

Green Bay/Fox River **Mass Balance Study**





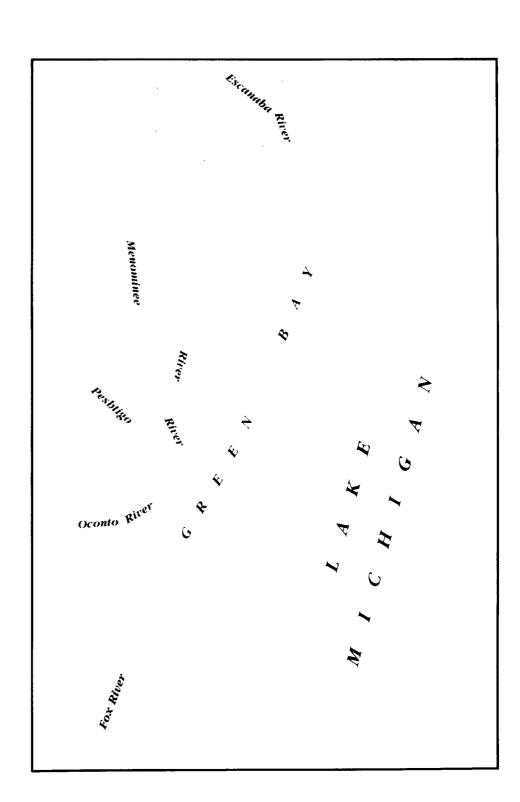












GREEN BAY MASS BALANCE STUDY PLAN: A STRATEGY FOR TRACKING TOXICS IN THE BAY OF GREEN BAY, LAKE MICHIGAN

U.S. Environmental Protection Agency Great Lakes National Program Office 230 South Dearborn Street Chicago, Illinois 60604

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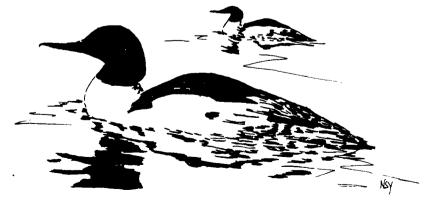


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PROCEDURE FOR STUDY MODIFICATIONS

The research project described in this document has not been conducted, as far as we know, on a geographic scale now being attempted. In no small way it encompasses the cutting edge of several facets of research regarding the fate of toxic substances in large aquatic ecosystems. For these reasons, the plan, as such, must be flexible. However, the successful outcome of the study requires a closely coordinated, multimedia and multidisciplinary effort, it is therefore essential that individual investigators or agencies do not unilaterlaly modify schedules or procedures. The following procedure will be followed prior to modification of any element of the Green Bay/Fox River Mass Balance Study.

- 1. Proposals for study modifications will be made in writing to the Chairman of the Technical Coordinating Committee (TCC).
- 2. The TCC, after consultation with the appropriate operational committees, will make the final determination on proposals of a technical nature which do not impact study or agency resources.
- 3. When resources are impacted, or modifications involve other than technical issues, the TCC will raise the issue to the Management Committee for resolution.

When modifications have been approved they will be incorporated into the Study Plan.

| <pre>Member:</pre> | Signature: | | |
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A. W. Andren and D. N. Edgington

University of Wisconsin-Madison and University of Wisconsin-Milwaukee

Application of the Mass Balance Approach to Green Bay: Sediment Loading, Fluxes and Redistribution of PCBs, Dieldrin and Other Chlorinated Hydrocarbons, Trace Inorganics and Radionuclides.

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Department of Geological Sciences University of Wisconsin-Milwaukee Milwaukee, WI 53201 Groundwater Flux in Western Green Bay

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Project Summary. Wastox, A Framework for Modeling the Fate of
Toxic Chemicals in Aquatic Environments; Part 2: Food Chain.

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NOAA/GLERL 2205 Commonwealth Blvd. Ann Arbor, MI 48105-1593 Resuspension and Particle Settling Velocities in Green Bay

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LLRS-USEPA 9311 Groh Road Grosse Ile, MI 24138 Water Column Station Locations

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USGS 6417 Normandy Lane Madison, WI 53719-1133 Prestudy for Green Bay Mass Balance Study

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Operation of a Master Atmospheric Deposition Measurement Site at Green Bay

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Measurement of Horizontal Sediment Flux and Sediment Resuspension

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USGS Field Operation Plan: Fox River at the Mouth and

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Nonparametric Evaluation of the Size of the Limnological Sampling

Networks: Application to the Design of a Survey of Green Bay

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Sediment Resuspension Quantification

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Application of Food Chain Model (Wastox: Part II) to Green Bay Lake Michigan: Screening and Sensitivity Analysis of PCBs in Lake Trout

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Operation of Master Atmospheric Deposition Measurement

Site at Green Bay

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Green Bay Modeling Committee LLRS/USEPA 9311 Groh Road Grosse Ile, MI 24138 Modeling Toxic Substances in Green Bay

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Water Volume Transport Measurements in Southern Green Bay

D. L. Swackhamer and S. J. Eisenreich

University of Minnesota, School of Public Health Box 1970, Mayo 420 Delaware Street SE Minneapolis, MN 55458 Intercomparison of Methodology for the Measurement of PCBs in Particulate and Dissolved Phases in Green Bay

T. C. Young

Department of Civil and Environmental Engineering Clarkson University Potsdam, NY 13676 Analysis of Green Bay Tributary Sampling Scenarios: The Fox River

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INTRODUCTION

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, in turn, allows informal prioritization and allocation of research, remedial actions and regulatory efforts for water quality management. The approach requires that the quantities of contaminants entering the system, less quantities stored, transformed or degraded within the system, must equal the quantities leaving the system. Once a mass balance budget has been established for each pollutant of concern, the long-term effects on water quality of the lakes can be simulated by mathematical modeling.

Mass balance modeling has been successfully applied to the regulation of nutrient loads in the Great Lakes during the past decade. However, the sources, pathways, and sinks for organic and inorganic toxic substances (toxics) are less well understood. It is, therefore, necessary to pilot the mass balance approach for toxics in a smaller ecosystem prior to expansion to whole lake situations. Toxicants of interest include PCBs (at the congener level), dieldrin, lead, and cadmium as representatives of classes of compounds. The physical/chemical models will be coupled with a food chain model to allow estimation of body burdens (Figure 1). The integrated model will then be used to predict concentrations in the water, sediment, and biota in response to differing regulatory and remedial action scenarios. The predictions will include long-term extrapolation from the short-term calibration.

The bay of Green Bay, Lake Michigan, will serve as the study site. Green Bay can be characterized as a long, relatively shallow extension of northwestern Lake Michigan (Figure 2). The Green Bay watershed drains land surfaces in both Wisconsin and Michigan, and contains about one-third of the total Lake Michigan drainage basin. The lower bay and Fox River have been recognized as a polluted

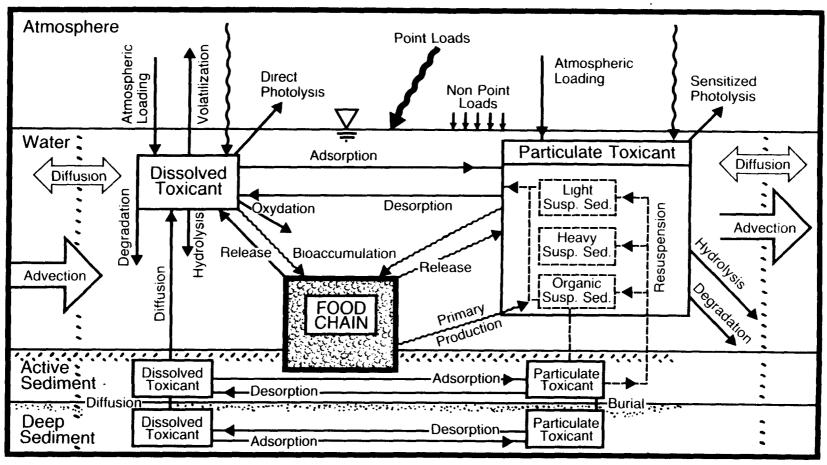
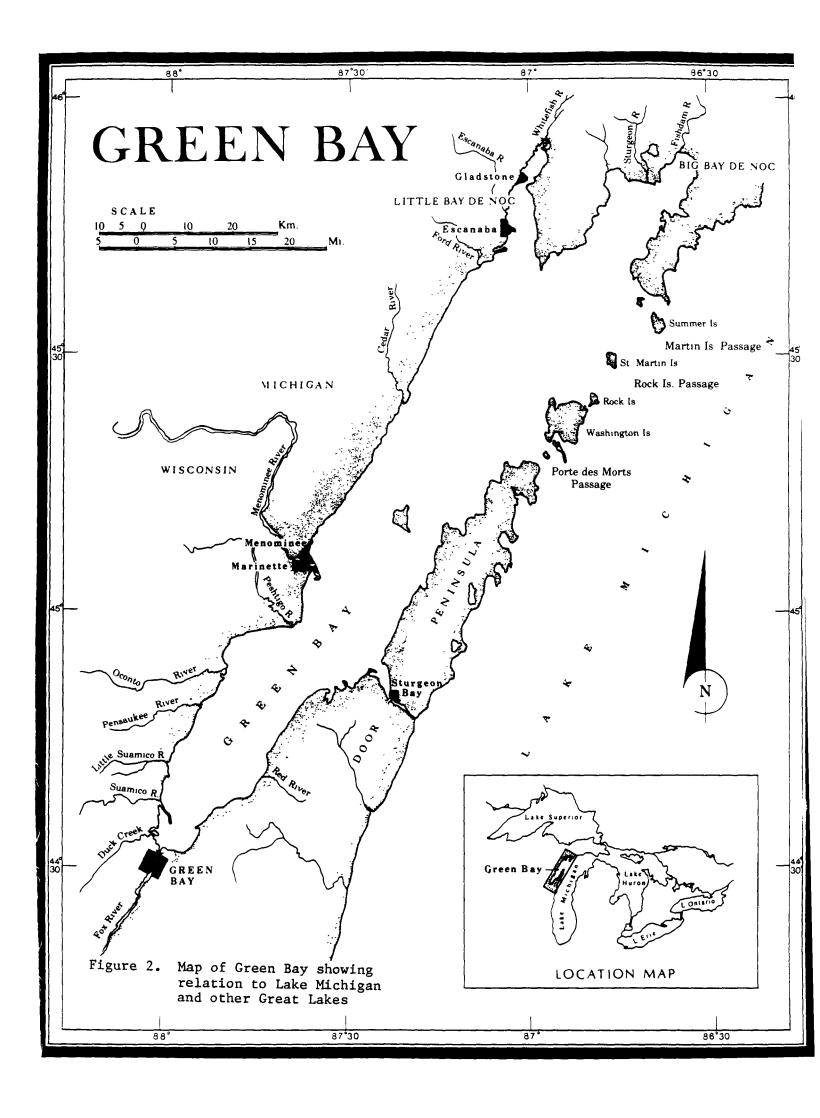


Figure 1. Graphic Mass Balance model showing pathways and fates of toxic substances in an aquatic ecosystem.



water system. The Fox River Valley is heavily industrialized and contains the largest concentration of pulp and paper industries in the world.

