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Report of the Surveillance Subcommittee

to the Great Lakes Water Quality Board

Proceedings of the Mass Balance Workshop

Kempenfelt Conference Centre Barrie, Ontario

March 7 - 9, 1990

A Report to the Surveillance Subcommittee

by the Mass Balance Workshop Steering Committee

March, 1991

ISBN 1-895085-22-5



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DISCLAIMER

to the Great Lakes Water Quality Board

The views expressed in this report are those of the Workshop participants and are not necessarily those of the Great Lakes Water Quality Board or the International Joint Commission.

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MASS BALANCE APPROACH TO LAKE TOXIC SUBSTANCE MANAGEMENT EXECUTIVE SUMMARY

The Great Lakes Water Quality Agreement continues to be refined and updated to reflect priorities in the Great Lakes basin and to promote new approaches to understanding ecosystem health. Annex 11 of the 1987 Protocol specifies that the surveillance program allow assessment of "total pollutant loadings to, storage and transformation within, and export from the Great Lakes System", i.e. the mass balance approach.

The existing surveillance program is not designed to collect the loading and independent verification data necessary to test and improve mass balance models for even the Critical [11] Pollutants. The new Great Lakes International Surveillance Plan (GLISP) (Surveillance Work Group 1987) represents an evolution toward acquiring some of these data and it is expected that programs will need to evolve if the mass balance approach is to be supported. The Surveillance Subcommittee (SSC) determined that it was necessary to bridge the gap between the existing surveillance programs and programs optimized for a mass balance analysis.

The SSC, in conjunction with the Loadings and Sources Subcommittee and the Science Advisory Board's Technological Committee, convened a workshop at the Kempenfelt Conference Centre in Barrie, Ontario on March 7-9, 1990 to improve the communication between modelers and the surveillance community, with the ultimate goal of developing specific recommendations that would lead to the application of the mass balance approach to specific contaminant problems/issues in the Great Lakes.

It was generally agreed at the workshop that the surveillance data are underinterpreted and that the application of a simple two-compartment (water column and sediment) mass balance model would greatly facilitate this interpretation. Such an application could be used, with relatively little expansion of the current surveillance programs, to conduct cursory level interpretations of the surveillance data and to begin to distinguish internal and external loads. Furthermore, it seemed the consensus of the participants that a Data Interpretation Group be formed to assist in the preparation of the State of the Lakes chapter for the Water Quality Board Report, and to ensure maximum utilization of the data generated.

Recommendations specific to each of the management issues presented to the work groups are summarized below:

1. <u>Group I</u>: Can simple mass balance models be applied to current surveillance data to provide useful information on current loads of the Critical 11 Pollutants? What further data would be required to improve and/or validate these models?

Group I added a sediment component to a single compartment (water column) model proposed by Dr. Don Mackay in a letter to the Great Lakes Science Advisory Board, in which he had used PCB trends in Lake Ontario fish and herring gull eggs to determine the bulk loss time constant. The output from the revised model would provide estimates of total internal and total external loadings with time. Some of the sampling needed for application of this simple mass balance model, while not currently being done, is called for in GLISP. Sampling components that were identified as being not entirely satisfied included dissolved contaminants in water, contaminants in bottom sediments and contaminants in actively resuspended sediments.

2. <u>Group II</u>: What change in (i) atmospheric, (ii) tributary and/or (iii) point source loading would be required to achieve 0.1 ppm total PCB in lake trout at an upper 95% confidence bound?

Group II required a more sophisticated model, one which related loadings to in-lake concentrations to fish body burdens, i.e. a food web model. For Lake Ontario, the required model divided the sediment compartment into multiple horizontal segments: there needed to be two epilimnetic segments, but only a single hypolimnetic segment. It was emphasized that more effort should be directed at the lower levels of the food chain.

To measure the atmospheric component for model input, Group II recommended implementation of the recommendations made in the IJC report, "A Plan for Assessing Atmospheric Deposition to the Great Lakes." Information from this atmospheric deposition network would need to be integrated with emissions data; receptor modeling techniques could then be used to provide information about sources.

The monitoring strategy proposed by Group II to determine the tributary component of the loadings matrix was based on a ranking of the major tributaries. The level of effort was proportional to the relative contribution of each tributary to the estimated total load (this figure could be determined from flow data and phosphorus loadings data. When possible, it is recommended that actual toxic contaminant data be used in identifying sampling schemes). For Lake Ontario, 11 tributaries would need to be monitored, with estimates supplied for the inputs from the Niagara River and Hamilton Harbour. Depthintegrated samples would need to be collected at a transect of stations near the downstream - most flow gauge, transverse to the direction of the flow; these samples would then be composited into a single sample. To keep the number of samples to a minimum, the group recommended several integration techniques which could aptly be applied to other monitoring components as well.

3. <u>Group III</u>: What is the loading to the open lake from nearshore regions, especially Areas of Concern?

Two generic nearshore areas were defined, which represented the extremes in the interface characteristics of Areas of Concern. The first type, a simple, well-mixed pipe, is dominated by advective flow, while the other extreme, a large, relatively open nearshore area, may be dominated by turbulent transfer at the interface. Each nearshore area must be considered unique, even though it may approach one of these extremes. It was recommended that, for either type, a one-time, intensive field data collection program be conducted for at least one year to determine the requisite loading flux parameters. The data analysis and modeling effort was determined to be extensive: an estimate of three person years was given. It was concluded that the absence of an adequate data base to accommodate the Areas of Concern component of a lakewide mass balance approach is not due to a lack of specification in GLISP¹ (with some refinements to the specifications for current/ hydrologic/physical data), but rather to a lack of implementation.

¹Which includes the "Guidance on Characterization of Toxic Substances Problems in Areas of Concern in the Great Lakes Basin" (Surveillance Work Group 1987). 4. <u>Group IV</u>: What is the relationship between concentrations of contaminants and that of conventional pollutants?

Group IV focused on sorbent compartments, as an accurate representation of the properties and dynamics of sorbent compartments is crucial to accurate toxics exposure modeling. They identified four sorbent compartments: plankton, non-living particulate organic carbon, dissolved organic carbon, and abiotic (allochthonous) particles, and specified that surveillance data were required to determine both the quantities of each of these sorbent compartments and the associated contaminant concentrations.

In fully implementing the mass balance approach, it is recognized that there are considerable gaps in knowledge regarding the transfer of contaminants through the ecosystem, that cannot be accommodated by [routine] surveillance programs. Four informal Research Work Groups were formed at the workshop to recommend improvements to research areas that would support the mass balance approach.

It was identified that there was generally a paucity of data to validate the current food web models; again, it was emphasized that data on contaminant levels in the lower trophic levels were lacking. A multi-year study of the movement of contaminants through food chains was recommended. Even more basic was a lack of knowledge of "who is eating whom, and how much?"

Direct measurements of fluxes at the sediment-water interface are needed, as are air/water and air/land exchange rates.

Finally, research is required to relate the dissolved contaminant concentrations to the biologically available fraction. To this end, we need to better understand the role of dissolved organic carbon in controlling the fate of contaminants.

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INTRODUCTION

In 1985, the Water Quality Board developed a two-track approach to address the toxic substances problem in the Great Lakes: a comprehensive track and a primary track. The comprehensive track was intended to evaluate all contaminants identified in the Great Lakes; those which were identified as representing an immediate threat to the ecosystem would then be promoted to the primary track. The purpose of the primary track was to identify, quantify and eliminate all significant sources of contamination. Immediately, 11 Critical Pollutants were identified for the primary track process.

The Board intends to support its two-track strategy through the use of predictive, scientifically valid mass balance models of toxic substances. Modeling can assist in quantifying as yet unknown, poorly quantified, or hard-to-quantify sources. In addition, modeling should make it possible to determine that mix of load reduction efforts to which the Great Lakes ecosystem would be most responsive, or which source reduction strategy would be most cost effective. Finally, modeling should provide an estimate of the time required to achieve a particular magnitude of decrease in a given media in response to implementation of a target load reduction before-the-fact, while monitoring could only reveal the effect of an actual load reduction after-the-fact.

The revised Great Lakes Water Quality Agreement of 1978, as amended by the Protocol of 1987, describes the development of Lakewide Management Plans for Critical Pollutants. It specifies that these plans shall include (in part):

(ii) "An evaluation of information available on concentrations, sources and pathways of the Critical Pollutants in the Great Lakes System, including all information on loadings of the Critical Pollutants from all sources, and an estimation of total loadings of the Critical Pollutants by modeling or other identified methods;"

and

(iv) "a determination of load reductions of Critical Pollutants necessary to meet Agreement Objectives;"

This consideration further emphasizes the need for surveillance programs to be responsive to the information requirements of the mass balance approach as applied to the Critical Pollutants.

Models are tools for synthesizing and interpreting data in a systematic way. Mathematical representations of complex ecosystems are based on relatively well understood physical, chemical and biological relationships developed from controlled laboratory or partially controlled field experiments. Models designed to predict lake response to known loads of contaminants have been rigorously tested in a workshop held by the Task Force on Chemical Loadings (IJC 1988) and the strengths and shortcomings of these models were described in detail. The consensus of the workshop was that the data were more flawed than the models. The models were judged to be fairly good, but they differed in detail in various areas, and they had different mass transfer coefficient values. Similar conclusions were reached at the Workshop on the Estimation of Atmospheric Loadings of Toxic Chemicals to the Great Lakes Basin (IJC 1987; Strachan and Eisenreich, 1988), which attempted to put atmospheric loads in perspective by developing whole lake mass balances.

Water quality managers are justifiably unsure of the value of model predictions. Until model validity can be objectively determined, they should be considered as one of a set of inputs to the decision-making process. Programs are being designed and implemented to improve and/or verify mass balance models. The Upper Great Lakes Connecting Channels Study has recently been completed (UGLCCS 1988) and an intensive program to mass balance PCBs, dieldrin, lead and cadmium in Green Bay is just beginning. In both of those programs, modelers were active in the design of monitoring and process studies. A joint United States-Canadian effort on Lake Ontario is underway to use best available models for estimating the load reductions necessary to achieve implemented or action level standards for toxics, such as concentrations of 0.1 ppm PCB in whole fish. These interactions among modelers, managers and the monitoring agencies will eventually lead to improved model fidelity and accuracy.

WORKSHOP GOAL AND OBJECTIVES

The existing surveillance program is not designed to collect the loading and independent verification data necessary to test and improve the mass balance models for Critical Pollutants. The Great Lakes International Surveillance Plan (GLISP) represents an evolution toward acquiring some of these data and it is expected that programs will need to evolve if the mass balance approach is to be useful. It is necessary to bridge the gap between existing surveillance programs and programs optimized for a mass balance analysis.

The Surveillance Subcommittee, in conjunction with the Loadings and Sources Subcommittee and the Science Advisory Board's Technological Committee, convened a workshop on March 7-9, 1990 to improve the communication between modelers and the surveillance community and to identify potential applications of the mass balance approach to contaminants.

The goal of the workshop was to:

Develop <u>SPECIFIC</u> recommendations that would lead to the application of the mass balance approach to specific contaminant problems/issues in the Great Lakes

The three workshop objectives were:

- o To have modelers and data gatherers exchange perspectives on the mass balance approach
- o To agree on the data (locations, frequency, quality, etc.) necessary to meet the requirements of different mass balance applications
- To determine whether these data are currently being collected or are being recommended to be collected within the surveillance programs, thereby identifying data gaps

The complete agenda for the workshop may be found in the Appendix.

The workshop objectives were addressed by dividing the participants into four groups. Each group was asked to recommend changes to the existing GLISP to provide data to answer a management question. Each group was given a "strawman" monitoring plan as a starting point.

The four management questions and associated "strawmen" were:

 Can simple mass balance models be applied to current surveillance data to provide (useful) information on current loads of the Critical 11 Pollutants? What further data would be required to improve and/or validate these models?

STRAWMAN: GLISP as currently implemented

2. What changes in (i) atmospheric, (ii) tributary and/or (iii) point source loadings would be required to achieve 0.1 ppm total PCB in lake trout at an upper 95% confidence bound? Are food web models/data required or is a bioconcentration factor sufficient? Specify confidence levels for these answers. How long will it take to reach the stated objective with the proposed strategy?

STRAWMAN: Green Bay Study and Lake Ontario Toxics Management Plan

3. What is the loading to the open lake from nearshore regions, especially Areas of Concern? What is the least information needed to estimate this amount? Can integrated samplers (biological or mechanical) be used? How? Is the technology available or being developed to monitor for this question? What frequency of sampling is needed?

STRAWMAN: 20 discrete water samples per month at the interface with open lake. Two Doppler current meters to identify direction and magnitude of flow at time of sampling. Average net load answers question.

4. What is the relationship (coupling) between concentrations of contaminants and that of conventional (e.g. nutrients, suspended solids) pollutants? How will management of these conventionals (and fisheries management) affect contaminant transport, uptake, residence times, etc.?

STRAWMAN: GLISP

Each group produced a report that summarized its discussions and recommendations.

The workshop participants were also asked to consider five research questions in a two hour evening session. The research questions and suggested discussion topics were:

1. TRANSFER OF CONTAMINANTS TO/THROUGH THE BIOTA

Topics for consideration:

o Are biota at/near steady state with the Critical 11 (C11) pollutants?

- o Are sediments a significant source of Cll to biota?
- 0 Are the existing surveillance programs measuring the best organisms and associated parameters (e.g. lipids)?
 - o Do surveillance programs need to measure Cll throughout the food web or are bioconcentration factors sufficient?
 - OTHERS defined by the work group 0

CONTAMINANT TRANSFER AT THE SEDIMENT-WATER INTERFACE 2.

Topics for consideration:

- o Do we have good numbers for rates of diffusive exchange for the Cll?
- Are benthos a significant vector for Cll transfer to top predators? 0
- OTHERS defined by the work group 0

CONTAMINANT TRANSFER AT THE AIR-WATER INTERFACE 3.

Topics for consideration:

- How reliable are present estimates of wet and dry deposition of the 0 C11?
- Is the existing monitoring/proposed network sufficient? What 0 accuracy/precision will come from the fully implemented network?
- 0 Can sources be identified with the existing/proposed monitoring program? If not, how will atmospheric loads be regulated?
- o OTHERS defined by the work group

4. UNCERTAINTY IN MODELING AND MEASUREMENTS

Topics for consideration:

- o What are the major inherent weaknesses in the models?
- 0 Using PCB as a test case and assuming perfectly known loads, what is the magnitude of inherent model errors?
- 0 Where are the major weaknesses in existing measurement programs? Be as specific as possible or develop recommendations for estimating them. OTHERS defined by the work group
- 0

IMPLEMENTATION OF RECOMMENDATIONS 5.

Topics for consideration:

- By what mechanism can simple mass balance interpretations be made of 0 current surveillance data (e.g. contract for 1991 WQB Report)?
- How will the recommendations from this workshop be used? Where do 0 they go next?
- Should the GLISP, with these recommendations, be independently 0 reviewed (e.g. NRC/NSB, IAGLR Technical Advisory Committee, contractor)?
- OTHERS defined by the work group 0

Each research discussion was summarized by a recorder.

WORKSHOP PROCEEDINGS

The following are the reports of the four groups examining management questions and the five summaries of research discussions. The actual viewgraphs of tables and figures used at the workshop are included whenever possible.

A list of the workshop participants as well as the membership on the steering committee may be found in the Appendix.

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<u>Don Mackay, Chairman</u> Barry Lesht, Recorder

STATEMENT OF MANAGEMENT QUESTION/ISSUE

Can simple mass balance models be applied to current surveillance data to provide (useful) information on current loads of the Critical 11 Pollutants? What further data would be required to improve and/or validate these models?

DISCUSSION OF THE MANAGEMENT QUESTION

Those responsible for "resource management" in the Great Lakes, particularly those involved with environmental assessment, regulation and contaminant control, need information about the lakes that may not, at present, be obtainable directly from measurement programs. In addition to futureoriented, process-related questions, such as "What will happen to the concentration of substance x in the lake if loads are reduced to level y?", seemingly simple questions such as "How much of substance x is being loaded into the lake now (or in the past)?" must be answered. Water quality models of varying complexity, based on a mass balance concept have been developed over the years in an attempt to answer the first type of question. Because measurement programs necessary for direct estimation of loads have not yet been implemented, it seems reasonable to ask whether mass balance models can be used to answer the second type of question as well. Simple models may also be useful for determining data quality objectives, for estimating likely environmental concentrations for comparison in advance with analytical detection limits, and for suggesting which environmental compartments should be sampled for tracking the flow of contaminants throughout the system.

If models can be used to infer quantities or information that cannot now be measured directly, we should examine the benefits, requirements and limitations of this approach. In the following paragraphs we discuss the concept of mass-balance-based models, the relationship between the models and field data, the application of the models to the question posed above, and the adequacy of current surveillance programs to support simple mass balance models.

