REPORT OF THE GREAT LAKES MASS-BALANCE PLANNING WORKSHOP

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I. EXECUTIVE SUMMARY OF THE LAKE MICHIGAN MASS-BALANCE PLANNING WORKSHOP

The Lake Michigan Mass-Balance Planning Workshop, held March 31-April 1, 1992, in Research Triangle Park, brought together representatives of two communities—scientists and end users—to discuss capabilities and needs in designing a mass-balance model for Lake Michigan. Their goals were to identify data collection and quality objectives, propose hypotheses that the mass-balance study should address, determine measurement protocols, and define key outputs.

After hearing presentations on the current status of monitoring efforts in the Great Lakes region, the participants divided into two work groups to discuss key elements of the mass-balance study, which were defined by the first day's presentations and discussions. Those elements were:

1. Data collection objectives (DCOs)
   - Pollutants of concern
   - Parameters considered essential for modeling
2. Data Quality Objectives (DQOs)
3. Hypotheses
4. Measurement
   - Methods and sampling frequency
   - Design
   - Cost, accuracy, other parameters
5. Location of sites
6. Key outputs

Although neither group presented recommendations for every element of the outline, the outline nonetheless provided a framework for the discussions and elicited new proposals and considerations that will benefit the design of the mass-balance effort.

Group 1 proposed the following target pollutants for the mass-balance model: PCBs, lead, atrazine, and trans-nonachlor The group also identified additional parameters as being essential for modeling:

- determinations of total suspended particles (TSP) in air;
- carbon inputs from air, precipitation, and tributaries; and
- nutrient cycling.

In addition, Group 1 recommended 7 land sites and 2 ship sites, which are discussed in detail in the group discussion section of this report.

Group 1 proposed the following hypotheses or issues to be addressed by the mass-balance study:

- whether measurements over land represent pollutants over water
- event-based sampling vs. monthly sampling
- dry deposition of large particles
- source information
- quality control (QC) issues, particularly regarding new compounds, such as atrazine
- importance of urban vs. regional inputs

The key output proposals for Group 1 were:

- atmospheric loadings to the Lake, plus information for modeling
- calibrated model

Group 2 proposed the following target pollutants for the mass-balance model: PCBs, dieldrin, lead, nonachlor, mercury, DDT, and PAHs. In addition to identifying these target pollutants, Group 2 devised a matrix of pollutants and criteria for their inclusion, which is presented in the detailed summary of the group discussions.

The group identified several additional parameters:

- use Green Bay target pollutant list as minimal base (PCBs at congener level, dieldrin, TSP, and organic and elemental carbon)
- review list and add parameters as needed
- determine source attribution
- determine air concentration over water and across air/water interface
- characterize precipitation chemistry
- determine phase distribution (vapor and particle)
- determine particle size distribution

Moreover, Group 2 identified the following DQOs:

- use the Green Bay Study as template for process of modeling Lake Michigan

- review and update all Standard Operating Procedures (SOPs) and Quality Assurance Project Plans (QAPjPs)
- establish centralized quality assurance (QA) authority
- consider requesting Office of Research and Development (ORD) to provide QA support
- offer more than one option to decision-makers, options that require varying levels of funding
- achieve lowest possible analytical detection limits

Group 2 proposed hypotheses that involve determining whether long-range transport has a significant effect on water quality, whether tributary loadings are significant, and what controls are required to achieve acceptable concentrations in fish. The proposed outputs were a mass budget and media contribution; prediction of the effect of control actions on biological/ecological systems; prediction of benefits from remedial actions; and the relation of benefits to regulatory action.

Although the two group presentations had little redundancy, the clear consensus was that the desired end product is a calibrated model that can be used to document human health or ecological effects of pollutants in the Great Lakes region, and thus spur regulatory action.

II. INTRODUCTION

The Lake Michigan Mass-Balance Planning Workshop was held in Research Triangle Park, NC, on March 31-April 1, 1992. The workshop agenda is given in Appendix A. The names, affiliations, and addresses of those who attended are listed in Appendix B.

The purpose of the workshop was to assemble two communities—scientists and potential data users—to discuss the capabilities, needs, and agendas in creating a Lake Michigan mass-balance program. The two communities are further defined as follows:

- Scientists—within the Environmental Protection Agency (EPA), the academic community, Environment Canada, and others in the Great Lakes region.
- Potential users—including those within EPA, representatives of legislative mandates, environmental groups, and state agencies.

Selected participants presented background information on monitoring efforts in the Great Lakes region This information consisted of:

- preliminary objectives for Lake Michigan Mass-Balance Model,
- an overview of current transport/fate and food-chain models for the Great Lakes;

- an estimation of wet deposition for mass-balance studies;
- an estimation of dry deposition for mass-balance studies;
- interface of atmospheric and aquatic models in design of mass-balance studies;
- an approach to measuring urban contributions to Great Lakes toxic loadings;
- use of source apportionment model results in mass-balance models;
- Great Lakes states' atmospheric measurement objectives and data needs;
- an overview of Lakewide Management Plan (LaMP)
- an overview of air toxics data need for LaMPs;
- Great Waters scientific and environmental measurement needs; and
- availability of sites.

On the first workshop day, presenters fielded questions and comments from participants. On the second day, participants divided into two groups to discuss study objectives. Their goals were to compile independent lists of target pollutants, to identify additional parameters deemed essential for viable modeling, and to propose central hypotheses that the mass-balance study should address.

III. DAY 1

A. Objectives

Mr. Dale Pahl opened the workshop by informing participants that their objective in the 2-day workshop was to discuss the capabilities, needs, and agendas in creating a Lake Michigan mass-balance model. He asked each participant to describe his or her position and work relating to the Great Lakes monitoring and modeling efforts.

B. Preliminary Objectives for Lake Michigan Mass-Balance Model

Mr. David DeVault of the EPA Great Lakes National Program Office (GLNPO) is responsible for planning, coordinating, and implementing monitoring programs. He gave an overview of GLNPO's current objectives for the mass-balance model. The project has received varying levels of support during the last 2 years, but now it is a priority to GLNPO and EPA. The field year for data collection is scheduled to be 1993. Sample analyses should be completed by December 1994. Mr. DeVault presented graphics explaining the basic principles of monitoring processes in the Great Lakes

Proposed toxic chemicals to be targeted are:

- PCBs
- dieldrin
- trans-nonachlor
- lead

GLNPO plans to study the loading of these compounds to the Lake and their concentrations in fish identified for their importance to the Lake Michigan sport or commercial fisheries. These fish are Lake Trout, Coho Salmon, and Bloater Chubs; they also represent differing exposure routes and histories.

Mr. DeVault stated that GLNPO, Region V, and the Great Lakes states need a mass-balance plan to determine loadings to Lake Michigan for various toxic chemicals. Once loadings are determined, building a model will be relatively simple and inexpensive (modeling costs represent about 10 percent of study costs). Mr. DeVault said a calibrated model is needed to provide predictability for remedial and regulatory actions and to reduce the amount of necessary monitoring, thus conserving resources. In addition, GLNPO seeks to establish a framework for collaboration among 25 or 30 agencies involved in Great Lakes research and regulation.

GLNPO's recommended approach for the mass-balance study is to use the calibrated model for the Green Bay Study and to focus 1992 data collection on loadings, process rates, and reactivity. The timeline for the study is being revised. Field work should start in spring 1993, and a draft study plan is targeted for completion by August 1992.

Lakewide Management Plan committees and Water Quality managers will provide funding for the study. It will be planned, managed, and coordinated by several technical committees.

Mr. DeVault expressed the hope that, during group discussions scheduled for the second day of the workshop, participants discard preconceived notions and focus on what is needed to make the mass-balance study "workable".

In response to a question about funding, Mr. DeVault said that GLNPO would propose funding adequate to meet the goals.

Mr. DeVault responded to Ms. Joanne Foy's question about the basis for the pollutants chosen by saying that the pollutants were shown to bioaccumulate in fish and would eventually have deleterious health effects to humans and non-humans who ingest the fish—thus, these pollutants were suitable for mass-balance modeling. Ms. Constance Hunt commented that all the pollutants mentioned appeared on Region V's critical pollutant list for Lake Michigan, although lead was listed as a lower-level pollutant.

Mr. Pahl said that modeling questions are not resolved, and that although management has given the choices much thought, he understood that the scientific community might not readily accept the choices.

A general discussion ensued about the choices of pollutants for modeling and about the importance of integrating atmospheric and aquatic pollutants in a well-designed model. Mr. DeVault noted that what managers need must be kept in balance with what the chemists believe is practicable.

C. Overview of Present Transport/Fate, Food Chain Models for the Great Lakes

Mr. William Richardson, Station Chief of the Office of Research and Development's (ORD's) Large Lakes Research Station, located at Grosse Ile, Michigan, has been involved with developing mathematical models for the Great Lakes for about 20 years. He currently is developing a management-level model that will assist with Lakewide Management Planning.

Mr. Richardson summarized two decades of modeling efforts in the Great Lakes. Successes were achieved in relating discharge of nutrients, such as phosphorus, to deficits in dissolved oxygen in Lake Erie with models developed through studies sponsored by ORD, GLNPO, and the International Joint Commission (IJC). These studies culminated in the late 1970s with the development of target loadings for phosphorus and a 10-year surveillance plan in the Great Lakes to monitor progress in restoring dissolved oxygen levels. The models were successful in relating loadings to concentrations.

Continued modeling efforts throughout the 1970s focused on determining how toxic chemicals behave in aquatic systems, using the phosphorus mass-balance model. A minimally funded effort in modeling at Grosse Ile for the Great Lakes was maintained during the 1980s. In 1988, a study by Lake Ontario Toxic Management Plan and Superfund focused on discharge levels of dioxin into Lake Ontario at Hyde Park. The Green Bay Mass-Balance Study focused on PCB levels in Lake Michigan, which remained high after PCBs were banned. The key issues in designing a mass-balance study are identifying the remaining sources of these toxic substances and the allocation of regulatory dollars to reduce their discharge.

Mr. Richardson said that the purpose of mass-balance modeling must be clear from the outset to provide management useful tools. He stressed that the Green Bay Study should be used as a basis for the Lake Michigan Mass-Balance Study.

Mr. Richardson then expressed the concern that managers do not clearly understand the need for mass-balance modeling. Ms. Constance Hunt noted that EPA managers see mass-balance as an academic exercise and are more interested in loadings, a misconception that

she hoped would be corrected when the results of the Green Bay Study are presented. Mr. Pahl suggested that "management system" could be substituted for "model" for greater effect, because a model, in essence, constructs a systematic view of reality. Ms. Hunt commented that the cost-effectiveness of models must be shown to persuade managers of their usefulness.

Mr. Richardson said that modeling is needed, for example, to predict PCB levels in the lower Fox River that result from reservoir flow events. Because the Fox River study is manageable, it can be used to convince management that modeling is valid. Mr. Richardson said that at Grosse Ile scientists are attempting to link modeling with GIS databases so that managers have tools they can use.

To arrive at a cost-effective program, Mr. Richardson said, a system is needed that would interact with sediments, watersheds, and atmosphere.

Mr. Richardson then presented a series of graphics, including a chemical modeling schematic; an explanation of chemical and biological processes involved in modeling toxic substances; bioaccumulation model processes; a food chain chart; PCB loadings; loadings relative to concentrations in Lake Ontario fish; the source of uncertainty in water concentration predictions; and the effect of seasonal differences in wind and temperature on volatilization (see Appendix M)

Mr. Richardson addressed the need for data in the system to compare simulated concentrations to measurements. He noted that the loading chart was constructed for PCBs because much historical data were available on PCBs. The graphic of relative loadings to concentrations in Lake Ontario fish showed an unacceptably large spread. To improve the model would require more experimental research in process rates and more data collection to calibrate the model.

Mr. Richardson noted that determining atmospheric loadings is a vital component of constructing an accurate model, and that the end product is a model that could calculate the concentration of pollutants over time

Mr. Pahl offered a summary of Mr. Richardson's presentation, stating that available data and existing models are identifying potential hypotheses that must be considered in the design of a mass-balance study.

D. Estimation of Wet Deposition for Mass-Balance Studies

Dr. Joel Baker of the Chesapeake Biological Lab, University of Maryland, described issues of the wet deposition project in Chesapeake Bay. Many of these issues are shared with the Great

Lakes project, including sampling methods and whether the atmosphere is a source of PCBs to the Lakes.

The necessary objectives of wet-deposition measurements must be clearly defined. If only gross loadings are needed, then that straightforward requirement can be met with moderate site density and monthly, integrated sampling. If exploring scavenging mechanisms, source attribution, or speciation of chemicals are high priorities, then event-based sampling and high-site density would become a priority. The latter study would require more money.

Dr. Baker described the need for, and difficulty of, studying scavenging mechanisms, source attribution, and speciation. It is not known precisely how and how much of the PCBs are scavenged from the atmosphere in wet deposition. To build a predictive model that starts with concentrations in the air, the mass-transfer processes must be understood to calculate the wet-deposition loadings. The distribution between the vapor phase and the aerosol phase also is extremely important and is a strong function of the ambient air temperature.

Data from Chesapeake Bay indicated that equilibrium partitioning with the ambient vapor phase accounts for only 2-3 percent of dissolved-phase PCBs in rain: The rain seems to be supersaturated with these compounds. Many additional mechanisms contribute, including:

- aerosol wash-out by precipitation
- temperature-driven disequilibrium
- rate of absorption at the air-water interface

Modeling pollutant scavenging is not as simple as scientists had hoped. Other mechanisms that are difficult to characterize are the exchange across air-water interfaces, volatilization, and meteorological influences on exchange rates. Temperature influences in particular are extremely important to vapor-aerosol distribution and the mass-transfer coefficient.

Speciation is important, Dr. Baker said, because the fate of a material is determined largely by its form at deposition. The varying effects of weather require data collection throughout the year.

Dr. Baker recommended that wet-deposition sampling for the Lake Michigan mass-balance study be characterized by:

- monthly sampling
- 2-3 remote sites
- event-based sampling in urban areas
- short-term intensive field work, coupled with meteorology

- study of speciation in precipitation and scavenging

Mr. Pahl asked whether Dr. Baker called for a study of microlayer measurements. Dr. Baker replied that he could not answer that question because the uncertainty in the mass-transfer coefficient is large. A general discussion ensued about the feasibility of event-based sampling.

E. Estimation of Dry Deposition for Mass-Balance Studies

Dr. Thomas Holsen, of the Illinois Institute of Technology's Environmental Engineering Department, studies dry deposition measurement and modeling. He opened his discussion of dry-deposition estimation by stating that:

- Realistic estimates of dry deposition can be made with existing models if complete mass-size distributions are obtained.
- Model predictions compare favorably with dry deposition measurements using surrogate surfaces.

Dr. Holsen presented various graphics illustrating sampling techniques to complete size distributions and deposition plates that directly measure dry-deposition flux He also presented slides of devices used to collect samples and described particle sizes monitored by each.

Dr. Holsen then described the method of calculating flux from atmospheric size distribution through mass-transfer coefficients, or deposition velocities: Size distributions multiplied by deposition velocities equal flux. Dr. Holsen presented three models to obtain deposition velocity.

Showing results of samples taken in Chicago, Dr. Holsen pointed out that although different mass-size distributions were found, flux distributions were similar Most of the flux in Chicago is attributable to large particles. If the mass-size distribution is divided into three sections (0.1-1 μm, 1-10 μm, and 10-100 μm), and if each concentration is multiplied by the appropriate deposition velocity and then summed, the result is cumulative flux. Data indicated that particles less than 1 μm are responsible in all cases for less than 1 percent of total flux; particles less than 10 μm are responsible for 10 percent of flux; and particles 10-100 μm are responsible for 90 percent of flux.

The significance of these findings is that the samplers typically used to estimate dry deposition collect small particles (i.e., < 10 μm), which in fact do not account for most flux. The same is true for metals and other compounds

The accuracy of the model was tested using PCBs, for which no complete mass-size distributions are available. Samples were analyzed under a microscope to determine size and group particles, and the models accurately matched counts on the plate.

Using nine Chicago dry-deposition samples with fairly equal distribution of fine and coarse particles, Dr. Holsen applied three different models and compared flux measure and atmospheric sizes. The three types of models used were:

- product model
- 1-step methods
- 9-step methods

The product model and one-step models accounted for only the fine-particle phase. The nine-step models accounted for coarse- and fine-particle phases and were most stable. The models that called for partitioning concentration by particle size and applying the appropriate deposition velocity for each size particle yielded results that matched plate counts. Dr. Holsen presented data from Chicago supporting the hypothesis that coarse particles are responsible for most flux.

Using the equation that total flux is the sum of flux for fine-particle phase and coarse-particle phase, scientists calculated flux by multiple regression for every element represented. The results agreed with model predictions.