The hydrodynamics of the bay are generally controlled by rotational, wind, and barometric forces. Currents tend to be counterclockwise with two main gyres in the upper and lower bay. Currents are heavily influenced by seiche activity, particularly in its southern portion. Central and northern portions of the bay are known to stratify.

Presently the bay ranges from hypereutrophic in the southern portion to mesotrophic-oligotrophic near the Lake Michigan interface. The extreme productivity in the southern basin results in deposition of organic material and associated hypolimnetic oxygen depletion in the central bay.

Toxic organic materials in the water, sediment, and biota of Green Bay has adversely impacted both utilization and management of the Bay's fishery. The commercial fisheries in the Bay, with the exception of yellow perch, are severely restricted by PCB contamination, and consumption advisories have been issued to anglers for most sport species. Due to exceedingly high PCB levels in all sizes, the commercial carp fishery has been closed by WDNR for the past 5 years. Fish eating birds have experienced reproductive failure and increased deformities apparently related to PCB contamination. The Fox River is estimated to contribute 600-1200 Kg of PCBs annually to the bay. Sediment contributions of PCBs to the water column within the bay are presently unknown.

The Green Bay Mass Balance Study (GBMBS) is intended to provide information to aid and support regulatory activities. However, its major goal is to (1) carry out a detailed mass balance of Great Lakes toxic substances, notably individual PCB compounds or congeners in Green Bay, and (2) based on the mass balance data, apply predictive tools that will aid resource managers evaluate the impact of management decisions. The GBMBS will serve as a pilot for future modeling studies of Great

Lakes ecosystems. The Green Bay Project will engage numerous investigators involved in project design, field collection, analysis and processing of data, quality assurance, data management and modeling activities. The project will be coordinated by the USEPA Great Lakes National Program Office (GLNPO), Chicago, Illinois. Modeling activities will be facilitated by the USEPA Large Lakes Research Station.

The Green Bay Mass Balance Study Plan (GBMBSP) is intended primarily as a communication device to link the activities of the standing technical committees ie. Field and Technical Operations Committee (FTO), Modeling Committee (MOD), Field and Analytical Methods Committee (FAM), and the Biological Committee (BC) to the required actions of the Technical Coordination Committee and ultimately to the Management Committee. It will serve to both guide the direction of the entire research effort and also to monitor the progress of the various "study components" and their attendent "work elements." The basis for the study plan eminates from past research efforts, the original Green Bay Mass Balance Work Plan (October, 1986), activities and reports of the Technical Committees since that time, project proposals from various agencies for particular work elements and several planning workshops.

The study plan has been organized to help insure that the data and information necessary to construct a mass balance for PCBs, dieledrin, cadmium, and lead (hereafter referred to as target chemicals) in Green Bay become available for model development in an orderly fashion. Essentially, the study plan is a design to gather the data needed to construct and drive the mass balance model.

Risk Assessment and Mass Balance Models

Ultimately, toxic substances are evaluated in terms of the risk posed to humans or other living organisms. The hazard posed to a natural water system by

a toxic chemical is governed by the uptake of the chemical by the resident biota and subsequent acute and chronic health effects. Evaluation of the risk involves three basic steps:

- 1) estimation of the chemical concentrations in the water and sediment
- estimation of the rate of uptake of chemical by segments of the resident biota
- 3) estimation of the toxicity resulting from uptake of the chemical

The GBMBSP considers only the first two steps of this risk assessment process, the third step goes beyond the bounds of the project. Execution of the first two steps requires consideration of the transport, transfer, and reaction of the chemical and the dependence of these processes on properties of the affected natural water system and its biota (Figure 1). Based on experimentation and theoretical development each process has been, or can be, described mathematically, specifying its functional dependence on specific properties. These expressions may be combined using the principle of conservation of mass to form a mathematical model that addresses one of the steps in the risk assessment.

Steps 1 and 2 of this risk assessment are addressed by the general modeling framework entitled WASPIV, an acronym for Water Quality Analysis Simulation for TOXics. This modeling framework is composed of two parts which may be termed the exposure concentration (physical-chemical) and food chain components, respectively. The exposure concentration component of WASPIV is the computational structure for applying step 1 to a specific natural water system. The food chain component of WASPIV is the computational structure for applying step 2 to a specific natural water system.

The physical-chemical model simulates water column response to various loading scenarios. The physical-chemical model is then coupled with a food chain model, eutrophication model and solids model to simulate biotic response to different

toxic loading scenarios. The biological end points chosen for Green Bay are tissue residues in various size classes of three fish species: walley, brown trout, and common carp. From simulations, the optimal strategy for remediation may be determined. Expected biological end points will be predicted target chemical concentrations found in the three species of fish.

Substantial "front end" planning has gone into the Green Bay Mass Balance. Reconnaisance level modeling has been conducted to evaluate and rank the impact of the various state variables and coefficients on model output. Surogate parameters have been used to model and optimize tributary load monitoring as well as collection frequency and station location in Green Bay proper. Additional studies have been undertaken to identify those tributaries requiring load monitoring and to delineate the forage base for the target species. The original goal of the Green Bay Mass Balance was to predict concentrations of PCB, dieldrin, Pb and Cd in walleye, brown trout and carp to within one half order of magnitude in order to make the model useful in management decisions. It is estimated that this level of accuracy (or better) will be achieved if major loading sources and compartments are monitored within ± 20-30% of the mean values. The tributary, atmospheric and open bay portions of this plan are designed to meet this ± 20-30% criteria.

STUDY PLAN ORGANIZATION

The GBMBSP is partitioned into six major divisions, each reflecting particular requirements to develop the mass balance model. These divisions are:

- I. Inputs
- II. Outputs
- III. Active Pools and Interfaces
- IV. Biota
- V. Quality Assurance and Data Handling
- VI. Administration

Divisions are further subdivided into particular "study components" eg. Tributary loading, point source loading, atmospheric loading, etc. Each study component is made up of particular "work elements" necessary to satisfy model development and operation.

The format of the study plan consists of an abreviated narrative for each study component addressing:

- -- sampling design, experimental procedures or information gathering activities
- -- responsible agency or individual to conduct study
- -- funding source

Details of individual work elements for particular study components will be contained in separate appendices and will be used as the basis of quality control and quality assurance review and will ultimately direct the field efforts. The GBMBSP is of necessity a dynamic plan since particular work elements will be phased in and out over a period of years, thus changing the action and progress status of these work elements. In order to keep all parties informed about the current status of particular work elements, a flow sheet containing all pertinent

information will be updated and circulated to all interested parties every two months. A narrative summary noting changes will accompany the flow sheet.

MODEL COMPONENTS AND WORK ELEMENT DESCRIPTIONS

I. INPUTS

Previous studies indicate that the Fox River contributes over 80 percent of the total PCB tributary load to Green Bay. Other tributaries known to contribute PCBs include the Oconto, Peshtigo, Menominee and Escanaba Rivers. Tributaries have not recently been sampled for dieldrin or other target toxicants. Consequently, a reconnaissance survey was conducted to identify those tributaries for which load monitoring will be required. Sampling was conducted by the U.S. Geological Survey starting in July, 1987, on the following tributaries to Green Bay: Duck Creek, Suamico River, Ford River, Days River, Rapid River, Whitefish River, Wilson River, and Fishdam River. The Oconto, Peshtigo, Menominee and Escanaba Rivers were not sampled because they have already been determined to be sources of PCBs and will require monitoring. Separate sampling was done for dieldrin on Egg Harbor tributary, Keger Creek, and the Red Riverbecause a likely source of dieldrin may be from orchard areas surrounding these streams.

Based on the findings of the reconnaissance survey, the Menominee, Escanaba, Oconto, Peshtigo, and Fox River, (Figure 2) will be monitored to determine loading of target chemicals into Green Bay.

A. 1. Tributaries

Sampling frequencies for different rivers varies according to volume flows and the delivery of suspended solids. The Peshtigo, Oconto and Escanaba Rivers will be sampled once monthly. Duplicate samples will be collected on six trips. The Menominee River will be sampled thirty-four (34) times during the open water

period and four (4) times during the winter. A total of 16 duplicate sampales will

be taken.

Water and suspended sediments will be sampled with a high-capacity submersible

The samples will be integrated over depth and cross-section.

analysis, samples will be filtered (glass fiber filter) and extracted at the sample

site. Extracts from prefilters and filters will be combined to produce one com-

posite particulate extract per sample. Dissolved phase organics will be extracted

using XAD-2 resin columns. PCB analyses will identify specific congeners as well

as quantify particulate and dissolved fractions. In addition to the other target

chemicals, water samples will be analyzed for several variables (see Table 1).

Daily suspended sediment loads will be determined for each tributary using

continuous discharge data and daily or weekly suspended sediment samples. Daily

samples will be collected by automated sampler on the Peshtigo, Menominee and

Escanaba Rivers, while weekly or daily high-flow samples will be collected by a

local observer at the Oconto River.