CONCEPTUAL APPROACH

Mass Balance Models and Surveillance Data

All water quality models currently in use are based on the same principle, namely conservation of mass. The differences between so-called simple mass balance models and more complicated models are reflected in the level of detail with which the modeled systems are represented. Models differ in:

- o the number of fundamental compartments in which mass is distributed (e.g. water column, sediment, biota)
- o the number of different state variables for which mass is tracked (e.g. nutrients, contaminants, biomass)

- o the number of distinct spatial segments
- o the methods of either specifying or calculating the intercompartment and inter-segment fluxes of the state variables

o the degree of temporal resolution desired

For example, a very simple contaminant model might track the mass of one state variable (the contaminant) in one compartment (e.g. the water column) in one spatial segment (considered a well-mixed reactor), with fluxes into the single compartment (loads) specified as an external forcing function and fluxes out of the single compartment calculated as directly proportional to the mass in the compartment (first order loss). In terms of concentration, such a model may be expressed with one ordinary differential equation

beelovel ezodt v(1)(1)

$$V dC/dt = E + F_iC_i - F_oC - kVC_i$$

in which V is the volume of the (well-mixed) spatial segment; C is the concentration of the contaminant; E is the external load [mass/time]; F_iC_i represents the load of the contaminant from upstream sources; F_O is the volumetric flow rate out of the segment and k is some bulk loss rate constant. More complicated models would require many more (coupled) differential equations and would involve many more parameters.

If the model parameters (e.g. F_i , F_o and k in Eq. 1 above) were accurately known, and if the segment and compartment fluxes were modeled correctly, mass balance models would be accurate transfer functions between the external forcing (loads) and the compartment masses. As such, they could be used to predict the effects on the model compartments of changes in the external load. In general, this function is the purpose for which mass balance models have been developed. Of course, model parameters are seldom, if ever, known accurately and in many cases the assumption that compartment fluxes are modeled correctly cannot be verified. Thus, the models are imperfect transfer functions, that must be evaluated by comparison of model predictions with field data.

Typically, water quality modeling proceeds in one of two directions. In some cases, models are formulated from "first principles" and simulations conducted in advance of (or without reference to) field data collection. Field data are used after the model has been developed to "calibrate" parameters and evaluate the model's success. In other cases, field data are collected first and models are formulated later in order to understand and explain the observations. We are primarily concerned with the second case (because the collection of data is dictated by other objectives of the surveillance program) and are interested in what may be considered the "information content" of the field observations. Because the field observations are to be interpreted within the context of a particular model, the information content will be, to a certain extent, model dependent. That is, there must be a contextual match between the data available and the model's complexity. It is easy to imagine that a set of simple field observations would be sufficient for application of one model, but insufficient for application of another. On the other hand, it may be impossible to use a simple model to explain a very detailed set of field observations.

Although the data have been collected for a variety of purposes, it is still reasonable to ask what management questions can be addressed by a model whose level of complexity is matched to the data. However, if the model complexity is stretched beyond the available data, reliable information can be lost. In other words, models for simulating the behaviour of natural systems are only as good as the data base on which they have been developed. If management questions of an increasingly complex nature need to be addressed, then data collection will have to be revised, with the requirements of more complex models in mind.

There are two reasons why the quality of the data base dictates the level of complexity of models. The first is that fundamental ecosystem theory is not developed to the point where models can be applied without site-specific calibration (i.e. test data from the actual location to be modeled). The other reason is that models are not just computer programs that describe a system, but rather an assembly of scientific and technical knowledge that evolves as new developments occur (i.e. better lab experiments and field sampling). Therefore, as data improve in both quality and quantity, confidence in using the model as a management tool increases.

Example Application to Lake Ontario

Mackay's (1989) discussion of PCBs in Lake Ontario provides a convenient starting point for examining the question of what kinds of information can be obtained by using a simple model to analyze surveillance data currently reported. Mackay used the simple model (Viewgraphs 1,2) described by Eq. (1), with observations of the concentration of total PCBs in fish (Viewgraph 3), to estimate the current loading ($E + F_iC_i$) of total PCBs, which is approx-imately 700 kg/year. Application of this model to the problem was facilitated by two features of the data. Mackay observed that the PCB concentration in Lake Ontario fish (and herring gulls) had undergone a period of exponential-like decline since the mid-1970s and had become almost constant in recent years. This information (time series of one state variable) was all that was required to estimate the bulk loss time constant, k, based on the decay portion of the record and, once the overall loss ratio F+kV was determined, to estimate the total loading from the steady state portion of the record (Viewgraphs 4,5).

Obviously, this application of a simple mass balance model is not without its limitations. In addition to the structural assumptions built into the model (e.g. single horizontally and vertically well-mixed water column, firstorder loss of PCBs from the water column, step function change in loadings from one constant value to another constant value), it is assumed that the concentration of PCBs in the fish is in equilibrium with the concentration of PCBs in the water. Finally, because this model does not have a compartment representing sediments, the internal load resulting from the recycling of sedimented PCBs is not modeled explicitly. Thus, the calculated total load probably overestimates the external load.

We may question the value of an estimate, inferred from the time series of concentration data, of the total load of PCBs into Lake Ontario. At least two answers come to mind. First, because the lake seems to be in a non-zero steady state with respect to PCB concentration implies that PCBs continue to be loaded (including internal sources) into the lake. Thus, managers may want to devote some effort to locating and quantifying the sources. Second, the

MACKAY SIMPLE MODEL AS DESCRIBED BY EQUATION (1)



 $V\frac{dc}{dt} = FC_I + E - FC - kVC$

Steady State Vdc/dt = 0 $\therefore C = \frac{FC + E}{\frac{1}{F + kV}}$

VIEW GRAPH 1

14

MACKAY SIMPLE MODEL AS DESCRIBED BY EQUATION (1), continued





VIEW GRAPH 3

- 16 -

ESTIMATE OF TOTAL LOADING FROM STEADY STATE (MACKAY)

Lake Ontario

 $V = 1.67 \times 10^{12} \text{ m}^{3} \qquad F \approx 0.21 \times 10^{12} \text{ m}^{3}/\text{year}$ $\therefore F/V = 0.126 \text{ y}^{-1} \qquad \text{or} \qquad V/F \approx 8 \text{ years.}$ But $\tau 1/2 \approx 2 \text{ years}$ $\therefore k_{o} \approx 0.693/2 \approx 0.347$ But $F/V \approx 0.126$ $\therefore k \approx 0.22 \qquad \text{or} \qquad \tau_{REM} \approx 3.1 \text{ years.}$ $F + Vk \approx 5.8 \times 10^{11} \text{ m}^{3}/\text{year}$

ESTIMATE OF TOTAL LOADING FROM STEADY STATE (MACKAY), Continued

VIEW GRAPH 4

- 17

ESTIMATE OF TOTAL LOADING FROM STEADY STATE (MACKAY), Continued

 $C \approx 1.2 \text{ ng/L}$ or $1.2 \times 10^{-6} \text{ g/m}^3$

But $C = \frac{FC_{I} + E}{F + kV} \leftarrow 5.8 \times 10^{11}$

 $\therefore FC_{I} + E = 700,000 \text{ g/year} \quad 700 \text{ kg/year}$

Niagara River Report 360 to 730

1974 C \approx 5 x this

 $\therefore FC_{I} + E \approx 700 \times 5 \text{ kg/year}$ 3500 kg/year

All CONC^w linearly related and proportional to $FC_I + E$ Loading Critical

Measurements of water column CONC?

Replication? Dissolved vs. Sorbed? Time Variation? Space Variation? RAP & Whole Lake Models Cost?

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estimate of the magnitude of the loading may help to evaluate other, independent estimates of loading and may help set priorities for whatever sampling and control programs may be designed. Such efforts may also benefit from the estimate of the effective time for removal of PCBs from the water column (which is much less than the hydraulic retention time) provided by the model solution.

A Second Simple Model

Adding a sediment compartment to the model described by Eq. (1) would make it possible to distinguish external and internal loads. The cost of this addition is that information about the mass of contaminant in the sediment is now required and, depending on the detail with which the intercompartment fluxes are modeled, several parameters are added. The new model (Viewgraph 6) could be represented by the two coupled ordinary differential equations,

$$V_w dC_w/dt = E + F_iC_i + w_rA_rC_s - F_oC_w - k_wV_wC_w - w_sA_sC_w$$
(2)

(3)

(4)

$$V_s dC_s/dt = w_sA_sC_w - w_rA_rC_s - k_sV_sC_s$$
,

where V_W and V_S represent the volumes of the water and sediment compartments; C_W and C_S are the concentrations in the two compartments; w_r is a resuspension velocity, representing the return of contaminant from the sediments; A_r is the effective area from which sediments are resuspended; k_W is a new (relative to the one segment model) first-order loss rate for the contaminant in the water; w_S is an effective settling velocity, representing removal of the contaminant from the water; A_S is the effect area over which sediments settle and k_S is a first-order loss rate for the contaminant in the sediment. The loading term E could be further subdivided so that

$$E = L + A_i - k_V C_W,$$

in which L is loading from unspecified sources (e.g. point, non-point, run-off); A_j is input from the atmosphere (both wet and dry) and the term $k_V C_W$ is a first-order representation of volatilization of the contaminant from the water.

Each of the terms on the right sides of Eqs. (2), (3) and (4) represent a flux (Viewgraphs 7, 8) that could (potentially) be measured in the field. These fluxes are not being measured by current surveillance programs, which are concentrated on sampling water column concentrations. Concentrations of contaminants in the sediments are not sampled routinely. Thus, although the simple two-compartment mass balance model could provide much of the needed information, data required to support this model are not currently collected.

Sampling Strategy

One of the major advantages of the simple models is that their data requirements are relatively modest. The two-compartment mass balance model could be supported with the following sources of information (Table 1).



 F_4

VIEW GRAPH 6

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FLUX REPRESENTATION FOR FIELD MEASUREMENT



VIEW GRAPH 7

FLUX RE	EPRESEN	NTATION F	OR FIELD ME	ASUREMENT	Continued
	GLISP- Concer	Derived	Chemical Masses	Process Rates	Rate Constants (Research)
	Water		kg	kg/yr	
VII	Fish &	∕Water :	Water	Trib in	1.
OME	Blota	∖Benthic	ic	Wat \rightarrow Atm	k
RAPH 8 - 22 -	Sedime	ents*		Wat \rightarrow Sed	k
	Actively Resusp.		Surface Seds.	Sed \rightarrow Wat	k
			W React	k k	
	Air	Aerosol		S React	k
	Rain			Outflow	k
	*Not enti- satisfied	irely l		Loadings	

TABLE 1

MASS BALANCE MODEL INFORMATION SOURCES

COMPARTMENT/DATA SOURCE	REQUIRED SAMPLING
Water Column	Five stations per lake, sampled annually during spring isothermal conditions, 10 m below surface. Contaminants determined for dissolved and particulate phases (total estimated by addition), also determinations for TSP, TOC, Chl-a and nutrients.
Sediments	Two or three sediment trap strings per lake, deployed annually during the overwinter (NovApr.) period. Surficial sediment (grabs) surveys done every 10 years. Periodic coring for research.
Fish	Annual sampling of salmonids and lake trout along with sculpin/smelt.
Gulls	Current GLISP program sufficient.
Air	Adopt the 1988 atmospheric deposition plan. Five stations per lake with analyses of air and particulate phase, rain/snow, determinations of TSP, carbon and nutrients in addition to contaminants.
Tributaries	Every major tributary sampled annually, others sampled selectively.
Loadings	Municipal and industrial sources should be monitored.

most be used of normality quantifying the exising status (huy, the group was divided into fear smaller groups (hree to address the loading data and one to consider and seent for organiate one conditions (open lake group) (he three loading protected and a groundwater loadings group (a order to eventightly control to the reduction in loadings of PCBs from tributaries and with the content is the reduction in loadings of PCBs from tributaries and with the reduction in loadings of PCBs from tributaries and with the reduction in loadings of PCBs from tributaries and with the reduction in loadings of PCBs from tributaries be determined on all the reduction in loadings of PCBs from estimates be determined for all tources to determine the relative contribution of each type of courts are thus target remediation possive accordingly. (the established, and remediation efforts for status from each of base sources can be established, and remediation efforts for status from each of these sources can be attracted reductions of other sources to grave the determine for these sources can be attracted reductions of other sources for still achieve the determed effect. This procedure also applies to developing a monthering sizeted to call in the

Recommendations

Some of the sampling needed for application of the simple mass balance models, while not currently being done, is called for in GLISP. Those areas that are not entirely satisfied by the planned sampling are (Viewgraph 8) listed below:

- o Dissolved contaminants in water
- o Contaminants in bottom sediments
- o Contaminants in actively resuspended sediments

Estimates of the concentration of contaminants provided by these measurements would greatly facilitate application of the simple mass balance models.

Additional Thoughts

A general concern shared by the members of this group was that surveillance data seemed to be "underinterpreted." It was generally agreed that formation of an "interpretation group" to assist in preparation of the surveillance sections of the Water Quality Board report would be worthwhile. It was not clear, however, how such a group should be formed or who its members should be. The group was also concerned about the apparent tendency of modelers and model supporters to assume that bigger is better. While very detailed models may give the impression of improved accuracy, that impression must be tempered by the understanding that very detailed models are much less well constrained than simpler models. Because sustained data collection (over many years) may be necessary for model comparisons and because it may be impossible to maintain the detailed data collection necessary to support complex models over such a period, simpler models should not be rejected because they are "too simple." It is important to separate the management utility of the modeling exercise from purely intellectual or academic interests.

GROUP II REPORT

<u>William Richardson, Chairman</u> Tim Bartish, Recorder

STATEMENT OF MANAGEMENT QUESTION/ISSUE

"What changes in (i) atmospheric (ii) tributary and/or (iii) point source loading would be required to achieve 0.1 ppm total PCB in lake trout at an upper 95% confidence bound? Are food web models/data required or is a bioconcentration factor sufficient? Specify confidence levels for these answers. How long will it take to reach the stated objective with the proposed strategy?"

DISCUSSION OF MANAGEMENT QUESTION

This question is answerable only using mass balance models that relate loadings to in-lake concentrations and to fish body burdens. Hence, the answer to this question requires that we assess the state of the mass balance models, choose the appropriate models, and design the data sets required to calibrate and validate the models.

The basic modeling framework is well established and has been or is being applied in several systems, including Saginaw Bay, Lake Ontario and Green Bay. For this exercise the framework considered is that used by Endicott et al. (1989; 1990) in two recent reports, which describe screening level models for Lake Ontario. This framework is depicted in Figures 1 and 2. There was general agreement among the workshop participants that this framework represents the present state of knowledge and accepted paradigm for exposure and food chain modeling.

The group also decided to apply the management question to Lake Ontario, since much discussion has occurred in various agencies that this most likely will be the lake where such a plan would be implemented first.

With the preferred model selected and the state variables known, addressing the issue of the change in loadings needed to meet objectives would reguire an estimate of the current loadings and the ambient (water column and biological tissue) concentrations. Obviously, a determination of reductions must be based on accurately quantifying the existing status. Thus, the group was divided into four smaller groups: three to address the loading data and one to consider data needs for open lake conditions (open lake group). The three loading groups were separated into a tributary/point source loads group, an atmospheric loadings group and a groundwater loadings group. In order to eventually conduct determinations of the reduction in loadings of PCBs from tributaries and point sources necessary to achieve a given objective, estimates of the current loading rates must be obtained. It is important that estimates be determined for all sources to determine the relative contribution of each type of source and thus target remediation measures accordingly. Once obtained, the overall reductions necessary from each of those sources can be established, and remediation efforts focused that, in conjunction with any scheduled reductions of other sources, will achieve the desired effect. This procedure also applies to developing a monitoring strategy to obtain the


NSOM: Non-settling Organic Matter

BASIC MODELING FRAMEWORK



current loading estimates from various sources. Granted, much of this information is lacking or poorly understood prior to conducting a monitoring program, and must often be estimated. The level of intensity/effort of the monitoring plan for each component (i.e. tributaries, point sources, atmospheric, groundwater) should be reflective of the relative percentage of contribution to the total load.

Even though relative contributions of each load are not currently available, monitoring programs were developed for tributary, point source and atmospheric loads, with the assumption that each component of the load was "significant;" the objective was to develop a monitoring program to quantify that load as well as possible.

Each group was to develop, based on the discussions of the modeling framework established, a sampling strategy that would provide values for addressing the management strategy, and to compare that strategy with what is currently called for in GLISP.

It was not the intent of the group to delve into all of the details, but rather to first outline all the requirements of a model-oriented surveillance effort, then discuss and recommend factors that should be included in a detailed design.

I. LAKE SUBGROUP REPORT

Figure 3 presents the choices for models examined by the group and the group's recommendation for Lake Ontario. Level 0 corresponds to the initial model suggested for Group I (prior to the workshop): a single segment, completely-mixed lake reactor. The notation in parentheses to the right of level refers to steady state (SS) or time variable (TV) assumptions for the water and biota, respectively. "OBS" and "BCF" refers to handling the biota in the models with an observed (from data) bioconcentration factor. Adding the sediment layer (level 1), which represents the storage reservoir, allows more realistic time variable computations for the lag time between loading changes and lake response. This result corresponds to the Group I model as agreed to at the workshop. The level 2 model includes a food chain model that represents the biotic response. The lag time of the fish response can be quantified at this level of modeling. The level 3 model divides the sediment compartment into multiple horizontal segments that represent the differing depths of the well-mixed layer. Two epilimnion and one hypolimnion segments are recommended to resolve the east-west gradient in lake trout data. The number of sediment segments will be determined by the range of well-mixed layer depth.