Models also accurately predicted deposition velocities for gas-phase compounds in a study of PCB and PAH samples collected in a 30-day period. Dr. Holsen noted that the data were more scattered for PCBs than for metals.

Dr. Holsen summarized research findings by repeating his introductory statements that dry-deposition estimates can be made if complete mass-size distributions are obtained and that model predictions compare well with measured dry deposition. He added that coarse particles are responsible for most dry-deposition flux.

Dr. Holsen then discussed the implications of these findings for the mass-balance study. Two methods are available to quantify dry deposition:

- measuring complete size distribution and applying deposition velocity models
- estimating dry deposition directly using flux models

Dr. Holsen stressed that using partial size distribution has little physical meaning because this method does not measure the particles responsible for deposition.

Using complete size distributions offers two advantages: an easy link with meteorological models and the application of deposition velocity models.

Coarse-particle samplers are short-term, making complete mass-size distributions difficult and expensive, and they do not provide direct measurement of flux.

The automated flux plate is simple and easy to use, provides direct measurement of flux, compares well to model data, and operates for long and short terms. A disadvantage, however, is that collected particles need to be counted to calculate mass-size distribution.

Dr. Holsen pointed out differences in samplers used in taking urban and non-urban samples. Dr. Holsen and Dr. Robert Stevens discussed various particle sampling methods, and Dr. Stevens questioned the validity of the Noll rotary sampler.

F. Interface of Atmospheric & Aquatic Models in Design of Mass-Balance Studies

Dr. William Benjey, with EPA in Research Triangle Park, NC, began discussing the interface of atmospheric and aquatic models by reviewing the Atmospheric Research and Exposure Assessment Laboratory's (AREAL's) toxic emission inventory compilations for regional dispersion and deposition modeling Because a detailed inventory is not available, compilations were derived from other databases, particularly the National Acid Precipitation Assessment Program (NAPAP) database. Results are compared with the Toxic Release Inventory System, which was conducted under the Clean Air Act Amendments (CAAA), Section 313. Dr. Benjey acknowledged that both databases are limited.

The purpose of the Interim Toxic Emissions Inventory is to make an initial, general assessment. Currently, QC procedures are being conducted, and emissions data are being merged from regional and local sources. The modeling application procedures being applied are geographic distribution and analysis by source type and category. Dr. Benjey then presented results of data gathered thus far on various pollutants (see Appendix I).

Dr. Benjey presented graphics that included a GIS-generated distribution map of mercury emissions and charts of various pollutant distributions in the Lake Michigan area and Detroit.

Dr. Benjey conceded that the data are by no means complete, especially data concerning volatilization. In addition, a model is needed to link these data with aquatic data. The data currently do not include banned pesticides, and no reliable method of reporting PCBs is available. EPA potentially could add any number of pollutants to the inventory, but knowledge of emissions and speciation factors is a limiting factor A research program initiated by the Office of Air Quality Planning and Standards (OAQPS) and AREAL will account for non-point source emissions.

Mr. Terry Clark, of AREAL in Research Triangle Park, has studied atmospheric modeling of toxic movements in the Great Lakes on a regional scale and has worked with Ms. Pamela Blakely of Region V in calculating atmospheric deposition of several toxins to Lake Michigan.

Mr. Clark presented modeling work being conducted, examples of how models can aid mass-balance efforts, and output for lead deposition in Lake Michigan.

Two models are in use in this work:

- Regional Lagrangian Model for Assessment of Pollutants (RELMAP)—which creates emission puffs that transport and disperse the pollutant, then dry- and wet-deposit the mass as it is transported downwind; and
- Regional Acid Deposition Model (RADM)—a comprehensive model that incorporates all known processes, operates in an episodic mode, and is very sophisticated, having undergone extensive peer review.

Mr. Clark noted that a version of the RADM is planned for use as a toxic deposition model in the future. Nevertheless, Mr. Clark focused on RELMAP, which uses emissions inventories and creates 3-hour puffs of pollutants in 40-km grid cells. The model was used to calculate wet removal based on wash-out ratios that are specific for each toxic pollutant. Dry deposition to land surfaces was calculated, as well as water surfaces within grid cells, and results were spatially integrated over the water-only portion of cells to determine total lake loading. Planned improvements to the model include adding processes that account for volatilization from land/water surfaces and resuspension from particles, as well as volatilization and possible deposition downwind from the water surface itself.

Mr. Clark then presented ways in which the model can assist in the mass-balance study; input requirements for atmospheric deposition models; and data on lead deposition to Lake Michigan (see Appendix J).

G. Approach to Measuring Urban Contributions to Great Lakes Toxic Loadings

Dr. Jerry Keeler presented research activities conducted at the University of Michigan at Ann Arbor. The University of Michigan has worked with EPA on the Lake Michigan Urban Air Toxics Study, and, in conjunction with the State of Michigan, has been studying toxics transport and deposition (especially for ambient mercury and lead) throughout the state.

Dr. Keeler stated that before site and pollutant discussions can begin, the scale of the management problem must be considered. Sources of pollutants may not be in the Great Lakes

Basin itself, which mandates a larger perspective. Historical evidence indicates that urban areas are important to deposition to lake surfaces.

The objectives of the Lake Michigan Urban Air Toxics Study are:

- to quantify levels of air toxics species
- to identify categories of sources
- to identify deposition to Lake Michigan
- to differentiate between urban sources around the Lake and those upwind

Dr. Keeler presented data from monitoring sites (see Appendix H) operated during the summer of 1991 in the lower Lake Michigan area. Four sites were used to sample for PCBs, PAHs, and metals. Three sites collected samples for mercury.

To characterize urban atmospheric loadings, Dr. Keeler recommended an emissions inventory and meteorology dispersion modeling. In addition, he recommended monitoring wet/dry deposition from samples in source areas, and upwind and downwind of urban areas. Coarse-particle loading should be considered, too.

Dr. Keeler stressed the importance of meteorological data and year-round measurement, and he noted that the following issues should be part of the design of a mass-balance study:

- overall goals
- perspective or scale
- pollutant list

Once those issues are resolved, determinations can be made regarding site selection, sampling frequency, analysis techniques, and surrogate/tracer compounds.

H. Use of Source Apportionment Model Results in Mass-Balance Models

Dr. Robert Stevens from EPA presented the attributes of various source apportionment methods. He began by discussing the effect of air toxics on the Great Lakes and presented a graphic describing the dispersion model and receptor model.

Dr. Stevens warned against taking a narrow view of sampling methods. He particularly spoke against using solely PM_{10} samplers because they include both acid and alkaline particles. He provided seven recommendations for improving sampling methodology:

1. Collect and analyze fine and coarse particles separately.
2. Use filters appropriate to the analysis.
3. Use denuders for collection and analysis of semi-volatile organic compounds (SVOCs).
4. Collect and analyze samples for VOCs.
5. Incorporate SEM analysis methods.
6. Use hybrid models.
7. Perform deposition experiments at the receptor site.

Dr. Stevens also advocated a dry-deposition program that would incorporate gas and particles to improve deposition estimates.

I. Great Lakes States' Atmospheric Measurement Objectives & Data Needs

Ms. Joanne Foy represents the State of Michigan Department of Natural Resources as the Great Lakes Air Program Coordinator. She serves as liaison for the other Great Lakes states in initiatives such as the Lake Michigan Mass-Balance Study.

Ms. Foy assured participants that the Great Lakes states' goals for controlling pollutants complement those outlined in the CAAA of 1990. The end result desired is the answer to the question "Are additional regulatory efforts required?" To achieve this, significant additional research should be done to evaluate both wet and dry deposition, air/water exchange flux dynamics, seasonal, and spatial variations, over lake vs. over land issues, standardized sampling and analytical protocols, and QA/QC concerns.

Michigan and other states have conducted toxics monitoring programs and have data to share. Also available will be VOC and meteorological data and transport analysis from the Lake Michigan ozone study Ms. Foy showed graphics depicting sites potentially available for sampling, which appear in Appendix C.

The Great Lakes Protection Fund provided the Michigan Department of Natural Resources a grant to conduct a baseline toxics monitoring study for compounds of concern in the Great Lakes, which tracked seasonal trends through monthly ambient air samples for PCB congeners, VOCs, pesticides and metals at 3 sites in Michigan. The data reviewed to date indicates seasonal and spatial differences. Ms. Foy vouched for the representativeness of the data by pointing out

that the findings matched levels and trends identified by other researchers. This network is being enhanced and expanded to include sampling every 6 days for at least 1 year, with back-trajectory analysis to be conducted by the University of Michigan.

Mr. Pahl asked whether the Great Lakes states were interested less in bioaccumulation than in regulating pollutants through the CAAA. Ms. Foy replied that the states certainly consider bioaccumulation a criteria in selecting pollutants of concern, but that the states are not able to effect much change for some pollutants, such as pesticides that were banned years ago. From a regulatory perspective, compounds of concern, such as benzo(a)pyrene and mercury, which have known air point sources, are of highest priority.

Ms. Melissa McCullough said that, whereas bioaccumulation (of any toxic chemical) is a concern, chemicals should be chosen for study that have deleterious effects to both ecosystems and human health and which can be controlled through air quality management techniques to optimize resources. Mr. Pahl replied that identifying compounds for study could be approached in two manners: relating bioaccumulation to human health; or taking a proactive role in choosing new compounds that may pose a problem in 5 to 10 years.

A general discussion ensued on the assessment, human health effects, and regulatory issues of PCBs. Ms. Foy said that the Great Lakes states have identified critical pollutants, including benzo(a)pyrene, alkylated lead compounds, and dioxins, but she noted that any critical pollutant would be of concern (critical in terms of listing in the Great Lakes Water Quality Agreement [GLWQA]).

J. Overview of Lakewide Management Planning

Ms. Constance Hunt, program Manager for LaMP in Region V of EPA in the Water Division, stated that the goals of LaMP are to.

- determine the critical pollutants in each of the Great Lakes and their sources;
- develop a plan to reduce loads of persistent, toxic compounds, and/or bioaccumulation of toxics; and
- prevent further release of those pollutants.

In pursuing these goals, Region V hopes to build a relationship with other organizations to avoid duplication of effort.

Ms. Hunt gave an overview of LaMP's history. The GLWQA, Annex II, identified critical pollutants as compounds that impair beneficial use of the Lakes, including conventional pollutants. Section 118 of the Clean Water Act (CWA) required EPA to lead GLWQA initiatives.

Identifying critical pollutants is a main concern to the LaMP program. Ms. Hunt noted that, ideally, the mass-balance study should be a reiterative process, evolving from new information as well as drawing on historical evidence.

Identifying pollutant sources will require an emissions inventory to estimate load reduction targets and to plan risk-based remediation action.

In response to Mr. David Cowgill's question regarding parameter criteria, Ms. Hunt said that LaMP will take whatever action is feasible based on two opportunities: regulation and voluntary pollution prevention. Ms. Hunt pointed out that the largest sources of pollutants may be non-point sources.

Ms. McCullough commented that another pitfall in decision-making is that the political climate may have changed by the time regulations are imposed. Mr. Richardson responded that science should not vacillate with politics. Ms. McCullough agreed that science always must be validated and advanced, but said that issues such as chemical targeting and defining effects as "adverse" typically are left to policy-makers.

Ms. Hunt then presented a graphic explaining LaMP's tiering concept for pollutants (see Appendix E). Level I pollutants are in violation of a numerical criteria such as water quality standards and fish consumption advisories. Level II pollutants have a strong association with beneficial use impairment. Level III pollutants have a moderate association with beneficial use impairment, and Level IV polutants have a possible association based on presence in the Lake and ability to impair uses. Pollutants may be shuffled among levels. For example, mercury was moved to Level I because of the concentration found in fish tissue in Upper Michigan. A screening process is ongoing to determine the top candidates for a mass-balance model.

K. Overview of Air Toxics Data Need for LaMPs

Ms. Pamela Blakely of EPA summarized Region V's need to understand the mass-balance theory and how it would affect the regulatory framework for pollutants. She addressed LaMP's air toxics data needs by stating a general goal of identifying and quantifying loadings for load reduction. She distinguished two phases of this goal. The short-term phase involves identifying source categories emitting critical pollutants to develop an action plan to reduce loads. The long-term phase involves determining a plan that will meet regulatory requirements within the various groups concerned with pollution in the Great Lakes.

Ms. Blakely stated that the mass-balance program is critical to achieving water quality standards. She then noted that there are three methods of controlling pollutants. Voluntary reduction provides an effective means of control, as does implementation of state programs outlined in CAAA 112 (l). Recommendations from the Great Waters Study also may provide means of controlling pollutants.

Ms. Blakely added that she supported the addition of mercury to the critical pollutant list because utilities appear to be primary sources of mercury and Title III may be the only means of utilities regulation.

Dr. Stevens stated that, whereas the purpose of a mass-balance study is to determine the distribution of pollutants from air and water, an emissions inventory would not allow an understanding of the major sources of air toxics. Mr. Pahl responded that if source category information is important, it will have profound implications for the study.

Ms. Foy said that the Great Lakes states have expressed a need for emissions inventories, monitoring, and modeling. Dr. Stevens said that sources can be identified through receptor modeling, particularly the hybrid model that combines dispersion and receptor modeling. Dr. Stevens emphasized that the hybrid receptor model was the tool of choice for quantitative analysis

L. Great Waters Scientific and Environmental Measurement Needs

Ms. Melissa McCullough of the EPA OAQPS, the leader of the Great Waters program, presented the mandates for the Great Waters Study set forth in Section 112(m) of the CAAA. She noted specifically that the CAAA require EPA to report to Congress in 1993 and every 2 years thereafter. Reports are to include an analysis of the relative atmospheric contribution of hazardous air pollutants (HAPs); and an identification of HAPs-caused effects. They also are to identify sources of HAPs and whether HAPs cause water violations. Finally, reports are to offer recommendations for regulatory revisions.

Ms. McCullough said the Great Waters Study will focus on those issues and will collect data that will support a logical and credible case for any recommended action.

The Great Waters program will consist of emissions inventory, monitoring, modeling, and effects assessment activities. Ms. McCullough stated that, whereas all groups associated with the Great Lakes have common goals, the Great Waters Study will rely on the scientific community to recommend a research strategy that will be endorsed by peer review.

The following have been defined as high-priority tasks for the Great Waters Study:

- compiling background information
- evaluating methodology for determining deposition/flux of toxic pollutants
- characterizing urban influences
- characterizing processes and parameters

Mr. Pahl asked what strategies the Great Waters Study planned to employ for interstate transport, given that Section 112(m) is a federal program allowing for state involvement. Ms. McCullough replied that recommendations will be included in the Great Waters Report, but by the time the report is submitted to Congress, the source category regulation schedule will be set.

The two main sources of funding for the Great Waters Study would be the OAQPS and the ORD Air Toxics Research Committee.

IV. DAY II

Mr. Dale Pahl opened the second day of the workshop session by announcing that the participants would divide into two groups, both charged with addressing the following issues defined by the first day's discussions and articulated by Mr. Pahl:

1. Data collection objectives (DCOs)
   - Pollutants of concern
   - Parameters considered essential for modeling
2. Data Quality Objectives (DQOs)
3. Hypotheses
4. Measurement
   - Methods and sampling frequency
   - Design
   - Cost, accuracy, other parameters
5. Location of sites
6. Key outputs

After a brief discussion, participants agreed that Dr. Clyde Sweet and Ms. Joanne Foy should present information on available sites before the group sessions.

A. Availability of Sites

Ms. Joanne Foy generally described available state sites around Lake Michigan. She stated that much time and money have been spent by the states on site searches for toxics and ozone monitors and that additional sites may be evaluated as monitoring funding becomes available.

Ms. Foy said that Great Lakes states are receptive to input on siting on states' monitors from the groups represented at this workshop and could assist EPA in finding appropriate sites for additional CAA monitors. Even though the Great Lakes air regulatory agencies have proceeded on their own in the past to establish air toxics monitoring sites in light of little or no previous federal funding or guidance, some of these sites may be appropriate to use for CAA implementation. Since these sites were established independently for various purposes, some might need to be relocated or enhanced in their monitoring capabilities to be compatible. Other sites considered comparable to EPA efforts may be appropriate to factor into EPA's sponsored programs as they exist.

The Great Lakes air regulatory agencies have formed an air monitoring coalition committed to monitoring planning and coordination, which includes states, local organizations, and Canadian organizations. This relatively informal coalition can serve as the coordination mechanism with the various organizations represented at the workshop if desired.

Dr. Clyde Sweet of the Illinois State Water Survey, which is associated with the University of Illinois in Champaign-Urbana, has worked under contract with GLNPO on various Great Lakes issues, including the air monitoring component of the Green Bay Mass-Balance Study. He currently manages the air sampling, chemical analysis, and data analysis for the Integrated Atmospheric Deposition Network's (IADN's) U.S. sites.

