

**LAKE MICHIGAN MASS BUDGET/MASS  
BALANCE**

**WORK PLAN**

**U.S. Environmental Protection Agency  
Great Lakes National Program Office**

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## **FOREWORD**

This study builds upon the Green Bay Mass Balance Study for toxic contaminants. That is, this study utilizes, as much as possible, the monitoring and modeling approaches and technology developed during the Green Bay Mass Balance Study. The Green Bay Mass Balance Study was supported by a large number of researchers, academic as well as governmental, and was termed an "unqualified success" by the portion of the scientific community involved in its review. Among their recommendations was that the approach now be attempted on a larger scale, namely one of the Great Lakes. For several reasons which will be elaborated in the text, we have chosen Lake Michigan.

## **ACKNOWLEDGMENTS**

Scientists from many state and federal agencies contributed to this workplan during and subsequent to a workshop held September 16 and 17, 1993. These scientists represented: the Illinois Department of Conservation, Indiana Department of Environmental Management, Michigan Department of Natural Resources, Wisconsin Department of Natural Resources, National Oceanic and Atmospheric Administration, U.S. Fish and Wildlife Service, U.S. Geological Survey, and several groups within the U.S. Environmental Protection Agency. We gratefully acknowledge the time and effort of the participants in the Workshop (see Appendix 1).



## **PURPOSE**

This document is the Workplan for conducting a Mass Balance Study for selected toxic contaminants in Lake Michigan. The mass balance effort is a part of the "Lake Michigan Enhanced Monitoring Program", which includes tributary and atmospheric load monitoring, source inventories, and fate and effects evaluations. We describe elements necessary to conduct a Mass Balance Study based upon the efforts of many Federal and State scientists and staff (see Appendix 1 for Participants) who participated in the initial planning workshop, as well as descriptions of components of the work modified from documents provided by principal investigators. The initial draft of the Plan was developed by Messrs. David DeVault of the EPA Great Lakes National Program Office (GLNPO) and Alan Hoffman of AREAL.

## **INTRODUCTION**

### **BACKGROUND**

This Mass Balance Workplan, part of a larger enhanced monitoring program for Lake Michigan, results from the convergence of a number of activities which address reductions in the release of toxic substances, particularly persistent, bioaccumulative substances, to the Great Lakes system. These activities provide information necessary for implementation of a Lakewide Management Plan (LaMP) for Lake Michigan. Development of LaMPs for all five of the Great Lakes were agreed to by the U.S. and Canada under the 1987 amendments to the Great Lakes Water Quality Agreement (GLWQA). The Lake Michigan LaMP has been developed by U.S. entities since the lake lies entirely within the boundaries of this country. Section 118 of the Clean Water Act (CWA) mandated its development and established deadlines regarding its completion. An example of the type of the activity supporting the LaMP is a study for the Great Waters Program mandated by Title III, Section 112(m) of the 1992 Clean Air Act Amendments (CAAA). The primary goal of this enhanced monitoring program is to develop a sound, scientific base of information to guide future toxic load reduction efforts at the Federal, State, Tribal, and local levels. In particular, the following specific objectives have been identified through various forums:

1. to identify relative loading rates of critical pollutants from major tributaries to the Lake Michigan basin in order to better target future load reduction efforts;
2. to evaluate relative loading rates by media (tributaries, atmospheric deposition, contaminated sediments) in order to better target future load reduction efforts and to establish a baseline loading estimate to gauge future progress;
3. to develop the predictive ability to determine the environmental benefits of specific load reduction scenarios for toxic substances and the time required to realize those benefits. This includes evaluation of benefits of load reductions from existing environmental statutes and regulations as required under Section 112(m) of the CAA, and Section 303 of the Clean Water Act (CWA), and;

4. to improve our understanding of key environmental processes which govern the cycling and bioavailability of contaminants within relatively closed ecosystems.

The Lake Michigan LaMP assesses the status of the Lake Michigan watershed and identifies pollutants impacting the system on a lakewide scale. The goal of the LaMP is to restore and protect beneficial uses (as defined by the GLWQA) of the Lake by prioritizing prevention, reduction, and remediation activities. By developing the predictive ability to determine the environmental benefits of specific load reduction options, the mass balance will allow Federal, State, and Tribal agencies to make more informed load reduction decisions.

USEPA intends the Lake Michigan LaMP to serve as the basis for development and submission of State Water Quality Management Plans (WQMPs) developed in accordance with Sections 208 and 303(b) of the CWA, as implemented through the requirements of 40 CFR 130.6. These WQMPs establish a process for continuous water quality planning which focuses on priority issues and geographic areas, and on the development of water quality controls leading to implementation measures. USEPA expects any new loadings data obtained during the development of LaMPs to be incorporated by the States when establishing or revising Total Maximum Daily Loads (TMDLs) and Wasteload Allocations (WLAs) for waters of the Great Lakes system. These new TMDLs and WLAs will then be appropriately reflected in subsequent revisions to NPDES permits. In this way, USEPA and the States will ensure reasonable progress in the overall improvement of the Great Lakes water quality and attainment of beneficial uses and water quality standards.

Pursuant to the Great Lakes Critical Programs Act of 1990 (GLCPA), USEPA published final Water Quality Guidance for the Great Lakes System (58 Federal Register 20802). The Guidance consists of water quality criteria for 29 pollutants to protect aquatic life, wildlife, and human health, and detailed methodologies to develop criteria for additional pollutants; implementation procedures to develop more consistent, enforceable water-quality-based effluent limits in discharge permits, as well as total maximum daily loads of pollutants that can be allowed to reach the Lakes and their tributaries from all sources; and antidegradation policies and procedures. A key part of the Guidance is the extensive documentation in support of the selection of 29 toxic pollutants for special focus. Included in the 29 contaminants are PCBs, chlordane, and mercury, three of the substances for which we will develop mass balances.

The water quality criteria and values proposed in the Guidance apply to all the ambient waters of the Great Lakes System, regardless of the source of pollutants to those waters. In this manner, the proposed water quality criteria and values provide the basis for integrating actions carried out under the range of environmental programs available to both Federal, State and Tribal regulators to protect and restore the Great Lakes ecosystem. The mass balance approach will facilitate this integration by evaluating multi-media load reduction actions required to ensure that Lake Michigan water quality meets the water quality criteria and values established in the final Guidance.

The CAAA specifically require EPA and NOAA to, among other things:

1. Conduct atmospheric monitoring for Hazardous Air Pollutants (HAPs)
2. Conduct research on monitoring methods
3. Determine the relative contribution of air deposition to total loadings

4. Evaluate the adverse effects from deposition, including the direct effect to health and the environment
5. Assess the contribution of such deposition to violations of water quality standards
6. Conduct biological sampling to identify the presence of HAPs that deposit from the air.

It is not possible, given the current state of the science and available resources, to meet these requirements or the specific objectives stated above, through a "brute force" monitoring approach. The CAAA and CWA requirements will best be met through a coordinated effort to quantify and understand the loadings, transport and fate of selected HAPs (hazardous air pollutants/contaminants) in a defined ecosystem and then transferring that knowledge to other ecosystems. A Mass Balance approach will allow the above requirements to be met in the most cost effective manner.

In a mass balance approach, the law of conservation of mass is applied in the evaluation of the sources, transport and fate of contaminants. This allows prioritization and allocation of research, remedial and regulatory actions for water quality management. The approach requires that the quantities of contaminants entering the system, less quantities stored or transformed within the system, must equal the quantities leaving the system. Once a mass budget for selected contaminants has been established and a mass balance model calibrated, additional contaminants can be modeled with limited data.

A mass balance study for hydrophobic organics was piloted on Green Bay, WI in 1988-1992 by USEPA and the Wisconsin Department of Natural Resources. The monitoring, analytical and modeling tools required by this approach on a whole lake basis were developed during the Green Bay Study. These techniques may now be applied to the Great Lakes, Lake Champlain and coastal estuaries. Lake Michigan will be the first full scale application and will serve as the basis of any future mass balance efforts.

### **CHEMICALS CHOSEN FOR MASS BALANCE**

A mass budget and mass balance model will be constructed for a limited group of hazardous air pollutants (HAPs)/contaminants which are present in Lake Michigan at concentrations which pose a risk to aquatic and terrestrial organisms (including humans) within the ecosystem, or which may accumulate to problematic concentrations in the future. The chemicals chosen cover a wide range of chemical and physical properties and are representative of other classes of compounds which pose current or potential problems. This approach will allow other chemicals to be modeled with limited data. The chemicals selected are:

**PCB congeners**

***Trans*-nonachlor**

**Atrazine and major breakdown products (de-ethyl atrazine, de-isopropylatrazine)**

**Total Mercury**

PCBs are present in some Lake Michigan fish species at concentrations which exceed US Food and Drug Administration tolerances, and have resulted in closure of commercial fisheries and the issuing of consumption advisories for sports fishermen. They also contribute to fish and wildlife reproductive problems and deformities (Mac 1988, Gilbertson 1988). PCB

congeners cover a wide range of physical and chemical properties, are relatively resistant to degradation, and are ubiquitous. These properties make them ideal surrogates for a wide range of organic compounds from anthropogenic sources (Eisenreich 1987).

*Trans-nonachlor* is the most bioaccumulative of the chlordanes present in fish at concentrations which exceed human health guidelines. As a technical chlordane constituent, it is also one of the chemicals addressed by the Great Lakes Initiative. *Trans-nonachlor* will serve as a model for the cyclodiene pesticides.

Unlike PCBs and *trans-nonachlor*, the manufacture and use of which have been banned or strictly controlled, atrazine is a commonly used herbicide in the Great Lakes basin and elsewhere in the United States. It has been reported at elevated concentrations in Lake Erie tributaries (Baker et al, 1988), in the open waters of the Great Lakes, and the atmosphere over the lakes (Steven Eisenreich, personal communication 1990). It's inclusion will provide a model for the more reactive, biodegradable compounds in current use. The model will not include a food chain component since atrazine does not bioaccumulate appreciably.

There is increasing concern about mercury in aquatic systems. It bioaccumulates, leading to increasing tissue concentrations up the food chain. Evidence from inland lakes indicates a trend of increasing fish tissue concentration (Sorensen et al. 1990), and increases through time in sediment cores. An understanding of the sources and fate of mercury and its potential as a problem in the Great Lakes is in keeping with the specific objectives of the study. Current sampling and analysis of mercury, however, present difficulties that are being addressed only at the research level. This is particularly true for analysis of the several chemical forms in which mercury appears in the environment. The estimation of transfer and process coefficients upon which much of mass balance modeling is based will require considerably more research than is possible through this study. Sampling and modeling, though less intensive than for organic contaminants, will provide new information on loads and fate of total mercury.

In addition, the Lake Michigan LaMP identifies each of these four contaminants as impacting, or having the potential to impact, the Lake Michigan watershed. Developing a mass balance for these substances will therefore assist the LaMP program by assessing the expected environmental benefits of load reduction options.

Resource limitations, quality assurance requirements, and analytical and data handling limitations preclude intensive monitoring and model calibration for more than the above described target chemicals. While the mass balance modeling will focus on the above parameters, determination of loadings and concentrations for other contaminants and compounds useful for source apportionment and deposition modeling will be undertaken as part of the Enhanced Monitoring Program (see Appendix 2 for list of analytes). The development of calibrated models will allow the listed CAAA requirements for other HAPs/contaminants to be met with limited monitoring data and future resources to be directed to other areas such as emission inventories and dispersion modeling.

## **COMPONENTS OF THE MASS BALANCE STUDY**

Components of the mass balance model will be designed to predict contaminant concentrations in the water column and target fish species over a 25 year period, relative to

loadings from significant sources. Predictions of concentrations of HAPs in three species of fish are desired as the final output from the models. The target fish species include:

lake trout (*Salvelinus namaycush*)  
coho salmon (*Oncorhynchus kisutch*)  
bloater chub (*Coregonus hoyi*)

These fish species represent a variety of life histories, food web dynamics, trophic levels, and contaminant exposure histories. Lake trout are native, top predators in Lake Michigan (despite the lack of sustained reproductive success) with a life span of greater than 8 years. Their food web is complex, including to varying degrees bloater chub, rainbow smelt (*Osmerus mordax*), alewife (*Alosa pseudoharengus*), slimy and deepwater sculpins (*Cottus cognatus*, *Myoxocephalus thompsoni*), benthic invertebrates (*Diporeia spp.*) and pelagic zooplankton (*Mysis relicta*), depending on life stage, season and geographic location (Miller & Holey, 1992). Lake trout provide an important recreational and commercial fishery. However, consumption advisories exist for certain size classes.

Coho salmon are non-indigenous, but are enjoyed by a vigorous sport fishery. They are hatchery reared for approximately one year (varying by state from 5 months to 17 months), live in Lake Michigan for two more years, then return to the tributaries to spawn and die. Their diet is largely alewife.

Bloater chub have had historical importance in the commercial fishery, and are an important component of the lake trout diet. Young chubs feed on zooplankton, but older age classes feed on benthic invertebrates (*Diporeia spp.*).

The calibration of the food web model(s) for these target species requires data on contaminant concentrations and fluxes not only in these species, but also in the supporting trophic levels. The forage fish feed largely on benthic invertebrates and on zooplankton. Alewife, in particular, feed heavily on pelagic Cladocera. At the base of the food webs being modeled is the mixed assemblage of phytoplankton.

Fish-eating birds represent another trophic level in the Lake Michigan ecosystem that is clearly impacted by toxic organic chemicals. However, the modeling of contaminant fluxes through aquatic birds is beyond scope and available resources for this study. Similarly, a clear understanding of the role of the microbial food web in the transport of organic contaminants to higher trophic levels would be highly desirable, but it is beyond the means of this study to undertake the research. The mass balance model for Lake Michigan could be modified or expanded at some future time to accommodate these other trophic levels when the ecological relationships are more clearly understood.

### **ACCURACY OF DATA COMPONENTS**

The level of accuracy in a mass budget and model required to make sound environmental management decisions is a subject of debate. For the Lake Michigan Mass Balance study, we propose that model output should be within a factor of 2 of the observed concentrations in the water column and target fish species. This level of accuracy is based on the likely use of risk assessment in making management decisions. As risk assessment methods are accurate, at best, to one order of magnitude, a factor of two, or one half order of magnitude is sufficient.

This will require a vertically and horizontally segmented water quality model coupled with a food chain model. The water quality model should be capable of differentiating between the nearshore and open waters of the lake on a seasonal time scale. The food chain model should be designed to predict peak contaminant concentrations in multiple age classes of the targeted fish species. From the Green Bay Mass Balance Study, it is estimated that the required level of model accuracy can be achieved if loadings and contaminant mass in significant environmental compartments are determined to within +/- 20 to 30 percent of the actual value.

### **SCOPE OF FIELD WORK**

Field data collection activities for the various parts of the Mass Balance Study are described further in the following sections. However, a brief description of these activities will provide perspective on the scope of the study. Field data collection activities were initially envisioned as a one year effort. However, it became evident early into the project that a longer collection period would be necessary to provide a full year of concurrent information on contaminant loads and ambient concentrations for modeling purposes. Therefore, field sampling will cover the period from April, 1994 through October, 1995.

#### **Loading Information:**

**Tributaries** - eleven Lake Michigan tributaries are being monitored intensively to determine the loads of the subject compounds to the lake. Sampling frequency varies from 12 to 45 samples per tributary in a year long period.

**Atmosphere** - nine sites are being monitored to determine atmospheric loads to Lake Michigan. Additional field activities, part of the Great Waters Study, will provide data to help determine the net atmospheric load. Additional atmospheric samples are taken during each Lake Guardian survey.

**Sediment** - one hundred and thirty-one sediment sampling sites will be visited, with the majority in sediment depositional zones. Surface sediment segments from box core samples will be analyzed for contaminants to determine the sediment contaminant inventory (available for resuspension and contaminant release to the water column). Additional studies will determine contaminants in sediment trap materials, and erodibility of sediment (resuspension).

#### **Ambient Concentration Information:**

**Water** - Five full (44 Station) and two abbreviated (15 Station) surveys will take place over the extended field season. In addition, a January, 1995 winter survey will visit 5 stations. Samples for analysis of contaminants in water and water-borne particulates will be collected at each of the stations. In addition, water quality and biological information required for modeling purposes is collected at each station.

**Upper Food Chain** - The National Biological Service will collect fish during five surveys over the extended season. These will concentrate on the top predator fish (lake trout), and also forage fish which comprise the predators' diet. Coho salmon are collected separately, and on a different schedule based on migratory patterns.

Lower Food Chain - As part of the seven lakewide surveys (see Water) samples of lower food chain organisms will be collected for contaminant analysis. The lower food chain is defined here as phytoplankton, zooplankton, *Mysis relicta* and *Diporiea* spp.

## **MODELING**

### **BACKGROUND**

The USEPA Great Lakes National Program Office has proposed a mass balance approach to provide a coherent, ecosystem-based evaluation of toxics in Lake Michigan (USEPA, 1993). The Lake Michigan Mass Balance Study (LMMBS) will also study hazardous air pollutants for the Clean Air Act Amendments' Great Waters Program. The mass balance approach, demonstrated in the Green Bay Mass Balance Study (GBMBS), provides a consistent framework for integrating load estimates, ambient monitoring data, process research efforts, and modeling, leading to the development of scientifically credible, predictive cause-effect tools. The primary goal of the mass balance study is to develop a sound, scientific base of information to guide future toxics load reduction efforts for Lake Michigan at the State and Federal levels. From this goal, a number of specific objectives have been identified. Several of the plan's objectives call for identifying and quantifying the sources of toxics to Lake Michigan, as well as establishing cause-effect relationships and developing forecasting tools:

1. Determine loading rates for critical pollutants from major source categories (tributaries, atmospheric deposition, contaminated sediments) to establish a baseline loading estimate to gauge future progress, and to better target future load reduction efforts.
2. Predict the environmental benefits (in terms of reducing concentrations) of specific load reduction alternatives for toxic substances, including the time required to realize the benefits.
3. Evaluate the environmental benefits of load reductions for toxic substances expected under existing statutes and regulations and, thereby, determine if there is a need for more stringent, future regulations to realize further benefits.
4. Improve our understanding of how key environmental processes govern the transport, fate, and bioavailability of toxic substances in the ecosystem.

The mass balance project will be based upon the Enhanced Monitoring Program (EMP), a comprehensive, 1.6-year synoptic survey for selected toxic chemicals in the Lake Michigan ecosystem. In support of the mass balance study, the Environmental Research Laboratory-Duluth (ERL-D) Large Lakes Research Station in cooperation with the Atmospheric Research and Exposure Assessment Laboratory (AREAL), the NOAA Great Lakes Environmental Research Laboratory (GLERL), and other cooperators, will develop a suite of integrated mass balance models to simulate the transport, fate and bioaccumulation of toxic chemicals in Lake Michigan. This work plan describes these models, the manner in which they will be integrated, the relationship between their development and the EMP data, and their intended application.

## **MODELING PURPOSE AND OBJECTIVES: MASS BALANCE APPROACH**

Development of effective strategies for toxics management requires a quantitative understanding of the relationships between sources, inventories, concentrations, and effects of contaminants in the ecosystem. A mass balance modeling approach is proposed in this work plan, to address the relationship between sources of toxic chemicals and concentrations in air, water, sediment, and biota. This approach integrates load estimation, ambient monitoring and research efforts within a modeling framework that is compatible with both scientific as well as ecosystem management objectives. The mass balance approach estimates the magnitude of mass fluxes that constitute the pathways for toxics transport into and out of the lake, that distribute toxics within the lake water column and sediment, and that lead to bioaccumulation of the aquatic food web. Based upon these estimates, the mass balance can determine the rate of change in concentrations and inventories of toxics as inputs such as atmospheric and tributary loadings are changed, or other aspects of the system are perturbed. Thus, the mass balance can serve as a useful tool to estimate or predict the outcome of alternatives under consideration for toxics management.

More specifically, the modeling efforts associated with the Lake Michigan mass balance project will meet the following objectives:

1. Provide a consistent framework for integrating load estimates, ambient monitoring data, process research efforts, and prior modeling efforts, leading to a better understanding of toxic chemical sources by media, transport, fate and bioaccumulation in Lake Michigan.
2. Estimate the loading of priority toxics, solids, and nutrients from major tributaries to Lake Michigan for the duration of the EMP study.
3. Estimate the atmospheric deposition and air-water exchange of priority toxics, including spatial and temporal variability over Lake Michigan.
4. Calibrate and confirm mass balance models for priority toxics using EMP data, based upon models for hydrodynamic and sediment transport, eutrophication/organic carbon dynamics, toxics transport and fate, and food web bioaccumulation.
5. Based upon the mass balance models, evaluate the magnitude and variability of toxic chemical fluxes within and between lake compartments, especially between the sediment and water column and between the water column and the atmosphere.
6. Apply the mass balance models to forecast contaminant concentrations in water and sediment throughout Lake Michigan, based upon meteorological forcing functions and future loadings based upon load reduction alternatives.
7. Predict the bioaccumulation of persistent toxic chemicals through the food web leading to top predator fish (lake trout and coho salmon) for specific fish populations in the lake, in order to relate mass balance predictions of water and sediment exposure to this significant impaired use.



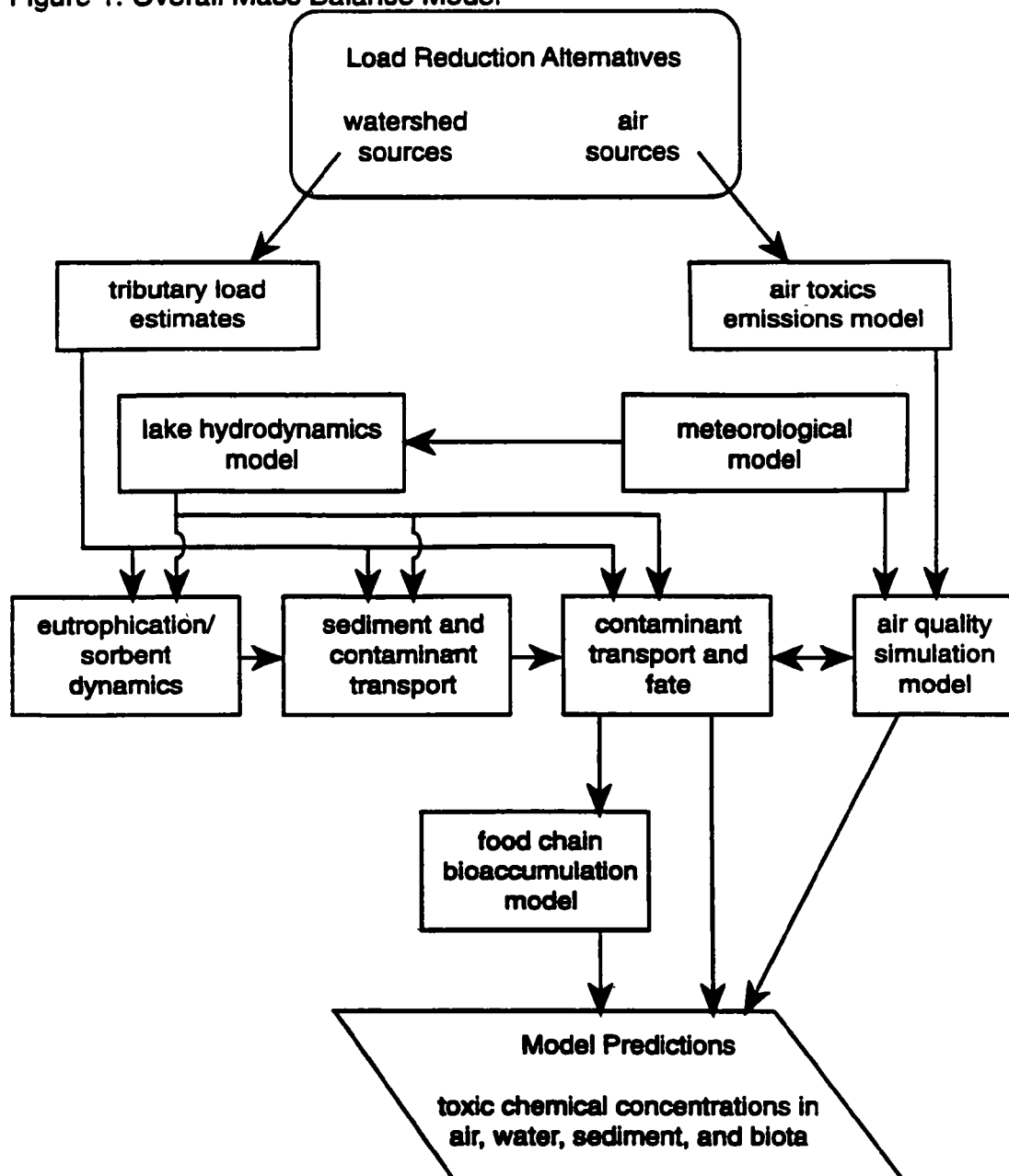
8. Estimate (quantify) the uncertainty associated with estimates of tributary and atmospheric loads of priority toxics, and model predictions of contaminant concentrations.
9. Identify and prioritize further monitoring, modeling, and research efforts to (1) address additional toxic substances, (2) further reduce uncertainty of predictions, (3) establish additional cause-effect linkages, such as ecological risk endpoints and feedbacks, and (4) evaluate additional source categories, such as non-point sources in the watershed.

The purpose of modeling will be to simulate the transport, fate and bioaccumulation of four priority toxics in Lake Michigan: PCB congeners, trans-nonachlor (TNC), atrazine, and total mercury. These toxics are collectively referred to as “contaminants” in this work plan.

### **MODELING FRAMEWORK**

The model design for the Lake Michigan Mass Balance Project is based upon the linked sub-model approach used in the Green Bay Mass Balance Study, and retains the same basic models: hydrodynamics, sediment transport, sediment bed dynamics, eutrophication/sorbent dynamics, contaminant transport and fate, and food web bioaccumulation. A schematic representation of the overall mass balance design is shown in **Figure 1**. The Lake Michigan submodels will be applied at several different levels of spatial resolution, and will incorporate predictive hydrodynamic and sediment transport simulations as the modeling “foundation”. This approach is consistent with other state-of-the-art ecosystem modeling exercises, such as the Chesapeake Bay Watershed Model (Linker et al., 1993), which emphasize increasing computational effort, complexity, and predictive resolution. As discussed below, linkages will also be established with atmospheric transport and watershed delivery models, to allow simulation of multimedia toxics transport as well as loads and boundary conditions to the lake. Ultimately, such linkages will be essential to relate watershed and “airshed” management to water quality. Descriptions of the lake process, atmospheric and watershed delivery model frameworks follow.

Figure 1. Overall Mass Balance Model



## **Lake Process Models**

The mass balance for toxics in Lake Michigan will be comprised of linked hydrodynamic, eutrophication/sorbent dynamics, particle transport, contaminant transport and transformation, and bioaccumulation simulations. Each of these models represents significant processes affecting the mass balance for toxic chemicals. The hydrodynamic model predicts water movements necessary to describe the 3-dimensional transport of dissolved and particulate constituents in the water column. The eutrophication model describes the production, respiration, grazing and decomposition of planktonic biomass within the lake. The particle transport model describes the resuspension, transport and deposition of particulate materials including sorbent phases necessary to describe the movement of particle-associated contaminants. The contaminant transport and fate model describes contaminant partitioning between dissolved and sorbed phases, transfer between media (air, water, sediment), and biogeochemical transformations. The bioaccumulation model simulates contaminant accumulation from water and sediments to predator fish via direct exposure and trophic transfer through benthic and pelagic food webs. Together, these submodels form an integrated description of toxic chemical cycling in the aquatic ecosystem, with which to predict the relationship between loadings and concentrations for contaminants of interest.

### **Hydrodynamics**

The Princeton Ocean Model (POM; Blumberg and Mellor, 1980 and 1987) will be used to compute three dimensional current fields in the lake. The POM will simulate large- and medium(km)-scale circulation patterns, vertical stratification and velocity distribution, seiche, and surface waves. This model will also be used to simulate a thermal balance for the lake, and will generate turbulent shear stresses for the sediment transport model. The POM is a primitive equation, numerical hydrodynamic circulation model that predicts three dimensional water column transport in response to wind stress, temperature, barometric pressure, and coriolis force. The POM has been demonstrated to accurately simulate the predominant physics of large water bodies (Blumberg and Mellor, 1983 and 1985; Blumberg and Goodrich, 1990). This model will be used to develop year-long simulations on a 5-km horizontal grid, with 15 sigma-coordinate vertical levels, at one-hour intervals for Lake Michigan. Observed and simulated meteorological data will be used to define model forcing functions. Extensive measurements of temperature, transmissivity, and current distributions collected in Lake Michigan during 1982-83 will provide the necessary data for model confirmation; measurements of daily surface temperature (from satellite) and temperature, transmissivity, and current distributions will also be used to confirm hydrodynamic simulations for 1994-95.

The hydrodynamic model is the appropriate transport foundation for an accurate lake mass balance model, for a number of reasons. A confirmed hydrodynamic model offers a credible basis for extrapolating transport, in terms of forecasting the response to expected and extreme meteorological forcing functions, that is desirable for a mass balance simulation. The hydrodynamic model results are scaleable to provide transport predictions at the desired spatial and temporal resolution. This is useful when considering that the various processes incorporated in the mass balance are not necessarily modeled at the same scale or resolution, yet all depend upon a consistent transport simulation. In

particular, the sediment and contaminant transport model described below, requires high resolution simulations of current- and wave-induced shear stress to predict sediment transport. Hydrodynamic models are also transportable, with little system-specific parameterization in comparison to traditional water quality models. A mass balance design based upon hydrodynamic transport is advantageous, for instance, when considering applying the mass balance model for Lake Michigan to the other Great Lakes.

### **Sediment and Contaminant Transport**

A 3-D version of the sediment transport model, such as SEDZL, will be used to simulate the movement of sediment particles in both the water column and sediment bed, including settling, resuspension, flocculation, transport and deposition. SEDZL will simulate the significant short- and long-term processes which transport sediment particles and particle-associated contaminants in the lake. SEDZL will be linked to hydrodynamic output from the POM, and will be based upon the same 3-D water column grid. State variables will include 3 particle classes (plankton/biotic solids, cohesive fine-grained sediment/detritus, and coarse-grained solids) and PCBs. SEDZL will simulate the 1982-83 and 1994-95 periods for which hydrodynamic forecasts will be available, as well as intensive confirmation data provided by sediment trap and radionuclide monitoring. Further confirmation data for 1994-95 will be provided by remote sensing, transmissometer arrays, and water intake monitoring. Sediment bed properties, particle resuspension rate parameters, flocculation parameters and settling properties necessary for the model will be determined by field measurements to be performed on Lake Michigan sediments, and by results of experiments conducted with other sediments from the Great Lakes. Allochthonous sediment loadings will be estimated for tributary export, shoreline erosion, and atmospheric particle deposition. Autochthonous production will be provided from the eutrophication/sorbent dynamics model, and input as loadings to the sediment transport model.

