for sediment toxic chemical concentrations in response to a step change in external loading. The model parameters used in this example were the following:

> Resuspension velocity =  $1.38 \times 10-4$  m/yr Burial velocity =  $1.25 \times 10-3$  m/yr Porosity = 0.90Particle density = 2.45 gm/cm3 Fraction organic carbon = 0.02Koc = 106 L/kg organic carbon Decay rate = 0Diffusion coefficient =  $3 \times 10-5$  cm2/sec.

The resuspension and burial velocities were taken from the Lake







Great Lakes Monograph No. 4

Ontario models presented at the above-mentioned UC Workshop. They correspond to a steady-state solids balance for the lake. Values for the other parameters are estimated, but fall within reasonable ranges for illustrative purposes. Mixed layer sediment depth was the independent variable.

Figure 5 illustrates 90% sediment response times as a function of assumed mixed layer sediment depth. Response time ranges from approximately two years for a sediment depth of 0.5 cm to approximately 65 years for a sediment depth of 5 cm. The principal point is not that these estimates are accurate, but that there is a large range of uncertainty in response time corresponding to a reasonable range of values for assumed mixed layer sediment depth.

This example supports the case for additional model complexity in the surface sediments. Specification of mixed layer sediment depth in simple models is somewhat arbitrary and is usually based on "best professional judgment". More realistic process representations would increase model accuracy and reduce prediction uncertainty for system response times. These processes should include vertical segmentation and explicit representation of advective and dispersive mass transfer processes within the sediment bed. Attempts should be made to parameterize these processes in terms of molecular diffusion, bioturbation and waves/currents.

Whole-Lake versus Near-Shore Scales

Another aspect to the case for additional model complexity in the surface sediments is the need to distinguish between near-shore and open-water zones. In addition, there are critical management questions that can not be answered with whole-lake models. The principal points to be made here are the following:

**1**. There are significant differences in resuspension potential between near-shore and open-water zones in large lakes.

2. In Lake Ontario, the open-water depositional zone represents approximately one- half of the total lake area.

3. In addition to whole-lake target loadings, there are critical management questions related to waste load allocations for individual sources in near-shore areas and embayments, including in-place pollutants.

Having established that load-response relationships are a sensitive function of sediment dynamics, it should be recognized that sediment-water exchange rates may differ greatly between near-shore and open-water zones due to differences in wave/current energies and animal densities/bioturbation. In Lake Ontario the open-water depositional zone represents only about half of the total lake area. Another argument supporting separation of these two zones is that most of the available sediment core data represent deposition areas, not highly-energetic near-shore areas. There do not exist "lake-wide average sediment cores" with which to



Great Lakes Monograph No. 4

#### compare output from lake-wide average models.

From a management standpoint, whole-lake models can only be used to establish lake-wide target loading objectives. Such models can not be used to allocate individual point and non-point source loadings at their primary control points. In particular, whole-lake models can not be used to set NPDES permit limits or to evaluate localized impacts of alternative remediation strategies for Great Lakes Areas of Concern.

Organic Carbon Dynamics and Sectiment-Water Gradients

For hydrophobic organic chemicals, the controlling environmental sorbent volume is organic carbon, not water column or bedded solids per se. Normalization of particulate phase toxic chemical concentrations to organic carbon produces interesting and somewhat complex ramifications in mass balance models. These ramifications directly impact both of the principal management questions. The principal points to be made here are the following:

**1**. Unequal fractions of particulate organic carbon between water column and sediment will generally cause unequal dissolved phase toxic chemical concentrations between water column and sediment, even at steady-state.

**2.** A given loading condition for a particular chemical may satisfy a water quality criterion but not necessarily a sediment quality criterion.

**3.** Toxic chemicals released in the nepheloid layer and/or at the sediment-water interface may "short circuit" slower sediment recycle processes and be recycled quickly back to the water column.

**4.** Toxic chemicals released within the sediment bed, if they are not buried into deeper sediment layers, will recycle back to the water column over a much longer period of time.

These points support the case that toxic chemical models for the Great Lakes must incorporate additional complexity to represent the mass balance cycle for organic carbon and the fate of associated toxic chemicals.

As another simple example, the conceptual model in Figure 2 was used to estimate the ratios of dissolved phase toxic chemical concentrations in the sediment to dissolved phase toxic chemical concentrations in the water column. The independent variable was fraction organic carbon content in water column particles (foc1). Fraction organic carbon content in the sediment (foc2) remained fixed at a value of 0.02. Sediment mixed layer depth was fixed at a value of 2 cm. All other parameters were the same as in the preceding example. All computations correspond to steady-state conditions.

Figure 6 illustrates that sediment:water dissolved phase



Great Lakes Monograph No. 4

concentration ratio ranges from 1 for foc1 = 0.02 to 17 for foc1 = 0.50. The reason for this behavior is that unequal organic carbon fractions produce unequal partitioning in the water column and sediment compartments, and hence unequal dissolved phase toxic chemical concentrations. It should be noted that this behavior is not a consequence of the "solids concentration effect" on partitioning. Water column and sediment partition coefficients (Koc1 and Koc2, respectively) were set equal in this example, consistent with the best current understanding that the "solids concentration effect" is not operative in stationary, bedded sediments. Apparent unequal partitioning occurs because in terms of organic carbon normalization, the operative partition coefficient is the product Kocfoc (= L/kg solids). Field observations confirm that foc1 is generally 5 to 10 times greater than foc2.

The significance of this example is that a given loading condition will produce different dissolved phase toxic chemical concentrations in the water column and sediment compartments, even at steady-state. Dissolved phase toxic chemical concentrations are generally considered to represent the bioavailable fractions of total chemical concentrations. Consequently, benthic and pelagic biota will have different toxic chemical exposure concentrations. With the advent of sediment quality criteria, determination of target loadings will become more complex because the external loading for a given chemical may satisfy the water quality criterion, but not the sediment quality criterion.

Simple models can and do account for the above behavior by assigning observed values for foc1 and foc2 to the water column and sediment compartments, respectively. However, hidden within this simple approach, and in the simple example presented here, is the assumption that the organic carbon associated with settled particulates decays completely within the sediment bed, thus releasing the associated toxic chemicals completely within the sediment bed. These toxic chemicals then re-equilibrate with sediment particulate organic carbon.

These simple assumptions ignore any organic carbon transformation and fate processes (and hence any toxic chemical recycle processes) that may occur in the benthic nepheloid layer and/or at the sediment-water interface. This distinction is not trivial because processes controlling water column dynamics are much faster than processes controlling movement of toxic chemicals within the sediment bed. Toxic chemicals released in the nepheloid layer may "short-circuit" slower sediment recycle processes and be recycled quickly back to the water column. Toxic chemicals released within the sediment bed, if they are not buried into deeper sediment layers, will recycle back to the water column over a much longer period of time. The ability to understand and predict these processes has direct bearing on the degree of certainty with which system responses can be predicted.

This example and associated discussion support the case for

additional model complexity to explicitly represent the mass balance cycle for organic carbon and the fate of associated toxic chemicals. More realistic process representations would increase model accuracy and reduce prediction uncertainty of system responses. These processes should include explicit representation of particulate and dissolved organic carbon as model state variables, and additional vertical segmentation to represent a separate benthic nepheloid layer.

Explicit inclusion of organic carbon dynamics in toxic chemical mass balance raises another important technical issue with direct management implications. Most of the organic carbon in the Great Lakes results from internal primary production, not external loadings. For example, in the ongoing Green Bay Mass Balance Study, it has been found that primary production is responsible for approximately 65% of the total organic carbon "loading". For Lake Ontario, even a larger contribution from primary production would be expected because it has a slower hydraulic flushing rate than Green Bay. Consequently, responses to nutrient loadings and toxic chemical loadings are potentially coupled by in-lake organic carbon dynamics. A need to address the question of toxic chemical impacts as a function of lake trophic state strengthens the case for explicit inclusion of organic carbon dynamics and nutrient load-response relationships in toxic chemical mass balance models for the Great Lakes.

Summary of Recommendations For Additional Model Complexity

To reduce uncertainties in answering critical management questions, the following recommendations are made for additional complexity in toxic chemical mass balance models for the Great Lakes in general, and Lake Ontario in particular:

1. Models should be fully time-variable and include coupled water column and sediment compartments with explicit representation of settling, resuspension, deep burial and sediment-water diffusive exchanges.

2. Vertical segmentation and explicit representation of advective and dispersive mass transfer processes within the sediment bed.

3. Sediment-water exchange processes should be parameterized in terms of molecular diffusion, bioturbation and shear stresses due to wave/current action.

4. Horizontal segmentation to distinguish between near-shore and open-water zones.

5. Explicit representation of the mass balance cycle for organic carbon and the fate of associated toxic chemicals. This should include explicit specification of internal organic carbon loadings due to primary production.

6. Vertical segmentation in the water column to explicitly represent processes in the benthic nepheloid layer.

# PROCESS PARAMETERIZATION UNCERTAINTY IN MODELS OF TOXICS IN THE GREAT LAKES

### PART 1: PROCESS PARAMETERIZATION IN CHEMICAL MASS BALANCE MODELS

#### Prepared for the Workshop on Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes Buffalo, New York February 3-5, 1992

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> > Great Lakes Monograph No. 4

### I. PREFACE

This white paper addresses the issue of process parameterization uncertainty in models of toxic chemicals in the Great Lakes. The paper is presented in two parts. The first part discusses parameter uncertainty in mass balance models; the second part considers parameter uncertainty in models of bioaccumulation.

The mass balance portion of the paper begins with an introduction to parameterization. This is followed by the description of a common mass balance formulation, and the identification of uncertainties in process parameterization. The impact of parameterization uncertainty on the results of a toxic chemical mass balance model is then presented as an illustrative example. Finally, prospects for reducing parameter uncertainty will be considered along with unresolved issues and questions.

#### II. INTRODUCTION

Parameterization may be defined as the selection of numerical values for input coefficients to a mathematical model. Obviously, uncertainty in parameterization will be reflected in uncertain model results. In a broader sense, however, parameterization must also consider the process description used in the model. In fact, parameterization is only meaningful in the context of a given process description. Similarly, examining uncertainty in a model process must extend beyond the uncertain parameter values themselves to consider the formulation used to describe the process. Modelers intend to accurately describe significant model processes, yet conceptual errors and errors in assumptions, omissions and formulations are still possible. In particular, a variety of process descriptions are relied upon

that, although commonly accepted, may be relatively unvalidated. As a result, uncertainty in models due to mis-specification of parameters is compounded by inaccuracies in the process descriptions. Therefore, the authors have chosen to address uncertainty in process description as well as in parameter values in this paper.

Parameterization of mass balance models is preferably achieved by calibration to a data set for the system being modeled. (Calibration data sets for mass balance models are the subject of another white paper prepared for this workshop). Calibration is the selection of model parameters that achieve an optimum fit between the model simulation and data for measured state variables. A variety of optimization or tuning methods are used for calibration, with "fit" being determined by visual inspection, objective function (such as sum-of-square error) or other criteria. The accuracy of parameterization achieved by calibration is strongly dependent upon the quality and particularly the completeness of the data. Mass balance models are very sensitive to the specification of external forcing functions, including loads and initial and boundary conditions. Erroneous calibration parameterization is likely if forcing functions contain even modest errors. Other sources of parameterization uncertainty may be introduced by bias or excessive variability in the calibration data, poor optimization, or insensitivity of some parameters to calibration. Calibration produces parameterization errors that are compensating; that is, error in one parameter will be offset or compensated by an error in another. The deviation of model calibration simulation from the calibration data serves as a lower-bound estimate of model uncertainty due to parameterization. A more comprehensive evaluation of model certainty is obtained by comparing model predictions to data independent of the calibration data set.

However, such verification of mass balance models has rarely been performed. The post-audit of eutrophication models for Lake Erie (Lam et al., 1987; Di Toro et al., 1987) and Saginaw Bay (Bierman and Dolan, 1986) represent the only documented verification of mass balance models in the Great Lakes. The lack of comprehensive data sets has prevented thorough calibration and verification of toxics mass balance models, and this lack of experience ultimately limits efforts to reduce model uncertainty.

For a variety of reasons, modelers rely upon other parameterization methods either in conjunction with or in place of calibration. Mass balance models are usually overparameterized; that is, the models contain more parameters than can be determined by calibration alone. As a result, calibration may yield a non-unique set of parameter values. Another case occurs when the calibration simulation is insensitive to one or more parameters; these parameters remain highly uncertain following calibration. These are circumstances in which parameterization by calibration alone may produce uncertain predictions as the conditions of the model system change. In these cases, calibration must be augmented by external specification of some parameters. Even for the parameter values that are obtained by calibration, independently-determined values are useful to assess the internal consistency of the model.

Other methods of parameterization include direct measurement, estimation by correlation and by the use of experimental data, or some combination of the latter. Direct measurement of process parameters in the system being modeled is certainly preferable to estimation. Most critical process parameters are not, however, directly measurable requiring that parameter estimation be used. Correlation estimates make use of relationships observed between

process parameters and properties of the chemical and/or the system. These include QSAR and other advanced computational estimates of chemical properties and reactivity. Some chemicaland system-specific parameters may be obtained directly from experimental data. Both correlations and experimental data have been reported extensively in the environmental literature. However, the accuracy of parameters obtained by either course is questionable. Correlation estimates of parameters may be highly sensitive to properties that are themselves uncertain, and are of course dependent of the accuracy on data used to construct the correlation. Estimates of the same parameter obtained by alternative correlations are sometimes significantly different. It is not unusual for some parameterization estimates to vary by as much as several orders of magnitude. Parameterization by experimental data is also difficult because much of the data found in the literature are difficult to interpret or conflicting, are not available for many systems and chemicals, require extrapolation or do not account for variables affecting the parameter in the system of interest. When forced to rely upon such approaches for process parameterization, it may be useful to construct a probability distribution for the parameter value using all reliable estimates and data. In some cases, this will provide a best estimate parameter value and suggest upper and lower confidence limits. In other cases, it may only be possible to bound the possible value of a parameter.

In some applications, mass balance models must be developed without extensive calibration. Calibration is most often precluded when forcing functions are unknown or uncertain, or when either the quality or quantity of the chemical data are insufficient to define state variable concentrations. In these cases, a majority of parameters must be estimated by correlation or experimental data. These applications include screening-level

models, where uncertain results may be acceptable, as well as extrapolation of existing models to different systems or chemical state variables. It is in such applications that defining parameter uncertainty and its relationship to model uncertainty becomes most critical. The specific model application presented below describes an approach used for dealing with parameterization uncertainty in this context.

#### III. MASS BALANCE MODEL FRAMEWORK

In order to introduce the formulation of mass balance processes found in the WASTOX, WASP4 and other water quality models, an example will be presented which is also the model used in the application presented below. This is the two-compartment model, the simplest framework that incorporates the significant processes for the mass balance of persistent toxic chemicals in a lake. This model simulates the chemical concentration in a completely-mixed water column  $(C_i)$  and underlying sediment layer  $(C_i)$ . The differential equation for chemical mass balance in the water column is:

$$V_{1} \frac{dC_{1}}{dt} = W$$

$$- QC_{1}$$

$$- v_{s}Af_{sl}C_{1} + v_{r}AF_{s2}C_{2} + K_{f}A[(f_{d2} + f_{b2})\frac{C_{2}}{n_{2}} - (f_{d1} + f_{b1})C_{1}]$$

$$+ A[(V_{wet} + v_{dry}f_{dp})C_{a} + k_{v}(f_{av}C_{a}/H - f_{dl}C_{1})]$$

$$- \Sigma k_{d}f_{dl}V_{1}C_{1} \qquad (Equation 1)$$

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

The accumulation of mass  $\{V_1 \frac{dC_1}{dt}\}$  equals the summation of the following terms: loading  $\{W\}$ ; water column exchange (in this case, outflow)  $\{-Q C_1\}$ ; sediment-water exchange  $\{-v_s A f_{sl} C_1 + v_r A F_{sl} C_2 + K_r A[(f_{sl} + f_{bl}) \frac{C_2}{n_c} - (f_{sl} + f_{bl}) C_1]\}$ ; air-water exchange  $\{+A[(v_{wer} + v_{dry} f_{cr}) C_a + k_r (f_{cr} C_s)/H - f_{sl} C_1]\}$ ; and transformation/-degradation  $\{-\sum_{k} f_{sl} V_1 C_1\}$ .

For the sediment layer the chemical mass balance equation is:

$$V_{2} \frac{dC_{2}}{dt} = v_{s} A f_{sI} C_{1} - v_{r} A f_{s2} C_{2} - K_{f} A [(f_{d2} + f_{b2}) \frac{C_{2}}{n_{2}} - (f_{dI} + f_{bI}) C_{1}]$$
  
-  $v_{b} A f_{s2} C_{2}$   
-  $\Sigma k_{ds} f_{d2} V_{2} C_{2}$  (Equation 2)

· • ·

Accumulation of mass in the sediment  $\{V_2 \frac{dC_2}{dt}\}$  equals sediment-water exchange  $\{v_A f_{zl} C_1 - v_r A f_{z2} C_2 - K_f A[(f_{z2} + f_{b2}) \frac{C_2}{n} - (f_{d1} + f_{bl}) C_1]\}$  minus burial  $\{v_b A f_{z2} C_2\}$  and sediment transformation/degradation  $\{-\sum_{k_{dr}} f_{d2} V_2 C_2\}$ .

The terms in these two equations have been arranged to group the mass balance processes in an organization of process categories that will be utilized for the balance of this paper. (Nomenclature is defined at the end of the paper.)

#### IV. IDENTIFICATION OF UNCERTAINTY IN PROCESS PARAMETERIZATION

### A. SEDIMENT-WATER EXCHANGE

Sediment-water exchange includes the processes of settling, resuspension and diffusion. Because it is usually associated with the other particle-transport terms, burial will be considered as a sediment-water exchange process, although it is
not. Similarly, the sediment layer volume will be considered as a sediment-water exchange process parameter. Accuracy in the description and parameterization of sediment-water exchange processes is critical in models of toxic chemicals in the Great Lakes, as toxics are persistent largely due to association with and accumulation in sediment. These processes define the long-term response of the Great Lakes to toxic chemical contamination and control efforts. Uncertainty in sediment-water exchange processes comes from uncertainty in both the process descriptions and parameterization.

### 1. Partitioning

A process of fundamental importance for sediment-water exchange is partitioning, which defines the distribution of chemical between different phases. Partitioning is represented in the mass balance formulations as fractions f of the total chemical in each phase. Examination of equations 1 and 2 reveals that partitioning fractions are distributed throughout the model. Partitioning affects nearly all other processes in the mass balance model by (1) defining particulate chemical fractions transported by particles, (2) defining dissolved chemical fraction subject to air-water exchange and transformation/degradation processes and available for direct uptake by biota and (3) defining mobile chemical fractions in sediment pore water. Uncertainty in partitioning parameterization propagates uncertainty throughout the mass balance formulation. Generally the effect of partitioning uncertainty is more pronounced in the water column, because practically all chemical in the sediment is in the sorbed (particulate) form.

Chemical fractions included in the model description of partitioning include freely dissolved  $(f_i)$ , sorbed  $(f_i)$  to one or

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study more particle classes and, in some models, colloidal "bound" (*f*<sub>s</sub>) phase. It is generally assumed that chemical partitioning reaches equilibrium rapidly, at least in comparison to other process rates. The chemical fractions are then related algebraically to the concentration of sorbent and partition coefficients defining the equilibrium chemical distribution between phases.

For example, the dissolved fraction in a simple two-phase (dissolved/sorbed) system is

$$f_d = \frac{1}{1 + K_p M/n}$$

where  $K_{p}(K_{p} = r/C_{d}; r = f_{a}C/M$ ,  $C_{d} = f_{d}C$ ) is the partition coefficient and Mis the particle concentration. For hydrophobic organic chemicals, organic carbon normalization generally reduces variability in partition coefficients observed for a chemical. Therefore,  $K_{p}$  is usually replaced by an organic-carbon partition coefficient,  $K_{\infty}(K_{\infty} = K_{p}/f_{\infty}; f_{\infty}$  is the organic carbon fraction) in models for hydrophobic organic chemicals (HOCs). (No similar normalization of partition coefficients for metals has been defined, a notable shortcoming.)  $K_{\infty}$  is either parameterized by calibration or estimated by regressions with chemical hydrophobicity, either solubility or octanol-water partition coefficient,  $K_{\infty}$ . Karikhoff's (1979) regression

 $\log K_{ac} = 1.0 \log K_{aw} - 0.2$ 

is a classic example; many other correlations may be found in the literature (Lyman et al., 1982). Considerable unexplained variability in partitioning apparently relates to the semi-empirical nature of  $K_x$ . Sufficient data suggests that

Great Lakes Monograph No. 4

organic carbon is not a uniform sorbent phase, and that the relationship between  $K_{\omega}$  and hydrophobicity varies among classes of HOCs. Order-of-magnitude variability in  $K_{\omega}$  is thus possible, based upon either measurements or estimation. In the case of  $K_{\omega}$  estimation, this variability is related to the fact that the hydrophobicity (expressed as  $K_{\omega}$ ) itself is an uncertain parameter for many HOCs of interest. The reliability of  $K_{\omega}$  measurements has been greatly improved by the development of generator column methods, which unfortunately have not been applied to many toxics of concern. Alternatively, estimation of  $K_{\omega}$  by correlation with molecular properties such as total molecular surface area (TSA) may improve reliability of chemical hydrophobicity determinations.

Uncertainty in the parameterization of partition coefficients also comes from the operational difficulties of making chemical separations consistent with the model process description. Particularly difficult is the separation of freely-dissolved chemical from the colloidal (or microparticulate) phase. Neither filtration nor centrifugation is apparently capable of cleanly separating the dissolved chemical fraction.

These conventional separation methods actually result in the measurement of a distribution coefficient K.

 $K_d = K_p / (1 + BK_b)$ 

where *B* is the concentration of colloid (usually measured as DOC) and *K*, is a binding coefficient  $(K_d = K_p/(1 + BK_p) \cdot K_p)$  is apparently related to chemical hydrophobicity in a manner analogous to *K*<sub>p</sub>. Depending upon the amount of colloidal material present and its

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

affinity for binding HOCs, measured K, may be several orders of magnitude smaller than K. This "third-phase" effect is apparently more significant in sediment pore water than in the water column. Although refined separation methods have been developed, they sometimes produce considerably different results, and none are practical for routine sample processing.

The third-phase effect was offered as an explanation for the observation that measured partition coefficients often vary inversely with sorbent concentration. Whether the "particle effect", first described by O'Connor and Connolly (1980), is adequately explained as an artifact of dissolved/colloidal separation is continuously debated. Di Toro (1935) has argued that colloidal binding alone cannot explain the magnitude of the particle effect. If so, then both the third-phase and particle effects must be retained in the description of the partitioning process. Regardless of the mechanism, the particle effect serves to reduce the sensitivity of  $f_i$  to variation in partition coefficients and sorbent concentrations, a useful outcome. Sorbed chemical fractions observed for HOCs in the Great Lakes are generally in the range of 20-50%.

Finally, the validity of the equilibrium partitioning assumption should be considered. Results of sorption/desorption rate experiments (Karickhoff and Morris, 1985; Wu and Gschwend, 1986; Coates and Elzerman, 1986) suggest that partitioning equilibria for HOCs may require from days to months to achieve, depending upon chemical hydrophobicity and sorbent particle size and concentration. If these rates are applicable to sorption/desorption in natural systems, then partitioning kinetics would be comparable or slower than other model process rates including particle transport, thereby invalidating the equilibrium partitioning assumption in at least some model applications. Furthermore, the results of many experiments conducted to measure partition coefficients are questionable because the duration of the experiments were considerably shorter than the equilibration times suggested by the sorption/desorption rate experiments. More research is necessary to confirm the kinetic data, and to develop rate data for a wider range of chemicals and experimental conditions. A number of partitioning process models incorporating kinetic effects are available, although for practical reasons, the equilibrium partitioning description is still employed in toxic chemical models.

### 2. Particle Transport

The three most important sediment-water exchange processes, settling, resuspension and burial, are controlled by particle transport. Settling and resuspension mediate the exchange of particulate chemical between the water and surficial sediment, and burial represents a loss process as particulate chemical is transported to deeper sediment layers (these deeper layers are sometimes added as additional model segments). Settling, resuspension and burial appear in the mass balance formulations as velocities  $(v_1, v_2, and v_3)$ , which are aggregate parameters representing a greatly simplified description of particle transport processes. In the simplest case, particle transport velocities are parameterized as annual average rates. Usually a steady-state mass balance for particles, either as a single class or multiple particle classes, is used to simulate the particle transport fluxes in toxic chemical models.

Because the sediment segment is treated as completely-mixed in the mass balance, its volume V, is properly defined by the thickness of the mixed sediment layer. The mixing of the surficial sediment is considered to be the result of

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study bioturbation. Dividing the mixed sediment layer thickness by the burial velocity determines the residence time of particles (and presumedly of particulate chemical) in this well-mixed layer. The sediment segment also represents the reservoir of particles and particulate chemical available for resuspension. The sediment residence time controls the accumulation rate in the sediment mass balance, and resuspension of particulate chemical ties the long-term water column accumulation to this rate as well.

Calibration of particle transport parameters in the 2-compartment model is based upon cesium-137 and plutonium-239/240, products of atmospheric bomb testing in the early 1960s. Accurate descriptions of the atmospheric loading of these constituents to the Great Lakes are available (Robbins, 1985a), as are measurements of water and sediment concentrations following their introduction to the lakes. Because Cs-137 and Pu-239/240 partition extensively, they serve as tracers for particle transport. Figure 1 illustrates the calibration achieved for 2-compartment models of each of the Great Lakes. It should be noted that this model fails to simulate the observed depletion of radionuclides during stratification, which isolates the epilimnion from resuspended sediment particles (Robbins and Eadie, 1991). Furthermore, this calibration is sensitive to the partition coefficients for Cs-137 and Pu-239/240 (Thommann and Di Toro, 1983), so mis-specification of partition coefficients results in errors in the calibration. The calibrated burial rates may be confirmed against sedimentation velocities determined by Cs-137 and lead-210 profile analysis in sediment cores, although analysis of a large number of cores may be necessary to define lake-wide averages. Similarly, settling and resuspension velocities may be confirmed by measuring particle accumulation in sediment traps. Calibrated sediment



Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

Figure 1

particle residence times are on the order of 20 years for all the Great Lakes, which is again confirmed by sediment core measurements of surface mixed layer depth.

The description of particle transport presented above has several limitations, which should be considered in the context of parameter uncertainty. First, this description provides no resolution on other than a whole-lake, annual basis. As one moves towards greater resolution, the process descriptions become more complex. For instance, study in the Great Lakes reveals that particle transport processes are subject to considerable spatial and temporal variability. Vertical transport rate varies considerably between nearshore and open-lake locations and at different depths in the water column. In addition, lateral particle transport, redistribution and accumulation result in distinct depositional patterns in the lake basins. Particle transport also varies temporally, both with seasonal processes and during storm events. Further complication is introduced by a predominance of cohesive sediments, which undergo aggregation/disaggregation during transport which alters their properties, and detrital particles which mineralize during settling. The significance of the nephloid layer upon particle and contaminant cycling is another phenomenon which has yet to be addressed in models. The potential influence of the complexity of particle transport on parameterization uncertainty in toxic chemical models is addressed by another paper prepared for this workshop. At a minimum, spatial and temporal variability of particle transport introduces parameter uncertainty via averaging errors in parameters obtained by measurement.