Dr. Sweet gave a historical overview of IADN's integrated monitoring program in the Great Lakes (including Lake Michigan area), a joint effort with Canada. He said that the pollutant list consists of selected toxic compounds found in fish in the Great Lakes area that can be monitored on a routine basis. The list includes PCBs, some pesticides (including dieldrin), PAHs, and lead. Mercury was rejected because the methods available for study would be difficult to implement for routine monitoring.

Sites chosen represented a compromise of the ideal and the economically feasible. Three or 4 sites—1 master and 2 or 3 satellite sites—on each of the Great Lakes are planned, although currently only the master sites are in place. Master sites are designed to support routine monitoring and research projects, and satellite sites are designed strictly for monitoring to supplement the master sites.

Dr. Sweet pointed out a need for quantifying urban input to the Lakes and said that three sites per Lake are not adequate to measure urban input. Because of this, IADN has focused on regional sites that reflect the atmosphere over the Lake as a whole. The mass-balance study is an opportunity to test urban influence on the Lakes by characterizing input in a 1-year study and extrapolating those results to other areas

IADN has been struggling to find a method of monitoring over the Lakes. Monitoring from a platform over the Lake or from a ship is expensive. Island sites may be feasible in some cases, but they do pose logistical problems. IADN has opted for shoreline sites, but new evidence suggests that these sites may reflect neither the land nor the water environment. The need for meteorological data at each site is becoming increasingly important.

Dr. Sweet presented slides of sites (see Appendix F) and reviewed issues associated with each, including proximity to major sources, staffing at stations, nearby use of pesticides, and relations with private land owners. In the process, he summarized IADN operational, available, and potential sites.

Dr. Sweet then presented data from air samples of total suspended particulates (TSP) at three Green Bay Study sites that indicate that urban pollutants may be transported by regional air masses.

B. Group Recommendations

The two groups discussed the issues outlined by Mr. Pahl and reconvened to share their recommendations. The groups used the elements defined by Mr. Pahl as a basis for discussion.

Dr. Sweet gave a brief overview of Group 1's discussion before presenting recommendations. Limiting the list of pollutants and obtaining a well-characterized and well-calibrated model were issues that were of prime concern.

The target compounds identified by Dr. Sweet's group were:

- PCBs
- lead
- atrazine
- trans-nonachlor

PCBs and lead were chosen because they were components of the Green Bay Study. Atrazine was chosen because it is a current-use pesticide, it has been identified as a potential problem and because it has a variety of ways in which to enter the Lake. In addition, it is reactive. Dr. Sweet expressed Group 1's hope that including atrazine would increase the model's

sophistication. Trans-nonachlor was chosen because it bioaccumulates and does not pose a significant analytical problem.

Additional parameters recommended were:

- TSP in air
- carbon inputs from air, precipitation, tributaries
- nutrient cycling

Site recommendations were:

- 7 land sites (1 in the north, 2 mid-Lake, and 4 around the South Basin)
- 2 ship sites (operational only part of the year)

The group recommended the high-volume (hi-vol) sampler with a filter and XAD vapor trap for monitoring air pollutants on a 12-day schedule for the 3 upper Lake sites and a 3-day schedule for lower Lake sites. For dry deposition, Group 1 recommended the Noll sampler. For precipitation, the group recommended a monthly composite and large-area sampler for event sampling. A denuder was suggested to help evaluate information from the standard hi-vol sampler.

Group 1 proposed the following hypotheses for the mass-balance study:

- whether measurements over land reflect pollutants over water
- event-based vs. monthly sampling
- dry deposition of large particles
- source information
- quality control issues, particularly regarding new compounds, such as atrazine
- importance of urban vs. regional inputs

Recommended outputs for the mass-balance study were:

- atmosphere loadings to the Lake, plus information for modeling
- calibrated model

Dr. Sweet stated that the calibrated model was the real goal of the study. A calibrated model is necessary to be able to predict the fate of pollutants entering the Lake from the atmosphere

and can be applied to new chemicals not included in the mass-balance study. The model will also predict the effects of controlling a particular source and will help determine which controls will have the most positive effect.

Mr. David Cowgill summarized Group 2's discussions, which focused on initiatives that would meet managers' needs and would win funding approval. Generally, the group advocated building on the Green Bay Study and choosing parameters that have transferability to other water bodies.

Group 2 identified the following pollutants of concern:

- PCBs
- dieldrin
- lead
- nonachlor
- mercury
- DDT
- PAHs

Mr. Cowgill presented his group's matrix, which listed identified pollutants on one axis and reasons for their selection on the other axis. A pollutant must meet one or more of these criteria to be useful to the mass-balance study (however, satisfaction of one or more criteria does not mandate a pollutant's inclusion in the study):

- has ecological significance to the Great Lakes
- is bioaccumulative
- can be measured in air and water
- has known modeling method
- can be regulated
- acts as a surrogate
- has known atmospheric source
- is a potential new pollutant that identifies an emerging problem

Group 2 provided several modeling parameters. The group suggested using the Green Bay Study target pollutant list as a minimal base and reviewing the list and adding parameters as needed. In addition, source attribution should be determined and precipitation chemistry, and the air concentrations over water and across air/water interface should be characterized. Finally, both phase distribution (air and precipitation) and particle size distribution should be determined.

Group 2's DQOs were:

- use Green Bay Study as template for Lake Michigan QA program
- review and update all SOPs and QAPjPs
- establish centralized QA authority
- consider requesting ORD to provide QA support
- offer more than one option to decision-makers, options that require varying levels of funding
- achieve lowest possible analytical detection limits

Group 2 formulated several hypotheses that the study should address·

- Long-range transport has a significant effect on the water quality of the Lakes (sources outside the Basin are contributing to loadings).
- Tributary loadings are significant.
- Once load reduction "y" is achieved, concentration in fish reaches acceptable levels in "x" number of years.
- Sign of air/water flux changes through seasons
- Saturated microlayer can form a barrier to limit atmospheric flux to the water.

The key outputs deemed significant by Mr. Cowgill's group were:

- mass budget and media contribution
- prediction of impact of control actions on biological/ecological systems
- prediction of benefits from remedial actions and relation of benefits to regulatory action

Mr. DeVault questioned the group's list of pollutants, pointing out that, although they are pollutants of concern, some are not good candidates for modeling, particularly mercury. Dr. Swackhamer asked to see the pollutant list/criteria for selection matrix again and reiterated Mr. DeVault's point, saying that pollutants that cannot be measured cannot be used to develop or validate a model. Mr. Cowgill replied that his group was aware of the problems in measuring mercury, but that it was important to start research on mercury because of public interest in this pollutant. Dr. Swackhamer replied that analytical research is being conducted on mercury, but it was nevertheless a poor choice for the validation of this mass-balance model. In a mass-balance model, she said, chemicals are the tools that make the model work A good data set is needed to calibrate the model.

Ms. McCullough said that the group's intent in including mercury was to present a well-supported case for regulatory action of a chemical that has a documented, validated human health or ecological impact. Dr. Swackhamer replied that many other chemicals would fill that need—atrazine, for example.

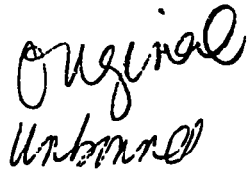
Dr. Swackhamer suggested prioritizing the selection criteria and completing the matrix for various pollutants, thus achieving a valid parameter list. The ability to measure and model pollutants would be the most significant selection criterion.

Mr. Pahl ended the workshop by observing that the group discussions were productive and spurred new ideas that would affect design of the mass-balance study. Mr. DeVault said that the next step for Region V was to complete the mass-balance study plan in 2-3 months and to start measurement work in spring 1993.

Mr. Pahl stated that this was the first of a series of mass-balance studies and that it would have a significant effect on all air and water quality plans.

APPENDIX A

MEETING AGENDA



LAKE MICHIGAN MASS BALANCE PLANNING WORKSHOP
FINAL AGENDA
GUEST QUARTERS SUITES
2515 MERIDIAN PARKWAY
RESEARCH TRIANGLE PARK, N.C.

TUESDAY MARCH 31,1992

10:30	Introduction	D. Pahl
10:40	Preliminary Objectives for Lake Michigan Mass Balance Model	D. DeVault
11:10	Overview of present transport/ fate, food chain models for the Great Lakes	B. Richardson
11:40	Estimation of Wet Deposition for Mass Balance Studies	J. Baker
12:15	LUNCH	
1:30	Estimation of Dry Deposition for Mass Balance Studies	T. Holsen
2:10	Interface of atmospheric & aquatic models in design of Mass Balance Studies.	T. Clark/ B. Benjey
2:45	Approach to measuring urban contributions to Great Lakes toxic loadings	J. Keeler
3:15	BREAK	
3:30	Use of Source Apportionment Model Results in Mass Balance Models	R. Stevens
4:00	Great Lakes States' atmospheric measurement objectives & data needs	J. Foy
4:15	Overview of Lakewide Management Planning	C. Hunt
4:30	Overview of air toxics data need for LaMP's	P. Blakely
4:45	Great Waters scientific and environmental measurement needs	M. McCullough
5:00	Adjourn /Social Hour/Raleigh Room	

WEDNESDAY, APRIL 1,1992

8:15	GROUP DISCUSSION: Identification of air data needs for Lake Michigan mass balance study and modelling (Pollutants, parameters, sampling frequency, analytic objectives, DQO's, Q.A.)	
10:30	BREAK	
10:45	Availability of sites	C. Sweet, J. Foy
11:15	Break into two teams to formulate preliminary monitoring plan	
12:00	Lunch	
1:00	Work group deliberations (continued)	
2:30	Work Group Presentations	
3:00	Wrap-up and summary	D. Devault/ A. Hoffman
3:30	Adjourn	