The sediment transport model is applied to predict the transport of particles in the lake, which predominantly carry hydrophobic contaminants from near-shore locations such as tributary mouths, to deposition zones usually in deep water. The transport of sediment and associated contaminants is a complex interaction of the properties of sediment particles and the sediment bed, circulation, bathymetry, and turbulent shear stresses applied by waves and current. Moving from shore to deep water, regimes of sediment transport are encountered, resulting in distinct distributions of grain size, bed thickness, sedimentation rate, and contaminant concentrations in the lake sediments. Contaminants move along this gradient associated primarily with the fine-grained sediments, yet their transport is influenced by the entire particle assemblage. In terms of resuspension and deposition, most sediment transport is associated with the sequence of short, infrequent events such as storms. SEDZL simulates the interactions and dynamics of sediment transport, and offers predictive capabilities beyond that obtainable by a calibrated-transport approach. Advantages include compatibility with the hydrodynamic simulation, high spatial resolution consistent with the spatial variability of the resuspension process, and verified process descriptions for the dynamics of sediment resuspension and deposition under event conditions which are the most difficult to model. SEDZL predictions have been confirmed mostly in tributary systems; in large water bodies simulations have been conducted for events, with only limited confirmation. Thus, significant development is still required for credible application of SEDZL in the Lake Michigan mass balance model. Sediment and

contaminant transport model predictions will require extensive confirmation against EMP data to ensure model credibility.

The alternative approach to treating sediment transport is descriptive, where direct calibration of Total Suspended Solids (TSS) and associated particle tracers is used to specify settling and resuspension fluxes. The descriptive approach ensures a model calibration that is consistent with available observations. However, the spatial complexity and event-responsive nature of sediment transport described above introduce too many degrees of freedom to allow model calibration to the data being generated by the EMP. This approach relies entirely upon fitting suspended constituent data, which will be too sparse (both in space and time) to allow accurate description of sediment transport fluxes. The second major disadvantage of descriptive transport, is that the resulting model has no forecasting basis other than replaying the calibration. Attempts to go beyond the calibration are, in general, weak emulations of predictive transport approaches.

### **Eutrophication/Sorbent Dynamics**

The eutrophication/sorbent dynamics (ESD) model predicts the production, transformation and decay of plankton biomass in response to seasonal dynamics of temperature, light, and nutrient concentrations. In the open lake, living and dead plankton comprise the majority of suspended particles and generate significant autochthonous loads of particulate and dissolved organic carbon (POC and DOC) to which PCBs and other contaminants preferentially partition (Richardson et al., 1983; DePinto et al., 1993). The ESD model simulates the non-conservative, seasonally-variable dynamics of the biotic organic carbon pool, which has a significant influence upon partitioning of HOCs (Dean et al., 1993). Such a model was applied to simulate the dynamics of organic carbon states in Green Bay as part of the GBMBS (DePinto et al., 1993). However, a more resolute, multi-class eutrophication model (Bierman and McIlroy, 1986) will be applied to Lake Michigan, and the linkage between plankton and organic carbon states will be refined. Model outputs include autochthonous solids loads (primary production), and transformation and decay rates, that will be used as inputs for the sediment transport and the contaminant transport and fate models. The biomass growth rates may also be linked to the plankton bioconcentration submodel of the food web bioaccumulation model.

The eutrophication/sorbent dynamics model is an important component of the mass balance model for hydrophobic contaminants, because it simulates the dynamics of a significant sorbent particle class (phytoplankton) in the water column. The dynamics of phytoplankton production and loss cannot be adequately described by seasonal EMP limnological monitoring, which will occur too infrequently to observe major events such as blooms, assemblage shifts, and die-offs. Furthermore, the ESD model component will allow forecasting for integrated toxics and nutrient management options, because mass balances for toxics and nutrients are coupled via eutrophication/sorbent dynamics processes. Finally, the ESD model is the appropriate framework for inclusion of zebra mussels in the mass balance model. Zebra mussels, which at high density can impact the lower food web and alter sediment and contaminant transport, are currently (1994) infesting Lake Michigan and are reaching high densities in areas of suitable habitat such as Green Bay.

## **Contaminant Transport and Fate**

The mass balance for toxic chemicals in the lake will be computed in a contaminant transport and fate (CTF) model which describes contaminant transport, intermedia exchange, phase distribution, and biogeochemical transformations, in both the water column and sediments. The CTF model will be calibrated and confirmed for each of the priority toxics: atrazine, mercury, selected individual and sum of PCB congeners, and TNC. Mass balance analyses will be performed for each contaminant, to evaluate the significant source, transport, and loss pathways. Effectiveness of alternative load reduction scenarios upon reducing toxic chemical concentrations, will also be forecast. Although calibration and confirmation will be limited to the period of available EMP data, the CTF model will be required to forecast contaminant concentrations for substantially longer periods: on the order of 20-50 years. Long simulations are necessary because of the substantial lag time associated with the chemical concentration response in the lake to changing loads. The lag time is associated with the residence time of contaminants in the surficial sediments, which is constrained by confirmation of CTF model hindcasts for cesium-137 and/or plutonium-239/240. These particle-associated radionuclides have been demonstrated as important tracers for the long-term transport of sediments and contaminants in Lake Michigan and the Great Lakes. Because their loading histories are known with relative certainty, available water and sediment data for these contaminants are directly useful for model confirmation. Such data are critical to develop of a model intended to make long-term forecasts, especially since EMP monitoring will be only 2 years in duration. Intensive sediment trap data collected in 1982-83 (Robbins and Eadie, 1991) and water column measurements from the same period, will provide further measurements for confirmation of particle transport fluxes.

A schematic diagram of the CTF model as applied for PCBs in Lake Michigan is presented in **Figure 2**. Chemical fluxes between model compartments are computed from advective and dispersive transport of aqueous and particulate contaminant fractions. The model will describe chemical partitioning between dissolved and particulate sorbent compartments, including multiple particle types, using an organic carbon-based equilibrium assumption. Both local equilibrium and first-order kinetic partitioning process descriptions will be tested. Chemical transformations such as hydrolysis and biodegradation are modeled as first-order or pseudo first-order reactions, with daughter chemicals retained in the mass balance as additional state variables (for atrazine, these include desethylatrazine and deisopropylatrazine). For mercury, a two-state (organic and inorganic) multiple-sorbent class framework proposed by Thomann (1993) will be applied.

The CTF model incorporates simulations of other submodels by the following linkages:

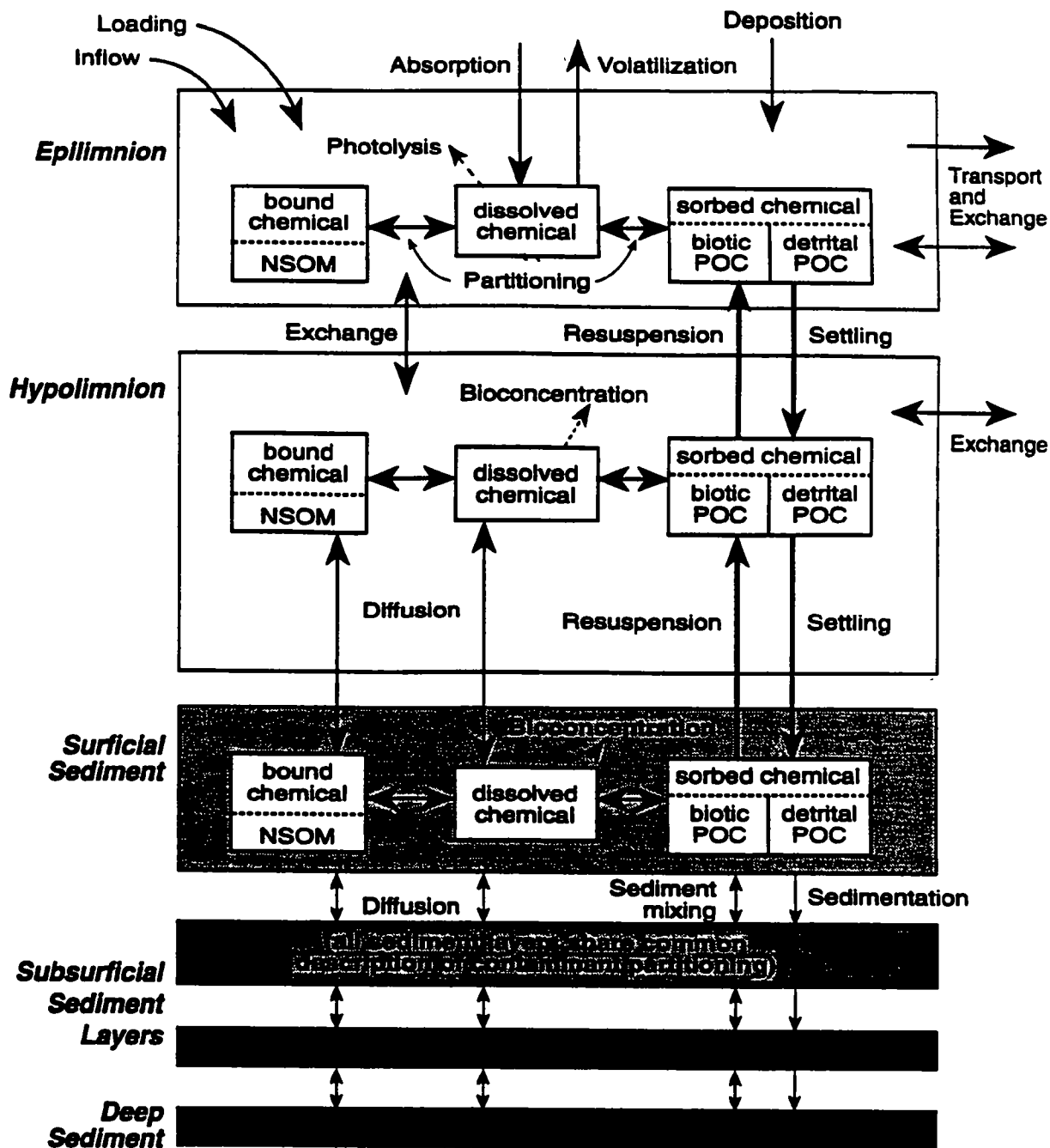
Table 1. Contaminant Transport and Fate Model Linkages

Submodel	Data Linkage
POM/SEDZL	hydrodynamic and sediment transport; water temperature
eutrophication/sorbent dynamics	autochthonous load; transformation and decay rates
meteorological model	wind and air temperature
atmospheric model	boundary conditions and fluxes
watershed delivery model	tributary loads

The CTF model will be linked to hydrodynamic and sediment transport simulations, by appropriate filtering and averaging of transport fields (Hamrick, 1987; Hall, 1989; Dortch et al., 1992). Total suspended solids (TSS) and SPCB (sum of congeners) simulations will be reproduced in both SEDZL and CTF models, providing computational "tracers" to validate the transport linkages.

The CTF model will be applied at an intermediate (Level 2) scale. In the water column, segment resolution is defined at a scale compatible with the definition of food web zones (approximately 20x40 km), with 2-5 vertical layers. In sediments, segmentation will be based upon deposition regime and contaminant distribution, with 1-cm vertical resolution. Fine-scale simulations are necessary for accurate predictions of hydrodynamic and cohesive particle transport as well as accurate simulation of short-duration event processes. However, the computational cost of fine-scale models is high and makes long-term (20 to 30 year) simulations infeasible, especially with the significant number of state variables required for multiple contaminants, sorbent phases, etc. Resolution at the scale of POM and SEDZL is also not appropriate for the mass balance objectives of this project. Intermediate scale models have substantially lower computational cost and have been demonstrated for contaminant transport and transformation over temporal and spatial scales appropriate for toxics exposure prediction and linkage to bioaccumulation models (DePinto et al., 1993; Connolly et al., 1992).

Figure 2. Schematic of Contaminant Transport and Fate Model  
**Watershed** **Atmosphere**





Although CTF model compartments are generally well-defined, no single framework presently available has the capacity to accurately predict all components of CTF while retaining the aggregate behavior of hydrodynamic and sediment transport simulations. To develop an appropriate framework for the LMMBS and future lake-wide analysis and management projects, existing and developmental mass balance water quality modeling frameworks such as those used for Chesapeake Bay (Cерco and Cole, 1993), Green Bay (Bierman et al., 1992; Velleux et al., 1994), and other projects (Richards et al., 1993; Katopodes, 1994) will be reviewed. Appropriate features of these models will be synthesized into a single framework and extended to meet the requirements of the LMMBS.

### **Food Web Bioaccumulation**

A bioaccumulation model simulates chemical accumulation in the food web in response to chemical exposure, based upon chemical mass balances for aquatic biota. The general form of the bioaccumulation equation is well defined, and equates the rate of change in chemical concentration within a fish (or other aquatic organism) to the sum of chemical fluxes into and out of the animal. These fluxes include direct uptake of chemical from water, the flux of chemical into the animal through feeding, and the loss of chemical due to elimination (desorption and excretion) and dilution due to growth. To predict bioaccumulation for top predator fish (the modeling objective here), the bioaccumulation mass balance is repeatedly applied to animals at each trophic level to simulate chemical biomagnification from primary and secondary producers, through forage species to top predators. Food web bioaccumulation models have been successfully applied for PCBs and other HOCs in several large-scale aquatic ecosystems (Thomann and Connolly, 1984; Connolly and Tonelli, 1985) and, most recently, for the GBMBS (Connolly et al., 1992). The model developed for that project, FDCHN, will be adapted for use in Lake Michigan. FDCHN is a time-variable, population-based age class model, incorporating realistic descriptions of bioenergetic, trophodynamic, and toxicokinetic processes. The general features of FDCHN are well-suited to a modeling application such as the Lake Michigan mass balance project.

For Lake Michigan, bioaccumulation of PCB congeners and TNC will be modeled for lake trout and coho salmon food webs. Food web bioaccumulation will be simulated for sub-populations of lake trout in three distinct biotic zones. The general structure of the lake trout food web in Lake Michigan is shown in **Figure 3**. In each zone, different food webs support lake trout, including benthic and pelagic food web linkages. Biotic zones are defined by the approximately 50-mile range of movement of lake trout. The coho salmon, in comparison, is strictly pelagic. Although the coho food web is simpler, the bioaccumulation simulation must account for significant migration over the two year lifetime of this stocked salmonid in Lake Michigan.

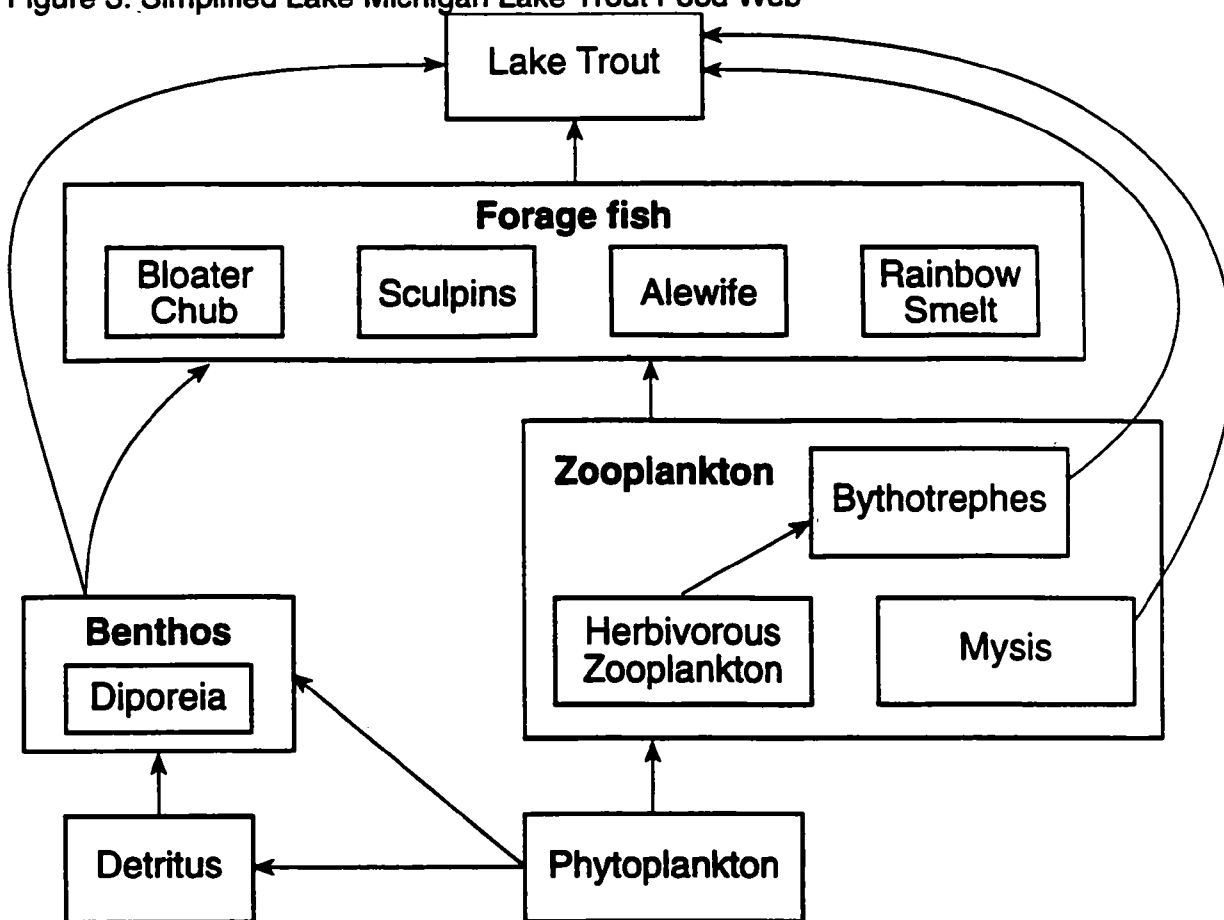
It should be recognized that FDCHN, and in fact all current food web bioaccumulation models, is not predictive in terms of the dynamics of the food web itself. In other words, the food web structure is described as model input. FDCHN does not predict changing forage composition, trophic status in response to nutrients, exotic species invasion, or fisheries management. Yet such factors have been demonstrated to alter food web structures in the Great Lakes, and these changes have been suggested to affect bioaccumulation in top

predators including salmonids. To address the sensitivity of bioaccumulation predictions to food web dynamics, the SIMPLE model (Jones, Koonce, and O'Gorman; 1993), a bioenergetic model for fish population dynamics in the Great Lakes, will be used to construct scenarios for food web change that will then be tested in FDCHN. While less satisfactory than an integrated population dynamics simulation, such testing will demonstrate the sensitivity of bioaccumulation predictions to food web dynamics in comparison to changes in contaminant concentrations in fish due to reducing exposure concentrations.

Atrazine bioaccumulation will not be modeled, because it is not expected to accumulate in biota due to its low hydrophobicity. It is not presently feasible to model bioaccumulation of mercury because a mass balance for the bioaccumulative fraction (the methyl species) is beyond present analytical and modeling capabilities. As identified in Mercury in the Great Lakes: Management and Strategy (Rossmann and Endicott, 1992), the development of such capabilities must initially take place on small, constrained ecosystems as opposed to the Great Lakes. This is consistent with the research approach of Porcella et al. (1992) in developing the EPRI Mercury Cycling Model, which was based upon data gathered from Little Rock Lake and other bog seepage lakes in Wisconsin.

A number of FDCHN enhancements will be considered in the Lake Michigan application. These include incorporating specialized sub-models for phytoplankton (Swackhamer and Skoglund, 1993) and *Diporeia* (Landrum et al., 1992), the organisms at the base of the pelagic and benthic food webs. The bioaccumulation process formulations of Gobas (1993), Barber et al. (1991), and Sijm et al. (1992) will be reviewed for possible updating of FDCHN toxicokinetic descriptions. The detailed bioenergetics model of Hewett and Johnson (1987, 1989), which is currently employed in simplified form in FDCHN, may also be more fully incorporated in the model.

Figure 3. Simplified Lake Michigan Lake Trout Food Web



## **Atmospheric Transport and Deposition**

Current estimates suggest that atmospheric deposition is the major source of several contaminants to Lake Michigan, including PCBs (Pearson et. al., 1994), and mercury (Rossmann, 1994). In addition, net volatilization to the atmosphere may be the predominant loss mechanism for semi-volatile contaminants such as PCBs from Lake Michigan (Endicott and Kandt, 1993) as well as Lake Superior (Jeremiason et al., 1994). Due to the importance of the deposition and exchange of toxics between Lake Michigan and the atmosphere, air-water fluxes of contaminants must be accurately predicted. This will be accomplished initially by observation-based interpolation/extrapolation of atmospheric monitoring data. A longer-term objective will be to model the deposition and exchange of contaminants by linkage and coupling between the CTF model and a compatible atmospheric transport model. The Regional Acid Deposition Model (RADM) will be adapted by the EPA Atmospheric Research and Exposure Assessment Lab (AREAL) for this application.

### **Observation-Based**

Observation-based interpolation/extrapolation of atmospheric monitoring data will be used to estimate over-lake wet deposition, dry deposition, and vapor phase contaminant concentration distributions. These estimates will be based upon: (1) routine monitoring at 9 land-based sites, (2) ship-board sampling in conjunction with open water monitoring, and (3) 3 intensive studies focusing on Chicago as an urban source of air toxics.

Measurements from the Integrated Atmospheric Deposition Network (IADN) and the Lake Michigan Enhanced Monitoring Project (EMP) will be used to drive the CTF model. An overview of the procedures to be used for deriving atmospheric loadings from monitoring data is provided in the Atmospheric Monitoring Overview and Appendix 3 of the Mass Balance Project Work Plan. The Lake Michigan Atmospheric Technical Workgroup will be responsible for calculating atmospheric loadings. This effort must be coordinated with the Modeling Workgroup to ensure compatibility with regard to contaminants of interest, simulation time periods, and spatial scales.

The primary use of observed atmospheric loadings will be to calibrate the CTF model using the best available information to characterize present conditions. Ambient gas phase observations above the water surface will be used in the air/water surface exchange calculations performed by the CTF model.

### **Atmospheric Transport and Deposition Model**

A version of RADM adapted for toxics (the Linear Chemistry Model, LCM) will simulate transport above the watershed and lake, the partitioning and transformations of contaminants in the atmosphere, and the significant deposition and exchange processes with the watershed and lake. Atmospheric transport in RADM is in turn driven by a meteorological model, which generates prognostic simulations of wind, temperature, insolation, etc. The atmospheric model will also generalize measurements of atmospheric deposition and vapor concentrations into fluxes on an appropriate spatial and temporal resolution. The volatile flux may be a significant mass balance component for

contaminants in both the lake and regional atmosphere. Because volatile flux is driven by the local concentration (fugacity) gradient between water and air, contaminant transport and fate models for lake and atmosphere must eventually approximate or achieve coupled simulations. The LCM will be used to predict the air component of contaminant transport and fate. This model will be linked and eventually coupled to the CTF model. LCM will compute transport, dispersion, gas-particle phase distribution, and chemical transformation of airborne contaminants. Meteorological model output is used to define wind and temperature fields for transport. Emission inventory data are used to define contaminant source inputs, although specified boundary condition data may be used to augment emission inventories. This model predicts wet deposition, dry deposition, and vertical air phase contaminant concentration distributions.

The diagnostic and analytic capabilities provided through atmospheric modeling can complement observation based loading calculations by providing enhanced temporal and spatial resolution of deposition during time periods consistent with observations. Although this potential for enhancing resolution of the observed input field is important, atmospheric modeling provides an objective method of linking atmospheric sources directly to watershed/water body impacts. Consequently, the atmospheric model should be a valuable tool in the regulatory decision-making process for assessing the aquatic impacts due to modifying emission releases in future or past scenarios. The role of atmospheric modeling and plans for model deployment are discussed further in Section 13.

### **Air/Water Linkage and Coupling**

The first stage of air process model development for the LMMBS is to link the RADM to the CTF model. The linkage outputs are wet and dry deposition contaminant fluxes and near surface atmospheric concentrations. The output fluxes and concentrations will be used to define input atmospheric loads and the gradient for gas exchange for the CTF model. Linkage can also occur in the other direction, where volatilization is treated as a source of contaminants to RADM.

Initially, the models will be linked, with one- and two-way transfer of flux output between RADM and the lake process models. The final goal is model coupling; the models will run simultaneously to simulate the bi-directional transfer and feedback of contaminant mass balances for air and water. Coupling is a dynamic, two-way process between the atmosphere and water surface. In this case, volatile exchange (volatilization or absorption) is computed based on conditions in both the atmosphere and water column. For both linkage and coupling, atmospheric and lake process inputs/outputs will be defined on compatible spatial and temporal scales.

### **Watershed Delivery**

Transport and fate frameworks may be applied to predict the multimedia delivery of toxics from the watershed to the lake. While contaminant loadings from major tributaries are being monitored as part of the LMMBS, these data alone may not be sufficient to accurately define contaminant inputs from the watersheds, tributaries, and harbors that adjoin the lake. Furthermore, quantifying tributary loads based upon monitoring at the river mouth does not identify sources of toxic chemicals. For instance, atmospheric deposition to the watershed will indirectly contribute to tributary loading. Depending upon the actual

source, toxics loading from the watershed may or may not decline over time without action, respond to meteorology, hydrology, or land use change. Modeling these significant loads would produce more complete and accurate load estimates and allow more realistic long-term forecasting ability.

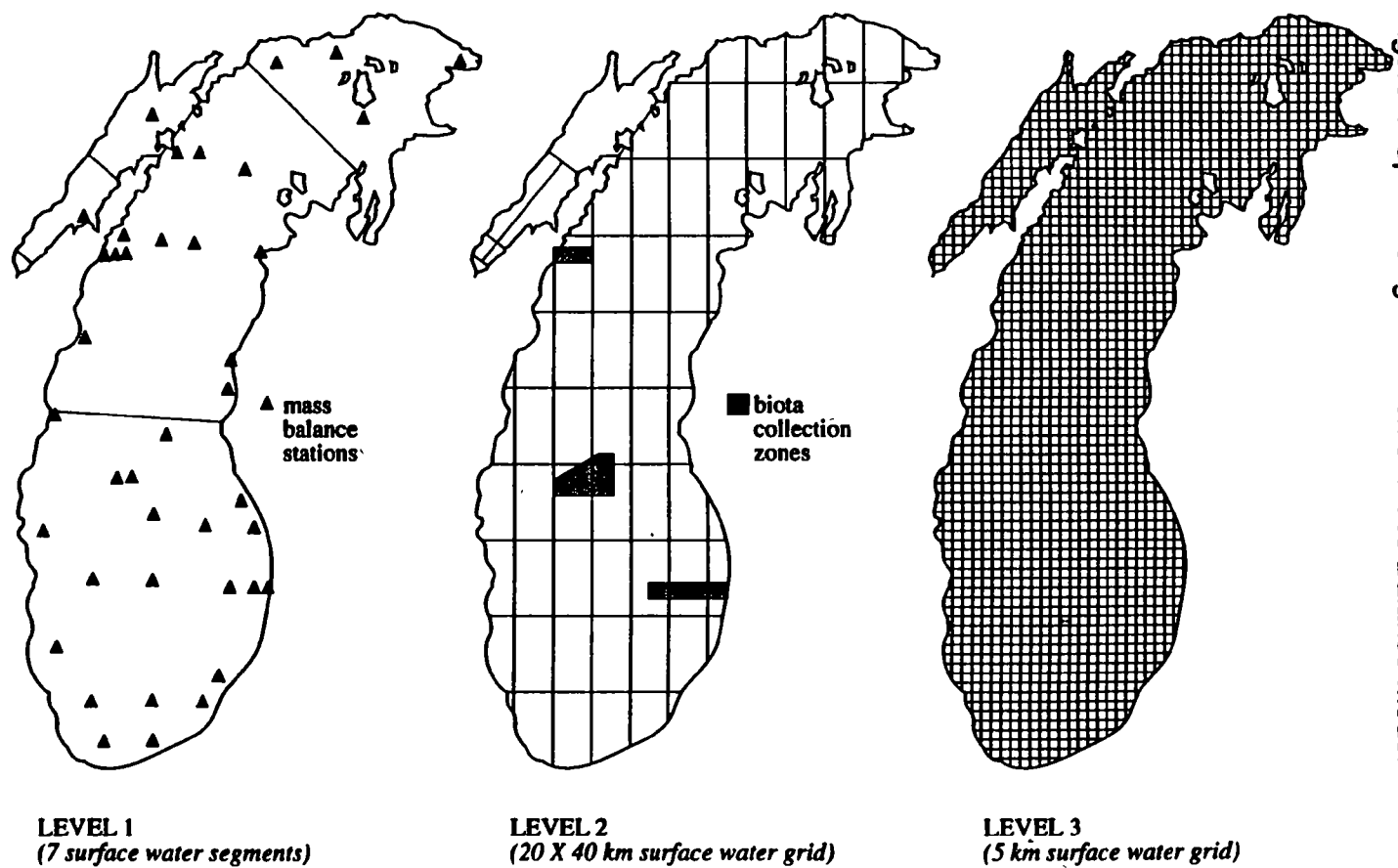
While such modeling capability is important for forecasting purposes, this development should be addressed separately due to the difficulty of managing such efforts within a project of this scope and duration. Development of watershed delivery models is distinct from the lake mass balance model development, because these models simulate toxics transport and fate at fundamentally different scales and have unique data requirements. Furthermore, it is not clear that watershed simulation on this scale is feasible at this time. Results of the LMMBS will be useful for identifying specific toxics and watersheds to prioritize for watershed delivery modeling, based upon the magnitude of tributary loading estimates.

### **MODEL RESOLUTION**

Model resolution is the spatial and temporal scale of predictions, as well as the definitions of model state variables. While factors such as data availability, model sophistication, and computer resources constrain resolution to a degree, different levels of model resolution are possible and, are in fact, necessary. Three "levels" of spatial resolution, indicated by the segmentation grid of the lake surface, are illustrated in **Figure 4**. Level 1 is resolved at the scale of lake basins (characteristic length,  $L = 150$  km), with an associated seasonal temporal resolution. This is a screening-level model resolution used in MICHTOX. Level 2 is resolved at a regional scale defined by food webs ( $L = 40$  km) including gross resolution of the nearshore and offshore regions; temporal resolution is weekly-to-monthly. This resolution is roughly comparable to that achieved by models developed in the Green Bay Mass Balance study. Level 3 is a hydrodynamic scale resolution ( $L = 5$  km), with associated daily temporal resolution. Level 3 is scaled to resolve and predict particle transport processes as well as hydrodynamic transport.

Although LaMP and Great Waters Program objectives are "lake-wide", these emphasize biotic impairments occurring primarily in localized, nearshore regions. LaMP objectives also require that the transport of contaminants from tributaries and other near-shore sources to the open lake be resolved. Therefore, the Level 1 model is not adequate for the study objectives. Level 2 resolution is adequate for most modeling objectives, but not for resolution of significant hydrodynamic and sediment transport events. Level 3 resolution is required for accurate hydrodynamic and sediment transport modeling and is desirable for predicting nearshore gradients, especially those formed by transients such as thermal bars, upwelling, and storm-induced resuspension, as well as more persistent features such as tributary plumes, thermal stratification, and the benthic nepheloid layer. Level 3 transport resolution would also be valuable in relating toxics loading from the 10 AOCs adjoining Lake Michigan, which must be addressed by the Remedial Action Plan (RAP) process, to the LaMP via the LMMBS.

The modeling design for the LMMBS will be based upon the development of several submodels, at two levels of resolution. The CTF model will be resolved at a level comparable to Level 2; the eutrophication model will be resolved at the same level. Because the CTF will be linked to atmospheric fate and transport model predictions, the two will share the Level 2 resolution at the Lake Michigan surface. The POM and SEDZL models will be Level 3 resolution. Results of these transport models will be spatially and temporally averaged prior to coupling to the CTF model. The rationale for specifying different resolutions is that hydrodynamic and predictive sediment transport models demand a Level 3 resolution, and these models offer the best capability for transport simulation and forecasting. A lower resolution is specified for CTF and ESD because these models have been demonstrated at this resolution, and the need for Level 3 toxics resolution is not clear.