One enhancement to the simple description of particle transport that appears significant for the accurate mass balance of toxic

Great Lakes Monograph No. 4

chemicals is the simulation of multiple particle classes. Multiple particle classes can be used to represent variations in transport and sorption properties of the principal components of the natural particle assemblage. For instance, this allows the accurate representation of partitioning of both suspended and transported particles in the water column. A multiple particle class formulation also facilitates the coupling of the toxic chemical model to simulations of biotic particle production and decay.

### 3. Sediment-Water Diffusion

The fourth sediment-water exchange process is diffusion between the two compartments. The diffusion process is considered to be a minor component of sediment-water exchange, although data to confirm this is lacking. The diffusive exchange coefficient,  $K_{r}$ , is often estimated by the chemical free liquid diffusivity modified for pathlength tortuosity. This produces a K, of 0.1 to 1 cm/d, a range of values also suggested by Thomann and Mueller (1987). Although a single exchange coefficient is applied to both dissolved and bound chemical fractions in the equations, K, for colloidal-bound chemical is probably smaller. Diffusive exchange cannot be uniquely determined in the calibration procedure, and the applicability of experimental measurements of K, to the field is uncertain. Either bioturbation, which would shorten the pathlength and lower the exchange resistance, or pore water transport by ground water infiltration could increase the flux of pore water chemical to the water column. Further research is necessary to develop and apply field measurement methods to measure diffusive exchange in situ, in order to remove uncertainty in parameterization of this process.

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

### B. AIR-WATER EXCHANGE

Air-water exchange includes the processes of rainfall washout, dry deposition, absorption and volatilization. Because these exchanges occur across an open model boundary and measurement is difficult, process parameterization is particularly uncertain. Rainfall washout and dry deposition represent the atmospheric load to the water column; both are described as deposition velocities  $(v_{and}, v_{and}, f_{and})$  multiplied by the total chemical concentration in air  $C_{c}$ . Since both deposition processes are usually specified as external forcing functions to water quality models they will not be considered further, except to note that both deposition velocities and air concentrations are difficult to measure, resulting in uncertain atmospheric loadings. The apparent spatial and temporal variability in depositional processes suggests that coupling the water quality model to simulations of atmospheric chemical transport may be particularly valuable in reducing this uncertainty.

The process descriptions for absorption and volatilization may be combined as an expression for net volatile exchange

## $A k_v (f_{av} C_a / H - f_{dl} C_1)$

the product of a volatilization rate k, and the gradient between atmospheric ( $f_{av}C_{a}/H$ ) and water column ( $f_{dl}C_{1}$ ) available chemical. Depending upon the direction of this gradient, net volatilization may represent either a source or sink of chemical. The two-film theory of Liss and Slater (1974) describes the volatilization rate as a function of serial mass transfer resistances in liquid and gas films at the air-water interface, with the overall rate constant given as:

 $k_{\nu} = \frac{1}{\frac{1}{K_{\nu}} + \frac{1}{K_{\mu}H}}$ 

where K, is the liquid film mass transfer coefficient [L/T], K, is the gas film mass transfer coefficient [L/T] and H is the dimensionless Henry's constant defining chemical equilibrium between vapor and dissolved phases. While there is general agreement in this description of volatilization, there is considerable uncertainty in its parameterization. Obviously, there are many parameters exerting influence upon the volatilization process. Henry's constant is particularly critical, as it defines the chemical gradient and determines which resistance controls k. For the semi-volatile chemicals of greatest concern in the Great Lakes, H is in the range 10<sup>-5</sup> to 10<sup>-3</sup> where direct experimental measurement is difficult and produces uncertain results. Estimating H as the ratio of solubility to vapor pressure is a questionable alternative, as these properties are themselves uncertain for many chemicals. Henry's constant is also fairly temperature dependent, so values measured or estimated at 25° must be adjusted to appropriate environmental temperatures. Factor of 5-10 variability in H is not uncommon; slightly less variability for extensively studied chemicals including PCBs and TCDD. QSAR estimates, available for some chemical classes (Brunner et al., 1990), may also provide more accurate values.

Liquid and gas-phase transfer coefficients are usually extrapolated from reaeration and evaporation rates for the water body of interest. Reaeration and evaporation have been studied extensively, and fairly reliable correlations with environmental

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

factors such as wind speed, drag coefficient and water and air viscosity have been developed. Correlations produce variable estimates of these rates, presumably due to a dependence of the rates upon scale. Correlations based upon data from large water bodies predict generally higher mass transfer coefficients. Extrapolation of the reaeration and evaporation rates to liquid and gas-phase transfer coefficients for a chemical is accomplished by scaling according to diffusivity ratios (Mills et al., 1982; Rathbun, 1990), based upon limited experimental data. Estimates of K, and K, can vary by 3-5, depending upon the particular method followed.

Volatilization rates determined in the calibration of mass balance models represent perhaps the best estimates for this process, although few examples can be cited. Richardson et al. (1983) determined volatilization rates of 0.2 and 0.05 m/d for Aroclors 1242 and 1260, respectively, in Saginaw Bay, Lake Huron. However, absorption of PCBs was neglected in that calibration; including absorption would have increased the calibrated k,s. Schwarzenbach et al.(1979) calibrated a volatilization rate of 0.24 m/d for dichlorobenzene in Lake Zurich. Considering the importance of volatilization in mass balance models, further field-scale determination of volatilization rates for the purpose of reducing parameterization uncertainty appears necessary. Simultaneous process calibration of air and water compartments should be considered in any such design.

### C. TRANSFORMATION/DEGRADATION

Transformation and degradation processes alter the mass balance for certain chemicals by biological and chemical reaction. Transformation is operationally defined as a process converting one constituent of concern to another; both will usually be

retained in the mass balance. Examples include mercury methylation, mirex photolysis, DDT transformation to DDE and PCB dehalogenation. Degradation is a transformation to constituents of no interest (or unknown chemical products) that are not retained in the mass balance. Transformation processes of concern include photolysis, hydrolysis, oxidation and aerobic and anaerobic biodegradation. Except for photolysis, which is limited to the upper water column, these processes may be particularly important in the sediment where even relatively slow transformation rates can alter chemical accumulation.

Transformation/degradation are described as first-order kinetic processes in the mass balance formulation, and are parameterized by a first-order reaction rate,  $k_{i}$ . For hydrolysis, oxidation and biodegradation this is an approximation since these are second-order reactions, although first-order with respect to chemical concentration. k, must usually be estimated from experimental data, although transformation rates have been inferred from vertical chemical distributions in sediment pore water (Oliver, Carlton and Durham, 1989). The reliability of transformation rate data and its applicability to environmental conditions make estimation of this parameter particularly uncertain. Practically, the observed persistence of a chemical can be used to define a probable upper bound for transformation rate; this may be essentially zero for many persistent toxics. If not, then uncertainty in estimates of k can exert a strong influence on the mass balance.

### D. WATER COLUMN EXCHANGE

Water column exchange includes the processes of advection and dispersion. In the 2-compartment model the only water column exchange process is outflow, which has a minor influence on the

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

mass balance for most chemicals. The completely-mixed assumption presumes that lake circulation is adequate to maintain uniform chemical concentrations throughout the water column. While this assumption may be valid on an annual basis, thermal stratification in particular may seasonally reduce circulation allowing concentration gradients to develop. Stratification alters particle transport, as previously mentioned. It may affect other processes as well because of their first-order relationship to chemical concentration. For example, a chemical transformation or volatilization rate will be effectively reduced if the chemical is depleted in the epilimnion during stratification. To simulate spatial variability in chemical concentrations requires additional model segmentation, and the addition of water column exchange processes to the model formulation.

In fact, equations 1 and 2 form a basis commonly used for more complex, multisegment models. Such models are made up of several water column and sediment compartments in which the mass balance equations 1 and 2 apply, with minor modification. This modification is necessary to account for mass exchange between water column segments. If segment 1 receives flow  $Q_u$  from an adjacent water column segment 3, and some degree of mixing (parameterized as a bulk dispersion coefficient,  $E'_u$ ) occurs between the segments, then the modification to equation 1 would be to add the terms

 $Q_{31}C_3 + E_{31}(C_3 - C_1)$ 

to the water column exchange term previously defined. Flows and dispersion coefficients are temporally varied to reproduce the observed circulation patterns. This is usually done by

Great Lakes Monograph No. 4

calibration, either to a conservative tracer such as chloride, or to temperature. Calibration is only possible if gradients in the tracer are observed; this limitation has prevented, for instance, the calibration of large-scale horizontal exchange in Lake Michigan (Rodgers and Salisbury, 1981). The predictive accuracy of calibrated exchange beyond the period of calibration may also be uncertain.

Hydrodynamic simulation has often been proposed as an alternative to calibration for exchange parameterization. Hydrodynamics offers the prospect of more accurate prediction of water column exchange, yet applications for mass balance model parameterization have been limited. Because hydrodynamic simulations take place on time and space scales much smaller than those of interest for mass balance, either hydrodynamic results must be averaged to produce exchange parameters or the mass balance equations must be solved on the hydrodynamic grid. The averaging schemes necessary to implement the first option are not generally developed, and the computational expense of the second option has been prohibitive. This latter option may become feasible with the growing availability of supercomputers and high-performance computer workstations.

## V. EXAMPLE: LAKE ONTARIO LEVEL 1 FATE OF TOXICS MODEL

A preliminary ("level 1") model for toxic chemicals in Lake Ontario was developed to support the Lake Ontario Toxics Management Plan development. The model was applied to predict the relationship between loading and chemical concentrations in water, sediment and biota for toxic chemicals of concern including chlordane, DDT, dieldrin, hexachlorobenzene, mirex, octachlorostyrene, PCBs (modeled as homologs) and TCDD. This model was based upon earlier models of radionuclides (Robbins,

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

1985b; Thomann and Di Toro, 1983), PCBs (IJC, 1988) and TCDD (Endicott et al., 1989) in Lake Ontario. The mass balance was based upon the two-compartment formulation presented above. The mass balance model was coupled to a bioaccumulation model to extend predictions to toxic chemical concentrations in biota, although the bioaccumulation model will not be discussed here. Because of limitations of the toxic chemical database, particularly the lack of reliable loading estimates, calibration of the model was not attempted. Loadings were treated as a single forcing function, including atmospheric deposition and absorption. The initial steady-state application of the model is presented here, although dynamic model applications have been subsequently developed.

Because of the preliminary, uncalibrated nature of this model estimation of predictive uncertainty was a particularly important aspect of this model application. Uncertainty analysis was used to relate parameter uncertainty to uncertainty in model predictions. Results of this analysis provided estimates of confidence for model predictions. Conceptual and descriptive errors in the model were neglected, because these factors relate to possibilities which would change model results to an unknown extent. Uncertainty due to these errors can only be identified by model calibration and verification, although some gense of the relative importance of model error was gained by comparing results to predictions generated by a conceptually-dissimilar model, TOXFATE (Halfon, 1990).

### A. ANALYSIS OF MODEL UNCERTAINTY

Uncertainty analysis may be performed by either first-order or Monte Carlo methods, the latter being used for this application. The Monte Carlo method allows direct analysis of the consequence

of model parameter uncertainty, since the model can be used to compute changes in concentration resulting from changes in parameter values. This is achieved by performing repeated simulations of the model with randomly selected values from defined probability distributions. For each simulation parameter values are chosen at random from specified frequency distributions. This is known as the Latin Hypercube method (McKay et al., 1979). The process is repeated for a number of iterations sufficient to converge upon an estimate of the frequency distribution of the output variables. Monte Carlo analysis allows a probabilistic statement of uncertainty to be made because a distribution of model predictions is produced (Gardner and O'Neill, 1983). The output probability distributions for 200 and 300 iterations were found to be the same; 300 iterations were used to assure convergence in the Monte Carlo analysis.

In Monte Carlo analysis probability distributions are used to represent the confidence, or uncertainty, in the parameter values. The selection of the probability distribution for each model parameter depends upon the information used to estimate the parameter. No distinction was made between parameters that were uncertain and those that were variable, because the level 1 model simulates only average conditions in the lake. Several probability distributions were used to represent parameter uncertainty in this exercise. If a parameter was based upon a number of data values, then the probability distribution of the sample mean was used. More often, however, parameter uncertainty was specified as a range of values. If it was assumed that the parameter could be anywhere in the range with equal probability, a uniform probability distribution was used. If instead the range was interpreted as confidence limits, with the actual value probably lying in the middle of the range, the normal or

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study lognormal distribution was used. There are several reasons for preferring the lognormal distribution (Endicott et al., 1989). For a narrow range the lognormal distribution approximates the normal, but for wide range the lognormal distribution is centered on the geometric mean and produces fewer extremely large values. In practice, the lognormal distribution is preferred because values generated are always positive. In a previous study the sensitivity of the Monte Carlo analysis to the assumed parameter distribution was investigated (Endicott et al., 1989). It was concluded that the choice of uncertainty probability distribution for the most sensitive model parameter (photolysis rate constant) did not significantly affect the results of Monte Carlo analysis.

The parameterization of the mass balance model followed the methods described above; details of the parameterization may be found in a report (Endicott et al., 1990). Probability distributions were also estimated for the parameters to quantify uncertainty in the values. System-specific parameterization is summarized in Table 1; the chemical-specific parameterization is presented in Tables 2, 3 and 4. Uncertainty was expressed in terms of the coefficient of variation (CV), a normalized measure of variability. For normal distributions, the coefficient of variation is the standard deviation ( $\sigma$ ) divided by the mean ( $\mu$ ):

$$CV = \frac{\sigma}{\mu}$$

For lognormal distributions the coefficient of variation is defined (Aitchison and Brown, 1969) as:

PARAMETER	UNITS	MEAN VALUE	CV	DISTRIBUTION
Volume	m <sup>3</sup>	1.68E+12		constant
Interfacial Area	m <sup>2</sup>	1.95E+10		constant
Flow	m³/s	6770	0.109	lognormal
Suspended Particle Concentration	mg/l	1.2	0.0932	lognormal
Sedimented Particle Concentration	mg/l	270000	0.266	lognormal
Particle Settling Velocity	⊒/đ	1	adjusted sediment fluxes	to balance particle
Particle Resuspension Velocity	mm/yr	0.741	0.430	lognormal
Particle Sedimentation Velocity	mm/yr	0.889	0.426	lognormal
Diffusive Exchange Coefficient	.cm/d	0.1	0.642	lognormal
Suspended Particle f <sub>ac</sub>		0.15	0.0937 -	legnormal
Sedimented Particle f <sub>oc</sub>		0.0323	0.236	normal
Water Column NSOM Conc.	mg/l	4	0.239	lognormal
Sediment Solids Density	gm/ml	2.4		constant
Solids Loading	kg/day	1.4E+07	adjusted water col fluxes	to balance umn particle

# TABLE 1. LAKE ONTARIO MODEL PARAMETERS

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

TABLE 2	2.	SELECTED	LOG	K <sub>ow</sub>	VALUES	FOR	CHEMICALS	0F	INTEREST
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CHEMICAL	log(K <sub>ow</sub> )	CV of K <sub>om</sub>
Chlordane	6.00	0.693
DDT	6.00	0.289
Dieldrin	5.50	0.990
нсв	5.84	0.475
Mirex	7.14	0.612
ocs	6.20	0.990
PCB-3	5.46	0.262
PCB-4	5.89	0.287
PCB-5	6.28	0.301
PCB-6	6.74	0.301
PCB-7	7.12	0.274
PCB-8	7.51	0.270
TCDD	6.76	0.422

Great Lakes Monograph No. 4

192

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TABLE 3. SELECTED VOLATILIZATION PARAMETERS FOR CHEMICALS OF INTEREST (10°C)

CHEMICAL	H (Pa/M)	CΛ	K1 (m/d)	cv	Kg (m/d)	cv	kv (m/d)	C
Chlordane	1.29	0.641 *	1.07	0.410	181	0.208	0.0910	0.617
DDD	0.311	0.641 *	1.10	0.410	186	0.211	0.0241	0.674
DDE	1.83	0.641 *	1.11	0.409	188	0.211	0.129	0.586
DDT	0.267	0.743	1.08	0.410	174	0.203	0.0194	0.760
Dieldrin	0.0284	0.976	1.09	0.410	177	0.204	2.13E-3	1.02
нсв	12.5	0.0880	1.26	0.407	201	0.219	0.577	0.227
Mirex	(0.102 -	9.31) **	1.00	0.408	188	0.211	0.0657	0.523
ocs	3.29	0.641 *	1.12	0.411	170	0.199	0,213	1.74
PCB-3	9.16	0.602	1.21	0.408	202	0.219	0.476	0.420
PCB-4	6.35	0.779	1.17	0.408	196	0.217	0.364	0.558
PCB-5	5.15	0.931	1.14	0.409	191	0.213	0.305	0.639
PCB-6	4.46	1.47	1.11	0.409	186	0.211	0.267	0.978
PCB-7	3.00	1.36	1.08	0.410	182	0.208	0.191	0.961
PCB-8	3.02	1.15	1.06	0.410	1.78	0.206	0.188	0.872
TCDD	1.85	0.396	1.12	0.409	1.78	0.204	0.124	0.403
	Phe width oq uniform	of the 95% probabili	confid ty dist	ence lir ributior	uits are for Mi	one ord rex II cl	ler of mag losen.	yn i tude.

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

CHEMICAL	kp (1/d)	DISTRIBUTION	CV
Chlordane	0		
DDT	7.9E-4	lognormal	1.73*
Dieldrin	4.2E-6	lognormal	1.73
нсв	2.1E-5	lognormal	1.73
Mirex	5.4E-5	lognormal	1.73
ocs	0		
PCB-3	0		
PCB-4	0		
PCB-5	0		
PCB-6	0	-	-
PCB-7	0		
PCB-8	0		
TCDD	2.3E-3	loguniform ov (2.3E-4 - 0.0	er 13)

TABLE 4. TRANSFORMATION (PHOTOLYSIS) RATES FOR CHEMICALS OF INTEREST

The 95% confidence limits are ± factor of 10.

Great Lakes Monograph No. 4

$$CV = \sqrt{e^{\sigma_l^2} - 1}$$

where  $\sigma_l$  = standard deviation of the natural logarithm of the parameter value.

B. RESULTS

Deterministic and Monte Carlo simulation runs were made with unit loadings of 1 kg/day. Sample Monte Carlo output histograms, in this case for TCDD, are presented in Figure 2. "Count " in the figure is the frequency of model predictions lying in a particular concentration interval, from a total of 300 Monte Carlo realizations. The model output distributions produced by Monte Carlo analysis were approximately lognormal for all chemicals. Reproducibility of the Monte Carlo output distributions was verified. The logarithmic mean, coefficient of variation (CV) and 95% confidence intervals of the distribution of model predictions are presented in Table 5. The confidence limits represent the model uncertainty as determined by Monte Carlo analysis. The logarithmic means of the Monte Carlo output distributions agree with the corresponding deterministic predictions. The variability of water and sediment concentrations are generally similar for each chemical, with CVs in the range of 0.2 to 0.7. Because the steady-state model relationship between total loading and concentration is linear, these predictions can be proportioned for any other total load to the lake. The load-concentration relationships can also be represented graphically, as shown in Figure 3.

The variability of model output may be compared to input parameter variability, to indicate whether input errors are accumulated or attenuated by the model. For each chemical, the

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study



Figure 2. Monte Carlo Output Distribution for TCDD

Great Lakes Monograph No. 4

# TABLE 5. SUMMARY OF MONTE CARLO RESULTS

## Predicted Steady State Concentrations for Total Lake Loading of 1 kg/day

CHEMICAL	DISE	OLVED W	ATER (p	g/l)Q	SORE	ED SEDIM	ENT (ng	g/g)
	log Mean	. <b>CV</b>	(95%	CI)	log MEAN	CV	(959	5 CI)
Chlordane	171	0.538	63.8	460	36.3	0.503	14.3	92.2
DDT	140	0.608	46.8	422	30.1	0.629	9.71	93.2
Dieldrin	387	0.661	119	1260	48.8	0.368	24.3	98.0
нсв	67.8	0.239	42.5	108	12.2	0.671	3.68	40.2
Mirex	77.6	0.710	22.2	272	53.4	0.451	23.0	124
ocs	111	0.487	44.9	274	29.0	0.596	9.84	86.3
PCB-3	87.0	0.345	44.2	171	10.5	0.728	2.94	37.9
PCB-4	93.8	0.436	41.4	212	17.7	0.703	5.12	61.4
PCB-5	90.3	0.473	37.4	218	25.9	0.567	9.20	72.9
PCB-6	75.9	Q.609	25.2	228	34.5	0.592	11.8	101
PCB-7	66.5	0.658	20.5	216	44.7	0.460	18.9	105
PCB-8	<b>_50.6</b>	0.640	16.0	159 -	50.6	0.403	23.7	108
Aroclor 1248	94.9	0.260	57.5	157	23.9	0.325	12.8	44.4
Aroclor 1254	87.1	0.354	44.4	171	32.7	0.369	16.2	65.8
TCDD	67.2	0.584	23.2	194	31.1	0.581	10.8	89.5

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study





Great Lakes Monograph No. 4

input parameter CVs were compared to the output concentration CVs. For water and sediment concentrations, the output CVs were generally similar or somewhat smaller than the input parameter CVs, indicating that input errors do not significantly accumulate through the mass balance model. For example, the large uncertainties in volatilization rate constant for DDT, dieldrin and mirex are not reflected in proportionately greater output variabilities of water and sediment concentration for those chemicals.

#### C. IDENTIFICATION OF CRITICAL PARAMETERIZATION UNCERTAINTY

Given that uncertainty in model predictions is large and, hence, confidence in predictions is low, how can the situation be improved? Aside from estimating the confidence intervals for model predictions, Monte Carlo analysis may be used to examine how confidence in model predictions is improved by reducing or eliminating uncertainty (variability) in the model parameters. An application of such analysis would be to prioritize research efforts intended to improve the accuracy of model predictions by accurately measuring one or more parameters. The degree of correlation observed between model inputs and outputs indicates the relative importance of input parameter uncertainty in contributing to predicted concentration variability. The Monte Carlo method is modified by simply redefining the uncertainty in the parameter or parameters of interest, and comparing the results to the original (base case) output distribution.

DDT, a chemical with significant variability in water and sediment concentration predictions, will be used to illustrate the method. Cross-correlation analysis of the base case Monte Carlo run identified the  $\log K_{\infty}$  regression error,  $\log K_{\infty}$  and the rates of transformation, volatilization and sedimentation as the

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study 199

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parameters most responsible for model variability. Three test cases, representing different levels of parameter uncertainty reduction, were prepared:

Case 1:	eliminate $\log K_{w}$ regression error (used to
	represent uncertainty in $K_{x}$ )

- Case 2: eliminate  $\log K_{r}$  regression error and uncertainty in  $k_{er}$ ,  $k_{r}$  and  $v_{r}$
- Case 3: eliminate  $\log K_{\infty}$  regression error and uncertainty in  $k_i$ ,  $k_i$ ,  $2v_i$ , and  $\log K_{\infty}$

Eliminating variability would be equivalent to perfectly accurate parameterization. A fourth case tested the impact of load uncertainty upon predictions:

Case 4: base case uncertainty plus uncertainty in the chemical load

Monte Carlo analysis was applied to each of these cases. The results, in terms of logarithmic mean and CV for the distribution of water predictions, are presented in Table 6. The first three cases test the impact of sequentially removing variability in the model parameters most affecting output variability. Variability in predicted water concentration is reduced 30% by eliminating the  $\log K_{\infty}$  regression error, and by 90% by additionally eliminating variability in  $k_{c}$ ,  $k_{c}$  and  $v_{c}$ . Eliminating variability in  $\log K_{\infty}$  has only marginal impact upon the uncertainty of predicted water concentrations.

CASE	log Mean	CV	95% CI
base case	140	0.608	46.8 - 422
case 1	146	0.492	58.4 - 363
case ?	176	0.089	148 - 210
case 3	177	0.069	155 - 203
case 4	139	0.771	36.6 - 532

## TABLE 6. MONTE CARLO OUTPUT FOR TESTS OF PARAMETER VARIABILITY REDUCTION FOR DDT

Dissolved water concentration (pg/l)

To this point, all model predictions have been made with a constant unit load. One should not lose sight of the fact that chemical loading is, in fact, another uncertain input to the model. Case 4 tests the significance of an uncertain load upon output variability. Loading is treated as having a lognormal is treated as having a lognormal probability distribution with a CV of 0.428 (the width of the 95% confidence interval for the loading distribution is a factor of five, similar to that for other important model inputs). The impact of load variability upon predicted water concentrations is significant; variability is increased by 60% over the base case.

The results of the parameter variability reduction analysis for DDT may be extended to the other toxic chemicals. Figure 4 illustrates the contribution of variability in key model parameters to variability in water concentrations. The square of the correlation coefficient, r is an estimate of the fraction of

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study



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Figure 4. Sources of Uncertainty in Water Concentration Predictions

Great Lakes Monograph No. 4

output variability attributable to each uncertain parameter. Variability is controlled by chemical loss rates  $(k_r, k_e$  and  $v_b$ ) and hydrophobicity ( $\log K_{er}$  regression and  $\log K_{er}$ ) although the relative importance of each parameter varies from chemical to chemical. In this figure the chemicals are ordered according to hydrophobicity; there is a general trend of increasing significance in partitioning uncertainty (" $K_{er}$  error") and a declining significance of volatilization and transformation rate for the more hydrophobic chemicals.

### D. IMPLICATIONS OF UNCERTAINTY ANALYSIS FOR MODEL APPLICATION

The uncertainty analysis performed on the "level 1" mass balance model indicates that predicted steady-state water and sediment chemical concentrations are confident to within about a factor of ten. This represents a large uncertainty in comparison to the potential accuracy of a calibrated model, where an accuracy on the order of ± 50% may be achieved. However, even with the factor-of-ten uncertainty, the results of the "level 1" model have apparently proven useful for preliminary applications in the Lake Ontario Toxics Management Plan. For instance, the load-concentration predictions confirm that virtual elimination, the stated goal of the Toxics Management Plan, must be achieved to meet stringent water quality criteria being developed for the Plan (Zafonte, 1990). Mass balance modeling will play a continual role in guiding toxics management efforts by predicting the effectiveness of loading reductions.

Even if model uncertainties were too large for predictions to be useful, the analysis of uncertainty is useful to identify critical uncertain parameters, which may be prioritized for further research investigation.

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

### E. IMPROVEMENTS

This mass balance application could be improved in a number of ways. Most importantly, the influence of non-steady state conditions and specification of atmospheric concentration and exchange, independent from loading, should be incorporated in the model results. Load-concentration diagrams incorporating these effects as well as parameterization uncertainty are being developed, to provide additional insight to the simulation of this critical relationship. Figure 5 illustrates how the linear steady-state load-concentration relationship, and its confidence limits based upon uncertainty analysis, compare to results under more complex and realistic conditions.

### VI. PROSPECTS FOR REDUCING PARAMETERIZATION UNCERTAINTY

Reducing parameterization uncertainty in mass balance models will require the development of a research strategy combining (1) the determination of critical process descriptions and parameters (including field measurement and verification) with (2) the further development of comprehensive data sets for model calibration, verification and post-audit. Critical parameterization uncertainties may be identified by the application of uncertainty analysis as well as by testing the sensitivity of model predictions to different process descriptions. More experimental process research will allow more advanced process descriptions to be used, as will more powerful computer resources. However, modelers will still rely upon the experience gained by calibration and verification to reduce parameterization uncertainty.