Table 2 presents the sampling plan for Lake Ontario. The number of stations per modeling segment in the water column and the number of cruises per year are based on the statistical analysis of the Saginaw Bay PCB data set (Richardson et al. 1983). This plan will be refined when the Green Bay data become available. The parameter list follows the Green Bay sampling program. An innovative sampling program for the sediment is proposed. A dense grid of sediment sampling is proposed to be done once. The key to the method is to analyze the Pb²¹⁰ data to find the depth of the well-mixed layer, and composite that depth of sediment for chemical analysis. Sampling of the resuspended material with sediment traps is recommended, using deployments

FIGURE 3

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Model Selection

Le	vel		# Segments	
		Water	Sediment	Biota
0	(SS, SS)	1	0	OBS, BCF
1	(TV, SS)	п	1	OBS, BCF
2	(TV, TV)	п	1	Food Chain
3	(TV, TV)	п	m	Food Chain
Re	commendat	ion:		

n = 2	East - West, Lake Trout Data
<i>m</i> = ?	Based on mixed layer distribution

TABLE 2

	WATER	SEDIMENT
# Stations	5/segment	200 sta. (A) 2 bottom sediment traps/seg (B)
Frequency	5/year	Once (A) 5/year (B)
Parameters	Diss., Part., POC, DOC, SS, N, P, Si, Chl	Pb ²¹⁰ , Part. %OC, Grain (AVS)
Rationale	Green Bay Design	Mixed layer Depth Critical Sediment Traps Efficient AVS → Metal Bioavailability

SAMPLING PLAN FOR LAKE ONTARIO TO SUPPORT GROUP II MODEL

- 30 -

during the sampling cruises. The measurement of acid volatile sulfide (AVS) and acid extractable metals in sediments is recommended because of the recent evidence that supports their use to determine metal bioavailability.

Figure 4 presents the design for the biota sampling program. It is suggested that the GLISP lake trout sampling frequency be reduced, and the species that are sampled increased to meet the requirements of the food chain modeling.

Figure 5 locates the sampling stations for the lake trout collections. We note the absence of a station on the United States shoreline. The algae-zooplankton sampling discrimination is made using a plankton net mesh size. The Green Bay parameter list is being recommended for this component.

II. LOADING PROGRAMS

The ideal monitoring program would, with the least cost and effort, estimate the population of interest with minimal bias and error and also account for loading from all "significant" sources and for temporal and spatial variability. In addition, it is critical in load determinations, that the methods used are adequate to detect the contaminant (e.g. PCB) at very low concentrations. Compliance monitoring programs (i.e. determing only whether a certain level is exceeded) are not suitable for these calculations.

Tributary Subgroup

A tributary monitoring program should focus on the "major" tributaries of the lake, ideally determined as those contributing the greatest quantities of biologically-available PCBs to the lake. In the absence of such information, an examination of the only loading data available - total phosphorus - revealed 11 tributaries contributing the greatest portion of the load (Great Lakes Water Quality Board, 1989a). These tributaries include the Oswego, Genessee and Black Rivers in New York, and the Welland, Trent, Twelve-Mile, Humber, Don, Credit and Moira Rivers, and the Welland Ship Canal in Ontario.

In addition, monitoring of the Niagara River (considered as a connecting channel and not a tributary) would be necessary. Other tributaries may be necessary, depending on the potential for sources within the watershed.

Depth-integrated sampling would be conducted near the flow gauge further downstream and upstream of the influence of the lake (lake effect or seiching). Unless it can be shown that no lateral variability occurs in the stream at the sampling site, multiple samples are to be collected transverse to the direction of the flow. These samples are then to be composited to a single sample.

The parameters to be analyzed include dissolved and particulate PCB, P, N, Organic C – dissolved and particulate, TSS, silica, chlorides, discharge flows, temperature and other state variables and those needed by the Open Lake monitoring group.

As stated earlier, it is imperative that the parameters, especially PCBs, are measured with extremely low detection levels, and will require the use of high volume analysis or centrifuging.

BIOTA SAMPLING PROGRAM

Biota

#Stations

Frequency

1/yr

1/yr

1/yr

1/yr

5/yr

Lake Trout

Alewife

Smelt

4 Sta. 25 Comp/Sta (US Shore?)

4 Sta. 10 Comp/Sta

4 Sta. 5 Comp/Sta

Sculpin

4 Sta. 5 Comp/Sta

Algae, Zoop Mysis, Pont

5 Sta/Seg

Rationale : Preliminary Analysis of GLISP Data & **Estimates**

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Lake Ontario TCDD Concentrations (ppt) in top 3 cm of Sediment Cores



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1

FIGURE 5

To adequately characterize the variability of the loading, each stream should be sampled approximately 30-40 times per year for all parameters except PCB, with most samples collected during periods of greatest variability (e.g. spring runoff). PCB samples are to be analyzed on at least 15 of the above samples and distributed according to the variability of the load. Flow (discharge) data are to be recorded continuously; daily averages are to be used in computing loading estimates.

For annual loads, the data should be post-stratified and Beale's Ratio Estimator applied to the strata, weighted for discharge, and combined. For PCB data, a multiple ratio estimator (Olkin 1958), using total suspended solids and flow as auxiliary variables, may be appropriate. For the monthly loading data needed by the PCB lake trout model, the data are to be handled such that a discharge-concentration regression model and monthly discharge observations are used, as is a multi-variate estimator for PCBs (i.e. both discharge and TSS).

To calculate loading from the unmonitored (downstream of the gauge) portion of the tributary, the upstream load for the unmonitored watershed area is to be increased by proportionate scaling. Point sources downstream of the gauge must be added as a direct load to the basin or included in the base load of the tributary.

This tributary program is fairly resource intensive and is a first step to collecting data to support the modeling effort. Subsequent modifications may require either a reduction of or an increase in the frequency, stations or other factors. Several alternate methodologies are recommended to attempt to limit the level of sampling. These involve the integration, both spatially and temporally, of samples through the use of:

- Solvent bags for monitoring the relative concentration of hydrophobic contaminants in small or hard-to-sample sources
- Automated sampling composited over fairly long time periods (the time period chosen depends on the type of analyses to be conducted on the sample)
- o Biomonitoring
- Cluster sampling, in which a geographical region is annually targeted for sampling (e.g. all streams in a given flow interval) at a greater rate for PCB and TSS, POC and DOC

Point Sources Subgroup

A point source monitoring program would focus on those sources discharging directly into the lake, as opposed to indirect point sources, which discharge into tributaries upstream of the sampling station, and are thus assumed accounted for in the tributary monitoring program. Thus, the geographic focus of point source monitoring is in harbor and nearshore zones. Monitoring of point sources for PCB loading, similar as it is to tributary monitoring, would ideally focus on the major contributors. However, since the contaminant has been banned from discharge, discharges that do occur are incidental and a whole range of point source types is suspect. The use of screening methodologies in an initial evaluation is recommended to determine the nearshore and harbor zones, to focus increased effort. Screening methodologies could include the presence of PCBs in ambient sediment, accumulation in tissues of resident aquatic biota such as spottail shiners, cladophora, mussels or benthos, or accumulation in tissues of caged organisms, such as mussels and fish. Care must be taken to ensure that the use of these screening methodologies is indicative of the nearshore/harbor area and not the open lake or tributary.

Once various areas are identified for further monitoring, procedures for estimating the loading of PCB should follow the detailed methodologies provided in "Guidance on Characterization of Toxic Substances Problems in Areas of Concern in the Great Lakes Basin (Surveillance Work Group 1987). Since PCB is a stable compound, selective use of compositing and integrating schemes could be implemented in a monitoring strategy. Surrogate sampling is also recommended.

Atmospheric Subgroup

Organic and inorganic chemicals are deposited in the Great Lakes from the atmosphere (directly onto the lake surface) by precipitation (rain and snow), dry deposition (particle) and vapor exchange at the air-water interface. These contaminants are lost from the water column of individual lake systems as a result of connecting channel or riverine outflows, sedimentation, volatilization and <u>in situ</u> degradation (e.g. biodegradation, hydrolysis, photolysis, photochemical degradation).

Gradually, the ambient atmosphere has been determined to be a substantial source of toxic substances through both wet and dry deposition. It is now recognized as an important contributor of anthropogenic organic compounds and toxic metals to the ecosystem burden of the Great Lakes.

Since many toxic chemicals are persistent and have relatively long atmospheric half-lives, emission sources beyond as well as within the Great Lakes basin may affect the lakes. Currently, information on the physical and chemical properties, processes, pollutant sources and environmental concentrations is insufficient to construct comprehensive models or budgets for the evaluation of the current state of the ecosystem or to predict its response to future changes in source strengths (Strachan and Eisenreich, 1988; IJC 1987). To reduce uncertainty in atmospheric deposition estimates and to fully understand the role which the atmosphere plays in contributing to the loadings of toxic substances into the waters of the Great Lakes, it is essential to (a) establish a data base of ambient monitoring data through field studies; (b) develop a comprehensive emissions inventory for the pollutants of concern and (c) apply atmospheric transport, dispersion and deposition models. These actions are discussed in more detail in the following sections.

A) Ambient Monitoring Data Base

1. Assessing Atmospheric Deposition. In July 1988, the International Joint Commission published "A Plan for Assessing Atmospheric Deposition to the Great Lakes". The plan, developed to meet the atmospheric component of GLISP, outlines a comprehensive program to quantify the atmospheric contribution of selected contaminants to the Great Lakes. The specific objectives of the plan are to:

- Determine concentrations of selected chemical contaminants and nutrients in precipitation and in the atmosphere
- Estimate annual deposition of these chemicals on each of the Great Lakes and basins
- Assess temporal and spatial trends in deposition of these chemical species

 Determine the relative contributions of these species from major sources or source regions to deposition at receptor areas within the Great Lakes basin

 Provide information on the occurrence of other toxic compounds in the atmosphere and in precipitation within the Great Lakes basin, to serve as an early warning of impending environmental problems

These objectives and the recommended monitoring to meet them are consistent with the charge of the Atmospheric Loading Subgroup of the workshop. The recommended program of monitoring, research and integration of information has three phases and is summarized in Table 3.

TABLE 3 ADDITION TO THE TABLE 3 ADDITION TO THE TABLE 3

A PLAN FOR ASSESSING ATMOSPHERIC DEPOSITION TO THE GREAT LAKES STRATEGY AND TIME LINES

O PHASE I Yrs	2 PHASE II Yrs	4 PHASE III 6 Ongoing Yrs Yrs Monitoring
-Provide Scientific Basis for Monitoring Activities	Initiate Monitoring Network	Implementation of Full-Scale Network
-Establish Two Master Stations	Establish Two Master Stations and 10 Satellite Stations	Establish 10 Additional Satellite Stations
	Continue Research	Continue Research

Phase I (two years), as quoted from the plan, outlines the research required to answer scientific questions relating to measurement and environmental processes and to develop interpretative models. These answers will be provided, in part, through monitoring activities conducted at two new master (research) sites, one each in Canada and the United States, located in the upper and lower basins. Specific outputs of Phase I are:

- o An assessment of atmospheric deposition methodology
- o A design for the routine monitoring network
- o Updated estimates of the atmospheric deposition to the Great Lakes

While monitoring capabilities are being enhanced, the continuation of existing and upgraded monitoring programs in the United States and Canada should continue in order to provide data for the on-going evaluation of temporal and spatial gradients.

Phase II (two years) incorporates information from Phase I to initiate an abbreviated monitoring network, involving both master (research) and satellite (routine) monitoring sites. A summary of equipment needs at each monitoring site is given in Tables 4 and 5. Scientific questions on measurement and deposition methodology will continue to be investigated during Phase II. Anticipated outputs of Phase II are:

- o A reassessment of atmospheric deposition methodology
- o A detailed design of a full-scale monitoring network
- o Optimates of atmospheric deposition into the Great Lakes

Phase III (on-going) involves deployment of an integrated atmospheric monitoring network. On-going reports will assess the effectiveness of the network and provide more precise estimates of atmospheric deposition on the Great Lakes every two years.

The unique feature of this plan is the establishment of master (research) sites during Phase I, which will focus scientific activities at particular locations. Measurements to evaluate the effects of spatial heterogeneity on siting can be made at any appropriate location, not necessarily a master site. Additional discrete laboratory and field studies to gain more information on the deposition process were also suggested. It will be necessary to emphasize the development and testing of integrated models as well as the parameters necessary to describe the deposition process. Data bases for environmental measurements and atmospheric source emissions will also be established.

Chemical species of interest are those identified as having either a demonstrated or potentially adverse influence on the aquatic ecosystem of the Great Lakes. The proposed program is flexible, allowing alterations in monitoring and measurement protocols as new pollutants are identified. At present, the focus is on organochlorines, other toxic compounds and selected trace metals, such as lead and mercury.

Some progress has been made in implementing this plan; it is outlined in the bilateral "Implementation Plan for the Integrated Atmospheric Deposition Network." Additional information, however, is required to establish a meaningful data base. This need is discussed in Section 2. Section 3 deals with the data base.

Parts B and C focus on the need for the development of emissions inventories and for the development and application of models to aid in the assessment of loadings (mass balance), trends in deposition (response) and source/ receptor relationships (control). For research needs and other aspects of modeling, the reader is referred to the original plan.

TABLE 4

EXAMPLE OF EQUIPMENT TO BE DEPLOYED AT THE MASTER SITES

NUMBER OF SAMPLERS	SAMPLING INTERVAL	DESCRIPTION OF EQUIPMENT
1	Weekly	Aerochem Metrics automatic sensing wet/dry precipitation collector (with standard Belfort rain gauge) for the collection of nutrients and trace metals
2	Biweekly	Wet-only integrating precipitation samplers with resin* extraction cartridges for the collection of organic compounds
1	Event	Wet-only event precipitation sampler with a resin extraction cartridge for the collection of organic compounds
3	24 Hours**	Hi-volume air samplers with filters and backup adsorbent* and wind sector controllers for the collection of organic compounds
nore informa- necesiary.to eff as the bases for	24 Hours	Anderson four-stage cascade impactor with backup adsorbent for the collection of organic compounds
1 Freedor Scher Basser meld bas	24 Hours	Hi-volume sampler for the determination of total suspended particles (TSP) and organic carbon (OC)
	Continuous	Meteorological equipment for continuous recording of rain intensity and amount, temperature, relative humidity, wind direction and velocity

*Resins and adsorbents will be XAD-2, XAD-5 or Tenax. **Air samples will be collected every sixth day. TABLE 5

NUMBER OF SAMPLERS	SAMPLING INTERVAL	DESCRIPTION OF EQUIPMENT
Ne hotj, Chadh Seoll ano tèorit oi staith Rigi du teichte	Weekly	Aerochem Metrics automatic sensing wet/dry precipitation collector (with standard Belfort rain gauge) for collection of nutrients and trace metals
2	Biweekly	Wet-only integrating precipitation samplers with resin* extraction cartridges for the collection of organic compounds
2	24 Hours**	Hi-volume air samplers with filters and backup adsorbent* and wind sector controllers for collection of organic compounds
(historical a ships from Hanowsfroment the location	24 Hours**	Anderson four-stage cascade impactor with backup adsorbent for collection of organic compounds

ENALGY EXAMPLE OF EQUIPMENT TO BE DEPLOYED AT THE SATELLITE SITES

*Resins and adsorbent will be XAD-2, XAD-5 or Tenax. **Air samplers will be collected every third day.

3. Out Starse and the termination of the sector main termination of the termination of termination of the termination of the termination of termination o

2. Ambient Measurement. The "Implementation Plan for the Integrated Atmospheric Deposition Network" deals essentially with the establishment of master and satellite sites for measuring concentrations of toxic chemicals. Some enhancements to this plan and implementation considerations are required to validate methodologies for estimating loadings into the lakes and basins. Those enhancements and considerations include:

- The need to provide information on the validity of current methods to 0 infer concentrations in air and precipitation of contaminants over water from land-based measurements (for estimation of load), to validate gradients (and loadings) predicted by current regional models and to infer/validate source/receptor relationships. To satisfy these needs, the existing array of sampling stations which are monitoring meteorological parameters as well as the concentration in air and precipitation of common ions, particulates (extend to fine and coarse fractions), lead and volatile organic compounds should be augmented by a small network of research sites on islands and floating platforms. The data obtained will be particularly useful in testing the ability to infer over-lake deposition from inland and shoreline observations. It is not suggested that such basic questions can be answered without using toxic chemicals measurements, but much useful information on these questions may be obtained less expensively.
- The need to conduct studies for a minimum of two seasons for two consecutive years.
- o The need for temporal resolution of the concentration measurements generally to be 24 hours. A few sites should operate with a minimum resolution of 12 hours to allow evaluation of source/receptor relationships.
- The need for the siting of monitors to be determined from inferred concentration and deposition patterns and from the availability of suitable islands/platforms.
- The need to consider using biological indicators in the Great Lakes to indicate spatial concentration and deposition patterns of toxic chemicals.
- o The need to conduct field studies over water to aid in parameterization/estimation of dry deposition and air/water exchange processes. Bouys and towers equipped for meteorological and chemical measurements are required.
 - o The need to investigate circulation-controlled processes at nearcoastal locations to estimate and account for their significance in the pollutant loading to the lakes by: 1) making intensive episodic field measurements in and around wintertime snow squall lines and sea-breeze fronts and (2) modeling (see Part C).