Investigating Agency - USGS

Funding Source - GLNPO/USGS

Contact person: Peter Hughs 608-276-3833

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TABLE 1. VARIABLES TO BE MEASURED IN A PARTICULAR MEDIUM AND MODEL COMPARTMENT

| Variable/Medium | Bay and Lower Fox | Tributary Loads Water | Atmosphere Loads Water | Bay and Lower Fox Sediments | Bay and Lower Fox Pore Water | Bay and Lower Fox Biota | Point Sources |
|-----------------------------------|----------------------|--------------------------|---------------------------|-----------------------------------|------------------------------------|-------------------------------|------------------|
| Diss. PCB Conge | x | x | x | | | | |
| Part. PCB Conge | x | x | x | | | | |
| Total PCB Conge | s | s | s | x | x | x | x |
| Diss. Dieldrin | x | x | x | | | | |
| Part. Dieldrin | x | x | x | | | | |
| Total Dieldrin | S | S | S | x | x | x | x |
| Diss. Lead | x | x | x | | | | |
| Part. Lead | x | x | x | | | | |
| Total Lead | S | s | s | x | x | x | х |
| Diss. Cadmium | x | x | x | | | | |
| Part. Cadmium | x | x | x | | | | |
| Total Cadmium | s | s | S | x | x | x | x |
| Total Phosphorus | x | x | x | x | | | |
| Sol. React. Pho | x | x | | | | | |
| Nitrate | x | x | | | | | |
| Ammonia | x | x | | | | | |
| TKN | x | x | | | | | x |
| Diss. Avail. Si | x | x | | | | | |
| Chloride | x | x | x | | | | x |
| Conductivity | x | x | x | | | | x |
| Temperature | x | x | x | | | | x |
| Suspended Solid Size Fractions | x | x | x | | | | x |
| DOC | x | x | | | x | | x |
| TOC | x | x | | х | | | x |
| POC | x | x | | | | | |
| Chlorophyll-a | x | | | | | x | |
| Mn | | | | | x | | |
| Fe | | | | | x | | |
| Hardness | x | x | x | | | | |
| pΗ | x | x | x | x | x | | x |
| Alkalinity | x | x | x | | | | × |
| DO | x | x | | | | | |
| Total Incid. Ra | x | | x | | | | |
| Light Extinction | x | | x | | | | |
| Porosity | | | | x | | | |
| Grain size | | | | x | | | |
| % solids | | | | x | | | |
| % water | | | | | x | | |
| Redox Pot. | | | | | x | | |
| Eh | | | | x | x | | |
| River Flow | | x | | | | | |
| Wind Vel. Direc | x | | x | | | | |
| Continuous Flow | | | | | | | x |
| Growth Rate/Age | | | | | | x | |
| Lipid | | | | | | x | |
| Stomach Contents | | | | | | Carp | |
| | | | | | | - | |

Legend: S = Sum of particulate and dissolved required

A.2. Contaminant Loading from the Fox River

An accurate determination of the particulate and dissolved load of PCBs transported into Green Bay by the Fox River is an essential component of the Green Bay/Fox River Mass Balance Project. It is feasible to estimate the PCB load from the Fox River by computing the load at the DePere Dam and adding the point source inputs downstream in addition to nonpoint source and sediment flux estimates. These data are then used in conjunction with the application of hydrodynamic and water quality models to the Fox River. However, the lower reach of the Fox River is affected by seiche and wind which results in bi-directional flow. hydrodynamic complexity and the wide range of possible loadings from the point sources, nonpoint sources, and in-place sediments can result in significantly different estimates of the contaminant load to Green Bay. Consequently, two methods of estimating the Fox River load are proposed. Both methods involve measurement and modeling. The first method (A.3) involves measurement of loads at the DePere Dam and modeling of the gradients of concentrations in the Fox River and Green Bay to determine loading. The second method (A.4) involves measurement of flows and concentrations at the Fox River mouth and modeling of the chloride concentrations (or other tracers) to determine which river mouth measurements represent upstream and downstream fluxes. Comparison of the two methods of load estimation will be used to determine which method would be more useful and practical to undertake on a larger scale.

A.3. Contaminant Loading -- Fox River/DePere Dam

This method requires an estimate of contaminant loading at the DePere Dam as a boundary condition to drive a model for the Lower Fox River. The U.S. Geological Survey will sample water 8.04 miles upstream of the mouth on the upstream side of the dam 39 times during the open water season and 3 times during the winter period.

The modeling effort will also use six stations in the river (Figure 3) between the DePere Dam and the mouth to collect depth integrated water samples which will coincide with the open bay sampling surveys.

Three stations (numbered 50 - 55) will be sampled three times (every 8 hours) during a 24 hour period as part of the Green Bay Mass Balance October Survey.

Sampling Location:

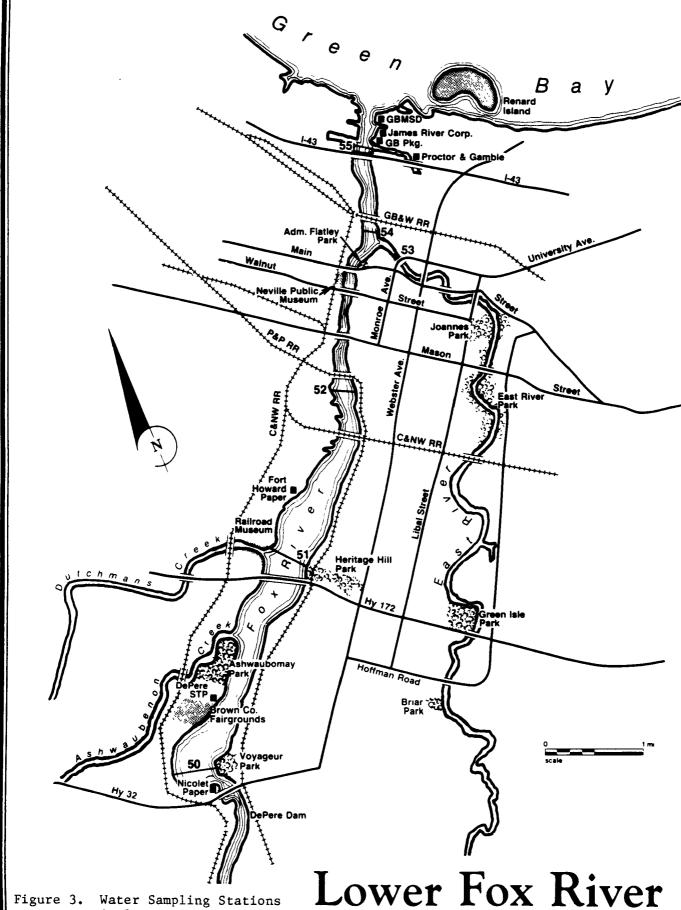
| STA. | west | center | east |
|------|-----------------------|--|-----------------------|
| 50 | 44^27.26′ | 44^27.23' | 44^27.20′ |
| | 88^04.19′ | 88^04.08' | 88^04.06′ |
| 51 | 44^28.78′ | 44^28.76' | 44 ²⁸ .72′ |
| | 88^02.74′ | 88^02.62' | 88 ⁰² .50′ |
| 52 | 44 ^{30.18} ′ | 44 ³⁰ .17′ | 44 ³⁰ .18′ |
| | 88 ^{01.49} ′ | 88 ⁰¹ .45′ | 88 ⁰¹ .40′ |
| 53 | | 44 ³¹ .10′ 88 ⁰⁰ .45′ | |
| 54 | 44 ^{31.39} ′ | 44 ³¹ .38′ | 44 ³¹ .36′ |
| | 88 ^{00.73} ′ | 88 ⁰⁰ .72′ | 88 ⁰⁰ .65′ |
| 55 | 44 ³² .16′ | 44 ³² .13′ | 44^32.13' |
| | 88 ⁰⁰ .46′ | 88 ⁰⁰ .44′ | 88^00.40' |

Sampling Points:

Station 53 located on the East River will be sampled at a single point, mid-channel, mid-depth. The remaining five stations will be sampled from mid-depth at three points along a transect perpendicular to the river, mid-channel and 1/3 the channel width on each side.

Compositing:

Equal volumes of water will be collected from each of the 3 sampling sites along the transect to provide a composite volume sufficient for the measurement of the parameters described in Table 1 of the variables to be measured.



Water Sampling Stations in lower Fox River.

Filtered Water Collection:

Station 53 will be sampled 3 times during the 24 hour period. At each of the 3 samplings 18 Liters of river water will be pumped through 2 Whatman GF/F filters (293 mm) and the filtered water collected in a glass carboy. Upon return to the R/V Simons the 18 Liters of filtered water will be pumped through an XAD resin column extracting the organic compounds from the water. The same XAD column will be used to extract each of the 3 collections from station 53. The XAD column will represent a composite organic extraction sample for the 24 hour period. The 6 filters used during the 24 hour collection period at station 53 will be wrapped in foil, labeled and placed in a plastic zip-lock bag and frozen.

At each of the remaining 5 stations 6 Liters of river water will be filtered at each of the 3 sampling points along the station transect and the filtered water composited in a glass carboy providing 18 Liters of filtered water. The 18 Liters of filtered water and 2 filters shall be treated as described for station 53.

Net tows as described in the biological work plan shall be collected once during the 24 hour period at stations 50, 51, 52, 54 and 55.

It will also be necessary to estimate the flux of contaminants from the sediments. Surficial contaminant concentrations will be measured at 25-30 stations in the lower river and fluxes estimated at three stations 3 times during the field season. Fluxes will be estimated at those stations having the highest contaminant concentrations. Estimates of point sources and urban non-point sources will be required (see I.B., D., E., and F.).

A.4. Contaminant loading -- Fox River/Mouth

Transport of contaminants (target chemicals) from the Fox River to Green Bay will be determined for the period March 1989 to February 1990. The field

water-quality sampling site for this element is at the mouth of the Fox River and is downstream of all but one point source discharger (GBMSD). Continuous streamflow data will be available from the USGS Acoustic Velocity Meter (AVM) gaging station located 0.75 miles upstream from the mouth.

For the purpose of contaminant load estimates, routine water samples will be collected on 36 days (33 open water and 3 winter) at the mouth of the Fox River. A total of 86 replicate samples will be taken. Intensive sampling events will also occur at the mouth with the following frequency:

Spring High Flow - 14 days, 2 samples/day

Summer Low Flow - 14 days, 2 samples/day

Fall Medium Flow - 14 days, 2 samples/day

In addition, automated pump samplers will be installed at the mouth to collect a minimum of three samples per day at two depths (0.2 and 0.8 times the normal total depth). Samples will be analyzed for total and volatile suspended solids and chloride. The solids data will be used to compute the suspended sediment load transported by the Fox River into Green Bay. The solids concentrations will also be statistically evaluated to determine their relationship to PCB concentrations. Chloride data will be used to track migration of water from Green Bay into the Fox River estuary during periods of flow reversal. Continuous monitoring for dissolved oxygen, temperature, conductivity and pH will be done at 0.2 and 0.8 times the total depth.

The field sampling and organic extraction procedure will be the same as those used for tributary sampling. The channel section at the mouth will be divided into a minimum of three approximately equal flow cells with the cell centroids identified on a field map or by Loran-C coordinates. At each of the cell centroids, water samples, dissolved oxygen, pH, conductivity, temperature, velocity and flow directions will be obtained at 0.2 and 0.8 times the total depth.