Figure 5. Impact of System Lag Time and Constant Air Concentration Upon Load-Concentration Relationships



Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

## VII. UNRESOLVED ISSUES/QUESTIONS

- A. WHAT UNCERTAINTY IS INTRODUCED BY COMMON ASSUMPTIONS IN MASS BALANCE MODELS?
  - 1. Equilibrium partitioning
  - 2. Mixed-layer sediment model
  - Constant settling/resuspension/deposition particle fluxes
  - 4. Completely-mixed water column
  - 5. Single sediment compartment
  - Single, constant air concentration (C<sub>s</sub>) driving air-to-water chemical fluxes
- B. DO UNCALIBRATED AND/OR SIMPLISTIC MASS BALANCE MODELS HAVE VALUE FOR DECISION MAKING?
- C. ARE THERE BETTER WAYS TO ESTIMATE/PRESENT MODEL UNCERTAINTY?

# MASS BALANCE NOMENCLATURE

$V_{1}$ , $V_{2}$	=	Water column and sediment layer volumes $[L^3]$
<i>C</i> <sub>1</sub> , <i>C</i> <sub>2</sub>	2	Chemical concentrations in water column and sediment $[M/L^3]$
W	-	Chemical loading rate
Q	3	Flow rate through lake
<i>C</i> <sub>3</sub>		Chemical concentration in water column segment 3 [M/L <sup>3</sup> ]
Q31	<b>=</b>	Flow rate from water column segment 3 to segment 1 $[L^3/T]$
E'31	=	Bulk dispersion coefficient between segments 3 and 1 [L <sup>3</sup> /T]
K <sub>f</sub>	=	Diffusive exchange coefficient between water column and sediment [L/T]
A	=	Interfacial area between segments [L <sup>2</sup> ]
$f_{4l}, f_{bl}, f_{cl}$	3	Dissolved, bound (to non-settling organic matter), and sorbed (to settling particles chemical fractions in water column
f 42, f 52, f 52	-	Dissolved, bound, and sorbed chemical fractions in sediment layer
<i>n</i> <sub>2</sub>	#	Porosity of sediment layer
<i>k</i> ,	-	Volatilization mass transfer coefficients [L/T]
k,	=	Transformation/degradation rate of chemical [1/T]
k <sub>de</sub>		Transformation/degradation of rate of chemical in sediment [1/T]
C <sub>ag</sub>	-	Gas phase atmospheric chemical concentration [M/L <sup>3</sup> ]
C.	=	Total atmospheric chemical concentration $[M/L_3]$
V <sub>wet</sub>	-	Wet deposition velocity [L/T]
V <sub>dry</sub>	=	Dry deposition velocity [L/T]

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

	H		=	Dimensi	onless	Henry'	s consta	ant		
	ν <sub>2</sub> , ν <sub>1</sub> , ν <sub>1</sub>		=	Solids	settli	ng velo	city, re	esuspensi	on	
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# PROCESS PARAMETERIZATION UNCERTAINTY IN MODELS OF TOXICS IN THE GREAT LAKES

## PART 2: Process Parameterization in Models of Chemical Accumulation in Aquatic Animals

Prepared for the Workshop on Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes

> Buffalo, New York February 3-5, 1992

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## SUMMARY OF THE PROCESSES

**Exposure to the Chemical.** The flux rate of chemical to an aquatic animal is dependent on the chemical concentrations in the two media contacting the animal; water and food. Bioaccumulation models explicitly specify the dissolved chemical concentration and, sometimes, the chemical concentration in the detritus or phytoplankton at the base of the food chain as forcing functions. In general, these concentrations are areal averages for a defined segment of the water body. Where concentrations vary spatially, such that a migrating animal experiences a significant temporal variation in exposure to the chemical, several segments are defined. Seasonal migration is accounted for by moving the migrating animal between the segments.

The model is usually directed to a top predator fish of commercial or sport fishing value. The chemical concentration in the prey of this fish is dependent on the concentration in the food of the prey, and so on to the base of the food chain. Thus, to correctly specify the chemical concentration in the food of the top predator it is necessary to define the food web below the top predator and to sequentially calculate concentrations from the base of the food chain through the top predator. The definition of the food web is generally simplified by using a single species as a representative of all the prey species inhabiting closely related ecological niches.

Uptake and Loss of Chemical. The accumulation of toxic chemicals by aquatic animals is generally described by the following equation (1):

$$-\frac{dv_i}{dt} = K_{ui}c + \sum_{j=1}^n \alpha_{ij}C_{ij}v_j - (K_i + G_i)v_j \qquad (1)$$

where

 $v_i$  = concentration of chemical in species i in the food chain [ug/g(w), where g(w) is grams wet weight]

 $K_{ui}$  = rate constant for chemical uptake across the gill of species i [L/g(w)-d]

 $K_i$  = rate constant for excretion of chemical by species i (1/d)

 $\alpha_{ij}$  = efficiency at which ingested chemical from prey j is assimilated by species i

 $C_{ij}$  = ingestion or consumption rate of species i on species j [g(w)prey/g(w)pred/d]

 $G_i$  = growth rate of species i (g(w)/g(w)/d)

c = dissolved chemical concentration (ug/L)

n = number of species (including different year classes of a single species) preyed on by species i

The first term of Equation (1) represents the direct uptake of chemical by the animal from water. The second term represents the flux of chemical into the animal through feeding. The third term is the loss of chemical due to desorption and excretion plus the change in concentration due to growth. Equation (1) is applied to each of the animals that comprise the food web. For the upper levels of the food web changes in chemical concentration with age are sometimes significant and each year class of the species at these levels is modeled separately.

The rate constant  $K_{ui}$  parameterizes the transport of chemical across the gill to the blood. It is essentially the body weight normalized product of a mass transfer rate constant and the gill surface area. Several equations have been proposed to define the mass transfer rate constant based on mechanistic descriptions of the processes occurring at the gill surface (2-4). A simpler approach that does not require explicit definition of the mass transfer rate defines  $K_{ui}$  from the uptake rate for oxygen (1). Oxygen transfer rate is defined by the respiration rate of the animal and the oxygen concentration of the water ( $c_{O2}$ ):

$$K_{ulo_2} = \frac{r'_i}{c_{o_2}} \tag{2}$$

where  $r_i$  is the respiration rate in units  $gO_2/g(w)$ -d. Mechanistically this uptake rate may be described in terms of a mass transfer rate constant at the gill ( $K_{UO_2}$ ), the gill surface area (A), and the weight of the animal, W:

$$K_{uio_2} = \frac{K_{uo_2}A}{W}$$
(3)

Similarly, the mass transfer rate for a chemical is:

$$K_{ui} = \frac{K_{ii}A}{W} \tag{(\div)}$$

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

If equations (2) and (3) are equated, solved for A/W and substituted into equation (4), the uptake rate of the toxicant may be written as:

$$K_{ui} = \frac{K_{Li}}{K_{Lio_2}} \frac{r'_i}{c_{o_2}}$$
(5)

From this equation it follows that the uptake rate of a chemical can be computed from the respiration rate of the animal if the ratio of the mass transfer coefficients for the chemical and oxygen is known. Estimates of the ratio may be obtained from measurements of chemical and oxygen uptake efficiencies. The ratio of mass transfer coefficients is equal to the ratio of uptake efficiencies measured when the body burden of the animal is zero.

The excretion rate constant  $K_i$  includes all of the processes by which the animal is able to depurate chemical. For most organic chemicals it appears that the gill is the major site of depuration (5) and that  $K_{ui}$  and  $K_i$  define the rates of uptake and elimination for a reversible diffusive process. The ratio of these rate constants defines the equilibrium condition for this process, or what is generally called the bioconcentration factor, N.

It has been demonstrated that the bioconcentration factor of neutral organic chemicals measured in laboratory studies can be predicted from the  $K_{OW}$  of the organic chemical (6-9). In fact, it appears that the lipid-normalized bioconcentration factor is approximately equal to  $K_{OW}$ , at least for log  $K_{OW}$  values up to about 6. Therefore, it is possible to compute N for a neutral organic chemical from the  $K_{OW}$  of the chemical and the fraction lipid of the animal (fL), i.e.,:

$$N_i = f_{\perp i} K_{ow} \tag{6}$$

Using this value of N for animal i in the food chain and the computed value of  $K_{ui}$  it is then possible to compute  $K_i$ :

$$K_i = \frac{K_{ui}}{N_i} \tag{7}$$

#### Great Lakes Monograph No. 4

Above a log  $K_{OW}$  value of 6 a loss of linearity has been observed in correlations of N and  $K_{OW}$  (10-12). N appears to reach a maximum in the log  $K_{OW}$  range 6.5 to 7 and begins to decrease at higher log  $K_{OW}$  values. Several hypotheses exist to explain this behavior. Gobas et al. (5) have reviewed and evaluated these hypotheses and have concluded that the dominant effects are the increasing importance of fecal elimination and a decrease in freely dissolved chemical (due to complexation with dissolved and colloidal organic material) as  $K_{OW}$  increases. The latter effect is an experimental artifact dependent on the concentration of organic matter in the water used in the experiment. Fecal elimination was shown to lower the slope of the N- $K_{OW}$  relationship but not cause a decreasing relationship.

Transfer of chemical across the gut wall is defined by an empirical constant; the chemical assimilation efficiency. This constant specifies the fraction of ingested chemical assumed to be transferred from the gut to the animal. The rate at which chemical is ingested is defined by the rate of food consumption  $C_i$  and the concentration of chemical in the food. The food consumption rate is calculated from the rate of energy usage. Energy usage is estimated from the rates of production and metabolism of body tissue by the animal. Growth rate defines the net production of body tissue (g(w)/g(w)/d). The rate of metabolism of body tissue,  $R_i$ , may be computed from the respiration rate by: 1) stoichiometricaily converting respiration from  $gO_2/g(w)/d$  to gC/g(w)/d; 2) converting carbon to dry weight by assuming all animals are 40 percent carbon on a dry weight basis; and 3) converting dry weight to wet weight using observed ratios. Given the caloric density of the animal's tissue in units cal/g(w),  $\lambda$ , the energy usage rate,  $P_i$ , is then;

$$P_i = \lambda_i (R_i - G_i) \tag{8}$$

Dividing  $P_i$  by the fraction of ingested energy that is assimilated, a, yields the rate of energy intake by the animal. The rate of consumption of food,  $C_{ij}$ , is the energy intake rate divided by the caloric density of the food,  $\lambda_i$ :

$$C_{ij} = \frac{\lambda_i R_i + G_i}{\lambda_j \alpha}$$
(9)

Where food is a lower trophic level animal, differences in caloric density are assumed to be related to differences in wet weight:dry weight ratio, i.e., the caloric density of dry tissue is assumed to be the same for predator and prey. The caloric density ratio in Equation (9) is

thus replaced by the ratio of the dry weight fractions of the predator and its prey. Doing this ignores differences in body composition, particularly differences in lipid content. While such differences do effect the caloric density ratio, they are much less significant than the effect of differences in water content.

For deposit feeding animals consumption is based on carbon rather than energy.  $C_i$  is computed as above except that caloric density is not considered,  $P_i$  is expressed as gC/g(w)/d using the conversion factors mentioned above and food assimilation efficiency, a, is interpreted as the fraction of ingested carbon that is assimilated. In the application of Equation (1)  $v_j$ , the chemical concentration in the food (i.e., sediment), is expressed as ug/gC.

Respiration and growth are defined by empirical relationships. Respiration is a specified function of weight and temperature, T, of the form:

$$R = \beta W^{\gamma} e^{\rho T}$$
(10)

An exponential growth rate that varies with age is assumed (see 1). The respirationweight-temperature function for each species is determined by regression of data from laboratory respiration studies. The growth rates are established from field observed length-weight, length-age and weight-age relationships.

## UNCERTAINTY IN PROCESS DESCRIPTION

Migration. Migration may be defined as the movement of fishes between three types of habitats: one suitable for reproduction, one suitable for feeding and one suitable as a refuge in periods of unfavorable abiotic or biotic conditions (13). The movement between habitats is strongly influenced by the diel pattern of light and dark, the annual temperature and photoperiod cycles and the age and sex of the fish. In addition, the habitats suitable for feeding and refuge may be different at different stages in the life cycle.

The general migration patterns of individual fish species can be determined from tagging studies. These data generally indicate that migration timing and extent vary greatly between individual fish. In addition, some species include a sub-population that do not participate in migration. For example, the Green Bay walleye include a sub-population that permanently resides in the Fox River and a sub-population that migrates between the river and the bay. Other species, such as stripped bass, only begin migrating after age two or three (14).

The variability of migration behavior within a fish population can make assignment of a single deterministic migration pattern problematic. An unquantified bias may be introduced into the model. Further, the comparison of computed and observed fish contaminant concentrations ignores possible differences between the movement history of the fish sampled and the migration pattern defined in the model. Also, the variability of migration behavior increases the variance of the contaminant concentration distribution in the population, particularly if the different habitats have significantly different exposure concentrations. These factors increase the inherent uncertainty of the calibrated model.

Migration uncertainty limited calibration in the modeling of Kepone in the stripped bass food web of the James River Estuary (15). Two migratory species were included in that model: stripped bass and Atlantic croaker. The croaker has a well-defined migration pattern and the model calibration was excellent Figure 1). The migration pattern of the stripped bass is more complicated because immature fish do not migrate and the age at which migration begins may vary between individual fish and between year classes (14). In addition, the timing of the migratory movements is somewhat variable. As a result, the temporal Kepone pattern in the stripped bass is less structured than that of the Atlantic croaker and the model calibration is weaker (Figure 1).

Additional aspects of migration that are not considered in the current models are the changes in energy expenditure and energy uptake. The activity level of the fish is increased during migration and feeding may cease. Fat reserves may be used and stored chemical may be released. The significance of these changes to the seasonal and annual contaminant concentration profile are uncertain.

Food Web Structure. The computed contaminant concentration in top predator fish is largely dependent on the structure of the food web. Of particular importance are the number of trophic levels in the food web and the association of the components of the food web with the water column and sediment environments.





The bioaccumulation models are generally built around the classical description of the aquatic food web; phytoplankton to zooplankton to forage fish to top predator fish. This description is now viewed as inadequate because of the demonstrated contribution of the bacteria to nanozooplankton to microzooplankton "microbial loop" to carbon flow (16). Figure 2 shows the classical food web and the positioning of the microbial loop. The significance of this microbial loop in contaminant accumulation has not been established. In freshwater systems the ability of cladocerans to graze the full microbial loop may reduce the impact that biomagnification through the loop has on higher trophic levels. In estuarine/marine systems the plankton food web is fairly linear and the microbial loop may be of greater importance.

Contaminated sediments are a dominant toxic chemical problem, and the pathway of chemical movement between these sediments and top predator fish is an important component in toxic chemical models. This pathway generally involves forage fish who feed at or near the sediment surface. These forage fish generally consume a variety of benthic animals including insect larvae, amphipods, oligochaetes, gastropods and bivalves. The benthic animals may live on the surface of the sediment or they may dwell in the subsurface. They may be suspension feeders, surface-sediment feeders or sub-surface sediment feeders. The water they take in for respiration and the particles they ingest may be characteristic of the overlying water column, the sediment or the benthic boundary layer. They may be selective feeders; ingesting particles whose physical characteristics and contaminant concentration are different from those of the bulk particulate material. Defining a prototype benthic food web component is difficult because of the variety of characteristics and because benthic ecologists have not yet determined these characteristics at the level required to define the contaminant exposure of the benthic animals. Uncertainty in defining the exposure regime of the benthic animals is of particular concern in model projections in which the rate of contaminant concentration change in the sediment is different from that in the water.

Transfer Across the Gut Wall. The equation describing contaminant uptake from food specifies the assimilation efficiencies of food and contaminant as independent parameters. Recent experiments with zooplankton (17) and polychaetes (18) indicate that these parameters are directly related and suggest that it is the contaminant released as tissue is digested that is available for transfer across the gut wall. Thus, model uncertainty could be reduced if empirical relationships between food and contaminant assimilation efficiencies were available.



Great Lakes Monograph No. 4

If only contaminant in digestible food is available for uptake, then the use of bulk food contaminant concentration is also a cause for uncertainty. The significance of this uncertainty will depend on the variability of the digestible food:bulk food contaminant concentration ratio. It may be most important for deposit feeding animals. These animals preferentially digest the more-labile components of the organic matter on the particles they ingest. A large fraction of this organic matter is bacterial. It is likely that the bacteria associated with sediment particles have a lower contaminant concentration per unit carbon weight than does the bulk sediment carbon; a consequence of their being composed of simpler carbon compounds than the bulk sediment carbon. Also, bacterial particulate organic carbon (POC) is essentially new carbon, whereas bulk sediment carbon is old carbon that has resistantly bound contaminant. Thus, only a small fraction of the ingested chemical is probably available for uptake and this fraction probably varies depending on the age of the sediment and the density of bacteria on the particles.

Growth. Growth rates used in the models are usually annual average values determined from measured weight and age data for fish from the water body being modeled. Because growth varies seasonally, the models tend to underestimate growth during the summer and overestimate growth during the winter. This error may not be significant because growth affects both uptake and loss of chemical concentration. An increase in growth will increase the rate of intake of contaminated food; but it will also increase the rate at which chemical is diluted by increasing body weight. Figure 3 shows computed annual cycles of PCB in three year old Green Bay walleye assuming either that the annual growth occurs uniformly throughout the year or only during the time that temperature exceeds 10°C. The hypothetical temperature profile used in the calculations is also shown. Restricting growth to a growing season results in a greater concentration wariability through the year, but the differences between the calculations are small. The differences, however, do not include the effects of the annual variability in fish lipid content, nor the effects of seasonal variability in exposure concentration. The growth related annual cycle of storage and metabolism of fat reserves will affect the rate at which contaminants are excreted and alter the contaminant patterns shown in Figure 3. Unfortunately, in most cases insufficient data are available to describe the lipid reserve cycle. In rivers, the seasonal flow variability will result in a seasonal exposure concentration variability. Depending on whether the contaminant is derived from an external source or from bed sediment, the exposure concentrations will be highest or lowest during the summer low flow period when maximum growth is occurring. This variability will tend to increase the effect of the seasonal growth variability.



Great Lakes Monograph No. 4

 $\overline{222}$ 

# UNCERTAINTY IN PROCESS DESCRIPTION PARAMETER VALUES

Bioaccumulation models have numerous coefficients that define the processes being described. Using the models developed by the Manhattan College group (1, 15, 19-21) as the paradigm, the coefficients are presented in Table 1. Previous applications of the models have indicated that sensitivity to the various coefficients is dependent on the particular contaminant being modeled. However, the contaminants may be categorized in three groups: metals (with the exception of mercury) and low to moderately lipophilic organic chemicals, lipophilic organic chemicals and super-lipophilic organic chemicals.

Models of Metals and Low to Moderately Lipophilic Chemicals. Most metals (excepting mercury), and organic chemicals with log  $K_{OW}$  values less than 5, do not biomagnify. The metals tend to be poorly absorbed from food (22), possibly because they are generally stored in relatively inert components of cells which are not readily digested (23). The lower  $K_{OW}$  organic chemicals are excreted sufficiently fast to limit their accumulation (20). Models of these contaminants are most sensitive to coefficients associated with uptake across the gill and excretion.

Respiration, contaminant:oxygen mass transfer ratio and bioconcentration factor are the controlling parameters. Since uptake from food is not important for this group of chemicals and excretion rate is usually greater than growth rate, the steady-state concentration is defined by the bioconcentration factor and the concentration of bioavailable contaminant in the water. Thus, uncertainty in the bioconcentration factor tends to dominate the model uncertainty. As discussed above, the bioconcentration factor for neutral organic chemicals can be estimated from the lipid content of the animal and the  $K_{OW}$  of the chemical. This relationship is probably accurate to factors of 2 or 3. Metals bioaccumulation factors are much more difficult to predict because of species specific enzymatic responses to metal accumulation.

Models of Lipophilic Organic Chemicals. Organic chemicals with log  $K_{OW}$  values in the range of 5 to 7 or 8 do biomagnify, with the extent of biomagnification increasing as  $K_{OW}$  increases (19-21, 24). This phenomenon occurs because uptake from food becomes an increasingly more significant flux of chemical to the animal as  $K_{OW}$  increases (20, 24). The increasing importance of food as a contaminant source is due to an increasing contaminant partition coefficient for the plankton and sediment that constitute the base of the food web. Thus, the coefficients associated with food consumption, the assimilation

efficiency across the gut wall and the partition coefficient at the base of the food web are the significant model parameters for these chemicals. In addition, growth dilution is important because the high lipid solubility of these chemicals results in very low aqueous blood concentrations and low excretion rates (19, 21).

Gut wall assimilation efficiency values used in the models are derived from laboratory experiments. We have compiled over two hundred published values encompassing a variety of organic compound classes including polychlorinated and polybrominated biphenyls, chlorinated insecticides, benzenes, toluenes, napthalenes and diphenylethers, polyaromatic hydrocarbons and polychlorinated dibenzo-p-dioxins and dibenzofurans. Approximately half of these values are for PCB congeners. Viewed in total the data are highly variable. Efficiencies range from less than 0.1 to greater than 0.9 with little correlation to  $K_{ow}$ , although values at the lowest and highest  $K_{ow}$  values tend to be toward the low end of the range. Within study variability is generally significantly less than cross study variability, suggesting that much of the variability is due to differences in methodology or differences between individual animals or species.

The significance of assimilation efficiency across the gut wall is illustrated by a model calibrated to PCB homologs 3, 4, 5 and 6 in the lobster and flounder food chains of New Bedford Harbor (21). The flounder is part of a largely benthic based food web. Sediment forms the base of this food web and its PCB homolog concentrations were fixed by observation. Polychaetes represented the deposit feeding animals that constitute the bulk of the flounder diet. To compute a PCB homolog distribution consistent with that observed in the polychaetes and the flounder the assimilation efficiency was decreased as PCB chlorine level increased. PCB homolog 3 through 6 assimilation efficiency values observed in laboratory studies exhibit little evidence of a dependency on chlorine level, although wide crossstudy variability exists (21). Calibration was not possible if the same assimilation efficiency value was used for all homologs. For example, applying the homolog 3 calibration assimilation efficiency to the other homologs results in an over prediction of as much as one and one-half orders of magnitude (Figure 4).

Values of the partition coefficient at the base of the food chain are generally calculated from  $K_{ow}$ . For non-living particulate material, a particulate carbon weight based partition coefficient is generally used. The uncertainty associated with this coefficient has



Figure 4. Computed and observed New Bedford Harbor flounder PCB homolog bioaccumulation factors in relation to K<sub>OW</sub>.

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

been discussed Part 1 of this paper. Published data indicate that the plankton bioconcentration factor for organic chemicals (BCF) is proportional to  $K_{OW}$  up to a log  $K_{OW}$  of about 5. At higher  $K_{OW}$  values the BCF tends to be independent of  $K_{OW}$ , although significant variability exists. For example, BCFs for various PCB congeners in Lake Ontario plankton show no trend with  $K_{OW}$  (Figure 5). These data were reported by Oliver and Niimi (25). Laboratory phytoplankton BCF data for PCB congeners (26-28) and other organic chemicals (29) show the same behavior (Figure 5b). Phytoplankton PCB data collected at various times over a year as part of the Green Bay Mass Balance Study (Debra Swackhammer, University of Minnesota, unpublished data) show relationships to  $K_{OW}$  that vary from a tendency to plateau at higher  $K_{OW}$ s to a continuous proportionality to  $K_{OW}$ .

Recent laboratory experimental studies (Debra Swackhammer, University of Minnesota, unpublished data) suggest that the depression of phytoplankton BCF below its expected linear relationship to  $K_{ow}$  is related to growth rate. These data show that as growth rate is decreased the BCF values approach the values defined by Equation (6). The mechanisms controlling the BCF-growth relationship have not been elucidated.

Alternately, it is possible that the observed BCF- $K_{OW}$  relationship is an artifact caused by the use of total dissolved chemical, rather than bioavailable dissolved chemical, in the BCF calculation. Dissolved or colloidal organic matter present in the water would decrease the bioavailable fraction of measured dissolved chemical in proportion to its concentration and the  $K_{OW}$  of the chemical. Such a "third phase" is known to cause apparent independence of partitioning and  $K_{OW}$ .

The significance of uncertainty in the phytoplankton bioconcentration factor value is illustrated using a steady-state bioaccumulation model of PCBs in the Lake Ontario lake trout food chain (30). A linear food chain of phytoplankton, zooplankton, alewife and lake trout was assumed. Consistent with the observed data, the phytoplankton bioconcentration factor was assumed to be constant across all of the PCB congeners. The observed and computed bioaccumulation factors for each level of the food chain are shown in relation to  $K_{OW}$  in Figure 6. Two computed lines are presented: the calibrated model with constant phytoplankton bioconcentration factor and a model that assumes a linear relationship between phytoplankton bioconcentration factor and  $K_{OW}$ . At log  $K_{OW}$  values less than 6 the models are nearly identical at all trophic levels above the phytoplankton. Above 6 the models begin to diverge. At log  $K_{OW}$  of 7 the computed concentrations in lake trout differ by about one order of magnitude. Assuming that the bioaccumulation factor varies



Figure 5. Relationship between observed BCF of various chemicals in phytoplankton and  $K_{\rm OW}$ .



Figure 6. Observed and computed PCB congener bioaccumulation factors in the Lake Ontario Food Chain. Solid line is the calibrated model. Broken line assumes phytoplankton BAF is proportional to Kow. Data from reference 25.

228

Great Lakes Monograph No. 4

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between the limits of the two assumptions used here, the use of either assumption may not be appropriate. However, use of a time-variable partitioning requires deriving a valid mechanistic description of the uptake and loss of contaminant by phytoplankton.

Models of Super-Lipophilic Organic Chemicals. Super-lipophilic organic chemicals ( $\log K_{ow} > about 7 \text{ to } 8$ ) have been shown to have reduced uptake efficiencies at both the gill and the gut, and appear to biomagnify somewhat less than the lipophilic chemicals. However, the available data are too limited to adequately model these chemicals. In particular, the lack of detectable dissolved concentrations tends to dominate the uncertainty of the models. Also, the limited data on gill versus gut uptake do not allow an assessment of the relative importance of these uptake routes and, thus, the relative significance of their associated parameters. Additional laboratory and field data are needed before a credible uncertainty analysis can be conducted for this class of chemicals.

#### PROSPECTS FOR REDUCING UNCERTAINTY

The most significant uncertainties relate to the following processes or parameters:

- (1) the species and contaminant specific uptake efficiencies and bioconcentration factors of metals,
- (2) gut wall assimilation efficiencies of lipophilic and superlipophilic chemicals and their relationship to food assimilation efficiency,
- (3) phytoplankton bioconcentration factors,
- (4) sources of contaminants to benthic animals,
- (5) migration, and
- (6) seasonal changes in animal growth and lipid content

Of these, the second, third and fourth on the list probably have had the most impact on the models that have been developed and are likely to be the most important sources of uncertainty in the modeling contemplated for Lake Ontario.

The greatest reduction in overall model calibration uncertainty would probably result from better quantification of gut wall contaminant assimilation efficiency. Laboratory studies directed to understanding the relationship between the assimilation efficiencies of contaminant and food will probably significantly reduce the uncertainty of this parameter.

The uncertainty associated with the phytoplankton bioconcentration factor could most easily be reduced by field sampling sufficient to describe seasonal variability in this parameter. In the short term these field data would be used to specify phytoplankton contaminant concentration in the model calibration. These data should also be coupled with laboratory studies in an effort to develop mechanistic descriptions of contaminant uptake and loss in phytoplankton. Such descriptions are necessary to reduce uncertainty in projections to conditions not represented by the calibration data set.