3. Data Storage and Accessibility. An interactive computerized data base for the Great Lakes measurements should be developed and supported. With the deployment of five master sites, 20 satellite sites and shorter term field studies, the information generated will rapidly outstrip existing resources for processing and interpreting such data. A common data base would ensure the quality of the data entry and compatability in data screening and calculation procedures. In addition, the time between taking the measurements in the field and making them available to a user should be shortened substantially. Currently such lag times often exceed two years.

Only the monitoring component is currently being addressed in the bilateral "Implementation Plan for the Integrated Atmospheric Deposition Network." The enhancements to this monitoring component discussed in this section should also be accomplished.

B) Emissions Inventory Data Base

Information on locations and amounts of toxic emissions from atmospheric sources is essential. Emissions estimates alone serve as indicators of the significance of atmospheric loading relative to other sources, such as direct industrial discharge to the lakes; provide guidelines for which compounds to measure in the atmosphere (emerging problems) and which sources or source categories to control; and are useful for interpretation of trends in biotic uptake and contamination of sediments. Emissions estimates are necessary inputs to models for quantification of deposition, establishment of trends (historical and predicted) and for determination of source/receptor relationships. Trend analyses are important for understanding and predicting response time of the lakes ecosystems to changes in pollutant loadings. Knowledge of the location of emissions sources is also important in determining the most suitable locations to site ambient monitors. Several air toxics emissions inventories have already been compiled for use in pollutant control programs.

Pollutants originating from anthropogenic and natural sources are introduced into the atmosphere through primary and secondary emissions. Primary emission includes direct emission from industrial stacks, incineration, residential chimneys and forest fires. For pesticides, it includes losses into the atmosphere through direct application of the pollutant and through volatilization of the pollutants from crop and soil during a relatively short period after application. Secondary emission includes recycling of material through resuspension and volatilization of previously deposited material. Pollutants can also be formed through chemical/photochemical reactions.

Once emitted into the atmosphere, the pollutants are subject to transport, dispersion, physical/chemical transformations and scavenging through wet and dry deposition processes. The distance from actual emission to removal (source to receptor) is a function of effective height of the release, meteorological conditions, properties of the pollutants and other factors. Many pollutants of concern to the Great Lakes ecosystem are persistent, slowly scavenged from the atmosphere and subject to long range transport. Toxaphene is a prime example of transport from the southern United States to the Great Lakes basin. Sulphur found in northern Canada has been linked to emissions in Eurasia. Hence, information on emissions of chemicals not only in the Great Lakes basin, but in North America and, indeed, the Northern Hemisphere, may be of importance. Several considerations should be made in the planning stages of emissions inventories. One choice regards the use of actual vs. allowable (by regulations) emissions. The inclusion of allowable emissions may be useful to an agency in certain modeling or control strategy evaluations. Another consideration is the use of annual vs. short term emissions. Annual emissions are generally used for estimation of annual long-term deposition while short term emissions estimates may be useful for modeling pollutant episodes and, maximum concentrations around certain sources. A third consideration is accidental vs. routine emissions. Routine emissions are typically predicted in inventories, but accidental emissions may be of interest in evaluating short term emergency situations. Both point and area sources should be considered in the inventory. Point sources are composed of stack and fugitive emissions. Area sources are smaller, more ubiquitous sources, such as automobiles and consumer solvent users. All inventory development should be for a common base year and future projection years.

A screening study is needed in the Great Lakes to develop preliminary estimates of emissions prior to beginning a detailed air toxics inventory. The screening study should define pollutants, source categories, geographic areas and the relative importance of major and minor point and area sources to loadings. A number of tools are currently available to help identify potential emitters of air toxics and to develop preliminary emission estimates. These tools include source category/pollutant cross indices, air toxic emission factors, speciation factors, conservative mass balance and existing source data/emission estimates (inventories developed under Section 313 of the Superfund Amendments and Reauthorization Act (SARA 313), state/provincial and local air toxics inventories and all other available data bases). For the list of critical pollutants, tools are available to estimate emissions from many of the major point and area sources. However, for non-traditional sources, limitations exist in preparing an emissions inventory. Some of these potential limitations for the Great Lakes include the lack of emissions estimating tools for specific sources or pollutants, the need for better emissions factors and test procedures, the need for tools (if possible) to develop an historical emission inventory for pesticides no longer in use in the United States, the lack of characterization of global or hemispherical emissions of specific compounds that are present in the Great Lakes, and the need for estimation procedures for atmospheric release of specific compounds from entrained dusts from landfills and waste drums. The resolution of these issues would improve the inventory in terms of providing inputs to air models for determining atmospheric loadings over the Great Lakes. These issues will require considerable effort and resources to resolve.

The effort to develop an air toxics inventory for the Great Lakes will be a formidable task. A phased approach should be taken to characterize an inventory of pollutants of concern in the Great Lakes. This approach should consist of an initial inventory of nearshore sources, an inventory of eastern United States and Canada and finally, an inventory of sources in the hemisphere. The first two inventories of nearshore and eastern United States and Canadian sources are essential for determining the loadings into the Great Lakes. The complexity of the development of an air toxics inventory will increase as the geographical area is increased from nearshore to hemisphere. It is recommended that existing inventory information be used when it is available: the SARA 313 inventory, the Southeast Chicago inventory, Wisconsin air toxics inventory, National Acid Precipitation Assessment Program inventory, National Air Toxics Information Clearing House data and the Ministry of the Environment Toxics inventory and Environment Canada data.

In Phase I of this study, a review of relevant literature and existing data bases pertaining to emissions of the critical pollutants should be made. In addition, time and cost requirements for compiling and computerizing a comprehensive toxic chemical inventory should be estimated. In Phase II, a thorough literature and data base review, with procurement, extraction and consolidation of emission-related information from available sources should be conducted with research and measurements as necessary to fill in data gaps where chemical specific emission factors and/or species factors are not available. The emissions data should then be gridded; temporal factors should be estimated; and the data should be shared on an interactive computerized data base.

Although there is an urgent need for present atmospheric emissions information as well as for trends in emissions of toxic chemicals, there has been no coordinated bilateral effort to compile this information and to establish an easily accessible data base. The creation of such a data base should be given high priority. It should be easily accessible to all Great Lakes researchers.

C) Transport, Dispersion and Deposition Modeling

Mass balance modeling of toxic chemicals in the Great Lakes has previously been limited to the physical boundaries of the lakes. Atmospheric input and inputs from tributaries, rivers, industrial discharge and groundwater seepage are usually estimated from only a few measurements. Consequently, they are often poorly characterized. Atmospheric deposition (wet and dry) has generally been inferred from a few measurements of pollutants in air and/or precipitation. Policy, assessment and management issues require that the sources of toxic materials be identified along with the pathways and magnitude by which they affect the lakes. Previous mass balance studies of lakes have indicated that for some lakes and toxic materials, atmospheric input is the major source of loading. Consequently, it is necessary for the atmospheric component to be extended to cover not only the lakes but the major source regions, which are currently poorly understood and may extend over regional and hemispherical scales.

Atmospheric "dispersion/deposition" and "receptor" models are major tools, that can help address source attribution of airborne toxic deposition into the Great Lakes. The models, however, require certain minimal input data to develop, evaluate and apply. GLISP must consider these data needs to adequately address the atmosphere component.

A description of "dispersion/deposition" and "receptor" modeling techniques is given below, along with a proposed staging of research and model applications and a brief discussion of benefits to be derived from the approach.

Modeling the Delivery of Airborne Toxics into the Great Lakes. An atmospheric dispersion model consists of a set of mathematical algorithms, which simulate the physical and chemical processes important in the emissions, transport, transformation and removal of air pollutants into and from the atmosphere. For some pollutants, e.g. acidic species and ozone, considerable resources have been directed to understanding these processes. These models have had various applications, ranging from studying physical and chemical processes to planning monitoring networks, interpolating monitoring data, spatially and temporally interpreting apparent trends in monitoring data, estimating ambient concentrations and deposition fields for data-sparse regions, and most importantly, allowing the assessment of the probable impact of changes in emissions on changes in ambient concentration and deposition fields.

Atmospheric dispersion/deposition models vary widely in sophistication. depending on their application, which, in turn, determines how physical and chemical processes are parameterized. For applications which require only long-term, seasonal or annual concentration fields, the models may contain a relatively simple parameterization of the chemical and physical process. For episodic models, that operate on a time scale as short as one hour, detailed treatment of the processes are necessary. For example, the comprehensive Regional Acid Deposition Model (RADM) and Acid Deposition and Oxidant Model (ADOM), currently being used in the assessment of acid deposition, contain over six vertical transport layers; consider more than 40 chemical species; and provide detailed treatment of the cloud and deposition processes. These Eulerian models simulate the physical/chemical processes on hourly time scales for about 80 km grid squares for the entire eastern United States and southeastern Canada. They require a super computer for the execution of multiple three-day episodes. Due to resource constraints, these episodes may then be aggregated to seasonal and annual averages.

On the other end of the scale are the simple Lagrangian models, such as AES-LRT, ENAMAP and ASTRAP. The latter is the Advanced Statistical Trajectory Air Pollution model, which has already been used in toxic applications. It is a Lagrangian model with a single vertical layer, which uses highly parameterized representations of chemical and physical processes. Seasonal meteorological statistics are generated and used to transport and disperse emissions over a spatial domain similar to that for the RADM. These models are relatively efficient to run and are appropriate for screening pollutants in the lakes, and for modeling the fate of non-reactive toxic byproducts, persistent toxics or toxics of pollutants following transformation for which emissions, transport and deposition processes are not well understood (i.e. more explicit representation of the processes are not justified).

The general modeling framework applied to acidifying species and ozone is also appropriate for toxic materials. However, the various components of the modeling system: emissions, transport, gas and aqueous phase chemical reactions, and removal by dry deposition and precipitation processes may be complex, depending on the specific species being addressed. Emissions of many toxics, for example, are poorly understood, relative to those for sulfur, nitrogen and volatile organic compounds. In general, a clear definition of toxics emissions will be difficult. Fugitive dust emissions and volatilization from the lakes and soils are poorly characterized in present inventories, and may be important for some toxic materials. These processes need further research and must be incorporated into the models.

The transport component of the models are generally consistent among all pollutant species. Those developed for acid deposition and oxidants will be

applicable for toxics. Gas- and aqueous-phase chemical processes will depend on the species being addressed. Non-reactive species will be relatively simple to model with existing models, whereas chemistry cogener composition, partitioning between particulate and vapor phase and similarly, dry deposition are poorly understood.

The spatial resolution of the "regional" models is 80 km. Deposition into the Great Lakes of some toxics may involve a contribution from local sources under complex small scale land-lake meteorological flows. Thus, nesting of models' scales, i.e. a local or mesoscale model nested within or driven by a regional model will probably be necessary for some applications. On the other end of the scale, hemispherical transport may be important for persistent toxic chemicals with long atmospheric residence times.

Thus, a set of regional models exists that can be adapted to issues of toxic transport to the Great Lakes region. However, there are features of source-receptor relations that are poorly understood and will require extensive study, e.g. emission chemistry and dry deposition. Nested scale modeling systems will probably be necessary to understand and predict the impact of toxic emissions on the lakes. In addition, local models are required for the assessment of suitability of monitoring/measurement sites and for interpretation of data.

Identification of Toxic Sources Through Receptor Modeling. The traditional method of estimating the ambient concentrations of air pollutants resulting from source emissions is based on dispersion/deposition modeling as discussed in the previous section. The accuracy of this approach is limited by uncertainty in the emission rates, the air flow field or lack of knowledge of the physical and chemical processes that influence the transport between source and receptor site.

"Receptor" modeling does not depend on details of source emissions or meteorology to make estimates of the ambient impacts of those emissions. Receptor models rely heavily on ambient measurements at the point of impact of chemical species that serve as quantitative tracers for the emissions from the sources of interest. The accuracy and resolution of a receptor model depends on the guality of the tracers. Two properties important in a tracer are uniqueness and stability. Uniqueness of a tracer to a source enables that source to be distinguished from others. Stability of a tracer ensures that the relative concentration of the tracer to the total mass emitted by a source remains constant between the source and the receptor (sampling) site. Examples of tracers are K and 14C for woodsmoke, Br and Pb (and certain VOCs) for mobile sources, Al and Si for wind-blown soil, V and Ni for oil-fly ash, Se for coal combustion, and morphology and composition for both coal-fly ash and fungal spores. Lead isotope measurements, together with back trajectories, have been used to identify regional sources of lead; cogener-specific measurements of toxic chemicals, coupled with trajectory analyses, have been used to distinguish fresh and aged sources and elucidate the source region. In the real world, tracers often are not ideal so mathematical procedures are used to construct linear combinations of measured species that are better source tracers than individual species.

In addition to the chemical species that are naturally present in the emissions of sources, receptor modeling has begun to make use of tracers that are artificially introduced into the source emissions. This procedure can be used to isolate the impact of a particular point source within a general source category or to determine the total impact of a source category for which no reliable natural tracers appear to exist. For example, in different enriched non-radioactive isotopes of the rare earth element, samarium, may be added to residential fuel oil, municipal bus fuel, and municipal truck fuel to determine the separate ambient impacts of these source categories. The method is exquisitely sensitive, requiring only a few grams of the enriched isotopes.

A powerful feature of the receptor modeling approach is that statistical analyses of the ambient species data can reveal which source categories are the principal contributors at a site, without relying on <u>a priori</u> assumptions, which may overlook a contributor.

"Dispersion/deposition" and "receptor" modeling approaches are complimentary in nature, each with its own strengths and weaknesses. A strength of receptor modeling is that source emissions and meteorological information requirements are minimized. A weakness is that it is not strictly predictive. That is, receptor models look only backward in time to describe what the source impacts were at the time when the ambient measurements were made, whereas dispersion models predict source impacts for any assumed meteorological scenario. Because of their complimentary nature, there has been considerable interest in recent years in devising ways in which the two approaches can be combined into what are called "hybrid" models. This is particularly appropriate in the case of the long distance transport of pollutants from sources, a situation which is difficult for either approach to deal with on its own. For example, an elementary way of combining the two approaches would be to perform ambient pollutant measurements at a site of interest for a series of successive periods; use dispersion modeling to compute back trajectories for each of the periods; stratify the pollutant measurement data into subsets, according to similar back trajectories to determine source region; and perform source impact estimates, based on receptor modeling, on the subsets to estimate source strength and later to develop different emissions scenarios. The last step is made easier and more reliable by the homogeneity and directionality information contributed by the dispersion modeling step. With important sources identified and their impacts estimated through receptor modeling, dispersion modeling then could be used to investigate control strategies under arbitrary meteorological scenarios.

A recent review of the present state of receptor modeling is available (Gordon 1988).

D) Sequencing of an Atmospheric Source Attribution Toxics Program

Developing an atmospheric modeling component for the Great Lakes toxic program is not a trivial task because little is known about the spatial distribution of emissions or the physical/chemical properties of the pollutants and deposition characteristics. The following steps are suggested as an approach to developing ambient monitoring and emissions inventory data bases, which through the application of transport and deposition models, will generate sufficient information to establish mass balance estimates for the atmospheric pathway:

- 1. First order modeling of the spatial and temporal fields of toxic deposition in the Great Lakes, using both simple and comprehensive models and incorporating simplified assumptions of emissions, chemistry and process parameterization. Local and hemispherical scale models may be required, depending upon the pollutants and their source distribution.
- 2. Use of the information from regional atmospheric models to assist in the selection of atmospheric monitoring sites for the surveillance program, as well as to provide first order estimates of atmospheric sources of toxic materials in the Great Lakes.
- 3. Investigation of circulation-controlled processes at near-coastal locations to estimate and account for their significance in pollutant loading into the lakes: Develop/apply models to evaluate the influence of the lake breeze and topographically-induced circulations on patterns of concentrations and deposition in the vicinity of large urban areas and point sources. Use models to assess the suitability of potential measurement/monitoring sites.
 - 4. Application of dispersion models, receptor models and meteorological analyses, with available toxic deposition measurements, to obtain estimates of source regions and types. Use of this information in the selection of additional sampling sites and as a basis for checking initial emissions estimates.
 - 5. Development of toxic emissions inventory on spatial scales of about 20 km or smaller and identification of significant point sources (major task).
 - 6. Modification of model chemistry and dry deposition parameterizations to address toxic aerosols. Evaluation of models, using selected components of the monitoring data base as well as special measurements.
 - 7. Development/application of regional and nested models to address toxic issues.
 - 8. Applications of simple and comprehensive models for atmospheric toxics to assess atmospheric source receptor relationships relative to toxic contributions to the Great Lakes. E) Recommendations

The atmospheric modeling component represents a major program, requiring emissions and monitoring data to implement. The immediate concern is how to structure the surveillance program to obtain a data base that will optimally feed the atmospheric modeling program.

o The atmospheric monitoring research and integration program recommended in "A Plan for Assessing Atmospheric Deposition to the Great Lakes" provides an excellent framework for the monitoring and research necessary to support atmospheric modeling. This program should be fully implemented in all three phases, while simultaneously addressing the suggested enhancements as discussed in Part A) above. A common data base should immediately be established to process and store data from the evolving network and field studies.