Investigating Agency - USGS/GLNPO/WDNR

Funding Source - USGS/GLNPO

Contact Person - Peter Hughes (608-276-3833)

B. Point Sources

The potential exists for all paper mills and some municipalities to discharge PCBs. The discharge of PCBs from point sources to the Fox River has primarily been attributed to paper mills recycling wastepaper. There are seven major point sources between the DePere Dam and the mouth of the Fox River. An additional 2 dischargers are located above the monitoring station on other tributaries. These nine point source dischargers will be monitored to determine the PCB loads. Seven dischargers will be monitored quarterly and two will be monitored monthly. Both influent and effluent samples will be obtained so that net loading can be determined.

Samples will be taken by the individual dischargers and will be 24-hour composites. Dischargers will be directed to collect the samples to coincide with river surveys when possible and also to provide continuous discharge flow measurements. Samples will be iced and shipped to the Wisconsin State Laboratory of Hygiene for analyses. Total sample size will be 1-4 liters. It is anticipated that this sample size will provide levels of detection of about 2-12 ng/L for individual PCB congeners. PCB analysis will be done on the particulate and dissolved fraction. Analysis will also be conducted for the other target contaminants.

Investigating Agency - WDNR

Funding Source - WDNR/GLNPO

Contact Person - John Konrad (608-267-7480)

C. Atomosphere

Three atmospheric sampling stations will be used to quantitate target chemical loads to Green Bay. These will include a Master Station comprised of three wet precipitation collectors with XAD-2 columns, two directionally operated high volume dry air samplers with absorbent columns to quantify vapor and particulate phase PCBs as well as other target chemicals. Additional "Master Station" equipment will also include a high volume collector dedicated to total suspended particulate and organic carbon, two cascade impactors and a meterological tower providing hourly data on wind speed, direction, humidity, temperature, precipitation, and solar radiation. Organic samples will be taken every 6 days for dry deposition and every 2 weeks plus events for precipitation (see Table 1 for other variables to be measured). The Master Station will be located on the University of Wisconsin-Green Bay campus approximately one-half mile inland on the east bay shore.

Routine monitoring stations will also be located at Fayette State Park in Upper Michigan and Peninsula State Park in Door County, Wisconsin. Each will provide trace organics from precipitation on a two week basis. In addition, routine sites include two wind directionally operated high volume samplers with XAD-2 resin cartridges for collection of trace organics in ambiant air every sixth day for a twenty-four (24) hour period.

Investigating Agency-Illinois State Water Survey,

DePaul University and USEPA

Funding Source - GLNPO

Contact Person - Edward Klappenbach (312-353-1378)

D. Evaluation of Potential Contribution of PCBs from Selected Landfills

Numerous waste disposal sites are located in the Lower Fox River and Green Bay watersheds. Present day regulations require the selection of environmentally compatible sites and use of engineering controls such as impermeable clay liners and leachate collection systems. Earlier landfills did not benefit from such planning. Most of these early sites were inappropriate for waste disposal. The Wisconsin Department of Natural Resources (WDNR) has inventoried the landfill and waste disposal sites within the Green Bay/Fox River mass balance study area. There are 16 abandoned landfills within this area. Several of the sites have monitoring wells installed, although in most cases the number of wells is insufficient to adquately evaluate the site.

There are three sites along the Fox River below the DePere Dam and along lower Green Bay which have monitoring wells. Samples will be collected from these wells and analyzed for PCBs, dieldrin, lead and cadmium. Approximately 6 monitoring wells exist at each site. During 1988-89, a total of 30 samples will be obtained. Some wells will be sampled once. Others will be sampled more often, since wells which are definitely not appropriate will not be sampled.

A separate research project has been developed to design a monitoring and evaluation protocol for waste disposal areas which do not currently have monitoring wells. This proposal is being considered for inclusion in WDNR's 1989-91 budget request. If funded, this project would develop methodology which would be applied to further monitoring and evaluation of landfill sites in the Lower Fox River and Green Bay area.

Investigating Agency - WDNR

Funding Source - WDNR

Contact Person - John Konrad (608-267-7480)

E. Evaluation of Potential Contribution of PCBs from Urban Areas

Estimates of PCB, dieldrin, cadmium and lead loading from the Green Bay Metropolitan Area will be done in two phases. The first phase will be a unit area load calculation based on existing data applied to the land use types found in Green Bay. A large data base exists for cadmium and lead in urban nonpoint source runoff. Unit area load calculations should provide accurate loading estimates for these parameters. Less information is available for PCB and dieldrin.

With respect to dieldrin, a unit area load calculation will not be performed. In urban nonpoint source studies, dieldrin is seldom detected and when detected its source is residential areas. Since dieldrin is banned as a pesticide and has not been detected to date in pre-surveys, it will be assumed that urban areas are not significant sources of dieldrin to the lower Fox River and to Green Bay.

PCB concentrations in urban stormwater runoff have been determined in several studies. The results obtained from the Nationwide Urban Runoff Program have been applied to the Green Bay area. PCB concentration in all but one out of 120 samples collected in commercial and residential areas in Milwaukee and other cities were below detection limits (0.021 to 0.50 ug/l). Because of these very low levels of PCB associated with commercial and residential areas, unit area loads for these land uses were not calculated. In industrial areas in Milwaukee, eight out of nine samples collected exceeded PCB detection levels (0.021 to 0.05 ug/l). The highest concentration was 7.9 ug/l with an average of 2 ug/l. These results indicate that industrial areas can be a significant source of PCBs.

The estimated annual nonpoint source PCB loading from industrial areas in Green Bay is 12 kilograms assuming the average concentration of 2 ug/l and 47 kilograms assuming the highest concentration (7.9 ug/l). The annual load of PCBs from the Fox River has been estimated at 600 to 1200 kilograms. The PCB loading from industrial areas in the City of Green Bay could account for 1 to 9 percent of

the annual load. These relatively low PCB loadings suggest that intensive monitoring is not warranted.

The second phase of the Nonpoint Source Element will be to inventory the existing industrial areas to determine similarities and differences from the areas monitored in Milwaukee. This inventory will document possible wet and dry weather sources of PCBs. For example, electrical transformers stored in an industrial yard are a potential wet weather source of PCBs and the heavy use of hydraulic fluid inside a plant is a potential source of dry weather PCBs. The survey will also delineate the subbasins the industries are in. The survey results will be used to determine the potential for PCBs from industrial sources. Residues from selected stormsewers will be analyzed for PCBs. These samples will be of sludge and/or scrapings from the wall of the stormsewers. The results of the industrial survey and the stormsewer residues will be used to determine if additional monitoring of urban stormwaters is necessary. All analyses will be for specific PCB congeners.

Investigating Agency - WDNR

Funding Agency - WDNR

Contact Person - John Konrad (608-267-7489)

F. Evaluation of Potential Ground Water Contributions

Existing information is currently being evaluated to summarize what is known about the groundwater flow system between the surrounding aquifers and the Bay. Special emphasis is placed on describing the shallow flow systems, since these will likely carry most of the pollutant load. This existing information has been supplemented with additional monitoring data and is being used to calibrate a groundwater flow model developed under the auspices of UW Sea Grant Institute. Once calibrated, this model will be applied to Door County and used to predict

contaminant loading to the Bay and the importance of these loadings as an input to the mass balance.

Groundwater and soil monitoring for PCBs, dieldrin, cadmium and lead was initiated during the spring of 1988. This monitoring will be continued during 1988-89. The additional samples will fill in where current efforts have identified data needs. These are areas of known contamination from lead and based on use patterns, areas of possible dieldrin contamination. New sample sites will be selected to define the area of Door County that could be contributing lead or dieldrin to the Bay. Additional sample sites for PCBs and cadmium will be targeted at suspected locations since documented contamination sites are not available. Suspected locations could include spill sites, old material handling locations, or waste disposal sites thought to contain cadmium or PCBs.

Investigating Agency - WDNR

Funding Source - WDNR

Contact Person - John Konrad (608-267-7489)

II. OUTPUTS

Contaminants in Green Bay can leave via a water route dissolved in the water or as suspended particles through the passages north of the tip of Door County. Biotic transport, although possible, has been evaluated as insignificant. Some may also leave by way of volitilization into the atmosphere or conversely by permanent burial in the sediments of Green Bay. To understand the true fate of contaminants in Green Bay, all routes must be monitored to establish the flux rates across the compartments of interest. Projects will be conducted to establish:

- 1) Water volume transport from the bay
- 2) Horizontal sediment flux and sediment resuspension
- 3) Particle settling velocities, and

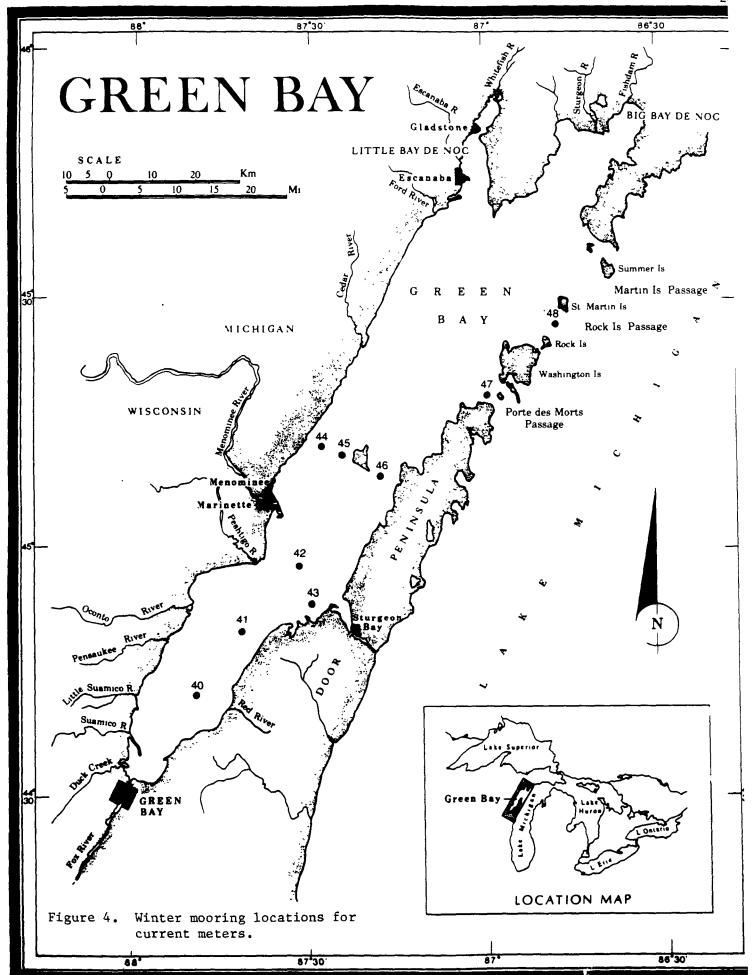
4) Desorption kinetics, sedimentation rates, and volitilization