APPENDIX B
WORKSHOP PARTICIPANTS AND AFFILIATIONS

LIST OF PARTICIPANTS

LAKE MICHIGAN MASS BALANCE PLANNING WORKSHOP

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March 31-April 1, 1992

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APPENDIX C

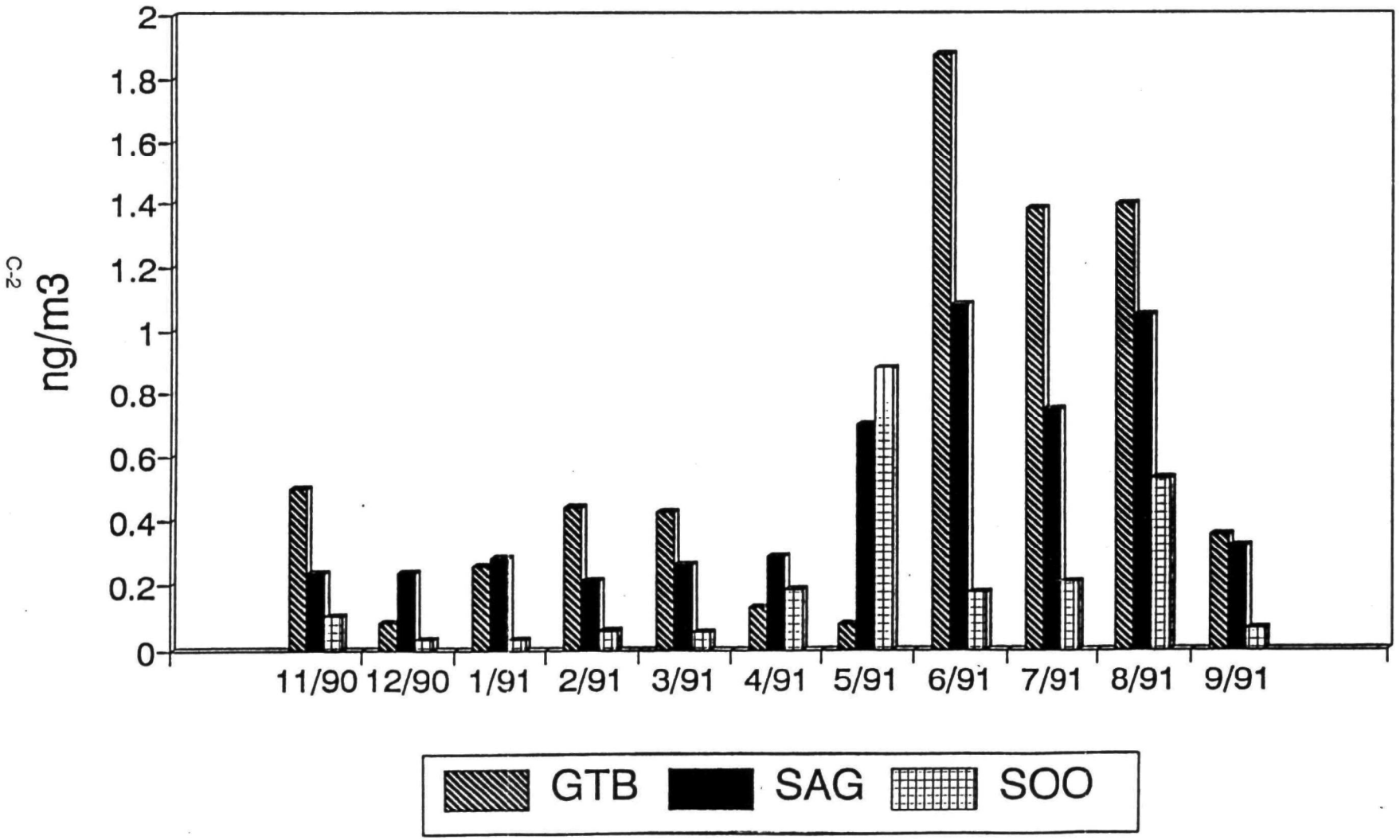
GREAT LAKES STATES' ATMOSPHERIC MEASUREMENT OBJECTIVES AND DATA NEEDS

PRESENTATION

MS. JOANNE FOY

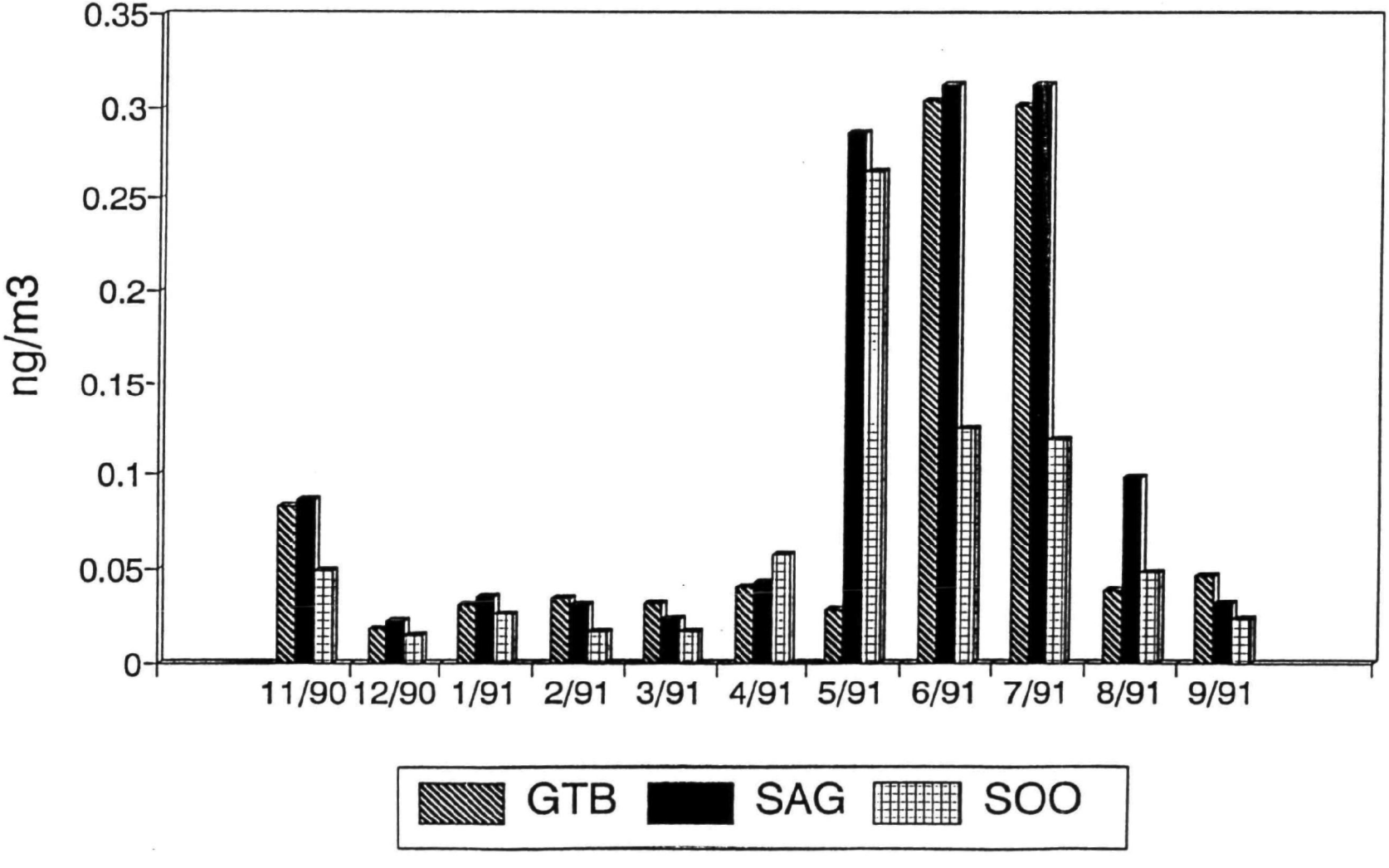
Great Lakes Toxics Monitoring

Total PCBs



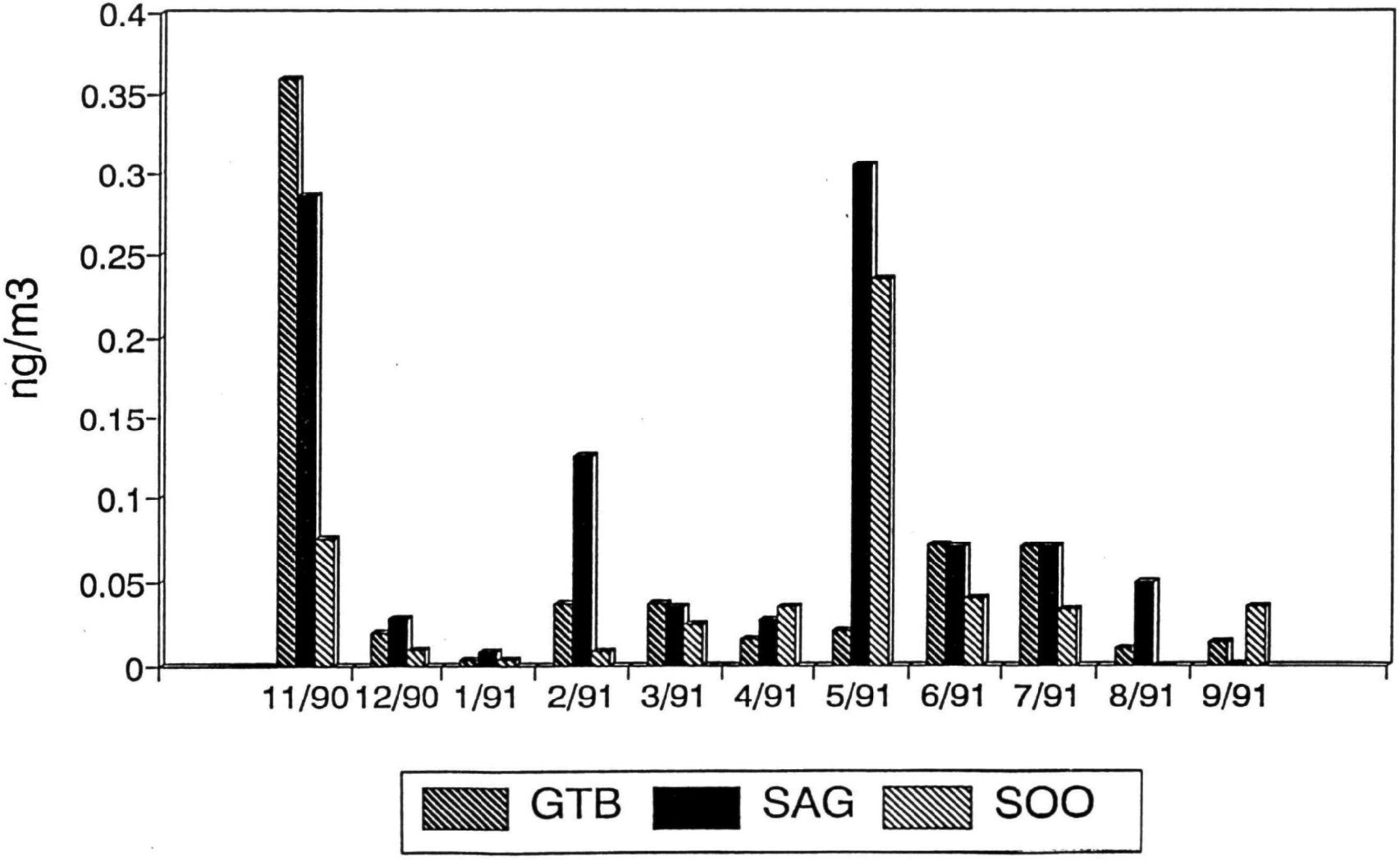
Great Lakes Toxics Monitoring

g-HCH



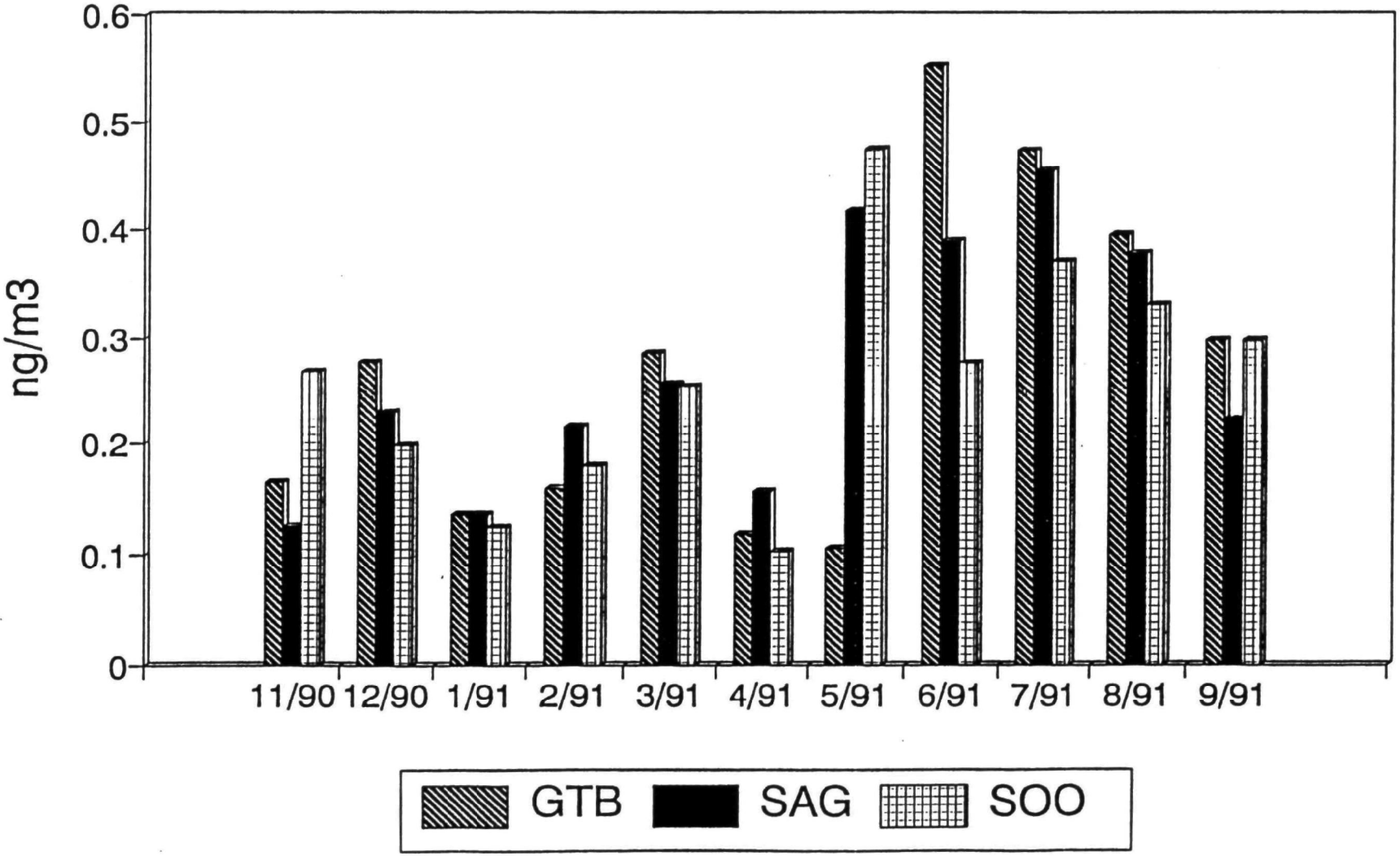
Great Lakes Toxics Monitoring

Dieldrin



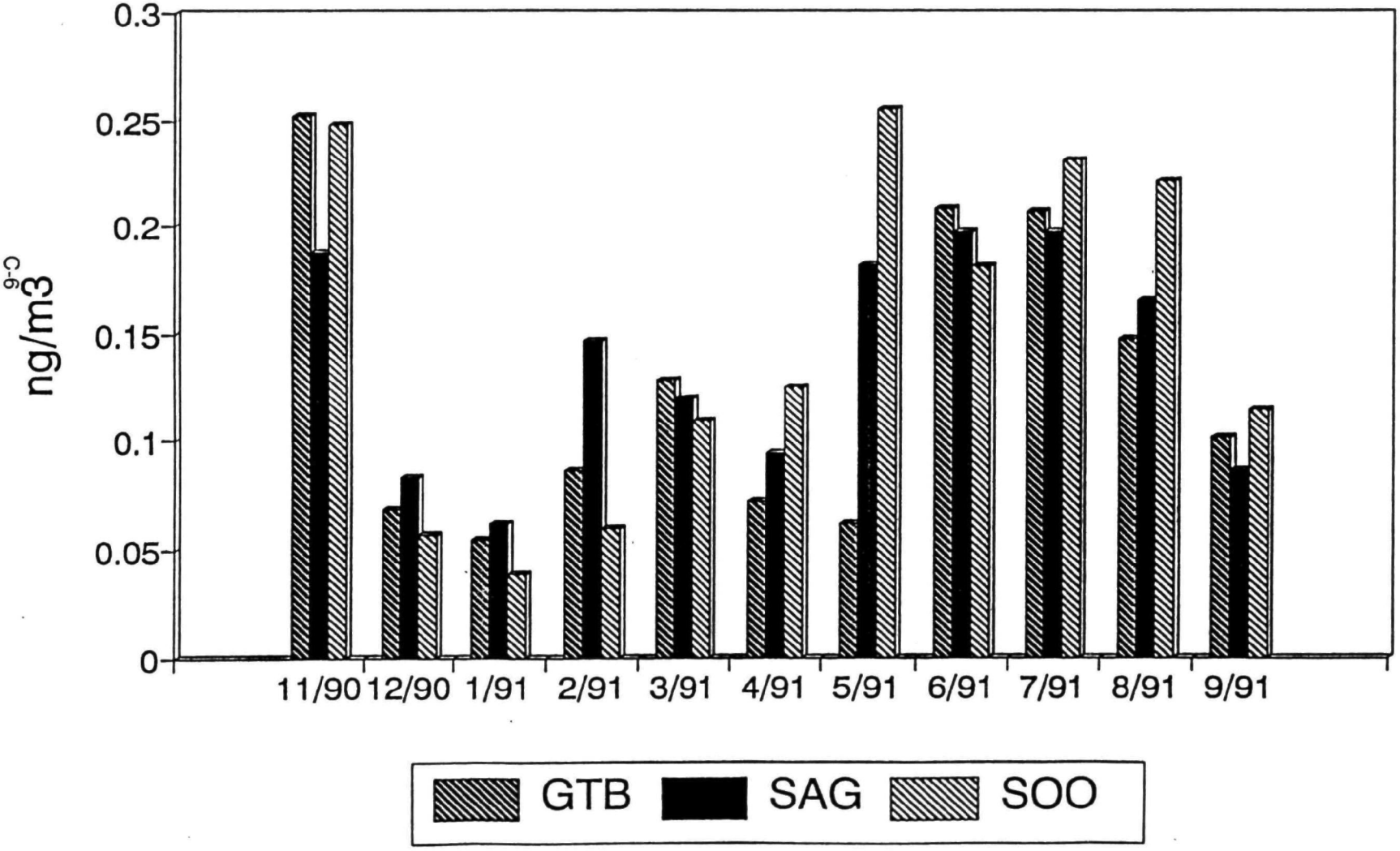
Great Lakes Toxics Monitoring

HCB



Great Lakes Toxics Monitoring

a-HCH



APPENDIX D
GROUP 2 DISCUSSION
SUMMARY

POLLUTANTS / DCO's OF CONCERN.

PCB's : BIOACC., ECO, SURROGATE

DIELDRIN : BIO, ECO, MEASURE

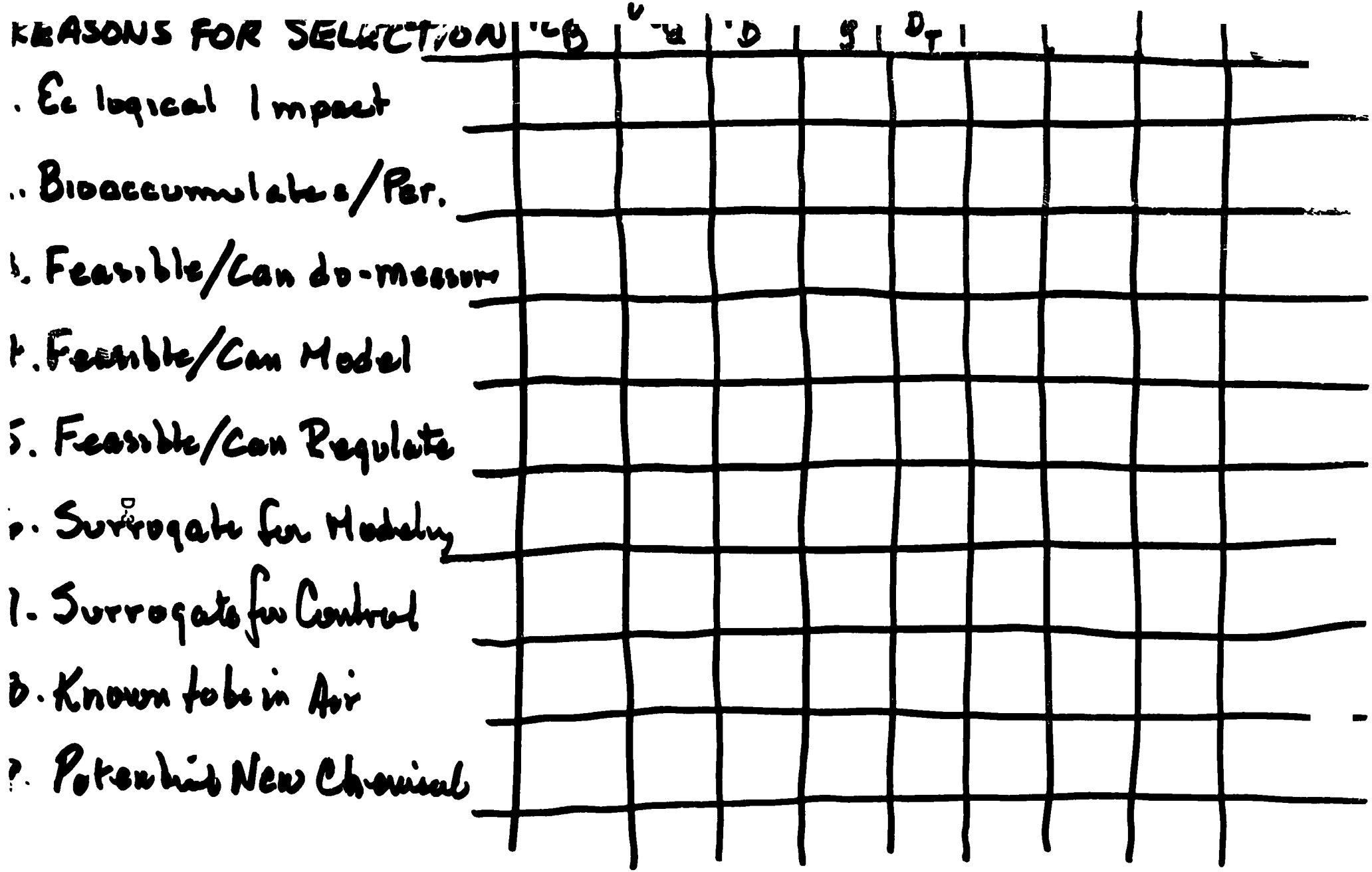
PB : ECO, measure

NONACHLOR : BIO, ECO, MEASURE

HG. : BIO, ECO, new problem, known AIR "Transferable"

DDT + MET : BIO, ECO,

PAH's :


REASONS FOR SELECTION
. Ecological Impact
.. Bioaccumulative/Per.
3. Feasible/Can do-measure
4. Feasible/Can Model
5. Feasible/Can Regulate
6. Surrogate for Modeling
7. Surrogate for Control
8. Known to be in Air
9. Potential New Chemical

PARAMETERS FOR MODELLING

1) MINIMUM: "GREEN BAY" LIST
(pg. 2 draft DeVaultp/a
+ SEDIMENTS)

2) NEED TO REVIEW LIST
IN LIGHT OF ADDITIONAL
PARAMETERS BEING
MEASURED (E.G. HG.)