- o A complete and comprehensive emissions inventory should be developed, consistent with the requirements discussed in Part B) above.
- o Utilize the data bases developed through ambient monitoring and the emissions inventories to develop, evaluate and apply atmospheric transport, dispersion and deposition models to derive mass balance estimates for the atmospheric pathway. Groundwater Subgroup

Groundwater transport directly into a lake (as opposed to transport into the tributary) could be a significant vector of contaminant loading, and indications of this occurrence have been observed in Lakes Superior and Erie. The use of groundwater flow models (MODFLOWSUTRA) and the incorporation of surveillance data (monitor wells, cores, "sniffers") would be needed to determine if this source of loading was significant. However, until it can be demonstrated that direct groundwater sources constitute a significant PCB load to the lake, no monitoring program is recommended.

RECOMMENDATIONS FOR SURVEILLANCE

A comparison of the monitoring programs developed to address the management question in Lake Ontario with the one currently called for in the Great Lakes International Surveillance Plan is illustrated in Table 6. The GLISP was examined only in terms of the data needs cited above; there was no intent to document the full scope of the programs outlined in GLISP.

The data requirements for the water monitoring portion of the Group II plan compare favorably with those in GLISP. The parameters represent a reduction and/or refocusing of sampling effort. For instance, the tributary monitoring plan calls for increased sampling frequency for PCBs, but on fewer streams than in GLISP, resulting in fewer samples. Similarly, sampling open lake water occurs less frequently than in GLISP. Fish tissue monitoring is comparable with that in GLISP and results in less effort than that currently expended.

The recommended data needs for open lake sediment represent a significant increase over those included in GLISP, especially in regard to the number and sampling frequency of trap stations, and the initial comprehensive coring survey. Increased frequency of invertebrate sampling would also be needed to achieve the Group II plan. For point sources and atmospheric sources, the recommendation of Work Group II was to follow GLISP (Surveillance Work Group 1987). Therefore, the recommendation and GLISP are identical.

For the most part, the sampling program recommended by Work Group II is less demanding than that called for in GLISP, but could require modifications to the existing station locations, sampling frequency and parameters analyzed. The most significant shortcomings are in the sediment and invertebrate sampling programs and in the methodologies used to measure PCB concentrations (e.g. whether they are sufficient to detect extremely low level concentrations). ments as discussed in Part A) shows. A common data preprint minediates by he established to process and store data from the evolving network and

	TABLE 6	
	MASS BALANCE WORKSHOP GROUP II REPORT	
<u>William Richardson, Chairman</u> <u>Tim Bartish, Recorder</u>		
MEDIA/PROGRAM/DESIGN	WORK GROUP II PLAN	GLISP
Tributary Monitoring Parameters	P, N, POC, DOC, Susp. Sols, silica, chloride, flow, PCB (diss. & part.)	P, Susp. Sols, organics, metals and others
# Stations	13 tributaries; 1 station/trib. Tribs include: Oswego, Genesee, Black, Welland, Trent, 12-Mile, Humber, Don, Credit, Moira & Niagara Rivers, and Welland ship canal.	23 tributaries; 1 station/trib. Tribs include: those under the WG II plan
Frequency (# samples/year)	15 for PCB; 30-40 for other parameters	12 for organics; 52 for others
Total # Tributary Samples	PCB -195; others 390 to 520	Organics - 276; others - 1,196
Open Lake Monitoring Parameters	PCB (dissolved & particulate), POC, DOC, Susp. Sols, P, N, silica, chloride	PCB, SS, chloride, P, N, POC, Si and others
# Stations	5/segment, 3 segments 10 epi 5 hypo	Organics: 23 - surface only at 20 stations; - epi, meta, hypo at 3
		Nutrients & chlorides: 97 – surface only in spring, 6 depths during summer

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Table 6 - cont'd.

Total # Samples

MEDIA/PROGRAM/DESIGN

Frequency (# samples/year) 5

75

WORK GROUP II PLAN

- 2 -

GLISP

Organics: 2 spring cruises at 20 surface stations 8 cruises at 3 -3 depth stations Nutrients & chlorides: 2 spring cruises 3 summer cruises

Organics: 112 Nutrients & chlorides: 1,880

SEDIMENTS Open Lake Parameters		NC Stepter NC Stepter Studeringe: Huces Burger Buk
Cores/grabs	Particulate PCB, %OC, grain size, (AVS) 210Pb	PCB, TOC, grain size, ²¹⁰ Pb, and others
Traps	Same as above	Fe, C, N, P
# Stations Cores/grabs Traps	200 2/segment	24 1
Frequency Cores/grabs Traps	One time sampling 5/year	Once every 10 years 2/year
Total # Samples Cores/grabs Traps	200 10x (x = # segments)	24/5 2

<u>Table 6 - cont'd.</u>

MEDIA/PROGRAM/DESIGN	WORK GROUP II PLAN	GLISP
FISH Open Lake		
Species	Lake trout, alewife, smelt, sculpin	Lake trout, salmon, white perch, others*
Parameters	РСВ	PCB and others
# Stations Composites	Lake trout - 4 stations: 25 fish/ station Alewife - 4 stations: 10 composites/ station Smelt/sculpin - 4 stations: 5 composites/ station	Number of stations stated as "sufficient to provide confidence in estimating a 25% change in abundance between sampling periods." 5 composites/station
Frequency	1/year	1/year
		*Also calls for "continued" monitoring of alewife and smelt
INVERTEBRATES	Follow GLISP (Sarvelliance Work Group	
Species	Mysis, Pontoporeia, algae, zooplankton	Pontoporeia, plankton, others
Parameters	PCB	PCB and others
# Stations	5/segment, 3 segments	Not stated, some need to correspond to fish sampling
Frequency	5/year	l/year (late summer)

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<u>Table 6 - cont'd.</u>	- 4 -	
MEDIA/PROGRAM/DESIGN	WORK GROUP II PLAN	GLISP
ATMOSPHERIC	Follow GLISP ("A Plan for Assessing Atmospheric Deposition to the Great Lakes") and the bilateral "Implementation Plan for the Integrated Atmospheric Deposition Network"	
POINT SOURCES	Follow GLISP (Surveillance Work Group 1987)	3 cienter trutses
Take a Kampler	2	Mitcheskik for Consined a
		1/year.

Table 6 - nont'd

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It must be kept in mind when conducting comparisons with GLISP, that GLISP was developed to address a multitude of objectives, not one, as attempted here. In addition, the GLISP plan calls for monitoring Lake Ontario fairly intensively for several years. Following each year, the information will be evaluated and the program modified accordingly. The intent of the plan detailed in GLISP is to conduct a pilot program so that an efficient monitor-ing program can be developed in the future. For example, the tributary portion of GLISP calls for suspended solids and total phosphorus data to be collected on 104 occasions for two years, after which, the data will be evaluated and the frequency for monitoring each tributary reassessed.

valatively complex to

Generic Marshore Areas

The characteristics of the nearshort area and areas of Concern differences considerably. As illustrated schematically in figure 6, the rest is considerably from a simple well-mixed also to a lense, relatively one terminer area, which integrates the imput; from many screen is a second size of the context as a simple source. A small tributary may been also second size of the context as transporters of the context as a second size of the size of the size of transporters are an open herbour, way as the second size of the size of the size of very farge interface with the take fact are the second size of the size of significantly or relating within the second size of the second factors which change the characteristics and the second size of the second factors It must be kept in mind when conducting comparisons with GLISP, that GLISP was developed to address a multitude of objectives, not one, as attempted here. In addition, the GLISP plan calls for monitoring take Ontario fairly intensively for several years. Following each year, the information will be evaluated and the program modified accordingly. The intent of the plan detailed in GLISP is to conduct a plict program so that an efficient monitor ing program can be developed in the future. For example, the tributary portion of GLISP calls for suspended solids and total phosphorus data to be collected on 104 occasions for two years, after which, the data wilf be evaluated and the frequency for monitoring each tributary reassessed. GROUP III REPORT

<u>Alex McCorquodale, Chairman</u> Mike Zarull, Recorder

STATEMENT OF THE MANAGEMENT QUESTION/ISSUE:

What is the loading to the open lake from nearshore regions, especially Areas of Concern? What minimum information is needed to estimate this amount? Can integrated samplers (biological or mechanical) be used? How? Is the technology available or being developed to monitor for this question? What frequency of sampling is needed?

DISCUSSION OF THE MANAGEMENT QUESTION

Objectives

Working Group III was charged with the task of determining how to design a sampling program to estimate the loading of contaminants into the open lake from the nearshore areas, with particular reference to Areas of Concern. On the surface it would appear to be a relatively simple task. However, it became obvious quickly that it was a very complex problem. Each nearshore area or Area of Concern is very different in terms of its hydrodynamics, chemical composition and potential importance as a source. Each of these factors dictates a very different approach to determining the loading of contaminants into the lake. No single sampling strategy (e.g. twenty discrete water samples per month and two Doppler current meters) is, therefore, adequate. This does not mean that the task is impossible, only that a single approach is not adequate to reliably obtain the data required. To address these problems, two generic nearshore areas were defined, which represent the extremes in the interface characteristics of the Areas of Concern. Three conceptual approaches were developed, which address the variable physical and chemical characteristics of the different nearshore areas and Areas of Concern: direct interface measurement, a simple parameterization model and a relatively complex system model.

Generic Nearshore Areas

The characteristics of the nearshore areas and Areas of Concern differ considerably. As illustrated schematically in Figure 6, they range in complexity from a simple well-mixed pipe to a large, relatively open nearshore area, which integrates the inputs from many sources and can be considered as a single source. A small tributary may behave as a well-mixed pipe, where the transport of the contaminant is dominated by advective flow. The other extreme, e.g. an open harbour, may be dominated by turbulent transfer at a very large interface with the lake, such that the contaminants are altered significantly or retained within the nearshore area. Very few Areas of Concern will fit either of the extremes and there may be seasonal factors which change the characteristics and their importance dramatically.



COMPLEX INTERFACE

OPEN INTERFACE

NARROW INTERFACE (WFIL-MIXED PIPE)

advective flow

turbulent transfer multidirectional flow

unidirectional flow no retention no transformation transformation within basin

flow homogeneous flow gradients single input multiple inputs within basin chemically homogeneous chemical gradients second plants when the second pretention within basin

FIGURE 6. GENERIC NEARSHORE ZONES

As an example, consider a harbour with a relatively confined entrance. During the spring, the water flow out of the mouth of the harbour may be unidirectional and uniform. Later in the season, the flows may be reduced and there may even be periods of flow reversal. The water column may be vertically or horizontally stratified, thus increasing the complexity of the system considerably. The result is that each nearshore area must be considered to be unique, even though it may approach one of the extremes.

CONCEPTUAL APPROACHES TO NEARSHORE-DERIVED LOADING TO OPEN LAKES

Approaches:

a) Interface Measurement:

As its name implies, the "Interface Measurement" approach involves the actual measurement of loading flux across the nearshore/open lake interface. Since contaminant loading is the product of volumetric flow rates and contaminant concentrations, both the flow rates and concentrations have to be measured at the interface. Further, since many of the critical pollutants are hydrophobic in nature, measurement of suspended sediment flux at the interface should also be determined.

To obtain accurate loading estimates, the spatial and temporal resolution for sampling should be sufficient to permit quantification of the variability for each of the three types of parameters: water flow rate, suspended sediment flux and pollutant concentrations. The details of this process are discussed in the "sampling strategy" section of the report.

In order to obtain representative loading estimates, it will be necessary to sample continuously, with respect to the variability periods of the three parameter types, using the "Interface Measurement Approach".

b) Parameterization:

In the "Parameterization" approach, 'limited measured data' are 'extrapolated', using 'derived relationships', to obtain an estimate of the loading flux between the nearshore region and the open lake. The 'limited measured data' would represent flow velocities and contaminant concentrations or appropriate concentration surrogates, measured at only a few locations and at specified times (less intensive with respect to the "Interface Approach"). The 'derived relationships' are mathematical equations, which are found to relate this 'limited measured data' to actual mass loading flux at the interface (i.e. the mass loading flux is parameterized, using this easily obtained but limited data).

The sampling requirements for the 'limited measured data' and the nature of the 'derived relationships' would be effectively determined only by first conducting a one-time, intensive field data collection program, likely for a period of at least one year. In this intensive program, detailed measurements of the mass flux crossing the interface would be made, along with appropriate 'surrogate' concentration and flow characteristics from within the nearshore region. Then, appropriate relationships between the mass flux of the contaminants of concern crossing the interface, and the surrogate concentrations and flow data from within the nearshore region are derived. Separate relationships will likely be required for each season of the year, but the exact number and surrogates involved would be designed to obtain the desired level of accuracy for the mass flux estimate. The number of surrogate stations would be sufficient to take into account the major sources of variance involved (i.e. data quality, spatial, temporal/seasonal, replication). Further details are discussed in the "Sampling Strategy" section of the report.

It is quite likely that this estimated contaminant mass loading from the nearshore to the open lake would take the form of a simple stochastic model, which would be some function of the mean and variable values of the surrogate concentrations and flows, obtained from the 'limited measured data'.

c) System Model:

The "System Model" approach would involve the application of hydrodynamic/ dispersion and contaminant fate and transport models to the entire nearshore region in question, (i.e. with the open lake representing the boundary of the application site). Thus, the mass loading in the open lake would be predicted using these models.

The main forcing functions of the model would include point source flows and mass loadings of contaminant, suspended solids and organic carbon. As a result, all significant point sources would have to be monitored with sufficient frequency to determine their loading rates in the nearshore region. The model would attempt to simulate the various transport and transformation processes, which would act upon discharged and/or in-place contaminants in a dynamic fashion until they leave the nearshore region (via transport to the open lake, volatilization, chemical transformation losses, etc.). The model would also have to simulate all sediment transport processes (settling, resuspension, sedimentation) as well as contaminant partitioning to the sediments. The nearshore region would be made discrete, with sufficient spatial detail to reflect any significant gradients in concentrations and/or process rates. The simulation time step would also be selected to assure it is smaller than the time scales of the key parameter variabilities. A good example of this approach would be the Green Bay Mass Balance Study.

Three levels of data collection would be necessary for the various stages of model application and use (i.e. calibration, verification and monitoring). These requirements are discussed in further detail in the "Sampling Strategy" section of the report. Selection of Approach

The appropriate approach for a given nearshore region (Area of Concern) would depend on many factors. Some of these include:

- the exact characteristics of the interface
- the type of contaminant, and concentration levels as they relate to sampling costs
- the nature of the contaminant loading as it relates to quantification of the sources (e.g. point source, in-place)
- the time scale of interest for open lake use of the information

Since there are many possibilities, depending upon the exact application, it is not worthwhile to consider the approach selection criteria in detail at this time. However, as a guide to selecting a satisfactory approach, it may be useful to list the key advantages and disadvantages for each approach.

a) Interface Measurement:

Advantages:

- i) It is a direct method of measuring mass flux at the interface.
- ii) It avoids both the need to measure the various point sources contributing to the nearshore region and the need to apply sophisticated models to predict transport through the interface.

Disadvantages:

- i) Accurate concentration measurements may be difficult or impossible, since levels at the interface (i.e. the low end of the gradient) may be near or below the detection limit.
 - ii) Hydraulics at the interface may be very complex, both spatially and temporally. Thus, several current metering stations may be required, with data collected on a continual basis (i.e. expensive monitoring).
- iii) The results will not address load allocation questions for sources to the nearshore region.
- iv) Nothing is learned regarding the system characteristics and the responses of the nearshore region.

b) Parameterization Method:

Advantages:

- i) The number of stations required for ongoing measurements (i.e. after the initial intensive gathering stage) is relatively small. They can also be supplemented with biomonitors.
- ii) It is a robust method since the modeling aspect is very simple.