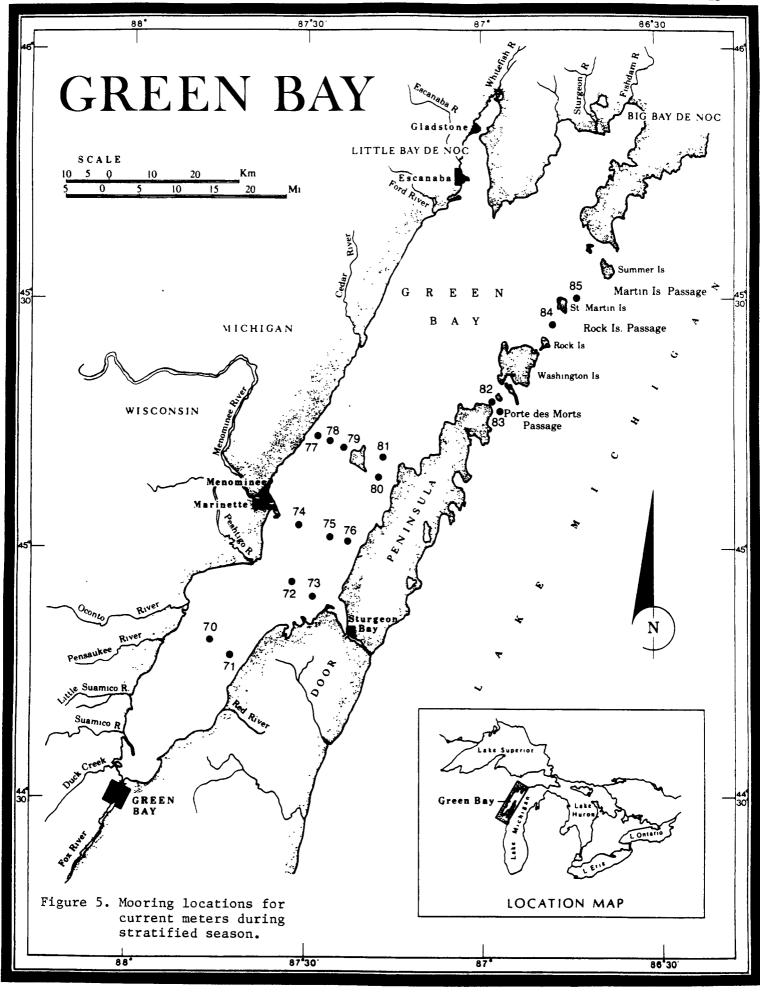
Three separate projects have been developed to address these modeling requirements. Two of these projects will be conducted by investigators from the Great Lakes Environmentnal Research Laboratory/National Oceanic and Atmospheric Administration (NOAA).

A. Water Volume Transport

The water exchange processes with Lake Michigan are very complex with, on the average, intense outflows of bay waters in the surface layers and inflows of Lake Michigan water penetrating deep into Green Bay in the near-bottom layers. The inflowing Lake Michigan waters can be identified flowing southward west of Chambers Island, causing accelerated flushing of the lower bay. Measuring water volume exchanges between the lower and upper bays with enough accuracy for use in the mass balance approach will require current velocity recordings in the channels on both sides of Chambers Island. Winter moorings (17 current meters total) will be installed at eight locations in September 1988 and retrieved in April 1989 (Figure 4). It is expected that after an energetic fall season of circulation in an unstratified water mass, currents under the ice will be driven mainly by the lunar tide and seiches interacting with northern Lake Michigan.

Moorings at sixteen locations and employing 37 meters total for the stratified season will be installed during May 1989 and retrieved during October 1989 (Figure 5). To extend the velocity profiles through the entire water column acoustic doppler current meters will be placed on the bay floor in the channels on both sides of Chambers Island. Measurements of flow in the surface layers of the water column are critical to the goal of computing water volume transports. Four thermistor chains placed at strategic locations will be used to measure water





temperature variations and thermocline depth.

Flow trajectories in the lower bay during varying surface wind stresses will be studied during a two-week long interval in June 1989 using combinations of satellite-tracked surface drifters and drogues, as well as a satellite transmitting meteorological station GLERL will install for the duration of these measurements. These measurements will establish a time history of the water volume exchange quantities between the upper and lower parts of Green Bay at Chambers Island. The volume fluxes will establish boundary conditions for improved hydrodynamics modeling and are necessary for the contaminant mass balance.

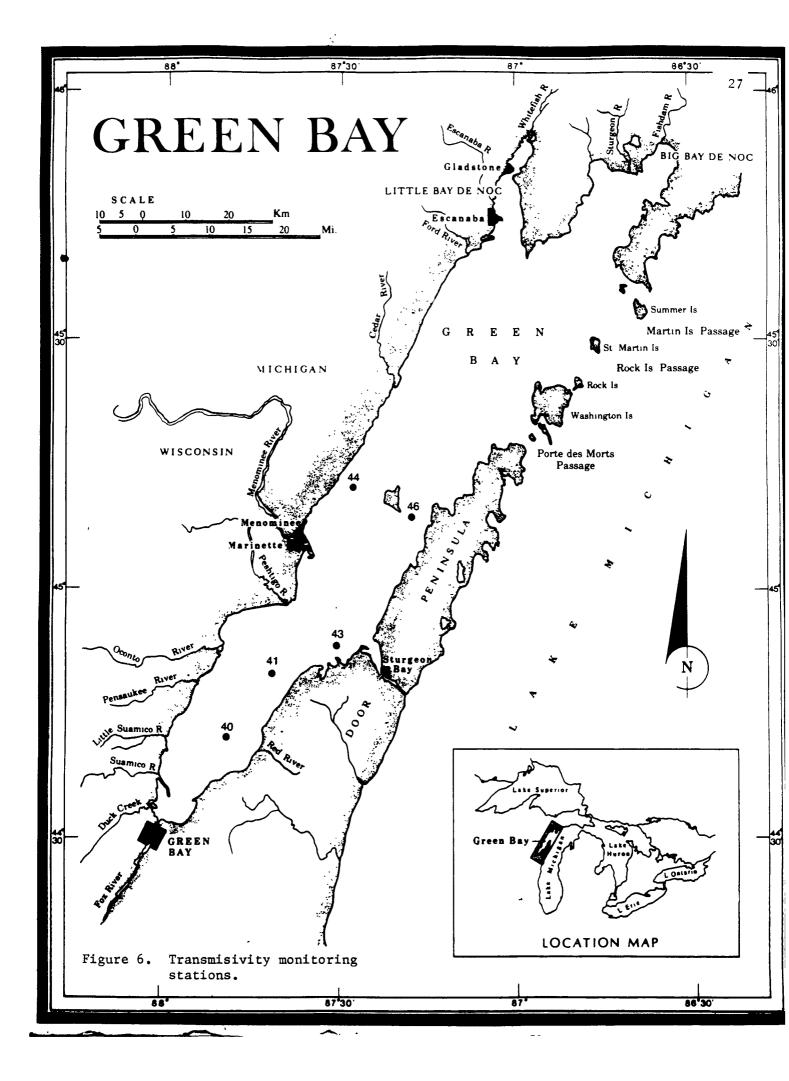
Investigating Agency - Great Lakes Environmental Research Lab (GLERL-NOAA)

Funding Agency - GLERL/GLENPO

Contact Person - J. H. Saylor (312-668-2118)

B. Sediment Flux and Resuspension

To measure horizontal sediment flux in and out of Green Bay and the amount of sediment resuspension, instrument packages will be deployed at several locations in the bay. Instruments that measure current velocity approximately one meter above the bottom, and water temperature, transparency, and conductivity one and five meters above the bottom and five meters below the surface will be deployed at five sites in Green Bay: Stations 40, 41, 43, 44, and 46 (Figure 6). Stations 40, 41, and 42 will be deployed beginning in May 1989, and will be maintained until May 1991 with the exception of station 40, which will be reviewed during the winter; the other stations will be deployed as soon as the necessary instruments are available (this is dependent on receipt of funding by GLERL and cannot be further specified at this time). The stations will be maintained at these locations until October, 1990 with the exception of station 40, which will be removed during the winter. All stations will be serviced monthly, except during the winter. Monthly



servicing will include retrieval of data, cleaning the transparency meters, and changing the power supplies.

A bottom-resting flume will also be deployed at selected sites to experimentally determine the bottom current necessary for sediment resuspension for various types of sediment (characterized by grain size distribution).

The time series data will be analyzed to determine an empirical criterion for sediment resuspension, and be combined with the water volume fluxes (GLERL Project II.A.) to calculate a time series of the horizontal mass flux of suspended material. All analyses will be in terms of measured velocities. The conductivity measurements will be used to identify the path of water coming from the Fox River.

The transparency meters will be calibrated by comparing the measurements to direct measurements of total suspended material (TSM) made by filtering known volumes of water through pre-weighed glass fiber filters. The decreased response of the meters due to material growing on the lenses during the summer will be monitored by making weekly profiles of water transparency using a clean meter at each of the deployment sites between May and October. These profiles, which will also measure temperature and conductivity, will also provide data on the vertical structure of these properties. These measurements will be used to develop a set of empirical equations relating sediment resuspension to current velocity for various bottom types (as defined by grain size) and an equation for the horizontal flux in and out of the bay.

Investigating Agency - NOAA

Funding Agency - GLNPO/NOAA-GLERL

Contact Person - Nathan Hawley (GLERL) (313-668-2273)

C. Sediment Resuspension Quantification

The above field measurements will be conducted by a battery of experiments designed to understand and characterize the physical and chemical processes affecting particle resuspension and the subsequent dynamics of particle size distribution and floc morphology of the resuspended material. The objective is a quantitative understanding of sediment resuspension as a function of sediment characteristics and bottom shear stress. This will involve vicometer experiments, settling studies, annular flume experiments and field resuspension experiments. The intent is to provide a synthesis of experimental results and field measurements into a mathematical framework that can predict the spatial and temporal distribution of solids and contaminants (solid and dissolved phases) that result from a resuspension event.

Investigating Agencies - GLERL.