3) SOURCE ATTRIBUTION
MEASUREMENTS.

4) PRECIP CHEM
AIR CONCS OVER H_2O
CONCS ACROSS AIR/H_2O INTERF.

PARAMETERS (CONT)

(5) PHASE DIST. AIR + PRECIP

(6) SIZE DIST. (PARTICLES)

DQO's

1. USE GREEN BAY STUDY AS TEMPLATE FOR PROCESS.

2. NEED TO REVIEW + UPDATE ALL SOP'S + QAPjP's.

3. CENTRALIZED QA CZAR TO OVERSEE / IMPLEMENT QA PROGRAM.

4. CONSIDER REQUESTING ORD TO PROVIDE QA TECH ASSISTANCE + SUPPORT

PROVIDE MGT WITH 2 OR 3 ALTERNATIVE LOE THAT REFLECT DIFFERENT LEVELS OF UNCERTAINTY AND SCIENTIFIC CREDIBILITY

HYPOTHESES TO BE TESTED.

① H_o: THERE IS NO SIGNIFICANT LONG RANGE TRANSPORT HAS SIGNIFICANT IMPACT ON LAKE WATER QUALITY

② H_o: WE CAN DETERMINE THE RELATIVE IMPORTANCE OF TRIB. DRAINAGE BASIN VS ATMOSPHERIC DEPOSITION VS SEDIMENTS LOADINGS TO THE LAKE.

③ H_o: ONCE "Y" LOAD REDUCTIONS ARE ACHIEVED, IT WILL REQUIRE "X" YEARS FOR CONCENTRATIONS IN FISH TO REACH ACCEPTABLE LEVELS.

(4) H_0: VOLATILIZATION FROM LAKE ~~MAY~~ CONTRIBUTES TO ~~CONCENTRATIONS~~ DEPOSITION DOWNWIND

(5) H_0: SIGN OF FLUX CHANGES BY SEASON.

(6) H_0: MICROLAYER CAN FORM BARRIER CURTAIL ATMOSPHERIC FLUX

KEY OUTPUTS

1. MASS BUDGET + MEDIA CONTRIBUTION

2. PREDICT IMPACT OF CONTROL ACTIONS ON BIOLOGICAL/ECOLOGICAL SYSTEMS

3. PREDICT BENEFIT OF REMEDIAL ACTION

APPENDIX E

OVERVIEW OF LAKEWIDE MANAGEMENT PLANNING

PRESENTATION

MS. CONNIE HUNT

LAKE MICHIGAN LAKEWIDE MANAGEMENT PLAN

Goal: To reduce loads of persistent, toxic, and/or bioaccumulative pollutants in order to restore beneficial uses to the Lake Michigan basin through an ecosystem-based, multi-media approach

Lake Michigan Lakewide Management Plan

Background

1. Great Lakes Water Quality Agreement Annex II
   a. provided mandate for Lakewide Management Plans for the Great Lakes

E3

2. Critical Programs Act
   a. mandates a proposed Lakewide Management Plan for Lake Michigan be published in January 1992
   b. mandates a final Lakewide Management Plan for Lake Michigan be published in January 1994

LAKE MICHIGAN LAKEWIDE MANAGEMENT PLAN

Participating Agencies

U.S. EPA

U.S. Fish and Wildlife Service

U.S. Geological Survey

U.S. Department of Agriculture

U.S. Army Corps of Engineers

Illinois EPA

Indiana DEM

Michigan DNR

Wisconsin DNR

Chippewa/Ottawa Treaty Fishery Management Authority

Proposed Critical Pollutants for Lake Michigan

Level I

Total PCBs

Dieldrin

Chlordane

DDT and Metabolities

Mercury

Level II

Dioxins

Level III

Furans

Level IV

Hexachlorobenzene

Toxaphene

PAHs

Cadmium, Chromium, Copper, Lead, Zinc

Critical Pollutants

Tiering Concept

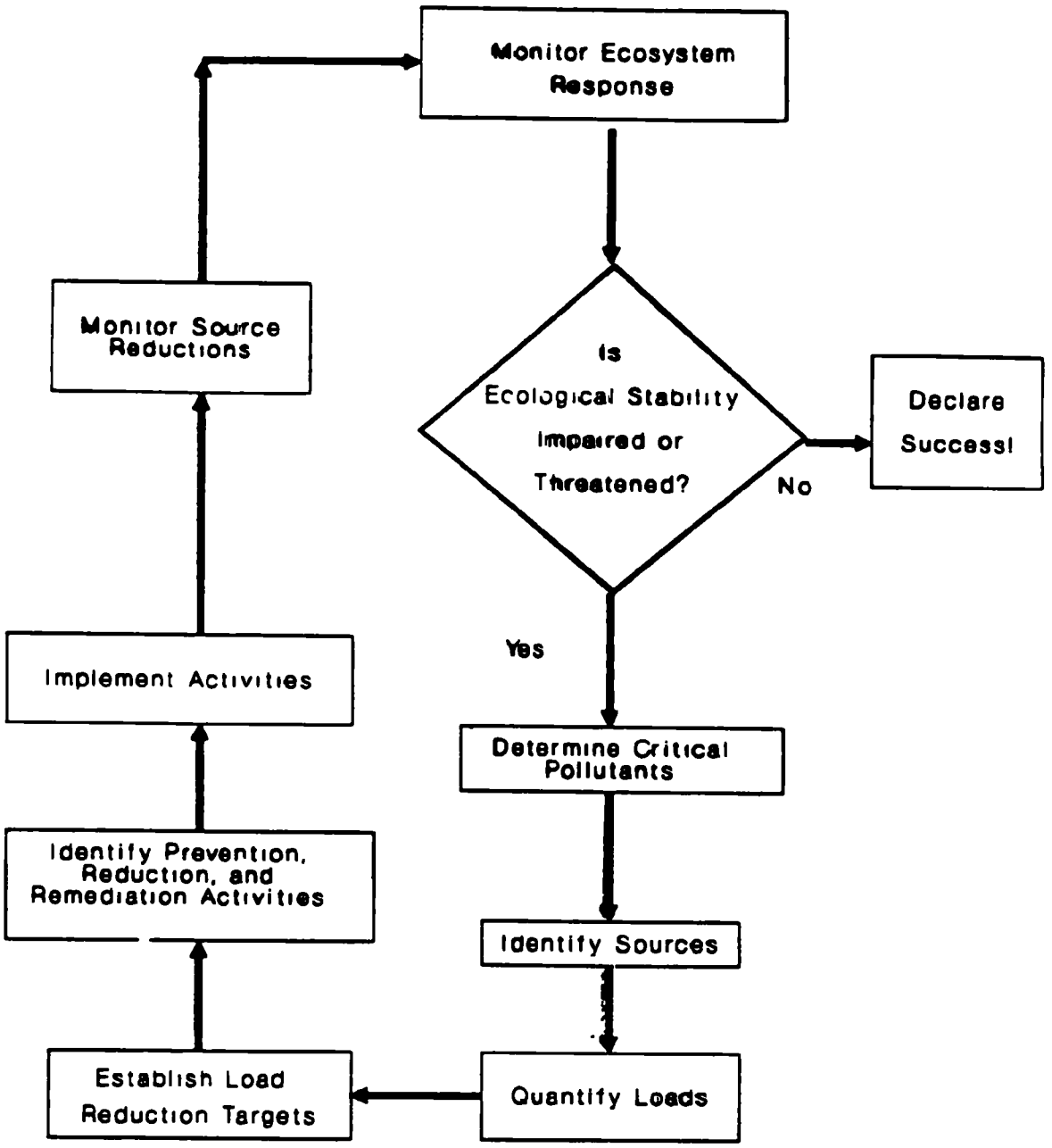
LEVEL I: Numerical Standard Violated ⟷ **LaMP Focus; Enforce Standards; Reduce Loads**

LEVEL II: Strong Association with Use Impairments ⟷ **LaMP Focus; Reduce Loads**

↑ ↑ ↑ --------CRITICAL POLLUTANTS-------- ↑ ↑ ↑

LEVEL III: Moderate Association with Use Impairments ⟷ **Develop Information Base; Encourage Load Reductions**

LEVEL IV: Possible Association with Use Impairments ⟷ **Develop Information Base; Encourage Pollution Prevention**


Monitor Ecosystem Response
Is Ecological Stability Impaired or Threatened?
No
Declare Success!
Yes
Determine Critical Pollutants
Identify Sources
Quantify Loads
Establish Load Reduction Targets
Identify Prevention, Reduction, and Remediation Activities
Implement Activities
Monitor Source Reductions

APPENDIX F

LAKE MICHIGAN AIR MONITORING—SITE SUMMARY PRESENTATION

DR. CLYDE SWEET

LAKE MICHIGAN AIR MONITORING - SITE SUMMARY
4-1-92

OPERATIONAL SITES*

Sleeping Bear Dunes (IADN Master Site)

Indiana Dunes (IADN Satellite Site)

Chicago 68th St. Crib (Offshore urban plume site)

AVAILABLE SITES*

Chicago (3 GLAD sites, IIT, urban sites)

Milwaukee UW (GLAD, urban site)

Green Bay UW (used in GBMB, PCB source area)

Sturgeon Bay Coast Guard Sta. (ship traffic, topography)

Beaver Is. (GLAD site, other potential sites on MDNR land)

Muskegon NOAA (paper mill, public beach nearby)

Benton Harbor (GLAD site, some industry nearby)

Manitowoc UW (GLAD site)

POTENTIAL SITES*

Peninsula State Park, WI (used in GBMB, tree cover)

Fayette State Park, MI (LMOS used a private site nearby)

Zion State Park, IL

Cana Light USCG

Mission School (MDNR Air Toxics Site, Traverse City)

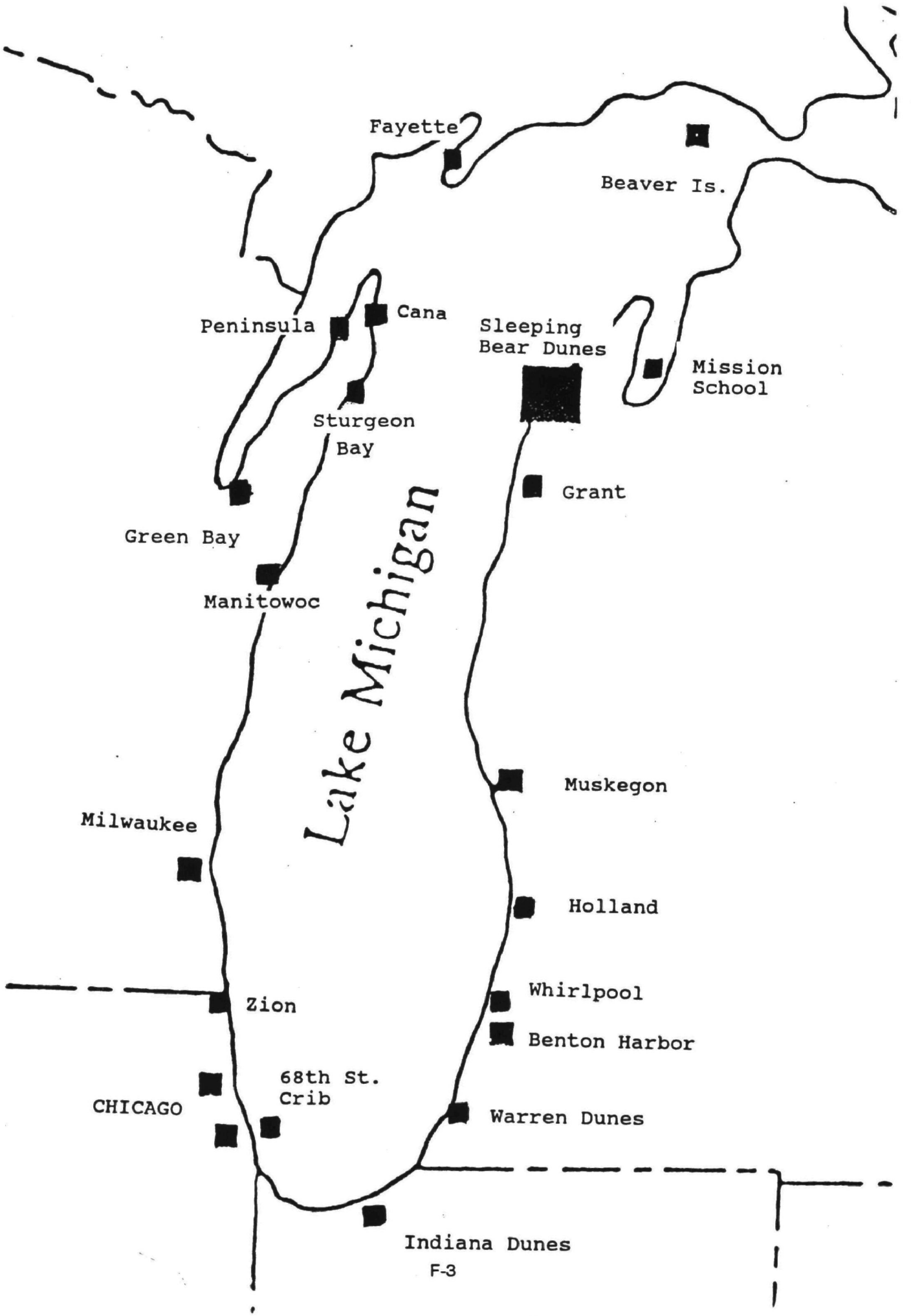
Grant Twp. (1991 LMOS Site)

Holland (1991 LMOS Site)