Disadvantages:

- i) The resulting accuracy of the mass flux estimates may be relatively low as compared with the other methods and/or the level of accuracy may be impossible to estimate.
- ii) It does not address any questions regarding load allocation within the nearshore region.
- iii) It does not provide a good insight into the system characteristics or response of the nearshore region, although it is likely to provide more such information than the "Interface Measurement" approach.
- c) System Model:

Advantages:

- i) It attempts to address the complexity of the nearshore region system.
- ii) It provides loading data for sources in the nearshore region, which can assist in any load allocation exercise. Therefore, it is more useful as a management tool.
 - iii) It provides good insight into the system characteristics and responses of the nearshore region.
- iv) It should provide higher accuracy, once calibrated and verified via intensive data gathering, since it can be used to predict continuous mass flux in the open lake (i.e. it can be used to 'interpolate' between limited measurement data, likely generated because of cost or logistical limitations on field work).

Disadvantages:

- i) It is initially costly because intensive field data for quantification of numerous modeling parameters are necessary.
 - ii) It requires a longer development period (for data gathering and model validation).
 - iii) It requires the use of 'specialists' for model development and application.
 - iv) All of the 'forcing functions' of the model (e.g. contaminant and sediment loadings to the nearshore region) must be measured on an ongoing basis.

SAMPLING STRATEGIES

Direct Measurement of Fluxes at the Interface Between the Area of Concern and the Open Lake

Formally, the annual load (mass) of contaminant species transported to the open lake across the defined interface section A, Figure 6 is given by the integral,

$$M_{S} = \int \int C_{S}(\vec{r}, t) V_{n}(\vec{r}, t) dA dt$$
(4)

where C_S is the concentration of species S; t is time; τ is the averaging period (1 year); dA is an element of cross sectional area; V_n is the component of velocity normal to the cross section, positive towards the lake. Both C_S and V_n are functions of location within the cross section (r) and time (t). For the direct measurement of contaminant transport to be feasible, the spatial distribution of V_n and C_S across A must be simple, with scales of variation not much smaller than the physical dimensions of A itself. The most complex situation would be expected in the summer if the depth of the cross section occurs (Hamilton Harbour), two-way exchange flows must be expected. From preliminary measurements of the distribution of C_S and V_n across A, made under a representative variety of seasonal conditions, wind-forcing situations and runoff conditions, it would be possible to divide the section A into a number of panels (i.e. vertical strips of area perpendicular to the flow) (identified as I), such that the integral above is approximated by the sum

$$M_{SIJ} = \sum_{j=1}^{J} \sum_{i=1}^{I_j} C_{Sij} V_{nij} A_{ij} \Delta t_j$$

and it is assumed that measurements of V_n and C_S are available for each of the I panels. The maximum number of panels, I, is a function of season as well as the size and geometry of A.

Mold oblyche bluedz 11 (vi (5)

(6)

An appropriate sampling strategy must now be considered for the temporal variations of flow and concentration in the section. Consider the average flux across a panel over the time T_a . Both the flow and concentration can be expressed as the sum of a value averaged over T_a and a fluctuating component. The average flux over the interval T_a is written in terms of the average values and their covariance

$$M = T_a \left\{ \overline{C}_S \overline{V}_n + \frac{1}{T_a} \int_t^{t+I_a} C_S V_n dt \right\}$$

where $V_n = \overline{V}_n + V_n$; $C_S = \overline{C}_S + C_S$ (the apostrophe denotes the fluctuating component).

For a given flow regime, it is possible to choose a T_a short enough so that the fluctuating components contribute negligibly to the flux over this interval. The averaging time, T_a, may be fixed at the value that produces acceptable results in all seasons or it may be adjusted to fit what has been determined from preliminary exploration about the temporal variations of the flow and concentration fields. In view of the costly analysis required to determine contaminant concentrations, a more easily measured tracer property, such as conductivity, chloride or an optical property might be employed to work out the time and space distributions of the concentration field if the contaminant and tracer fields had equivalent statistical properties in space near the interface section. Current meter measurements, especially with modern microprocessor-controlled devices, are readily converted to averages over selected Tas. Water samples would have to be composited or derived from integrating samplers to form the appropriate average. In Table 7 we present the number of water samples for contaminant analysis that would be produced in a year under various assumed time and space variabilities.

The numbers of measurement panels and samples for contaminant analysis are not the only operational considerations. The mechanisms for maintaining and servicing the measurement program must be in place for the monitoring period (assumed to be at least a decade). Physical exposure of current meters, sampling devices, and other equipment to shipping and storm conditions must be considered. It is likely that the network would be out of service from time to time. Backups and/or redundancy sufficient to avoid unacceptable losses of data add very significantly to the costs.

Parameterized Exchanges

Over long time scales it would seem possible to estimate the loading flux in terms of five slowly varying parameters (Boyce and Hamblin, 1975): an outflow velocity; an eddy diffusivity; two concentrations, one representative of the Area of Concern (AOC), the other of the adjacent ambient conditions in the lake, and a cross-sectional area. Thus,

$$F_{S} = A \left(v_{0} C_{S0} + (C_{S0} - C_{SL}) K_{L} \right)$$
(7)

where F_S is the flux of substance S; A is the cross sectional area of the interface (note that A is variable if stratified flow occurs); v_O is the average outflow velocity of "basin" water normal to the section; C_{SO} is a concentration representative of the basin; C_{SL} is a concentration representative of the basin; C_{SL} is a concentration representative of the basin and the lake; and K_L is an eddy diffusion coefficient. In some situations it might be possible to treat all parameters as annual averages; here we consider that seasonal changes are important, particularly if stratification is involved. Thus, the averaging period implied in [4] above may be taken as one or several months.

 v_0 , K_L and A can be specified if the hydrodynamics of the exchange flow is known. Under homogeneous conditions, v_0 could be derived from a water budget of the AOC. Flow measurements made in support of the direct measurements (above) would serve to define the hydrodynamic parameters. A numerical
TABLE 7

NUMBER OF WATER SAMPLES PER YEAR FOR CONTAMINANT ANALYSIS FOR DIRECT FLUX MEASUREMENT METHOD

A	VERAGING PERIOD	1	2	3	4	over se
ARR # 24.34	4 hr	2190	4380	8760	17520	
	1 dav	365	730	1460	2920	
	1 wk	52	104	208	416	
	1 mo	12	24	48	96	
	de for the at	ala al el t	age Manace	in eneme a	Seem Surres	1912194

Typical	Numbers:	Toronto Harbour	15000
		Hamilton Harbour	3000
		Niagara River	300

	is torms of five slowly earying parameters (flowing of the share a
	out low velocity; an eddy diffusivity that educer " a fear any and the
	TABLE 8
	MEASUREMENT ARRAY FOR METHOD 2
9	4 Current Meters c/w Temperature Sensors (10 min sampling)
or	2 Doppler Profiling Current Meters
	2 Thermistor Arrays or Equivalent Temperature Profilier (e 1/2 m)
	4 Recording Conductivity Meters (1/2 III Averaging and Sampring)
	2 Water Level Gauges (1/2 nr averaging and sampling)
	1 Wind Speed and Direction Recorder with Corresponding Air and Water Surface Temperature (1/2 Averaging and Sampling)

WEEKLY LAUNCH SAMPLING - Conductivity, Temperature and Contaminants

VD. E. and A can be specified if the hydrodynamics of the archange. Actor is known. Under homogeneous conditions, vo could be derived from a veter budget of the AGL. Flow measurements made in support of the direct measurements (above) would serve to define the hydrodynamic parameters. A numerical

hydrodynamic model of the exchange flows, verified by field data, might be the most efficient. If the currents were known at a point in the interface (monitored), the model could be made to "fit" the flow measurements by the adjustment of parameters, such as friction factors. The diffusivity, KI, can be determined from the fluctuations of current in the interface area. Each episode of unidirectional flow can be described by an average velocity and particle excursion length (average velocity times the time interval of the flow episode). The diffusivity can be expressed as a suitable average of the product of the velocity scale and the excursion length. The episodes that contribute significantly to exchange are those where the excursion length is comparable to or larger than the length, L, of the interface. The weighting scheme for adding the effects of the flow episodes of variable scales could be developed from limited segments of direct flux measurements from method 1 (above) or from transport models and/or other engineering experience. The concentrations, C_{SO} (AOC) and C_{SL} (lake ambient), could de determined from limited pooled sampling within and without the AOC. The larger the data set available at the time of parameterization, the more accurate the results will be. Nevertheless, common sense applied even to a limited data base should yield numbers that have the correct order of magnitude and the method, once standardized, should give consistent results for comparative purposes.

Data collection for this approach divides into two phases: calibration and verification of the parameterization or model and long term monitoring activities.

The first phase would require segments of data roughly equivalent to those collected in the pursuit of method 1 (above). Since the goal of this phase is to establish a model or parameterization of the physical transport, the water mass tracer could be a simply-measured conservative tracer, such as conductivity or chloride. Table 8 lists an array of data required over a year's time. Sampling intensity might vary: perhaps four intensive, month-long periods with more reduced monitoring in between. The data analysis and modeling effort is considerable: three persons for a year would be reasonable. A verification stage might be considered, whereby the computed exchanges of contaminant species are compared with a direct measurement of the flux, using method 1 over one or two months.

The second phase would require "continuous" measurement of currents and temperatures at the control section and perhaps four composite water samples taken from a few (5?) stations both inside and outside the AOC at weekly intervals (a morning's launch-based sampling per week). Roughly 250 chemical analyses (totals, both dissolved and particulate matter) per year would be required.

Mass Balance Model of Area of Concern

The transfer of contaminants to the open lake could be computed from a mass balance model of the AOC. If inputs of contaminants to the AOC from local sources were known and if transfers of contaminants to the sediments and atmosphere could be determined, the quantities carried to the open lake would appear as a residual. The integrating time-scale of this method would be long: annual averages would seem reasonable. The model-building phase of this approach involves much more data gathering and analysis than the other methods, but no gain in accuracy could be promised. Justification of this approach would not be based on accuracy or expediency, but rather on the increased understanding of the natural system which the project would yield. Loading to the open lake would be, in effect, a by-product.

The calibration phase of the study would entail a year's measurement of flux according to method 1, in addition to concurrent measurements of loadings from local sources and study of distributions in the AOC itself. With this data, the losses to the atmosphere and sediments could be determined and parameterized, at least in principle. Table 9 summarizes the data requirements for this method in a general way, and assumes that an independent data set would be collected for model verification. A monitoring program, particularly of distributions of materials in the AOC would seem prudent and would, in any case, be part of RAPs.

RECOMMENDATIONS FOR GLISP

The sampling requirements (both component or parameters and the point of sampling) are presented in Table 9 for the calibration, verification and monitoring phases of the program, which ascertains the contribution of material from nearshore regions, especially Areas of Concern. The work group concluded that because of the many fundamental differences among Areas of Concern, it is not possible to specify a single plan for sampling an Area of Concern; instead, the Work Group ranked the requirements for sampling information on each component and suggested a minimum number of surveys necessary to develop an adequate data base.

The Great Lakes International Surveillance Plan also concluded that "because of the varying nature of the problems as well as the geographic nature of the locations (e.g. harbours and embayments versus tributaries and connecting channels) each will have to be dealt with in the individual plans on a case-by-use basis." In some cases, the individual task forces felt that there was sufficient problem definition (through intensive studies, which had already taken place) to produce a surveillance plan, at least for the enrichment (nutrient) and bacteriological components. Some of the areas for which the plans were produced include Saginaw Bay, Michigan (Lake Huron); Hamilton Harbour, Ontario and Toronto Harbour, Ontario (Lake Ontario). However, most areas were described as having insufficient characterization to propose a surveillance plan at present and a "special studies" approach was advocated. The Lake Erie Task Force perhaps summed up the situation best: "Due to a lack of any quantitative data base for any of the areas (except River Raisin) [applies to Lake Erie only], it is currently not possible to design any effective surveillance programs for these impacted areas. Since each Area of Concern differs in physical and hydrological features, as well as having specific pollutants, it is not possible to design a standard model for routine monitoring. Therefore, it is imperative that each Area of Concern be subjected to an intensive study prior to the formulation of a routine monitoring program. Consequently the task force recommends that as a pragmatic approach, each Area of Concern undergo an intensive study similar to the open lake schemes outlined in the original GLISP. Precedence for such efforts include: Green Bay, Saginaw Bay and the River Raisin."

As a direct result of these recommendations and because of a lack of information on toxic substances in all Areas of Concern, the Surveillance Work Group sponsored a workshop (October 1985) and subsequently produced a report

MODEL STAGE	CA	LIBRATION		VI	ERIFICATIO	N	M	ONITORING	199338
COMPONENT LOCATION →	BOUNDARY CONDITION	POINT SOURCES	AMBIENT	BOUNDARY CONDITION	POINT SOURCES	AMBIENT	BOUNDARY CONDITION	POINT	AMBIENT
Flow - Currents	A(1)	A(1)	A(1)	A(1)	A(1)	в	A(1)	A(1)	С
Phase – Sus. Separation – Diss.	A A	A A	A A	A C	A C	A D	A D	A D	A D
P.O.C.	А	A	A	A	A	A	В	В	В
D.O.C.	A	A	A	А	A	A	В	В	В
Temp.	A(1)	A(1)	A(1)	A(1)	A(1)	A(1)	A(1)	A(1)	A(1)
Conventionals	А	А	A	A	A	A	A	A	С
Low KoW - Total	А	A	A	A	A	A	B/C	А	B/C
High KoW – Total Centrifuge	A A	A A	A A	A A	A A	A A	B/C B/C	A A	B/C B/C
Metals	A	A	A	A	A	А	B/C	А	B/C
Benthos (enumeration)			С						С
Sediment - Traps			A(2)			с			A
Sediment - Surficial			A(2)			С			В
Sediment - Cores			A	D	D	D	D	D	D
Biomonitoring			B(R)			B(R)			B(R)
Minimum Number of Surveys/Yr.	4+	4+	4+	4+	4+	4+	0.5	HF	0.5
+Sampling – Synoptic		1 - 2 4	A	- Essential			22228	128 3	

SAMPLING	REQUIREMENTS	FOR	METHOD	3	(SYSTEM	MODEL)
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TABLE 9

¹Continuous measurement ²Sample along the gradient from inside the area to outside ³Clams or caged fish

B - Useful
C - Nice to know
D - Waste of effort

R – Research need HF – High frequency (unspecified) All survey samplings require 20% replication

i 65 -

"Guidance on Characterization of Toxic Substances Problems in Areas of Concern in the Great Lakes Basin" (March 1987) to assist the agencies in collecting enough of the necessary data to define the local problems as well as to track and quantify sources of contaminants. This document, which is part of Volume III of GLISP, provides detailed information on study design, analytic techniques and statistical considerations. If there is one weak aspect of the guidance document, it is in its lack of detail on setting up a hydrological/ physical study of water movement and mass transport at the boundary between the Area of Concern and the adjacent lake. The report does, however, stress the need for such information.

On the basis of the Stage 1 remedial action plans, which have been submitted to the IJC, few have employed this document or similar intensive study approaches for examining enrichment problems and none has described the movement of contaminants or the actual or potential impacts from such contaminants on the adjacent lake.

The inescapable conclusion is that the absence of an adequate data base to accommodate the Areas of Concern component of a lake-wide balance approach (as described in this section) is not due to a lack of specification in GLISP (Volumes II & III), but rather to a lack of implementation of what is required. All of the data necessary to implement the mass balance approach could be available if GLISP were implemented (especially the guidance document), with some additional refinements to the specifications for current/hydrologic/ physical data.

GROUP IV REPORT

Joseph V. DePinto, Chairman David M. Dolan, Recorder

STATEMENT OF MANAGEMENT QUESTION/ISSUE AND DISCUSSION

Before stating the management question being addressed by this group, we feel that it is necessary to make two statements regarding the approach of our group in addressing our question. First, we feel that our deliberations are providing input to the conceptual models being developed by the other groups. In that sense we are not developing a single conceptual model on our own, but rather a conceptual framework within which a range of models (varying in complexity) can be used to address our question. Second, we consider that there are basically two type of data needs for toxic mass balance modeling:

- Model <u>Development</u> Data intensive, coherent field observation and process experimentation used for model calibration and verification (e.g. the Green Bay Project)
- Model <u>Application</u> Data less intensive, more routine monitoring and surveillance for such needs as post-audit testing of the success of regulatory or remediation programs, assessing long-term, system-wide trends and facilitating the transfer of toxics exposure models to other systems (e.g. GLISP).

We see our role in suggesting strategy as providing for the model application data needs rather than the model development needs.

With the above two qualifications, we would state our problem in the following manner:

What is the relationship (i.e. coupling or linkage) between concentrations of contaminants and that of conventional (phosphorus and suspended solids) pollutants? How will management of these conventionals (e.g. P control, point and non-point solids control, fisheries management) affect contaminant fate and transport?

CONCEPTUAL APPROACH

Goals: _____

- To identify the linkages causing the response of contaminants to the management of conventional pollutants and fisheries
- o To understand or explain the observed response in terms of sorbent compartments
- o To understand emerging problems in terms of unusual occurrences, such as exotic species invasions and extensive ice cover

Figure 7 is a diagram of the conceptual approach. The boxes can be thought of as models of in-lake processes. The two-way arrows are the linkages between the processes, which could also be models. The one-way arrows are the management options that affect these processes. Data to describe the ambient phosphorus and contaminant processes are currently available from GLISP or will be required by other groups in the workshop. Group IV focuses on the sorbent compartments.