Food webs that include a benthic animal component are subject to uncertainty associated with defining a prototype for that component. A means to reduce that uncertainty may be to analyze stomach contents of the animals feeding on the benthos. However, not all animals in the stomach are easily identified and a biased estimate could result from this type of data. Stable isotope data may allow a determination of the extent to which the bottom feeding animals are receiving water column associated or sediment associated carbon in their diet. Such data could be used to define the sources of contaminant to the benthic component.

## UNRESOLVED ISSUES/QUESTIONS TO BE DISCUSSED AT THE WORKSHOP

A number of issues have been raised in this paper and, although, several approaches to reducing uncertainty are suggested, most issues remain unresolved. These issues do not encompass all of the parameterization related sources of uncertainty in models of chemical accumulation in aquatic animals, however, they provide a basis for discussion. A summary of the principal questions follows.

- (1) What are the major sources of uncertainty in models of super-lipophilic chemicals?
- (2) What types of experiments are needed to progress towards a mechanistic description of contaminant uptake and loss by phytoplankton?

- (3) What types of experiments are needed to permit the development of a better description of gut wall contaminant assimilation efficiency and its relationship to food assimilation efficiency?
- (4) How can migration be better quantified; both in terms of the time-location relationship and changes in bioenergetics that occur during migration?
- (5) How can the differences in chemical content between digestible and bulk food be determined, particularly for deposit-feeding animals?
- (6) What is the significance of the "microbial loop" in models of biomagnifying chemicals?
- (7) How should the uptake and loss (bioconcentration) of metals be described? Should species-specific enzymatic processes be considered?
- (8) How important is fat storage and metabolism to contaminant dynamics, and how should this process be described in the models?
- (9) How significant are seasonal differences in growth rate to contaminant uptake and loss, particularly in river systems?

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Process	Coefficients
Oxygen Uptake Rate	Weight & Temperature Dependent Respiration Rate Dissolved Oxygen Concentration
Food Consumption Rate	Respiration Rate Growth Rate Food Energy Assimilation Efficiency Dry Weight:Wet Weight Ratio of Predator and Prey
Contaminant Uptake Rate Across the Gills	Oxygen Uptake Rate Contaminant:Oxygen Mass Transfer Coefficient Ratio
Contaminant Uptake Rate Across the Gut	Food Consumption Rate Contaminant Assimilation Efficiency
Whole Body Contaminant Excretion Rate	Animal Lipid Content Contaminant Uptake Rate Across the Gills Contaminant Bioconcentration Factor
Dilution of Contaminant Concentration	Growth Rate
Contaminant Accumulation in Plankton at Base of the Food Web	Partition Coefficient
Food Web Structure	Number of Prey Fraction of Food Consumption on Each Prey
Migration	Annual Pattern of Movement Between Spatial Compart- ments

Table 1. Coefficients Included in the Food Chain Model

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Organic Contaminants In Lake Ontario, 1968-1991: A Review and a Data Base

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## Abstract

Introduction

concentration data of toxic organic contaminants in Lake Ontario (Throughout the search, it was often discovered that the same data were published in a variety of sources. Whenever possible the primary article is referenced, and exclusion of the secondary sources has occurred, thus the reference list is much smaller than those read and reviewed). This search has been limited to "published" data readily available to the scientific community. Of interest are the concentrations in water, sediments (at the bottom and in suspension), and in biota (plankton, benthos and fish) over time. All these concentrations have now been collected into a freely distributable data base (The data base also contains food web information in energy terms). We have found that comprehensive data, meaning data in all compartments mentioned above and for many years, exist only for very few chemicals; mainly PCBs, dleidrin, Mirex, DDT, and some chlorobenzenes. Data exist for many other chemicals (various di-, tri-, tetra- and penta chlorobenzenes, HCBD, HCE, various PCB congeners, lindane, OCS, PCP, chlorotoluenes, photomirex, PCT, TTCP, HCE, heptachlor epoxide and methoxychlor) but in a much more limited form. The existence of published data is important to modellers for comparison with their simulations, and to statisticians involved with trend analysis. As of December 1991, most available data are for 1990 and previous years: this lag is due to both analytical work and publication delay.

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Approximately 500 publications have been reviewed for

In the past two decades the presence of toxic organic contaminants in Lake Ontario has been reported: hundreds of them might be present. Eadle (1984), Shear (1984), Strachan and Edwards (1984), Biberhofer and Stevens (1987), Thomas <u>et al.</u> (1987), Allan and Ball (1990) and the Government of Canada (1991) made comprehensive reviews of contaminants in the Great Lakes region.

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

One of the drawbacks, for modellers and statisticians alike, has been the lack of a readily available data base to compare simulations with and to assess trends. This review tries to overcome this problem. An extensive literature search on the organic contamination of Lake Ontario was performed. Approximately 500 papers were reviewed. A small part of the data can be made available in printed form here, but all data are freely available in PARADOX, QUATTRO PRO, LOTUS 1-2-3, ASC II, and DBASE II, III, III PLUS, or IV formats.

The data base contains information not only on concentrations of toxic contaminants in Lake Ontario but also information on the food web (Schito and Halfon, 1992). Once a fate model, TOXFATE (Halfon and Oliver, 1990; Halfon, 1992a), was completed, we realized that the food chain models in TOXFATE (plankton - alewife - lake trout; benthos - sculpin - lake trout) did not include the complex food web realities in the lake. Transfer of contaminants to the top fish predators was dependent on the knowledge of how energy collected by plankton was transferred to the top five predators in the lake. This food web has been published and its data are also available.

As a final point we acknowledge the fact that the systematic name of <u>Pontoporeia</u> <u>hovi</u> has recently been changed to <u>Diporeia</u> sp. (Bousfield, 1989). However, in this paper we refer to it as <u>Pontoporeia</u> <u>hovi</u>, the name commonly used by Great Lakes researchers.

Methods

Data presented here are available in the literature (1970 to 1991). A major drawback is that not much recent data was discovered in the literature. Our database contains information as current as 1990 (published up to 1991). As a norm, contaminant data take about a year to be analyzed in a laboratory. Publication usually adds a two year delay.

Data sources

Throughout the search, it was often discovered that the same data were published in a variety of places. Whenever possible the primary article is referenced, and exclusion of the secondary sources has occurred. The number of articles cited here is therefore much smaller than those read and reviewed. Data from the same government agencies are not always published in the same report series and had to be tracked down.

#### Data omission from data base

Sometimes it was necessary to omit published concentrations from the data base. Potential data was rejected if the year of sampling was not explicitly stated in the article, or if the concentration in an organism was not measured on a whole organism basis. For example, concentrations measured in the muscle portion or a standard fish fillet were not included. In the event that the reported concentration was based on a sampling plan that spanned a number of years, the most recent year was assumed to be the year that the concentration level occurred.

This approach has provided a data base that spans a period of approximately two decades and contains the observations from many different researchers. Therefore, the concentrations of toxicants in the various compartments are not always directly comparable; one must consider the experimental conditions associated with each reported value. Furthermore, some older data were measured using obsolete analytical methods. Some very high concentrations published in the 1970's have been weeded out, but some are still present. Users should carefully screen old data before using them.

# Data conversion to a standard basis

The reported data were converted to ng/L (for water) and ng/g dry weight (for all other compartments). This conversion was necessary to be able to compare data with simulations. When necessary, concentrations on a wet weight basis were converted to dry weight. This conversion was done using the following assumptions: the dry weight of phytoplankton and zooplankton is 10% of wet weight, the dry weight of benthas is 15% of wet weight (Strayer and Liken, 1986), the dry weights of <u>Mvsis</u> and <u>Pontoporeia</u> are 21 and 27% of wet weight, respectively (Evans and Landrum, 1983), and the dry weights of all fishes are 25% of wet weight.

# The Data Base

Separate datafiles were constructed for each of the following: fishes, <u>P</u>. <u>hovi</u>, benthos, <u>Mvsis</u>, plankton, sediments, and water. All datafiles include "standard" fields with the sampling location and year, number of samples, toxicant, reported concentration, and converted concentration. There is also a reference datafile, which is linked to the above datafiles by a field called "reference #". In addition to the "standard" fields, the fish datafile includes fields for fish age, weight, and length. These fields are used when data are available from the literature.

The datafiles for benthos and  $\underline{P}$ , <u>hovi</u> are essentially the same. Both datafiles include the "standard" fields, as well as a field to record the depth of the site sampled. The benthos datafile includes one additional field: a field to record the type of benthic organism used in the contamination monitoring (for example, an amphipod or oligochaete).

The plankton datafile contains the "standard" fields, in addition to

fields for organism type (i.e. zooplankton, phytoplankton, or both, and minimum size of the organisms, if available), depth of site, and depth of sampling below the water surface.

The <u>Mysis</u> datafile is more limited than the plankton datafile; it does not contain fields to record either the depth of site, or the depth of sampling. These fields were eliminated from the datafile because no researcher identified these variables in their reports.

The water datafile contains information regarding the site depth, in addition to the information provided by the "standard" fields.

Besides the "standard" fields, the sediment datafile contains a field called "sediment type" that is used to specify whether the contaminant is measured in suspended, surficial, or bottom sediments. Depth of site, depth of sampling below water surface, and depth into sediments are also recorded when available.

Results

Even though the data base includes many contaminants, to reduce the amount of printed information, Tables 1 to 8 present only concentrations of polychlorinated biphenyls (PCBs), dieldrin, Mirex, and chlorobenzenes (1,2,3-TCB, 1,2,3,4-TeCB, and HCB) in Lake Ontario water, sediments, and aquatic life (excluding macrophytes). These contaminants were chosen since they are found widely in Lake Ontario, the data base is fairly complete, and past loadings have been computed (Halfon and Oliver, 1990) to drive a model. Since most information of interest to readers is the data base, the results section only mentions points of interest, such as the availability (or missing measurements) of recent data in selected compartments.

Surprisingly, a full data base is only available for a few of the many contaminants in Lake Ontario. Concentrations of BHC, various chlorobenzenes, chlordane, DDT and metabolites, dieldrin, hexachlorobutadiene, lindane, Mirex, octachlorostyrene, photoMirex, and total PCBs in Lake Ontario biota, water, and sediments were found in the literature. Less information is available on the concentrations of other chemicals (for example dioxins, pentachlorotoluene, and TTCP) in various compartments. Tables 1 through 6 provide a summary of the occurrence of selected contaminants in Lake Ontario biota. Water concentrations are summarized in Table 7 and concentrations in Lake Ontario sediments are in Table 8.

## **PCBs**

**Biota** 

The largest numbers of data were found for PCBs in biota, water, and sediments. Table 1 shows concentrations in biota. Most data are averages reported in the literature: authors of each report should be contacted for the raw data. Figure 1 shows PCBs

Great Lakes Monograph No. 4

concentrations in lake trout; this species is among the best documented. The fish datafile contains close to 100 records on concentrations of PCBs in spottail shiner, slimy sculpin, rainbow smelt, alewife, brown trout, lake trout, and rainbow trout (Haile <u>et al</u>., 1975; Borgmann and Whittle, 1983; Whittle and Fitzsimons, 1983; Shear, 1984; Strachan and Edwards, 1984; Whittle, 1986; Oliver and Niimi, 1988; Stevens, 1988; Niimi and Oliver, 1989; Borgmann and Whittle, 1991). Data for PCBs in alewife are very scarce; only one value was reported for 1982 (Oliver and Niimi, 1988), while all other reported values were for 1973 (Haile <u>et al</u>., 1975). Niimi and Oliver (1989) were the only researchers that reported concentrations of PCBs in brown and rainbow trouts.

PCB concentrations in <u>P. hovi</u> (Borgmann and Whittle, 1983; Whittle and Fitzsimons, 1983; Oliver and Niimi, 1988; Stevens, 1988) have been reported from 1978 through to 1985 (with the exception of values for 1982 and 1984). No literature was located with concentrations after 1985.

PCBs in Lake Ontario benthos have been investigated thoroughly (Cook and Johnson, 1974; Haile <u>et al.</u>, 1975; Fox <u>et al.</u>, 1983; Strachan and Edwards, 1984; Oliver and Niimi, 1988; Stevens, 1988). The majority of data is for amphipods or oligochaetes and reported for the years 1972 to 1985.

The datafile for <u>Mysis</u> contains 11 records on the concentration of PCBs. These values have come from a variety of sources (Borgmann and Whittle, 1983; Whittle and Fitzsimons, 1983; Oliver and Niimi, 1988; Stevens, 1988), and cover the years 1977 to 1984 (Fig. 2).

The majority of concentrations found for PCBs in other planktonic organisms were from years before 1980 (Haile <u>et al</u>., 1975; Borgmann and Whittle, 1983; Strachan and Edwards, 1984; Stevens, 1988). Whittle and Fitzsimons (1983) report two concentrations in net plankton sampled from the lake in 1981. A concentration from 1982 was reported by Oliver and Niimi (1988).

Water

Concentrations of PCBs in water are contained in approximately 30 records (Fig. 3). The vast majority are samples taken in 1973 (Haile <u>et al.</u>, 1975) or 1983 (Biberhofer and Stevens, 1987; Stevens, 1988). There is one record for each of the years 1975 (Glooschenko and Glooschenko, 1975), 1984 (Oliver and Niimi, 1988), and 1986 (Stevens and Neilson, 1989). Serge L'Italien (NWRI, Burlington) provided a large amount of data (to 1990) not yet available in the literature.

#### Sediments

A concentration of PCBs in suspended sediments from Lake Ontario in 1986 (Oliver and Niimi, 1988) was the only value found. PCB

concentrations in surficial sediment (0 - 3 cm) are available for the years 1968 (Frank <u>et al.</u>, 1979), 1974 (Thomas, 1983), 1981 (Bourbonniere <u>et al.</u>, 1986; Oliver <u>et al.</u>, 1987), and 1982 (Oliver <u>et al.</u>, 1989). Measurements in the upper 2 cm were reported by Stevens (1988) for the year 1981. Note that caution must be used when comparing data in the sediment datafile; earlier collection techniques, and storage of samples has apparently yielded concentrations lower than the actual ones.

*Dieldrin* This chemical is water soluble and is quite widespread in Lake Ontario. The data base is quite comprehensive.

Biota

About 75 records exist in the fish datafile. A large portion of these records is the result of lake trout (Fig. 4) monitoring (Whittle and Fitzsimons, 1983; Shear, 1984; Whittle, 1986; Borgmann and Whittle, 1991). Concentrations of dieldrin (Table 2) in alewives were only found for 1973 (Haile <u>et al</u>., 1975). Over half the records for slimy sculpin was for the year 1973 (Haile <u>et al</u>., 1975), while only one record was for data collected in the 1980s (Stevens, 1988).

Concentrations of dieldrin in the amphipod <u>P. hovi</u> were only found for the years 1978 to 1983 (Whittle and Fitzsimons, 1983; Stevens, 1988). Likewise, no data was found in the literature for dieldrin concentrations in benthos sampled after 1983 (Cook and Johnson, 1974; Haile <u>et al.</u>, 1975; Stevens, 1988).

The literature search provided eight concentrations of dieldrin in <u>Mysis</u>, from the years 1977 to 1982 (Whittle and Fitzsimons, 1983; Stevens, 1988). No source provides insight into the more recent concentrations in this zooplankter (Fig. 5). Data regarding the concentration of dieldrin in other planktonic species is also limited before 1982 (Haile <u>et al.</u>, 1975; Whittle and Fitzsimons, 1983; Stevens, 1988).

#### Water

Of the 27 records in the water datafile that are concerned with the concentrations of dieldrin (Fig. 6), eight refer to samples taken in 1973 (Haile <u>et al.</u>, 1975), and 18 to samples taken in 1983 (Biberhofer and Stevens, 1987; Stevens, 1988). The remaining record is for samples taken in 1986 (Stevens and Neilson, 1989). Vast amounts of data (to 1990) not yet available in the literature was provided by Serge L'Italien (NWRI, Burlington).

#### Sediments

The database on dieldrin concentrations in Lake Ontario sediments is extremely limited. No published values were found for suspended sediments. Concentrations in surficial sediments (0 - 3 cm) were only reported for 1968 (Frank <u>et \_al</u>., 1979) and 1974 (Thomas, 1983). Concentrations in bottom sediments (depth into sediment not specified) from various locations throughout the lake were reported for 1973 (Haile <u>et al.</u>, 1975).

## Chlorobenzenes

Chlorobenzenes enter Lake Ontario mainly from the Niagara River (Halfon and Oliver, 1990). Halfon (1992b) reports a large source of dichlorobenzenes from Toronto. Dichlorobenzenes are used in public lavatories as disinfectants. Several chlorobenzenes (Tables 3 to 5) are found in Lake Ontario: trichlorobenzenes (TCB), tetrachlorobenzenes (TeCB), pentachlorobenzene (QCB) and hexachlorobenzene (HCB). Data for these chemicals is quite extensive and the computation of past loadings since 1909 (Halfon and Oliver, 1990) allows the driving of fate models. A comparison of model simulations and data is in preparation (Halfon and Schito, 1992). The following section shows some interesting data features.

#### Biota

Data on specific chlorobenzenes concentrations in Lake Ontario biota are incomplete. Data on HCB are the most widely published. Chlorobenzenes in biota have been measured since 1980 (Oliver and Nicol, 1982; Fox <u>et al</u>., 1983; Oliver and Niimi, 1988; Niimi and Oliver, 1989), with the exception of 1978 values reported for HCB in coho salmon, and lake (Fig. 7) and rainbow trouts (Niimi, 1979).

Fox <u>et al</u>. (1983) reported chlorobenzene concentrations in both amphipods and oligochaetes collected from the western basin in 1981. Oliver and Niimi (1988) sampled benthic organisms from the Niagara basin in 1985, and they reported concentrations much smaller than those reported by Fox <u>et al</u>. (1983). These two are the only articles found that pertain to chlorobenzenes concentrations in benthos from Lake Ontario. Tables 3 to 5 present the available data for 1.2.3-TCB, 1.2.3.4-TeCB and HCB.

Fox <u>et al</u>. (1983) and Oliver and Niimi (1988) investigated the level of chlorobenzenes contamination in <u>Mysis</u>. HCB (Fig. 8), 1,2,3-TCB, and 1,2,3,4-TeCB concentrations were reported for samples taken in 1981 (Fox <u>et al</u>., 1983) and 1982 (Oliver and Niimi, 1988).

Water Concentrations of HCB (Fig. 9), 1.2.3-TCB, and 1.2.3.4-TeCB in Lake Ontario water have been reported by Oliver and Nicol (1982), Biberhofer and Stevens (1987), Stevens (1988), Oliver and Niimi (1988), and Stevens and Neilson (1989). The majority of the chlorobenzene records in the water datafile have come from samples collected in 1983 (Biberhofer and Stevens, 1987; Stevens, 1987), while a limited number is for samples from 1984 (Oliver and Niimi, 1988), and 1986 (Stevens and Neilson, 1989). The 1983 open lake concentrations of specific chlorobenzenes reported by Biberhofer and Stevens (1987) are well within the 1983 ranges reported by Stevens (1988). Serge L'Italien (NWRI, Burlington) provided large amounts of data (to 1990) not yet available in the literature.

Sediments Some chlorobenzenes concentrations in suspended sediments have been reported for 1982 (Oliver and Chartton, 1984) and 1986 (Oliver and Niimi, 1988). As for bottom sediments, Oliver and Nicol (1982) were the only researchers to report on chlorobenzene vertical distribution within a core sample. They reported concentrations based on a core sample taken from the Niagara basin in 1980.

Concentrations of chlorobenzenes in surficial sediments (0 - 3 cm) were only located in the literature for 1981 (Oliver and Nicol, 1982; Bourbonniere <u>et al.</u>, 1986; Oliver <u>et al.</u>, 1987), and 1982 (Oliver <u>et al.</u>, 1989). For 1981, Oliver <u>et al.</u> (1987) reported values that were all lower than the lowest values reported by Bourbonniere <u>et al.</u> (1986) also for 1981. Stevens (1988) summarized chlorobenzene concentrations in samples of surficial sediments (top 2 cm only) collected in 1981.

Overall Contamination

Table 6 shows Mirex concentrations in Lake Ontario biota. Mirex is a chemical extensively studied by Kaiser (1978) and his co-workers. Comba <u>et al</u>. (1992) has recently computed past loadings of Mirex since 1952 and therefore this chemical is a good object for modeling work.

Tables 7 and 8 summarize water and bottom sediment concentration of the PCBs, Mirex, dieldrin and chlorobenzenes. As mentioned above, more data on other chemicals are available in the data base. Also in these tables we note the lack of published recent concentrations.

Discussion

A large time gap exists between data collection, analysis and publication. Some selected data might be published with short delays, but complete data bases that include all water, sediment, and biota compartments, take many years before being properly

published. A complete data set exists for few chemicals. Even when a complete data base exists, often some compartments are rarely sampled, for example, contaminants in alewives. A careful review of the data base shows that even water concentrations are not often reported in the literature. A flurry of activity has occurred in the early 1980's when the importance of the contaminants problems was realized and large data collections programs were organized. These large efforts must be repeated in the 1990's. All compartments must be measured for as many contaminants as possible to obtain reference data. Since these efforts are very expensive, we recommend that these be repeated only every ten year. Smaller surveillance programs on toxic contaminants should be done every year and should focus on compartments where few data are available even now. Some compartments were contaminant data are missing are the alewives, benthic organisms, all salmonids but lake trout, plankton and suspended sediments. We will try to keep this data base as current as possible and we invite any interested parties, including agencies and individuals to provide us with the organic contaminant data in a prompt fashion so that they can be made available in electronic form to the scientific community at large.

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

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Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study



**Total PCBs Concentration** 

Figure 1.Mean whole fish concentrations (ng/g dry weight) of total PCBs in lake trout from Lake Ontario. See Table 1 for values and sources.



### **Total PCBs Concentration**

Figure 2.Mean concentrations of total PCBs in <u>Mysis relicta</u> from Lake Ontario. See Table 1 for values and sources.

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study



Figure 3.Mean concentrations (ng/L) of total PCBs in water from Lake Ontario. See Table 7 for values and sources.



**Dieldrin Concentration** 

Figure 4.Mean whole fish concentrations (ng/g dry weight) of 'dieldrin in lake trout from Lake Ontario. See Table 2 for values and sources.

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study



## Great Lakes Monograph No. 4



Figure 6.Mean concentrations (ng/L) of dieldrin in water from Lake Ontario. See Table 7 for values and sources.

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- **Lake Ontario Case Study** 



Great Lakes Monograph No. 4



## HCB Concentration

Figure 8.Mean concentrations (ng/g dry weight) of HCB in <u>Mysis</u> <u>relicta</u> from Lake Ontario. See Table 3 for values and sources.

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study



Great Lakes Monograph No. 4

TABLE 1.

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# Summary of the concentration of PCBs in various Lake Ontario biota. (See footnotes for comments and assumptions).

	· · · · · · · · · · · · · · · · · · ·		Co	nverted Co	nc. <sup>2</sup>
Organism	Location	Year	Mean Concentration <sup>1</sup>		(ng/g dry) Source <sup>3</sup>
plankton			, , , , , , , , , , , , , , , , , , ,		
net >153um	Lake Ontario	1972	7.17 ug/g dry weight	7170	Stevens, 1988
		1977	0.19 ug/g dry weight	190	
		1978	0.26 ug/g dry weight	260	
		1979	0.15 ug/g dry weight	150	
net >64um	midlake, Lake Ontario	1973	10.6 ug/g dry weight	10600	Haile et al., 1975
	Hamilton, Lake Ontario	1973	3.4 ug/g dry weight	3400	
	midlake, Lake Ontario	1973	3.6 ug/g dry weight	3600	
	midlake, Lake Ontario	1973	6.0 ug/g dry weight	6000	
	Cobourg, Lake Ontario	1973	7.6 ug/g dry weight	7600	x
	Deep Hole, Lake Ontario	1973	11.8 ug/g dry weight	11800	
net	Lake Ontario	1973	6.1 ug/g dry weight	6100	Strachan and Edwards, 1984
		1975	1.9 ug/g dry weight	1900	
net >153um, n <sup>4</sup> =2	Eastern Lake Ontario	1981	110 ng/g dry weight	110	Whittle and Fitzsimons, 1983
net >153um, n=5	Western Lake Ontario	1981	280 ng/g dry weight	280	
n=3, 10m depth	Lake Ontario	1982	50 ng/g wet weight	500	Oliver and Niimi, 1988
zooplankton >153u	m				
n=20. 1m depth	Eastern Lake Ontario	1979	0.20 ug/g dry weight	200	Borgmann and Whittle, 1983
n=4, 1m depth	Western Lake Ontario	1979	0.31 ug/g dry weight	310	
<u>Mvsis</u> relicta					
n=25	Lake Ontario	1977	0.31 ug/g dry weight	310	Stevens, 1988
n=25		1978	0.44 ug/g dry weight	440	
n=32		1979	0.64 ug/g dry weight	640	
n=15		1980	0.76 ug/g dry weight	760	
n=25		1981	0.60 ug/g dry weight	600	
n=22		1982	0.58 ug/g dry weight	580	
n=12	Eastern Lake Ontario	1979	0.29 ug/g dry weight	290	Borgmann and Whittle, 1983
n=4	Western Lake Ontario	1979	0.39 ug/g dry weight	390	-
n=12	Eastern Lake Ontario	1981	150 ng/g dry weight	150	Whittle and Fitzsimons, 1983
n=5	Western Lake Ontario	1981	580 ng/g dry weight	580	

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

n=2	Lake Ontario	1984	330 ng/g dry weight	. 330	Oliver and Niimi, 1988
benthos					
•					
n=3 n=11	Western Lake Ontario	1972 1983	0.98 ug/g dry weight 1.57 ug/g dry weight	980 1570	Stevens, 1988
	Oswego, Lake Ontario	1973	97 ng/g dry weight	97	Cook and Johnson, 1974
no details	Lake Ontario	1973	0.47 ug/g dry weight	470	Strachan and Edwards, 1984
mixed, includes <u>P</u> . <u>hovi</u>	Rochester, Lake Ontario Hamilton, Lake Ontario	1973 1973	341 ng/g dry weight 976 ng/g dry weight	341 976	Haile <u>et al</u> ., 1975
amphipods no details	Lake Ontario	1975	9.0 ug/g dry weight	9000	Strachan and Edwards, 1984
amphipods mixed, includes <u>P. hovi</u>	Western Lake Ontario	1981 1981 1981 1981 1981 1981 1981 1981	2600 ng/g dry weight 4700 ng/g dry weight 5200 ng/g dry weight 5300 ng/g dry weight 6600 ng/g dry weight 7900 ng/g dry weight 11000 ng/g dry weight 17000 ng/g dry weight	2600 4700 5200 5300 6600 7900 11000 17000	Fox <u>et al</u> ., 1983
-li					
no details	Lake Ontario	1975	1.9 ug/g dry weight	1900	Strachan and Edwards, 1984-
oligochaetes no details	Western Lake Ontario	1981 1981 1981 1981 1981 1981 1981 1981	930 ng/g dry weight 1400 ng/g dry weight 1500 ng/g dry weight 1800 ng/g dry weight 2000 ng/g dry weight 2400 ng/g dry weight 2600 ng/g dry weight 5300 ng/g dry weight	930 1400 1500 1800 2000 2400 2600 5300	Fox <u>et al</u> ., 1983
oligochaetes					
n=6	Niagara basin	1985	180 ng/g wet weight	1200	Oliver and Niimi, 1988
Pontoporeia hovi					
n=16 n=13 n=5 n=5 n=11	Lake Ontario	1978 1979 1980 1981 1983	1.73 ug/g dry weight 1.84 ug/g dry weight 1.26 ug/g dry weight 1.89 ug/g dry weight 1.35 ug/g dry weight	1730 1840 1260 1890 1350	Stevens, 1988
n=4 n=8	Western Lake Ontario Eastern Lake Ontario	1979 1979	1.67 ug/g dry weight 1.70 ug/g dry weight	1670 1700	Borgmann and Whittle, 1983