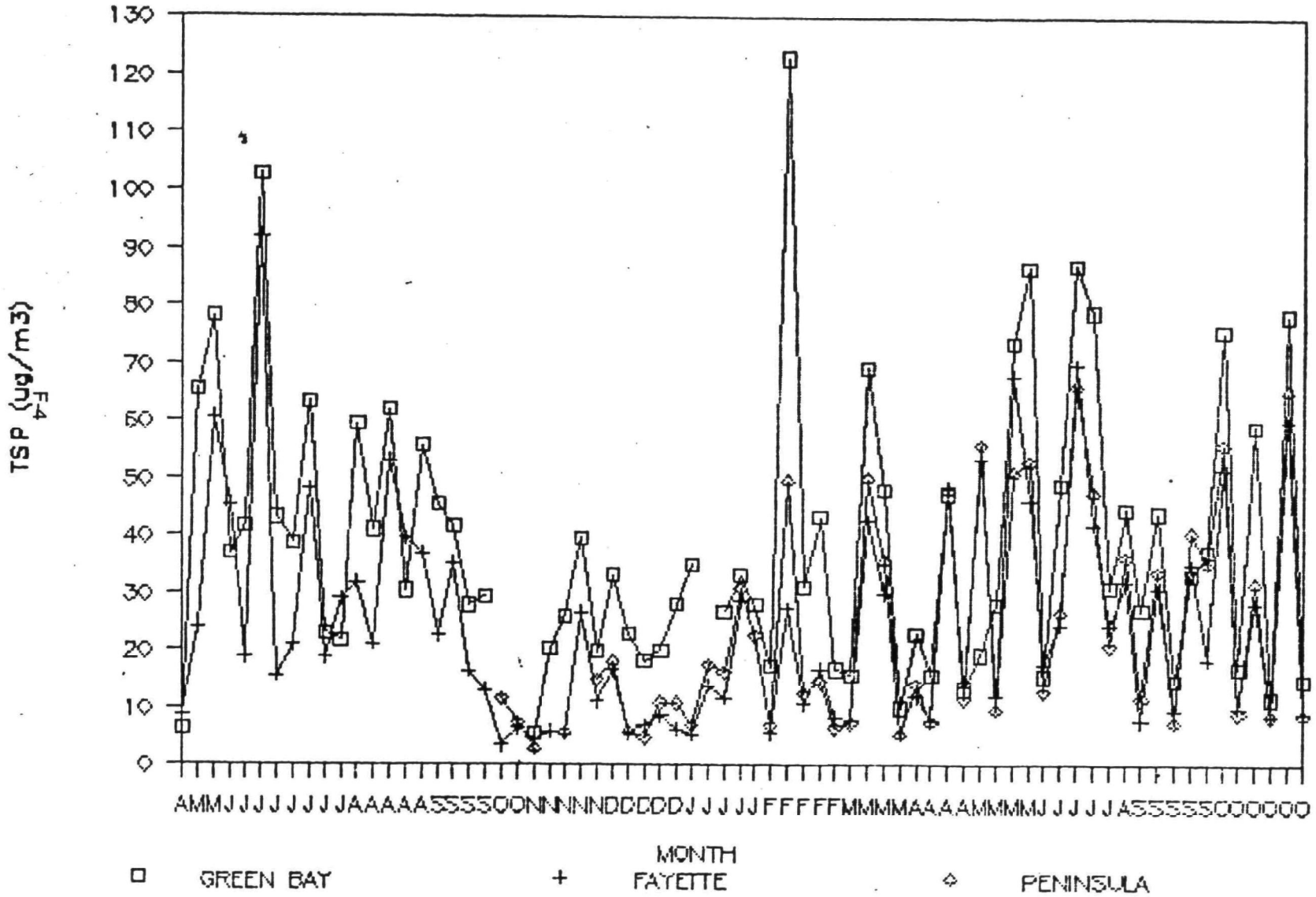
Whirlpool Corporation

Warren Dunes State Park, MI

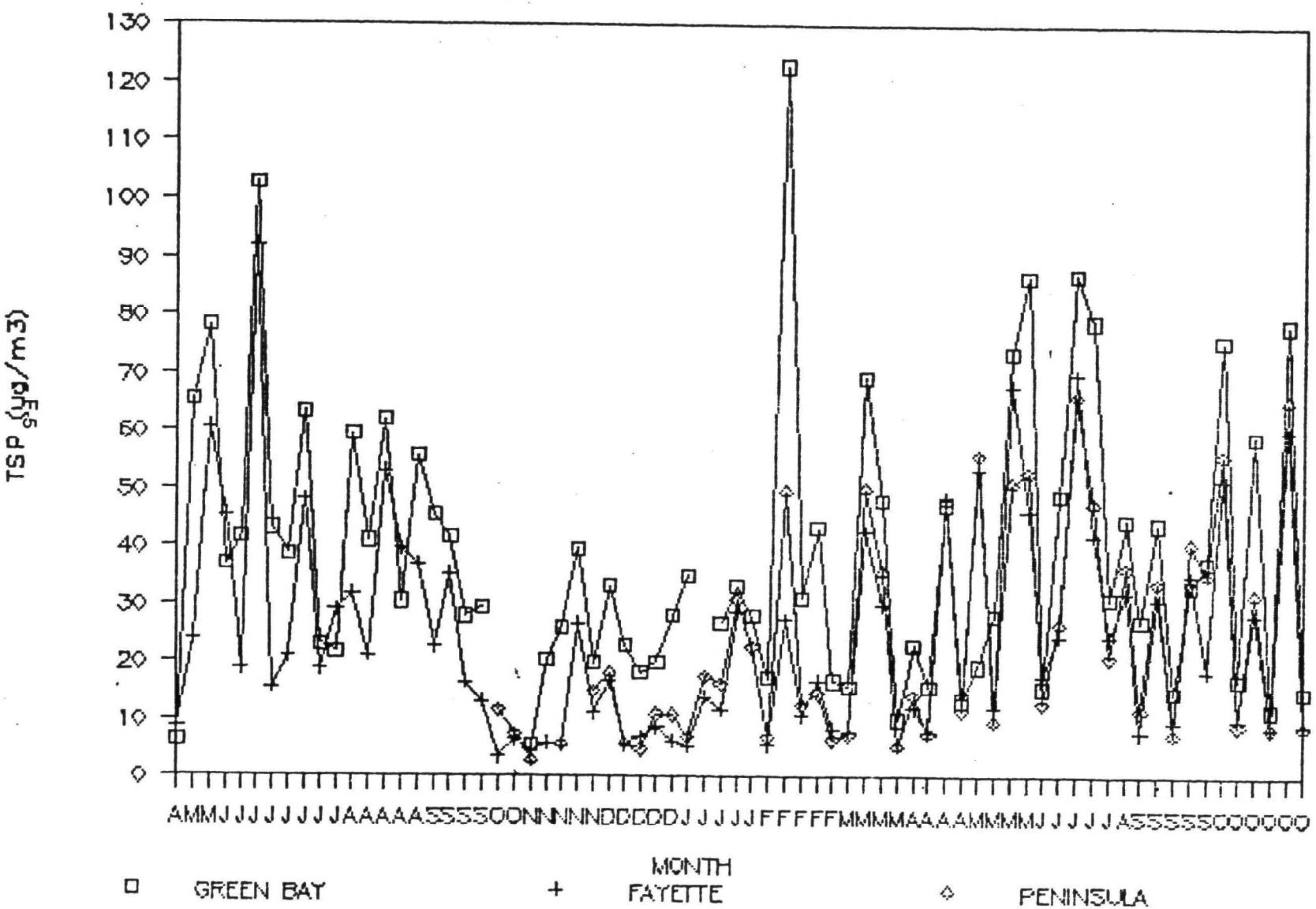
* OPERATIONAL = Now in operation or operations planned for 1992.
AVAILABLE = Written or verbal approval has been obtained.
POTENTIAL = No approval has yet been obtained.

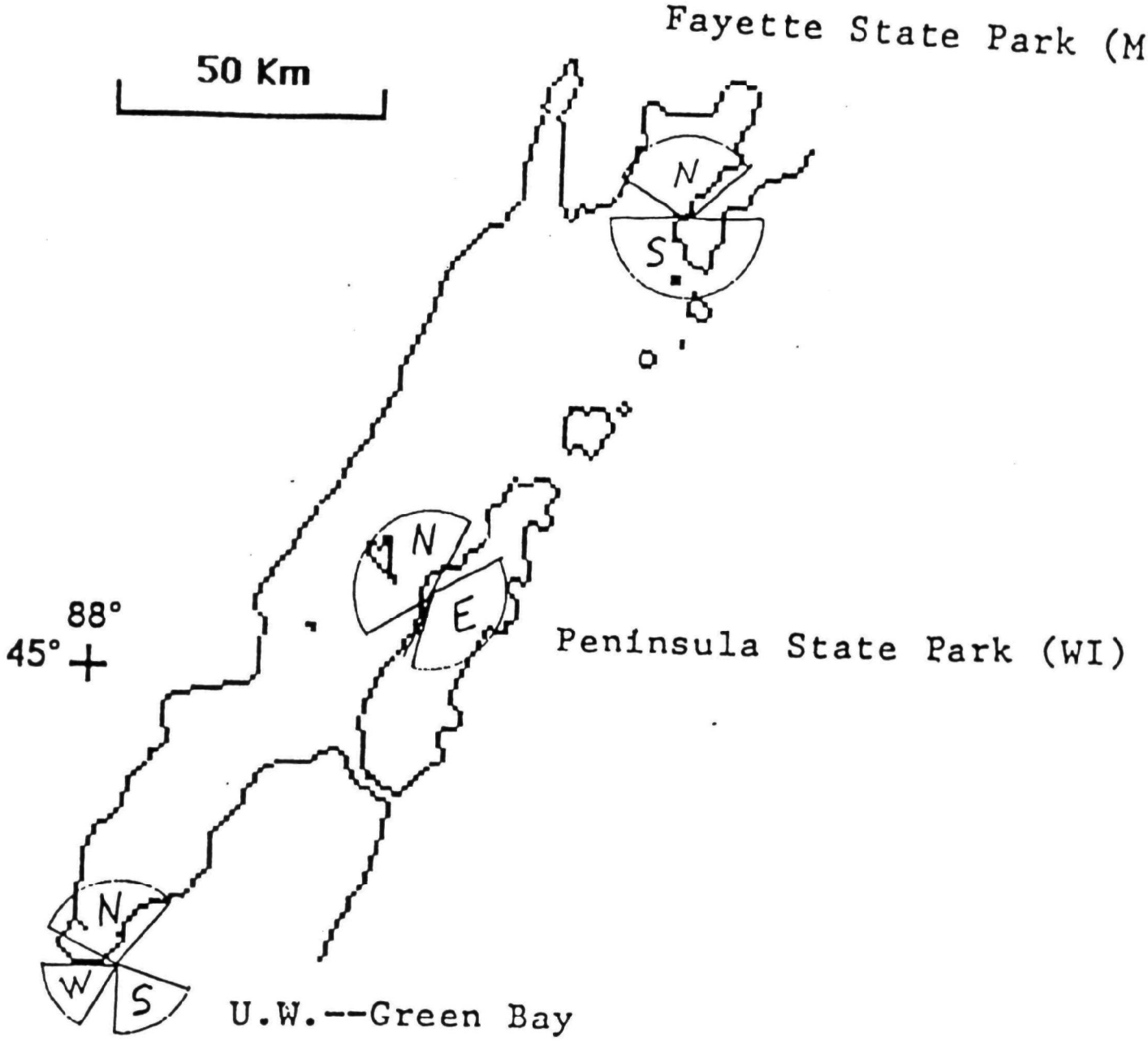

Fayette
Beaver Is.
Peninsula
Cana
Sleeping
Bear Dunes
Mission
School
Sturgeon
Bay
Grant
Green Bay
Lake Michigan
Manitowoc
Muskegon
Milwaukee
Holland
Whirlpool
Zion
Benton Harbor
68th St.
Crib
CHICAGO
Warren Dunes
Indiana Dunes

GREEN BAY PROJECT TSP VALUES 1988—1989



GREEN BAY PROJECT TSP VALUES 1988–1989

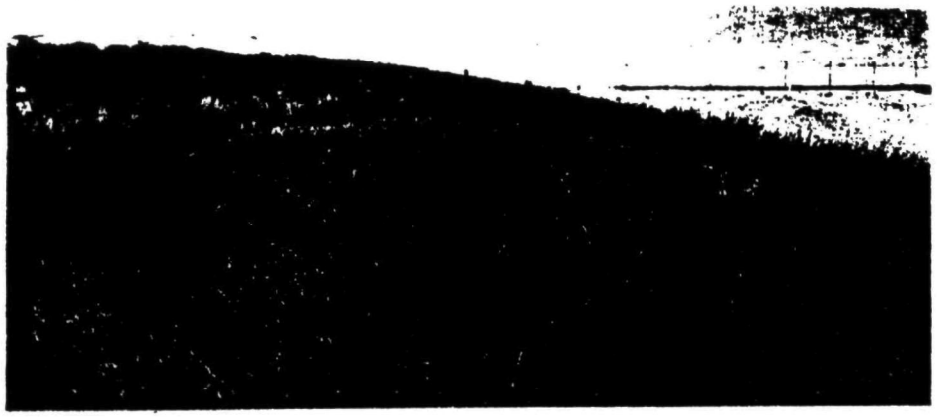



Fayette State Park (MI
50 Km
N
S
N
E
88°
45°
Peninsula State Park (WI)
N
W
S
U.W.--Green Bay

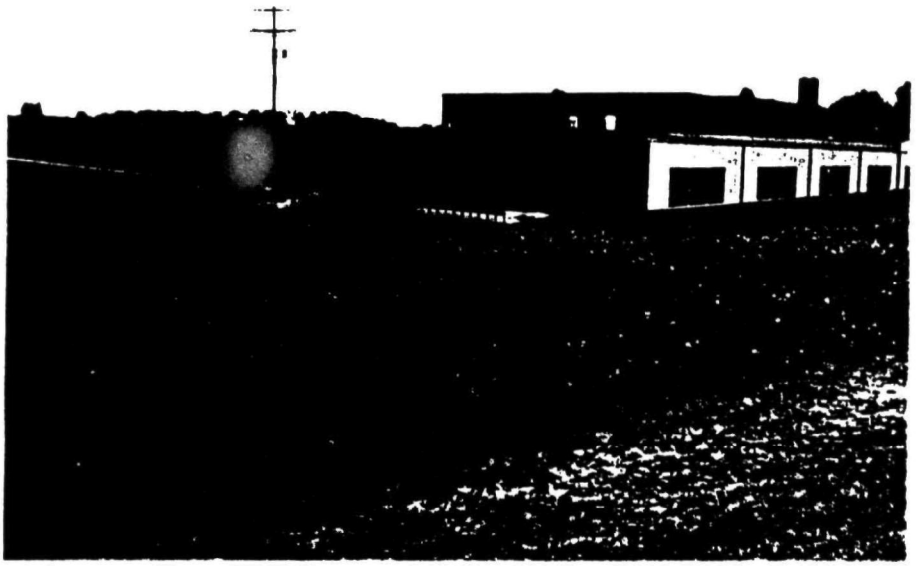
BEAVER ISLAND (GLAD)

MUSKEGON (NOAA)

BENTON HARBOR (GLAD)

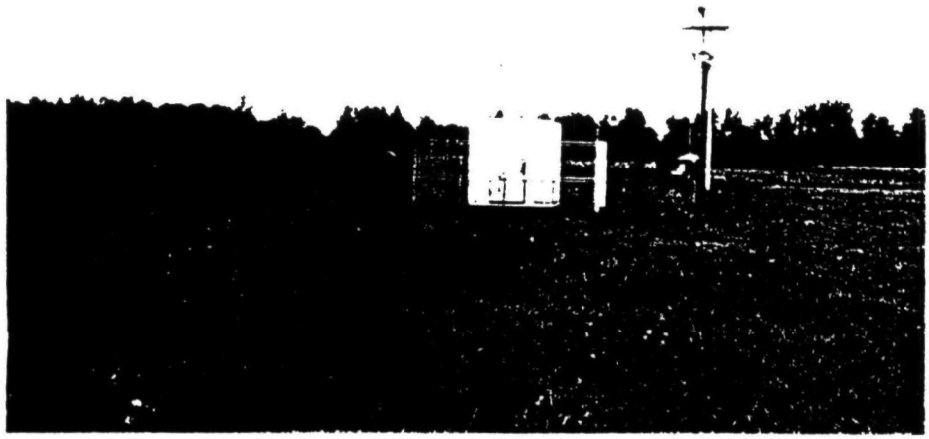


MISSION SCHOOL (MDNR)

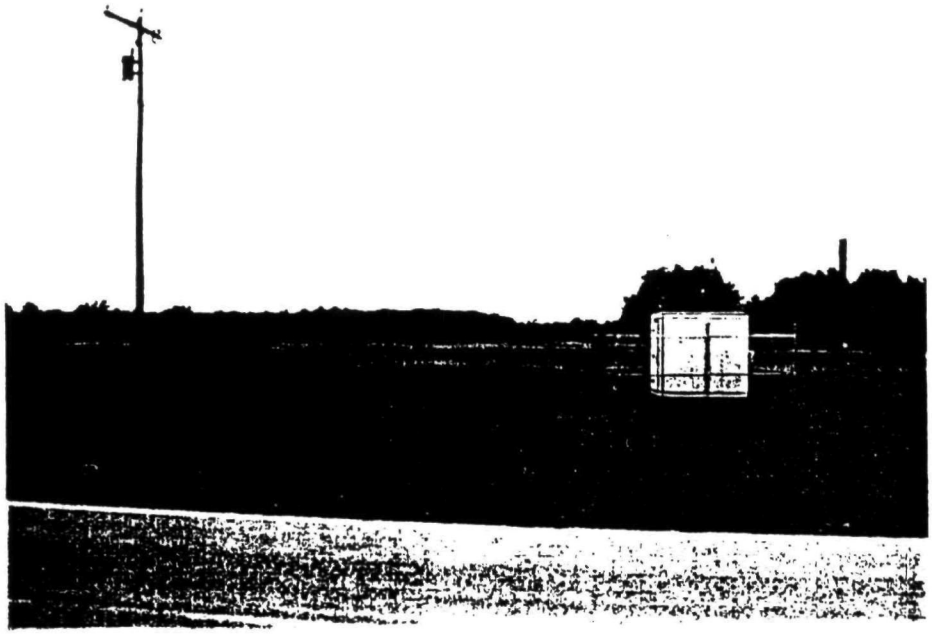


WHIRLPOOL CORP.