PREMISE FOR CONCEPTUALIZATION

- o Linkage between conventionals management and toxics management is provided professional design of the conception of the second s by sorbent compartments.
- o Accurate representation of properties and dynamics of sorbent compartments is crucial to accurate toxic exposure modeling.
- o Differentiation among sorbent compartments may be important for the following reasons:
 - differences in transport characteristics
 - differences in partitioning 100 Della
 - differences in spatial and temporal gradients, resulting from 1 different source functions and internal transformation processes
 - different responses to different management strategies
 - may facilitate food chain bioaccumulation models 07800<u>1</u>0 8

Four sorbent compartments were identified:

- Plankton (Living Particulate Organic Carbon (POC)) 0
- Non-living Particulate Organic Carbon (POC) (FOC) 0
- Dissolved Organic Carbon (DOC) 0
- Abiotic Particles (allochthonous) 0

The plankton compartment is meant to include living matter, primarily phytoplankton and zooplankton. The non-living POC compartment includes detritus. The DOC compartment is system-dependent, but includes organic matter that passes through filters. The DOC compartment will represent a wide range of molecular weight, compound structure and degradability; hence, there may be significant system-specific differences in the fate of DOC and, in particular, in its effectiveness in binding toxic organic chemicals. Abiotic particles consist of allochthonous material derived primarily from land runoff. Each of these compartments has different sorbent characteristics. For each compartment, surveillance data is required to answer two questions:

- How much of each sorbent compartment is present and how much is 0 entering the system from external sources?
- How much contaminant is present in each compartment? 0

SAMPLING STRATEGY

With the above conceptual approach in mind, Table 10 contains the necessary elements of the sampling strategy to answer the question of nutrient-contaminant interactions. The different media required to be measured are listed at the top of the table and include water column (unfiltered, filtered and

GROUP IV CONCEPTUAL APPROACH



PARAMETERS	WATER COL. UNFILT. FILTRATE RESIDU	E SEDIMENTS ATMOSPHERI	C LOADS	FIS	SH PREDATOR	BENTHOS
TP (SRP)	1/G	GLISP+	GLISP			
TSS	Seasonal (4 cruises)		GLISP			
Chl a	epi & hypo	M.S. (surf.)	M.S.			
POC	5 stat./seg.		M.S.			
DOC (or lipid for biota)			M.S.	GLISP	GLISP	1/G
Part. Ca, Fe, Al, Mn			M.S.			
Radioisotopes	1/G	M.S. (core)				
Total Contam.	1/G	1/G-surf. GLISP+ M.Score		GLISP	GLISP	1/G
Four sorbed phases	M.S.	M.S. (surf.)				
"truly dissolved" contaminant	M.S.	M.S. (surf.)			1. J 43	12172

PROPOSED GLISP TO SUPPORT QUESTION #4

TABLE 10

- 70 -

particulate), sediment, atmosphere, tributary, fish (forage and predators) and benthos. The parameters are listed in the left column. Although many of the parameters will be required to answer other mass balance questions, the measurements critical to answering this question are the sorbent-related parameters (TSS, Chlorophyll a, POC, DOC, particulate calcium, iron, aluminum and manganese) and radioisotopes. The results of the sorbent-related measurements, together with knowledge of typical ratios for different lakes and different seasons, will allow the estimation of the quantities of sorbent present in each compartment. The radioisotopes will allow the question of rates of solid dynamic exchange between water column and sediments to be addressed.

Some of the notations on Table 10 require explanation. 1/G refers to one annual (refer to Group II) generic lake plan. GLISP means that the measurement is currently required by the plan. M.S. refers to master stations, which are a subset of total GLISP stations (both in space and in time, if necessary), where the more detailed work described in this strategy would be performed. The last three parameters are the different phases of a contaminant for which a mass balance is being performed. The contaminant concentrations in each of the four sorbed phases should be based on a subset of stations as well as on the amount of "truly dissolved" contaminant. These measurements require physical separation of enough of each sorbent compartment to measure its contaminant level. Accomplishment of this separation on a routine basis requires additional research. The Green Bay Mass Balance Study includes research efforts on this subject.

RECOMMENDATIONS

- o It is recommended that the parameters included in Table 10 be added to GLISP and monitored at the spatial and temporal intensity specified.
- The resulting data on sorbent compartments should be routinely interpreted by a standing work group (perhaps in a workshop format) so that the results will be available for use by mass balance modelers.

particulates, section i, atmosphere, tributary, fish (forenee and predators) and benthos. The parameters are jisted in the left column. Although many of the parameters will be required to answer other mass belative questions, the measurements critical to answering this question are the content-related parameters (ISS, Chlorophyll &, TOC, DOC, particulate calcium, from sluminum and manganese) and radioisotopes. The results of the sorbent-related measure treats, together with knowledge of typical ratios for different lates and different seasons, will allow the estimation of the question of the different present in each compartment. The radioisotopes will allow the direction of retes of solid dynamic exchange between water column and sediments to be addressed

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by a standing work group (perhaps in a workstop format) so that the results will be available for were by mere belonge created and the

MASS BALANCE APPROACH RESEARCH NEEDS

RESEARCH QUESTIONS

It is recognized that there are considerable gaps in knowledge regarding the transfer of contaminants through the ecosystem that cannot be accommodated by [routine] surveillance programs. Five informal Research Work Groups were formed at the workshop to recommend improvements to research areas that would support the mass balance approach.

GROUP A - TRANSFER OF CONTAMINANTS TO/THROUGH THE BIOTA

The discussion of the group focused on the need to understand the movement of contaminants through the ecosystem in order to be able to interpret the data being generated by the monitoring programs. All of the questions presented to the working group were more or less related to modeling the food chain transfer of contaminants. Everyone in the group strongly agreed that we did not have much field data to validate the current models. Although the literature data currently available supports a food chain transfer, there is such great variation in the contaminant concentrations in each trophic level that there is very little statistical confidence in the results of the models. There has been a focus on the higher trophic levels and very little data is available for the lower trophic levels, where bioconcentration may be important. The models usually make several assumptions about the bottom of the food chain

Major Research Needs

The research needs go beyond the monitoring program. Research is needed to give confidence to the interpretation of the data collected.

- A multi-year study of the movement of contaminants through food chains leading to the organisms being monitored. This study would include both chemical and biological parameters.
- A study of the role of DOC in limiting the bioavailability of contaminants to lower organisms in the Great Lakes.
- A collection of DOC as a regular conventional parameter.

Specific Questions

- 1. The group thought that the Critical 11 Pollutants were <u>not</u> in equilibrium for several reasons: changing condition and lipid content of biota, a lag in the response of top predators because of the filtering through the food chain and rapid changes in the availability of the contaminants. The chemicals, in some cases, may be approaching equilibrium.
- 2. The sediments could be a source of contaminants to some biota, but not others, depending on the chemicals and the habits of the organism. The sediments may reflect the concentrations of these chemicals in the lower trophic levels.

- 3. The existing programs do seem to measure adequate numbers and species of fish. There is some concern that the programs focus on top predators. The way that the fish are sampled/subsampled differs with different labs, a situation which makes it difficult to compare results.
- 4. The surveillance program does <u>not</u> need to measure Critical 11 Pollutants throughout the food chain on a regular basis. However, the strongest recommendation of the group was that a multi-year study be conducted to document, in the <u>field</u>, the concentration of the Critical 11 Pollutants in a variety of food chains. This effort would have to include seasonal sampling. Emphasis is needed on the lower trophic levels, which are sensitive to the water concentration (and possibly sediment concentration) and for which we have very little data. The basic biological parameters need to be defined better: "who is eating whom and how much?".
- 5. The role of dissolved organic matter (DOC) in limiting the availability of contaminants is poorly understood, even though it may have a significant influence. Research is required to relate the "dissolved" contaminant concentrations to the "truly dissolved" or biologically-available fraction. We need to better understand the role of DOC in controlling the fate of trace contaminants. DOC is a conventional parameter that <u>must</u> be collected.

6. Question the current focus on hydrophobic chlorinated organics.

GROUP B - CONTAMINANT TRANSFER AT THE SEDIMENT-WATER INTERFACE

There was general agreement that sediment sampling techniques are well established. Box corers can be used by experienced personnel to collect undisturbed sediments.

Adequate techniques do not exist for the direct measurement of fluxes at this boundary. A combination of measurement and modeling must be used. For this effort, the following are required:

- o physical exchange processes and needs
 - Comprehensive lake-wide estimates (with confidence intervals) of the ratio of the surface sediment mixed layer to the sediment accumulation rate. This ratio represents the time constant for removal via burial beneath the "active zone". Values of this time constant (with standard errors) should be estimated for each lake (team of experts) from existing information. A detailed research sampling project should then be developed.
 - Near-bottom sediment traps can be used to collect samples of the active sediment zone. We do not know how large an area such a trap samples. Research on this question should be pursued since traps are being considered as surveillance sampling devices.

o biological transfer and needs

How well do we know the partition coefficients for the Critical 11 Pollutants? Is the uptake pathway of benthic invertebrates the sediment or the water?

How much of the body burden of the Critical 11 Pollutants in fish comes from the consumption of benthos? Measurement of sediments (NAA, ICP) in the stomachs of fish

Do we have good estimates of diffusion of the Cll from the sediments? Need good numbers for dissolved pore water concentrations and diffusion coefficients.

has - hee Comprehensive measurement of fallout radionuclides in fish (salmonids and others) in whatever older fish are available (1960 - present) transfer function from well-known loads to fish.

Post depositional diagenesis of organics and carbonates. Are trace water. organics remobilized by this process?

Focusing factors - evaluate the concept that the sediment accumulation of a well-characterized constituent (e.g. Pb²¹⁰, Cs¹³⁷) can be used to estimate the load of poorly-characterized compounds (e.g. BaP).

GROUP C - CONTAMINANT TRANSFER AT THE AIR-WATER INTERFACE

o How reliable are present estimates of wet and dry deposition of the Cll?

Poor for best known (PCBs) (factor of 3 to 5)

Less than poor for others (factor of 10) -

Is the existing/proposed monitoring network sufficient? 0

> Yes, to obtain atmospheric loading estimates (wet + dry particle) of perhaps 70% of the Cll in areas distant from source areas (continental background).

No, not sufficient to estimate the Cll chemicals proximate to source areas.

No, not sufficient to estimate air/water exchange of the Cl1 za-zan. chemicals.

No, not sufficient for 30% of the Cll chemicals.

o Can sources be identified with the existing/proposed monitoring program?

- No, not directly.

records.

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o Major research recommendations:

- Air/water exchange of the Cll chemicals.
- Air/land exchange of the Cll chemicals.
- Modeling near-scale atmospheric deposition on lakes/land within 50 km of large source areas (e.g. Chicago, Gary, Toronto, Hamilton)

GROUP D - UNCERTAINTY IN MODELING AND MEASUREMENTS RESEARCH RECOMMENDATIONS

The following is a summary of the discussion held by the Uncertainty in Modeling and Measurements Group:

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Verify the Models

Lack of knowledge is the inherent weakness of toxics modeling. This problem will be resolved only when the necessary data is collected to verify model predictions. Since there is no demonstrative example of toxics model verification, questions of "inherent model errors" cannot be answered. This situation may be contrasted with the eutrophication modeling experience. Eutrophication modeling was a success because there was abundant data collected for model calibration and verification, a situation which led to confidence in model use.

For verification, several kinds of data are needed. First, we need loading data. Loads are key to testing models because they drive the predictions. Then we need ambient data, with measurements that can be related to the model state variables. Finally, some process experimental data may be needed to remove the remaining degrees of freedom from the model.

The group discussed the possibility of identifying contaminants for which past loadings could be reconstructed by means of production or usage records, peat cores or other means. Such loading functions would make existing ambient data useful for model testing. Aside from the fallout radioisotopes, which have already been exploited for model calibration, lead and mirex were suggested as potentially useful for the verification of a toxics model.

The view was expressed that the necessary effort to verify the models will only be made when regulators seriously ask for the target loads to meet toxics goals. Some questioned whether toxics regulations will, in fact, be guided by rational decision making, as opposed to other methods (i.e. calls for zero discharge). However, if practicality dictates that toxics goals drive load reductions, then verified models will be essential for the management of toxics.

The group concluded that it could not answer the question, "What is the magnitude of inherent model errors?" because it did not know.

Fix the Chemistry

Chemical analytic methods and load monitoring strategies are weaknesses of existing measurement programs. The group recommended that no new monitoring or surveillance programs begin until issues of reliability, detection and cost of chemical analysis can be resolved. Current designs specify too many samples (Green Bay was cited as an example), creating problems of both logistics and expense. The number of samples gets out of hand because replicate variability is high so a number of samples are needed to produce one confident measurement, and load monitoring strategies are sample-intensive. What is needed is simpler, cheaper and more reliable (less analytic variation) chemistry methods. \$100 per sample analysis was proposed as a goal for cost. Obviously, surveillance and research dollars would go much further if analytical costs were reduced to this level.

Further development of methods for quantifying loadings is necessary. The methods must work with fewer analyses, while still identifying and distinguishing "big" loads. The method must also be acceptable to regulators and dischargers.

Identify the Uncertainties

Uncertainty in toxics goals should be considered when deciding how good model predictions need to be. Models with predictive errors of \pm 10% are unnecessarily precise if they are used in conjunction with a goal incorporating a 100-fold or greater safety factor. To manage toxics optimally, all components of the problem relating control strategies to endpoints (i.e. cancer risk or ecosystem viability) should carry comparable levels of uncertainty. This situation may require the integration of toxics modeling with goal setting and risk assessment.

Several areas of uncertainty in the toxics models themselves were also identified. Long-term model simulations of the response of water quality to loading changes apparently do not agree with trend data for toxics in the Great Lakes. Because these long-term responses are controlled by sedimentwater column exchange, the formulation and parameterization of this process may require further investigation. Predicting the bioaccumulation of high-K_{OW} chemicals is a second weakness of current models.

GROUP E - IMPLEMENTATION OF RECOMMENDATIONS

- Need to come out with a common front to managers and the public so that constructive debate in the scientific community is not seen as confusion, i.e. come out with a single model (note, this effort does not mean that model development should stop).
- o The framework should consider the following five questions:
 - How is the problem to be defined (i.e. benchmark, such as concentrations in fish exceeding health protection guidelines)?
 - What are the current total loads of chemicals of concern?
 - How much do the loads have to be reduced to alleviate the problem?
 - new How long will it take for load reductions to produce the required Conceffect?
 - Where do we most effectively apply the controls?
- Once model needs are defined, we need to examine the flexibility of GLISP in terms of meeting the model needs (i.e. what is currently in place; what gaps need to be filled?)
- The report from the workshop needs to discuss the model AS WELL AS go through examples of how the model works. It should also state the models' limitations.
- o To ensure that the current exercise continues, we need two groups: 1) under the IJC structure a joint Data Interpretive Group (e.g. SAB Technological Committee and Water Quality Board (WQB) Surveillance Subcommittee) should perhaps use models in putting together a chapter for the 1991 WQB Report and 2) under the Parties a bilateral group should ensure implementation of the components needed to use the models as well as to interpret data. [Note: Don Mackay suggested at a plenary session that maybe there should be a third party group and source of funding]. Perhaps the lakewide management plan process currently being developed by the Parties constitutes such a third party. The bottom line would appear

to be that for the results of the workshop to be successful there needs to be a mechanism in place to ensure continued dialogue between the data gatherers (i.e. surveillance and monitoring people) and the researchers (including the modeling community).

o Finally, it was recommended that the report be given wide distribution, especially to the public (public interest groups).

Some additional concerns that were expressed:

*

Air and water programs should be coordinated better.

There is no additional funding for implementation.

- The relative source of uncertainties in model inputs (e.g. not to collect air data to four significant figures when tributary data known only to one) need to be known.

- * Wayne Willford pointed out that a "Modeling" Group had been proposed on the United States side.
 - Steven Eisenreich recommended that a group be specifically funded to perform the "data interepretation" to ensure that the job is completed.

It needs to be understood that no single model will provide all the answers and as the process gains acceptance, we start refining models (i.e increase complexity) to start obtaining more detailed information.