*note: surface sediment segmentation is similar but not identical to surface water segmentation. Biotic zones in bioaccumulation model are superimposed on mass balance model segments.*

**Figure 4. Spatial Segmentation of Mass Balance Model**



## **GOALS FOR ACCURACY**

The stated goal for model accuracy is prediction of lakewide average concentrations of toxics in water (volume-weighted average), surficial sediment (spatial average), and top predator fish (average fish in each biota zone) within a factor of two of the average concentrations based upon monitoring data. To achieve this model accuracy, loadings and contaminant mass in each compartment must be determined to within 25% of the actual lakewide, annual average value. Approximately 20% of the samples for toxics analyses should be replicates, as a basis for estimating measurement variability. (In this context, replication refers to multiple observations per model segment and sampling interval). In addition, 75% of loading and ambient samples in all compartments must be quantified for each contaminant (completeness). These data quality objectives are based upon expert opinion, and experience gained in the GBMBS. Failure of the EMP to achieve these goals will degrade the accuracy of the mass balance and model predictions.

## **ANALYSIS OF UNCERTAINTY**

It should be recognized that model accuracy refers to a comparison of model predictions to data collected during the EMP. In a forecasting application, the accuracy of model predictions will degrade over time. In either case, parameterization error is a significant source of model prediction uncertainty. To evaluate and quantify the effects of parameterization error, uncertainty analysis will be performed for selected model simulations. The parameter variance-covariance estimation procedure of Di Toro and Parkerton (1993) will be applied to estimate data, parameter, and model error components.

With these estimates, confidence intervals for model predictions will be generated using Monte Carlo/Latin Hypercube simulation. Uncertainty analysis will also provide a check on the quality of model parameterization and calibration, via the estimation of parameter errors, which will be applied periodically during model development.

## **LONG TERM SIMULATIONS**

Long term simulations will include both hindcast and forecast applications. CTF forecasts will be performed to determine time to steady state, for both continuing and discontinued loads. Forecasts will also be run to evaluate reductions in exposure concentrations resulting from elimination of tributary and/or atmospheric loading. These forecasts will be propagated through the food web bioaccumulation model for PCBs and TNC, to estimate time for sport fish contaminant concentrations to decline below criteria limits. As described previously, SIMPLE model scenarios will be used to test the sensitivity of long-term bioaccumulation predictions to food web dynamics. Based upon the results of long term simulations, graphs will be developed to illustrate the fundamental loading-concentration relationships, for both transient and steady state conditions.

## **SCHEDULE**

A two year project period is proposed for modeling, with model development coincident with data collection. However, the schedule for completion of model development and applications must be contingent upon availability of data from the Mass Balance study, because many aspects of model development cannot proceed without data. In other

words, model final reports will be completed two years after receipt of all data identified above. Delays in data analyses and reporting will cause equal delays in modeling.

## **MODEL COMPONENTS AND WORK ELEMENT DESCRIPTIONS**

### **INPUTS**

#### **TRIBUTARY LOADS**

##### **Background**

Tributaries discharging to Lake Michigan are a major source of nutrients, conservative ions (IJC, 1987), and PCBs (Marti and Armstrong, 1990). Therefore, estimates of contaminant loads from the tributaries will be an important component of the mass balance model. Tributary load estimates of critical pollutants that are not part of the mass balance modeling effort will be measured along with mass balance model parameters. These critical pollutant loads will provide Lake Michigan environmental managers with information necessary to set priorities for load reduction activities.

The objectives of the tributary monitoring are:

1. to identify relative loading rates of critical pollutants from major tributaries to the Lake Michigan basin in order to better target future load reduction and remedial efforts; and
2. to compare tributary loading rates to other media (atmospheric deposition and contaminated sediments) in order to better target future load reduction efforts and to establish a baseline loading estimate to gauge future progress.

Pollutant loads from tributaries must be accurately and precisely determined in order to: 1) quantify the contaminant loads from each tributary; 2) prioritize tributaries for potential remediation based on contaminant load, and; 3) provide an estimate of the total contaminant load from tributaries for comparison with loads from atmosphere and open lake sediments. In order to address the study objectives, the tributary monitoring plan has been designed to obtain load estimates of target compounds to within +/- 25 to 30 percent of the actual loads.

The tributary monitoring program is intended to assess the contribution of a number of critical pollutants to Lake Michigan from the major tributaries. The critical pollutants were identified in the draft Lake Michigan Lakewide Management Plan for toxic pollutants (LaMP) and are listed in Appendix 2 of the Mass Balance Work Plan. Achieving the objectives of the tributary monitoring plan will address the needs of the mass balance model and the Lake Michigan LaMP as driven by the federal Clean Water Act and the Federal Clean Air Act Amendments.

This study will not provide data on the specific sources (pipes, nonpoint, sediment, etc.) which contribute to a tributary's load: attempts to answer that question are beyond its scope. However, additional source identification work will occur through the Lake

Michigan LaMP process. Any additional source identification work within the tributaries could build upon the Mass Balance Model database.

## **Sampling Design**

Detailed Quality Assurance Project Plans (QAPjP) outlining sampling and analytical procedures have been developed and approved. These QAPjPs are available upon request. However, a brief overview of the sample design and sampling methods is provided below.

With the exception of a study by Marti and Armstrong (1990) for PCBs in the early 1980's, very little work has been done to estimate organics and metals loads from Lake Michigan tributaries. It is, therefore, necessary to use data from other media (e.g. contaminants in resident fish) to determine which tributaries are potential sources of the target contaminants. In addition, the use surrogate parameters such as suspended solids and flow is necessary to develop a sampling scheme necessary to meet the objective of monitoring the loadings with an accuracy of +/- 25 to 30 percent.

The tributaries in Table 2, with the exception of the Pere Marquette, were selected because of elevated concentrations of one or more of the target contaminants in resident fish collected in 1981-82 (De Vault, 1985; USEPA unpublished data). The Pere Marquette River was selected because it has a fairly large and pristine watershed. Samples collected from the Pere Marquette River could be used to estimate loads from significant portions of the Lake Michigan watershed that will not be monitored.

The tributary samples will be collected by three crews lead by the United States Geological Survey (U.S.G.S). One crew will be based in Madison, Wisconsin and collect samples from the Milwaukee, Sheboygan, Fox and Menominee Rivers. A second crew will be based in Grayling, Michigan and collect samples from the Muskegon, Pere Marquette and Manistique Rivers. The third crew will be based in Lansing, Michigan and collect samples from the Grand, Kalamazoo, St. Joseph and Grand Calumet Rivers.

Sampling sites will be located as far downstream as is practical to monitor the accumulated point and nonpoint source loads (**Figure 5**). Flow will be monitored continuously at each of the sites. Acoustic velocity meters (AVMs) will be used to monitor flow reversals at sites that are impacted by seiches. Continuous turbidity monitoring and automated suspended solids sampling will be employed to assess particulate loads from each tributary.

Each sample collected for analysis of organic pollutants will consist of separate samples for dissolved (<0.7 microns) and particulate (>0.7 microns) organics. Analysis of non-polar organic samples collected during pilot work at four tributaries has indicated that quarter point sampling of the tributaries is appropriate. Quarter point sampling includes preparing composite samples of subsamples collected at 0.2 and 0.8 of the river depth at three locations in a cross sectional transect. The three points on the transect will be located at 0.25, 0.5 and 0.75 the length of the transect. Non-polar organic samples will be filtered through Whatman GF/F filters in a pentaplate filter. The filters will be used to analyze contaminants in the particulate phase. Filtered water will be passed through XAD2 resin columns to extract the dissolved contaminant fraction. Total sample volume will range

from 80 to 160 liters, depending on expected contaminant concentrations at the sites and logistical constraints faced by field crews.

Atrazine samples will be collected using the same quarter point sampling methods. Samples will be collected using carbopak resin cartridges. Atrazine samples will be collected between April 1 and October 31, 1995, coinciding with the normal atrazine application period.

Metals sampling will include collection of a sample for total metal analysis and a filtered sample for analysis of dissolved (<0.45 microns) metals. Analysis of samples collected during pilot monitoring at four tributaries indicated that sampling at two depths at the centroid of the tributary is appropriate. Samples will be collected at 0.2 and 0.8 the depth of the centroid.

Due to the hydrophobic nature of the nonpolar organic critical pollutants, we assume that they will behave similarly to suspended sediment and be event responsive. Therefore, the tributary monitoring plan was designed to focus sampling effort on high flow events. Polar organics such as atrazine may also respond to high flow events, mainly as runoff from agricultural lands, directly entering tributaries. Loads of herbicides calculated for tributaries to Lake Erie indicate event responsiveness and seasonal dependence (Baker and Richards 1989). At present, the behavior of mercury and other metals on the critical pollutant list during a precipitation event is unknown.

The flow variability of each tributary was used to predict the level of sampling required to achieve a load estimate with the given level of accuracy and precision. The Lake Michigan tributaries targeted for sampling fall into three categories of flow variability as described by Richards (1990): super stable, stable, and variable. The level of sampling required increases from super stable to variable. Table 2 indicates the classification of selected tributaries by Richards. Work done by Dolan (1981) for phosphorus and Day (1989) for several parameters indicates that the number of samples required from most Michigan tributaries (Grand, Pere Marquette, St. Joseph, Muskegon) to determine loads with 95 percent confidence levels +/- 20% to 30% would be 20 to 30 per year. Based on the suspended solids and nutrient loading work the estimated sample sizes necessary to calculate critical pollutant load with the required precision and accuracy range from 16 to 45 (Table 2). Super stable tributaries will be sampled 16 times, 26 samples will be collected at the stable tributaries and 45 samples will be collected at the variable tributaries. The only exception to this sampling strategy is the Grand River, where 36 samples will be taken. The potentially large load of contaminants (due to high flow volume) from the Grand River warrants the additional effort.

The two tributaries to Green Bay, which deliver the largest load of contaminants to the Bay, namely the Fox and Menominee Rivers, will be monitored at a frequency of 26 samples per year. However, sedimentation, volatilization, and other processes may prevent pollutant loads from Green Bay tributaries from reaching Lake Michigan. The Green Bay Mass Balance Model will be used, along with monitored boundary conditions to estimate the pollutant load from Green Bay to Lake Michigan.

Approximately two-thirds of the samples will be collected during high flow events. High flow events have been defined in advance to include any event that exceeds the upper

twentieth percentile of flow based on historical flow records maintained by the U.S.G.S. The high flow monitoring frequency has been predicted based on the expected number of high flow days in an average year and the estimated number of samples for each tributary. The estimated high flow sampling frequency will range from one sample every 6.5 days for the super stable Pere Marquette River to one high flow sample every 2.5 days from the variable Milwaukee and Sheboygan Rivers (Table 3). These high flow sampling frequencies were estimated to provide guidance to the field crews charged with collecting samples. However, the field crews have the discretion to temporarily alter sampling frequencies in order to respond to any unique situations that may occur. The estimated total number of samples to be collected is 314. An additional 10 percent for quality assurance will bring the total number of samples to 345. However, the sampling guidance outlined above will allow crews flexibility to collect more samples if the project period is unusually wet and fewer samples if the project period is unusually dry. Low flow samples will be scheduled and collected during base flow periods after the sampling crews have determined that the sampling locations are not being influenced by seiches.

Sample collection on the Grand Calumet River will be scheduled in advance and not based on flow conditions in the river. Industrial discharges contribute the majority of flow to the Grand Calumet River and effectively stabilize the flow hydrograph at the mouth. Scheduled sampling runs are preferred at the Grand Calumet River since the flow is stable and scheduled sampling runs are logistically easier to plan and implement than event monitoring strategies.

These sample numbers are estimates, based on optimizing crew availability and logistics, weather conditions, and government funding and quality assurance review. However, several of these factors combined during water year 1994 to delay and hamper the collection of the expected samples. In order to provide accurate and precise load estimates for a complete year, tributary sampling has been extended through October 1995. The sampling intensity for the one year period ending in 1995 will be the same as our initial estimate for 1994. That is, the sample numbers for that year will be those listed in the following tables. The samples collected up to October, 1994 will be analyzed and will provide less precise load estimates for that period.

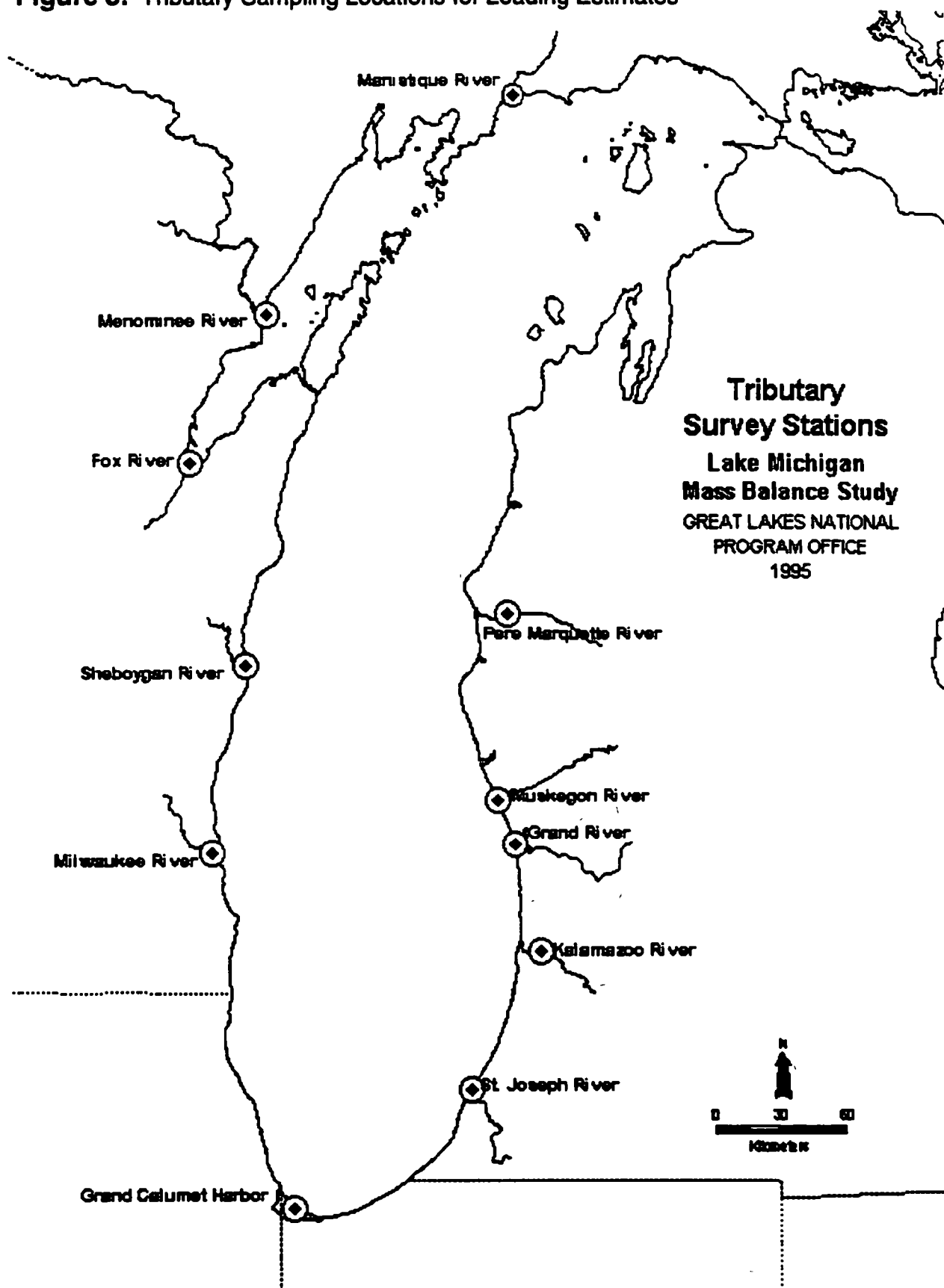
Table 2. Tributaries to be Monitored For Loadings		
Tributary	Event Responsiveness	Number of Samples
Grand River, MI	Stable	36
Kalamazoo River, MI	Stable	26
St. Joseph River, MI	Stable	26
Muskegon River, MI	Stable	16
Manistique River, MI	Stable	16
Pere Marquette, MI	Super Stable	16
Milwaukee, WI	Variable	45
Sheboygan River, WI	Variable	45
Fox River, WI	Stable	26
Menominee River, WI	Stable	26
Grand Calumet River, IN	Super Stable	16

**Table 3. Estimated sample volumes, sample sizes and sampling frequency.**

Tributary	Sample Volume	Sample Size		Total	Frequency
		High Flow	Low Flow		
Grand Calumet	80 liters	all samples scheduled		16	
Pere Marquette	80 liters	11	5	16	1/6.5 days
Muskegon	80 liters	18	8	16	1/4 days
Kalamazoo	80 liters	18	8	26	1/4 days
St. Joseph	80 liters	18	8	26	1/4 days
Grand	160 liters	24	12	36	1/3 days
Manistique	160 liters	18	8	16	1/4 days
Menominee	80 liters	18	8	26	1/4 days
Fox	80 liters	18	8	26	1/4 days
Milwaukee	80 liters	30	15	45	1/2.5 days
Sheboygan	80 liters	30	15	45	1/2.5 days

Indicates the frequency at which high flow samples should be collected. These frequencies are estimated to provide guidance to the field crews.

**Figure 5. Tributary Sampling Locations for Loading Estimates**



## **Tributary Load Calculations**

Load calculation methods are presented in detail in the QAPjP. However, a general overview is presented below.

The load will be calculated using short term averages (5 to 15 minutes) of flow volume and direction for dissolved phase contaminants. Along with flow measures, short term averages of turbidity will be utilized for particulate load calculations. In order to determine the relationship between turbidity and suspended solids concentration, an automated, ISCO sampler will be programmed to take three water samples per day. These water samples will be analyzed for suspended solids concentration, and linear regressions of suspended solids versus turbidity measurements made at sample collection times will be developed, stratified by season and flow. Continuous turbidity monitoring and suspended solids sampling will be conducted at a single location in each tributary. In order to establish the representativeness of the locations, cross-sectional samples will be taken for suspended solids during regular sampling visits, and compared with values obtained from ISCO samples.

### **Point Source Loadings**

Tributary monitoring sites have been selected, purposely, to be downstream of most major point source discharges. The Great Lakes States are currently evaluating the potential contribution of point sources on Great Lakes tributaries as well as point source contributions direct to Lake Michigan. The approach taken is to utilize any available concentration measurements for the contaminant of interest sampled from the point sources. Where contaminant concentrations are below the limit of detection (LOD) a range of estimates using the LOD, one-half the LOD, and zero will be evaluated against estimated total tributary loads. Point source loadings are an important component of watershed models, which may follow the mass balance modeling effort.

### **Research Issues**

An area of research being planned is the use of automated Infiltrix samplers for continuous monitoring of toxic organic compounds. The samplers are self-contained, employing a pump and in-line filter cartridge and XAD2 resin column (small), controlled by a programmable microprocessor. As part of the regular sampling program, Infiltrix samplers will be evaluated against quarter point sampling to determine the representativeness of samples taken at a single point. There is some potentially cost saving in using these samplers as an alternative to sampling crews on standby for sampling during rain events. The automated samplers will be installed in selected tribs in spring 1995.

## **ATMOSPHERIC MONITORING OVERVIEW**

### **Introduction**

Atmospheric deposition has been shown to be a significant source of target organic compounds to the Great Lakes, particularly the upper lakes, Superior, Michigan and Huron



(Strachan and Eisenreich, 1988; Eisenreich and Strachan, 1992). Atmospheric monitoring for the Lake Michigan Mass Balance will be conducted to assess the contribution of atmospheric deposition and exchange to the concentration of toxic contaminants in the lake. The atmospheric data set will be used to calculate the atmospheric load to the system and to calibrate air models linked with the mass balance water models.

Contaminants are removed from the atmosphere as wet and dry deposition and exchanged across the air-water interface through vapor absorption and volatilization. To address these processes, the atmospheric monitoring to be conducted on Lake Michigan consists of several components: approximately one and one-half year of routine land-based monitoring, and special research/monitoring studies necessary for the mass balance. The special studies include the following: intensive seasonal monitoring and research studies off of Chicago; over-water atmospheric monitoring from the R/V Lake Guardian during intensives and open-water surveys; and mercury monitoring at four land-based sites for the 1.5 year period of the loading study and extensive land-based and over-water monitoring during the intensive studies.

These studies have been designed to:

- Assess the impact of the Chicago urban area on atmospheric deposition and exchange with Lake Michigan including categorization of major urban source categories.
- Compare over-water and land-based sites to assess whether land-based sites are representative of the bulk deposition to the lake surface.
- Estimate the air-water exchange of contaminants including seasonal direction and magnitude.
- Improve estimates of dry deposition including the large particle contribution from urban areas.

Relatively little is known of the spatial and temporal variability of atmospheric concentrations of the target compounds over Lake Michigan. It is therefore not possible to design the atmospheric network to assess loads with predetermined accuracy and precision. Measurement uncertainty (sampling and analytical) is minimized through the use of the best sampling and analytic techniques available. For modeling purposes, the goal of the data collection is a combined sampling and analytical uncertainty of  $\pm 20\text{-}30\%$  at 90% confidence.

### **Parameters**

The parameters for the atmospheric component of the mass balance are those previously identified: congener-level PCBs, *trans*-nonachlor, atrazine, and mercury on a research basis. The longer list of parameters in Appendix 2 will also be monitored for the atmospheric loading study for Lake Michigan and, in some cases, to provide supplemental information for the mass balance. Data collection for the loading study list of parameters will allow estimates of the ratio of the atmospheric load (wet and dry deposition) to the total load (tributaries and atmosphere). Meteorological data collected includes air

temperature, wind speed, wind direction, relative humidity, and solar radiation. Additional research and ancillary data will also be collected for the special studies.

### **Routine Monitoring at Land-based Sites**

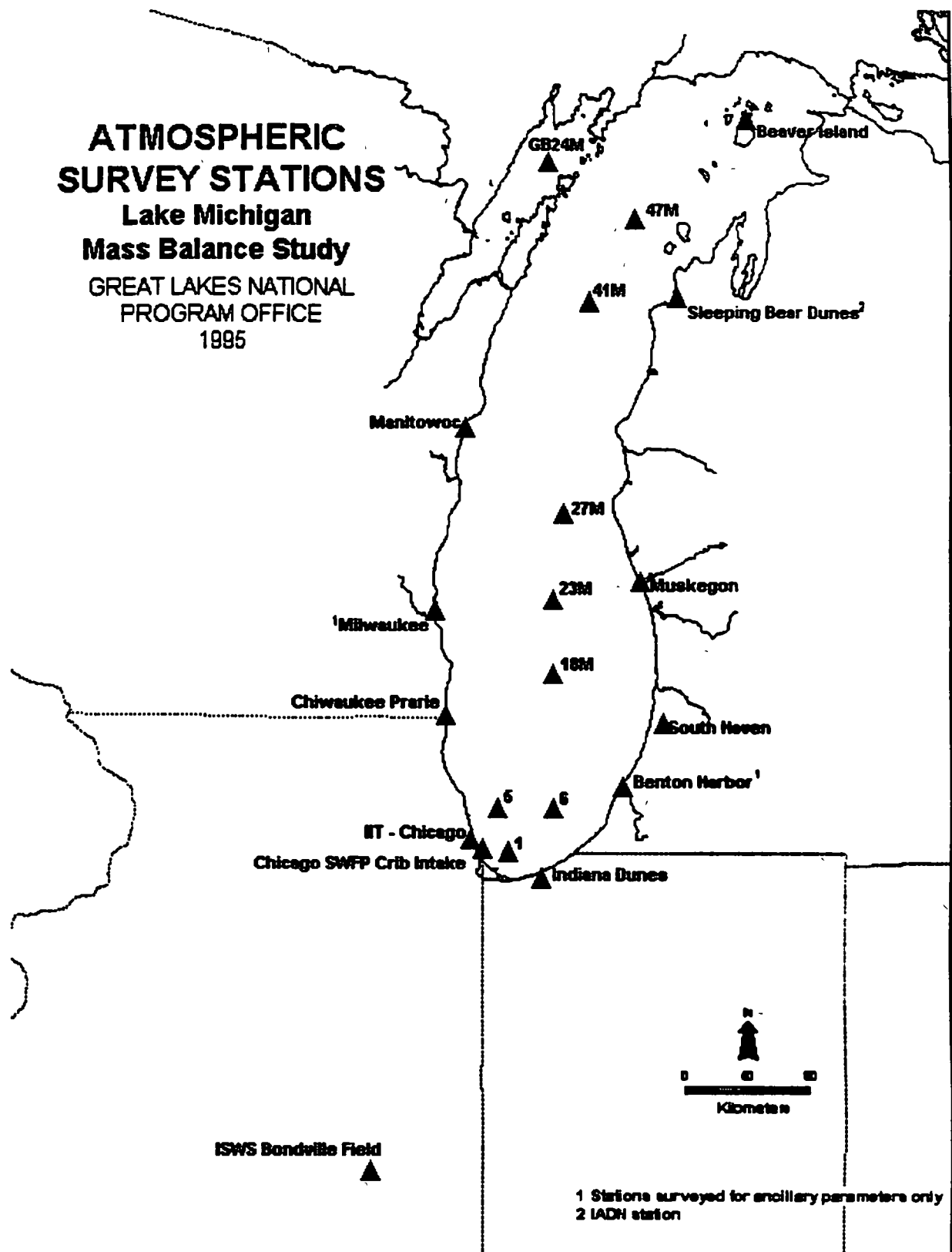
Data collected during the routine monitoring portion of the mass balance will be used to estimate annual and seasonal loadings and calibrate deposition models. Routine monitoring will be conducted at nine land-based sites for the period beginning February 1994 and ending October 1995 (**Figure 6**). The number and location of the sites were chosen at workshops and through discussions with experts working on atmospheric deposition in the Great Lakes (USEPA, 1992a and b). Unpublished data (Steve Eisenreich personal communication, 1992) indicate that the atmospheric concentrations of PCBs exhibit a strong gradient over Lake Michigan, with concentrations in the southern portion of the lake approximately 3 to 5 times that in the north. A higher density of sites is located in the southern portion of the lake due to the higher contaminant concentration and load variability attributable to urban areas.

The site classifications (urban/urban-influence, rural/background and remote) correspond to proposed sampling frequency and are identified in Table 4. The urban site is located at Illinois Institute of Technology in Chicago, Illinois, with a background site located upwind at Bondville, Illinois to monitor the impact of contaminants carried to the Chicago urban area from outside the region (i.e., St. Louis area). Duplicate samplers will be located at the IADN and/or IIT sites. The possible inclusion of a routine site located on a NOAA buoy is being explored.

**Table 4. Atmospheric Monitoring Sites and Sampling Frequency**

<b>LM Mass Balance\Loading Study Atmospheric Monitoring Sites</b>							
Site	State	Category	IADN	Mercury	Intensive	GLAD	Installation
Beaver Island	MI	Remote				X	~10/93
Sleeping Bear Dunes	MI	Remote	X	X		X	12/91
Muskegon	MI	Rural					9/93
South Haven	MI	Rural		X	X		7/93
Indiana Dunes	IN	Urban Infl		*		X	11/92
IIT - Chicago	IL	Urban		X	X	X	1/93
Chiwaukee Prairie	WI	Urban Infl		*			~11/93
Manitowoc	WI	Rural				X	~11/93
Bondville	IL	Background			X		9/93
R/V Lake Guardian					X		
* Total mercury will be monitored at one of these two sites							

Figure 6. Land-based and Intensive Atmospheric Sampling Sites Land-based and Intensive Atmospheric Sampling Locations<sup>1</sup>



Particle-phase, gas-phase and precipitation samples will be collected at each routine site according to the frequencies in Table 5. A modified Andersen high-volume sampler (flow rate of 20 cfm) with GF/F glass fiber filter and XAD-2 resin cartridge will be used to collect the particulate and gas-phase SVOCs, respectively. The average sampling frequency for particulate and gas-phase concentrations is once every six days based on a range of every twelfth day for rural sites to every three days for urban sites. Modified hi-vol samples will be composited on a monthly basis at all sites during the routine monitoring. This sampling scheme is intended to address the variability expected in urban areas without increasing the required laboratory capacity. Precipitation is collected as an integrated monthly sample using a modified MIC with XAD-2 resin column which is analyzed for the SVOCs.

During the period of routine sampling, dry deposition plates will be located at those sites also identified for the mercury studies. Each dry deposition sampler consists of two plates pointed into the prevailing wind by a wind vane. Four greased Mylar strips are located on each of the plates for a total of eight per sampler. The samplers will collect integrated monthly samples. One strip from each site will be analyzed for trace metals. Strips are weighed before and after sampling to determine the total mass collected. The compositing and analysis schemes for the other strips has not yet been determined.

Additional parameters are collected at the routine sites either as support for the mass balance or the loading study. A dichotomous sampler is used to collect coarse and fine particulate for trace metal analysis by XRF. Precipitation is collected weekly in a modified Aerochem Metric sampler with a Teflon coated sampling train and analyzed for trace metals using ICP/MS. Nutrients and major ions are collected weekly at the GLAD sites only. Meteorological data is recorded continuously and averaged for hourly values at all land-based sites.

Specific details of the sample collection and analysis will be covered in the Quality Assurance Project Plans (QAPjPs) and Standard Operating Procedures (SOPs) developed for the mass balance and loading studies. The QAPjP and SOPs will be based on the procedures and quality assurance/quality control measures that were used in the Green Bay Mass Balance Study (Swackhamer, 1988) and those which are currently used for the Integrated Atmospheric Deposition Network (IADN) (Sweet, 1992). XAD-2 resin is used to concentrate the vapor phase and dissolved (precipitation) phase SVOCs. Whatman GF/F filters are used to collect particle phase SVOCs. Each sample is analyzed for all the loading study parameters including PCBs, *trans*-nonachlor and atrazine. Following extraction, a portion of the sample is analyzed for atrazine and its two major degradation products, de-ethylatrazine and de-isopropylatrazine, using gas chromatography/mass spectrometry (GC/MS) with

Table 5. Atmospheric Monitoring Sampling Frequency

<b>Table 5</b>		
<b>Atmospheric Monitoring Frequency - Routine Monitoring</b>		
<b>Parameter</b>	<b>Sampler</b>	<b>Frequency</b>
<b>Precipitation</b>		
PCBs, pesticides, PAHs	Modified MIC - XAD column	28 days - composite
trace metals	Modified Aerochem - Teflon	7 days (Tues) - composite
(a) nutrients, inorganics	Standard Aerochem	7 days (Tues) - composite
precip. volume	Belfort/nipher	7 days (Tues) - composite
<b>Air</b>		
PCBs, pesticides, PAHs	Mod Hi-Vol - GFF/XAD cartridge	urban/urban infl - 24 hrs every 3 days background/rural - 24 hrs every 6 days remote/IADN - 24 hrs every 12 days
trace metals	Dichotomous sampler	96 hr composite/month - 24 hrs every 6 days
TSP/TOC	Std. Hi-vol	every sixth day
trace metals, SVOC, mass	Dry deposition plates	monthly composites - limited # of sites
<b>Meteorology</b>		
T, RH, SR, WS, WD	Campbell/Tower	continuously-averaged hourly
(a) Only at GLAD sites		

<b>Parameter</b>	<b>Sampler</b>	<b>Frequency</b>
<b>Intensive Study</b>		
PCBs, pesticides, PAHs		
Vapor/particulate	Mod Hi-Vol - GFF/XAD cartridge	2 - 12 hr samples daily
Precipitation	Baker Sampler	event-based
trace metals (coarse/fine)	Dichotomous sampler	2 - 12 hr samples daily
TSP/TOC	Std. Hi-vol	
Carbon - elemental / volatile	Fine Particle Sampler	
<b>Mercury Study</b>		
Mercury - total	Hg sampler Modified MIC - B	air - 24 hrs every sixth day precipitation - weekly or event
Mercury - speciation	Hg sampler Modified MIC - B	air - precipitation - daily, as warranted

selected ion monitoring (SIM). The remaining sample is separated into two fractions with silica column chromatography. The first fraction is analyzed by gas chromatography/electron capture detection (GC/ECD) for PCBs, DDE, HCB and aldrin, while the second fraction is analyzed by GC/MS for the PAHs, *trans*-nonachlor, chlordane, dieldrin, DDT and DDD.