HOLLAND (LMOS)



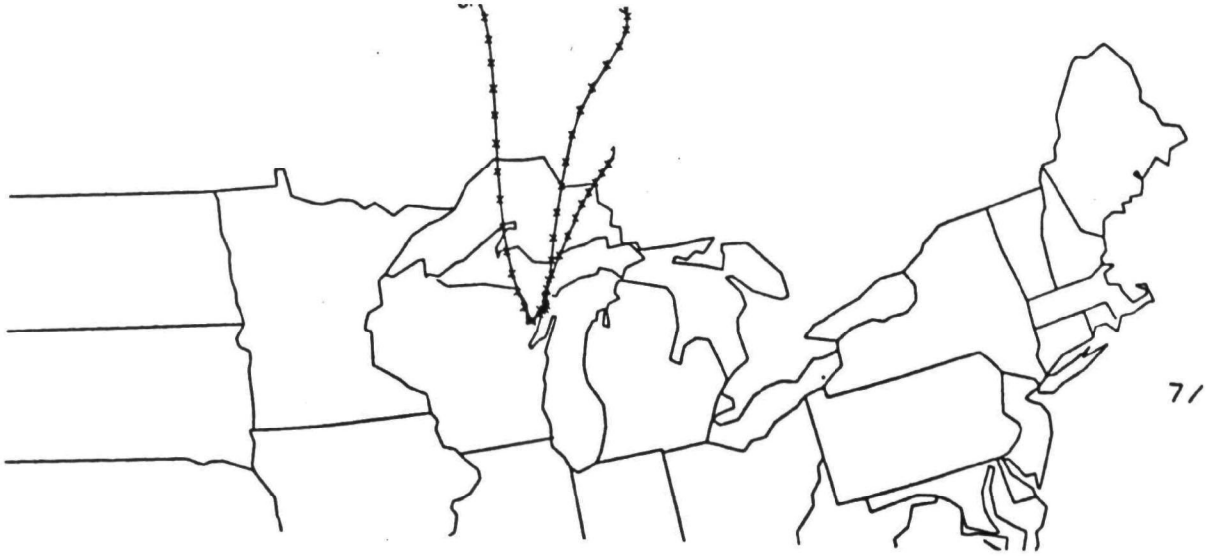
GRANT TWP. (LMOS)



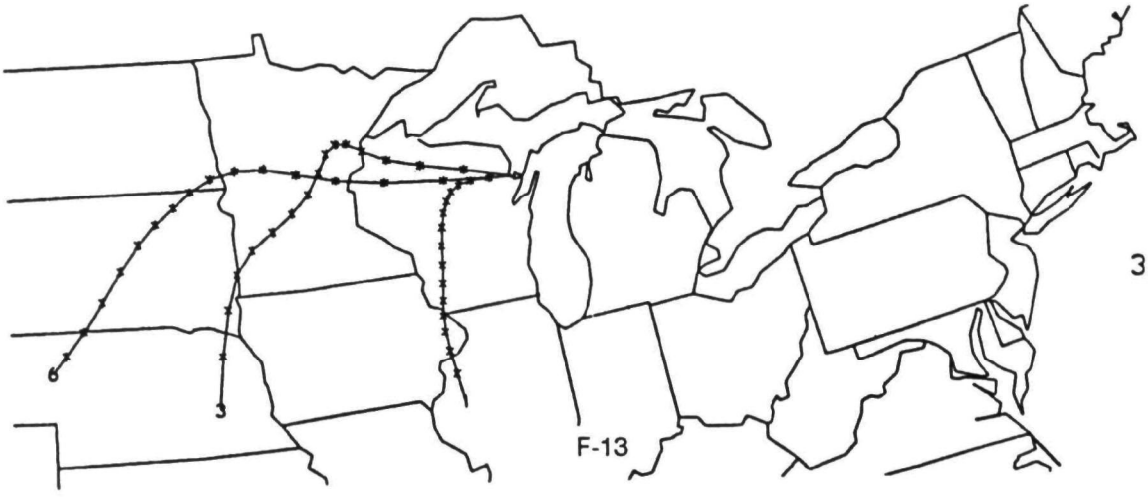
INDIANA DUNES NATIONAL LAKESHORE (NADP)

LOW TSP

9/13/89

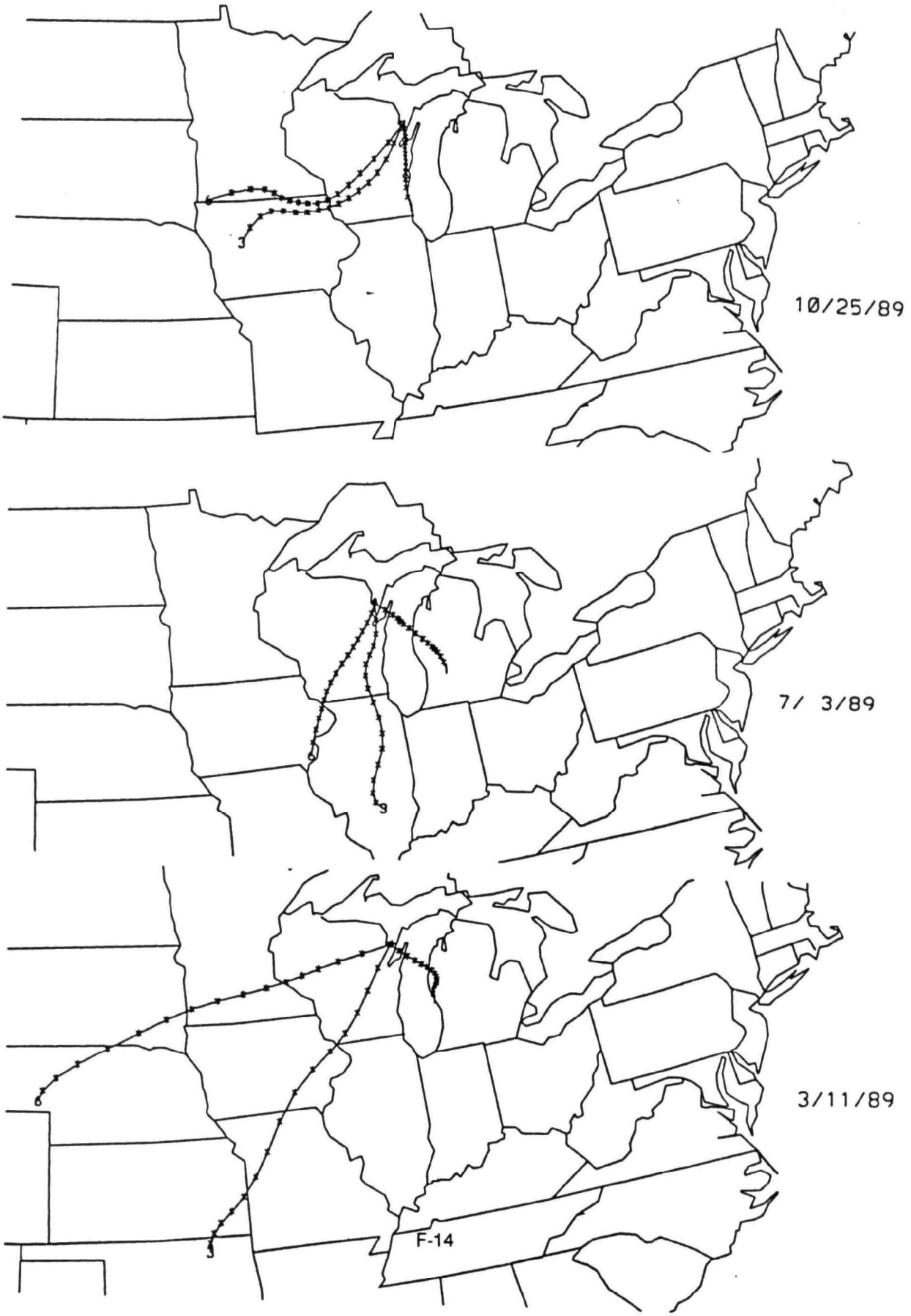


7/15/89



3/29/89

HIGH TSP



APPENDIX G

USE OF SOURCE APPORTIONMENT MODEL RESULTS IN MASS-BALANCE MODELS

PRESENTATION

DR. ROBERT STEVENS

GREAT WATERS AIR TOXIC DEPOSITION RESEARCH PROGRAM

Recommendations for Sampling and Analysis

Collect and Analyze Fine & Coarse Particles Separately

Use Filters Appropriate for Analysis

Use Denuders for Collection and Analysis of SVOCs

Collect and Analyze VOCs

Incorporate SEM Analysis Methods

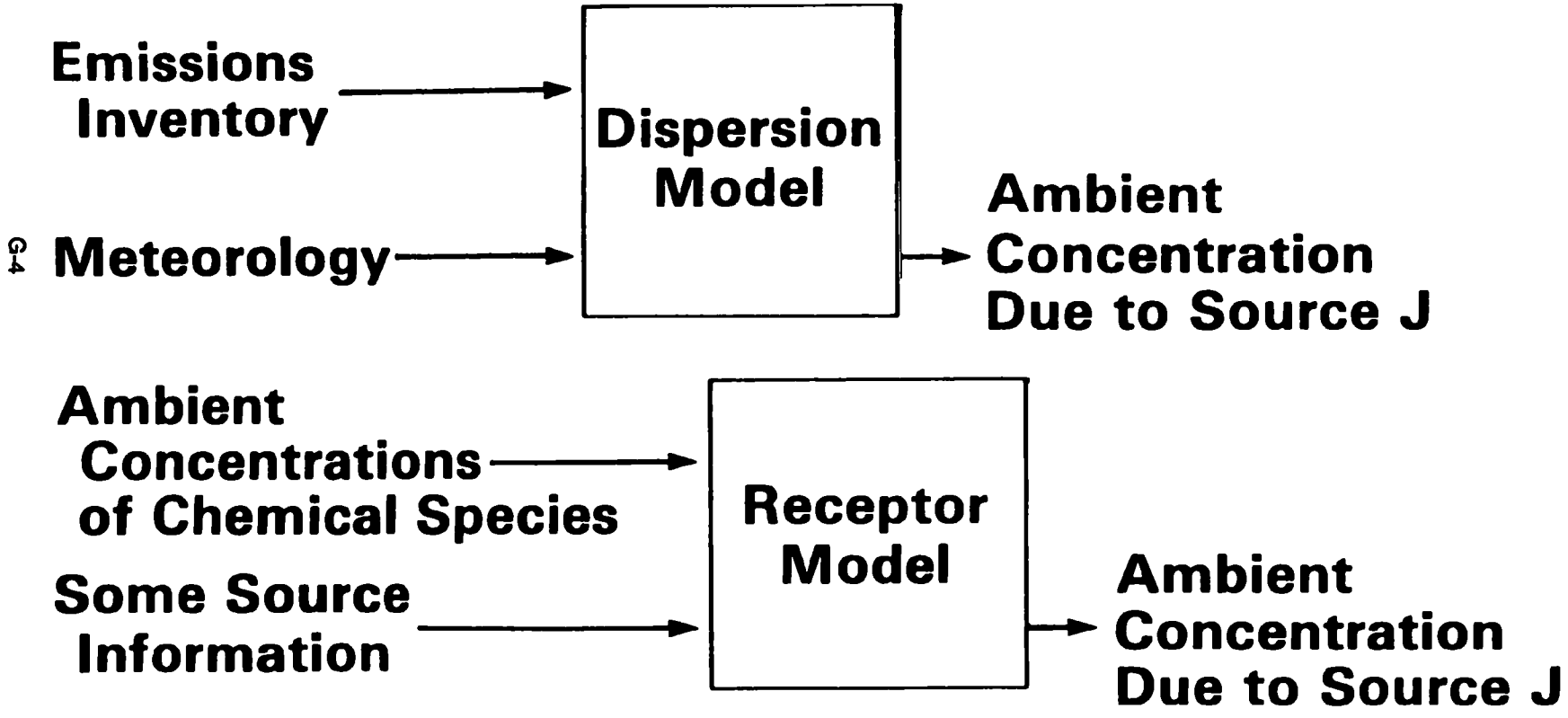
Use Hybrid Models

Perform Deposition Experiments at Receptor Sites

HYBRID RECEPTOR MODEL

ANY PROCEDURE FOR ESTIMATING THE SOURCES OF AMBIENT AIR POLLUTANTS AT A RECEPTOR (AMBIENT) SITE, WHICH COMBINES ELEMENTS OF BOTH RECEPTOR AND DISPERSION MODELING APPROACHES.

Source Apportionment Methods



APPENDIX H

APPROACH TO MEASURING URBAN CONTRIBUTIONS TO GREAT LAKES TOXIC LOADINGS

PRESENTATION

DR. JERRY KEELER

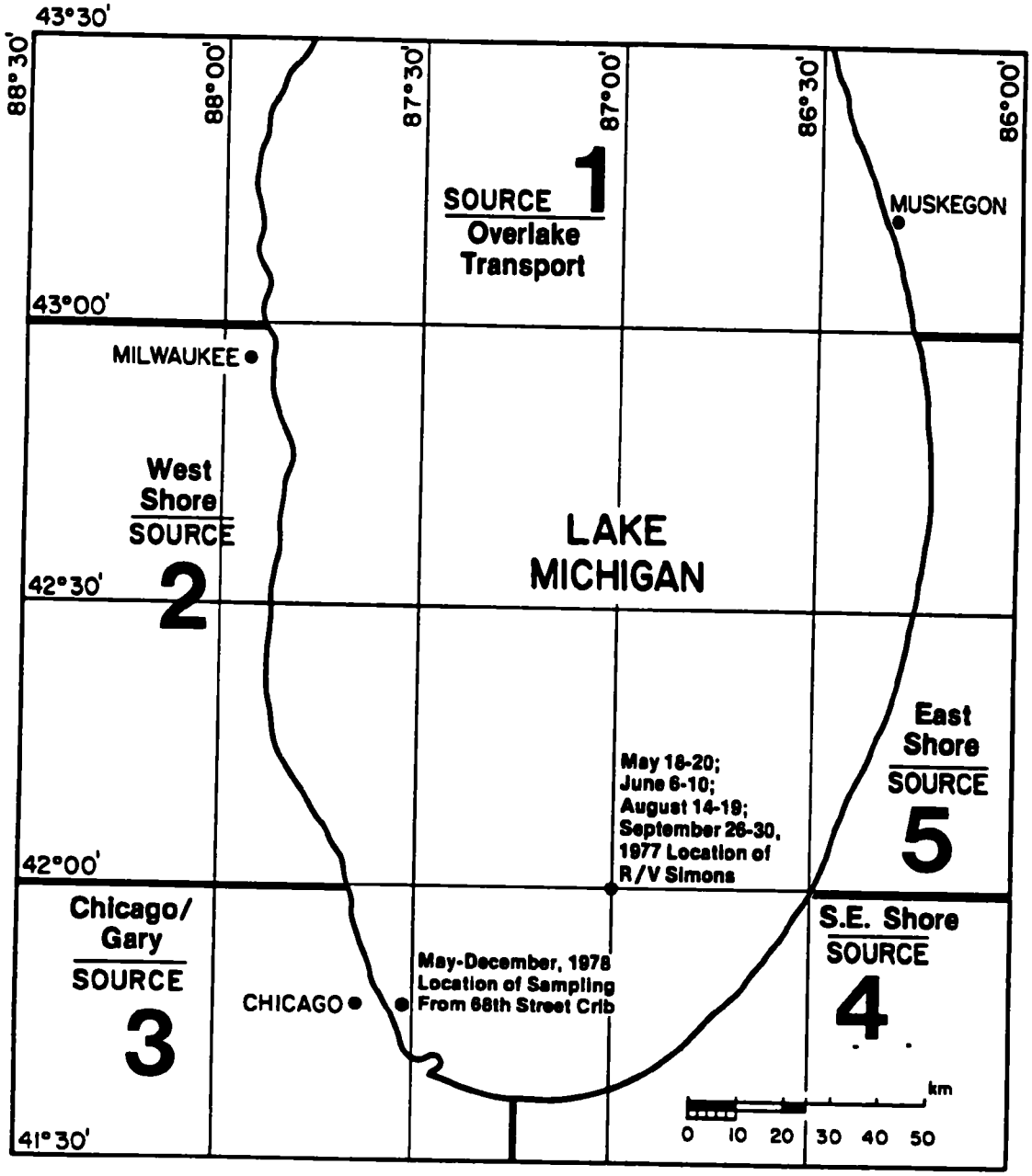
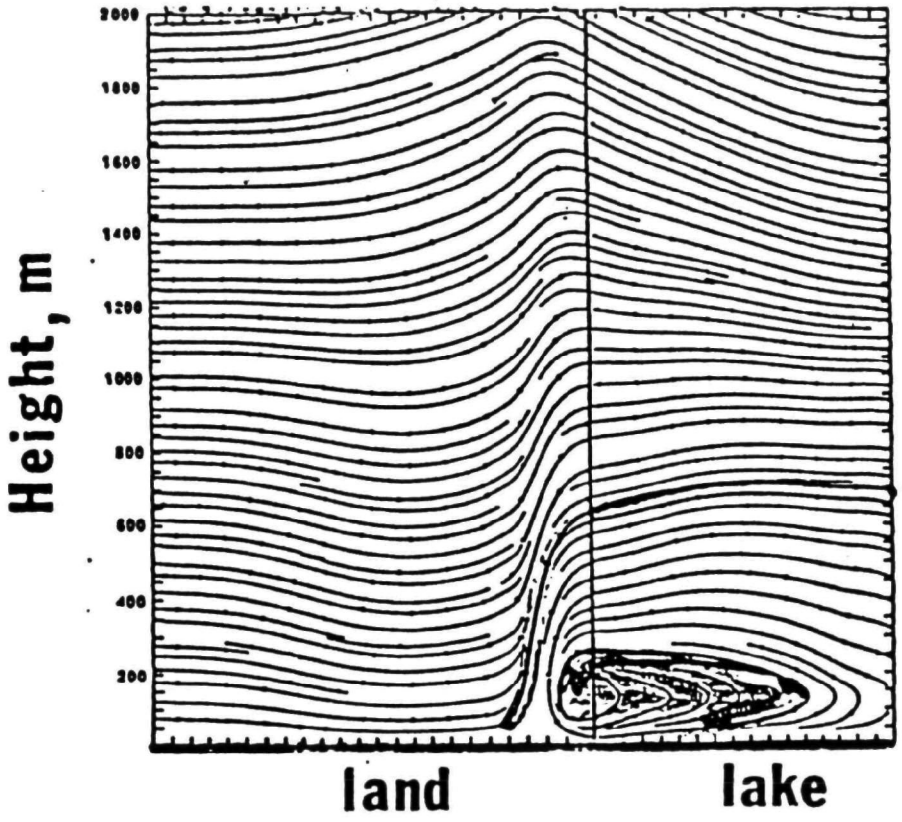


FIGURE 1. Location of Source Regions and Sampling Data.