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Great Lakes Monograph No. 4

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n=5	Western Lake Ontario 1	981	1378 ng/g dry weight	1378	Whittle and Fitzsi	mons 1983
n=13	Eastern Lake Ontario 1	981	1849 ng/g dry weight	1849		
n=6	Niagara basin 1	985	790 ng/g wet weight	2926	Oliver and Niimi,	1988
			-			
spottail shiner						
	Lake Ontario 1	975	0.69 ug/g wet weight	2760	Shear, 1984	
	19	977	0.65 ug/g wet weight	2600	, 2001	
	19	978	0.32 ug/g wet weight	1280		
	19	979	0.15 ug/g wet weight	600		
	1	980	0.27 ug/g wet weight	1080		
n=5,58mm length	Glenora, Lake Ontario 19	975	111 ug/kg wet weight	444	Suns, 1986	
n=5.58mm length	Darlington Lake Ontario 19	975	420 ug/kg wet weight	1680		
n=6,54mm length	Presqu'ile Lake Ontario 10	075	505 ug/kg wet weight	2020		
n=5.58mm length	Twelve Mile Creek I ake On	) / _) 1f	1075	2020	) ug/kg wet weight	3560
n=3,36mm length	Darlington Lake Ontario 10	11 076	360 ug/kg wet weight	1440	, aging wer weight	3200
n=10,00mm longth	Burlington, Lake Ontario 19	970 077	922 ug/kg wet weight	2220		
n=9,55mm length	Humber Diver Lake Ontario	711	1077	2222	19 ug/leg wat waight	2077
n=0,02111111  length	Cabaurz Crack Lake Ontario		1977	22.	lo ug/kg wei weigin	1090
n=0,49 min length	Trustue Mile Creek, Lake Ontario		1970	2/1	Jug/kg wet weight	1206
n=8,51mm length	I weive Mile Creek, Lake On	10	1978	54	9 ug/kg wet weight	1390
n=8,00mm length	Credit River, Lake Ontario		1978	29	Jug/kg wei weight	∠300 11750
n=8,58mm length	Humber River, Lake Untario		1978	29.	sa ug/kg wet weight	11752
n=5,45mm length	Rouge River, Lake Untario		1979	84	ug/kg wet weigens	440
n=8,55mm length	Outlet River, Lake Ontario		1979	11.	2 ug/kg wet weight	448
n=8,49mm length	Presqu'ile, Lake Ontario 19	979	122 ug/kg wet weight	488	· • · · · ·	
n=8,56mm length	Credit River, Lake Ontario		1979	18	b ug/kg wet weight	744
n=8,53mm length	Bronte Creek, Lake Ontario		1979	18	8 ug/kg wet weight	752
n=3,49mm length	Gages Creek, Lake Ontario		1979	19	7 ug/kg wet weight	788
n=8,51mm length	Twelve Mile Creek, Lake On	nt	1979	27	l ug/kg wet weight	1084
n=8,60mm length	Humber River, Lake Ontario		1979	12	23 ug/kg wet weight	4892
n=7,61mm length	Duffrin Creek, Lake Ontario		1980	11	l ug/kg wet weight	444
n=7,48mm length	Twelve Mile Creek, Lake On	n	1980	14	B ug/kg wet weight	592
n=7,53mm length	Outlet River, Lake Ontario		1980	18	5 ug/kg wet weight	740
n=7,62mm length	Credit River, Lake Ontario		1980	238	3 ug/kg wet weight	952
n=7,47mm length	Burlington, Ontairo 19	980	250 ug/kg wet weight	1000		
n=6,62mm length	Humber River, Lake Ontario		1980	62	1 ug/kg wet weight	2484
n=7,57mm length	Ganaraska River, Lake Ont		1980	12	02 ug/kg wet weight	4808
n=6,54mm length	Twelve Mile Creek, Lake On	nt	1981	20:	5 ug/kg wet weight	820
n=6,62mm length	Humber River, Lake Ontario		1981	95	4 ug/kg wet weight	3816
n=5,68mm length	Mimico Creek, Lake Ontario	I.	1981	10	51 ug/kg wet weight	4204
n=6,54mm length	Wolfe Island, Lake Ontario		1982	12	1 ug/kg wet weight	484
n=7,49mm length	Outlet River, Lake Ontario		1982	12	8 ug/kg wet weight	512
n=7,48mm length	Welland Canal, Lake Ontario	2	1982	15	8 ug/kg wet weight	632
n=7,52mm length	Credit River, Lake Ontario		1982	18	3 ug/kg wet weight	732
n=4,56mm length	Oshawa Creek, Lake Ontario	)	1982	22	7 ug/kg wet weight	908
n=7,41mm length	Twelve Mile Creek, Lake On	nt	1982	27	9 ug/kg wet weight	1116
n=6,58mm length	Humber River, Lake Ontario		1982	· 35	3 ug/kg wet weight	1412
n=7,65mm length	Wolfe Island, Lake Ontario		1983	81	ug/kg wet weigbt4	
n=7,63mm length	Welland Canal, Lake Ontario	0	1983	22	9 ug/kg wet weight	916
n=7,64mm length	Twelve Mile Creek, Lake Or	nt	1983	23	6 ug/kg wet weight	944
n=7,60mm length	Credit River, Lake Ontario		1983	32	9 ug/kg wet weight	1316
n=7,57mm length	Burlington, Lake Ontario 1	983	375 ug/kg wet weight	1500		
n=7,68mm length	Humber River, Lake Ontario	· .	1983	53	7 ug/kg wet weight	2148
n=7,70mm length	Mimico Creek, Lake Ontario	)	1983	54	2 ug/kg wet weight	2168
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Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study 259

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n=6.66mm length	Mimico Creek, Lake Ontari	0	1983	572 u	g/kg wet weight	2288
n=7.58mm length	Wolfe Island, Lake Ontario		1984	90 ug	/kg wet weiß160	
n=7,43mm length	Outlet River, Lake Ontario		1984	112 u	g/kg wet weight	448
n=6.33mm length	Burlington, Lake Ontario	1984	113 ug/kg wet weight	452		
n=6.48mm length	Welland Canal, Lake Ontar	io	1984	157 u	ig/kg wet weight	628
n=6.54mm length	Twelve Mile Creek, Lake C	Ont	1984	267 u	ig/kg wet weight	1068
n=6.69mm length	Mimico Creek, Lake Ontari	0	1984	378 u	ig/kg wet weight	1512
n=7.57mm length	Weiland Canai, Lake Ontar	io	1985	255 0	ig/kg wet weight	1020
n=7.57mm length	Bronte Creek, Lake Ontario	)	1985	317 u	ig/kg wet weight	1268
n=4.57mm length	Twelve Mile Creek, Lake (	Ont	1985	337 ı	ig/kg wet weight	1348
n=7.41mm length	Burlington, Lake Ontario	1985	502 ug/kg wet weight	2008		
n=7.64mm length	Humber River, Lake Ontari	0	1985	-524 u	ig/kg wet weight	2096
n=5.74mm length	Toronto main STP. Lake O	nt	1985	676 u	ig/kg wet weight	2704
n=10,62mm length	Credit River, Lake Ontario		1986	1315	ug/kg wet weight	5260
	·			07.00		-d- 1004
	Lake Ontario	1975	0.69 ug/g wet weight	2760	Strachan and Edw	ards, 1984
		1976	1.3 ug/g wet weight	5200		
		1977	1.5 ug/g wet weight	6000		
		1978	1.1 ug/g wet weight	4400		
		1979	0.46 ug/g wet weight	1840		
		1980	0.31 ug/g wet weight	1240		
•						
slimy sculpin						
no details	Lake Ontario	1972	4.63 ug/g wet weight	18520	Stevens, 1988	
n0.00000000000000000000000000000000000		1972	1977	0.74	ng/g wet weight	2960
m=10,mean wet=5.10	/g		1070	1.09	ug/g wet weight	4360
n=3, mean wet=4.54g	7		1092	1.07	ug/g wet weight	6960
n=11,mean wet=7.47	/g		1902	1./4	agyg wer wergin	0,00
no details	Prince Edward Point	1973	1.58 ug/g wet weight	6320	Haile <u>et</u> <u>al</u> ., 1975	•••
	Hamilton, Lake Ontario	1973	2.89 ug/g wet weight	11560		
	Galloo-Stoney, Lake Ont	1973	3.33 ug/g wet weight	13320		
	Rochester, Lake Ontario	1973	4.32 ug/g wet weight	17280		
	Mexico Bay, Lake Ontario	1973	6.49 ug/g wet weight	25960		
	Olcott, Lake Ontario	1973	9.17 ug/g wet weight	36680		
n=53, mean dry=.66	g Eastern Lake Ontario	1979	3.82 ug/g dry weight	3820	Borgmann and W	hittle, 1983
· · · · · ·		1004		6400		1000
5 fish composite	Lake Untario	1980	1000 ng/g wet weight	0400	Oliver and Nilmi,	, 1988
rainbow smelt						
	T. I 0	1070	0.65	10600	Sharran 1000	
no details	Lake Untario	19/2	2.00 ug/g wet weight	10000	Sievens, 1988	
	• • • •	1984	1.73 ug/g wet weight	0920		
no details	Lake Ontario	1977	1.50 ug/g wet weight	6000	Shear, 1984	
		1978	1.82 ug/g wet weight	7280		
		1979	0.80 ug/g wet weight	3200		
		1980	1.12 ug/g wet weight	4480		
n=73,mean wet=24.4	4g Lake Ontario	1978	1.74 mg/kg wet weight	6960	Whittle 1086	
n=47,mean wet=28.3	3g		1981	0.00	mo/ko wet weight	3600
n=48,mean wet=31.9	9g		1982	1 66	moles wer weight	6640
n=36,mean wet=29.8	Sg		1983	1 /12	maka wat waish	5020
n=56,mean wet=21.9	90		1984	1.40	myrk wei weigni	1040
n=49,mean wet=17.2	2g		1985	0.55	maka wei weight	4040 2200
,				0.00	melve wet weight	2200

Great Lakes Monograph No. 4

260

I.

n=109,mean dry=4.22 n=50,mean dry=6.90	2g Eastern Lake Ontario Western Lake Ontario	1979 1979	2.38 ug/g dry weight 6.75 ug/g dry weight	2380 6750	Borgmann and Whittle, 1983
n=23,mean wet=18.3 n=12	g Western Lake Ontario Eastern Lake Ontario	1981 1981	858 ng/g wet weight 1000 ng/g wet weight	3432 4000	Whittle and Fitzsimons, 1983
20 fish composite 6 8-fish composite	Vineland, Lake Ontario Port Credit	1982 1986	1400 ng/g wet weight 620 ng/g wet weight	5600 2480	Oliver and Niimi, 1988
alewife					
no details	Prince Edward Point Mexico Bay, Lake Ontario Olcott, Lake Ontario Hamilton, Lake Ontario Galloo-Stoney, Lake Ont Rochester, Lake Ontario	1973 1973 1973 1973 1973 1973	0.14 ug/g wet weight 0.94 ug/g wet weight 1.73 ug/g wet weight 3.12 ug/g wet weight 3.81 ug/g wet weight 4.36 ug/g wet weight	560 3760 6920 12480 15240 17440	Haile <u>et al</u> ., 1975
12 fish composite	Lake Ontario	1982	1300 ng/g wet weight	5200	Oliver and Niimi, 1988
brown trout					
n=10,mean wt=1430 and Oliver, 1989	g	Vineland	d, Lake Ontario	1986	2380 ng/g dry weigha80
acho salmon				,	
cono samion				-	
n=206, mean dry=43	4g Western Lake Ontario	1 <b>97</b> 9	9.14 ug/g dry weight	9140	Borgmann and Whittle, 1983
no details	Lake Ontario	1977 1978 1979 1980	3.03 ug/g wet weight 3.00 ug/g wet weight 1.21 ug/g wet weight 2.3 ug/g wet weight	12120 12000 4840 9200	Shear, 1984
no details	Lake Ontario	1975 1976 1977 1979	0.69 ug/g wet weight 1.3 ug/g wet weight 1.5 ug/g wet weight 2.8 ug/g wet weight	2760 5200 6000 11200	Strachan and Edwards, 1984
n=10, total wt=3026	g Lake Ontario	1981	4.24 ug/g wet weight	16960	Whittle and Fitzsimons, 1983
n=9, mean wt=3330g and Oliver, 1989	5	Credit F	liver, Lake Ont	1986	4650 ug/kg dry weii6550
n=10, mean wt=1190	)g Vineland, Lake Ontario	1986	1970 ug/kg dry weight	1970	· .
lake trout					
n=216, mean dry=24 n=110, mean dry=17	6g Eastern Lake Ontario 7g Western Lake Ontario	1979 1 <b>979</b>	14.1 ug/g dry weight 20.7 ug/g dry weight	14100 20700	Borgmann and Whittle, 1983
no details	Lake Ontario	1977 1978 1979 1980 1981	4.95 ug/g wet weight 7.10 ug/g wet weight 3.79 ug/g wet weight 4.79 ug/g wet weight 2.82 ug/g wet weight	19800 28400 15160 19160 11280	Shear, 1984

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

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					· · · · · · · · · · · · · · · · · · ·	
n=32,mean wet=210	02g Lake Ontario	1977	8.00 mg/kg wet weight	32000	Whittle, 1986	
n=11,mean wet=120	00g		1978	5.06	mg/kg wet weight 20240	
n=72,mcan wet=200	68g		1979	4.73	mg/kg wet weight 18920	
n=82,mean wet=17	92g		1980	4.77	mg/kg wet weight 19080	
n=83,mean wet=15.	38g		1981	3.67	mg/kg wet weight 14680	
n=36,mean wet=18	62g		1982	5.87	mg/kg wet weight 23480	
n=46,mean wet=17	69g		1983	6.44	mg/kg wet weight 25/60	
n=47, mean wet=15	47g		1984	5.91	mg/kg wet weight 23040	
n=14,mean wet=17	14g		1985	2.80	mg/kg wet weight 11200	
n=10, age=4+yrs	Eastern Lake Ontario	1981	2370 ng/g wet weight	9480	Whittle and Fitzsimons,	1983
n=98, age=4+yrs	Western Lake Ontario	1981	3890 ng/g wet weight	15560		
n=10,mean wt=241 and Oliver, 1989	Og	Port C	redit, Lake Ont	1986	5 9970 ug/kg dry wengn70	Nii
o	Lake Ontaria	1077	5.84 ug/g wet weight	27360	Borgmann and Whittle	1991
48c=+A12	Lake Omario	1078	8 04 ug/g wet weight	32160	Dorgmann and Winnie,	
		1070	3 67 hala wet weight	14680		
no detaile	Cobourg Lake Optania	1080	3 31 ug/g wet weight	13740		
no derans	Eastern Lake Optatio	1020	2.51 ugg wei weight	11520		
	Hamilton Lake Ontario	1020	4.90 ug/g wet weight	19600		
	Vingston basin	1020	3 47 ug/g wet weight	13880		
	Lake Optimie :	1020	3.47 ug/g wet weight	15760		•
	Niagon Diver Lake Opt	1090	3.08 ug/g wet weight	15020		
	Port Credit Lake Ont	1080	5.35 ug/g wet weight	21000		
ngen lurr	I ake Ontario	1081	2.85 ug/g wet weight	11400		
age+y15	Earc Ontario	1087	5.31 ug/g wet weight	21240		
		1083	5.43 ug/g wet weight	21270		
		108/	4 84 ug/g wet weight	10360		
		1025	2.54 ug/g wet weight	10160		
		1004	2.54 ug/g wet weight	12520		
-		1980	3.13 ug/g wet weight	12020		
		1987	2.54 ug/g wet weight	13720		
	597 del alte Ontario	1091	2.05 wala wat weight	12000	Stoward 1099	
n=178 mean wet=1	460 0g	1901	1022	1000	367618, 1988	
n=144	1400.0g	1983	5.30 ug/g wet weight	21200		
rainbow trout n=12, mean wt=33 n=8, mean wt=114	80g Credit River, Lake Ont 0g	1986 Vin <del>c</del> ia	5660 ug/kg dry weight Ind, Lake Ontario	5660 198	Niimi and Oliver, 1989 6 1450 ug/kg dry weight	1450
n=8, mean wt=114 'In most cases only <sup>2</sup> All reported value	Og y mean concentrations report s converted to ng/g dry weig 1. dry weight of plankton	Vinela ed; conta ght using is 10%	act author(s) for raw data the following assumption its wet weight	198 	6 1450 ug/kg dry weight	1450
	2. dry weight of <u>Mysis</u> is 3. dry weight of benthos	21% IIS is 15% i	ts wet weight (Evans and L ts wet weight (Strayer and	anurum, 19 d Liken, 19	86)	
	4. dry weight of Pontopon 5. dry weight of all fishes	reia is 27 is 25%	7% its wet weight (Evans its wet weight	and Landru	ım, 1983)	
	and an and an an and an and an and an and an					
<sup>3</sup> Sources includ	le published literature from I	970 to 1	991 only.			
n = number of	samples for plankton, Mysis	s, <u>Ponto</u>	poreia, or benthos, and n	= number o	f organisms for all fishes.	

Great Lakes Monograph No. 4

262

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# TABLE 2

Summary of the concentration of dieldrin in various Lake Ontario biota (See footnotes for comments and assumptions).

ranism	Location	Year	Mean Concentration <sup>1</sup>	. u usu CO	(nala dev) Saural
9-44-444		1 .01	Steam Concentration		(ug/g or i) Source.
ankton					······································
t >135um					
-7	Lake Ontario	1077	0 13 ng/g den meight	130	Starrang 1009
	Care Charlo	1077	0.05 ug/g dry weight	100	Stevens, 1988
		1977	0.05 ug/g dry weight	20	
-22		19/8	0.03 ug/g dry weight	30	
-19		1979	0.01 ug/g dry weight	10	
:20		1982	0.01 ug/g dry weight	10	
t >64um	Deep Hole, Lake Ontario	1973	0.02 ug/g dry weight	20	Haile et al. 1975
	Rochester, Lake Ontario	1973	0.02 ug/g dry weight	20	
	midlake. Lake Ontario	1973	0 16 ugin dry weight	160	
	midlake entr I aka Ont	10	0.19 ug/g dry wolght	190	
	Monare cast Lake Uni	1044	orro of a cia meridiat	100	
	riamition, Lake Untario	1973	0.24 ug/g ary weight	240	
	midlake west. Lake Ont	1973	0.25 ug/g dry weight	250	
>153um, n=5	Western Lake Ontario	1981	17 ng/g dry weight	17	Whittle and Fitzsimons, 1983
>153um, n=2	Eastern Lake Ontario	1981	19 ng/g dry weight	19	
relicta					
	false Ormais		0.10	100	S
÷.	Lake Untario	1977	0.10 ug/g dry weight	100	Stevens, 1988
-5		1973	0.15 ug g dry weight	150	
2		1979	0.03 ug g dry weight	30	
5		1980	0.05 ug/g dry weight	50	
5		1981	0.06 up a dry wainin	60	
-		1007	0.00 ugig diy weight	70	
-		1307	o.o. në a në meidut	70	
<b>,</b>	Western Lake Ontario	1981	10 ng/g dry weight	10	Whittle and Fitzsimons, 1983
	Eastern Lake Untario	1981	1/ ng/g dry weight	17	•
nthos					
<del></del>					
.I	Western Lake Ontario	1972 1983	0.15 ug/g dry weight 0.27 ug/g dry weight	150 270	Stevens, 1988
			oilly age ally reagan		•
	Oswego, Lake Ontario	1973	3.0 ng/g dry weight	3	Cook and Johnson, 1974
red, includes	Hamilton, Lake Ontario	1973	14.8 ng/g dry weight	14.8	Haile <u>et al.</u> , 1975
novi	Kocnester, Lake Ontario	1973	2.9 ng/g dry weight	2.9	
Pentoporeia hov	<u>i</u>				
n=16	Lake Ontario	1978	0.13 ug/g dry weight	130	Stevens, 1988
n=13		1070	0.38 ug/g dry weight	380	• • • • •
		1020	0.23 ug/g dry weight	730	
		1001	0 13 ug/g uty weight	0ئند 10،	
=2		1981	0.45 ug/g dry weight	÷30	
=i1		1983	0.28 ug/g dry weight	280	
<b>z=</b> 5	Western Lake Ontario	1981	226 ng/g dry weight	226	Whittle and Fitzsimons, 198
a=13	Eastern Lake Ontario	1981	376 ng/g dry weight	376	
slimy sculpin					
slimy sculpin 10 details	Lake Ontario	1972	0.06 ug/g wet weight	240	Stevens, 1988
slimy sculpin no details n=10,mean wet=i	Lake Ontario 5.10g	1972	0.06 ug/g wet weight	240 0.	Stevens, 1988 08 ug/g wet weight 320
slimy sculpin no details n=10,mean wet=4. n=5,mean wet=4.	Lake Ontario 5.10g 34g	1972	- 0.06 ug/g wet weight 1977 1979	240 0. 0.	Stevens, 1988 08 ug/g wet weight 320 14 ug/g wet weight 560

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

	,				-
no details	Galloo-Stoney, Lake Ont	1973	0.04 ng/g wet weight	160	Haile et al., 1975
	Rochester, Lake Ontario	1973	0.05 ug/g wet weight	200	
	Olcott, Lake Ontario	1973	0.06 ug/g wet weight	240	
	Mexico Bay, Lake Ontario	1973	0.10 ug/g wet weight	400	
	Prince Edward Point	1973	0.11 ug/g wet weight	440 440	
rainbow smelt					
no details	Lake Ontario	1972. 1084	0.04 ug/g wet weight	160	Stevens, 1988
2	. <del>.</del>	1904	0.04 ug/g wet weight	100	
no details	Olcott, Lake Ontario	1973	0.02 ug/g wet weight	80	Haile et al. 1975
· · ·	Rochester, Lake Ontario	1973	0.03 ug/g wet weight	120	<b></b>
	Hamilton, Lake Ontario	1973	0.04 ug/g wet weight	160	
	Prince Edward Point	1973	0.06 ug/g wet weight	240	
	Galloo-Stoney, Lake Ont	1973	0.07 ug/g wet weight	280	
no deroile	Lake Omorio	1077	0.02 vaia wet weight	80	Shear 108.t
	THE ATTRIA	1978	0.05 ug/g wet weight	200	windly LFUT
		1979	0.04 ug/g wet weight	160	
		1980	0.04 ug/g wet weight	160	
n=47,mean wet=25	3.3g	Lake Or	mario	1981	0.06 mg/kg wet weight
Whittle, 1986	-				<u> </u>
n=48,mean wer=31	1.9g		1982	0.05	mg/kg wet weight 200
n=56,mean wet=29	1.8g		1983	0.03	mg/kg wet weight 120
n=0.mean wet=2	1.9g 7 2-		1984	0.03	mg/kg wet weight 120
n=49,mean wei=17	/- <u>-</u> g		בפען	0.02	myrkg wet weight 80
n=12	Eastern Lake Ontario	1981	65 ng/g wet weight	260	Whittle and Fitzsimons, 198
n=23,mean wet=18	3.3g	Western	Lake Ontario	1981	70 ng/g wet weight 289
	Olcott, Lake Ontario Prince Edward Point Galloo-Stoney, Lake Ont Hamilton, Lake Ontario	1973 1973 1973 1973	0.03 ug/g wet weight 0.03 ug/g wet weight 0.04 ug/g wet weight 0.04 ug/g wet weight	120 120 160 160	11000 <u>- 91</u> , 1979
	Rochester, Lake Ontario	1973	0.04 ug g wet weight	160	
coho saimon					
no details	Lake Ontario	1977	0.07 ug/g wet weight	280	Shear, 1984
		1978	0.10 ug/g wet weight	400	
		1979	0.05 ug/g wet weight	200	
		1980	0.07 ugig wet weight	U	
iake trout					
no detaile	Lake Ontario	1977	0.04 mg/g wet weight	160	Shear, 1984
	LARG UMAIN	1978	0.18 ug/g wet weight	720	
		1979	0.20 ug/g wet weight	800	
		1980	0.10 ug/g wet weight	400	
		1981	0.15 ug/g wet weight	600	
30e=4v1*	Lake Ontario	1977	0.05 ug/g wet weight	200	Borgmann and Whittle, 19
aRc=+12		1979	0.19 ug/g wet weight	760	
no details	Niagara River, Lake Ont	1980	0.08 ug/g wet weight	320	
	Eastern Lake Ontário	1980	0.09 ug/g wet weight	360	
	Kingston basin, Lake Out	1980	0.09 ug/g wet weight	360	
	Lake Ontario	1980	0.09 ug/g wet weight	360	
	Port Credit, Lake Ont	1980	0.09 ug/g wet weight	360	
	•				
	Hamilton, Lake Ontario	1980	0.11 ug/g wet weight	440	

Great Lakes Monograph No. 4

age=4yrs	Lake Ontario	1981 1982 1983 1985 1986 1987 1988	0.18 ug/g wet weight 0.13 ug/g wet weight 0.13 ug/g wet weight 0.10 ug/g wet weight 0.11 ug/g wet weight 0.11 ug/g wet weight 0.09 ug/g wet weight	720 520 520 400 440 440 360	
n=11,mean wet=120 Whittle, 1986 n=72,mean wet=200	00g 68g	Lake C	1979	19 · 0.	078 0.21 mg/kg wet weight84023 mg/kg wet weight920
n=82,mean wet=17	92g		1980	0.	12 mg/kg wet weight 480
n=83,mean wet=15	38g		1981	0.	19 mg/kg wet weight 760
n=36,mean wet=18	62g		1982	0.	15 mg/kg wet weight 600
n=46,mean wet=17	69g		1984	0.	14 mg/kg wet weight 560
n=47,mean wet=15	47g		1984	0.	15 mg/kg wet weight 600
n=14,mean wet=17	14g		1985	0.	11 mg/kg wet weight 440
n=10, age=4+yrs	Eastern Lake Ontario	1981	190 ng/g wet weight	760	Whittle and Fitzsimons, 1983
n=98, age=4+yrs	Western Lake Ontario	1981	190 ng/g wet weight	760	
n=213,mean wet=1 Stevens, 1988	587.4g	Lake C	Intario	19	981 0.20 ug/g wet weigh£00
n=144		1983	0.12 ug/g wet weight	480	

<sup>1</sup>In most cases only mean concentrations reported; contact author(s) for raw data.

<sup>2</sup>All reported values converted to ng/g dry weight using the following assumptions;

1. dry weight of plankton is 10% its wet weight

2. dry weight of Mysis is 21% its wet weight (Evans and Landrum, 1983)

3. dry weight of benthos is 15% its wet weight (Strayer and Liken, 1986)

4. dry weight of Pontoporeia is 27% its wet weight (Evans and Landrum, 1983)

5. dry weight of all fishes is 25% its wet weight

<sup>3</sup>Sources include published literature from 1970 to 1991 only.

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n = number of samples for plankton, <u>Mysis</u>, <u>Pontoporeia</u>, or benthos, and n = number of organisms for all fishes.

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

# TABLE 3

Summary of the concentration of HCB in various Lake Ontario biota (See footnotes for comments and assumptions).