### **Atmospheric Component of the Open-water Surveys**

Air and water samples above and below the air-water interface will be collected simultaneously to assess the volatilization of HOCs. This sampling component is similar to that used for the volatilization study conducted as part of the Green Bay Mass Balance (Achman, 1993; Hornbuckle 1993). A modified high-volume sampler will be mounted on the bow of the Lake Guardian for collection of 12-hour air samples (approximately 400 m<sup>3</sup>). Concurrent water samples are collected as discussed in the plan's section on Open-Water sampling. Air and water temperature, wind speed and direction, barometric pressure and wave height are also recorded while on station. Depending on the sea conditions, the ship will be at anchor while on station to ensure that prevailing winds are from the bow of the ship and to minimize contamination from the ship's exhaust. Alternately, the sampler will be operated only when wind is <60° off of the bow. All station locations have not yet been selected but include the master stations for the open-water survey as a minimum. The magnitude and direction of the flux is estimated by comparison of the vapor-phase air and dissolved water concentrations with the expected equilibrium values as discussed in the section on atmospheric loading calculations.

We will evaluate the representativeness of land-based sites as surrogates for over-water measurements. Land-based samples (hi-vol and dichot) will be collected concurrently with over-water samples (hi-vol and dichot) when the ship is on a station near to that land site. This will allow for the comparison of over-water and over-land samples and an assessment of the representativeness of land-based sites.

During the survey, event-based precipitation samples for SVOCs will be collected using a 1 m<sup>2</sup> steel funnel draining to an XAD-2 resin column. This is a modification of the Baker sampler, which allows for manual operation.

### **Intensive Study**

The Lake Michigan Urban Air Toxics Study (LMUATs) indicated that the concentrations of several contaminants were significantly higher in the Chicago urban area than at sites upwind (Kankakee, IL) and downwind (South Haven, MI) (Keeler, 1993). In addition, a study of dry depositional flux of PCBs indicated that the flux from the Chicago urban area may be up to three orders of magnitude higher than that of nonurban areas. (Holson, 1991) The intensive studies are designed to further assess the impact of the Chicago Urban area on the atmospheric deposition to the lake, to address process oriented research issues, and to provide data in support of source apportionment and trajectory modeling.



Three intensive studies were conducted: spring 1994, summer 1994 and winter 1995. Monitoring locations include three land-based sites: IIT (urban), South Haven (downwind), and Champaign/Bondville (upwind) and one over-water site, the R/V Lake Guardian approximately 5 miles off of Chicago. During each intensive, the R/V Lake Guardian was used for a period of one to two weeks for frequent sampling. The land-based sites operated for several additional days on either side of the Lake Guardian operations, resulting in approximately three to four weeks of intensive sampling at land-based sites. These sampling periods are to provide information to track plumes/events over and across the lake.

The monitoring equipment included versions of that used at the routine monitoring sites and additional equipment for research studies and source apportionment analysis. Precipitation was sampled for SVOC and trace metals on a daily (24-integrated) basis, as warranted. Vapor and particulate phase SVOCs were collected, at a minimum, as two 12-hour samples each day of the intensive. Two 12-hour integrated aerosol samples (coarse and fine) were collected each day for trace metal analysis. Meteorological data and dichotomous sampler data were used to select those samples to be analyzed and to define any compositing scheme which may be employed for the intensive studies. Dry deposition plates and a micro-orifice impactor/Noll rotary impactor combination collected 24-hour integrated samples daily. The latter equipment is included to address the impact of large particle deposition collecting size segregated aerosol up to 150  $\mu\text{m}$ . Mercury speciation was determined in precipitation, vapor, aerosol less than 2.5 microns, and total aerosol. Fine particulate samplers for carbon (elemental and volatile), VOC canisters, and annular denuders for acid gases were used during the intensives for source apportionment analysis. Open water samples were collected to address exchange at the air-water interface. Additional research was conducted to address the research issues discussed below. The intensive studies were coordinated with the open-water surveys so that during the two weeks following or preceding the intensives, atmospheric monitoring was conducted aboard the R/V Lake Guardian during the open water surveys.

Water column data collected in 1976-77 indicate strong gradients off Chicago for several conventional water quality parameters (Rockwell, et. al., 1980). As there is no consistent hydrologic connection between Chicago and Lake Michigan, the origin is likely atmospheric. Sediment traps radiating from Chicago are also proposed to monitor the impact of atmospheric deposition from the Chicago Urban area. The details of this sediment monitoring are discussed in the sediment section of the study plan.

### **Loading Calculations**

Atmospheric deposition and exchange with a lake, which includes wet and dry deposition, net gas transfer, resuspension from the lake and the atmospheric component of the tributary contribution, may be expressed as the equation in Appendix 3.

The atmospheric component of the Green Bay Mass Balance Study divided the bay into four surface segments corresponding to the nine used for the surface water. Wet deposition was calculated as an external input to each of the four segments using monitoring data to generate the input series. The volatilization was incorporated in the water balance model. Two air-water mass transfer sub-models (O'Connor (1983) and Mackay and Yeun (1983)) were evaluated to compute the overall mass transfer coefficient. Predictions from both models were compared with measurements of instantaneous air-water fluxes. Results from the O'Connor model were found to be in better agreement with observations, particularly at high wind speeds. This sub-model coupled the atmosphere and water.

Based on the ambient data, wet and dry deposition loads to the lake and the atmospheric boundary conditions will be assessed. In the simplest terms, wet deposition is assessed from the concentration in the precipitation, amount of precipitation, and area of lake covered by precipitation. The dry deposition flux is calculated by dividing the particle distribution into a number of intervals and assigning the appropriate deposition velocity. (Holsen 1993) The flux for each interval is summed for the total deposition. Several models exist for the determination of the deposition velocity and the intensive studies are expected to advance the state of these models. The volatilization component will be addressed as a sub-model as in the Green Bay Mass Balance. However, it will be improved upon by the specific research studies of the Lake Michigan Mass Balance and calibrated with ambient data.

Linking an atmospheric mass balance/transport model with the water mass balance model requires emission inventories and process information which are not presently available for comprehensive atmospheric models. Simple atmospheric deposition models are currently being developed, such as RELMAP which is being developed to use a mercury emission inventory. However, while these models are being developed, the Lake Michigan Mass Balance model will use loads based on ambient data.

### **Research Issues/Areas**

Process related atmospheric research to improve mass balance estimates for SVOCs include (approximately in order of importance by category):

#### **Wet deposition:**

- Gas/aerosol distribution, and aerosol scavenging coefficients
- Total atmospheric concentration
- Total precipitation concentration
- Gas scavenging coefficient

#### **Dry deposition:**

- Aerosol deposition velocity
- SOC aerosol size distribution

## **Gas Exchange:**

**SOC speciation in water**

**Mass transfer coefficients, including the applicability of existing mass transfer coefficients to the Great Lakes**

**Total SOC concentration in water**

**Henry's Law constant/temperature dependence**

**Comparison of different models (two film vs. surface renewal)**

**Investigation of surface microlayer in gas exchange**

## **OUTPUTS**

There are three potential removal paths for the targeted chemicals in Lake Michigan. These are burial in the bottom sediments, volatilization to the atmosphere (see Atmospheric Loadings), and discharge through the Straits of Mackinaw. Volatilization is covered under Atmospheric Loadings and discharge through the Straits will be calculated from water column measurements. This section will describe monitoring to quantify sedimentation.

### **SEDIMENT AND PARTICLE FLUX**

#### **Data Quality Objective**

The goal is to measure the sediment-water exchange of the target compounds to within an error of 30% with a confidence level of 90%. All data collected will be acquired with generally acceptable or peer reviewed sample/data collection, handling and analytical techniques. All of the data to be collected for this program will be subject to EPA QA/QC oversight.

#### **Sediment Project Components**

The annual cycle of particle production and transport plays a major role in the seasonal and long term behavior of contaminants in lakes. Compounds entering the lakes are removed to the sediments at a rate proportional to their affinity for settling particles. Since particle residence times in the water column are relatively short (even in deep systems, such as Lake Michigan, particle settling times are less than one year), particle-associated contaminants are efficiently scavenged and removed to the sediments. After reaching the bottom, the settled materials are mixed by the feeding activities of bottom dwelling organisms into an homogenized pool representing years to decades of recent sedimentation (Robbins, 1982). It is apparent from the relatively slow decline in the concentrations of particle-associated constituents in water and biota in recent years, that sediments are a leaky sink; small concentrations persist in the water for decades because of processes that remobilize materials from the bottom.

In regions where sediments are accumulating, the extent of this pool is the sediment mixed layer (except for constituents with a rate of decomposition greater than the layer mixing time (approx. seasonal). In regions where there is no apparent long term accumulation of sediments, the exchangeable pool is the material temporarily

deposited and in transit to the depositional regions. The critical parameters required to estimate the sediment-water exchange of contaminants are:

- 1. the concentration of total contaminant in the sediment mixed layer (the material available for exchange);**
- 2. the time constant (sediment accumulation rate/thickness of the mixed layer) for changing the concentration within this layer;**
- 3. the amount of resuspension of the local sediments;**
- 4. the distribution coefficients for the contaminant in local sediments;**
- 5. the gross downward sediment and associated contaminant flux;**
- 6. the dissolved and DOC bound contaminant sediment-water exchange.**

#### Sediment Core and Surface Sediment Analyses

Many of the target compounds in this LMMB Program accumulate in sediments of lakes and, as a result of resuspension/benthic food web processes, this exchangeable inventory effectively buffers the temporal behavior of these contaminants to changes in loadings. In order to model the behavior of the programs' target compounds, a careful measurement of the concentrations in the sediment mixed-layer and long term burial must be made. Radionuclides, principally <sup>210</sup>Pb and <sup>137</sup>Cs, have been used to: 1) determine the geochronology over the last 100-120 years of such sediment records; 2) estimate the extent of surficial mixing due to physical or biological process; to estimate the rate of movement of contaminated sediment from non-depositional to depositional areas (focusing); and 3) calculate fluxes to the sediments and relate them to input functions. Radionuclide measurements will be used to address:

- 1. the concentration and inventory of target contaminants in the sediment mixed layer (the material available for exchange) through determination of the thickness of the mixed layer, and**
- 2. the time constant (sediment accumulation rate/thickness of the mixed layer) for changing the concentration within this layer**

This project will consist of four components:

- (a) the collection of vertically undisturbed sediment cores representative of all of the depositional zones in Lake Michigan;
- (b) the sampling of these cores in the best manner to provide samples that:

- (i) may be used to measure the sedimentation rate and mixed-layer depth;
- (ii) will be analyzed for mercury and specific organic compounds in the mixed layer;
- (c) the analysis of samples from fully-sectioned cores for water content,  $^{137}\text{Cs}$ , and  $^{210}\text{Pb}$ ;
- (d) the evaluation of the data on a core-by-core basis obtained in component (3) and the calculation of sedimentation rates and mixed depths using established best practice.

### **Sampling**

A sampling grid covering all depositional areas of the lake has been established based on the locations of the 40 stations already created for the EMAP program. A comparison of these stations with the grid established by Argonne National Laboratory in 1972, and expanded upon in 1982 and 1992 by the Center for Great Lakes Studies, University of Wisconsin-Milwaukee and NOAA-GLERL is shown in Figure 7. Representative samples will be collected at each station on the complete EMAP grid provided there is a sufficient depth of sediment to sample using the CGLS-UWM Box Corer. In addition sediment samples will be collected at approximately 30 stations sampled last in 1992 where the  $^{137}\text{Cs}$  distribution, and therefore the effectiveness of this particular location to reflect focusing of contaminated sediment and the depth of the mixed layer, is already known. This arrangement will provide materials that are already known to reflect significant focusing and permit the timely start for the analysis of organics (and mercury) in the mixed layer during the first year of the study without having to wait for the evaluation of the samples from the new stations based on the EMAP grid. (The selection of stations will be arranged among the P.I.'s involved based on an analysis of both published and unpublished information).

Each retrieved box core, one per station, will be sub-sampled to provide 4 - 10 cm diameter cores using best practices to prevent core shortening. The disposition of these cores will be as follows:

**Sub-core 1** This core will be sectioned at 1 cm intervals to the bottom and the samples analyzed for water content,  $^{137}\text{Cs}$ , and  $^{210}\text{Pb}$ , diatoms (EMAP) and mercury

**Sub-core 2** The core will be sectioned in a similar manner to the one above, frozen, and archived.

**Sub-core 3 and 4** These cores will be sectioned in 1 cm intervals and combined in order to provide sufficient sample for the analysis of the organic compounds included in the Lake Michigan Mass Balance Program.

## Sediment Resuspension

### ***3. quantifying the resuspension of sediments,***

The sediment-water exchange component is critical and all current approaches to quantifying sediment resuspension are imperfect. To add confidence to these estimates, three approaches will be taken:.

- a. Laboratory flume measurements of sediment resuspension potential or initiation velocity have been made and will be continued. Undisturbed cores will be collected and limited measurements will be made. These would be useful in constraining any modeling.
- b. In-situ flume measurements of sediment resuspension will be made at several locations in sediment depositional areas.
- c. In-situ time series of light transmission (calibrated to TSS) and current velocity provide the only direct evidence of resuspension events. Vertical arrays of transmissometers and sediment traps (which passively sample the settling particle pool) can provide information on the vertical extent of the bottom nepheloid layer during the stratified period and directly measure the resuspended particle flux during the period when the lake is well-mixed. Sites will be located near water column master stations. The quantity of resuspended sediment in traps can be estimated by measuring their <sup>137</sup>Cs activity. This tracer is all sediment associated and virtually all <sup>137</sup>Cs in traps has come from sediment resuspension (Eadie et al., 1984).

Fine-grained sediments are transported primarily as suspended load, so once the material is in the water column a circulation model can be used to track the movement of the sediment, but determining under what conditions the sediment is deposited or eroded is considerably more difficult. This effort will consist of field measurements designed to establish the conditions necessary for the resuspension of fine-grained bottom sediments in Lake Michigan and to assess the relative importance of local resuspension versus advective processes in the deeper parts of the lake.

- (a) Instrument platforms have been deployed at various locations in the lake. The platforms support sensors that measure water temperature and water transparency at several heights above the bottom, as well as current velocity and water depth. The attached Table 6 shows the positions of the sensors at the three stations deployed for the winter on October 31, 1994. For logistical reasons the three tripods were deployed near Muskegon, MI in water depths of 30, 58, and 100m along a transect running from Muskegon harbor to Brian Eadie's sediment trap station. The 100m station is near Brian Eadie's set of sequencing traps, while the shallower stations will allow the observation of both the changes in conditions with depth and the amount of cross-shelf transport. Weekly vertical temperature and transmissometer profiles taken during the summer, 1995, will be used to correct the time series measurements for any fouling that may occur, and to assess the representativeness of the

observations. Beginning May 1995, the tripods will be serviced at approximately 4 week intervals until October 1995, so that a full year of data is collected. Supporting weather data will be obtained from NOAA's NOMAD buoys and CMAN stations, and from the weather station established at NOAA's Muskegon facility.

Moorings have been deployed at three sites; the instruments at each site are at the following elevations above the bottom (in meters, mab). All instruments will sample for one minute every hour at one Hertz. The average of these measurements will be recorded. The current meters are electromagnetic (either Marsh-McBirney 585s, or Interocean S4s). Temperature measurements are made using YSI thermocouples. Water transparency measurements are made using either Sea Tech transmissometers (25 cm pathlength) or Sea Tech light-scattering sensors. Paroscientific pressure sensors are being used to record water depth.

Table 6. Sensor Array Information

<u>Height (mab)</u>	<u>Station 24 (30m)</u>	<u>Station 27 (58m)</u>	<u>Station 19 (100m)</u>
0.5	Current velocity Temperature Water depth	Current velocity	Current velocity
0.9	Water transparency Temperature	Water transparency Temperature	Water transparency Temperature
1.1		Water depth	Water depth
7	Water transparency Temperature	Water transparency Temperature	Water transparency Temperature
17	Water transparency Temperature	Water Transparency Temperature	Water transparency Temperature
35		Current velocity Water transparency Temperature Water depth	Current velocity Water Transparency Temperature
65			Current velocity Water transparency Temperature Water depth

(b) Data from the tripods will be augmented by measurements from a bottom-resting flume. This device allows in-situ measurements of the critical velocity required for erosion by creating a controlled flow across the bottom and monitoring when sediment resuspension occurs (Hawley, 1991). Using this device will allow the critical erosion velocity to be measured at a large number of sites in a relatively short time. Deployments will first be made at the tripod sites so that the flume results can be compared to naturally- occurring erosion events.

Once this is done the flume can be used at other sites in the lake, so that the erosion velocity of different sediment types can be determined. Box cores will also be taken at each site where the flume is deployed in order to determine the sediment properties. These will include porosity and grain size.

## Contaminant Distribution Coefficients

### ***4. the distribution coefficients and bioavailability of the target contaminants in mixed-layer sediments,***

The coupling of a physical sediment model with concentrations of contaminants associated with sediment particles will provide an estimate of the sediment-water exchange of persistent hydrophobic contaminants. Equilibrium phase distribution coefficients are available for the PCBs from the Green Bay monitoring program (DiPinto et al., 1991). other Great Lakes field measurements (Baker et al., 19xx) and from laboratory experiments (Eadie et al., 1990). Attempts to measure distribution coefficients for phytoplankton were pioneered as part of the Green Bay Mass Balance Study and are continuing for Lake Michigan.

## Downward Flux of Sediments and Contaminants

### ***5. the gross downward sediment and associated contaminant flux***

The objectives of this effort are:

- a) to measure the gross downward fluxes of particulate material and organic carbon and
- b) to collect samples of the resuspendable pool of materials in regions of the lake where modern sediments do not accumulate and
- c) to provide samples of these materials for target compound analysis.

In the Great Lakes, as in most aquatic systems, the rapid and efficient processes of sorption and settling scavenge contaminants from the water column with the result that the largest fraction of persistent trace contaminant inventories reside in sediments. However, studies of the long-term behavior of certain fallout radionuclides and stable contaminants in the Great Lakes have shown that higher levels persist in the lakes than expected if settling and burial were the sole transport process. Materials return from sediments due primarily to resuspension. Constituents initially transferred to sediments are homogenized via bioturbation creating a mixed layer corresponding to a decade or more of accumulation. These are resuspended back into the water column during the isothermal period and are available for uptake by pelagic biota. It is now accepted that the internal recycling caused by the coupled processes of bioturbation and resuspension is responsible for the continuing elevated concentrations of trace contaminants (e.g. PCB, DDT) in fish and the lag in lake response to nutrient abatement.

Since 1977, GLERL has been examining the processes of particle flux and resuspension through the use of sediment traps, passive cylinders deployed to intercept materials settling to the bottom. Traps provide an efficient tool for the collection of integrated samples of settling materials for detailed analysis. Measuring



the mass collected allows us to calculate the gross downward flux of particulate matter and associated constituents and to calculate settling velocities.

Twelve traps having sequencing capability for multiple samples per deployment, (autosequencing sediment traps) will be deployed with eight in four 2 trap arrays (5m above bottom, and 30m below surface). The remaining 4 traps will be deployed at 5m above bottom in regions of the lake that do not accumulate recent sediments and are not suitable for coring. These will provide samples of the mobile pool of particulate matter in the benthic nepheloid layer, materials resuspended during the unstratified period and materials settling out of the epilimnion during stratification. **Figure 7** shows trap locations and the attributes of the selected stations are listed in Appendix 7.

For this project, the samplers will be programmed as described in Appendix 7. The simpler design is also an 8" diameter, but only has 10 sample capacity with a programmable, but constant, collection time. This will be set to 30 days until mid-June, 1995 when they will be retrieved and redeployed for ten, consecutive, 15 day collections. There will be traps located at 5m above the bottom at all 8 stations. These will sample the mobile (resuspendible) sediments on 15-30 day intervals. In addition, there will be traps at 30-35m below the surface at stations 5-8. These traps will sample resuspended materials during the unstratified period and material settling through the thermocline during the stratified period. The mass, carbon and contaminant fluxes determined by this sampling will be directly incorporated into the model.

The sample locations in **Figure 7** and Appendix 7 were selected to meet a number a criteria established in meetings/discussions with modelers, the sediment workgroup, and others with a technical interest in this part of the LMMB program. Samples were desired that would provide information on: the mobile sediments in the areas of the lake not presently accumulating sediments (sta 1-4) and therefore not good candidates for coring as well as the following particular reasons:

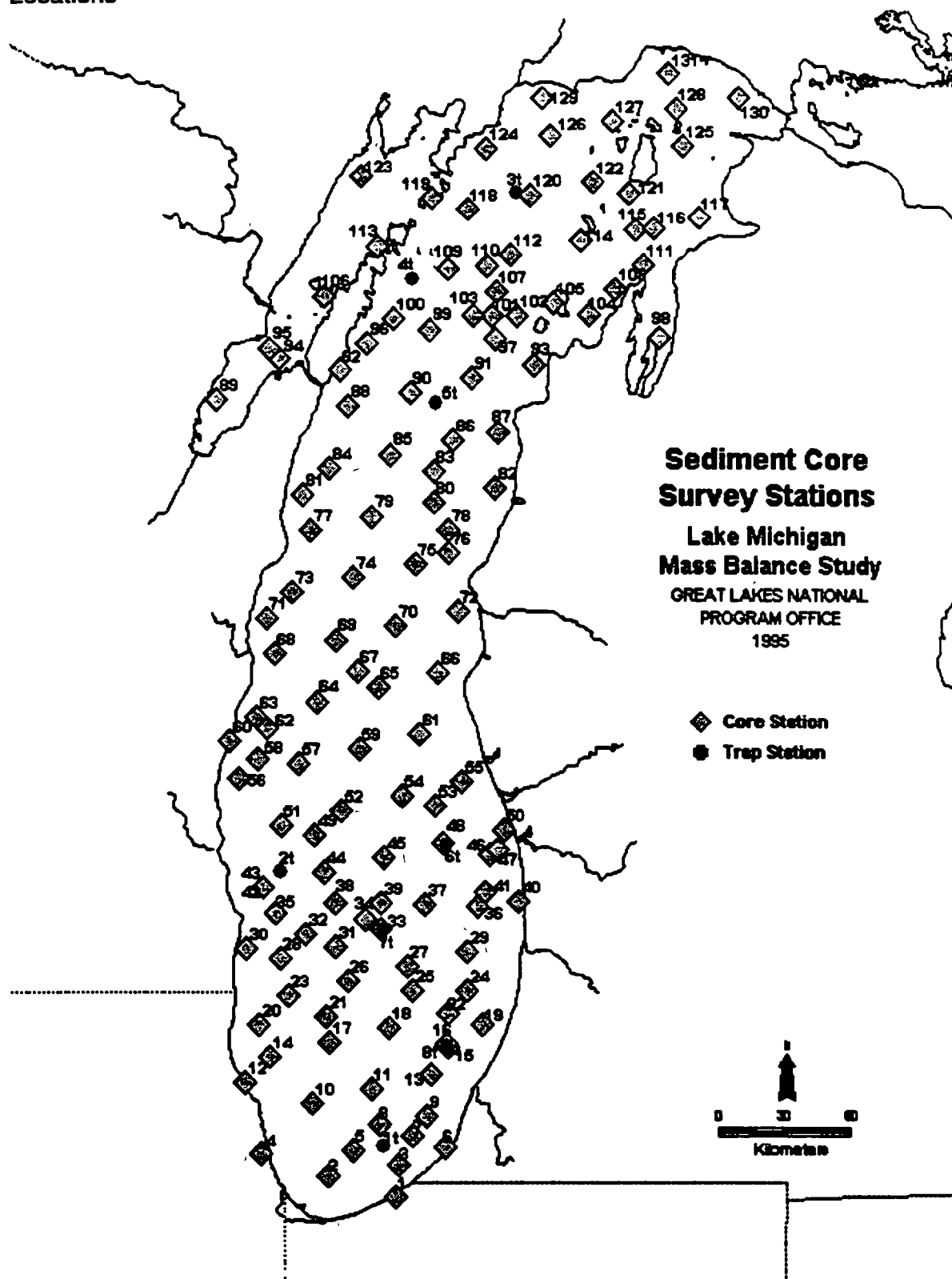
- a site off Chicago which should intercept materials from that urban source. This site also was selected because of the high concentration of PCB observed by Swackhammer and Armstrong (1986);
- the region off Milwaukee (sta 2) which should intercept some of the bluff erosion that is the major source of particulate material to Lake Michigan;
- a site at the major outflow of Green Bay which should intercept materials from that source;
- sites (sta 5-7) coincident with LMMB water column master stations;
- sites that have some former trap data (see Appendix 7);
- the area of maximum deposition (sta 8) where satellite imagery has shown regular intense spring plumes

Assuming all of the traps operate properly and are retrieved, there will be a total of 270 samples collected. Upon retrieval, the samples will be split and known portions will be made available for target organic compound (Pat Van Hoof) and total mercury (Ron Rossmann) analysis. A third portion will be allowed to settle, the overlying water siphoned off and the slurry will be freeze dried in an ultra clean freeze drier. Samples will be weighed and fluxes calculated. Finally, organic carbon will be measured on each sample as a surrogate for HOC. The remaining materials will be stored frozen at NOAA's Great Lakes Environmental Laboratory or at EPA's Large Lakes Research Station.

***6. the dissolved and DOC bound contaminant sediment-water exchange.***

These values will be estimated based on literature review. No additional effort is anticipated in this area.

Figure 7. Sediment and Sediment Trap Sampling Locations



## **ACTIVE POOLS**

### **OPEN-LAKE WATER COLUMN STRATEGY**

#### **Introduction**

Water column samples in the open lake will be collected and analyzed to produce the calibration data base for the water column portion of the mass balance model. The open lake data for the chemicals selected for mass balance will be critical for the transport and hydrodynamic model components. The sampling plan for the open lake will consider both nearshore and offshore areas, and the water column will be resolved both horizontally (spatially) and vertically (with depth). The working definition of nearshore for this study is based on the movement of bottom sediments by wave action. A guideline of 25-30 meters depth will be used for distinguishing nearshore and offshore.

#### **Parameters and Methods**

The parameters to be monitored in the water column are listed in Table 7. Some samples, such as large-volume hydrophobic organic contaminant (HOC) samples, will be taken as operationally-defined dissolved and particulate phases. The dissolved phase will be that portion of a water sample that passes through a 0.7 micron GF/F glass fiber filter, and the particulate phase will be the material that is retained on the filter. Particulate-phase organic carbon (POC), dissolved-phase organic carbon (DOC), and total suspended solids (TSS) will be sampled along with the large-volume samples. All filtered organic parameters will be sampled with the same type and pore size filter for consistency. Nutrient concentrations and traditional water quality parameters, such as pH and alkalinity, will be monitored in addition to targeted pollutants for mass balance. Nutrient data are required for the development of the eutrophication model. In addition, conductivity, temperature, and depth (CTD) profiles for each sampling station will be obtained by over-board casts (*i.e.*, with a Seabird). Casts using transmissometry and fluorometry will be used to observe water column profiles of suspended solids and chlorophyll.

Specific details of sampling and analytical chemistry are covered in the Quality Assurance Project Plans (QAPjPs) and Standard Operating Procedures (SOPs) that will be used for the mass balance. The SOPs and the QAPjPs are initially based on the procedures and quality assurance/quality control measures that were used in the Green Bay Mass Balance Study (Swackhamer, 1988), and they are developed by the principal investigators (PIs) involved in the study. Overall, the SOPs are a combination of "cook-book" methods, such as the filtering of total suspended solids (TSS), and performance-based methods, such as the congener-specific analysis for PCBs. It is important to emphasize uniformity of sampling and analytical procedures where possible. For that reason, XAD-2 resin will be used to pre-concentrate dissolved-phase target HOCs, which are PCBs and *trans*-nonachlor. This is consistent with the sampling procedures for the tributary dissolved-phase and atmospheric vapor-phase samples. Open-lake, dissolved-phase water samples will be obtained by passing the sample filtrate through XAD-2 resin columns. The resin column volume will be on the order of 600 cubic centimeters of resin. This relatively large volume of resin is used to allow sampling flow

rates in the range of 1 liter per minute and to prevent sample breakthrough. Typical dissolved-phase sample volumes will be in the range of 200 to 300 liters. Particulate-phase sample volumes will start at 400 liters and are scaled up from there, depending on the in-lake concentrations of suspended solids and analytical requirements. Samples for dissolved-phase and particulate-phase PCBs and *trans*-nonachlor will be analyzed by gas chromatography (GC) with electron-capture detection (ECD).

Atrazine and its two major degradation products, de-ethylatrazine (DEA) and de-isopropylatrazine (DIA), will be sampled using solid-phase extraction (SPE) with analysis by gas chromatography/mass spectrometry (GC/MS) with selected ion monitoring (SIM). There is evidence that atrazine exists primarily (95%) in the dissolved phase in surface waters (Thurman, et. al., 1992). So, the measurement of atrazine and its major degradation products will be focused on the dissolved phase. Water samples for atrazine, DEA, and DIA will be taken separately from those for PCBs and *trans*-nonachlor. The sample volume for atrazine will be in the range of 2 to 3 liters due to breakthrough problems on SPE cartridges. (Thurman, et. al., 1990). Also, atrazine is not amenable to a full mass balance because it is not measurable in all media, such as fish tissue. Thus, a bioaccumulation model is not possible. However, it is expected that a water column mass balance model is attainable.

### **Sampling Site Selection**

The data quality objectives (DQOs) for the open-lake water column are based on the best sampling techniques and analytical chemistry available. A combined sampling and analytical uncertainty of  $\pm 20$ -30% at 90% confidence is the goal of this component of the mass balance. There are currently few open-lake data on HOCs in the open lake (Swackhamer and Armstrong, 1987; Lefkowitz, 1987; Pearson and Swackhamer, 1993; Anderson, 1994). Therefore, surrogate parameters, such as solids concentrations, were used to determine the number of open-lake sampling stations that are required to meet the DQOs. Solids data from approximately 100 stations in 1976-1977 were used (Rockwell, et. al., 1980).