University of California Santa Barbra

Funding Agency - GLNPO

Contact Persons - Wilbert Lick (805-961-4295)

D. <u>Desorbtion Kinetics</u>, <u>Sedimentation Rates and Volitilization</u>.

The total mass of contaminants in the sediments and water column influence the rates of contaminant exchange between the sediment, water and air. Most of the mass of pollutants such as PCBs, dieldrin, Pb and Cd reside in the sediments of the Green Bay ecosystem. The concentration of pollutants in the sediments will exert a dominant effect on the concentrations in other compartments. Consequently, it is necessary to:

- 1) Quantify the spatial distributions of PCBs, dieldrin, Pb and Cd, both horizontally and vertically. This also includes:
 - a) Development of a strategy to determine the total mass of

these pollutants in the Bay, and for PCBs, the mass of each individual congener. If possible, other hydrophobic pollutants will be included.

- b) Determination of sedimentary organic carbon and particle size distribution (sand and clay/silt fractions) to examine the relationship between these parameters and pollutant concentrations.
- 2) Determine sedimentation rates and surface mixed-layer thicknesses throughout Green Bay using 137Cs and 210Pb geochronology.
- 3) Using data generated from the tasks of objective 2, calculate:
 - a) the mass of active sediments (i.e. sediment effectively remaining in contact with the overlying water) in the bay and the rate of leakage to the permanently buried sediments;
 - b) the mass of PCBs, both as total Aroclors and on an individual congener basis, in the active and inactive sediment layers.
- 4) Evaluate diffusive fluxes of PCBs across the sediment/water interface and the effects of changes in the partitioning of PCBs between interstitial water and sediment on these fluxes as a result of variations in the concentration of dissolved organic carbon.
- 5) Evaluate the importance of volatilization of these compounds from the water when a mass balance is considered.

In order to meet the requirements of objectives enumerated above, a two-tiered sediment sampling and analysis program is proposed covering two field seasons.

In the first year of the study (1988) sediment cores will be retrieved from approximately 50 stations, chosen to provide an initial best estimate of the spatial distribution of the mass of PCBs in the whole Bay and a first estimate of the sediment mass balance (Objectives 1, 2, and 3). These stations will include

10 from south of Long Tail Point and 5 from the extreme northern end of the Bay where samples have not previously been taken (Figure 7a & b). A variety of coring devices will be used and cores obtained typically are sectioned in 1 cm intervals down to 10 cm, in 2 cm intervals down to 30 cm and in 5 cm intervals down to the end of the core.

While all cores will be sectioned in their entirety, and the gamma-ray spectra of radionuclides will be measured on as many sections as are required to reach sediments that are older than 200 years before present, it is planned that to meet objective 1 for the mass balance 8 sections will be analyzed from each core for base/neutral organic compounds. The numbers of individual sections to be composited into each single sample to be analyzed for PCBs, other organics, as well as Cd and Pb, will be determined on the basis of the observed depth of the 1952 horizon of 4137_Cs in each core.

In addition to providing the first estimate of the total mass of PCBs present in the sediments and their areal and vertical homogeneity, these results will provide the basis for the Green Bay Modeling Committee to recommend refinements to the sediment sampling program for the second field season (summer 1990).

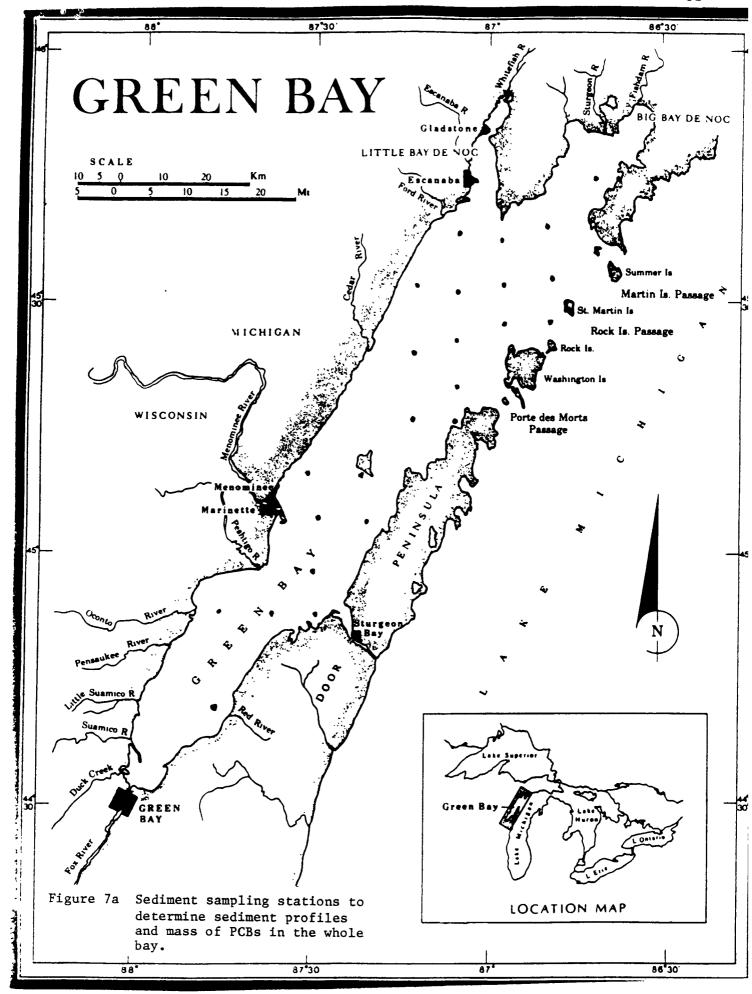
Investigating Agency - UW Sea Grant Institute,

Madison/Milwaukee

Funding Agency - UW/GLNPO

Contact Person - Anders Andren (608-262-0905)

David Edgington (414-649-3008)



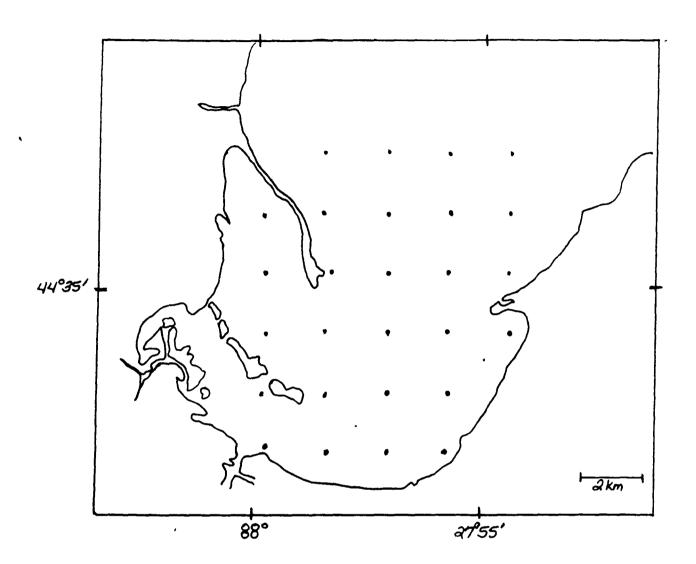


Figure 7b. Sediment sampling stations to determine sediment profiles and mass of PCBs in the whole bay.

III. ACTIVE POOLS AND INTERFACES

A. Lower Fox River Sediments

The sediments below the DePere Dam are known to be contaminated with PCBs. Suspension and subsequent transport of these contaminated sediments could result in significant PCB loading to Green Bay. The soft sediments in this portion of the river will be characterized based on core samples. Approximately 36 cores will be obtained using a private contractor. Each core will be divided into four sections. Particle size, % solids, total organic carbon and total PCBs will be determined on all samples; lead, Cd and Dieldrin concentrations will be determined. Specific congener PCB analyses will be conducted on 10% of the core samples. The results of this activity will provide needed information to link the Fox River PCB transport model with the model developed for Green Bay.

Investigating Agency - WDNR

Funding Source - WDNR

Contact Person - John Konrad

B. Water Column

B. 1. Method Evaluation

Measuring minute quantities of PCBs in natural water bodies presents some formidable problems. The best method to separate particulate and dissolved phases of PCBs has heretofore not been well defined. Consequently, research to evaluate two methods of particulate PCB isolation, including continuous flow centrifugation and high volume flow filtration was undertaken. Investigators evaluated three methods of isolating dissolved phase PCBs (high volume liquid-liquid extraction, batch extraction, and XAD column extraction), both in combination with centrifugation or filtration so that the best combination of dissolved / particulate separation methods could be determined.

This work was conducted in November 1987 in preparation for the 1988 field testing. It was determined that while high volume liquid to liquid extraction holds substantial promise, it currently is not develoed to the extent necessary for this study. Dissolved phase organics will therefore be determined by extraction on XAD-2 resin.

B. 2. Water Column - Bay

In general, water and suspended sediments will be collected on each of five surveys per year during the 1989 navigable season. If possible, a winter (under ice cover) survey will also be conducted in the winter of 1989-1990. The frequency of frontal passage (3-4 days), the large number of sampling stations twenty-seven (27), and requirements for synoptic surveys (6 days or less) will require the use of a vessel capable of operating 24 hours a day for periods of up to one week.

Twenty-seven (27) stations (Figure 8) were selected for monitoring contaminants and conventional variables in the water columns.

Approximate survey schedule for 1989 will be (to be modified based on phytoplankton and thermal events):

- 1. February 15 (under ice) 4. June 26
- 2. April 15

5. August 14

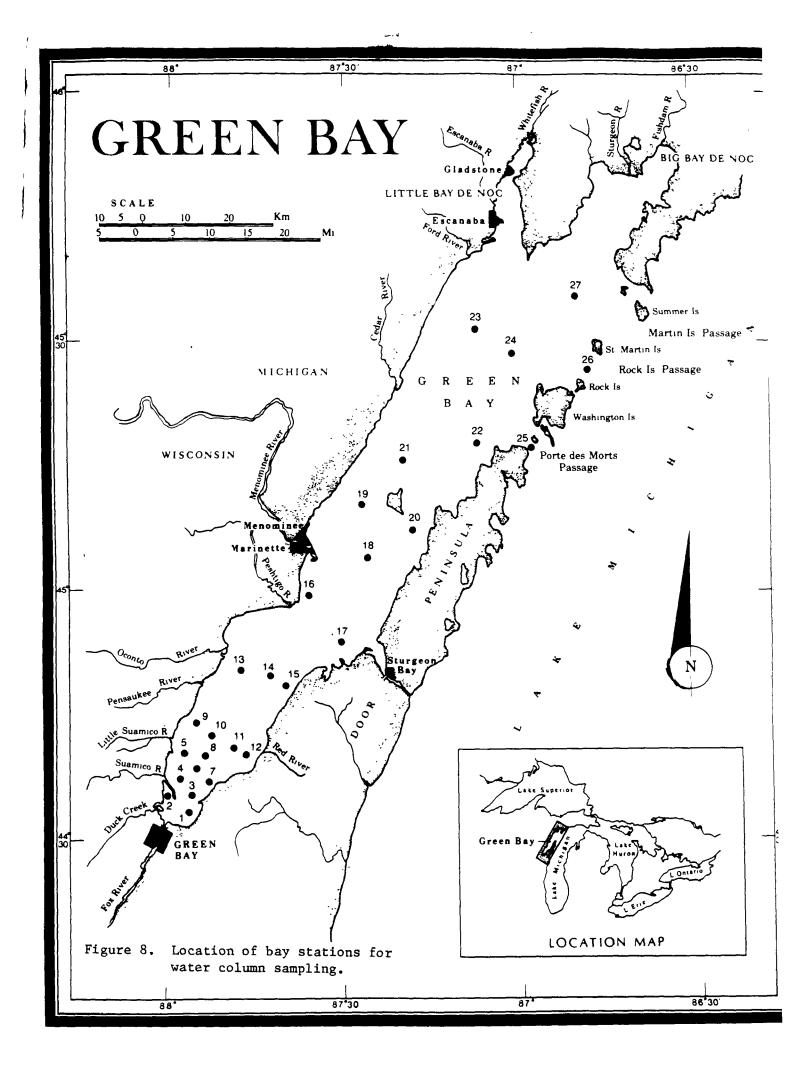
3. May 15*

6. October 16

* May be modified depending on "ice out" date.