			Converted Conc. <sup>2</sup>			
Organism	Location	Year	Mean Concentration <sup>1</sup>	.011761.264	(ng/g dry) Source <sup>3</sup>	
plankton			· · · · · · · · · · · · · · · · · · ·		<u> </u>	
n <sup>4</sup> =3, 10m depth	Lake Omario	1982	1.6 ng/g wet weight	16	Oliver and Nilmi, 1988	
<u>Mysis relicta</u>						
no details	Western Lake Ontario	1981	96 ng/g dry weight	96	Fox <u>et al</u> ., 1983	
a=2	Lake Ontario	1982	4.0 ng/g wet weight	19	Oliver and Niimi, 1988	
penthos						
amphipods mixed, includes <u>2. hovi</u>	Western Lake Ontario	1981 1981 1981 1981 1981	90 ng/g dry weight 157 ng/g dry weight 190 ng/g dry weight 230 ng/g dry weight 260 ng/g dry weight 260 ng/g dry weight	90 157 190 230 260	Fox <u>et al</u> ., 1983	
		1981 1981 1981 1981 1981	370 ng/g dry weight 724 ng g dry weight 1200 ng g dry weight 1400 ng g dry weight 1600 ng g dry weight	370 724 1200 1400 1600		
oligochaetes ao details	Western Lake Ontario	1981 1981 1981 1981 1981	63 ng/g dry weight 69 ng/g try weight 75 ng/g dry weight 140 ng/g dry weight 181 ng/g dry weight	63 69 75 140 181	Fox <u>=: al</u> ., 1983	
		1981 1981 1981 1981	250 ng/g dry weight 270 ng/g dry weight 480 ng/g dry weight 1200 ng/g dry weight	270 480 1290		
n=6	Niagara basin, Lake Ont	1985	3.5 ng/g wet weight	13	Oliver and Niimi, 1988	
Pontoporeia affin	is					
n=6	Niagara basin, Lake Ont	1985	18 ng/g wet weight	67	Oliver and Niimi, 1988	
imy sculpin						
fish composite	Grimsby, Lake Ontario	1986	38 ng/g wet weight	152	Oliver and Niimi, 1988	
ainbow smelt						
) tish composite 8-fish composites	Vineland, Lake Ontario Port Credit, Lake Ont	1982 1986	14 ng/g wet weight 7.6 ng/g wet weight	56 30.4	Oliver and Niimi, 1988	
lewiſe						
2 fish composite	Vincland, Lake Ontario	1982	20 ng/g wet weight	80	Oliver and Niimi, 1988	

266

Great Lakes Monograph No. 4

#### brown trout

n=10,mean wet=1430 and Oliver, 1989	)g	Vinelar	nd, Lake Ontario	1986	25 ug/kg dry weight	25	Mi
coho salmon							
n=20,mean wet=3.56 1979	kg	Credit	River, Lake Ont	1978	36 ng/g dry weight	36	Mai
n=9,mean wet=3330; and Oliver 1989	g	Credit	River, Lake Ont	1986	24 ug/kg dry weight	24	Mi
n=10,mean wet=119	Og	Vinela	nd, Lake Ontario	1986	26 ug/kg dry weight	26	
lake trout							
n=14,mean wet=1.02 1979	`kg	Eastern	a Lake Ontario	1978	80 ng/g dry weight	80	Ж
n=1, age=4+yrs n=1, age=6+yrs	Point Petre, Lake On: Niagara basin, Lake Ont	1980 1980	61 ppb dry weight) 127 ppb dry weight)	61 127	Oliver and Nicol, 19	82	
n=10,mean wet=241 and Oliver, 1989	Og	, Port C	edit, Lake Ont	1986	90 ug/kg dry weight	90	Nii
rainbow trout							
n=15,mean wet=2.33 1979	2kg	Port H	ope. Lake Ont	1978	62 ng g dry weight	62	Y
n=1, wet weight=2.39 and Niimi, 1983	Эkg	Ganara	ska R., Lake Ont	1981	15 ng/g dry weight	15	G
n=1,wet weight=1.80	Skg		1981	20 п	g/g dry weight20		
n=1,wet weight=4.6	7kg		1981	20 n	g/g dry weight20		
n=1,wet weight=1.52	2kg		1981	21 п	g/g dry weight21		
n=1,wet weight=2.86	δkg .		1981	27 п	g/g dry weight27		
n=1,wet weight=4.0	7kg		1981	28 n	g/g dry weight28		
n=1.wet weight=3.03	Skg		1981	40 n	g/g dry weight40		
n=1,wet weight=3.94	4kg		1981	48 n	g/g dry weight+8		
n=1, wet weight=3.7.	3kg		1981	50 n	g/g dry weight00		
n=1,wet weight=3.8	skg		1981	28 n	g/g ary weights		
n=8,mean wet=1140 and Oliver, 1989	g	Vinela	nd, Lake Ontario	1986	20 ug/kg dry weight	: 20	Nii
n=12,mean wet=338	Og	Credit	River, Lake Ont	1986	i 42 ug/kg dry weight	: 42	

'In most cases only mean concentrations reported; contact author(s) for raw data.

<sup>2</sup>All reported values converted to ng/g dry weight using the following assumptions;

- 1. dry weight of plankton is 10% its wet weight
- dry weight of <u>Mysis</u> is 21% its wet weight (Evans and Landrum, 1983)
  dry weight of benthos is 15% its wet weight (Strayer and Liken, 1986)

- 4. dry weight of <u>Pontoporeia</u> is 27% its wet weight (Evans and Landrum, 1983) 5. dry weight of all fishes is 25% its wet weight

<sup>3</sup>Sources include published literature from 1970 to 1991 only.

n = number of samples for plankton, <u>Mysis</u>, <u>Pontoporeia</u>, or benthos, and n = number of organisms for all fishes.

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

# TABLE 4.Summary of the concentration of 1,2,3-TCB in various Lake Ontario<br/>biota (See footnotes for comments and assumptions).

•	<b>*</b>	<b>1</b> 7	Con	verted Ca	)nc.'
Organism	Location	Year	Mean Concentration'		(ng/g dry) Source
plankton	<u></u>		<u> </u>		· · · · · · · · · · · · · · · · · · ·
1 <sup>4</sup> =3, 10m depth	Lake Ontario	1982	0.03 ng/g wet weight	0.3	Oliver and Niimi, 1988
Mysis relicta					
ao details	Western Lake Ontario	1981	20 ng/g dry weight	2	Fox et al., 1983
1=2.	Lake Ontario	1982	0.1 ng/g wet weight	0.48	Oliver and Niimi, 1988
Denth05					
imphipods nixed, includes 2. hovi	Western Lake Ontario	1981 1981 1981 1981	2.9 ng/g dry weight 6.7 ng/g dry weight 9.0 ng/g dry weight 9.5 ng/g dry weight	2.9 6.7 9.5	Fox <u>et ai</u> , 1983
		1981 1981 1981 1981 1981	10 ng/g dry weight 14 ng/g dry weight 19 ng/g dry weight 20 ng/g dry weight 29 ng/g dry weight	14 19 20 29	
aligochaetes	Western Lake Ontario	1981 1951 1981	1.3 ng/g dry weight 6.3 ng/g dry weight 7.5 ng/g dry weight 9.3 ng/g dry weight	13 63 75	Fox <u>et al</u> , 1983
		1981 1981	11 ng/g dry weight 13 ng/g dry weight	11 13	
Pontoporeia hovi					
1=0	Niagara basin. Lake Ont	1985	1.5 ag/g wet weight	5.56	Oliver and Niimi, 1988
pottail shiner					
ake trout					
	Point Petre, Lake Ont	1980 1980	0.2 ppb wet weight) 1 ppb wet weight	0.8 4	Oliver and Nicol, 1982

Great Lakes Monograph No. 4

268

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# TABLE 5.Summary of the concentration of 1,2,3,4-TeCB in various Lake Ontario<br/>biota (See footnotes for comments and assumptions).

			Сол	verted C	onc. <sup>2</sup>
Organism	Location	Year	Mean Concentration <sup>1</sup>		(ng/g dry) Source <sup>1</sup>
plankton	•••••••••••••••••••••••••••••••••••••••				
=3, 10m depth	Lake Ontario	1982	0.4 ng/g wet weight	4	Oliver and Nilmi, 1988
Mysis relicta					
an detaile	Western I ake Ontario	1091	19 pg/g dry weight	10	For at al. 1983
	Vesteri Lake Ontario	1901	15 mg/g dry weight		
1=1	Lake Untario	1984	Lo ng/g wet weight	7.14	Oliver and Nilmi, 1988
<b>Sentra</b> OS					
amphipods	Western Lake Ontario	1981	9.0 ng/g dry weight	9	Fox et al., 1983
nixed, includes		1981	13 ng/g dry weight	13	
<u>2. bovi</u>		1981	18 ng/g dry weight	18	
		1981	24 ng/g dry weight	24	
		1981	48 ng/g dry weight	8 74	
		1091	00 ng/g dry weight	70	
		1981	95 ng/g dry weight	90	
		1981	130 ng/g dry weight	130	
oligochaetes	Western Lake Ontario	1981	9.3 ng/g dry weight	9.3	Fox <u>et 11.</u> , 1983
30 details		1981	19 ng/g dry weight	19	
		1981	20 ng/g dry weight	20	
		1981	21 ng/g dry weight	21	
		1981	25 ng/g dry weight	25	
		1981	38 ng/g dry weight	38	
		1981	42 ng/g dry weight	42	
		1981	69 ng/g dry weight	69	
<b>126</b>	Niagara basin. Lake Ont	1 <b>985</b>	0.3 ng/g wet weight	2	Oliver and Niimi, 1988
Pontoporeia hovi					
<b>3=</b> 0	Niagara basin, Lake Ont	1985	6.1 ng/g wet weight	22.6	Oliver and Niimi, 1988
	-				
limy sculpin					
i fish composite	Grimsby, Lake Ontario	1986	0.9 ng/g wet weight	3.6	Oliver and Niimi, 1988
ake trout					
=1, age=6+yrs	Niagara basin, Lake Ont	1980	12 ppb wet weight	12	Oliver and Nicol, 1982

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- **Lake Ontario Case Study** 

rainbow trout		
n=1,wet weight=2.39kg	Ganaraska R., Lake Ont	1981 0.4 ng/g dry weight 0.4 Gr
and Niimi, 1983		•
n=1,wet weight=4.67kg	1981	0.6 ng/g dry weight 0.6
n=1,wet weight=1.86kg	1981	0.6 ng/g dry weight 0.6
n=1 wet weight=1.52kg	1981	0.7 ng/g dry weight 0.7
n=1 wet weight=4.07kg	1981	0.9 ng/g dry weight 0.9
n=1 wet weight=3.05kg	1981	0.9 ng/g dry weight 0.9
n=1, wet weight=3.94kg	1981	1.2 ng/g dry weight 1.2
n=1, wet weight=2.86kg	1981	1.4 ng/g dry weight 1.4
1 mot weight=2.73kg	1981	14  ng/g dry weight $1.4$
n=1,wei weight=3./3kg	1001	1 A ng/g der weight 1 A
n=1,wet weight=3.88kg	1981	1.4 ng/g dry weight 1.4

'In most cases only mean concentrations reported; contact author(s) for raw data.

<sup>2</sup>All reported values converted to ng/g dry weight using the following assumptions;

1. dry weight of plankton is 10% its wet weight

2. dry weight of Mysis is 21% its wet weight (Evans and Landrum, 1983)

3. dry weight of benthos is 15% its wet weight (Strayer and Liken, 1986)

4. dry weight of Pontoporeia is 27% its wet weight (Evans and Landrum, 1983)

5. dry weight of all fishes is 25% its wet weight

<sup>3</sup>Sources include published literature from 1970 to 1991 only.

n = number of samples for plankton, <u>Mysis</u>, <u>Pontoporeia</u>, or benthos, and n = number of organisms for all fishes.

Organism	Location	Year	Conv Mean Concentration	erted ( 1 <sup>1</sup>	Conc. <sup>2</sup> (ng/g dry)	Source <sup>3</sup>
plankton			<u> </u>			
n <sup>4</sup> =3, 10m depth Oliver and Niim	i, 1988	Lake (	Ontario	1982	2 1.3 ng/g wet	weight 13
<u>Mysis relicta</u>						
n=2	Lake Ontario	1984	330 ng/g wet weight:	571	Oliver and Niir	ni, 1988
benthos						
oligochaetes n=6	Niagara basin	1985	6.9 ng/g wet weight	46	Oliver and Niir	ni, 1988
<u>Pontoporeia</u> ho	<u>vi</u>					
n=16 n=13 n=5	Lake Ontario	1978 1979 1980	0.08 ug/g dry weight 0.04 ug/g dry weight 0.12 ug/g dry weight	80 40 120	Stevens, 1988	
n=13 Whittle and Eite	Eastern Lake Ontario	,	1981	41 1	ng/g dry weight	41
n=5	Western Lake Ontario	0	1981	228	ng/g dry weigh	228
n=6	Niagara basin	1985	12 ng/g wet weight	44	Oliver and Nii	mi, 1988

TABLE 6.Summary of the concentration of mirex in various Lake Ontario biota<br/>(See footnotes for comments and assumptions).

spottail shiner

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

•
n=10.mean wet=9.11g
Skinner, 1988
n=10,mean wet=10.6g
n=10,mean wet=11.1g
n=9,mean wet=11.8g
n=10,60mm length
1986
n=8,62mm length
n=9,55mm length
n=8,49mm length
n=8,58mm length
n=8,51mm length
n=8,60mm length
n=3,49mm length
n=8,53mm length
n=7.57mm length
n=7.55mm length
n=7,40 mm length
n=7,52mm length
n=6.54mm length
n=4.56mm length
n=7.41 mm length
n=7.60mm length
n=7.57mm length
n=7.65mm length
n=7,64mm length
n=6,48mm length
n=7,43mm length
n=6,54mm length
n=7,58mm length
n=10,62mm length

Lake Ontario

1975 0.013 ug/g wet weigh62 1978 0.029 ug/g wet weigh16 1979 0.001 ug/g wet weight 4 1980 0.011 ug/g wet weigh14

Salmon River, Lake Ont

Oswego Harbor, Lake Ont Black R. Bay, Lake Ont Salmon River, Lake Ont

Darlington, Lake Ontario

Humber River, Lake Ontario Burlington, Lake Ontario Cobourg Creek, Lake Ont Humber River, Lake Ontario Twelve Mile Creek, Lake Ont 1978 Credit River, Lake Ontario Gages Creek, Lake Ontario Outlet River, Lake Ontario Ganaraska River, Lake Ont Outlet River, Lake Ontario Welland Canal, Lake Ontario Credit River, Lake Ontario Outlet River, Lake Ontario Wolfe Island, Lake Ontario Oshawa Creek, Lake Ontario Twelve Mile Creek, Lake Ont 1982 Credit River, Lake Ontario Burlington, Lake Ontario Wolfe Island, Lake Ontario Twelve Mile Creek, Lake Ont 1983 Welland Canal, Lake Ontario Outlet River, Lake Ontario Twelve Mile Creek, Lake Ont 1984 Wolfe Island, Lake Ontario Credit River, Lake Ontario

Shear, 1984

1984 3.5 ng/g wet weight 141984 3.8 ng/g wet weight 15.2

1984 3.9 ng/g wet weight 15.6 1985 4 ng/g wet weight 16

1976 6 ug/kg wet weight 24Ss

1977 5 ug/kg wet weight 20 1977 9 ug/kg wet weight 36 1978 6 ug/kg wet weight 24 1978 15 ug/kg wet weight60 20 ug/kg wet weight80 1978 28 ug/kg wet weight12 1979 6 ug/kg wet weight 24 1979 10 ug/kg wet weight40 1980 6 ug/kg wet weight 24 1980 8 ug/kg wet weight 32 1982 6 ug/kg wet weight 24 1982 7 ug/kg wet weight 28 1982 7 ug/kg wet weight 28 1982 8 ug/kg wet weight 32 1982 9 ug/kg wet weight 36 21 ug/kg wet weight84 1983 5 ug/kg wet weight 20 1983 7 ug/kg wet weight 28 1983 7 ug/kg wet weight 28 8 ug/kg wet weight 32 1984 5 ug/kg wet weight 20 1984 6 ug/kg wet weight 24 7 ug/kg wet weight 28 1984 7 ug/kg wet weight 28 1986 32 ug/kg wet weight28

Great Lakes Monograph No. 4

slimy sculpin

n=10,mean wet=5.10g Lake Ontario 1977 0.0 n=5,mean wet=4.34g 197		0.06 ug/g wet weigh240 1979	Stevens, 1988 ug/g wet weighi20			
5 fish composite Oliver and Niin	e ni, 1988	Grims	by, Lake Ontario	1986 57 ng/g wet weight228		
rainbow smelt	· · · ·					
no details	Lake Ontario	1977 1978 1979 1980	0.11 ug/g wet weight40 0.06 ug/g wet weigh240 0.06 ug/g wet weigh240 0.08 ug/g wet weigh620	) ) )	Shear, 1884	
n=73,mean wet	=24.4g Lake Ontario	1978	0.05 mg/kg wet weight	)	Whittle, 1986	
n=73,mean wet	=24.2g		1979	0.05	mg/kg wet weight	200
n=33,mean wet	=28.7g		1980	0.04	mg/kg wet weight	160
n=47,mean wet	=28.3g		1981	0.04	mg/kg wet weight	160
n=48,mean wet	=31.9g		1982	0.02	mg/kg wet weight	80
n=36,mean wet	=29.8g		1983	0.05	mg/kg wet weight	200
n=56,mean wet	=21.9g		1984	0.01	mg/kg wet weight	40
n=49,mean wet	=17.2g		1985	0.01	mg/kg wet weight	40
no details	Lake Ontario	1981	0.06 ug/g wet weigh240	)	Strachan and Edwards	s, 1984
n=12 Whittle and Fit:	Eastern Lake Ontario		1981	50 n	g/g wet weight 200	
n=23,mean wt=18.3g		Weste	rn Lake Ontario	1981	35 ng/g wet weigh	t140
20 fish composition	ite ni 1988	Vinela	nd, Lake Ontario	1982	53 ng/g wet weigh	t212
6 8-fish composites Port Credit, Lake (		Ont	1986	26 n	g/g wet weight 104	

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- **Lake Ontario Case Study** 

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## alewife

1982 45 ng/g wet weight180 Vineland, Lake Ontario 12 fish composite Oliver and Niimi, 1988 brown trout. Vineland, Lake Ontario 1986 77 ug/kg dry weight 77 m n=10,mean wt=1430g and Oliver, 1989 coho salmon Lake Ontario 1977 0.16 ug/g wet weigh640 Shear, 1984 no details 1978 0.08 ug/g wet weigh620 0.10 ug/g wet weight400 1979 0.10 ug/g wet weigh#00 1980 Strachan and Edwards, 1984 Lake Ontario 1981 0.04 ug/g wet weight60 no details Credit River, Lake Ont 1986 203 ug/kg dry weig203) n=9,mean wt=3330g and Oliver, 1989 1986 45 ug/kg dry weight 45 Vineland, Lake Ontario n=10,mean wt=1190g

lake	trout
------	-------

no details	Lake Ontario	•	1977 1978 1979 1980 1981	0.27 x 0.21 x 0.23 x 0.18 x 0.15 x	18\8 18\8 18\8 18\8 18\8	wet wet wet wet wet	weigh0 weigh8 weigh9 weigh0 weigh6	80 40 20 20 20	Shear, 198	34
n=32,mean wet=	2102g	Lake (	Ontario				1977	0.49	mg/kg we	t wł£gfn
willie, 1900	1200		1078				015	malka	wet weigh	+ 600
n-72 mean wet-	200g 2069g		1979				0.15	mg/kg	wet weigh	t 1000
n=82 mean wet=	1792g		1980				0.14	mg/kg	wet weigh	t 560
n=83 mean wet=	15839		1982				0.16	mo/ko	wet weigh	t 640
n=36 mean wet=	1862g		1983				0.21	mg/kg	wet weigh	t 840
n=46 mean wet=	1769g		1984				0.08	mg/kg	wet weigh	t 320
n=14,mean wet=	1714g		1985				0.13	mg/kg	wet weigh	t 520
age=4yrs	Lake Ontario	1977	0.38 u	g/g we	t we	ig∎ð	20	Borgm	ann and Wh	ittle, 1991
no details	Cobourg, Lake Ontari	io	1980			-	0.14	ug/g w	vet weighti6	0
	Eastern Lake Ontario		1980				0.09	ug/g w	vet weight6	0
	Hamilton, Lake Ontar	rio	1980				0.19	ug/g w	vet weigh16	0
	Kingston basin	1980	0.12 u	g/g we	et we	igh <b>t</b> l	-80			
	Niagara River, Lake (	Ont	1980				0.14	ug/g w	vet weighi6	0
	Port Credit, Lake Ont	t	1980				0.16	ug/g w	vet weighi4	0
age=4yrs	Lake Ontario	1981	0.12 u	g/g we	et we	ight	80			
		1983	0.18 u	g/g we	et we	ight7	20			
	۲	1984	0.07 u	g/g we	et we	igh2	.80			
		1986	0.06 u	g∕g we	et we	igh2	.40			
		1987	0.10 u	g∕g we	et we	ight	00			
		1988	0.17 u	g/g we	et we	ight	80			
n=141,mean wet Stevens, 1988	=956.7g Lake Ontario		1978				0.18	ug/g w	vet weigh12	:0
n=176,mean wet	=1554.8g		1979				0.22	ug/g w	vet weight8	0
n=133,mean wet	=1660.4g		1980				0.17	ug/g w	vet weight8	10
n=178,mean wet	=1460.0g		1982				0.17	ug/g w	vet weight8	0
n=144		1983	0.17 u	g/g we	et we	ight	80			
no details	Lake Ontario	1981	0.14 u	g/g we	et we	ighð	60	Stracha	an and Edwa	ards, 1984
n=10, age=4+yrs Whittle and Fitze	simons, 1983	Easter	n Lake	Ontari	io		1981	. 130	ng/g wet w	veighfi20
n=98, age=4+yrs		Wester	rn Lake	e Onta	rio		1981	. 150	ng/g wet v	veigh100
n=10,mean wt=2 and Oliver, 1989	410g	Port C	redit, L	.ake O	nt		1986	5 430	ug/kg dry	weig <b>13</b> 01 <b>ii</b>

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

# rainbow trout

n=12,mean wt=3380g	Credit River, Lake Ont	1986	246 ug/kg dry weigB46bin
and Oliver, 1989			
n=8,mean wt=1140g	Vineland, Lake Ontario	1986	51 ug/kg dry weight51

<sup>1</sup>In most cases only mean concentrations reported; contact author(s) for raw data.

<sup>2</sup>All reported values converted to ng/g dry weight using the following assumptions;

1. dry weight of plankton is 10% its wet weight

2. dry weight of Mysis is 21% its wet weight (Evans and Landrum, 1983) ,

3. dry weight of benthos is 15% its wet weight (Strayer and Liken, 1986)

4. dry weight of Pontoporeia is 27% its wet weight (Evans and Landrum, 1983)

5. dry weight of all fishes is 25% its wet weight

<sup>3</sup>Sources include published literature from 1970 to 1991 only.

n = number of samples for plankton, <u>Mysis</u>, <u>Pontoporeia</u>, or benthos, and n = number of organisms forall fishes.

TABLE 7.

Summary of the organic contaminant concentrations in Lake Ontario water (See footnotes for comments).

	·····					
Contaminant and Location ; Source'	# of	samples	Year	Mean	Concentration <sup>1</sup>	ng/L²
PCBs						
Toronto, Lake Ontario		1973	35 ng/L	35	Haile <u>et</u>	<u>al</u> ., 1975
Rochester, Lake Ontario		1973	40 ng/L	40		
Olcott, Lake Ontario		1973	44 ng/L	44		
Cobourg, Lake Ontario		1973	45 ng/L	45		
Hamilton, Lake Ontario		1973	49 ng/L	49		
Deep Hole, Lake Ontario		1973	56 ng/L	56		
Oswego, Lake Ontario		1973	77 ng/L	77		
Niagara River, Lake Ontario		1973	97 ng/L	97		
Lake Ontario		1975	30 ng/L	30	Glooschen Glooschen	ko and ko, 1975
open lake, Lake Ontario	14	1983	0.430 ng/L	0.43	Biberhofe	r and
open lake, Lake Ontario		1983	0.320 ng/L	0.32	Stevens.	1987
open lake, Lake Ontario		1983	1.140 ng/L	1.14		
eastern Lake Ontario		1983	0.320 ng/L	0.32	Stevens.	1988
Kingston basin, Lake Ontario		1983	0.430 ng/L	0.43	000,000,	
midlake. Lake Ontario		1983	0.430  mg/L	0.43		
Bochester basin Lake Ontario		1983	0 430 pg/L	0 43		
Rumber Diver Lake Ontario		1983	0 590 pg/L	0.45		
Gewege Lake Ontario		1983	0.300  mg/L	0.30		
Bay of Quinta Take Ontario		1093		0.70		
Lake Ontario		1093		0.72		
Niagara Piwer Lake Ontario		1083		0.93		
nerthebore Lake Ontario		1093		0.03		
Welland Canal Lake Ontario		1093		0.04		
18 Mile Creek Lake Ontario		1993	1 010 ng/L	1 01		
western Lake Ontario		1983	1 140 ng/L	1 14		
Black Biver Lake Optario		1093	1 920 ng/L	1 97		
Burlington, Lake Ontario		1983	3.100 ng/L	3.10		
Lake Ontario	31	1986	1.41 ng/L	1.41	Stevens a Neilson,1	nd .989
Lake Ontario	. 7	1984	1100 pg/T	1.10	Oliver an	d Niimi.
	•	2001	1100 29/1		1988	
Toronto, Lake Ontario	94	1987	1.33 ng/L	1.33	ELI Eco L	ab., 1988
Lake Ontario	33	1988	1.18 ng/L	1.18	L'Italien	, pers.
	46	1990	1.31 ng/L	1.31	comm.	
dieldrin					•	
Deen Hole, Lake Ontario		1077	1 3 70/1.	1.7	Haila at	al., 1975
Niagara River, Lake Ontario		1077	2.1 ng/L	2.1		
Rochester, Lake Ostario		1077	2.2 na/1.	2-2		
Hamilton, Lake Ontario		1977	3 1 ng/1	3.1		
Toronto, Lake Ontario		1977	3 5 77/1	3.5		
Olcott. Lake Ontario		1077	3.9 mm/T.	3 9	4 - 1 	
Cobourg, Lake Ontario		1973	9,9 na/T.	9.9		
Antero Isko Astanio		1077		12.6		

open lake, Lake Ontario open lake, Lake Ontario open lake, Lake Ontario	14	1983 1983 1983	0.259 ng/L 0.361 ng/L 0.470 ng/L	0.259 0.361 0.470	Biberhofer & Stevens, 1987
Bay of Quinte, Lake Ontario western Lake Ontario Black River, Lake Ontario Rochester, Lake Ontario 18 Mile Creek, Lake Ontario eastern Lake Ontario Oswego, Lake Ontario Lake Ontario Niagara River, Lake Ontario Burlington, Lake Ontario Midlake, Lake Ontario Welland Canal, Lake Ontario Humber River, Lake Ontario Kingaton basin, Lake Ontario Northebore, Lake Ontario		1983 1983 1983 1983 1983 1983 1983 1983	0.047 ng/L 0.259 ng/L 0.300 ng/L 0.325 ng/L 0.352 ng/L 0.361 ng/L 0.442 ng/L 0.443 ng/L 0.453 ng/L 0.450 ng/L 0.510 ng/L 0.527 ng/L 0.538 ng/L	0.047 0.259 0.300 0.325 0.352 0.361 0.442 0.442 0.448 0.453 0.456 0.470 0.510 0.527 0.538 0.631	Stevens, 1988
Lake Ontario	31	1986	0.331 ng/L	0.331	Stevens and Neilson, 1989
Lake Ontario	33 46	1988 1990	0.36 ng/L 0.28 ng/L	0.36 0.28	L'Italien, pers. comm.
mirex					
Lake Ontario	7	1984	31 pg/L	0.031	Oliver and Niimi, 1988
Toronto, Lake Ontario	95	1987	0.0071 ng/L	0.0071	ELI Eco Lab., 1988
Lake Ontario	33 46	1988 1990	0.013 ng/L 0.0029 ng/L	0.013 0.0029	L'Italien, pers. comm.
нсв					
Lake Ontario		1980	0.06 ng/L	0.06	Oliver and Nicol, 1982
open lake, Lake Ontario open lake, Lake Ontario open lake, Lake Ontario	14	1983 1983 1983	0.033 ng/L 0.036 ng/L 0.043 ng/L	0.033 0.036 0.043	Biberhofer & Stevens, 1987