There are 41 sampling stations. Ten of these stations are identified as master stations where increased resolution sampling will strengthen the calibration data set. The sampling station locations are shown in Figure 8. There is a need to have both nearshore (water depth < 25-30 meters) and offshore stations in order to characterize contaminant concentration gradients, as well as in-lake processes, such as the occurrence of the thermal bar. With regard to thermal profiles, remote sensing data for temperature is planned to augment the ship survey data. This satellite data will be ground-truthed. In summary, the focus of station location will be on measuring the concentration gradients.

Other aspects of the station location rationale can be summarized. The offshore stations were selected near existing GLNPO monitoring stations, when possible. One master station was located in Green Bay, while two of the Lake Michigan master stations correspond to existing NOAA weather buoys. The master station off of Grand Haven, Michigan is a NOAA Great Lakes Environmental Research Laboratory (GLERL) station that has several years of existing suspended solids data, as well as other parameters. The non-master stations have been located near some of the monitored

tributaries, as well as at sites away from tributaries. The two Green Bay passages with the highest transport of solids are chosen, as well as one site in the Straits of Mackinaw.

The vertical resolution at the sampling stations will vary. During non-stratified periods (isothermal), a mid-water column depth will be used. Water-column transparency profiles will be used to identify any additional vertical resolution which may be needed. During stratification, all stations will be sampled at the mid-epilimnion and at a depth in the hypolimnion that corresponds to the median particle mass, as measured by transmissometry. Continuous monitoring devices will also be used in some cases to measure the transport of solids.

The proposed master stations are identified in **Figure 8**. The master stations will be sampled at two additional depths during stratification. When they occur, the deep chlorophyll layer (DCL) and the benthic nepheloid layer (BNL) will be located using fluorometry and transmissometry, respectively, and sampled for all parameters. Care must be taken to sample the BNL without disturbing and/or sampling the bottom sediments. Because of uncertainties involved with sampling the BNL from a ship platform, the BNL has been identified as a research area. The BNL may not always exist at the master stations, and it may also occur during non-stratified periods (Hawley and Lesht, 1993). Transmissometry will be critical for detection of the BNL. Investigation of the short-term variability of the BNL using transmissometry casts is planned. Nearshore master stations have been ruled out, based on the working definition of nearshore as 25-30 meter depth.

During implementation of this plan, it will be important to coordinate the water column sampling with sampling for atmospheric contaminants, as well as with phytoplankton and zooplankton sampling. The air/water exchange flux calculations will depend upon a close synchronization of the measurement of the contaminants in the two media. The logistics for performing these tasks have been considered. The emphasis at this point is that all field data must be collected in the same yearly hydrologic cycle, and for open water components, comprehensively during each survey. At a minimum, seasonal coordination is needed for the open lake and tributary monitoring. There are nearshore open-lake stations located near the mouths of some of the monitored tributaries (**Figure 8**) as mentioned above. Also, the open lake water and plankton sampling should be coordinated temporally and spatially.

The fluxes of contaminants to/from Green Bay will be determined. The horizontal and vertical resolution needed to accurately measure this flux will be estimated based on transmissometry data. A master station in Green Bay will also be monitored. Data from these stations will be used in conjunction with the Green Bay Mass Balance Study model to determine the Green Bay/Lake Michigan fluxes. The fluxes at the Straits of Mackinaw will be investigated using acoustic Doppler current profilers (ADCPs), if the procurement and budget constraints of the program will allow it. It has been noted that the flux from Green Bay is a more critical parameter than the flux through the Straits of Mackinaw.

## **Sampling Schedule**

The limnological cycle will be the basis for the temporal aspects of the sampling plan. The planned number of lake surveys is 4 in 1994, and 3 in 1995. The first survey during each year will be at the earliest "ice out" in the late Winter or early Spring. The second survey in 1994 should capture the lake in early stages of stratification (late Spring). Surveys in the late Summer or early Fall, 1994, and perhaps 1995, and late Fall surveys in 1994 and 1995 to measure the lake at late stratification round out the seven major surveys. The scope of the late Summer/early Fall survey in 1995 is under discussion at present. The rationale for these time frames is the need to capture lake events as accurately and precisely as possible. The depth of the thermocline and the occurrence of overturn are key variables. Previous GLNPO surveys indicate that Lake Michigan does not turn over until the middle or end of December. A Winter survey, of limited spatial coverage, may be included if conditions are such that it is safe to sail. Finally, it will be important to capture Spring run-off for atrazine due to its present application schedule.

## **Open-Lake Water Column Research Areas**

The benthic nepheloid layer (BNL) is an area of research. Important questions include:

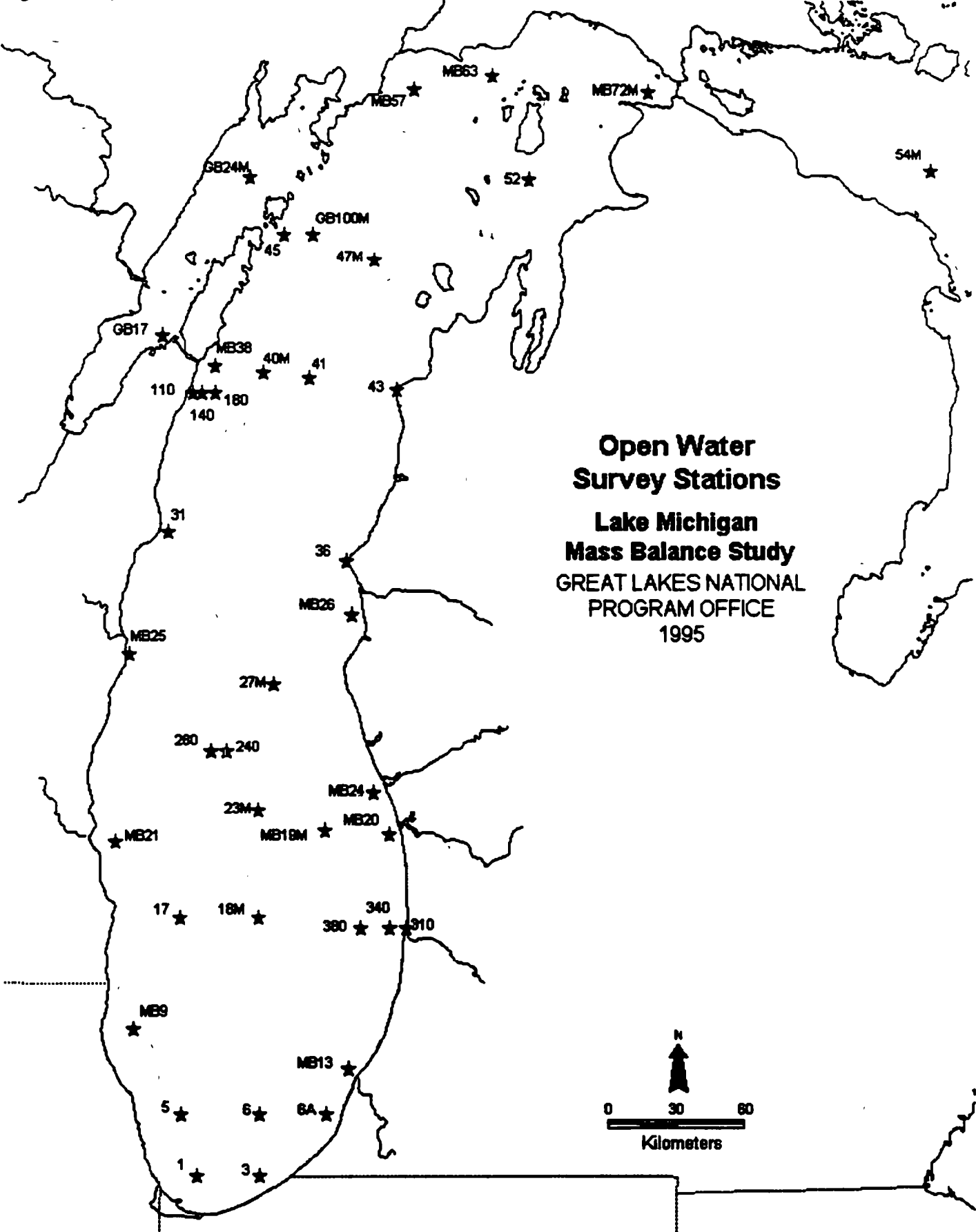
1. How accurately can we measure contaminant concentrations in the BNL?
2. How accurately can we measure particle transport in the BNL?
3. How is the BNL/food chain connection to be quantified/estimated?
4. How important is the BNL in the offshore transport of particles?
5. What is the short-term variability of the BNL?

Table 7. Variables to be Measured						
Variable	Atmosphere			Lake	Tributaries	Sediments
	wet	dry	gas			
Diss. PCB	X	na	na	X	X	
Part. PCB	na	X	na	X	X	X
Vapor PCB	na	na	X	na	na	na
Dis. nonachl	X	na	na	X	X	na
Part. nonachl	na	X	na	X	X	X
Vapor nonachl	na	na	X			
Diss. Atrazine, DEA, DIA	X	na	na	X	X	na
Part. Atrazine, DEA, DIA	na	X	na	X	X	X
Vapor Atrazine, DEA, DIA	na	na	X	na	na	na
Diss. Hg	X	na	na	X	X	na
Part. Hg	na	X	na	X	X	na
Vapor Hg	na	na	X			
Total P	X	X	na	X	X	X
Nitrate	na	na	na	X	X	X
Ammonia	na	na	na	X	X	X
TKN	X	na	na	X	X	X
Diss. Si	X	na	na	X	X	na
Chloride	X	X	na	X	X	X
DOC	na	na	na	X	X	na
POC	na	na	na	X	X	na
TOC	X	X	X	na	na	X
Conductivity	X	na	na	X	X	na
SPM 0.7µm	X	na	X	X	X	na
Temperature	na	na	na	X	X	na
Chlorophyll a	na	na	na	X	X	na
Diss. Oxygen	na	na	na	X	X	na
pH	X	na	na	X	X	na
Alkalinity	X	na	na	X	X	na
Incid. Solar Radiation				X	na	na
Light Extinction				X	na	na
Porosity				na	na	X
% Water				na	na	X
% Solids				na	na	X
Redox. Potent.				na	na	X

All filterables at 0.7µm, Whatman GF/F filters.



Figure 8. Open-Lake Sampling Station Locations



## BIOLOGY

### **Summary of Biology Data Needs and Sampling Approaches**

Three of the five Management Objectives presented in the Introduction to this Work Plan directly involve the biota:

- to develop the predictive ability to determine the environmental benefits (i.e., reductions in fish tissue concentrations) of specific load reduction scenarios for toxic substances and the time required to realize those benefits (i.e. trend analysis of organic contaminants in fish);
- to develop the ability to evaluate the environmental benefits (i.e. reductions in fish tissue concentrations) of load reductions for toxic substances that will occur under existing environmental statutes and regulations; and
- to improve our understanding of key environmental processes which govern the cycling and *bioavailability* of contaminants within relatively closed ecosystems.

To achieve these objectives, a food web model will be constructed and calibrated for predicting the total body burden of the target contaminants in representative fish species. The model will be linked to the physical-chemical model for Lake Michigan.

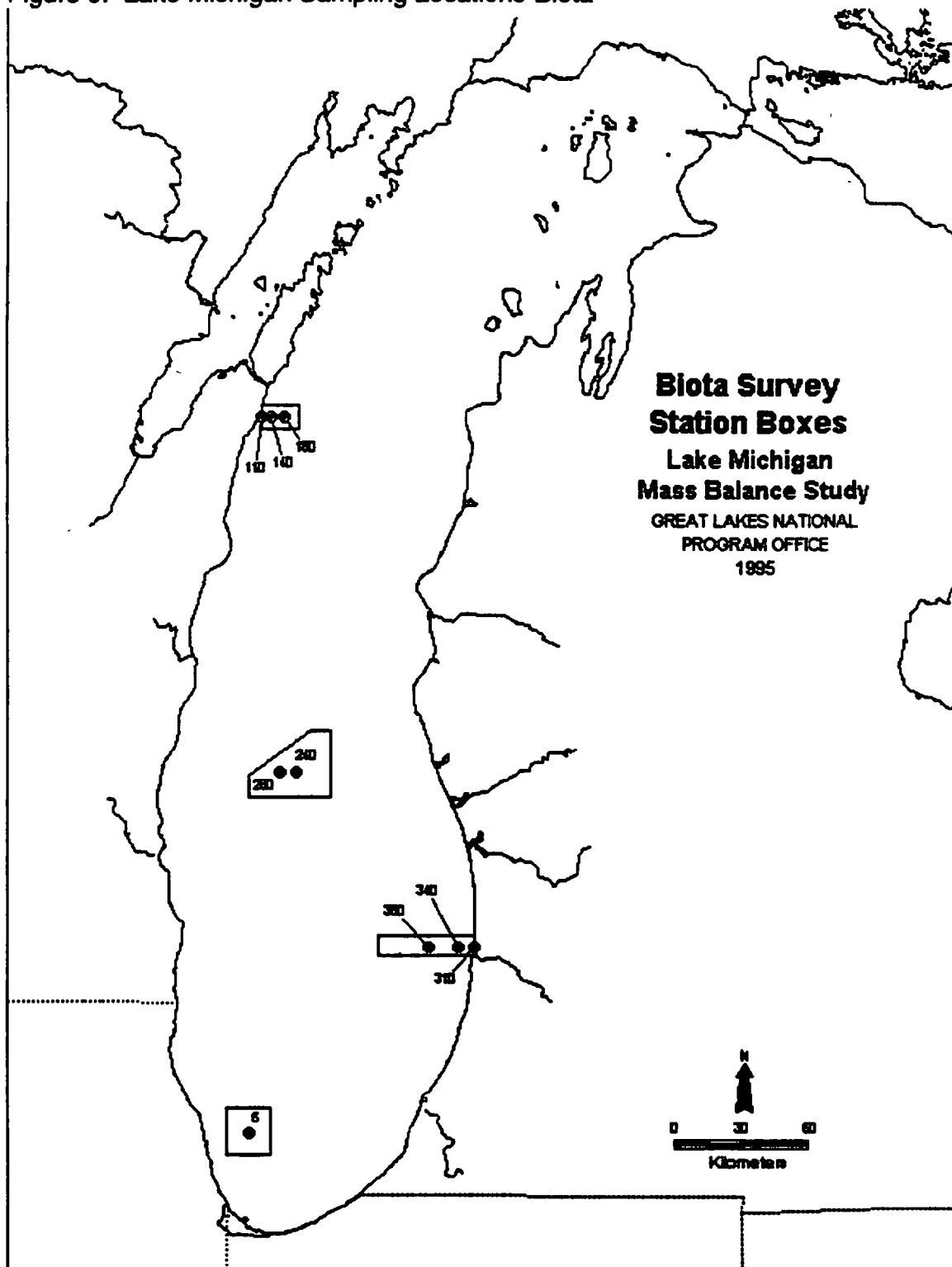
The food web model is intended to predict the concentration of the target chemicals (PCBs, *trans*-nonachlor, atrazine) in the fish species of interest (lake trout, coho salmon, bloater chubs) as a result of contaminant concentrations in the water column. The results for each species will be dependent on the size or age class of the species being modeled, concentrations of contaminants in the water, food chain dynamics, and other seasonally-varying factors that influence the exposure history of the target species. For example, diet studies indicate that in Lake Michigan coho salmon consume primarily alewife and some invertebrates, while the diet of lake trout is more diverse, consisting of alewife, bloater chub, rainbow smelt, sculpin species, *Diporeia* spp., and *Mysis relicta*. The relative percentage and amount consumed of each forage species in the lake trout coho salmon diets vary, however, between seasons and between different geographic locations in Lake Michigan. In order to adequately model the flow of contaminants from the water through each of the target food chains, data are needed for each of the listed components of the food chains for each representative area of Lake Michigan for different seasons.

Each of the named species and groups will be collected concurrent with the early spring, midsummer and late fall surveys of the open water column. Phytoplankton and zooplankton will be collected at some of the open water sites. Fish collections will be primarily at three selected locations for the lake trout food chain, i.e., the so-called "biota boxes" near Saugatuck, MI, the mid-lake reef near Port Washington, WI, and near Sturgeon Bay, WI (Figure 9). Coho salmon collection sites will vary seasonally. *Diporeia* and *Mysis* will be collected within the lake trout collection areas and at one additional site northeast of Chicago, IL. Phytoplankton and zooplankton will be collected at the biota box stations and at some of the open water master station sites.

In addition, studies will be conducted to further define and quantify food web interactions. An analysis of the stomach contents of lake trout, coho, bloater chub and the forage fish species will elucidate the diet of these fish, including quantity, species consumed and seasonal changes. Phytoplankton and zooplankton species composition, abundance and biovolume will be determined the biota box sites and at the open water master stations to support refinements in the modeling of food web interactions at the lower trophic levels.

A **Data Requirements** matrix is presented in Table 8 which displays for each species and group the specifications for age and size, the seasons to be collected, the location of sampling sites, requirements for coordination with other data elements, and a reference to a list of measurements to be obtained from each sample. A listing of the parameters to be measured for each data group is displayed in Table 9, **Biology Measurements and Data Groups**.

Figure 9. Lake Michigan Sampling Locations-Biota



**TABLE 8. BIOLOGY DATA REQUIREMENTS**

BIOTIC ELEMENT	SPECIFICATIONS		SEASONS <sup>1</sup>			LOCATION OF SAMPLING <sup>2</sup>	SAMPLING COORDINATION	NOTES
	Age/Size	Data <sup>3</sup> Group	SP	SU	FA			
Lake Trout	2-4 yr, 300-550 mm	A	XX	X	XX	Saugatuck; Sturgeon Bay; Port Washington	Forage fish assessment	
	5-7 yr, 600-700 mm	A	XX	X	XX	Saugatuck; Sturgeon Bay; Port Washington	Forage fish assessment	20 yr trend data available
	8-10 yr, 725-800 mm	A	XX	X	XX	Saugatuck; Sturgeon Bay; Port Washington	Forage fish assessment	
Coho salmon	17 months, hatchery	B	XX			Platte River hatchery, Michigan		Prior to release into Lake Michigan
	1+ yr	A			XX	Platte River, Kewaunee River, Southeast and Southwest Lake Michigan	Forage fish assessment: alewife	Follow coho migration
	2+ yr	A	XX			Southeast and Southwest Lake Michigan	Forage fish assessment: alewife	Follow Coho migration
	2+ yr	A		X		East-central and West-central Lake Michigan	Forage fish assessment: alewife	Follow Coho migration
	2+ yr	A			XX	Near Platte River and Kewaunee River	Forage fish assessment: alewife	Follow Coho migration, Beginning of fall run at the weirs
Bloater Chubs	0-2 yr < 150 mm	B	XX	X	XX	Saugatuck; Sturgeon Bay; Port Washington	Lake trout assessment	
	4+ yr > 200 mm	A	XX	X	XX	Saugatuck; Sturgeon Bay; Port Washington	Lake trout assessment	If collect larger fish, analyze as older age, but not available to lake trout
Alewife	60-120 mm	C	XX	X	XX	Saugatuck; Sturgeon Bay; Port Washington	Lake trout, coho assessment	
	120+ mm	C	XX	X	XX	Saugatuck; Sturgeon Bay; Port Washington	Lake trout, coho assessment	
Smelt	>100 mm	C	XX	X	XX	Saugatuck; Sturgeon Bay; Port Washington	Lake trout, coho assessment	

<b>Sculpin</b>	<b>Slimy</b>	<b>C</b>	<b>XX</b>	<b>X</b>	<b>XX</b>	<b>Saugatuck; Sturgeon Bay; Port Washington</b>	<b>Lake trout assessment</b>	
	<b>Deepwater</b>	<b>C</b>	<b>XX</b>	<b>X</b>	<b>XX</b>	<b>Saugatuck; Sturgeon Bay; Port Washington</b>	<b>Lake trout assessment</b>	
<b><i>Mysis</i></b>	<b>mixed</b>	<b>D</b>	<b>XX</b>	<b>XX</b>	<b>XX</b>	<b>Saugatuck; Sturgeon Bay; Port Washington; Chicago</b>	<b>Water sampling for organics</b>	<b>Benthic trawl near water stations in biota boxes</b>
<b><i>Diporeia</i></b>	<b>mixed</b>	<b>D</b>	<b>XX</b>	<b>XX</b>	<b>XX</b>	<b>Saugatuck; Sturgeon Bay; Port Washington; Chicago</b>	<b>Water sampling for organics</b>	<b>Benthic trawl near water stations in biota boxes</b>
<b>Zooplankton, mixed</b>	<b>mixed</b>	<b>E</b>	<b>XX</b>	<b>XX</b>	<b>XX</b>	<b>Saugatuck; Sturgeon Bay; Port Washington; Chicago</b>	<b>Water sampling for organics</b>	<b>Collect at water stations in biota boxes</b>
<b>Phytoplankton, mixed</b>	<b>mixed</b>	<b>E</b>	<b>XX</b>	<b>XX</b>	<b>XX</b>	<b>Saugatuck; Sturgeon Bay; Port Washington; Chicago</b>	<b>Water sampling for organics</b>	<b>Collect at water stations in biota boxes</b>

<sup>1</sup>X = 1994 only, XX = 1994 + 1995

<sup>2</sup>Biota Box Areas are designated Saugatuck, Sturgeon Bay, Port Washington and Chicago.

<sup>3</sup>Refer to the Table 9 Biology Measurements and Data Groups for a list of data elements to be measured for each Data Group

**Table 9. BIOLOGY MEASUREMENTS AND DATA GROUPS**

MEASUREMENT	DATA GROUP				
	Group A	Group B	Group C	Group D	Group E
<b>FIELD SAMPLES</b>					
Concentration of contaminant in COMPOSITE WHOLE FISH WITHOUT STOMACHS	X	X			
Concentration of contaminant in COMPOSITE WHOLE FISH INCLUDING STOMACHS			X		
% lipid in sample	X	X	X	X	X
Sex of fish	X	X	X		
Age of fish	X	X	X		
Length of fish	X	X	X		
Weight of fish	X	X	X		
Concentration of contaminant in non-fish biomass				X	X
Biomass of sample				X	X
% moisture in sample	X	X	X	X	X
Gut contents	X	X	X		
Species identifications					X
Species abundance and biovolume					X
<b>LAB STUDIES - LITERATURE or CALCULATED VALUES</b>					
Rate of uptake of contaminants from water (through gills or whole organism)	X	X	X	X	X
Rate of uptake of contaminants through food ingestion	X	X	X	X	X
Respiration rate	X	X	X	X	X
Elimination rate	X	X	X	X	X
Exposure to contaminants in food	X	X	X	X	X
Exposure to contaminants in water	X	X	X	X	X
Growth rate	X	X	X	X	X
<b>LAB STUDIES REQUIRED TO BETTER ESTIMATE MODEL VARIABLES</b>					
Contaminant assimilation through gut wall	X	X	X		
Back excretion of contaminant through gut wall	X	X	X		
Contaminant uptake across gill	X	X	X		
Contaminant loss across gill	X	X	X		
Variability of contaminant concentration between individual fish	X				

Group A	Lake trout; coho salmon from Lake Michigan; bloater chubs > 200 mm
Group B	Bloater chubs < 150 mm
Group C	Alewife; smelt; sculpin; coho salmon from hatchery(except no gut content analysis)
Group D	<i>Mysis</i> ; <i>Diporeia</i>
Group E	Zooplankton (Cladocera); phytoplankton



## **Sampling Locations**

**Lake trout and forage fish.** Three geographic areas of Lake Michigan will be sampled for lake trout, bloater chubs, alewife, smelt and sculpins (Figure 9). Each area is expected to contain trout populations representative of different habitat and food chain characteristics. Trout from an area east of Sturgeon Bay, WI., will represent northern, nearshore conditions. Those from the mid-lake reef east of Port Washington, WI., will be typical of those from deep water populations, and those southwest of Saugatuck, MI., will represent nearshore, southern basin fish. The bloater chubs and forage fish species will be collected from within the same biota box areas as for the lake trout.

**Coho salmon.** Sampling locations for coho salmon were selected to follow the typical seasonal migration of planted coho. Spring sampling will be conducted in the southeastern region near St. Joseph, Mi., and in the southwestern region near Waukegon, IL. Young coho also will be collected directly from the Platte River hatchery, where the majority of coho are raised or originate. Mid-summer sampling will be conducted in both the east central and west central regions of the lake. Late fall sampling will be conducted to coincide with the fall spawning run up Lake Michigan tributaries. Collections will be made from the returns of mature coho (both age 1+ and 2) to rivers from two general regions of the lake: the northeastern side in the vicinity of the Platte River, and the western side in the vicinity of the Kewaunee River. Fall collections will also be made of immature coho from the southeastern and southwestern regions of the Lake.

***Mysis* and *Diporeia*.** These crustaceans will be collected by bottom trawls within each of the lake trout biota box areas. Collections will be made in the vicinity of 40m and 80m depths in each of the biota boxes and at station No. 5 near Chicago. Biota box stations at 10m generally are too dynamic (wave action) or warm to support large populations of these macroinvertebrates.

**Zooplankton and phytoplankton.** These trophic levels will be collected for analysis of contaminant concentrations at each of three stations within the biota boxes and at station 5 near Chicago. The stations will be located at 10m, 40m and 80m depths. Phytoplankton and zooplankton will also be collected for quantitative analysis of species identification, abundance and biovolume at each visit to the 9 biota box stations and to the 10 open water master stations. *Bythotrephes* will be collected when abundant during sampling operations for the predator and forage fish.

**Primary productivity.** The rate of fixation of carbon by algal populations, i.e., primary productivity, will be determined by ship-board incubations using the radiotracer C14 at each visit to the 9 biota box stations and to the 10 open water master stations.

#### **Sampling Schedule**

Fish, invertebrates and phytoplankton will be collected at each of the designated sites during three (3) seasons: early spring, midsummer, and late fall. The invertebrates and phytoplankton will be sampled at the same time as the corresponding open water survey for organic contaminants. Collections of fish will be conducted at approximately the same time, but not necessarily coincidental with the surveys for organics contaminants, invertebrates and phytoplankton. Given that fully successful collections of biota can be obtained during the first field season, some reduction of effort can be achieved if a second field year is required. In that case, fish collections would be conducted during the spring and fall seasons, but the lower food chain components would continue to be collected during all three seasons.

#### **Quantity or Biomass of Samples**

Quantitative data on the spatial and temporal variability of organic contaminants in the designated trophic levels in Lake Michigan are not currently available. Experience gained from the GLNPO monitoring program for fish contaminants and from the results of the Green Bay Mass Balance Study have been used to design the following sampling guidelines.

#### **For Contaminant Analysis:**

**Individual fish:** 25 specimens per age grouping per site (biota box) per season, e.g., 25 lake trout in each of age groupings 2-4 yr, 5-7 yr and 8-10 yr; 25 bloater chubs in each age group 0-2yr, 4+yr; etc.

**Composite fish samples:** 5\_ composite samples per age grouping per site (biota box) per season, each consisting of 5 fish. However, each composite will contain only fish of the same age, e.g., 2 yr old, 3 yr old, etc. Some exceptions to the numbers of fish per composite may be made based upon availability of fish of certain ages or sizes.

***Mysis*, *Diporeia*, *Bythotrephes*, zooplankton (*Daphnia*), and phytoplankton:** 10 grams, wet weight (drained), per site (each station within the biota boxes) per season, without accompanying sediment and detritus. *Bythotrephes* may be abundant only in late summer or early fall. Ten percent of the samples will be collected in duplicate for quality control assessment. The required quantity of

biomass may change during the study depending on the concentration of contaminants found in the samples and on the sensitivity of the laboratory methodology.

For fish samples, the basic unit for analysis of chemical contaminants will be composites of 5 fish each. Five (5) such composites will be analyzed for each designated size class of each species from each biota box each season. Appendix 4 displays a summary of the number of organisms to be collected and the number of analyses to be performed for this study. Analysis of contaminants in individual fish is recognized to be preferred over the composite samples in order to assess the variability in contaminant burdens within each fish population of interest. However, if each fish were analyzed individually, 1350 analyses would be required for lake trout, coho and chubs alone! The analytical effort needed to accommodate that number of samples is beyond the scope of this project. Therefore, the composite fish sample approach appears to be a reasonable compromise. Supporting studies to estimate the variability in contaminant burdens among fish of similar age/size and collected from the same area at the same time will be conducted on a limited basis.

#### For Diet Composition

Quantitative data on the simultaneous diets of the predator fish (lake trout and coho salmon) and of the forage fish (bloater, alewife, smelt, slimy and deepwater sculpin) in Lake Michigan are not currently available. Specimens for diet analysis therefore will be taken concurrently with those for contaminant analysis. Twenty specimens will be collected per age group per site (biota box) per season, 10 of which will be analyzed for diet composition. If more than 3 of the 10 specimens in a forage fish group have empty stomachs, the other specimens will be analyzed. Because of the high percentage of empty stomachs usually found in the predator fish, all specimens of the predator fish will be analyzed. Each prey fish from a stomach will be identified to species, measured for total length if intact, and weighed. Innovative procedures, such as measuring vertebrae for conversion to total length, will be conducted for prey fish not intact. Invertebrate food items will be sorted into the lowest taxa practicable, and weighed in the aggregate. Then 10 individuals per taxon will be measured (total length) and converted to biomass based on regressions from the literature. Stomachs of prey fish are weighed before and after food items are removed to obtain total weight of prey eaten.

### **Sampling Methodology**

A brief summary of collection methods for each species and group follows:

<b>Lake trout.</b>	Gill nets
<b>Coho salmon.</b>	Hook and line, or state-operated hatchery and weir collections.
<b>Bloater chub.</b>	Trawling.
<b>Forage fish.</b>	Trawling.
<b>Benthic invertebrates.</b>	Bottom sleds, trawling.
<b>Zooplankton.</b>	Vertical net hauls.
<b>Phytoplankton.</b>	Pumping into stationary nets, with separation screening for zooplankton.

### **Additional Model Requirements**

Not all data inputs to a food web model will be determined from empirical field measurements. Although laboratory studies on some parameters would provide data to better define and reduce uncertainty in food chain bioaccumulation models (Thomann & Connally 1984; Endicott *et al.* 1992; Connally *et al.*, 1992), such research is beyond the scope of this project. Therefore, much of the data for physiological and ecological processes and for contaminant flux rates will be gleaned from the peer reviewed literature for Lake Michigan (first option), peer reviewed literature for other locations (second option), or from other reports and unpublished studies (third option). This approach will be taken to obtain values for:

- Rate of uptake of contaminants from the water through the gills (fish) or through the whole organism (invertebrates and algae).
- Rate of uptake of contaminants through food ingestion at each trophic level.
- Rate of elimination of contaminants from the organism
- Organism respiration rate
- Other factors related to organism exposure to contaminants through food (diet composition) and water
- Fish migration patterns
- Effects of compositing fish samples on estimates of mean and variance of contaminant concentrations

## **MERCURY**

Based upon a recommendation of the original Mass Balance Workshop, total mercury was agreed upon as a target analyte of the LMMB by the Steering Committee in November, 1993. Recognizing the difficulty of achieving modeling results at the level of accuracy expected for organic contaminants, we will attempt a less extensive data collection and modeling effort for mercury than for the organochlorine contaminants. A main difficulty in modeling mercury is the rudimentary state of knowledge of the processes and rates of conversion of mercury among its several forms, particularly its rate of uptake and transformation in biota. These are critical research questions which, unfortunately, are beyond the scope of the LMMBS.