Parameters to be measured at each station are found in Table 1.

At each of the 27 stations lake water is pumped on board through polyethylene pipe or tubing of approximately one inch diameter by use of a submersible centrifugal pump. A portion of this water is filtered through a 293 mm diameter glass fiber filter to collect a suspended solids sample of about 50 mg. The filtrate from this filtration is collected in a suitable storage container (glass,



stainless steel, or Teflon) for extraction with XAD resin columns. A mid-depth sample is taken from non-stratified water columns, and mid-hypolimnion and mid-epilimnion samples are collected from stratified water columns. The samples are filtered while at the sampling location. The filtrate is subjected to the extraction while enroute to the next sampling location. The collected sediment on the filter is retained in a glass jar with Teflon lined closure.

IV. BIOTA

A. Food Chain Model

General biological study components to meet modeling requirements will include: contaminant body burden determinations of primary fish species and their respective supporting food chains, phytoplankton species composition and abundance estimates, chlorophyll a measurements, and bioenergetic characters for biotic components.

Six major morphometric zones (Figure 9) have been identified for the study which exhibit and correspond to physical/chemical/biological gradients in the Bay; these include eutrophication, chemical contaminant, forage, and habitat gradients. Besides the gradient factors, zonation has been based on distribution of fish populations, availability of fish, and the number of samples which could be reasonably collected and analyzed during this study.

Biota will be sampled three times during the navigational period and represent three general seasons: April--June 20th, June 21--September 20, and September 21--November. Walleye, brown trout, and carp have been chosen as the target species for the Green Bay study. These species meet most or all of the criteria for target species selection. The study of these species and their respective, supporting food chains will be the primary biological effort in the Green Bay study.

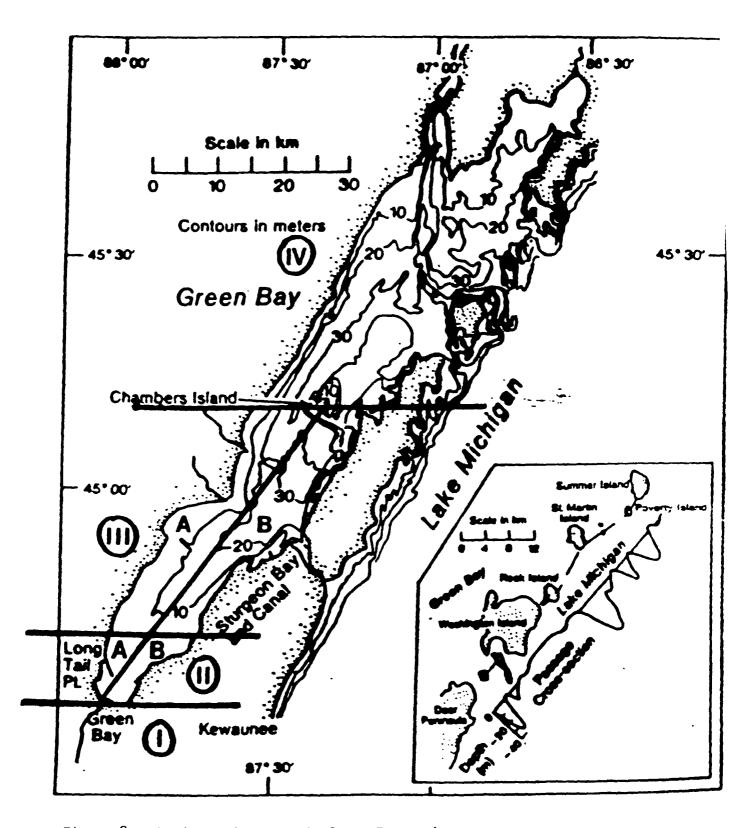


Figure 9. Morphometric zones in Green Bay to be used for sampling biota.

The major biological field effort for the Green Bay study will be to collect specimens for contaminant analyses for all biological components in food chain models. Beyond specimen collections for body burden analyses, the weight, length, and age (target species only, forage species to be separated by size groups) of fish will be determined in order to calculate bioenergetic parameters for modeling (See Table 2 for biota parameters).

Gut content analyses were conducted in 1987 to determine the species-specific forage bases of walleye and brown trout in several areas of the Bay; these data have been used to determine the sampling strategy for forage species. Results of gut content analyses indicated that rainbow smelt and alewife were the primary forage bases of walleye and brown trout and gizzard shad were a forage component of walleye in zones I, IIA, and IIB (Figure 9). Carp gut contents will be excised from specimens collected to represent their forage base because of the difficulty in obtaining meaningful information on the feeding of carp. Target and forage species will be collected from each zone during the 3 time windows outlined previously. Multiple size classes of each species of fish will be required for modeling and sought; however, it is recognized that not all size classes for each species, in each zone, for each seasonal sampling period will be available and this has been factored into the sampling scheme and number of samples to be collected. For walleye and carp three size classes will be sampled, for brown trout two size classes in addition to fall and spring stock specimens, for alewife and smelt two size classes, and for gizzard shad one size class.

For target species, five replicate samples per zone per season will be obtained for each size class. Each replicate will consist of 5 fish (5-fish composite) and weigh a minimum of one-half pound. For the forage species, five replicate samples per zone per season will be obtained for each size class. One half pound of each size class will be collected and represent one sample/replicate.

Table 2. SUMMARY OF GREEN BAY BIOTA SAMPLES AND VARIABLES TO BE MEASURED

| | WALLEYE | BROWN | CARP | SMELT | ALEWIFE | SHAD | PHYTOPLANKTON | ZOOPLANKTON |
|-------------|---------|-------|------|-------|---------|------|---------------|-------------|
| WEIGHT | x | x | x | x | x | x | | |
| LENGTH | x | x | x | x | x | x | | |
| AGE | x | x | x | | | | | |
| LIPID | x | x | x | x | x | x | x | x |
| PCB | x | × | x | x | x | x | x | x |
| DIELDRIN | x | x | x | x | x | x | x | x |
| Cd | x | x | × | x | x | x | x | x |
| Pb | x | x | x | x | x | x | x | x |
| Al | | | | | | | x | x |
| Fe | | | | | | | x | x |
| Chlorophyll | | | | | | | x | |
| Phaeophytin | | | | | | | x | |

For target species, each fish collected will be weighed and measured. A scale sample or fin spine will be taken in order to age each fish. Each fish will remain whole and will not be eviscerated. Stomach contents of carp will be excised from partially thawed carcasses. Five stomachs from each carp composite will be ground, homogenized, and subsampled in the same manner and quantities as the fish tissue.

Phytoplankton and zooplankton samples for food chain modeling will be collected from the R/V Roger R. Simons or associated support vessels. Size fractionation and manual separation will be the two techniques used to allow analyses of these biotic compartments. Three seasonal sampling periods will be used for collections representing the spring, summer, and fall and will coincide with the Green Bay Mass Balance cruises scheduled for these seasons. Seasonal collection windows will be May-June, July-September and September-October; phytoplankton-zooplankton sampling will not occur during all Mass Balance cruises, only 3 designated cruises. Similarly, stations to be sampled will be the same as for the Green Bay Mass Balance, with some exclusions.

Stations to be sampled include 23 of the 27 Green Bay Mass Balance stations in the Bay proper plus 5 stations in the lower Fox River for a total of 28 stations; these will be collected during three cruises. Five replicate samples (each representing 5 phytoplankton and 5 zooplankton samples) will be required from each of the biological zones for the size fractionation technique. Phytoplankton-zooplankton samples will be collected concurrently using a double net apparatus. A coarse mesh net (100-130 um), with an approximate length:width ratio of 3:1, mounted inside a fine mesh net (10 um), with an approximate length:width ratio of 5:1, will allow simultaneous collection of both biotic compartments from the water column. The nets must be detachable for appropriate processing. Collection jars will be attached to the bottom of each respective net. A flowmeter will be mounted

at the mouth of the double net apparatus to measure water volume filtered.

Manual separation of phytoplankton and zooplankton in the laboratory will be accomplished through a combination of sieving and picking when appropriate; this necessitates preservation with formalin. Whether seiving is applicable or not, the zooplankton will be separated from the phytoplankton using binocular scopes at a magnification of 100-400X. After all large zooplankton are removed from a particular aliquot (this may include Ponteporeia or other invertebrates suspended in the water column), the remainder of the sample is added to the phytoplankton fraction originally collected in the fine mesh net. When sufficient mass is obtained, these phytoplankton and zooplankton fractions will be analyzed. During the separation process, the dominant genera of phytoplankton and zooplankton will be recorded.

A summary of all samples/analyses are presented in Table 3. Although the sampling scheme has been developed with the consideration that all samples will not be obtained for each zone, season, size class, or sample type, additional samples may not be obtained. This possibility is evident for all fish species as well as phytoplankton and zooplankton collections. Considering this factor, it is anticipated that approximately 75% of the projected samples will be collected.