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Hater Quality Modeling Section
Div. of Water Quality Planning and Assessment
Ohio Environmental Protection Access P. O. Box 1043, 1800. Holesattric Br Columbus, Ohio 48268-0140 (614) 644-2884

Me Tim M. Bartich Great Laiss Regional Colles International Joint Consistion 100 Ouellighte Avenue, 3th Floor Findsor, Ontario 426 513 19197 256-7821 Minesce 13137 226-2170 Decroit

He Hans Elberborr Inland Maters Directorals Levinonment Ganada Canada Gentra for Schud Ma = 2, 80x 5050, 861 Long box Surlington, Ortacio 178 Am 0415) 335-4515

Aug Dorgeane Mpartment of Fisheries & Demon anede Centre for Inland Heters 50. Box 5050. 867 Lengshore Co Griington, Optario 178 465

Hendy Bournique Dev of Rater Obelity Planning and As gissment Dato Environmental Protection Agency D.O. Box 1040 1990 Recentark Dr Columbus Obto 412000-0149 (614) 644-2800

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Research Triangle Bark, North Carolina 27711 (919) 541-3660 FTS::629-3560

HC. Hickael D'Antris Ontario Hintstry of The Chelrogen 135 St. Clair Avenue Htgl Toronto, Ontarie 148 Aler G4161 123-4960

Sobers Day Lobers Neter Pasiity Division Cleas Later Section Richigan Dept. of Satural Resources Office Building, South Towar F 6. Box 30028 Lansing, Michigan 48909 (517) 325-3318

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APPENDIX

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MASS BALANCE WORKSHOP PARTICIPANTS BARRIE, ONTARIO MARCH 7-9, 1990

Mr. Seif Amragy, Manager Water Quality Modeling Section Div. of Water Quality Planning and Assessment Ohio Environmental Protection Agency P.O. Box 1049, 1800 WaterMark Dr. Columbus, Ohio 43266-0149 (614) 644-2884

Mr. Tim M. Bartish Great Lakes Regional Office International Joint Commission 100 Ouellette Avenue, 8th Floor Windsor, Ontario N9A 6T3 (519) 256-7821 Windsor (313) 226-2170 Detroit FTS: 226-2170

Mr. Hans Biberhofer Inland Waters Directorate Environment Canada Canada Centre for Inland Waters P.O. Box 5050, 867 Lakeshore Road Burlington, Ontario L7R 4A6 (416) 336-4512

Uwe Borgmann Department of Fisheries & Oceans Canada Centre for Inland Waters P.O. Box 5050, 867 Lakeshore Rd. Burlington, Ontario L7R 4A6 (416) 336-4559

Randy Bournique Div. of Water Quality Planning and Assessment Ohio Environmental Protection Agency P.O. Box 1049, 1800 WaterMark Dr. Columbus, Ohio 43266-0149 (614) 644-2856

Mr. Farrell Boyce National Water Reserach Institute Environment Canada Canada Centre for Inland Waters P.O. Box 5050, 867 Lakeshore Rd. Burlington, Ontario L7R 4A6 (416) 336-4921 Mr. C. H. Chan Water Quality Branch IWD, Ontario Region Environment Canada Canada Centre for Inland Waters P.O. Box 5050, 867 Lakeshore Rd. Burlington, Ontario L7R 4A6 (416) 336-4644

John F. Clarke Atmospheric Sciences Modeling Division MD-80 U.S. EPA Research Triangle Park, North Carolina 27711 (919) 541-3660 FTS: 629-3660

Mr. Michael D'Andrea Ontario Ministry of the Environment 135 St. Clair Avenue West Toronto, Ontario M4V 1P5 (416) 323-4960

Mr. Robert Day Surface Water Quality Division Great Lakes Section Michigan Dept. of Natural Resources Ottawa Building, South Tower P.O. Box 30028 Lansing, Michigan 48909 (517) 335-3314

Mr. Dave DeVault Great Lakes National Program Office 5GL-TUB-10 U.S. Env'l. Protection Agency 230 South Dearborn Street Chicago, Illinois 60604 (312) 353-1375 FTS: 353-1375

Dr. Joseph V. DePinto Department of Civil and Environmental Engineering Clarkson University Potsdam, New York 13676 (315) 268-6532 FAX: (315) 268-6570

Dr. Dominic M. DiToro Environmental Engineering OLMATHO JIARAS Great Lakes Institute Department Manhattan College Bronx, New York 10471 (212) 920-0276

Mr. David M. Dolan Great Lakes Regional Office International Joint Commission 100 Ouellette Avenue, 8th Floor Windsor, Ontario N9A 6T3 (519) 256-7821 Windsor (313) 226-2170 Detroit FTS: 226-2170 941510 .1 1000

Mr. Richard Draper Great Lakes Section New York Department of Environmental Conservation Room 310 50 Wolf Road Albany, New York 12233-3501 (518) 457-0669

Dr. Brian J. Eadie Head, Synthetic Organics & Particle Dynamics Group GLERL/NOAA 2205 Commonwealth Blvd. Ann Arbor, Michigan 48105 (313) 668-2281

Dr. Steven J. Eisenreich Environmental Engineering Sciences Dept. of Civil & Mineral . Engineering University of Minnesota Minneapolis, Minnesota 55455 (612) 625-3082 FAX: (612) 624-0293

Mr. Douglas D. Endicott Large Lakes Research Station U.S. Environmental Protection Agency 9311 Groh Road Grosse Ile, Michigan 48138 (313) 692-7613 FTS: 378-7613 FAX: (313) 692-7603

401 Sunset Avenue Windsor, Ontario N9B 3P4 (519) 253-4232, X-2731

> Dr. Rav Hoff Atmospheric Environment Service R. R. #1 Egbert, Ontario LOL 1NO (705) 458–1141

> > Mr. Marvin E. Hora Minnesota Pollution Control Agency 520 Lafayette Road North St. Paul, Minnesota 55155 (612) 296-7215

> > Mr. Joe Hudek Surveillance and Analysis Division U.S. EPA, Region II Woodbridge Avenue Edison, New Jersey 08837 (201) 321-6713

Mr. Peter Kauss Surveillance Unit Great Lakes Section Water Resources Branch Ontario Ministry of the Environment 135 St. Clair Avenue West Toronto, Ontario M4V 1P5 (416) 323-4952 FAX: (416) 965-9807

Dr. Barry M. Lesht, ER/203 Center for Environmental Research Biological, Environmental, and Medical Research Division Argonne National Laboratory 9700 South Cass Avenue Argonne, Illinois 60439 (708) 972-4208 FTS: 972-4208

Dr. Donald Mackay Department of Chemical Engineering and Applied Chemistry University of Toronto 200 College Street Toronto, Ontario M5S 1A4 (416) 336-4921 (416) 978-4019

Dr. J. Alex McCorquodale Department of Civil and Environmental Engineering Great Lakes Institute University of Windsor 401 Sunset Avenue Windsor, Ontario N9B 3P4 (519) 253-4232

Mr. Gil McRae 1915 West Michigan Saginaw, Michigan 48602

Dr. Thomas J. Murphy Department of Chemistry DePaul University 25 E. Jackson Blvd. Chicago, Illinois 60604-2302 (312) 341-8191, X-8180 - University FAX: (312) 341-5324

Mr. Carlton Nash, Chief Ambient Assessment Unit Air and Radiation Division U.S. EPA, Region V 230 South Dearborn Street Chicago, Illinois 60604 (312) 886-6030 FTS: 886-6030

Mrs. Melanie T. Neilson Water Quality Branch, Ontario Reg. Environment Canada Canada Centre for Inland Waters P.O. Box 5050, 867 Lakeshore Rd. Burlington, Ontario L7R 4A6 (416) 336-4963

Dr. Peter Nettleton Great Lakes Section Ontario Ministry of the Environment 1 St. Clair Avenue West Toronto, Ontario M4V 1K6 (416) 323-4964

Mr. Phillip O'Brien
Bureau of Monitoring and
Assessment
New York Department of
Environmental Conservation
Room 328
50 Wolf Road
Albany, New York 12233-3503
(518) 457-2672

Ms. Ann O'Toole Atmospheric Environment Service 4905 Dufferin Street Downsview, Ontario M3H 4T5 (416) 739-4867 FAX # (416) 739-4224

> Ms. Ann Pope MD-15 U.S. EPA Research Triangle Park, North Carolina 27711 (919) 541-5373 FTS: 629-5373

Dr. Don Poulton Great Lakes Section Ontario Ministry of the Environment 135 St. Clair Avenue West Toronto, Ontario M4V 1P5 (416) 323-4954

Mr. William L. Richardson Chief Large Lakes Research Station U.S. EPA 9311 Groh Road Grosse Ile, Michigan 48138 (313) 692-7611 FTS: 378-7611 FAX: (313) 692-7603

Dr. John A. Robbins GLERL/NOAA 2205 Commonwealth Blvd. Ann Arbor, Michigan 48105 (313) 668-2283

Mr. David C. Rockwell Great Lakes National Program Office 5GL-TUB-10 U.S. Env'l. Protection Agency 230 South Dearborn Street Chicago, Illinois 60604 (312) 353-1373 FTS: 353-1373

Mr. Mark Servos
Great Lakes Laboratory for Fisheries & Aquatic Sciences
Department of Fisheries & Oceans
Canada Centre for Inland Waters
P.O. Box 5050, 867 Lakeshore Rd.
Burlington, Ontario L7R 4A6
(416) 336-4708 Mr. Keith Sherman Investigations and Surveillance Unit Great Lakes Section Water Resources Branch Ontario Ministry of the Environment 135 St. Clair Avenue West Toronto, Ontario M4V 1P5 (416) 323-4951

Dr. William C. Sidle U.S. EPA, Region II 26 Federal Plaza, Room 805 New York, New York 10278 (212) 264-5352 FAX: (212) 264-2194

Mr. Warren Stiver Department of Chemical Engineering and Applied Chemistry University of Toronto 200 College Street Toronto, Ontario M5S 1A4 (416) 978-6764

Dr. Kenneth Stromborg Green Bay ES Field Office U.S. Fish and Wildlife Service 1825 South Webster Avenue Building No. 2 Green Bay, Wisconsin 54301 (414) 433-3803 FTS: 360-3803 FAX: (414) 433-3882 or FTS: 360-3882

Dr. Eva Voldner Atmospheric Environment Service 4905 Dufferin Street Downsview, Ontario M3H 4T5 (416) 739-4670 FAX: (416) 739-4224

Mr. Wayne A. Willford Chief, Surveillance and Research Staff Great Lakes National Program Office 5GL-TUB-10 U.S. Env'l. Protection Agency 230 South Dearborn Street Chicago, Illinois 60604 (312) 353-1369 FTS: 353-1369 FAX: (312) 353-2018 Mr. Don J. Williams Surveillance Program Manager Inland Waters Directorate Ontario Region Environment Canada P.O. Box 5050, 867 Lakeshore Road Burlington, Ontario L7R 4A6 (416) 336-4534 FAX: (416) 336-4906

Dr. Thomas C. Young Department of Civil and Environmental Engineering Clarkson University Potsdam, New York 13676 (315) 268-4430

Dr. Michael A. Zarull National Water Research Institute Lakes Research Branch Environment Canada P.O. Box 5050, 867 Lakeshore Road Burlington, Ontario L7R 4A6 (416) 336-4999

MASS BALANCE WORKSHOP STEERING COMMITTEE

Head, Synthetic Organics & Particle Mrs. Melanie T. Neilson Dynamics Group GLERL/NOAAWater Quality Branch, Ontario Reg2205 Commonwealth Blvd.Environment CanadaAnn Arbor, Michigan 48105Canada Centre for Inland Waters(313) 668-2281P.O. Box 5050, 867 Lakeshore Rd.FTS: 378-2281Guilington, Ontario L7R 4A6 FTS: 378-2281 OMNET: NOAA.GLERL FAX: (313) 668-2055

Dr. Barry M. Lesht, ER/203 Center for Environmental Research Biological, Environmental, and Medical Research Division Argonne National Laboratory 9700 South Cass Avenue Argonne, Illinois 60439 (708) 972-4208 FTS: 972-4208 BITNET: B2905@ANLVM or LESHT%ANLER@ANL FAX: (708) 972-5498

Mr. William L. Richardson Chief Large Lakes Research Station U.S. EPA 9311 Groh Road Grosse Ile, Michigan 48138 (313) 692-7611 FTS: 378-7611 FAX: (313) 692-7603

Mr. Carlton Nash, Chief Ambient Assessment Unit Air and Radiation Division U.S. EPA, Region V 230 South Dearborn Street Chicago, Illinois 60604 (312) 886-6030 FTS: 886-6030 FAX: (312) 886-9096

Monitoring & Surveys Section Dynamics Group Water Quality Branch, Ontario Reg. (416) 336-4963 TELEX: 061 8296 FAX: (416) 336-4906

> Dr. Donald Mackay Department of Chemical Engineering and Applied Chemistry University of Toronto 200 College Street Toronto, Ontario M5S 1A4 (416) 978-4019 TELEX: 06-218915 FAX: (416) 978-8605

Secretary

Mr. David M. Dolan Great Lakes Regional Office International Joint Commission 100 Ouellette Avenue, 8th Floor Windsor, Ontario N9A 6T3 (519) 256-7821 Windsor (313) 226-2170 Detroit FTS: 226-2170 ENVOY: IJC.Windsor DIALCOM: 163:IJC002 FAX: (519) 256-7791

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IJC SURVEILLANCE SUBCOMMITTEE WORKSHOP MASS BALANCE APPROACH TO LAKE TOXIC SUBSTANCE MANAGEMENT

KEMPENFELT CONFERENCE CENTRE BARRIE, ONTARIO MARCH 7-9, 1990

PROGRAM

<u>GOAL</u>: Develop <u>SPECIFIC</u> recommendations that will lead to the application of the mass balance approach to specific contaminant problems/issues in the Great Lakes

OBJECTIVES:

- 1. Have modelers and data gatherers exchange perspectives on the mass balance approach.
- 2. Agree on the data (locations, frequency, quality, etc.) necessary to meet the requirements of different mass balance applications.
- 3. Determine whether these data are currently being collected or are being recommended to be collected within the surveillance programs thereby identifying data gaps.

DAY 1: WEDNESDAY, MARCH 7, 1990 (10:00 a.m. - 10:00 p.m.)

THERE WILL BE MORNING SHUTTLES FROM TORONTO AIRPORT TO THE MEETING. CONTACT DAVE DOLAN (U.S. 313-226-2170; CDN. 519-256-7821) FOR INFORMATION SCHEDULE AND RESERVATION.

LATE MORNING REGISTRATION

12:00 - 12:45 LUNCH

- 1:00 CONVENE AND INTRODUCTIONS
- 1:15 WORKSHOP OBJECTIVES AND SCHEDULE MELANIE NEILSON AND STEERING COMMITTEE
- 1:30 BACKGROUND DESCRIPTION OF MODELS
- DOM DiTORO
- 2:00 BACKGROUND DESCRIPTION OF THE GREAT LAKES INTERNATIONAL SURVEILLANCE PLAN (GLISP), INCLUDING CURRENT IMPLEMENTATION DON WILLIAMS
- 2:30 RESPONSE TO THE 1989 WQB REPORT ON CONTAMINANTS DON MACKAY

3:00 BREAK

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WASS BALANCE APPROACH TO LAKE TOXIC SUBSTANCE MANAGEN

DAY 1: Cont'd. 3:15 STRATEGIES DEVELOPED IN WORKSHOP I AND CHARGE TO PARTICIPANTS BRIAN EADIE AND STEERING COMMITTEE 3:45 CONVENE MANAGEMENT STRATEGY WORK GROUPS <u>RECOMMENDED FOCUS</u>: Conceptual approaches to addressing assigned management question/issue

- 5:45 ADJOURN
- 6:00 DINNER
- 8:00 SOCIAL

DAY 2: THURSDAY, MARCH 8, 1990 (7:30 a.m. - 10:00 p.m.)

- 7:30 8:15 BREAKFAST
- 8:30 RECONVENE MANAGEMENT STRATEGY WORK GROUPS
- 9:30 PLENARY; PROGRESS REPORTS ON MANAGEMENT STRATEGY; CONCEPTUAL APPROACHES
- 10:45 BREAK
- 11:00 RECONVENE MANAGEMENT STRATEGY WORK GROUPS <u>RECOMMENDED FOCUS</u>: Revisions to ideas; begin thinking about data collection strategies
- 12:00 12:45 LUNCH
- 1:00 UNSTRUCTURED, FREE TIME; INFORMAL DISCUSSIONS ENCOURAGED
- 3:00 RECONVENE MANAGEMENT STRATEGY WORK GROUPS <u>RECOMMENDED FOCUS</u>: Sampling strategy to support conceptual approach(es) to your assigned management question/issue
- 5:00 PLENARY; PROGRESS REPORTS ON MANAGEMENT STRATEGY; SAMPLING STRATEGY
- 5:45 ADJOURN
- 6:00 DINNER
- 8:00 CONVENE RESEARCH WORK GROUPS UPSTAIRS LOUNGE (CASH BAR)
- 10:00 ADJOURN

DAY 3: FRIDAY, MARCH 9, 1990 (7:30 a.m. - NOON)

7:30 - 8:15 BREAKFAST

- 8:30 PRESENTATION BY THE IMPLEMENTATION WORK GROUP How will the results of this workshop be used by the IJC-WQB and/or the Parties? WILLFORD AND WILLIAMS
- 9:00 RECONVENE MANAGEMENT STRATEGY WORK GROUPS <u>RECOMMENDED FOCUS</u>: 1. Revise sampling strategies
 2. Compare with current monitoring program and identify sampling gaps; codify as critical or desirable
- 10:30 BREAK
- 10:45 WORK GROUPS RECONVENE; DRAFT FINAL REPORTS
- 12:00 ADJOURN; LUNCH IS OPTIONAL