As part of the Enhanced Monitoring Program, mercury was included as a target analyte in the original parameter list for tributary and atmospheric monitoring. It has received much attention in the Great Lakes Basin (Sills, et. al., 1992). As stated in the introduction, mercury is a pollutant of concern based on trends in loadings obtained from sediment cores from inland lakes, as well as fish tissue concentrations, which require consumption advisories in some inland waters. After some discussion of the utility and desirability of lead as a chemical for mass balance, and its eventual removal from the list, the workshop participants felt that there should be some effort made to obtain the data needed to for a Total Mercury mass balance model. This model would have less certainty associated with it than will the mass balances for the other chemicals, because sampling would occur at fewer locations in the Lake than for the other chemicals, and there are significant research questions to be answered before the rate and transfer functions needed for the models can be derived. Because of sampling requirements (clean techniques, clean rooms, etc.) and the cost of analysis, the inclusion of mercury as a mass balance chemical would require a considerable increase in expenditure. The decision to whether or not to proceed with a total mercury mass balance is that of the managers.

The outline of the work necessary for a mass balance for mercury is taken from conversations with Dr. Ronald Rossman and Mr. Douglas Endicott of U.S. EPA, Large Lakes Research Station, as well as discussions that took place at the Workshop.

## **TRIBUTARIES**

Monitoring of total mercury in the dissolved and particulate phases, for load calculations, is planned as part of regular sampling of the tributaries. That is, total mercury samples will be taken at each sampling visit. Clean techniques will be used, including teflon samplers. Little or no additional sampling will be required for the mass

balance model, as samples will be taken as a regular part of the intensive monitoring program.

### **ATMOSPHERE**

Total mercury will be monitored at four sites (IIT, South Haven, Sleeping Bear Dunes and Chiwaukee Prairie or Indiana Dunes). Vapor and particulate phase mercury will be collected for a period of 24 hours every sixth day. Mercury in precipitation will be a composite weekly sample. The mercury monitoring conducted for Lake Michigan will be coordinated with a ten site network which will monitor for vapor and particulate mercury for a one year period proposed to begin in approximately October 1994. This basin-wide network will include the five US and Canadian IADN sites and five additional sites. Sampling frequency will be the same as that proposed for Lake Michigan. Sampling methods for the mass balance are currently being developed under a research proposal with EPA-AREAL. Total mercury will be monitored as part of the atmospheric monitoring to be conducted for load estimates for Lake Michigan.

### **SEDIMENT**

Surficial sediment (top 1 - 2 cm) from all depositional zone box core samples collected as part of the sediment sampling program (see Sediment section) will be analyzed for total mercury. It is anticipated that a subset of the (dated) sediment cores to be taken for analysis of other mass balance chemicals would be analyzed for mercury to determine historic loading trends. The subset of cores would depend on data quality objectives determined for the mercury mass balance, but would probably be 10 to 15. A limited number of sediment trap samples will also be analyzed for mercury to determine current particulate mercury fluxes.

### **OPEN LAKE**

Total mercury samples (mercury in dissolved and particulate fractions) will be taken at master stations and at one station in each of the biota boxes on all planned mass balance surveys. One (unstratified water column) or more (stratified water column) samples will be taken at each station as part of the Open Lake surveys (see Open Lake Section). Clean techniques will be used for sample collection, and clean area aboard the R/V Lake Guardian will be used for sample processing and handling.

## **BIOTA**

### **Upper Food Chain**

A small subset of the lake trout and coho salmon sample collected by NBS and USFWS will be analyzed for total mercury.

### **Lower Food Chain**

Samples of zooplankton and phytoplankton, taken concurrently with those to be analyzed for organic contaminants, will be analyzed for total mercury. A subset of the *Mysis relicta* and *Diporeia* samples will also be analyzed.

## **RESEARCH**

There are several areas of research which must receive attention for successful completion of a mercury mass balance. Most are cogent to the fate and effect (food chain) portion of the work. Methyl mercury is the chemical specie which is most toxic and most bioconcentrated. While total mercury will be measured in all media, methyl mercury will not. Understanding the relationship between methyl mercury and total mercury is important to the understanding of mercury bioaccumulation in fish. For this purpose, methyl mercury measurements, along with total mercury, should be made at a research level, to begin to define both loads of methyl mercury, and concentrations, seasonally in the water. It may also be necessary to measure several species of mercury in open water and over-water atmosphere to determine flux of mercury into and out of the water: this is equivalent to work performed for the Green Bay Mass Balance which has led to a rethinking of role of the Bay as a source or sink of PCBs. In the case of mercury, several species would be measured, namely:  $\text{Hg}^0$ ,  $\text{Hg}^{2+}$ , total-Hg and methyl-Hg. A final area of research relevant to mercury uptake by biota is the measurement of selenium.

## **QUALITY ASSURANCE PROGRAM**

The EMP directors and managers will make decisions based upon the interpretive results of this program. These decisions will depend on qualitative and quantitative measurements derived from various environmental data collection activities (EDCA) including modeling. Measurements are never true values and always contain some level of uncertainty. Therefore, decision makers must be sufficiently comfortable with the uncertainty in data to risk making an inappropriate decision. This is the basis for the quality assurance program: minimizing the risks of making inappropriate decisions, thereby maximizing the potential for improvement of the environment.

The EMP QA Program's goal is to assure that the data that are produced meet defined standards of quality within a specified level of confidence. Data quality will be defined, controlled, and assessed through activities implemented within the various technical resource groups. The following sections will provide a brief discussion of the major planning, implementation and assessment aspects of the EMP QA Program. Detailed information can be found in the EMP QA Program Plan.

### **THE QA WORKGROUP**

The QA workgroup is composed of a coordinator (QAC), a lead from each technical resource group, various agency QA representatives, principle investigators, and technical experts, to ensure that data are of acceptable quality. The QA program will also hire support personnel for the verification and validation of data prior to official acceptance into the main data repository. The QA workgroup serves two functions; support and oversight. As a support group, the QA workgroup responsibilities will include:

- Assisting in the development of program objectives, data quality objectives, and measurement quality objectives;
- Assisting in the development of the EMP Study Plan;
- Developing and implementing the EMP QA Program Plan;
- Providing technical guidance to principle investigators on the development of QA Project Plans; and
- Assisting in the development of verification techniques



Oversight functions include:

- Reviewing and approving QA Project Plans;
- Tracking progress on QA Project Plan development;
- Coordinating and implementing assessments;
- Developing integrated data quality reports; and
- Verifying/validating data.

## **QA PROGRAM PLANNING**

As in all substantive data collection efforts, planning is essential. The QA program will assist in four major planning/development activities: 1) data quality objectives, 2) measurement quality objectives, 3) the EMP QA Program Plan, and 4) the QA project plans.

### **DATA QUALITY OBJECTIVES (DQOs)**

Central to a sound QA program is the development of data quality objectives (DQOs). DQOs are the full set of performance constraints needed to design a project, including a specification of the level of uncertainty that a decision maker (data user) is willing to accept in the answers to the questions of the study. This is data that, when evaluated, provides the decision maker with enough certainty that he/she is willing to risk making an inappropriate decision. Therefore, the data quality attributes that are associated with data are necessary for any educated ecological management decision.

Uncertainty can be illustrated as follows:

$$S_o^2 = S_p^2 + S_m^2 \quad (\text{equation 1})$$

Where:

o= Overall Uncertainty

p= Total Population Uncertainty (spatial and temporal)

m= Measurement Uncertainty (data collection)

The estimate of the allowable overall uncertainty is the DQO. The term "uncertainty" is used as a generic term to describe the sum of all sources of error associated with a given portion of the measurement system. Since variance is additive, we can see that

every input to the mass balance model (MBM) will add to the overall uncertainty of the model. Therefore, the MBM is only as good as the data inputs. At a specific input, confidence in the estimate of population uncertainty can be controlled through the use of statistical sampling design techniques. The goal of QA program is to understand and control measurement uncertainty to an acceptable level through the use of various quality control and evaluation techniques.

The modeling section and subsequent sections relating to each ecological resource (air, open lake etc.) have stated that the DQO for each input to the model to be within 20-30% of the mean at the 95% confidence interval. The QA workgroup will strive to attain a level of measurement uncertainty that will meet the DQO.

### MEASUREMENT QUALITY OBJECTIVES

Equation 1 can be further viewed as:

$$\begin{array}{lcl} \text{For:} & S_o^2 = S_p^2 + S_m^2 & \text{(equation 1)} \\ & \text{(DQO)} & \text{(MQO)} \end{array}$$

This equation serves to illustrate that DQOs are the sum of both the population and measurement uncertainties. The terms data quality objective (DQO) and measurement quality objective (MQO) have been added to equation 1. This serves to distinguish the fact that an MQO is not a DQO and that the EMP QA programs main priority is to control and assess measurement uncertainty by establishing MQOs.

MQOs are addressed in terms of 6 attributes: precision, accuracy, detectability, completeness, representativeness, and comparability. These attributes are defined in the EMP QA Program Plan and will be addressed in detail in resource specific QA project plans.

Comparability of data across the various ecological resources is important for the mass balance as well as for other uses of the EMP data. Since each resource group will be measuring primarily the same parameters, it is important that detection limits, accuracy, and precision are comparable. There are two ways of controlling comparability: 1) requiring the use of specific methods, or 2) requiring consistent method performance criteria. The QA workgroup will assist the ecological resource groups on attaining data comparability

## **THE EMP QA PROGRAM PLAN**

The document around which the QA program revolves is the EMP QA Program Plan (QAPP). The EMP QAPP describes the program's minimum requirements to which all organizations collecting data must adhere. These minimum requirements are developed in order to meet the EMP objectives. The goal of the program plan is to present the program, the data quality objectives (DQOs), and the rationale for them, and to establish the consistent use of QA techniques among the various agencies collecting data for the EMP. In order for the program to successfully meet the EMP objectives, all cooperators must adhere to the guidance and policy set forth in the QAPP. Major elements of the QAPP include:

- Quality Assurance Policy Statement
- Data Quality Objectives
- Information Management
- Organizational Structure
- QA Program Implementation
- QA Reports

The QAPP will be developed in cooperation with all program workgroups and approved by the Program Directors.

## **QA PROJECT PLANS**

The EMP requires every EPA funded EDCA to have written and approved quality assurance project plans (QAPjPs) prior to the start of the EDCA. The purpose of the QAPjP is to specify the policies, organization, objectives, and the quality evaluation and quality control activities (QE/QC) needed to achieve the DQOs of the EMP.

Each program cooperator will be provided guidance documentation for the development of QAPjPs. The QAC and support staff will also be available for one-on-one consultation in order to assist in the QAPjP development.

## **QA PROGRAM IMPLEMENTATION**

QA program implementation includes the following areas that will subsequently be addressed:

- QA project plan review and approval
- Assessments
- Reporting
- Training/certification
- Data verification/validation

## **QA PROJECT PLAN REVIEW AND APPROVAL**

Review of the QAPjP will include the principle investigator (PI), the resource workgroup's QA lead, the EPA Project Officer, and the EPA QA manager (QAM). The EPA QAM will review each QAPjP for the required elements and the soundness of the planned QA activities. The QAM will provide written comments within 15 working days from submission. Data collection may not proceed without an approved QAPjP.

## **TRAINING/CERTIFICATION**

Training is essential to the success of data collection activities. Training enables personnel to complete each aspect of an EDCA according to design and management objectives and in a standardized manner.

Prior to the start of any EDCA, a training session shall be conducted. Training will include practice with each of the SOPs and shall include some level of certification by the trainer that individuals are performing the EDCA properly.

The resource workgroup QA lead will oversee the training aspects of their resource groups, attend the training exercises for assessment purposes, and report on the activities accomplishments.

## **ASSESSMENTS**

An audit or assessment is a formal evaluation of performance to pre-determined standards and the evaluation and documentation to effect change towards improved performance. Audits are the principal means to determine compliance and to control systems in a real-time manner to improve performance. Three types of audits are defined: 1) technical systems audits (TSAs), 2) data quality audits (DQAs), and 3) performance evaluations (PEs). These audits will be utilized in the EMP.

### **Technical Systems Audits (TSAs)**

Technical systems audits (TSAs) are qualitative on-site evaluations of a complete phase of an EDCA (i.e., sampling, preparation, analysis). This audit can be performed prior to the data collection activity, in order to verify the existence and evaluate the adequacy of equipment, facilities, supplies, personnel, and procedures that have been documented in the QAPjP. TSAs are also employed during the data collection activity in order to verify and evaluate the EDCA.

## **Data Quality Audits (DQAs)**

A data quality audit (DQA) focuses on collected data. It is used to determine if enough QA information exists with the data set to evaluate the quality of the data and whether this quality satisfies the stated DQOs of the EDCA. It is also used to assess the ability of the QAPjP to produce data of known and satisfactory quality.

## **Performance Evaluations (PEs)**

Performance evaluations (PEs) are a means of independently verifying and evaluating the quality of data from a measurement phase, or the overall measurement system. This is accomplished through the use of samples of known composition and concentration. These samples can be introduced into the measurement system as single blind (identity is known but concentration is not) or double blind (concentration and identity unknown). These samples can be used to control and evaluate accuracy and precision and to determine whether DQOs or MQOs have been satisfied. PEs can also be used to determine inter- and intra-laboratory variability and temporal variability over long projects, and to evaluate laboratories prior to contract awards.

Another performance evaluation method that may be employed in the EMP are interlaboratory comparisons studies in which reference or a homogenous matrix samples are sent to all analytical participants in order to determine data comparability.

## **DATA VERIFICATION/VALIDATION**

Data verification is a process used to determine and control measurement uncertainty in order to produce accurate and reliable data. A method must be developed within each QAPjP that takes the various QE/QC information that has been included in the QA design and evaluates this data in a consistent manner. Data not meeting acceptance criteria is flagged. Depending on the types of flags associated with the routine samples, data may be reanalyzed (if possible) or flagged in a manner that will inform the user of the data quality. This process should not be considered as a means to eliminate subjective decisions made by the principal investigator (PI), but will allow for a consistent data review using the MQO samples. In fact, if a verification system is properly developed, it should capture many of the thought processes used by the PI during his/her review of data.

Each resource group will use a consistent set of flag codes. This set contains mandated standard EPA codes. As new codes are needed, they will be developed and

distributed to all EMP cooperators. PIs developing QAPjPs must identify the codes they will use to flag data.

Data validation is a process whereby either the PI or the technical workgroup review the project data and the associated flags in terms of the program requirements and determine what data will be placed into the central data base to answer the program objectives. At present this procedure has not been developed. However, once it has, it must remain consistent throughout the program's duration. If not, all previous data must be processed through any modified procedure.

### **QA REPORTING**

The following types of QA documentation will be developed during the EMP.

- QA Program Plan      - QA Project Plan
- Assessment Reports   - QA Reports

The first three have been discussed in previous chapters and will not be presented here. More details on all QA documentation is included in the EMP QA Program Plan.

The QA report is a document that describes a project's quality assurance program, including the verification techniques, and provides an assessment of the quality of the routine data, based upon the evaluation of measurement quality samples. The QA report is directed primarily towards the users of the data who will be analyzing the data and making various interpretive conclusions. Depending on the type of report (interim or final), the QA report will include the following:

**Overview:** The time sequence that the report covers, the activities that the report covers, a brief description of the program and reference to the appropriate QAPjP, and the structure of the report.

**QA Summary:** Summary of the QA program, its implementation, and accomplishments, and a summary of corrective actions taken.

**Audits:** Results of all audits during the appropriate time span. Actual audit reports should be included in an appendix.

**Data Assessment:** Assessment in terms of precision, accuracy, detectability, representativeness, completeness, and comparability in terms of the DQOs/MQOs, estimates of overall measurement uncertainty the statistical techniques used to make

the assessments, a discussion of whether the DQOs/MQOs were met, and the resulting impact on decision making, limitations on the use of the data and identification of invalid data (flagged data) for the program.

**Conclusions:** Assessment of the QA program both positive and negative and recommended changes for improvement of the program.

Each QAPjP will identify the frequency of these reports and the specific content of progress and final reports.

## **Lake Michigan Enhanced Monitoring Program - Data Management Strategy -**

The Lake Michigan Mass Balance (LMMB) and Lake Michigan Enhanced Monitoring projects represents considerable opportunity to improve data management practices for environmental monitoring information collected under the Great Lakes Program. The data management mission for these projects is to provide a data entry, storage, access, and analysis system to meet the needs of mass balance modelers and other potential users of the data. This document outlines elements of a data management plan for the Lake Michigan Enhanced Monitoring Program (LMEMP).

### **Background**

Because the LMEMP will involve over 25 investigators in collecting and analyzing samples, data management and the quality assurance program will be pivotal in maintaining consistency and comparability across the program. Fortunately, in planning the LMEMP, the need for rigorous data management was recognized early. Since then, a data management strategy has been evolving for the LMEMP.

In planning for this project, GLNPO has taken the responsibility to develop and implement a data management plan for information supporting the LMEMP in cooperation with Region 5 and the States of Illinois, Indiana, Michigan and Wisconsin. These responsibilities include: data management, data base administration, and development/administration of the system which houses these data. Project Officers for laboratory contracts and grants which create data and the LMEMP work groups are responsible for the quality of the data. Staff support is provided by GLNPO and contract staff, Region 5, and the US Army Corps of Engineers.

### **LMEMP Data Management Philosophy**

The data management plan for this project is being developed under several guiding principles including:

- **Cross-program/project utility and long-term value:** The data collected under the LMEMP will represent the largest, and highest quality toxics data ever generated in the Great Lakes Basin. It is therefore critical to the Great Lakes Program that the data be useful to investigators outside the scope of the original project.
- **Store data of known quality:** In order to make the data useful beyond the original scope of the project, users have expressed the need to be able to understand the quality of each data set in the data base. To support this requirement, the LMEMP data base will store information describing the project, the data quality objectives, and the quality assurance information associated with each data set.



- **Avoid duplication of effort:** Because the LMEMP includes monitoring of all major environmental media (sediment, water, air and biota), there will be a significant challenge to make all of these data available within a single system. In fact, there is currently no single system which could manage all of these data types. GLNPO has therefore formed a partnership with USEPA Office of Water, where the STORET Modernization Project is being completed. The STORET Modernization Team shares GLNPO's vision for a comprehensive monitoring database focusing on longevity, integration, and data quality. By becoming a pilot project for STORET Modernization., LMEMP is capitalizing on a national-scale user requirements analysis and on the efforts to integrate with other major environmental monitoring data systems. GLNPO has utilized existing resources wherever they exist in developing this data base.

### **The LMEMP Data Base**

The LMEMP Data Management Plan centers on the use of a relational data base that is designed to store and organize data so that the data are consistent, and so that redundancy is eliminated whenever possible. Relational data bases strive to maintain a single copy of the information and refer to it using pointers that indicate where related information is used. This helps not only to ensure efficient storage and consistency, but allows quick access to the data. Relational also means that relationships between different sections of the data base are not restricted when the data base is created. For example, if sampling and station information are stored in separate locations in the data base, one can create a query using both.

Based on an extensive requirements analysis for this multi-media monitoring project, a relational database has been designed to accommodate all of the information that will be necessary to utilize these data far into the future. For the first time, GLP data users will have a comprehensive monitoring data base that will provide information about the project objectives, the participants, the monitoring stations, the sample collection/analytical procedures, the analytical results AND the supporting quality assurance/quality control data. By storing all of this information in a single data base, the data can be used to support projects beyond the original scope of the LMEMP. Because extensive project description information will be included in the data base, secondary users will not have to make phone calls or track down supplemental reports in order to determine whether these data might be of use in their projects. The useful life of the data will extend beyond the careers of the scientists that collected the data. As the GLP monitoring program matures, the LMEMP data base is expected to be expanded to house *all* major Great Lakes environmental monitoring project data.

### **Standardized Data Reporting & Data Entry**

Because there are over twenty-five organizations producing data through collection and analysis of samples, a tremendous amount of forethought was necessary to ensure that data will be submitted in a consistent and comparable format. For the LMEMP the two major outside sources for data are the field sampling crews and the analytical laboratories. For both of these groups of data generators, required formats for data reporting (data reporting standards) were developed. The data reporting standards are designed to take ASCII text flat files (like spreadsheets) and convert them to the relational structure of the data base. Each data standard specifies the formatting rules by which data must be submitted, and in many cases, allowable values for a given field are defined (i.e.: mercury shall be reported as "Hg", Atropine shall be reported as "Art", etc.). By requiring consistency in data reporting, the allowable value lists reduce the amount of processing necessary upon receipt.

The data reporting standards were designed to minimize the number of data elements reported from the field crews and lab analysts. All of the "Project" and "Station" data, as well as any data that can be gleaned from the Quality Assurance Project Plans will be entered using a data entry application at the Program Office. The data elements and attributes which are required by either the data reporting standards or the data entry applications will make up the minimum data requirements for the LMEMP data base. The minimum data requirements will be particularly useful in determining which additional monitoring studies can be added to the LMEMP data base.

### **Data Access**

The LMEMP data base is being designed to support a variety of uses. The primary users will be the LMEMP project team and the environmental modelers associated with the project. The data base will also be accessible to anyone who can benefit through the use of high-quality toxic data. Among the anticipated customers are the Lakewide Management Teams, Remedial Action Plan committees, and government/non-government entities focused on developing load reduction strategies. The data base will include documentation of methods, quality assurance, quality control, data quality objectives, and other information needed for meaningful interpretation.

Clearly, toxic chemical data can be difficult or impossible to interpret for those not trained in organic chemistry. Therefore, all summary documents and data analyses will be made available to those who request it both via the Internet and through the mail. GLNPO is committed to working with State and other customers to improve access to Great Lakes environmental monitoring information. The LMEMP data base will be a major step toward fully meeting the needs of Great Lakes data users.

### **Project Communications and Internet Access**

LMEMP work group members can now communicate through Internet electronic mail. A "listserver" (basically an electronic mailing list) has been established to facilitate group communications. To communicate via the listserver with project participants owning Internet addresses, send your email to the following address:

**GLIN-LMMB@great-lakes.net**

To subscribe to the LMEMP listserver, send an email message to:

**GLIN-Majordomo@great-lakes.net**

and in the body of the email, simply type: **subscribe GLIN-LMMB .**

Members who do not have Internet mailboxes can get one from the Great Lakes Information Network (GLIN). Ron Emaus at CICNet (313)998-6419 can help provide electronic mail services or required connectivity to members of LMEMP work groups.

The Great Lakes Information Network includes Internet "Gopher" and "World Wide Web" servers containing various information about the Great Lakes, including environmental information and information about environmental activities in the Basin. The Lake Michigan Mass Balance and Enhanced Monitoring Work Plan and other LMEMP documents/reports will be posted on the Great Lakes Network and will be available for downloading by interested parties. The following Internet addresses provide access to the LMEMP and other Great Lakes information:

**<http://epawww.ciesin.org/>**

**<http://www.great-lakes.net:2200/>**

**<gopher://glnpogis2.r05.epa.gov>**

Additionally, an anonymous FTP site is available at: **<ftp://glnpogis2.r05.epa.gov>** .

Please inform the Data Management Committee chair when you have electronic copies of documents to be posted on the GLIN.

### **Systems Development Environment**

- |   |                               |
|---|-------------------------------|
| • Relational data base management system: | ORACLE                        |
| • Application development tools:          | MS Access, PowerBuilder       |
| • Data base platform:                     | Data General 5240 UNIX server |
| • CASE tool:                              | ORACLE CASE                   |

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- |  |                      |                |
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## Appendix 2. Parameters and Measurements Proposed for EMP

Parameter	Specific	Measurement
PCB Congeners PCB Aroclors	65 Peaks	A/P/T F
Pesticides	Oxychlordan a-HCH g-HCH p,p' DDT o,p' DDT p,p' DDE HCB Aldrin Dieldrin Trans/cis-nonachlor Atrazine Toxaphene a-Chlordane g-Chlordane	A/P/T A/P/T A/P/T A/P/T/F A/P/T/F A/P/T/F A/P/T/F A/P A/P/T/F A/P/T/F A/P/T P/T/F A/P/T/F A/P/T/F
PAHs	acenaphthylene acenaphthene fluorene phenanthrene anthracene fluoranthene pyrene chrysene benzo(a)anthracene benzo(b)fluoranthene benzo(k)fluoranthene benzo(a)pyrene indeno(123cd)pyrene dibenzo(a,h)anthracene benzo(ghi)perylene naphthalene retene cyclopenta(cd)pyrene coronene benzo(e)pyrene	A/P/T A/P/T A/P/T A/P/T A/P/T A/P/T A/P/T A/P/T A/P/T A/P/T A/P/T A/P/T A/P/T A/P/T A/P A/P A/P A/P A/P
Octachlorostyrene <sup>a</sup>		A/P/T/F
Metals	Cd Pb Hg <sup>b</sup> Cr Cu Zn Cl P Si S	A/P/T A/P/T A/P/T/F A/P/T A/P/T A/P/T A/P/T A/P/T A/P/T A/P/T
2,3,7,8 TCDD/TCDF <sup>a</sup>		A/F
Conventional/Physical	Total Organic Carbon Part. Organic Carbon Diss. Organic Carbon	A A/T T

	VOC	A
	Elemental Carbon	A
	Hardness	T
	Alkalinity	T
	Chlorophyll a	T
	Suspended Solids	T
	Particle Size	A
	Temperature	A/T
	Dissolved Oxygen	T
	Conductivity	P/T
	pH	P/T
	Water Clarity	T
	Turbidity	T
	Speed	A/T
	Direction	A/T
	Volume	A/P/T
	Weight	A/P/F
	Length	F
	Age	F
	Location	A/P/T/F
	Relative Humidity	A
	Solar Radiation	A

A=Air, P= Precipitation, T=Tributary(water), F=Fish

a = Lake superior only b= only collected at three sites for air

### Appendix 3. Atmospheric Loading Calculations

The equation for modelling the atmospheric component of mass loadings used in the IADN program is as follows (from IADN QA Program Plan modified from Baker and Eisenreich, 1990):

$$L = L_t + P + G + D + RS$$

where:

$L$  = total atmospheric loading as  $g\ yr^{-1}$

$L_t$  = Atmospheric component of tributary loading to lake  
 $= F_t C_t \phi_t$

$P$  = Precipitation component of loading to lake  
 $= 10^3 C_p R_p A_p$

$G$  = Net gas phase transfer component  
 $= 10^9 A K_{aw} [(1-\phi_a) C_a RT/H - 10^6 (1-\phi_w) C_w]$

$D$  = Dry deposition of particles to lake  
 $= 10^9 \phi_a A C_a V_a$

$RS$  = Resuspension of particles from lake  
 $= \phi_w C_w F$

with:

$A$  = Area of lake ( $m^2$ )

$A_p$  = Area of lake covered by precipitation ( $m^2$ )

$C_a$  = Concentration in air ( $ng\ m^{-3}$ )

$C_p$  = Concentration in precipitation ( $\mu g\ l^{-1}$ )

$C_t$  = Concentration in tributary ( $\mu g\ l^{-1}$ )

$C_w$  = Concentration in water ( $\mu g\ l^{-1}$ )

$F$  = Resuspension flux function (not currently available in functional form)

$F_t$  = Tributary flow ( $10^3\ m^3\ yr^{-1}$ )

$H$  = Henry's law constant ( $Pa\ m^3\ mol^{-1}$ )

$K_{aw}$  = Air-water mass transfer coefficient ( $m\ yr^{-1}$ )

$R$	= Gas constant ( $\text{Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1}$ )
$R_p$	= Rate of precipitation ( $\text{m yr}^{-1}$ )
$T$	= Ambient temperature (K)
$V_d$	= Particulate deposition velocity ( $\text{m yr}^{-1}$ )
$\phi_a$	= Particulate fraction of concentration in air
$\phi_t$	= Fraction of tributary loading which is atmospheric in nature
$\phi_w$	= Particulate fraction of the concentration in water

The estimates of atmospheric deposition calculated by Eisenreich 1992 used the Junge-Pankow model for determining the fraction of chemical in the particle phase.

$$\phi_a = c\Theta / (P_i + c\Theta)$$

where  $c = 17.2 \text{ Pa-cm}$  and  $\Theta$  is the surface area per unit volume of air

#### Appendix 4. Number of Biology Samples for Collection and Analysis

BIOTIC ELEMENT	GROUP	No. COLLECT	No. per COMPOSITE ANALYSES	No. ANALYSES	No. SITES	No. SEASNS	TOTAL COLLECT	TOTAL ANALYSES
LAKE TROUT	2-4 yr	25	5	5	3	5	375	75
	5-7 yr	25	5	5	3	5	375	75
	8-10 yr	25	5	5	3	5	375	75
TOTAL LAKE TROUT							1125	225
COHO	Hatchery	25	5	5	1	1	25	5
	1+	25	5	5	2	1	50	10
	2+ adults	25	5	5	2	5	250	50
TOTAL COHO							325	65
BLOATER	0-2 yr	25	5	5	3	5	375	75
CHUB	4+ yr	25	5	5	3	5	375	75
TOTAL CHUBS							750	150
ALEWIFE	60-120 mm	25	5	5	3	5	375	75
	>120 mm	25	5	5	3	5	375	75
TOTAL ALEWIFE							750	150
SMELT	>100 mm	25	5	5	3	5	375	75
TOTAL SMELT							375	75
SCULPIN	Slimy	25	5	5	3	5	375	75
	Deepwater	25	5	5	3	5	375	75
TOTAL SCULPIN							375	75

TOTAL FISH							3700	740
BIOTIC ELEMENT	GROUP	No. SAMPLES	No. BIOTA BOX	No. SITES/BX	No. SEASNS	No. REPS/SN	TOTAL COLLECT	TOTAL ANALYSES
MYSIS	mixed	1	3	2	6	1	42	42
		1	1	1	6	0	6	6
TOTAL MYNIS							48	48
DIPOREIA	mixed	1	3	2	6	1	42	42
		1	1	1	6	0	6	6
TOTAL DIPOREIA							48	48
PLANKTON								
Bythotrephes	> 2500 um	1	3	1	2	0	6	6
		1	1	1	2	0	2	2
Crustaceans	100 - 2500 um	1	3	3	6	1	60	60
		1	1	1	6	0	6	6
Phytoplankton	10-100 um	1	3	3	6	1	60	60
		1	1	1	6	0	6	6
TOTAL PLANKTON							140	140
TOTAL LOWER FOOD WEB							236	236

## **Appendix 5. Format for Reporting Analytical Results**

### **Introduction**

As the amount of data from sources outside EPA grows, finding the time and resources to translate data files into a central database becomes increasingly difficult. By requesting data in a standard electronic format, EPA's efficiency in processing and integrating information is dramatically increased in this time of scarce resources. This document describes the format for electronic data transmission only.

### **General Requirements**

1. Results will be submitted to GLNPO in electronic media (i.e. diskette, magnetic tape, CD ROM, Internet transmission). All results submitted in electronic format will have been verified against laboratory records and will agree exactly with any hard copy submissions. Records of the verification should be made.
2. All files shall be submitted in comma delimited ASCII format.
3. Field lengths should only be as long as necessary to contain the data; packing with blanks is not necessary. Missing or unknown values need not have anything entered (,) but as this is a order format the place will need to be held.
4. Subdirectories should be used to segregate information. All sample results and batch data for a particular batch and analyte should be together in the same subdirectory. Each different batch and analysis should have a separate subdirectory. For complex analyses such as PCBs, GC or GCMS, Batch Data files can be created for each of the compounds and placed in one subdirectory. Any samples found to have any of these compounds are then reported in the same subdirectory. The analyte field in the Results records will prevent confusion both in single and multiple compound instances. Stations or facilities with their associated samples should also be in separate subdirectories.
5. Numeric fields may contain numeric digits, a decimal place and a leading minus (-) sign. A positive (+) sign is assumed and must not be entered into any numeric field. The size of the numeric field indicates the maximum number of characters including digits, decimal and minus sign, if needed, that can appear in the field at the same time. The number reported may need to be rounded using EPA rounding rules to fit into the field. The rounding should maintain the greatest significance possible within the field length limitation.