Oswego, Lake Ontario Black River, Lake Ontario eastern Lake Ontario Kingston basin, Lake Ontario Bay of Quinte, Lake Ontario midlake, Lake Ontario eastern Lake Ontario Rochester, Lake Ontario western Lake Ontario Lake Ontario 0.017 ng/L 0.019 ng/L 0.033 ng/L 0.031 ng/L 0.034 ng/L 0.036 ng/L 1983 0.017 0.019 0.033 0.031 0.034 1983 1983 1983 1983 1983 1983 1983 0.036 0.036 ng/L 0.04 ng/L 0.042 ng/L 0.05 ng/L 0.05 ng/L 0.05 ng/L 0.052 ng/L 0.04 0.042 1983 0.043 0.05 0.05 0.05 0.052 Lake Ontario 1983 midlake, Lake Ontario western Lake Ontario Welland Canal, Lake Ontario 1983 1983 1983

Stevens, 1988

278

Great Lakes Monograph No. 4

Burlington, Lake Ontario northshore, Lake Ontario western Lake Ontario Humber River, Lake Ontario Niagara River, Lake Ontario 18 Mile Creek, Lake Ontario western Lake Ontario		1983 1983 1983 1983 1983 1983 1983	0.068 ng/L 0.068 ng/L 0.08 ng/L 0.089 ng/L 0.095 ng/L 0.103 ng/L 0.12 ng/L	0.068 0.068 0.08 0.089 0.095 0.103 0.12	
Kingston basin eastern basin eastern basin midlake, Lake Ontario western basin Niagara basin Niagara basin		1983 1983 1983 1983 1983 1983 1983 1983	0.03 ng/L 0.03 ng/L 0.03 ng/L 0.04 ng/L 0.05 ng/L 0.05 ng/L 0.08 ng/L 0.12 ng/L	0.03 0.03 0.04 0.05 0.05 0.08 0.12	Oliver, 1984
Lake Ontario	7	1984	150 pg/L	0.15	Oliver and Niimi, 1988
Lake Ontario	31	1986	0.063 ng/L	0.063	Stevens and Neilson,
1909					
Toronto, Lake Ontario	95	1987	0.063 ng/L	0.063	ELI Eco Lab., 1988
Lake Ontario	33 46	1988 1990	0.068 ng/L 0.087 ng/L	0.068 0.087	L'Italien, pers. comm.
1,2,3-TCB					
Lake Ontario		1980	0.1 ng/L	0.1	Oliver and Nicol, 1982
open lake, Lake Ontario open lake, Lake Ontario open lake, Lake Ontario	14	1983 1983 1983	0.024 ng/L 0.065 ng/L 0.140 ng/L	0.024 0.065 0.140	Biberhofer & Stevens, 1987
Black River, Lake Ontario Welland Canal, Lake Ontario midlake, Lake Ontario Say of Quinte, Lake Ontario Oswego, Lake Ontario northshore, Lake Ontario Rochester, Lake Ontario astern Lake Ontario Burlington, Lake Ontario Humber River, Lake Ontario Niagara River, Lake Ontario 18 Mile Creek, Lake Ontario Lake Ontario	7	1983 1983 1983 1983 1983 1983 1983 1983	0.008 ng/L 0.020 ng/L 0.024 ng/L 0.040 ng/L 0.055 ng/L 0.055 ng/L 0.056 ng/L 0.065 ng/L 0.065 ng/L 0.084 ng/L 0.111 ng/L 0.133 ng/L 0.140 ng/L 170 pg/L	0.008 0.020 0.024 0.040 0.048 0.055 0.056 0.056 0.056 0.065 0.084 0.111 0.133 0.140 0.672 0.170	Stevens, 1988 Oliver and Niimi, 1988
Lake Ontario	31	1986	0.097 ng/L	0.097	Stevens and Neilson, 1989
Toronto, Lake Ontario	86	1987	0.072 ng/L	0.072	ELI Eco Lab., 1988
Lake Ontario	33 <b>46</b>	1988 1990	0.110 ng/L 0.660 ng/L	0.110 0.660	L'Italien, pers. comm.

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

1,2,3,4-TeCB

Lake Ontario		1980	0.1 ng/L	0.1	Oliver and Nicol, 1982
open lake, Lake Ontario	14	1983	0.082 ng/L	0.082	Biberhofer & Stevens,
open lake, Lake Ontario		1983	0.086 ng/T.	0.086	1987
open lake Lake Optario		1983	0 091 pg/T	0 091	
open taxe, bake oncarto		1900	Grobit ng/D	0.051	
Bay of Quinte, Lake Ontario		1983	0.014 ng/L	0.014	Stevens, 1988
Kingston basin, Lake Ontario		1983	0.017 ng/L	0.017	• • • •
Welland Canal, Lake Ontario		1983	0.034 ng/T	0.034	
Burlington, Lake Ontario		1983	0.037  pg/T	0 037	
porthebore Lake Ontario		1983	0 037 56/1	0.037	
Bochaston Iska Ostania		1003		0.037	
Rochester, Lake Untario		1903	0.057 ng/L	0.057	
Oswego, Lake Untario		1983	0.058 ng/L	0.058	
eastern Lake Ontario		1983	0.07 ng/L	0.07	
eastern Lake Ontario		1983	0.08 ng/L	0.08	
Niagara River, Lake Ontario		1983	0.081 ng/L	0.081	
western Lake Ontario		1983	0.082 ng/L	0.082	
midlake. Lake Ontario		1983	0.086 ng/L	0.086	
eastern Lake Ontario		1983	0 091 ng/L	0 091	
eastern Lake Ontario		1092		0.001	
Hastern Lake Untario		1903		0.11	
Humber River, Lake Untario		1983	0.125 ng/L	0.125	
Lake Ontario		1983	0.13 ng/L	0.13	
midlake, Lake Ontario		1983	0.15 ng/L	0.15	
western Lake Ontario		1983	0.16 ng/L	0.16	
western Lake Ontario		1983	0.27 ng/L	0.27	
18 Mile Creek, Lake Ontario		1983	0.572 ng/L	0.572	
·					
Kingston basin		1983	0.07 ng/L	0.07	Oliver, 1984
eastern basin		1983	0.08 ng/L	0.08	
eastern basin		1983	0.09 ng/L	0.09	
eastern basin		1983	0.11 ng/L	0.11	
midlake Lake Ontario		1983	0.15 pg/L	0 15	
Niegawa bagia		1000		0.10	
Miagara basin		1963		0.10	
Niagara basin		1983	0.16 ng/L	0.16	
Western Dasin		1983	0.27 ng/L	0.27	
Lake Ontario	7	1984	140 pg/L	0.14	Oliver and Niimi,
					1700
Lake Ontario	31	1986	0.104 ng/L	0.104	Stevens and Neilson,
					1909
Toronto, Lake Ontario	94	1987	0.095 ng/L	0.095	ELI Eco Lab., 1988
Lake Ontario	33	1988	0.132 ng/L	0.132	L'Italien, pers-
	46	1990	0 070 pg/L	0 070	
	40	2320	0.070 Hg/H	V.V/V	

<sup>1</sup>In most cases mean concentration reported; contact author(s) for raw data. <sup>3</sup>All reported values converted to ng/L. <sup>3</sup>Published literature from 1970 to 1991 only.

280

Great Lakes Monograph No. 4
TABLE 8.

Summary of the organic contaminant concentrations in Lake Ontario sediments (See

# footnotes for comments).

Chemical & Details Source <sup>3</sup>	# of samples	Year	Mean Concentration <sup>1</sup>	ng/g dry weight <sup>2</sup>
PCBs				·

bottom sediments

• • <u>·</u>					
0 - 3, CM	770	1969	71 meh dagi melaht		Transla et al. 1070
	443	1050	51 ppb dry weight	51	Frank <u>et al</u> ., 1979
Lake Untario		1000	37 ppb dry weight	37	
Mississauga Dasin		1768	11 ppp dry weight	77	
Dasin zone		1968	as ppp dry weight	85	
Niagara Dasin		1969	sa bbp gið mardur	89	
Rochester basin		1968	sa bbp gið merdur	89	
Cobourg		1973	43 ng/g dry weight	43	Haile <u>et al</u> ., 1975
midlake		1973	79 ng/g dry weight	79	
Olcott		1973	80 ng/g dry weight	80	
Rochester basin		1973	84 ng/g dry weight	84	
Niagara basin		1973	155 ng/g dry weight	155	
Oswego		1973	158 ng/g dry weight	158	
Welland Canal		1973	245 ng/g dry weight	245	
0 – 2 cm					
Lake Ontario		1981	260 ng/g dry weight	260	Stevens, 1988
		1981	380 ng/g dry weight	380	· •
		1981	470 ng/g dry weight	470	
		1981	670 ng/g dry weight	670	
		1981	680 ng/g dry weight	680	
		1981	730 ng/g dry weight	730	
		1981	810 ng/g dry weight	810	
		1991	840 ng/g dry weight	840	
-1		1701	and which get werdure	940	
0 - 3 cm			·		
Rochester basin	1	1981	630 ng/g dry weight	630	Bourbonniere <u>et al</u> .,
1986					
Niagara basin		1981	874.8 ng/g dry weight	874.8	
Niagara basin		1981	910 ng/g dry weight	910	
Mississauga basin		1981	1041 ng/g dry weight	1041	
Niagara basin		1981	1100 ng/g dry weight	1100	
Rochester basin		1981	1500 ng/g dry weight	1500	
0 – 3 cm					
Niagara basin	35 .	1981	360 ng/g dry weight	360	<u>Oliver et al</u> , 1987
Rochester basin		1981	400 ng/g dry weight	400	
Mississauga basin		1981	430 ng/g dry weight	430	
0 – 3 cm					
Kingston basin	35	1982	200 ng/g dry weight	200	Oliver <u>et</u> <u>al</u> ., 1989
Niagara basin		1982	510 ng/g dry weight	510	
Rochester basin		1982	630 ng/g dry weight	630	
Mississauga basin		1982	690 ng/g dry weight	690	
suspended sediments					
Lake Ontario	10	1986	440 ng/g dry weight	440	Oliver and Niimi, 1988
	30	1007			1000
ISCONCO, LARE UNTAFIO	20	1381	Jon bbr	JERT CC LEC	i3,, T300
dieldrin					
bottom endiments					
SUCCESS STULLEDULE					

SACCON BACITURICS

0 - 3 cm Lake Ontario

1968

229

0.6 ppb dry weight

Frank <u>et</u> <u>al</u>., 1979

0.6

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- **Lake Ontario Case Study** 

0 – 3 cm		1000			1 1087
Alagara basin		1768	2.8 ng/g dry waight	TROBAS C	<u>c ar</u> ., 1983
midlake		1973	0.5 ng/g dry weight	0.5	Haile et al, 1975
Cobourg		1973	0.6 ng/g dry weight	0.6	
Oswego		1973	0.8 ng/g dry weight	0.8	
Olcott		1973	0.9 ng/g dry weight	0.9	
Rochester basin		1973	0.9 ng/g dry weight	0.9	
Niagara basin		1973	1.4 ng/g dry weight	1.4	
midlake-east		1973	2.1 ng/g dry weight	2.1	
Weiland		1973	2.6 ng/g dry weight	2.6	
mirex					
bottom sediments					
0 – 3 cm			<i></i>		
Lake Ontario	16	1968	5.6 ppp ary weight	5.5	Holdrinet et al., 1978
Oswego anomaly	27	1300	1.3 ppb dry weight	1.3	
Alagara anomaly	50	1300	in bbp gth merdur	TO	
Western Lake Ontario	1	1980	8.2 ppb dry weight	8.2	Kaminsky et al., 1983
		1980	16 ppb dry weight	16	
		1980	17 ppb dry weight	17	
		1980	20 ppb dry weight	20	
		1980	33 ppb dry weight	33	
		1980	57 ppb dry weight	57	
		1980	es bbp gra werduc	94	
0 - 3 cm					
Niagara basin	1	1981	45.7 ng/g dry weight	45.7	Bourbonniere <u>et</u> <u>al</u> .,
Rochester basin		1981	59.0 ng/g dry weight	59.0	
Rochester basin		1981	93.0 ng/g dry weight	93.0	
Mississauga basin		1981	98.1 ng/g dry weight	98.1	
Niagara basin		1981	110.0 ng/g dry weight	110.0	
Niagara basin		1981	110.0 ng/g dry weight	110.0	
0 - 3 cm					
Niagara basin	35	1981	18 ng/g dry weight	18	Oliver <u>et</u> <u>al</u> ., 1987
Rochester basin		1981	23 ng/g dry weight	23	
Mississauga basin		1981	25 ng/g dry weight	25	
Niagara basin	12	1982	48 ng/g dry sediments	48	Oliver and Charlton, 1984
U - 3 CM Vinceton basin	95	1002	E & and a dame was	<i>с</i> ,	
Mingston Dasin	23	1962	20 sa(a day weight	 	OTIVET EL al., 1989
Bidyara basin Bochester basin		1997	33 ng/g dry weight	30	
Mississauga basin		1982	38 ng/g dry weight	38	
			<u></u> , <u>.</u>		
suspended sediments					
Niagara basin	21	1997	5.7 na/a dry weight	5.2	Oliver and Charlton
1984	44	1796	are which and wording	J + 4	Server and Charlebolly
		1982	7.3 ng/g dry weight	7.3	
		1982	9.3 ng/g dry weight	9.3	
		1982	re udid only merdur	Τø	
Lake Ontario	10	1986	15 ng/g dry weight	15	Oliver and Niimi, 1988
Toronto, Lake Ontario	8	1987	14 ppt	12LI Eco	Lab., 1988

282

Great Lakes Monograph No. 4

HCB

bottom sediments

Western Lake Ontario	1	1980 1980 1980 1980	7.6 ppb dry weight 7.7 ppb dry weight 10 ppb dry weight 17 ppb dry weight 47 ppb dry weight	7.6 7.7 10 17	Kaminsky <u>et al</u> ., 1983
		1980	51 ppb dry weight 52 ppb dry weight	51 52	
		1980	57 ppb dry weight	57	
		1980	58 ppb dry weight	58	
		1980 1980	65 ppb dry weight 89 ppb dry weight	65 89	·
0 - 3 cm Lake Ontario		1980	97 ppb	97	Oliver and Nicol, 1982
Niagara basin			Oliver	and Nicol, 198	2
0 - 1 cm	1	1980	270 ppb	270	
1 - 2 cm		1980	460 ppb	460	
2 - 3 cm		1980	160 npb	160	
4 - 5 cm		1980	76 ppb	76	
5 - 6 cm		1980	16 ppb	16	
6 - 7 cm.		1980	0.8 ppb	0.8	
7 - 8 cm		1980	0.5 pps	0.5	
0 - 2 cm Take Optanic		1981	62 ng/g dry weight	62	Stevens, 1988
Lake Oncario		1981	71 ng/g dry weight	71	
		1981	73 ng/g dry weight	73	
		1981	110 ng/g dry weight	110	
		1981	120 ng/g dry weight	120	
		1981	210 ng/g dry weight	210	
		1981	250 ng/g dry weight	250	
		1981	840 ng/g dry weight	840	
0 - 3 cm					
Rochester basin 1986	1	1981	150.0 ng/g dry weight	150.0	Bourbonniere <u>et</u> <u>al</u> .,
Niagara basin		1981	188.9 ng/g dry weight	188.9	
Niagara basin		1981	200.0 ng/g dry weight	200.0	
Rocnester Dasin Mississance basin		1981	228.0 ng/g dry weight	228.0	
Niagara basin		1981	380.0 ng/g dry weight	380.0	
0 - 3 cm					
Niagara basin	35	1981	42 ng/g dry weight	42	Oliver at al., 198/
Rochester basin		1981	64 ng/g dry weight	64	
0 - 3 -					
Kingston basin	35	1982	14 ng/g dry weight	14	Oliver <u>et al</u> ., 1989
Rochester basin		1982	100 ng/g dry weight	100	
Niagara basin		1982	110 ng/g ary weight	110	
Mississauga basin		1982	130 ng/g dry sediments	130	
Niagara basin 1984	12	1982	110 ng/g dry <del>we</del> ight	110	Oliver and Charlton,
0 - 3 cm					
Lake Ontario		1983	100 ng/g dry weightfon a	andlO@iver, 199	0
suspended sediments					
Niagara basin	21	1982	26 ng/g dry weight	26	Oliver and Charlton,
1984		1002	97	77	
		1982	2/ ng/g ary weight 41 ng/g dry weight	41	
		1982	42 ng/g dry weight	42	
Niagara basin	6	1982	14 ng/g dry weight	Qliver, 198	4
Lake Ontario	10	1986	36 ng/g dry weight	36	Oliver and Nilmi, 1988
Toronto, Lake Ontario	13	1987	4.1 ppt	ILI Eco La	b., 1988

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

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1,2,3-TCB

botton sediments

Niagara basin 0 - 1 cm 1 - 2 cm 2 - 3 cm 3 - 4 cm 4 - 5 cm 5 - 6 cm 6 - 7 cm 0 - 3 cm Lake Ontario 0 - 2 cm Lake Ontario	1	1980 1980 1980 1980 1980 1980 1980 1980	<pre>18 ppb 11 ppb 10 ppb 3 ppb 2 ppb 3 ppb 1 ppb 7 ppb Oliver 7.2 ng/g dry weight 7.2 ng/g dry weight 8.6 ng/g dry weight 10 ng/g dry weight 11 ng/g dry weight 11 ng/g dry weight 14 ng/g dry weight</pre>	18 11 10 3 2 3 1 and Micol, 19 7.2 7.6 8.6 9 10 11 14	Oliver and Nicol, 1982 82 Stevens, 1988
Niagara basin	12	1981 1982	25 ng/g dry weight 9 ng/g dry weight	25 9	Oliver and Charlton,
1984					
suspended sediments					
Niagara basin	21 .	1982	6.9 ng/g dry weight	6.9	Oliver and Charlton,
1984		1982 1982 1982	7.7 ng/g dry weight 7.8 ng/g dry weight 64 ng/g dry weight	7.7 7.8 64	
1,2,3,4-TeCB					
botton sediments					
0 - 3 cm Lake Ontario		1980	33 ppb	33	Oliver and Nicol, 1982
Niagara basin 0 - 1 cm 1 - 2 cm 2 - 3 cm 3 - 4 cm 4 - 5 cm 5 - 6 cm 6 - 7 cm 7 - 8 cm	l	1980 1980 1980 1980 1980 1980 1980 1980	76 ppb 68 ppb 32 ppb 12 ppb 9 ppb 4 ppb 1 ppb 0.5 ppb	76 68 32 12 9 4 1 0.5	Oliver and Nicol, 1982
0 - 2 cm Lake Ontario		1981 1981 1981 1981 1981 1981 1981 1981	23 ng/g dry weight 31 ng/g dry weight 32 ng/g dry weight 34 ng/g dry weight 39 ng/g dry weight 46 ng/g dry weight 49 ng/g dry weight 110 ng/g dry weight	23 31 32 34 39 46 49 110	Stevens, 1988
g - 3 GM Rochester basin 1956 Niagara basin Rochester basin Niagara basin	I	1981 1981 1981 1981	37.0 ng/g dry weight 41.8 ng/g dry weight 50.0 ng/g dry weight 52.0 ng/g dry weight	37.0 41.8 50.0 52.0	Bourbonniere <u>et al</u> .,
Niagara basin Mississauga basin		1981 1981	53.0 ng/g dry weight 53.5 ng/g dry weight	53.0 53.5	

284

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0 -	3 cm				
	Niagara basin	35	1981	17 ng/g dry weight	17 Oliver et al., 1987
	Mississauga basin		1981	20 ng/g dry weight	20
	Rochester basin		1981	20 ng/g dry weight	20
198	Niagara basin 4	12	1982	41 ng/g dry weight	41 Oliver and Charlton,
0 -	3 cm Lake Ontario		1983	36 ng/g dry weig <b>E</b> alfon and	<b>GLiver</b> , 1990
#U.S	pended sediments				
198	Niagara basin 4	21	1982	20 ng/g dry weight	20 Oliver and Charlton,
			1982	21 ng/g dry weight	21
			1982	23 ng/g dry weight	23
	Niagara basin	6	1982	5.3 ng/g dry weight	O <b>LiBer</b> , 1984
	Lake Ontario	10	1986	15 ng/g dry weight	15 Oliver and Niimi, 1988
	Toronto, Lake Ontario	8	1987	17 ppt	lELI Eco Lab., 1988

<sup>1</sup>In most cases mean concentration reported; contact author(s) for raw data. <sup>2</sup>All reported values converted to ng/g dry weight. <sup>3</sup>Published literature from 1970 to 1991 only.

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

# The Importance of Large Events

by

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Great Lakes Monograph No. 4

#### Abstract

1

Sediment resuspension in rivers and lakes is a very nonlinear function of the currents in these systems. It is shown here that because of this and other nonlinear transport processes, large events such as storms on lakes and large run-offs in rivers, despite their infrequent occurrence, are responsible for most of the sediment transport in rivers and lakes.

It is also demonstrated that the flux of contaminants from the bottom sediments to the overlying water due to resuspension and deposition of sediments is generally larger, sometimes by as much as several orders of magnitude, than the fluxes due to bioturbation and molecular diffusion. As a result, large events are also responsible for most of the contaminant transport in rivers and lakes.

For many hydrophobic chemicals, the assumption of chemical equilibrium during resuspension/deposition is not valid. Therefore, in order to predict the flux of hydrophobic chemicals accurately, the rates at which adsorption and desorption occur and the parameters on which these rates depend must also be determined accurately, especially as they affect the partitioning of these chemicals between solids and water during large resuspension/deposition events.

The transport of sediments and contaminants is a very dynamic process with the fluxes changing continuously in magnitude and direction. There is no steady state. Because of this and the nonlinearity of the processes involved in this transport, an average state is difficult to define and may not be meaningful. It is the time-dependent event, especially the large run-off and/or storm, that must be considered in the modeling and prediction of the transport and fate of sediments and contaminants.

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

#### Introduction

In geology, in particular in the interpretation of the stratigraphic record, there has been a long standing controversy between the uniformitarionists and the catastrophists. The uniformitarionists believe in the 'gentle rain from heaven' theory; that is, sedimentary conditions and rates are uniform with time, and the stratigraphic record can be interpreted from a knowledge of the present day conditions and rates. Catastrophists on the other hand believe that the sedimentary record is primarily determined by large episodic events separated by long periods of time where very little occurs.

The history of this controversy is quite fascinating with the original confrontation occurring during the nineteenth century between people with strong religious beliefs (catastrophists) and presumably more logical scientists (uniformitarionists). The religious sector believed that God intervened in the day-to-day affairs of man and caused catastrophic events from time to time (for example, the great flood of Noah's time), and that these events were observable in the stratigraphic record. The scientists had a somewhat more logical approach; however, their approach was based on an over-simplified idea of the invariance of natural laws which was then extended to the presumption of uniform rates and conditions in the past. In the latter part of the nineteenth century, the emphasis on God's intervention decreased, the uniformitarionists were able to satisfactorily interpret much of the geologic record, and catastrophe theory became less favored.

However, in more recent times, the importance of large events in geology has received increasingly more attention. Ager (1981), in a delightful book entitled, "The Nature of the Stratigraphical Record", is a strong and persuasive proponent of the importance of large events in the interpretation of the stratigraphic record. In the book, he presents information on numerous catastrophic events and their effects on the stratigraphic record and emphasizes the spasmodic nature of sedimentation.

Of many events that he describes in detail, let me mention only a few. (1) The floods from the glacially-dammed Lake Missoula in the northwestern part of the United States

which occurred during the Pleistocene Epoch, about one to two million years ago. During this time, catastrophic floods from Lake Missoula occurred several times. An event was typically initiated when a 2000 ft. glacial dam broke; this was followed by a flood of water up to 800 ft. deep which ran for about 2 weeks from Lake Missoula to the Pacific Ocean about 430 miles away. Basins as deep as 135 ft. were scoured out, the Upper Grand Coulee (25 miles long) was formed, boulders many feet in diameter were rolled for miles, and current ripples up to 10 ft. in height were formed. (2) Turbidity currents in the Italian Apennines. For this region, it has been proposed that large turbidity currents caused the formation of sedimentary beds up to 20 m thick, all deposited by a single 'whoosh' of turbid water. (3) Hurricanes in the Gulf of Mexico. In more recent times, it is estimated that there is a 95 per cent probability that a hurricane will pass over any particular point on the coast of the Gulf of Mexico at least once every 3000 years. The maximum amount of sediment deposited over that period is estimated to be about 30 cm. But hurricanes, by resuspension and subsequent deposition, can certainly rearrange that amount of sediment. In other words, the rare hurricane is probably the main event recorded in the stratigraphy of this region and probably of other similar parts of the world, even in the present time.

Ager describes many other large and rare events and also the causes of these events, including tsunamis, meteorites, climatic changes, and plate tectonics. As far as catastrophic events are concerned, he concludes that "Nothing is world-wide, but everything is episodic."

Of course, as far as pollution in rivers and lakes is concerned, the spatial and especially the temporal scales of concern are much smaller than those described by Ager. Nevertheless, a careful examination of present-day sediment dynamics at the smaller spatial and temporal scales of interest in pollution problems also leads to a recognition of the importance of the large and rare event in the transport and fate of sediments. More importantly, it follows that the large event is also of major significance in the transport and fate of contaminants and in the resultant exposure of organisms to these contaminants. The specific hypothesis that will be argued here is that large episodic events such as storms on lakes and large run-offs in rivers, despite their infrequent occurrence, are responsible for

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

most of the sediment and contaminant transport in rivers and lakes. A corollary to this is that, over a long enough period of time, exceptional events are not the exception but the rule.

In the following, recent work on the effects of large events on sediment transport and fate in rivers and lakes is briefly discussed. The fluxes of contaminants from the bottom sediments to the overlying water due to resuspension/deposition, bioturbation, and molecular diffusion (as well as the effect of non-equilibrium sorption on these processes) are then briefly described and compared. A summary and concluding remarks are presented in the final section.

#### Sediment Transport

#### Lake Erie

The resuspension and transport of fine-grained sediments in Lake Erie has been calculated for a variety of wind conditions (Lick et al, 1991). The emphasis was on the effects of major storms. Calculations were made for different constant wind speeds and wind directions and also for the Armistice Day storm in November 1940, one of the largest in the last century. Only a brief summary of the results will be presented here; the report by Lick et al. should be consulted for the details.