Investigating Agencies - EPA-GLNPO, Duluth Lab, WDNR

Funding Agency - EPA

Contact Person - Dave Rockwell (312-353-1373) Russell G. Kreis (313-675-7706)

Table 3. Summary of Green Bay Biota Samples for Food Chain Modeling: 6 zones, 3 seasons, 5 replicates per zone, each replicate a 5-fish composite, and number of age classes.

| | | e Class | Wt (1k | os) | Length | (in) | <pre># of samples/ analyses Whole:</pre> |
|-------------------|--------------------------------------|----------------------------|---------------|-----------|----------------------------|-----------------------|--|
| WALLEYE | | 1+ 3+ 4+ | | | 8 - 15 - > | 18 | 90 90 90 |
| | # of individual fi | sh = 1350 | | | | | 270 |
| BROWN TROUT | stocked yearling (stocked fingerling | | 3 - 10 - | 8 13 | 8 - 5 - 17 - 10 - | 8 23 | 5 5 45 45 |
| | # of individual fi | - | 10 | 10 | 10 | | 100 |
| CARP | - | 1+ 7+ 10+ | < 5 - > | 6 | < > ; | 21 | 90 90 90 |
| | # of individual fi | .sh = 1350 | | | | | 270 |
| ALEWIFE | | YOY Adult | | | < 100 > 100 | | 90 90 180 |
| RAINBOW SMELT | | YOY dult | | | < 100 > 100 | | 75 75 150 |
| GIZZARD SHAD | - | YOY | | | < 13 | o mm | 45 |
| CARP GUT CONTENTS | 3 | | | | | | 90 |
| ANALYSES | | | | | | SUBTOTAL TOTAL FIS | 1,105 SH 1,375 |
| PHYTOPLANKTON | | Size Fracti Manual Sepa | onation | | | | 90 24 |
| ZOOPLANKTON | | Size Fracti Manual Sepa | onation | (>100-130 | mm) | | 90 24 |
| | | | | | | Plankton Ana | _yses 228 |
| Expected 75% Succ | | | | | | TOTAL ANALY | SES 1,603 503 = 1,202 Analys |

V. QUALITY ASSURANCE AND DATA HANDLING

The GBMB will generate hundreds of samples in different media which will be analyzed by different laboratories. This, coupled with the fact that parameters such as PCB congeners have not previously been monitored on a large scale, requires an aggressive quality assurance component to the study. High quality, comparable data will be assured by:

- 1. Requiring all participating laboratories to follow the procedures and meet the criteria defined in "Quality Assurance Plan, Green Bay Mass Balance Study: I. PCBs and Dieldrin and II: Lead and Cadmium." This includes the analysis of a series of blindly coded QA samples.
- 2. Requiring that all Green Bay projects be reviewed and approved by the Green Bay Quality Assurance Coordinator (GBQAC) prior to implementation. This is in addition to any QA review procedures required by funding agencies.

Following completion of conditions 1 and 2, sample collection and analysis may proceed. As data sets are completed, the data and supporting QA information will be forwarded (on a quarterly basis) to the GBQAC for acceptance or rejection. Rejection will result in the implementation of appropriate corrective actions including, if necessary, reanalysis. Data sets which are accepted will be transferred to U.S. EPA, LLRS for electronic storage.

VI. ADMINISTRATION

Planning and ultimately the conduct of the Green Bay Mass Balance Study has and will continue to require close cooperation between government and university scientists and managers. Members of the Management Committee, Technical Coordinating Committee and four Operational Committees are listed in Figure 10. For "network purposes" a list of contacts is included in Appendix A.

VII. SCHEDULE FOR GREEN BAY/FOX RIVER MASS BALANCE STUDY

Generally, study activities are being conducted during a four year study period beginning in 1987 and continuing until the end of 1991. A summary of the anticipated schedule is shown in Table 4.

Figure 10. GREEN BAY MASS BALANCE ORGANIZATION CHART

MANAGEMENT COMMITTEE RESPONSIBILITY Carol Finch - USEPA GLNPO Co-chair Lyman Wible WINR Co-chair Overall management WDNR Thomas Robrer Anders Andren -Wisconsin Sea Grant Coordination of interagency planning Al Beeton NOAA GLERL Gilman Veith - USEPA GLERL, Duluth Funding commitments - USEPA Water Division Ken Fenner - USEPA Waste Management Division Mary Gade Bruce Robertson- Green Bay Citizens Advisory Council Warren Gebert - USGS TECHNICAL COORDINATING COMMITTEE RESPONSIBILITY - USEPA GLNPO - WDNR Wayne Willford Co-chair John Konrad Co-chair Coordination of technical activities of William Richardson - USEPA LLRS operational committees William Sonzogni - WI State Lab of Hygiene - USEPA LLRS Russ Kreis Recommend study design to management - WDNR George Boronow committee - Wisconsin Sea Grant Anders Andren - University of Wisconsin - University of Minnesota Hallett Harris Recommend resolutions of technical disputes Deborah Swackhamer to management committee David Devault - USEPA GLNPO - USGS Peter Hughes MODELING DUTIES William Richardson, Chair Thomas Fontaine Define modeling requirements John Paul Dale Patterson Direct the modeling effort David Dolan Steve McCutchen Review and evaluate proposals for compliance with modeling Victor Bierman, Jr. goals and objectives John P. Connolly Joseph DePinto Dominic DiToro Douglas Endicott Russell Kreis, Jr. James L. Martin Paul W. Rodgers William Roth FIELD AND TECHNICAL OPERATIONS DUTIES Anders Andren, Chair John Sullivan Review monitoring plan and procedures for water and sediments John Filkens Nathan Hawley Assist in planning and corrdinate field operations Hallett Harris David Devault Review and evaluate proposals for technical procedures and investigator competency BIOTA DUTIES Russ Kreis Co-chair George Boronow Co-chair Prepare biota monitoring plan Michael Mac David Devault Review and evaluate proposals for technical procedures and Brian Belonger investigator competency Lee Liebenstein Terrence Lychwick FIELD AND ANALYTICAL METHODS DUTIES William Sonzogni Chair Larry Burkhart Evaluate and recommend field and analytic methodology Steven Eisenreich

Development and oversight of QC program

Provide AQ evaluation of proposals and monitoring plan

Mike Mullin

Ron Rossman

Anders Andren Deborah Swackhamer

Table 4. SCHEDULE OF ACTIVITIES FOR THE GREEN BAY/FOX RIVER MASS BALANCE STUDY

| | FY'87 | FY'88 | FY'89 | FY'90 | FY'91 |
|----------------------|-------|-------|-------|-------|-------|
| Study Plan | x | x | | | |
| Quality Assurance | | x | x | x | x |
| Field Reconnaissance | x | x | | | |
| Modeling | x | x | x | x | x |
| Monitoring | | x | x | x* | |
| Sample Analysis | | x | x | x | |
| Interim Reports | | x | x | x | |
| Data Evaluation | x | x | x | x | |
| Final Reports | | | | | x |
| | | | | | |

^{*} Additional monitoring as required



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APPENDIX B. GREEN BAY STATIONS

| STATION NUMBER | LATITUDE LONGITUDE LORAN | | | AN | WATER DEPTH (M) | COPTER SITE | NUMBER OF SAMPLES STRAT UNSTRAT | |
|-------------------|--------------------------|------------|---------|---------|-----------------------|----------------|---------------------------------------|----|
| | | | | | | | | |
| 1 | 44^32'45" | 087^56'48" | 32486.8 | 48274.0 | 3 | P | 1 | 1 |
| 2 | 44^35'01" | 087^59'45" | 32486.8 | 48240.0 | 3 | | 1 | 1 |
| 3 | 44^34'57" | 087^57'29" | 32474.0 | 48251.6 | 1 | P | 1 | 1 |
| 4 | 44^36'22" | 087^57'16" | 32470.9 | 48235.9 | 6 | | 1 | 1 |
| 5 | 44^39'31" | 087^57'45" | 32456.5 | 48201.4 | 5 | s | 1 | 1 |
| 6 | 44^37′50" | 087^55'35" | 32456.9 | 48225.3 | 6 | s | 1 | 1 |
| 7 | 44^36'24" | 087^57'32" | 32455.6 | 48248.8 | 5 | P | 1 | 1 |
| 8 | 44^40'20" | 087^53'43" | 32435.4 | 48206.3 | 7 | | 1 | 1 |
| 9 | 44^43'40" | 087^54'01" | 32420.3 | 48171.4 | 6 | s | 1 | 1 |
| 10 | 44^42'37" | 087^51'19" | 32414.5 | 48191.9 | 9 | s | 1 | 1 |
| 11 | 44^40'40" | 087^48'29" | 32413.0 | 48221.9 | 8 | S | 1 | 1 |
| 12 | 44^39'29" | 087^46'27" | 32410.4 | 48241.1 | 7 | S | 1 | 1 |
| 13 | 44^52'11" | 087^47'30" | 32350.7 | 48106.3 | 5 | s | 1 | 1 |
| 14 | 44^51'02" | 087^43'40" | 32340.8 | 48131.2 | 15 | P | 2 | 1 |
| 15 | 44^49'44" | 087^39'27" | 32329.6 | 48159.6 | 14 | s | 2 | 1 |
| 16 | 45^01'02" | 087^34'18" | 32252.7 | 48062.5 | 15 | | 2 | 1 |
| 17 | 44^53'49" | 087^30'08" | 32270.0 | 48149.6 | 21 | | 2 | 1 |
| 18 | 45^05'27" | 087^24'41" | 32190.6 | 48050.8 | 30 | P | 2 | 1 |
| 19 | 45^11'01" | 087^28'36" | 32180.5 | 47981.3 | 23 | | 2 | 1 |
| 20 | 45^07'07" | 087^18'30" | 32156.0 | 48055.1 | 21 | | 2 | 1 |
| 21 | 45^19'30" | 087^18'55" | 32100.1 | 47930.9 | 27 | | 2 | 1 |
| 22 | 45^17'36" | 087^09'54" | 32069.4 | 47980.1 | 27 | | 2 | 1 |
| 23 | 45^31'41" | 087^10'34" | 32010.4 | 47841.1 | 19 | | 2 | 1 |
| 24 | 45^29'37" | 087^01'58" | 31981.2 | 47889.5 | 19 | P | 2 | 1 |
| 25 | 45^18'00" | 086^58'07" | 32015.2 | 48014.6 | 37 | | 2 | 1 |
| 26 | 45^26'54" | 086^48'03" | 31930.5 | 47960.3 | 35 | | 2 | 1 |
| 27 | 45^34'24" | 086^48'08" | 31898.7 | 47889.4 | 18 | | 2 | 1 |
| | | | | | | | | |
| | | | | | | TOTAL | 41 | 27 |

Secretary of the second second second