6. The records formats are intended to be general for a variety of media, but some special considerations apply to certain common media. Diskettes shall bear one or more external labels, collectively supplying the following information: batch ID, creation date, name and address of submitter, brief description of contents and subdirectories.
7. All temperature fields are in centigrade. All times will be given on a 24 hour clock, known as military time. Dates are given numerically as MM/DD/YY. All fields are alpha-numeric unless remarks state otherwise.
8. Consistency in station naming is crucial for GIS and modeling use of information. EPA designated names shall be used when they exist.
9. If the data generator finds it necessary to change the format, notification of the exact nature of the differences should be discussed with an EPA representative and accompany the submission.
10. This standard is intended to be as efficient as practical. Suggestions for improvement are welcomed.



### Specific Instructions

**Delivery Header Record** - The Delivery Header Record shall be included as a separate file in the root directory and appears once on each disk, tape or transmission from the same GLNPO program.

### FORMAT for Delivery Header Record

Record Position	Max. Length	Field Contents	Remarks or Explanation
1	30	Requestor	Name of Requestor
2	40	Program	ex. IADN, GLAD, Limnology
3	8	Date disk made	Date format, Release_date
4	40	Laboratory	Laboratory name, Lab_title
5	30	Sampling Organization	Sampling_Org
6	12	Contract or Grant #	Assignment
7	40	Data contact person	and phone number

**Sample Batch Data Record** - All sample results and batch data for a particular batch and analyte should be together in the same subdirectory. Each different batch and analysis should have a separate subdirectory. For complex analyses such as PCBs, GC or GCMS, Batch Data files can be created for each of the compounds and placed in one subdirectory. Any samples found to have any of these compounds are then reported in the same subdirectory. The analyte field in the Results records will prevent confusion both in single and multiple compound analyses.

**FORMAT for Sample Batch Data**

Record Position	Max. Length	Field Contents	Remarks or Explanation
1	12	Batch ID	Sample_Batch_ID
2	8	Analyte	Analyte
3	10	CAS number	Chemical Abstracts System number
4	10	Matrix	Matrix_type
5	9	Detection Limit	Detection_Limit, Numeric
6	16	Units	Units
7	12	Method	Analysis Method
8	12	Instrument	Instrument
9	8	Date of analysis	Analysis_date, Date format
10	3	Submission number	

**Sample Results** - This type of record will be repeated for each result reported for the compound or analyte listed in the Batch Data Record. For complex analyses such as PCBs, GC or GCMS, Batch Data files can be created for each of the compounds and placed in one subdirectory. Any samples found to have any of these compounds are then reported in the same subdirectory. The analyte field in the Results records will prevent confusion both in single and multiple compound instances.

**FORMAT for Sample Results**

Record	Max.	Field	Remarks or Explanation
--------	------	-------	------------------------

Position	Length	Contents	
1	12	Sample ID	Sample_ID
2	8	Analyte	Analyte
3	40	Result	Results_Reported
4	50	Identifier	Sample, Field Blank, etc. Prompt
5	12	Qualifier	Qualifier, Use EPA standard 3 character qualifiers up to 4
6	8	Dilution factor	Dilution_factor
7	80	Comments on data	If desired

**Field Data Record** - The field records may not be available to the data generator. This section need not be filled out in that case. Stations or facilities with their associated Field Data Records should be in separate subdirectories. It is not the intention to add further work, but to capture all the information available at the earliest source. If field results (pH, etc.) are being reported, Sample Batch Data and Sample Results formats are used. The Batch ID in Sample Batch Data becomes FIELD.

**FORMAT for Field Data Record**

Record Position	Max. Length	Field Contents	Remarks or Explanation
1	12	Sample ID	Sample identifier
2	30	Station	Station or Facility
3	8	Sampling Method	Sampling technique
4	6	Depth	Depth sample taken
5	8	Start of sampling	Sampling start date
6	8	End of sampling	Sampling end date
7	4	Type of sampling	Grab or Composite (Comp)

**Field Station Record** - The field records may not be available to the data generator. This section need not be filled out in that case. Stations or facilities with their associated Field Data Records should be in separate subdirectories. For locational information, latitude is always given before longitude. The standard form of degrees, minutes, seconds and decimal portions of seconds will followed. For more information see the EPA Agency Locational Data Policy, Information Resources Manual, Chapter 13 and Appendix A.

**FORMAT for Field Station Record**

Record Position	Max. Length	Field Contents	Remarks or Explanation
1	30	Station	Facility or Station
2	30	Description	Description
3	30	Address	Address1
4	30	Address	Address2
5	25	City	City name
6	2	State	State 2 letter code
7	9	Zip	Zip code
8	11	Latitude	Latitude
9	12	Longitude	Longitude
10	5	Coordinate type	Point, line or area
11	8	Date coordinates determined	
12	10	Source of coordinates	
13	5	Accuracy	Accuracy of coordinate determination + or -
14	8	Units for accuracy	minutes, seconds
15	16	FINDS ID	EPA FINDS number if available

## Appendix 6. Modeling Requirements and Studies

This section defines field data requirements for the Lake Michigan mass balance modeling effort, in terms of how data will be used for model development, confirmation and application. Substantially greater detail of the EMP design may be found in the LMMBS Work Plan. Through work group involvement, the modeling committee has offered input to the EMP design to maximize the utility of the sampling and analytic effort, within the overall project constraints defined by GLNPO. It should also be noted that data management and database development are the responsibility of GLNPO.

Data may be categorized in three groups, according to their usage in the modeling process:

Loadings, boundary and initial conditions, and forcing functions - Data that is specified externally (based upon observations or other models), and input to the model. Loadings are external sources of mass for constituent state variable, including contaminants, sediments, sorbents, and nutrients. Boundary conditions are state variable concentrations in media adjacent but external to the model (i.e., the atmosphere and Lake Huron water across the Straits of Macinaw). Initial conditions are the concentrations of state variables at the beginning of the model simulations. Forcing functions include other data to which the model responds, such as meteorology.

Constituent observations in water, sediment, and biota - Data that are compared to model predictions of state variable concentrations; they may be either observations of the state variables themselves, or of other constituents used as surrogates for state variables. Model performance is principally evaluated in terms of the residuals (differences) between observations and predictions for state variables. Appropriate spatial and temporal allocation of the point observations is necessary for comparability with model predictions, which are spatially and temporally continuous.

Process data - Data that are used to confirm particular aspects of the model formulation and parameterization. Process data are usually specific in terms of constituents and media, and are based upon field and/or laboratory experiments. Process data is particularly useful in confirming aspects of the model parameterization which is unconstrained by other observations.

loadings, boundary conditions, and forcing functions

Loadings and boundary conditions necessary for the toxics, solids, and nutrient mass balances will be based upon monitoring data for the atmosphere, tributaries, and Lake Huron. Continuous estimates of loads, for the 1994-95 EMP period, will be required for the parameters listed in Table 1. Atmospheric loads from dry and wet deposition will be resolved as weekly averages on the level 2 model grid. Tributary loads will be computed as daily (for events) or weekly (non-event) averages, for each river. The computation of load estimates is considered the responsibility of Atmospheric and Tributary Workgroups.

Table 1. Parameters required for atmospheric and tributary loads

parameter	atmosphere	tributary
PCB congeners, TNC, atrazine (+ DEA and DIA), mercury (+methyl if available)	vapor concentration, wet and dry deposition fluxes	tributary load
Total Suspended Solids	particle size and deposition velocity, wet and dry deposition fluxes	tributary load
Particulate Organic Carbon	wet and dry deposition fluxes	tributary load
Dissolved Organic Carbon		" "
Total Phosphorus	wet and dry deposition fluxes	" "
Soluble Reactive P	" "	" "
Total Dissolved P		" "
Nitrate-Nitrite	wet and dry deposition fluxes	" "
Total Kjeldahl N	" "	" "
Ammonia		" "
Dissolved Silica	wet and dry deposition fluxes	" "
Biogenic Silica		" "
Chlorophyll a		" "
Chloride		" "
Hardness		" "



parameter	atmosphere	tributary
		"
Conductivity		"
Alkalinity		"
Other Data	Rainfall, Snowfall, pH, T, relative humidity, solar radiation, wind speed and direction, wave height	Flow, velocity, stage, T, transmissivity, pH, D.O.

Boundary conditions of concern to the mass balance include vapor-phase air concentrations, and concentrations of state variables in Lake Huron water. Over-water air concentrations will be estimated, based upon the routine (shore-based) and Air Intensive monitoring data. Water quality data from Station 54M, located in northern Lake Huron, will be used to describe the lake boundary condition.

Meteorological data including wind speed and direction, temperature, and solar radiation will be collected from land and ship-based atmospheric monitoring, NWS surface observing stations, and NOAA mid-lake weather buoys. These data will be used to synthesize overwater momentum and heat flux fields, forcing functions for the hydrodynamic model. Ice cover data will also be used as a model forcing function.

#### water column

Water column monitoring will be conducted to determine the spatial distribution and inventory of mass balance state variables in the lake, on a seasonal sampling basis. State variables to be measured in the water column are listed in Table 2. The basic monitoring program consists of sampling on 8 cruises conducted aboard the Lake Guardian. Five cruises (April, August, and October '94; April and September '95) will sample the 41 EMP stations; three other cruises (June '94; January and August '95) will sample a station subset. On all cruises, enhanced vertical sampling resolution will be obtained at 9 open-water master stations. In addition to discrete samples for the parameters in Table 2, continuous vertical profiles of conductivity, temperature and transmissivity will be recorded at all stations. Supplemental water column monitoring data will be provided by NOAA-GLERL (weekly-monthly sampling at several southern basin stations), Air Intensive studies, biota sampling, and municipal water intake components. The parameters of interest from these data sources are identified in Table 3.

Table 2. Water column state variables

parameter	phases / comment
PCB congeners	dissolved and particulate
Trans-nonachlor	dissolved, and particulate
Atrazine (+ DEA and DIA)	dissolved and particulate (master and biota stations)
Mercury	dissolved and particulate (master and biota stations)
Total Suspended Solids	
Particulate Organic Carbon	
Dissolved Organic Carbon	
Phosphorus	total, total dissolved and soluble reactive
Nitrate-Nitrite	dissolved
Total Kjeldahl N	total
Ammonia	dissolved
Dissolved Silica	dissolved
Biogenic Silica	particulate (will not be done)
Chlorophyll a	
Chloride	
Hardness	
Alkalinity	
pH	
Secchi Disk	
Light Extinction	
C-14 Primary Production	Master Stations
Phytoplankton (abundance and biovolume)	Master Stations

parameter	phases / comment
Zooplankton (abundance and biovolume)	Master Stations
Temperature, conductivity, D.O., beam attenuation	Seabird instrument (vertical water column) profiles
Incident Solar Radiation	
Wave Height	

Table 3. Supplemental water column monitoring data

study component	parameter
NOAA-GLERL monitoring	Total Phosphorus
	Soluble Reactive Phosphorus
	Nitrate, Ammonia
	Dissolved and Particulate Silica
	Chlorophyll a
	Particulate Organic Carbon
	Dissolved Organic Carbon
	Chloride
	Temperature
	Secchi Disk
	Bacteria, Phyto- and Zooplankton Counts
Air Intensive	Wind and Wave Height
	Volatile Flux (PCB congeners, mercury)
	Overwater Deposition Fluxes (PCB congeners, TNC, atrazine, and mercury)
Plankton sampling (phyto-, zooplankton, and detritus)	dry weight/volume

study component	parameter
particle fractions)	
	PCB congeners, TNC
	mercury
Remote Sensing (NOAA)	Surface Temperature and Reflectance
municipal water intake	Temperature and Transmissivity (calibrated to TSS)

PCB concentrations (in all media) are to be reported using a standard congener list , according to GLNPO Data Reporting Standards. Surrogate recovery data as well as below-detection limit and below-quantification limit results are required for modeling data reduction. Mercury data will be reported for total mercury and methylmercury (if available).

#### sediment

Sediment sampling will be conducted to estimate the distribution of sediments, contaminants, nutrients, and selected other parameters in surficial sediments throughout the lake, as well as the fine-scale vertical distribution of contaminants in selected sediment cores. The primary use of this data is to define initial conditions, as the sediments contain the largest inventory of contaminants in the system. More than 100 box cores, gravity cores and PONAR grab samples will be collected, providing nearly uniform coverage of Lake Michigan sediment locations and types. Parameters of interest in sediment samples are listed in Table 4. The top centimeter of cores will be sampled as the surficial sediment, as will surface grab samples. Approximately 30 sediment cores from deposition basins will be sampled at 1-cm intervals and analyzed for lead-210, cesium-137, and ancillary sediment parameters; 10 of these cores will also be analyzed for contaminants. Trap material from four near-bottom sediment traps will also be analyzed for parameters in Table 4, to better define constituent concentrations for resuspendable sediments in non-depositional zones. This data will be augment prior sediment surveys conducted by Cahill (1968), Edgington and Robbins (1975), and Eisenreich et al.(1991-92).

Table 4. Sediment parameters of interest

parameter	surficial sediment	sediment cores	sediment traps
PCB congeners	all	selected	composite
Trans-nanoclor	" "	" "	" "

parameter	surficial sediment	sediment cores	sediment traps
Atrazine *	selected		
Mercury	all	selected	composite
Total organic carbon	" "	" "	all
Cumulative dry weight		" "	
Gross particle downflux			all
% moisture	all	all	
Porosity (derived)	" "	" "	
Grain Size	" "		
Pb-210 and Cs-137	" "	all	all
Total Phosphorus	" "		" "
Extractable/bioavailable Phosphorus	" "		" "
Total Nitrogen	" "		" "
Ammonia	" "		
Total Kjeldahl N	" "		
Biogenic Silica	" "		all

\* Selected sediment samples should be analyzed for the presence of atrazine, even though this contaminant is not believed to associate with sediments.

## biota

Biota will be sampled in defined food webs and zones, on a seasonal basis. The top predators of interest, lake trout and coho salmon, will be sampled as discrete age classes. Based upon the collection success in a particular season and zone, individual as well as composite fish may be analyzed for the parameters in Table 5. Individual-based sampling provides better information as to the source of contaminant variability. Forage fish will be collected in conjunction with top predators, and analyzed as composites according to size. Invertebrates (mysis and diporeia) will also be sampled at the same times and locations as fish; phytoplankton and zooplankton will be sampled in conjunction with water sampling cruises.

Table 5. Biota parameters

parameter	top predator s	forage fish	inverteb rates	phyto-, zooplankton, and detritus fractions
age	x			
weight	x	x	x	
length	x	x		
sex	x			
% moisture	x	x	x	x
% lipid	x	x	x	x
POC				x
PCB congeners	x	x	x	x
TNC	x	x	x	x
mercury	x			x
atrazine				x

## transport

Additional data will be required to confirm transport simulations. Remote sensing of lake surface temperature and reflectance (a surrogate for suspended solids at the lake surface), municipal water intake measurements of temperature and transmissivity (correlated to

suspended solids), and vertical instruments arrays measuring temperature, transparency, depth and current velocity will provide information about water and particle transport transients at a resolution not attainable by conventional ship-based sampling. Wave height data from ship and buoy observations will be used to confirm the wave submodel used in the transport simulations.

#### particle and contaminant fluxes

To obtain accurate mass balance results, large-magnitude contaminant and particle fluxes between the atmosphere and the lake, and the lake and the sediment, will be monitored. These include atmospheric wet and dry deposition, net volatilization flux, and net settling and resuspension rates. Monitoring for wet and dry deposition fluxes will be conducted during routine and intensive atmospheric sampling; volatilization flux at the lake surface will also be monitored during intensive ship-based sampling. Sequencing sediment trap arrays will be deployed at deep water locations, to measure settling and resuspension fluxes for solids, POC and selected nutrients (Table 4). Sedimentation fluxes will be determined from Pb-210 profiles in sediment core samples, sediment mixing depth from Cs-137 profiles, and sediment focusing factors from Pb-210 and Cs-137 inventories.

#### contaminant partitioning

All water column contaminant samples will be separated into dissolved and particulate fractions by filtration, and will be accompanied by measurements of TSS, POC, and DOC. Although this data will provide the basis for confirming the description of partitioning in the CTF model, additional data will be required to define the contaminant distribution between sorbent phases within these fractions. These include the organic carbon partition coefficient,  $K_{oc}$ , the dissolved organic carbon partition coefficient,  $K_{d,DOC}$ , and the biotic and detrital fractions of POC. The partition coefficients will be treated as contaminant-specific parameters, and will be based upon the literature as well as process data from laboratory experiments. POC fractions will be based upon surrogate measures, including chlorophyll, developed from phytoplankton sampling and biovolume data. Contaminant partitioning in sediment pore water will be described using data from the literature and from field and laboratory experiments.

#### contaminant transformation

Transformation between state variables is of concern for atrazine, mercury, and PCB mass balances. Because atrazine is known to degrade in soil as well as water, the concentration of diethylatrazine (DEA) and deisopropylatrazine (DIA) will be measured with the parent compound in all tributary and water samples. These data will confirm the location and rates of atrazine transformation. Mercury methylation and demethylation rates are not being measured

for the LMMBS, consistent with the total mercury mass balance objective. Operationally, a sediment equilibrium constant between organic and inorganic mercury states will be defined for CTF modeling, based upon the literature. PCB congener dehalogenation rates will be estimated from data in the literature. Prior modeling efforts, including the PCB mass balance models for Green Bay and the Fox River, as well as process research (Rhee et al., 1993) have suggested that dehalogenation is probably negligible for the range of PCB sediment concentrations observed in Lake Michigan.

#### resuspension

The relationship between shear stress and resuspension rate is critical for sediment transport modeling, and must be measured for representative sediments throughout the lake. Although a number of flume devices have been used in the laboratory for this purpose, the bottom-resting seaflume (Hawley, 1991) has been deployed previously in the Great Lakes. For this project, the seaflume will be modified to improve quantitative results, and deployed to test sediment resuspension properties at master stations, sediment trap and vertical instrument array locations, and other locations to obtain data for a variety of sediment substrates. This information will be used to estimate resuspension properties throughout the lake, based upon the spatial distribution of sediment physical properties.

#### eutrophication

Specialized process measurements required for the eutrophication model include C-14 primary production, phytoplankton and zooplankton abundance and biovolume, light extinction, and incident solar radiation.

#### bioconcentration and bioaccumulation

Species- and contaminant-specific toxicokinetic parameters required for the bioaccumulation model, will be based upon the literature and prior modeling studies. This parameterization will be refined by calibration to biota contaminant data.

Data for movement and migration patterns, feeding habits, and seasonal growth rates of fish are also required for the bioaccumulation model. Fish are not perfect integrators of lake-wide toxics exposure; rather, their contaminant burden reflects their exposure (particularly through diet) along a chemical gradient defined by their movements over seasons and years. National Biological Survey (NBS) personnel interviews, reports and file data will be used to construct fish migration patterns. Feeding habits will be based upon gut contents analysis for top predator and forage fish. Age-weight relationships will be developed for the collected fish, to define their rate of growth at each collection location.



### Supporting Studies List

A draft LMMBS work plan was distributed for public comment by GLNPO in October, 1993. A substantial number of comments were received, including suggestions for research and additional monitoring to support the mass balance objectives. These suggestions were organized, and the following list of candidate "supporting studies" was developed:

<b>Candidate supporting studies for LMMBS</b>
<b>Measure contaminant concentrations in plankton; confirm separation of phytoplankton, zooplankton, detritus</b>
<b>Monitor movement/migration of food web fish species</b>
<b>Gut contents analysis (diet composition by weight; gut fullness) to define food web structure and seasonal variance</b>
<b>Measure rates of contaminant uptake by phytoplankton, including relationship between uptake and growth</b>
<b>Measure seasonal changes in invertebrate growth and lipid</b>
<b>Routes of contaminant transfer to benthic organisms; linkages between food web structure and contaminant concentrations in invertebrates; Dietary composition and feeding behavior of diporeia and mysis</b>
<b>Measure rates of uptake (diet/ dermal/ respiration) and elimination (respiration/ excretion/ metabolism) for PCB congeners and TNC in lake trout, alewife and smelt</b>
<b>Study role of lipid transfer and synthesis upon hydrophobic contaminant accumulation by invertebrates</b>
<b>Research of sediment bioturbation by sculpins, mysis, diporeia, etc.</b>
<b>Improve biotic carrier (birds, insects, fish) flux estimates for contaminants</b>
<b>Measure transformation rates of atrazine in Lake Michigan</b>
<b>Measure air-water exchange fluxes for contaminants</b>
<b>Determine effect of chemical hydrophobicity/lipophilicity (<math>K_{ow}</math>) upon XAD-2 resin separation efficiency for dissolved and DOC-bound phases</b>
<b>Research the effects of sampling equipment upon dissolved HOC measurements and blanks</b>
<b>Study fate and bioavailability of atmospheric particulate matter in the water column</b>

<b>Candidate supporting studies for LMMBS</b>
<b>Measure methyl mercury in water, sediment and biota for understanding mercury cycling and bioaccumulation</b>
<b>Analyze PCDD, PCDF and coplanar PCB congeners in sediment and fish</b>
<b>Process research on mercury species transformation, sorption, and bioaccumulation</b>
<b>Measure sediment nutrient fluxes</b>
<b>Study organic carbon sorbent kinetics (especially particle degradation/mineralization rates): vertical resolution in water column/BNL/sediments</b>
<b>Improve measurements or estimates of flow across Straits of Mackinaw</b>
<b>Acquire/interpret remote sensing data for surface temperature, TSS and chlorophyll</b>
<b>Water intake monitoring for temperature and transmissivity</b>
<b>LMMBS integration with UM/NOAA thermal fronts study</b>
<b>Measure tributary contaminant loading during high-flow events</b>
<b>Estimate solids load from shoreline and bluff erosion</b>
<b>Monitor other significant point source loads for evaluating effectiveness of load reduction efforts</b>
<b>Research and estimation of contaminant loading from storm sewers/urban runoff</b>
<b>Model coupling of atmospheric and lake mass balances for hazardous air pollutants</b>
<b>Watershed deliver modeling to estimate present and future tributary loading of nutrients, solids and contaminants</b>
<b>Develop methods of distinguishing and separating particles into biotic and abiotic, as well as functional organic carbon sorbent classes</b>
<b>Fine-scale mapping of density, porosity, particle size and organic carbon content of surficial sediments based upon acoustical profiling or sediment surveys</b>
<b>Measure sediment mixed layer depth, particle residence time, and sedimentation velocity throughout depositional zones by coring and Cs and Pb-210 radiodating</b>
<b>Measure particle and contaminant exchange between sediment and water column: sediment trap measurement of vertical fluxes of solids, POC, Cs &amp; Be, chlorophyll, nutrients, and selected contaminants</b>
<b>Measure sediment resuspension properties as function of shear stress</b>

<b>Candidate supporting studies for LMMBS</b>
<b>Measure rates of contaminant desorption from resuspended sediment particles</b>
<b>Sampling and analysis of sediment pore water chemistry</b>
<b>Measure in-lake temperature, current and suspended solids profiles</b>
<b>Measure particle settling velocity (including effects of flocculation)</b>
<b>Research and measurement of dissolved and DOC-bound contaminant exchange between sediment and water</b>

The final selection of supporting studies necessary to support the modeling effort for the LMMBS, was based upon prioritization of modeling data requirements, utility in relationship to the model paradigms, and availability of demonstrated methods. Several supporting studies have been funded, as described below. However, at this time a number of high-priority efforts have not been initiated, due to lack of adequate time for planning, funding and personnel shortfalls, and constraints upon extramural modeling vehicles. These efforts are described below:

#### **eutrophication/sorbent dynamics (research and submodel)**

The eutrophication/sorbent dynamics model will require development or modification of existing models, to refine the relationships between biotic and organic carbon state variables, and to incorporate linkages to hydrodynamic and sediment transport submodels. In addition, research of specific processes related to understanding and modeling the dynamics and transformations of organic carbon states in Lake Michigan will be important to develop an accurate, scientifically-defensible toxics mass balance model. In Lake Michigan, the loss and transformation of particulate organic carbon states appears to be particularly significant (Eadie et al., 1983; Eadie and Robbins, 1987). Accurate simulation of the sorbent dynamics is critical, because the major transport, fate and bioaccumulation processes for toxics are all mediated by partitioning.

#### **sediment transport process measurements**

Measurement of sediment resuspension properties is essential for accurate sediment transport simulation. The measurements should establish the relationship between resuspension rate and applied shear stress, for an appropriate range of shear stresses both above and below the critical shear stress, including consideration of the effects of sediment ageing, compaction, and armoring. Methods for extrapolation of results to the whole lake, such as acoustical impedance,

should be tested in conjunction with sediment coring. This research should evaluate the variation in sediment resuspension properties both vertically and areally (at different spatial scales), as well as the relationship between resuspension properties and sediment contaminant concentrations. Although aspects of this process may be addressed by deployment of the seaflume, continued development will be necessary to ensure compatibility with modeling requirements.

#### estimates of shoreline erosion load: dynamics and variability

According to both contemporary (Colan and Foster, 1994) and historical sources, bluff and shoreline erosion is the major component of sediment loading to southern Lake Michigan. Although the majority of the erosional load is sand, as much as 25% is fine-grained material. Both components are probably significant influences upon sediment and contaminant transport. To be useful for modeling, the estimates of coarse- and fine-grained erosional loading must be resolved in terms of both temporal and spatial distribution. Estimates based upon relationships to factors such as wind and wave intensity, and water level, could be incorporated in the sediment and contaminant transport model. Survey of the literature reveals no such estimation methods, however.

#### vertical contaminant concentration profiles in sediment

Analysis of the top 1-cm of sediment cores, was recommended by the Sediment Workgroup as the optimum method to sample the distribution of toxics in the surficial mixed layer of lake sediments. From a mass balance perspective, this data will provide an adequate measure of the resuspendable toxic chemical associated with the sediment. Additional sampling of deeper sediment layers will be necessary to measure sediment-associated toxics at locations in the lake where greater than 1 cm of sediment resuspension is predicted, as well as to define vertical contaminant gradients which will increase contaminant fluxes via sediment mixing, bioturbation, and benthic irrigation processes. Analysis of sediment cores collected in 1991-92 may satisfy this latter need, at least for PCBs. However, sediments subject to greater than 1 cm of resuspension will be located in shallower lake regions, areas where coring and vertical profile analyses have not been performed. Because sediment core samples will be archived, it may be possible to defer analysis until estimates of maximum resuspendable depth can be obtained from the sediment transport model.

#### volatilization mass transfer rate

The volatile exchange of semivolatile toxics is driven by the local concentration gradient between the water and air, at a rate specified by a volatilization mass transfer coefficient ( $k_v$ ).  $k_v$  is generally estimated using semi-empirical relationships based upon two-film, surface renewal,

and penetration mass transfer descriptions. Depending upon the relationship chosen,  $k_v$  estimates can vary by as much as a factor of 5-10, directly influencing the computation of volatile flux. Furthermore, the different relationships vary in terms of  $k_v$  sensitivity to environmental variables including wind speed, wave height, fetch... For semivolatile contaminants in Lake Michigan, this variability introduces considerable uncertainty into the mass balance. Although measurements of volatile flux have been performed for toxic chemicals in the laboratory, and for tracers ( $O_2$ ,  $CO_2$ ,  $H_2O$ , Rn...) in streams, lakes, and oceans, direct environmental measurements are necessary in Lake Michigan to measure volatile exchange of hazardous air pollutants, especially PCBs and mercury.

#### tributary sampling during sediment resuspension/transport events

Highly-resolved monitoring and detailed modeling of sediment and contaminant transport in Great Lakes tributaries, has demonstrated that tributary loading is strongly related to extreme high flow events for contaminants originating from tributary sediments (Gailani et al., 1992; Velleux and Endicott, 1994). Unless the EMP monitoring program samples such events in tributaries with significant in-place pollutants, it is likely that tributary loading will be significantly underestimated. It is unclear whether the EMP tributary sampling effort can adequately address this requirement, in particular the "first flush" of contaminants which occurs on the rising limb of the hydrograph.

#### watershed contaminant delivery model

The need for a watershed component to the LMMBS was described previously. Depending upon the specific toxic chemical, watershed delivery encompasses a number of source and transport pathways. For atrazine, the source is spring agricultural application; runoff and groundwater transport from cultivated land are principal transport mechanisms. For PCBs and mercury, some combination of atmospheric deposition, nonpoint sources, and contaminated sediments appear to serve as watershed sources. Unless mass balance analysis is applied on the watershed, as it will for the atmosphere and lake, relationships between sources and tributary loading necessary for load reduction efforts will not be established. The severity of such a limitation upon the utility of the modeling results for each contaminant, will depend upon the magnitude of the watershed load relative to both air/water and sediment/water mass fluxes. Relative magnitudes of contaminant loads and mass fluxes will be determined as part of the mass balance project, suggesting that a watershed contaminant monitoring and modeling effort be designed and conducted subsequent to this project. Tributary monitoring and load estimates will also serve to identify specific watersheds for contaminant delivery modeling efforts.

#### development of user interface and model integration system

The drawback of the linked submodel framework, is that model execution and data transfer become a complex, repetitive series of computer operations. Thus, use of the models is beyond the general capabilities of scientists and decision makers, thereby limiting interaction with the models for both scientific and managerial interests. This situation would be greatly improved if the processes of model development and application was systematized and automated. To this end, a computer-based model integration system should be developed for the LMMBS models, with graphic user interfaces constructed for data analysis, model visualization, scenario management, etc... Such development would greatly facilitate the accessibility and utility of the models.

#### In-House Plan (LLRS/ERL-D)

The LLRS/ERL-D inhouse modeling team will lead the lake mass balance modeling effort. They will be responsible for the following tasks:

#### Screening-level (MICHTOX) analysis

The screening-level mass balance analysis performed for PCBs will be extended to the other toxics of concern: atrazine, mercury, and TNC. This will provide an operational model for evaluating transport and fate pathways for the different contaminants, testing air model linkages, and rapid incorporation of toxics loading and ambient monitoring data into the mass balance. The screening model will continue to serve its present function as a means of communicating and demonstrating the mass balance paradigm.

#### Submodel development and linkage

The inhouse team will lead development of the sediment and contaminant transport, CTF, and food web bioaccumulation models and model linkages.

#### Green Bay prototype application

The integrated submodel framework will be prototyped on Green Bay, using the GBMBS data for testing and confirmation. Sediment and contaminant transport, CTF, and food web bioaccumulation submodels will be linked to simulate the 1989-90 mass balance for PCBs and lead in the Fox River/Green Bay ecosystem. The extensive data for suspended solids, PCBs, and lead will allow for comprehensive testing of the Lake Michigan submodels, except that GBOCS (DePinto et al., 1993) will be substituted for the eutrophication/sorbent dynamics model. Such a test application is necessary for productive model development in advance of the EMP data.