However, before considering a few of the results, it is informative to consider a qualitative argument for the relative importance of large storms in resuspending and transporting large amounts of sediments. Consider the forcing of currents and/or wave action in a lake by a wind with speed U. The magnitude of the steady-state wind-driven currents and/or wave action is approximately proportional to the wind speed. It is also well known that the bottom shear stress  $\tau$  due to currents and/or wave action is approximately proportional to the square of the magnitude of the currents and/or wave action. From this it follows that  $\tau$  is proportional to the square of the wind speed, i.e.,

Great Lakes Monograph No. 4

(1)

Recent experimental evidence has demonstrated that the amount of sediment resuspended  $\varepsilon$  is proportional to the cube of the shear stress, i.e.,

 $\varepsilon \sim \tau^3$ 

From the above equations, it follows that the amount of sediment resuspended for a particular wind speed is approximately proportional to the sixth power of the wind speed, i.e.,

$$\varepsilon \sim U^6$$
 (3)

For example, when the wind speed is doubled, the amount of sediment resuspended is increased by a factor of 64; when the wind speed is increased by four, the amount of sediment resuspended is increased by a factor of 4096. It can be readily seen that the resuspension of bottom sediments is a very nonlinear and rapidly increasing function of the wind speed. The amount of sediment transported of course depends on the amount of sediment resuspended as well as the currents and is therefore also a very nonlinear function of the wind speed.

In order to quantify these arguments, calculations of sediment transport were made for winds of 11 mph (the average wind at the Buffalo airport), 22.5 mph, and 45 mph (the approximate maximum sustainable winds during the year). For each of these wind speeds, calculations were done for a southwest wind (the dominant wind direction throughout the year), a northeast wind (the dominant wind during large storms), a southeast wind, and a northwest wind.

In the middle of the Eastern Basin, cores have been taken and analyzed by Robbins et al. (1978). Geochronological data from these cores will be referred to below. For purposes of comparing the effects of different wind magnitudes and directions, the net deposition at this core location has been calculated and is shown in Table 1. For the average 11 mph wind, net deposition at this location is less than  $10^{-6}$  gm/cm<sup>2</sup> for all wind

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study 5

(2)

directions. For the 22.5 mph wind, the net deposition is largest for the southwest wind  $(0.01 \text{ gm/cm}^2)$  and decreases to 0.0003 gm/cm<sup>2</sup> for the southeast wind. For the 45 mph wind, net deposition is relatively large for all wind directions, is largest for the southwest wind (2.4 gm/cm<sup>2</sup>), and is least for the northeast wind (0.7 gm/cm<sup>2</sup>), but is generally on the order of 1 gm/cm<sup>2</sup>. The very nonlinear effect of increasing wind speed is quite evident as is the lesser effect of wind direction.

For purposes of verification, calculations of sediment deposition were then compared with the <sup>210</sup>Pb and <sup>137</sup>Cs data at the Eastern Basin core location. The data indicates that deposition at this site was very non-uniform with time with infrequent large depositions caused by major storms which were separated by long periods of time in which very little deposition occurred. The results of the calculated deposition are consistent with this idea, thus substantiating the model and the approximations used in the model. Depositions at this site due to major storms (defined as about a once-in-five year storm) typically are on the order of a few centimeters.

From the above and other similar calculations, it can be shown in general that winds with average and below average speeds cause negligible transport compared to the 1940 storm or any equivalent large storm. As the wind speed increases, the probability of an event with this speed decreases, but the net transport of sediment caused by all events with a given wind speed increases. The largest storms, despite their infrequent occurrence, cause the most transport of any class of wind events, and are responsible for more of the transport in Lake Erie than the total of all of the lesser storms and wind events.

#### Fox River

Sediment transport in the lower Fox River (defined as the part of the River from the DePere Dam to Green Bay) has been studied intensively as part of the Green Bay Mass Balance Program. As part of the sediment transport study, calculations were made of the concentrations of suspended sediments in the Fox at steady high, medium, and low flow rates as well as for time-varying flow events (Gailani et al, 1991). In particular, three large flow events were modeled in detail, and the results of the calculations were then compared

with observations. Excellent agreement between the calculations and observations was obtained, thereby validating the model and the description of the physical processes implied in the modeling. Calculations are presently being extended to include other storms, bed load, and the changes in sediment bed thickness due to resuspension and bed load. At the present time, reasonable agreement between the calculations and observations of the changes in sediment bed thickness is being obtained.

In the lower Fox under almost all conditions, the source of most sediment is the suspended sediment in the flow over the DePere Dam and not the resuspension/deposition of bottom sediments. As the flow rate increases, the sediment transport in the River increases even more rapidly due to higher sediment concentrations in the flow over the Dam as well as the increased flow. Erosion also increases rapidly with flow rate, for similar reasons to those described above for a lake.

The flow in the Fox is controlled by dams so that natural extreme high and low flows do not occur. Nevertheless, for the 1989-90 period examined by us in detail, approximately 80% of the sediment transport occurred in 20% of the time. For other rivers which are not controlled, a much larger fraction of the transport can be caused by fewer events. For example, the ratio of the once-in-five year flow rate to the median flow rate for the Fox is about 4; in the Buffalo River, this ratio is about 60; while in the Saginaw River, this ratio is about 30. In these latter rivers, because of these much higher ratios and because of the very nonlinear response of sediment resuspension to flow rate, it is expected that a much greater fraction of the sediment transport will occur during the large but rare event compared to the Fox. A preliminary estimate indicates that in these rivers a once-in-five year flow will transport an amount of sediment comparable to, or perhaps more than, the amount of erosion during a once-in-five year flow will be far greater than that caused by all other flows during that period.

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

### **Chemical Fluxes**

Chemical fluxes from the bottom sediments occur primarily by a combination of three processes: resuspension/deposition, bioturbation, and diffusion. Each of these processes is quite complex and also is distinctly different from the others. In general, they occur simultaneously, and there are interactions between them. However, for simplicity, each of these processes will be briefly described below independently of the others. In many realistic situations, one of the processes is dominant over the others and so, to a good approximation, can be considered independently. Other possible flux mechanisms are (a) diffusion and convection of chemicals adsorbed on colloids in the interstitial waters of the bottom sediments and (b) convection of dissolved chemicals in the interstitial waters. Convection of the pore waters is possible due to pressure differences caused by oscillatory wave action. These latter two flux mechanisms have not been investigated quantitatively, but are thought to be less important than the three mechanisms mentioned above and so will not be discussed further here.

Chemical reactions can significantly affect the sediment-water fluxes. For hydrophobic organic chemicals (HOCs), the adsorption/desorption process (especially its non-equilibrium nature) is particularly significant. Because of this, its effect on the flux is also briefly discussed below.

### Resuspension/Deposition

As bottom sediments are resuspended, the contaminants associated with these sediments are also transported into the water column where they may adsorb or desorb depending on the conditions in the overlying water relative to the conditions in the bottom sediments. This sorption does not occur instantaneously but at a finite rate. This will be discussed further below. Significant amounts of contaminants can be fluxed in this manner compared to bioturbation and diffusion.

For example, in Lake Erie during major storms, up to a meter or more of sediment

can be eroded from near-shore areas while up to 20 cm of sediment can be deposited in other areas further off shore (Figure 1). It should be noted that almost all areas in the Lake are neither uniquely erosional nor depositional; erosion generally occurs in almost all areas at the beginning of the storm while deposition occurs later in the storm. It is the difference between these two which determines whether there is net erosion or deposition at a particular site.

For the Fox, there is a similar 'conflict' between erosion and deposition with erosion occurring primarily at the beginning of the flood while deposition occurs later, especially during moderating and low flows. In the Fox, the amounts of sediment disturbed during a large run-off are somewhat smaller than in Lake Erie during a large storm. Figure 2 shows the net changes in bed thickness due to large flows in the period from October 27, 1989 to September 20, 1990. It can be seen that more than 50 cm of sediment have been eroded in some areas while up to 20 cm of sediment have been deposited in other areas. For rivers which are not as controlled as the Fox, greater changes in bed thickness due to resuspension/deposition are expected.

### **Bioturbation**

Bioturbation is another significant factor in the flux of contaminants from the bottom sediments. Benthic organisms burrow in the sediments and also plow through the sediments; in the process, they stir the sediments, force water through pores and burrows in the sediments, disrupt the existing sediment fabric, change the water content, and secrete mucus within the sediments. Their effects are many, quite diverse, and depend on the organism. In order to be specific, the vertical mixing of the bottom sediments by tubificid oligochaetes in Lake Erie (Fisher et al, 1980) is discussed here as a typical example of bioturbation. Tubificid oligochaetes are vertically oriented subsurface deposit feeders; they feed at depth and defecate at the surface, thus mixing the sediments by a combination of vertical transport due to feeding and diffusion due to slumping and closing of old burrows and development of new burrows.

From the activity of these organisms as measured in the laboratory and from their

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

densities as measured in the Lake, a reworking rate (reported as a subduction velocity) can be calculated and is shown in Figure 3. In most of the Western Basin and in the near-shore areas of the Central and Eastern Basins, the subduction velocities are about  $1.0 \times 10^{-2}$ cm/day. In most of the off-shore areas of the Central Basin, these subduction velocities decrease to about  $0.5 \times 10^{-2}$  cm/day, while in the center of the Eastern Basin, these velocities are still lower, about  $0.1 \times 10^{-2}$  cm/day. In a few isolated areas (mouths of the Detroit, Maumee, Sandusky, and Cuyahoga Rivers), the subduction velocities may be as high as  $5 \times 10^{-2}$  cm/day.

#### **Diffusion**

The flux of chemicals from the bottom sediments can also occur by diffusion; in fact, all of the chemical flux from the bottom sediments is quite often attributed to this process. In the absence of resuspension/deposition, bioturbation, and chemical reaction, diffusion can be described relatively simply, i.e., the flux q is given by

$$q = -D\frac{\partial C}{\partial z} \tag{4}$$

where  $\partial C/\partial z$  is the vertical concentration gradient in the sediment at the sediment-water interface, and D is the molecular diffusion coefficient. When chemical sorption is present, molecular diffusion is retarced because of this sorption. If sorption rates are sufficiently rapid that equilibrium is attained, then an effective diffusion coefficient which includes this sorption equilibration can be defined by (Berner, 1980)

$$D_{eff} = \frac{D}{1 + \left(\frac{1 - n}{n}\right)\rho K_p}$$
(5)

where  $K_p$  is the equilibrium partition coefficient defined as the ratio of the concentration of the sorbed chemical to the concentration of the dissolved chemical,  $\rho$  is the density of the solid particles, and n is the porosity of the sediment bed. For hydrophobic chemicals, this effective diffusion coefficient will be many orders of magnitude less than the molecular diffusion coefficient.

## Sorption

In quantifying the transport and fate of HOCs in aquatic systems, it is necessary to know the extent to which these chemicals sorb to particles in the water. In most previous work, it has been assumed that chemical equilibrium exists and that this equilibrium can be quantified by means of the partition coefficient K<sub>p</sub>. However, in recent work, it has been noted that although the initial adsorption or desorption of a hydrophobic chemical can be quite rapid, with time scales of minutes to hours, the final equilibration may take days to weeks or even longer (Karickhoff and Morris, 1985; Coates and Elzerman, 1986; Van Hoof and Andren, 1991). For example, it has been demonstrated that an equilibration time for hexachlorobenzene may be one to two months while equilibration times for PCBs may be months to years. By comparison, the time of transport of a sediment particle in a river or lake may be as short as minutes to hours. Because of this, the assumption of chemical equilibrium for HOCs sorbed to bottom sediments after these sediments are resuspended and as they are transported in an aquatic system may not be valid. Even the assumption of sorption chemical equilibrium in the surficial bottom sediments may be questionable when it is noted that the times between resuspension events (hours to days) may be quite small compared to sorption equilibration times. For these reasons, it follows that the rate of sorption as well as the equilibrium partition coefficient is a significant quantity and needs to be determined, both for suspended solids and for deposited bottom sediments.

In quantifying the rate of sorption, significant processes that must be considered are the convective-diffusive mass transfer from the water to the particle and the diffusion of the contaminant into the interior of the particle. The available data is consistent with the idea of a rapid mass transfer from the water to the surface followed by a slow diffusion into the interior. In both cases, the size of the particle is an important parameter. Since finegrained particles exist as flocs, the effective sizes and densities of these flocs are also significant in determining sorption rates.

## Comparison of Fluxes

A comparison of the relative effects of resuspension/deposition, bioturbation, and diffusion is difficult because these processes affect transport in different ways and on different time scales. Molecular diffusion is probably simplest to quantify. It occurs continuously. Molecular diffusion coefficients for non-reacting substances, e.g. NaCl, are typically about  $10^{-5}$  cm<sup>2</sup>/s. For reacting substances, the diffusion coefficients can be considerably lower. For example, for PCBs, the effective diffusion coefficients are on the order of  $10^{-12}$  cm<sup>2</sup>/s (from Eq. (5) or Fisher et al, 1983). An effective distance  $\Delta z$  over which diffusion affects the sediments is given by

$$\Delta z = \sqrt{D \,\Delta t} \tag{6}$$

where  $\Delta t$  is the time interval. Consider the depth of penetration in a one-year period (approximately  $3 \times 10^7$  s). For non-reacting substances (D =  $10^{-5}$  cm<sup>2</sup>/s),  $\Delta z$  is then approximately 17 cm. If D is  $10^{-12}$  cm<sup>2</sup>/s, then  $\Delta z$  is reduced to  $5 \times 10^{-3}$  cm.

Benthic organisms mix the sediments down to a depth of about 10 cm. This does not occur instantaneously but over a period of time that depends on the reworking rate, which in turn depends on the concentrations of the organisms and their activities. For a subduction velocity of  $10^{-2}$  cm/day (as for tubificids in Lake Erie), it would take 1000 days for the sediments to be well-mixed to a depth of 10 cm. In order to compare bioturbation with molecular diffusion, an effective diffusion coefficient can be defined as

$$D = \frac{\Delta z^2}{\Delta t}$$
(7)

For the present case, D would be about  $10^{-6}$  cm<sup>2</sup>/s. This is somewhat smaller than the molecular diffusion coefficient for non-reacting substances, but much larger than the

effective diffusion coefficients for strongly reacting substances.

In many areas of lakes, it has been assumed that benthic organisms are primarily responsible for the mixing of the upper layers of the sediments. The justification for this has been the well-mixed surficial layers deduced from the radiometric dating of the sediments. From a consideration of sediment dynamics, an alternative and more plausible explanation in many instances is that this mixing is due to episodic resuspension/deposition events.

The effects of resuspension/deposition are highly variable in space and time, depending on water depth, topography, and meteorological conditions. During calm periods and average winds, the effects of resuspension/deposition are relatively small and are probably comparable with the effects of bioturbation and diffusion. However, major storms can cause mixing of sediments to depths much greater than that possible by benthic organisms or chemical diffusion. The release of contaminants from the bottom sediments due to this resuspension/deposition and subsequent desorption would also then be much greater than that due to bioturbation or diffusion.

The effects of contaminant sorption on resuspension/deposition, bioturbation, and diffusion depend on the particular transport process as well as the rates of adsorption and desorption, but have not yet been quantified. However, consideration of the differences in the fluxes for the two limiting cases of fast sorption (equilibrium partitioning) and slow sorption (frozen partitioning) shows that the effects of sorption rates can be significant and must be considered in determining the flux of contaminants.

### **Concluding Remarks**

Some geologists, in their version of catastrophe theory, have recently emphasized the importance of the large but rare event and believe that the sedimentary record is primarily determined by large episodic events separated by long periods of time where very little occurs. A careful examination of present-day sediment dynamics at the smaller spatial and

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study temporal scales of interest in pollution problems also leads to a recognition of the importance of large events. In the present paper, it is specifically argued that large episodic events such as storms on lakes and large run-offs in rivers, despite their infrequent occurrence, are responsible for most of the sediment and contaminant transport in rivers and lakes.

Quantitative results were presented for Lake Erie which demonstrated (a) the very nonlinear response of sediment transport and fate to the wind speed over the Lake, (b) that major storms can be identified in the geochronological record, and (c) that major storms are responsible for most of the sediment transport in the Lake. For the Fox River, detailed and verified calculations of sediment transport have demonstrated that a few large run-off events are responsible for most of the transport in the River, despite the fact that the River is controlled and the natural extremes of flow do not occur. For other rivers which are less controlled, even a greater fraction of the transport would be caused by fewer events. For example, for the Buffalo and Saginaw Rivers, preliminary calculations indicate that a oncein-five year flow will transport more sediment than all the other flows during that same five year period.

The importance of the effects of resuspension and deposition of bottom sediments on the flux of nutrients and contaminants from the lake bottom to the overlying water was also emphasized. In fact, it was argued that the net chemical flux due to resuspension/deposition is generally larger, in some cases by several orders of magnitude, than the chemical flux due to both molecular diffusion and bioturbation. In order to predict the net flux accurately, the finite rate at which sorption occurs and the parameters on which this sorption depends must also be determined accurately.

A generalized conclusion that follows from these studies is that, during any specified period of time (whether it is one year or twenty years), the largest event (either storm or run-off) expected during that period is responsible for more of the sediment and contaminant transport than all of the other events during that period. In other words, during a one-year period, the once-in-a-year high flow or storm will cause more sediment and contaminant transport than all the other flows or storms during that year. During a

five-year period, the once-in-five year high flow or storm will cause more sediment and contaminant transport than all the other flows or storms during that five-year period, i.e., more than the five once-in-a-year high flows or storms. During a twenty-year period, the once-in-twenty year high flow or storm will cause more sediment and contaminant transport than all the other flows or storms during that twenty-year period, i.e., more than four once-in-five year high flows or storms and more than twenty once-in-a-year high flows or storms.

The above statements may be repetitive and may even be slightly over-stated for some cases, but the repetition is meant in order to make a point. In attempting to predict the trend of water quality in rivers and lakes over long periods of time, it is the large run-off and/or storm that must be considered in the modeling and prediction of the transport and fate of sediments and contaminants. This of course is contrary to the conventional wisdom which emphasizes the uniform deposition of sediments and the chemical flux from the bottom sediments due to diffusion. In contrast, the above studies emphasize the dynamic nature of sediment and contaminant transport and the importance of large events in this dynamics. There is no steady state. Because of this and the nonlinearity of the processes, an average state is difficult to define and may not be meaningful.

From this it follows that, in order to predict sediment and contaminant transport more accurately, data and modeling relevant to large storm and run-off events are needed. In particular, data is needed on the resuspension of sediments at high shear stresses, the changes in bathymetry due to erosion/deposition during large events, the variation of sediment properties with depth and not just near the sediment-water interface, and weather conditions, flows, and sediment and contaminant concentrations during large storms and run-offs. More accurate information on the probability of the occurrence of a large event of a certain magnitude is also needed. The non-equilibrium nature of HOC sorption needs to be investigated, first as a rate process and second as it affects the partitioning and flux of contaminants during large events controlled by resuspension/deposition.

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- **Lake Ontario Case Study** 

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# Deposition in Eastern Basin of Lake Erie (gm/cm<sup>2</sup>)

Wind	Wind Magnitude (mi/hr)					
Direction	11	22.5	4 5			
Southwest	< 10-6	.01	2.4			
Northeast	< 10-6	.0008	0.7			
Northwest	< 10-6	.005	1.6			
Southeast	< 10-6	.0003	1.0			

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Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

# Appendix C

# **Workshop Participant Roles**

**Steering Committee** 

Robert Beltran Jack Manno Charles Zafonte Joseph V. DePinto William L. Richardson Michael Zarrull

Work group 1

# Loading and Forcing Functions

Keith Bedford Dave Devault Andy Ernest Gary Kohlhepp Jack Manno Gerry Mikol Griff Sherbin Jeff Steuer Stewart Taylor Thomas Young Robert Beltran Dave Dolan Rajeev Jain, *Support* John Konrad J. Alex Mccorquodale Dale Patterson William Sonzogni, *Facilitator* William Strachan Shirley Thompson

# Work group 2

In Situ Field Observations and Measurements

Dieter Busch Dominic DiToro Brian Eadle Steven Eisenreich John Hassett Barry Lesht Melanie Neilson, *Facilitator* William Richardson Ralph Rumer Donald Stewart Philip Cook Dick Draper David Edgington Efraim Halfon Joe Hudak Joseph Makarewicz John Paul Jack Rosenfeld Natalie Schito Scott Underhill, Support

# Workgroup 3

# **Model Paradigms**

Victor Bierman Steven Chapra Joseph DePinto Frank Gobas Donald Mackay Steven McCutcheon Nicholas Nikolaidis Ramesh Raghunathan, Support Robert Thomann Wayne Willford Bill Booty Maxine Dakins Kurt Fedra Charles Hall James Martin, *Facilitator* Peter Nettleton Donald O'Connor William Schertzer John Toll Charles Zafonte

# Workgroup 4

#### Process Paramaterization

James Bonner Terry Clark Doug Endicott Jim Kramer, *Facilitator* Paul Rodgers Deborah Swackhamer Michael Zarrull Chen-Yu Cheng, Support John Connolly Efraim Halfon Wilbert Lick William Snodgrass Kent Thornton

**Closing Panel** 

Brett Kaull William L. Richardson Charles Zafonte Donald O'Connor Wayne Willford Michael Zarrull

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

Appendix D

# Summary of Post-Conference Survey Results

Question 1: If you were organizing this conference next time, what would you do differently? The conference was aimed at reducing uncertainty in mass balance models but specific models were not presented nor discussed in any detail. Qualitatively, the uncertainties will differ from toxicant to toxicant -- different loadings via different routes and different processes governing their fates. The workshop might have benefited by being more specific in its charges to the participants. A selection of pollutants with different properties and modes of import and export could have been given which covered the span for substances to be encountered; a definition or comparison of the sorts of model (and therefore the inputs) to be considered would have helped focus the discussions.

- Smaller working groups with more specific charges.
- A prior budgeting for a follow up meeting to be held the following year.
- Invite speakers to introduce the notion of value of information as a framework for guiding mass balance modeling research.

Examples of such work:

Reichard and Evans, 1989. "Assessing the Value of Hydrogeologic Information for Risk Based Remedial Action Decisions," <u>Water Resources Research</u> 25(7):1451-60.

Knopman and Voss, 1987." Behavior of Sensitivities in One-Dimensional Advection-Dispersion Equation: Implications for Parameter Estimation and Sampling Design," <u>Water Resources Research</u> 23(2):253-275.

In retrospect, I think I would do the following:

Provide more detailed guidance to the working groups and facilitators. There seems to be some confusion as to what the actual goals of the workshop were. As a result, it seems that the working group discussions and reports were either biased by facilitator's pre-conceptions of what he/she thought the workshop goals were, or dominated by particular individuals, who, in the absence of more definite guidance, put forth their own agendas.

- I thought I understood the workshop goals from reading the prospectus and from discussions with the organizers in advance of preparing a white paper. However, most people focused on what I think of as application and implementation issues only (e.g., which chemicals should be monitored, how many cruises should we have) instead of more technical issues (e.g., how do we quantify uncertainty, how does model uncertainty affect management decisions). Both issues are important and I think that the workshop was intended to deal with them both. However, I think the technical issues should have been dealt with first. An understanding of these more basic problems would put the implementation questions into a more general and manageable context. However, given the time that we had, it would have been very difficult to consider both.
- My second suggestion is that I would have allowed more time for the workshop and perhaps involved fewer people. I thought the plenary presentations on the first afternoon were excellent and a great way to start off the conference but all of the work of the meeting was done on day 2. The size of the working groups (about 15 people) was too large to really work efficiently and it was very difficult to get into any great depth about the questions the groups were charged with. I think this is why the groups tended to focus on fairly narrow implementation issues rather than on the broader technical issues. If more time was allowed (maybe another day) and if we had spent the first day on the fundamentals and the second day on the specifics of a Lake Ontario model, I, for one, would have been more satisfied with the result. I realize, of course, that it is hard

Reducing Uncertainty in Mass Balance Models of Toxics in the Great Lakes- Lake Ontario Case Study

enough to get people to a meeting for three days, to say nothing of four. Perhaps if the original group were smaller it could have been done.

- A strawman proposal for Lake Ontario would have focused discussion a bit better. This should have included samples per year, tributary schedule, lake stations, biota sampling, process experiments, etc.
- I thought the conference went well and was exactly what was needed, however next time I would hope we could get more managers to participate. With many workshops like this the results get stuck and never get communicated to those who can implement the recommendations. Let's make sure we put a presentation package together for use by the key organizers and perhaps as a group we could present it to different management groups. I would hope that each participant would take the results to appropriate forums.
- The conference was very well organized and run. One suggestion for next time professional facilitators in the work group meetings would have helped keep groups on track. Group leaders could be "resource persons" for technical input. A recorder could have just kept notes. Asking a group leader to do all three jobs is almost impossible.
- More time with small groups. Possibly smaller groups.
- I might have made it a bit more structured, i.e., posed a series of questions to focus each workgroup.
- Have more of the Managers integrated into the workgroups.
Question 2: In retrospect, what point do you wish you had made? Effective treatment of uncertainty in mass balancing modeling of Great Lakes toxics requires supplementing best available mass balance models with sensitivity/uncertainty and decision analytic methods to produce a more useful policy research tool. Sensitivity/uncertainty and decision analytic methods provide rigorous documentation of objectives and modeling assumptions and a rational framework for thinking about the value of reducing uncertainty in mass balance models.

The effectiveness/usefulness of models in regulating pollution sources is diminishing. The real value is in understanding the ecosystems so that the necessary societal changes can be made with respect to persistent toxic substances.

That modelers and experimentalists interested in water quality evaluation and forecasting must work together to develop holistic models. Piecemeal research never results in a complete systems approach and can lead to confusion, contradiction, and poor decision making.

Given that the workshop was to address reducing the uncertainties in mass balance models, I feel that the role of the biota in the models should not have been included -- except as a check on predictions or a surrogate for some other aspect of the models. It would be nice to have "the mother-of-ail-models" but the resources to validate (or even develop) such a model are not and will not be made available. We should learn to walk before we run. If we cannot predict/account for 90% of the disposition of chemicals, how then are we going to do 99.99% of them?

I feel that a sensitivity analysis of the models to each of the different process parameters and the input functions should be done. There are some which need only be known roughly and others which should be more precise. This might help in determining the source(s) of the uncertainty.

The point I tried to make is that there are contaminant data from Lake Ontario to compare models with and there are loading data that can be used to drive the models. There is a white paper with data, a published paper with data up to 1983 and the later loadings from the Niagara river are available from CCIW. In a paper in preparation we will show that those loadings for four chlorobenzenes, PCB's and mirex can drive the model well enough to match the data well. The model was calibrated with 1983 data and therefore a good match with post-1983 data can be considered a post-audit.

The modeling proposals are only incremental improvements over the Green Bay Study. While I welcome the progress that Bob Thomann and others have made in their thinking, we need to go still further in improving the state of the art. We should not be distracted by the difficulties of the Green Bay Study. Many of these problems can be avoided by the improved management of resources and investigators that was being learned during the study as quickly as new things were being learned about modeling.

Up-front planning and understanding of objectives by all study participants is essential. Omission of mercury from the list because it is difficult to analyze is irresponsible and naive.

When models are well understood, pathways and kinetics well documented, rates known etc., the model is no longer needed. Once we understand how a system works, we can effectively manage it and make intelligent decisions. It is precisely where we don't understand, have the highest uncertainty and least insight where models are needed the most. A mass balance model exposes our lack of knowledge in ways individual research projects never could. The discussion on mercury is a case in point. We know less about mercury than most other toxics. Trying to do a mass balance model will very clearly show what our knowledge needs are.