### Model development for Lake Michigan

The inhouse team will perform data reduction, construction of input data sets, calibration and confirmation of the sediment and contaminant transport, CTF, and food web bioaccumulation models. Linkages with the eutrophication/sorbent dynamics and atmospheric transport models will be established.

### Lake Michigan model application

The integrated submodel framework will be applied to Lake Michigan, including both short- and long-term simulations for both scientific and managerial objectives.

### Extramural Plan

The expertise of a large number of extramural researchers will be required for a successful LMMBS modeling effort. Academic, consultant, and government collaborators will be funded to provide specialized expertise including: submodel process formulation, experimental design and conduct, data analysis, model development, and scientific peer review. Several cooperative agreements are in progress to develop and parameterize transport, fate and bioaccumulation process descriptions, funded by an ERL-Duluth/LLRS initiative for reducing uncertainty in toxic chemical models for the Great Lakes. These include:

Colloid Mediated Transport of Hydrophobic Organic Contaminants Across the Sediment-Water Interface in the Great Lakes Ecosystem (Yu-Ping Chin, Ohio State University) Development and application of methods to characterize and quantify organic colloidal matter residing in the pore water of Great Lakes sediments, study the effect of pore water colloids upon HOC distribution, and estimate on the basis of experimental measurements the ability of porewater colloids to facilitate the exchange of HOCs between the sediment bed and the overlying water column.

Reducing the Uncertainty in Modeling Dietary Transfer of Hydrophobic Contaminants (Robert Thomann, Manhattan College) Investigation of the dietary accumulation process of HOCs from detrital organic carbon to a benthic invertebrate species, leading to an improved submodel for macrobenthos bioaccumulation.

Sorption, Flux and Transport of Hydrophobic Organic Chemical (Wilbert Lick, University of California) Study of sorption process for HOCs on fine-grained sediment particles and incorporation of this information into CTF models. Experiments will be performed to measure equilibrium partition coefficients and chemical sorption

rates to and from sediments, under well-controlled conditions, in both suspended solids and deposited bottom sediments.

Uptake and Loss of PCBs by Phytoplankton: Importance to Mass Balance Models (Deborah Swackhamer, University of Minnesota) Investigation of the relationship between phytoplankton growth and HOC uptake kinetics, and HOC loss from phytoplankton by desorption and exudation. A submodel describing the dynamics of HOC accumulation in phytoplankton will be developed to incorporate this experimental data.

An interagency agreement between ERL-Duluth/LLRS and the NOAA Great Lakes Environmental Research Laboratory has been established to fund the following research:

Accumulation and Mixing of Recent Sediments in Lake Michigan Collection and dating of sediment cores taken at various locations in the lake, to generate lakewide distributions of sedimentation rate, mixed layer thickness, and Cs-137 and excess Pb-210 inventories.

Bioaccumulation of Organic Contaminants by Diporeia spp.: Kinetics and Factors Affecting Bioavailability Investigation and modeling of bioaccumulation rates of PCB congeners, including factors such as temperature, sediment composition, and availability of fresh detritus. Rates of porewater irrigation by Diporeia will also be measured.

Hydrodynamic Model of Lake Michigan Development and confirmation of a 3-dimensional hydrodynamic model, as described previously.

Sediment Resuspension and Transport in Lake Michigan Instrument platforms will be deployed to measure vertical water column distributions of temperature, transparency, and current at selected locations in the lake. Seaflume device will be deployed to measure sediment resuspension properties.

Use of Sediment Traps for the Measurement of Particle and Associated Contaminant Flux in Lake Michigan Deployment of sequential-sampling sediment traps, to measure gross downward fluxes of particulate matter and organic carbon, and to collect and analyze samples of the resuspendable sediment pool from selected depositional and non-depositional regions of the lake.

Additionally, several aspects of the EMP sediment sampling program (sediment core collection, radiometric dating, analysis for contaminants) have been coordinated with other programmatic



missions and funding sources, including the ERL-D/LLRRB Mercury Fate and Accumulation Project and the ERL-D Great Lakes EMAP Project.

A number of vehicles may be used to address the needs for additional supporting studies already identified. These include solicitation and competitive selection of cooperative agreements, funding work assignments through existing Agency contracts, and interagency agreements.

### Schedule

The schedule for LMMBS model development is complicated, for it must accommodate a number of incongruous objectives and factors: substantial model development lead time, uncertainty as to the schedule of data delivery, potential disruption of extramural vehicles, lack of funding to initiate necessary modeling tasks, and institutional requirements to rapidly develop interim and final results. In particular, timely project completion will be contingent upon stable funding, staffing, and extramural vehicles. IAG, cooperative agreement, and inhouse model development efforts have already begun, with additional model development efforts initiated in FY95. It is expected that a reasonably complete EMP data set will not be available until 1997, allowing two years for model development and testing, Green Bay prototype application, and conduct of supporting research. Initial simulations from the hydrodynamic and sediment transport models will provide transport linkages to eutrophication/sorbent dynamics and CTF models in late 1995 and 1996. By 1997 the linked submodels will be operational, although confirmation and refinement of simulations for the EMP period (1994-95) will require another year. Long-term model simulations will be conducted in 1998. Project completion, including preparation of final reports and transfer of the modeling system to GLNPO, is expected in 1999.

### Atmospheric Modeling Plan

#### Introduction

Atmospheric modeling provides a direct link between air toxics emissions and the greater Lake Michigan watershed. The Atmospheric model should be viewed as a comprehensive system, including not only the air quality simulation model (AQSM) which provides concentration and deposition fields, but also the meteorological and emissions models required to drive the AQSM. The atmospheric modeling system provides the following information useful to the aquatic mass balance model:

1. direct wet and dry deposition loadings,

2. near-water, ambient gas phase concentrations used in mass balance surface exchange calculations, and
3. meteorological fields of wind speed and direction, air temperature, heat flux, and radiation to drive hydrodynamic processes influencing sediment/water exchange, air/water exchange, and water column advection and dispersion.

The interaction between the air/water interface is bidirectional. During certain time periods, volatilization of PCBs from the lake surface will increase ambient concentrations over water, and may act as a major source in itself for downwind receptors. Atmospheric modeling will assist near-term program specific tasks and process oriented research by:

1. providing concentration and deposition fields for aquatic mass balance inputs,
2. supporting regulatory analyses addressing impacts resulting from various emission control strategies, and
3. serving as an integrator of available information (e.g., emissions, meteorology, ambient air chemistry) to enhance our understanding of transformation and deposition processes and provide direction for continued research.

The following plan describes the near-term (1995-96) and long-term approaches for regional scale atmospheric modeling within the Mass Balance Project.

### Air Quality Simulation Model

#### Model description

A dual track model development effort will address near-term program needs and research interests for the Lake Michigan Mass Balance Study. Modeling will be based on variations of the Regional Acid Deposition Model (RADM), which utilizes a gridded Eulerian framework to treat the relevant transport, transformation and deposition processes. The dual track reflects an immediate model development objective to be program responsive and the ongoing interest in enhancing the scientific credibility of the modeling efforts toward reducing uncertainty and improving process level understandings. The operational and research grade models will be based on similar geometric frameworks, thus minimizing the interfacing with meteorological, emissions and aquatic mass balance models. Generally speaking, the operational model will incorporate highly parameterized and available chemical transformation, particle description, and deposition schemes. Research grade modeling will build upon operational-grade models

by incorporating improved process characterizations utilizing process-related observed data and more sophisticated, mechanistic treatment.

Spatial scales. The modeling domain will extend throughout the continental U.S. (perhaps extending westward only to the Rocky Mountain region) and consist of a double-nested horizontal grid arrangement of 54 km and 18 km grids (this may change to a 36/12 configuration). The 18 km grid would overlay the Great Lakes basin. Generally 15 vertical layers will be used to represent the atmosphere through 100 mb (roughly 15 km). Some preliminary modeling may be conducted with 80-km grid cells and 6 vertical levels to test newly coded parameterization schemes. Certain research grade models may be based on 25 vertical levels for improved characterization of meteorological processes affecting vertical mixing and transport.

#### Operational Model

The operational model will be based on simplified, highly parameterized treatments of particle characterizations, chemical transformations and deposition. Gas phase chemistry of oxidants and relevant radical initiation/destruction processes will be parameterized, rather than calculated explicitly with complex chemical mechanisms. For example, particle concentrations and size distributions will be explicit model inputs (e.g., sulfate based particle fields) with limited growth and decay controlled by fluctuations in ambient moisture content. Phase distribution between particles and gas-phase will be based on best available thermodynamic data. Similarly, deposition processes will utilize existing algorithms and available data. Basically, "off-the-shelf", highly parameterized components will be used to economize model development and CPU times, respectively. For discussion purposes, the operational model will be referred to as the linear chemistry model (LCM) version of RADM. A working version of the LCM should be available in 1995.

#### Research-grade Modeling

Using the same general platform as the LCM, the model would be enhanced through continual updating of parameterization schemes and the incorporation of mechanistic chemistry and particle characterization algorithms. The research grade model will be referred to as the Regional Particulate Model (RPM), a derivative of RADM including treatment of sulfur, nitrogen and organic-based aerosols relying on more deterministic treatments of gas and aqueous-phase chemistry and phase distribution processes.

#### Utilization of Observed Data

The intensive monitoring programs will be collecting precipitation, particle and gas phase data over multiple locations. These data will be the basis for University research supporting development of deposition models and treatment of air/water exchange phenomena. In turn, these model components will be adopted for use in the atmospheric model to upgrade existing process schemes and input fields with current, area-specific data. The process entailing data collection, quality assurance, interpretation and algorithm development likely will extend over a 3-5 year period.

Observed data will also be used for model evaluation, as described below.

### Meteorological Modeling

#### Model description

Meteorological information for the toxics transport and deposition modeling will be obtained from the Penn State/NCAR Mesoscale Modeling System - Generation 4 (MM4) and Generation 5 (MM5). The MM4 and MM5 are Eulerian-grid, primitive-equation meteorological models which can employ four-dimensional data assimilation (FDDA) for diagnostic applications to constrain their simulations to the observed conditions. They can also be used for prognostic applications, but typical model error growth limits these forecast periods to about 48 hours. The MM5 has been developed as an extension of the MM4 to allow non-hydrostatic modeling of atmospheric physics. This Eulerian model, when using the non-hydrostatic physics, can resolve horizontal scales down to 4 km. It has improved computational grid nesting capabilities to allow up to 9 simultaneous grids with the capability of moving nests to follow small-scale phenomena of interest (squall lines, mesoscale convective complexes, etc.) Initial applications will use existing model output from the MM4 at an 80-km horizontal grid scale and 15 vertical levels. Meteorological information on a smaller horizontal scale will be produced using objective spatial analysis schemes and interpolation. MM5 applications should be possible beginning in late 1995.

Inputs required by the MM4 and MM5 models include: hemispheric-scale meteorological model analyses from the U.S. National Meteorological Center (NMC) and/or from the European Center for Medium-Range Weather Forecasting (ECMWF), terrain height and surface type information at the horizontal scale of the modeling grid, observed meteorological data at the Earth's surface (at 3-hour intervals for FDDA applications), and observed meteorological data at various vertical levels in the atmosphere (at 12-hour intervals for FDDA applications). Normal model outputs include: horizontal wind vectors, temperature, water vapor mixing ratio, atmospheric pressure, convective (sub-grid-scale) precipitation and non-convective (resolvable grid-scale) precipitation. Special model outputs obtainable without code modification include

cloud water and cloud ice density. Modifications can be made to extract the heat and momentum flux variables that are currently internal to the model code.

The RADM and LCM currently use a meteorological data pre-processor to read MM4 output data and format them for air-quality model input. The MM4 has normally been operated with the same horizontal and vertical grid definition as the air-quality model to which data is provided. Thus the meteorological data pre-processor is used to simply modify the computational data format. At this point there are no plans to allow feedback of chemical and aerosol results from the air-quality model to the meteorological model. However, it has been realized that aerosol loading of the atmosphere does affect radiative energy transfers, and these feedback mechanisms could be significant.

We envision that the meteorological model would supply both the air-chemistry model and the hydrodynamic model with meteorological inputs, but both links would be forward only (one-way). We realize that water surface temperature and roughness (wave height) information from the hydrodynamic model could be used to provide feedback forcing to the meteorological model, but such two-way linking would require the same level of effort as two-way linking to the air-chemistry model, which has thus far been beyond the scope of our research and development projects. However, two-way linking of the water- and air-quality models will be investigated.

#### Meteorological scenarios

Time periods for modeling will be determined by considering availability of processed MM4 simulations and relevance to the LMMBS. Currently, MM4 has been exercised for 1990 as part of the Interagency Workgroup on Air Quality Modeling (IWAQM) and initial modeling will therefore be restricted to that year. Issues to be resolved include the identification of meteorological periods and the method of producing annual estimates. Limitations on CPU time and storage media may restrict full, 365 day simulations. Consideration will be given to aggregating meteorological episodes to represent reasonable distribution of events in order to reduce total execution time. These computational savings become more important as we progress from operational to research-grade models.

#### Emissions data and modeling

Emissions data at the county level by season are available for mercury and atrazine. These data will be gridded into RADM compatible formats using standard GIS procedures. Eventually, these emission files should be updated as information becomes available from the Regional Air Pollutant Inventory Database System (RAPIDS). The availability of that inventory

ultimately will influence the selection (if any) of additional substances to be modeled beyond these two toxics.

Emissions data are not available for restricted/banned chemicals such as PCBs and TNC. The types of modeling analyses for these toxics will be restricted to determining transport patterns from lake surfaces.

#### Proposed model simulations

Mercury Mercury modeling has been conducted with the Regional Lagrangian Model for Air Pollution (RELMAP) for the continental U.S. To provide continuity and comparison with the RELMAP effort and to take advantage of the available mercury emissions inventory, LCM simulations producing annual 1990 deposition totals and concentrations for mercury will be exercised, as well as episodic periods corresponding to the 1994 intensive studies. Transformation and deposition processes will be based on the RELMAP effort (Bullock, 1994). Emissions of elemental mercury,  $Hg^0$ , divalent mercury,  $Hg^{++}$ , and particulate mercury,  $Hg_{part}$ , are apportioned by source category. Only the aqueous phase transformation of dissolved  $Hg^0$  to  $Hg^{++}$  through ozone oxidation was considered in determining the relative fractions of wet deposited mercury. Particle/gas phase transformations and gas phase transformations were not considered in dry deposition calculations.

PCBs Given the high level of interest in PCBs, a modeling effort to track the transport of PCBs from lower Lake Michigan to other areas will be conducted. The lake surface would effectively be considered the only emissions source and the relative impact due to subregion lake volatilization on other Lakes and lake subregions would be assessed. Since volatilization events exhibit strong episodic patterns, a short, perhaps 2-4 week period, would be modeled. Because this effort does not require an emissions inventory and extends over a short modeling period, this exercise could serve as an early example of interfacing atmospheric and aquatic systems. Changes in gas-particle phase distributions would be treated using available adsorption isotherm data following the general procedures intended for the RPM (Binkowski, 1994). Characterization of available particle area would be based on a simplified description of sulfate aerosol formation built into existing RADMLCM versions.

Atrazine Atrazine modeling would consider the same meteorological period as mercury (1990) and consider particle-gas phase interactions.

trans-nonachlor Modeling is not planned for TNC. The LMMBS may want to consider supporting emission inventory work for banned substances such as

trans-nonachlor and PCBs. The value of atmospheric modeling of banned substances for regulatory purposes requires clear definition and understanding before committing large resources.

### Interfacing/Linking Issues

#### Unidirectional linking

The initial modeling efforts, with exception of PCBs, will provide unidirectional inputs from the atmosphere to the Lake. The model output will consist of hourly wet and dry deposition and ambient gas phase concentration estimates above the lake surface on an 18 km (or other) basis. An interfacing system needs to be developed to interpolate the atmospheric estimates over comparable lake area domains. Note that the output will include concentration data above the lake surface required for air/water exchange calculations in the mass balance models. An interface should also be developed between the MM4 output files and the hydrodynamic model used in mass balance modeling. Analogous interpolation and extrapolation needs to be performed on monitoring data that are used to provide atmospheric loadings to the aquatic mass balance models. However, the large output files and consistent framework associated with the atmospheric models suggests that a specific, perhaps user friendly, software be developed for this interfacing, particularly if future technology transfer efforts are to be conducted with State agencies.

#### Bidirectional linking

A longer term objective is the more complete interactive operation of the aquatic and atmospheric models in which the interfacing is imbedded in the modeling construct and the lower atmosphere is impacted by air/water exchange of gaseous species. This linkage is being addressed through EPA's High Performance Computing (HPCC) program. The end product will be the capability to perform direct source to aquatic effect simulations incorporating more realistic physical treatment of exchange processes, without intermediate interface processing steps.

#### Model Evaluation

Model evaluation will be limited by the data available for comparisons with model estimates. The intensive monitoring data collected over and near the Great Lakes will be used to improve deposition and particle-gas phase distribution schemes in the atmospheric model. These data will be used to evaluate the ability of the model to partition between wet and dry deposition events and particle and gas phases. Such evaluations will be highly subjective, however, because the data will be used to improve the parameterization schemes used in the model.

Thus, the data will be used in a "nudging" manner to influence the modeled fields to reflect physical observations, rather than to independently confirm the predictions.

The observed data also will be used in a more classical approach to determine if the modeled concentration and deposition fields characterize observed fields. The utility of this exercise will be limited by the available data. Lacking an adequate upwind monitoring network, it will be difficult to trace the source/causes of disagreements between model predictions and observations. Episodic time-scale evaluations should be conducted to take full advantage of the observed data set and provide insight into the strengths and limitations of the modeling system. Evaluations on an annual scale should be performed to uncover systematic biases from season to season.

Without a dedicated field exercise to evaluate model performance, it will be difficult to associate poor model performance with difficulties in emissions, meteorology or process characterizations in the model. Nevertheless, the adequacy of emission inventories will be debated. Receptor modeling approaches might be integrated with the dispersion modeling to improve, or at least identify problems with, local emission sources. Eventually, resource decisions balancing the value of atmospheric modeling for decision-making and improved scientific understanding with the cost required for reducing model uncertainty will need to be addressed.

### 13.8 Atmospheric Modeling Schedule

time frame	products
1/95-12/95	RADM/LCM mercury output files for 1990
	RADM/LCM PCB output files for selected 1990 episodes
4/95 - 1/96	RADM/LCM PCB output files for selected 1994 episodes (coincident with field intensives)
	RADM/LCM atrazine output
	Additional mercury and atrazine simulations based on recommendations of Steering and Modeling Committees
1/96 - 1/97	Construction of model deposition and phase distribution algorithms based on field data and related University cooperative research
	Episodic runs for 1994 intensive period to evaluate model performance for Hg and atrazine



time frame	products
	Refinement of operational LCM
	Initial testing of RPM adopted for SVOCs

## Appendix 7. Sampling Locations for All Mass Balance Components

### LMMB Program Sediment Sampling Site

Site From	LMMB #	EMAP #	Depth	Lon	Lat
Nalepa-EMAP	1	75060	6	-86.929	41.706
Nalepa-EMAP	2	76622	25	-87.293	41.79
Special	3			-86.907	41.833
Nalepa-EMAP	4	79710	1	-87.659	41.872
EMAP 1	5	76620	43	-87.154	41.886
Nalepa-EMAP	6	73492	16	-86.649	41.899
EMAP 1	7	75050	50	-86.831	41.941
Nalepa-EMAP	8	76611	64	-87.014	41.983
TNh20	9		55	-86.753	42.014
EMAP 1	10	78190 *	54	-87.38	42.066
Nalepa-EMAP	10	78190 *	54	-87.38	42.066
EMAP 1	11	76610	83	-87.056	42.121
Nalepa-EMAP	12	79772	10	-87.747	42.148
EMAP 1	13	75040 *	75	-86.732	42.175
Nalepa-EMAP	13	75040 *	75	-86.732	42.175
EMAP 1	14	79770	43	-87.607	42.245
Special	15			-86.634	42.283
TNeg18	16		57	-86.643	42.293
EMAP 1	17	78180	101	-87.283	42.301
EMAP 1	18	76600	129	-86.958	42.356
Nalepa-EMAP	19	73472	52	-86.449	42.367
TNb7	20		45	-87.667	42.367
Special	21			-87.3	42.4
EMAP 1	22	75030	70	-86.633	42.41
EMAP 1	23	79760	100	-87.51	42.481
PVH-DNE-92	24		73	-86.53	42.5
PVH-DNE-92	25		125	-86.833	42.5
EMAP 1	26	78170	145	-87.185	42.536
EMAP 1	27	76590	147	-86.859	42.59
Nalepa-EMAP	28	79752	81	-87.554	42.619
EMAP 1	29	75020	84	-86.532	42.644
EMAP 1	30	81350	20	-87.739	42.66
PVH-DNE-92	31		122	-87.25	42.667
EMAP 1	32	79750	110	-87.413	42.716

Site From	LMMB #	EMAP #	Depth	Lon	Lat
Trap	33		159	-87	42.733
EMAP 1	34	78160	151	-87.086	42.771
TNc7	35		55	-87.575	42.792
TNc3	36		77	-86.474	42.819
EMAP 1	37	76580	99	-86.759	42.825
PVH-DNE-92	38		122	-87.25	42.833
PVH-DNE-92	39		149	-87	42.833
Nalepa-EMAP	40	73452	18	-86.246	42.835
EMAP 1	41	75010	72	-86.431	42.878
EMAP 1	42	81340	51	-87.642	42.895
Nalepa-EMAP	43	81340	51	-87.642	42.895
EMAP 1	44	79740	92	-87.315	42.951
EMAP 1	45	78150	88	-86.987	43.005
PVH-DNE-92	46		74	-86.406	43.017
TNh31	47		46	-86.364	43.033
EMAP 1	48	76570	103	-86.658	43.059
Nalepa-EMAP	49	79732	73	-87.358	43.089
Nalepa-EMAP	50	75000	30	-86.329	43.112
EMAP 1	51	81330	79	-87.545	43.13
EMAP 1	52	79730	80	-87.216	43.185
Special	53			-86.7	43.2
EMAP 1	54	78140	114	-86.886	43.24
EMAP 1	55	76560	86	-86.556	43.293
EMAP 1	56	82930	79	-87.776	43.309
EMAP 1	57	81320	115	-87.446	43.365
PVH-DNE-92	58		118	-87.667	43.383
EMAP 1	59	79720	77	-87.116	43.42
Nalepa-EMAP	60	82922	8	-87.82	43.447
EMAP 1	61	78130	125	-86.785	43.474
PVH-DNE-92	62		126	-87.617	43.5
EMAP 1	63	82920	73	-87.678	43.544
EMAP 1	64	81310	133	-87.347	43.6
EMAP 1	65	79710	146	-87.015	43.655
EMAP 1	66	78120	99	-86.683	43.709
PVH-DNE-92	67		145	-87.125	43.715
EMAP 1	68	82910	47	-87.579	43.78
EMAP 1	69	81300	85	-87.246	43.835
EMAP 1	70	79700	166	-86.913	43.889
Nalepa-EMAP	71	82902	32	-87.623	43.918
EMAP 1	72	78110 *	36	-86.579	43.943
Nalepa-EMAP	72	78110 *	36	-86.579	43.943
EMAP 1	73	82900	55	-87.479	44.015

Site From	LMMB #	EMAP #	Depth	Lon	Lat
EMAP 1	74	81290	147	-87.145	44.07
EMAP 1	75	79690	160	-86.81	44.124
PVH-DNE-92	76		169	-86.625	44.165
EMAP 1	77	82890	46	-87.378	44.25
PVH-DNE-92	78		220	-86.625	44.254
EMAP 1	79	81280	234	-87.043	44.304
EMAP 1	80	79680	242	-86.707	44.358
Nalepa-EMAP	81	82882	40	-87.422	44.388
EMAP 1	82	78090	136	-86.37	44.411
PVH-DNE-92	83		262	-86.705	44.475
EMAP 1	84	82880	101	-87.276	44.484
EMAP 1	85	81270	235	-86.939	44.539
EMAP 1	86	79670	263	-86.602	44.592
PVH-DNE-92	87		200	-86.354	44.623
EMAP 1	88	82870	76	-87.174	44.719
Nalepa-EMAP	89	86112	2	-87.894	44.746
EMAP 1	90	81260	207	-86.835	44.773
EMAP 1	91	79660	187	-86.496	44.826
Nalepa-EMAP	92	82862	1	-87.217	44.857
Nalepa-EMAP	93	78070	19	-86.157	44.878
Special	94			-87.55	44.9
Nalepa-EMAP	95	86101	15	-87.601	44.94
EMAP 1	96	82860	23	-87.07	44.954
PVH-DNE-92	97		160	-86.367	44.975
Nalepa-EMAP	98	74920	17	-85.475	44.98
EMAP 1	99	81250	173	-86.73	45.008
Nalepa-EMAP	100	82851	60	-86.922	45.05
EMAP 1	101	79650	194	-86.39	45.06
PVH-DNE-92	102		96	-86.25	45.062
PVH-DNE-92	103		200	-86.492	45.064
Nalepa-EMAP	104	76482	70	-85.857	45.068
EMAP 1	105	78060	39	-86.049	45.112
Nalepa-EMAP	106	84470	20	-87.306	45.134
PVH-DNE-92	107		197	-86.364	45.154
EMAP 1	108	76480	101	-85.707	45.163
EMAP 1	109	81240 *	57	-86.624	45.242
Nalepa-EMAP	109	81240 *	57	-86.624	45.242
PVH-DNE-92	110		183	-86.409	45.25
Nalepa-EMAP	111	76471	28	-85.556	45.257
EMAP 1	112	79640	157	-86.282	45.294
Nalepa-EMAP	113	82842	33	-87.009	45.327
EMAP 1	114 ?			-85.9	45.35

Site From	LMMB #	EMAP #	Depth	Lon	Lat
EMAP 1	115	76470	128	-85.596	45.396
Special	116			-85.5	45.4
EMAP 1	117	74900 *	52	-85.252	45.445
Nalepa-EMAP	117	74900 *	52	-85.252	45.445
EMAP 1	118	81230	66	-86.517	45.476
Nalepa-EMAP	119	82831	21	-86.71	45.519
EMAP 1	120	79630	127	-86.173	45.528
Nalepa-EMAP	121	76462	44	-85.636	45.535
EMAP 1	122	78040	55	-85.829	45.579
Nalepa-EMAP	123	84450	8	-87.097	45.603
Nalepa-EMAP	124	81220	14	-86.409	45.71
Nalepa-EMAP	125	76451	9	-85.331	45.723
EMAP 1	126	79620	71	-86.063	45.761
EMAP 1	127	78030 *	31	-85.718	45.812
Nalepa-EMAP	127	78030 *	31	-85.718	45.812
EMAP 1	128	76450	29	-85.371	45.862
Nalepa-EMAP	129	79612	16	-86.105	45.9
Nalepa-EMAP	130	74880	13	-85.024	45.91
Nalepa-EMAP	131	76442	18	-85.411	46.001

# Lake Michigan Mass Balance Study - Open Lake Stations

Lake	Station #	Latitude			Longitude		
		Deg	Min	Sec	Deg	Min	Sec
Lake Huron	54M	45	31	0	83	25	0
Lake Michigan	MB72M	45	48	20	84	55	0
	MB63	45	52	0	85	45	0
	52	45	29	0	85	33	24
	MB57	45	49	0	86	10	0
	45	45	16	12	86	51	24
	GB100M	45	16	20	86	42	0
	47M	45	10	42	86	22	30
	* 110	44	40	50	87	20	24
	* 140	44	41	2	87	16	23
	* 180	44	40	59	87	13	29
	MB38	44	47	0	87	13	20
	* 40M	44	45	36	86	58	0
	* 41	44	44	12	86	43	18
	* 43	44	41	50	86	16	20
	31	44	10	18	87	28	24
	36	44	3	36	86	32	0
	MB26	43	51	40	86	30	0
	27M	43	36	0	86	55	0
	MB25	43	43	0	87	40	40
	* 240	43	20	58	87	10	11
	* 280	43	21	16	87	14	50
	23M	43	8	0	87	0	0
	MB24	43	11	50	86	23	20
	MB20	43	2	30	86	18	20
	MB19M	43	3	23	86	38	47
	18M	42	44	0	87	0	0
	17	42	44	0	87	25	0
	MB21	43	1	0	87	45	30
	* MB9	42	19	11	87	42	34
	* 310	42	42	6	86	13	49

Lake	Station #	Latit			Lon		
		Deg	Min	Sec	Deg	Min	Sec
	* 340	42	41	22	86	18	54
	* 380	42	41	5	86	27	27
	5	42	0	0	87	25	0
	6	42	0	0	87	0	0
	6A	42	0	0	86	39	0
	1	41	46	0	87	20	0
	3	41	46	0	87	0	0
	* MB13	42	10	2	86	32	2
Green Bay	GB17	44	53	49	87	30	8
	GB24M	45	29	37	87	1	58

Key: MB prefix indicates that the station is near an existing GLNPO station of the given number. GB prefix indicates that the station was part of the Green Bay Mass Balance Study. The M suffix indicates a master station. Other prefixes or suffixes were assigned during previous efforts and have no special meaning for this study.

## EPA Lake Michigan Mass Balance Trap

### Trap Locations

	1	2	3	4	5	6	7	8
Latitude	41.904	42.957	45.542	45.203	44.735	43.057	42.732	42.287
Longitude	86.995	87.553	86.249	86.82	86.693	86.643	86.997	86.642
Station Depth (m)	50	82	132	58	250	101	160	56
GLERL Trap # @ 30m below surface					3 AO3		5	7
GLERL Trap # @ 5m above bottom	8	9	0	1	2 AO2		4	6
Years of trap data at/near station	1	1	0	0	3	14	6	2



## Lake Michigan Mass Balance Atmospheric Monitoring

Station	Longitude	Latitude
<b>Land-base</b>		
Beaver Island	-85.5404	45.7274
Sleeping Bear Dunes	-86.0583	44.7606
Muskegon	-86.3392	43.2269
South Haven	-86.1686	42.4644
Indiana Dunes	-87.0875	41.6317
IIT - Chicago	-87.6247	41.8344
Chiwaukee Prairie	-87.8092	42.5047
Manitowoc	-87.6553	44.065
ISWS Bondville Field	-88.3714	40.0525
Milwaukee	-87.8839	43.0753
Benton Harbor	-86.475	42.1167
Chicago SWFP Crib Intake	-87.5333	41.7861
Brule River	-91.605	46.7469
Eagle Harbor	-88.1497	47.4631
<b>Open Water</b>		
1	-87.3333	41.7667
6	-87	42
5	-87.4167	42
18M	-87	42.7333
23M	-87	43.1333
27M	-86.9167	43.6
41M	-86.7217	44.7367
47M	-86.375	45.1783
GB24M	-87.0328	45.4936

# **Lake Michigan Mass Balance Tributary Monitoring Sites**

<b>Longitude</b>	<b>Latitude</b>	<b>NAME</b>
-87.5894	45.0953	Menominee River
-88.0089	44.5286	Fox River
-87.71	43.7472	Sheboygan River
-87.8983	43.0244	Milwaukee River
-87.4558	41.6575	Grand Calumet Harbor
-86.4853	42.1133	St. Joseph River
-86.1067	42.6514	Kalamazoo River
-86.2403	43.0603	Grand River
-86.3394	43.2275	Muskegon River
-86.2786	43.945	Pere Marquette River
-86.2338	45.9486	Manistique River