URBAN AIR TOXICS COMPONENT

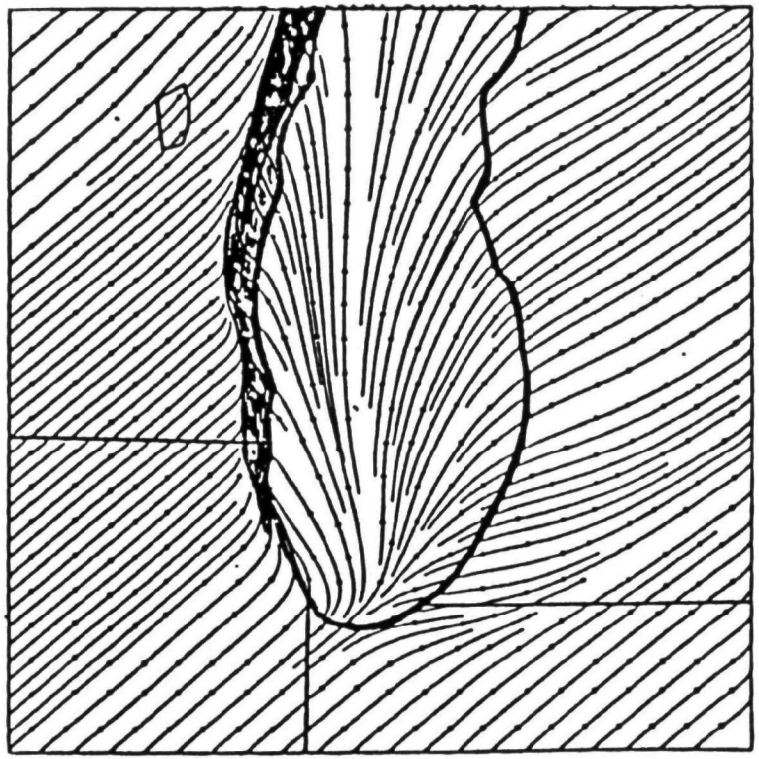
DESIGN CONSIDERATIONS:



OFFSHORE MIXING ZONE-VERTICAL PROFILE

URBAN AIR TOXICS COMPONENT DESIGN CONSIDERATIONS

SUMMERTIME EPISODIC WIND PROFILE:



SHADED AREA ON WESTERN SHORE-MAX O3

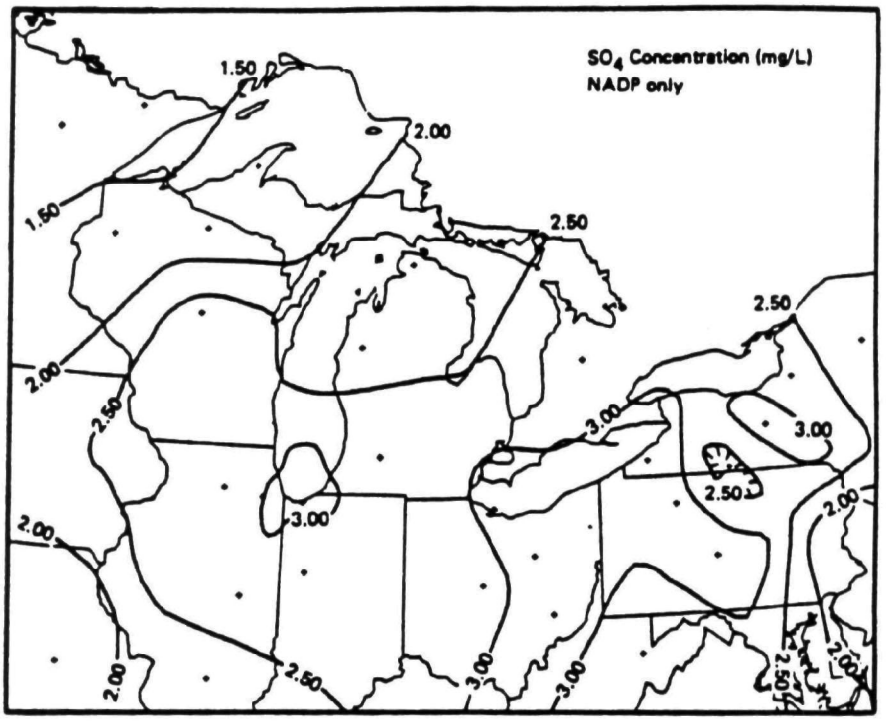


Figure 8(a). Spatial distribution of volume-weighted SO_4 concentrations in the Great Lakes region, using NADP data for 1982-83.

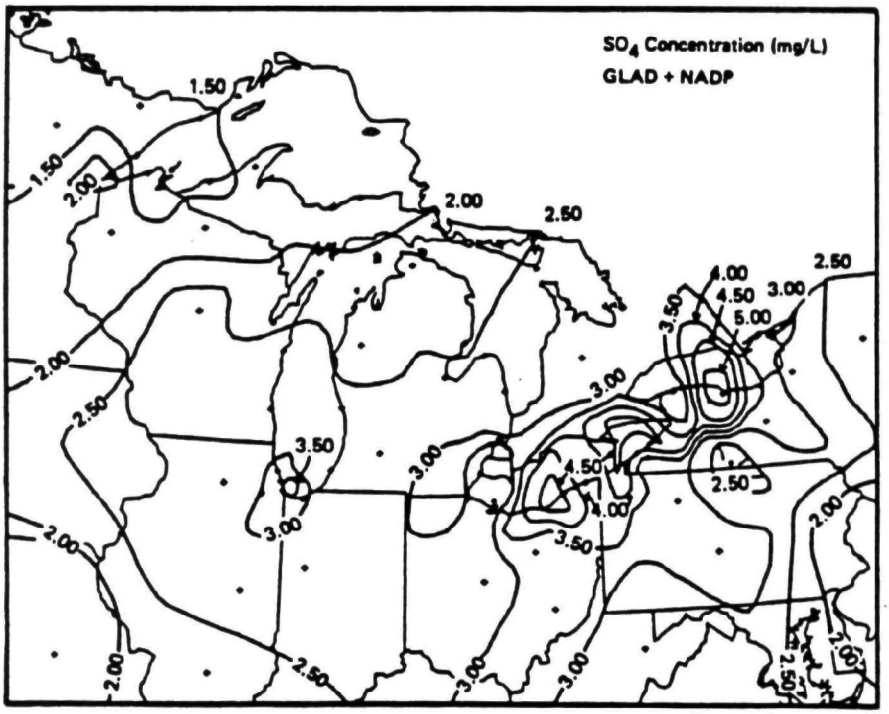


Figure 8(b). Same as (a), but using the combined GLAD/NADP data set.

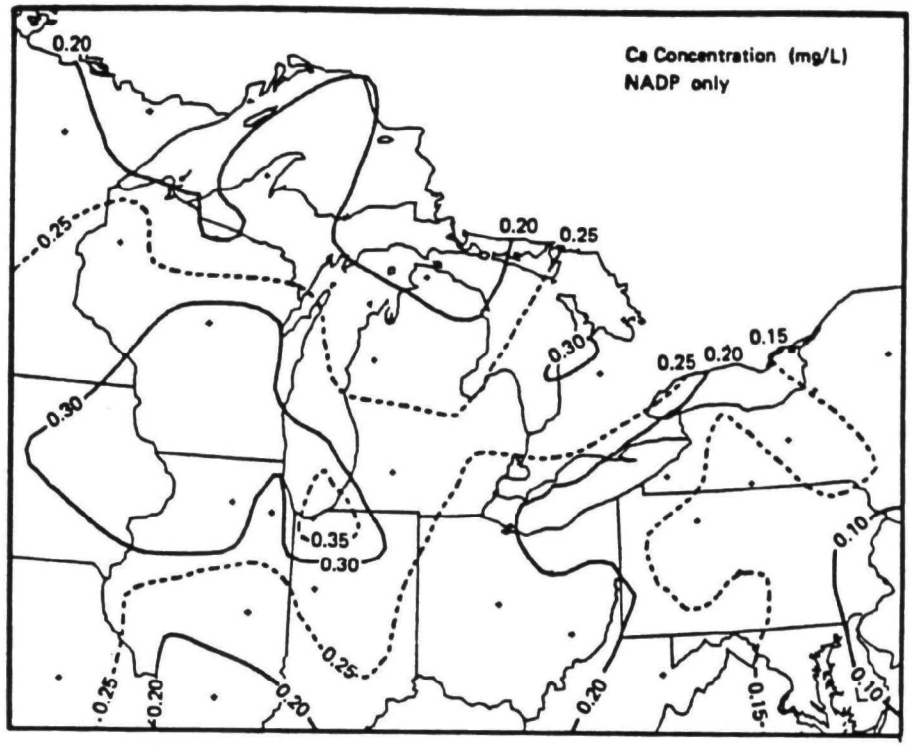


Figure 9(a). Spatial distribution of volume-weighted Ca concentrations in the Great Lakes region, using NADP data for 1982-83.

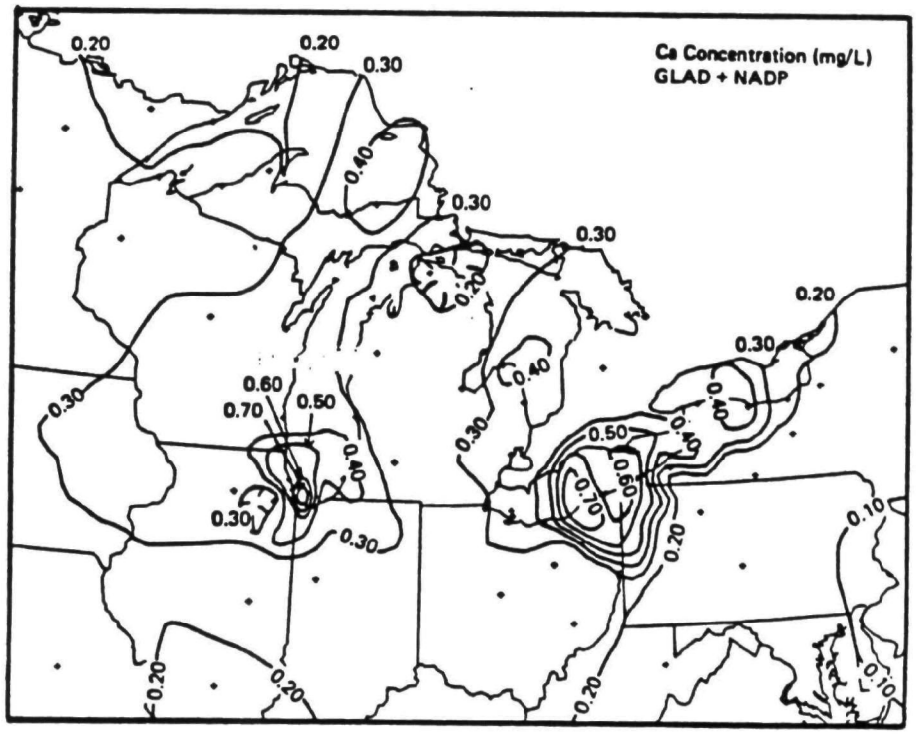


Figure 9(b). Same as (a), but using the combined GLAD/NADP data set.

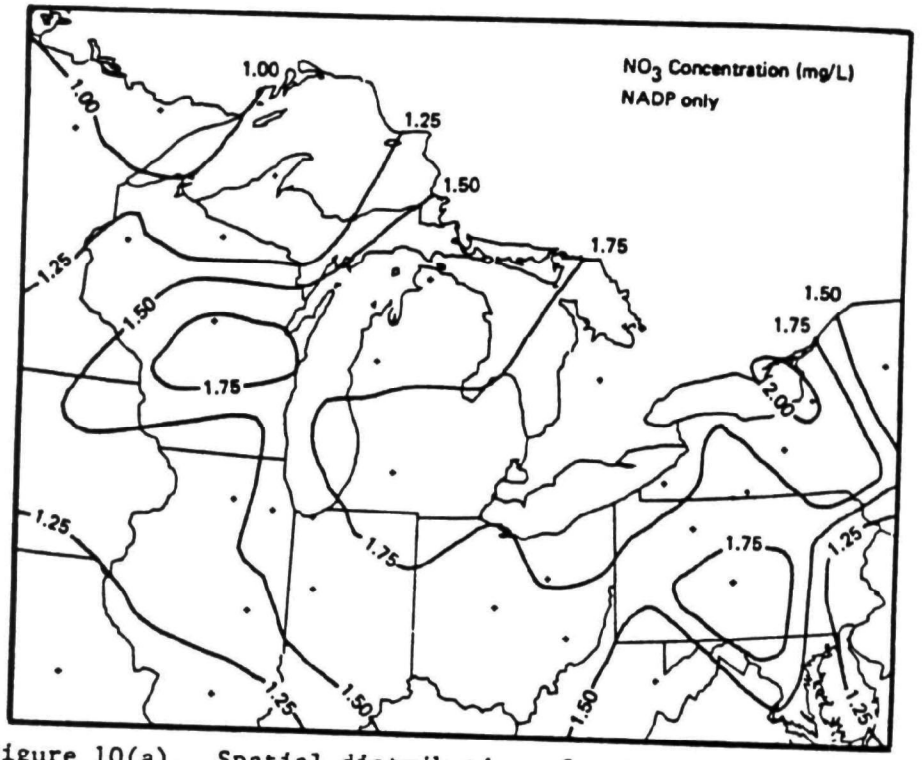


Figure 10(a). Spatial distribution of volume-weighted NO_3 concentrations in the Great Lakes region, using NADP data for 1982-83.

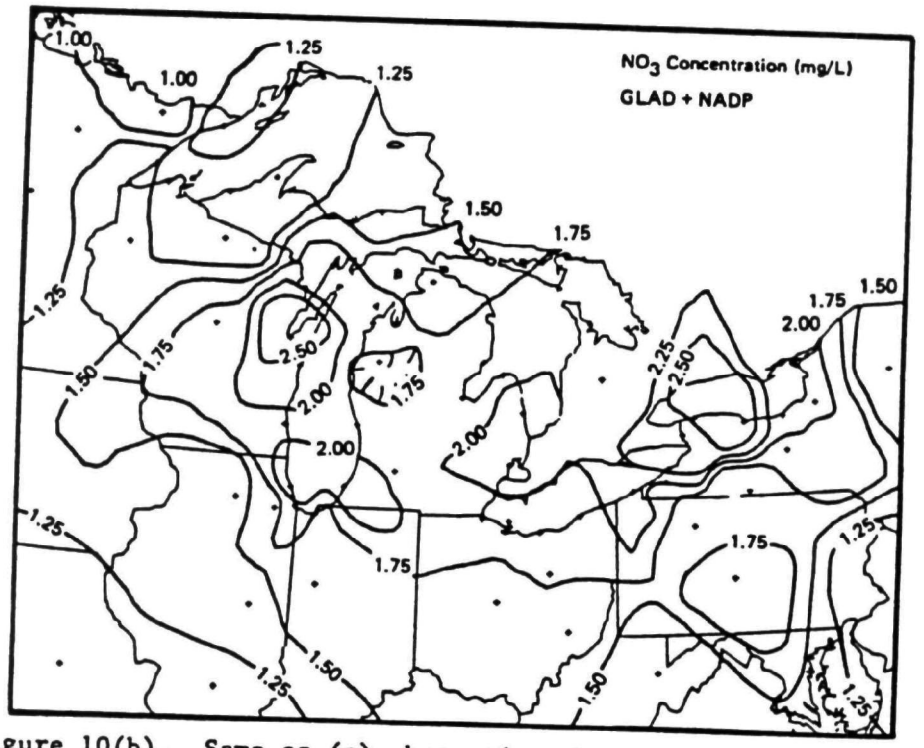
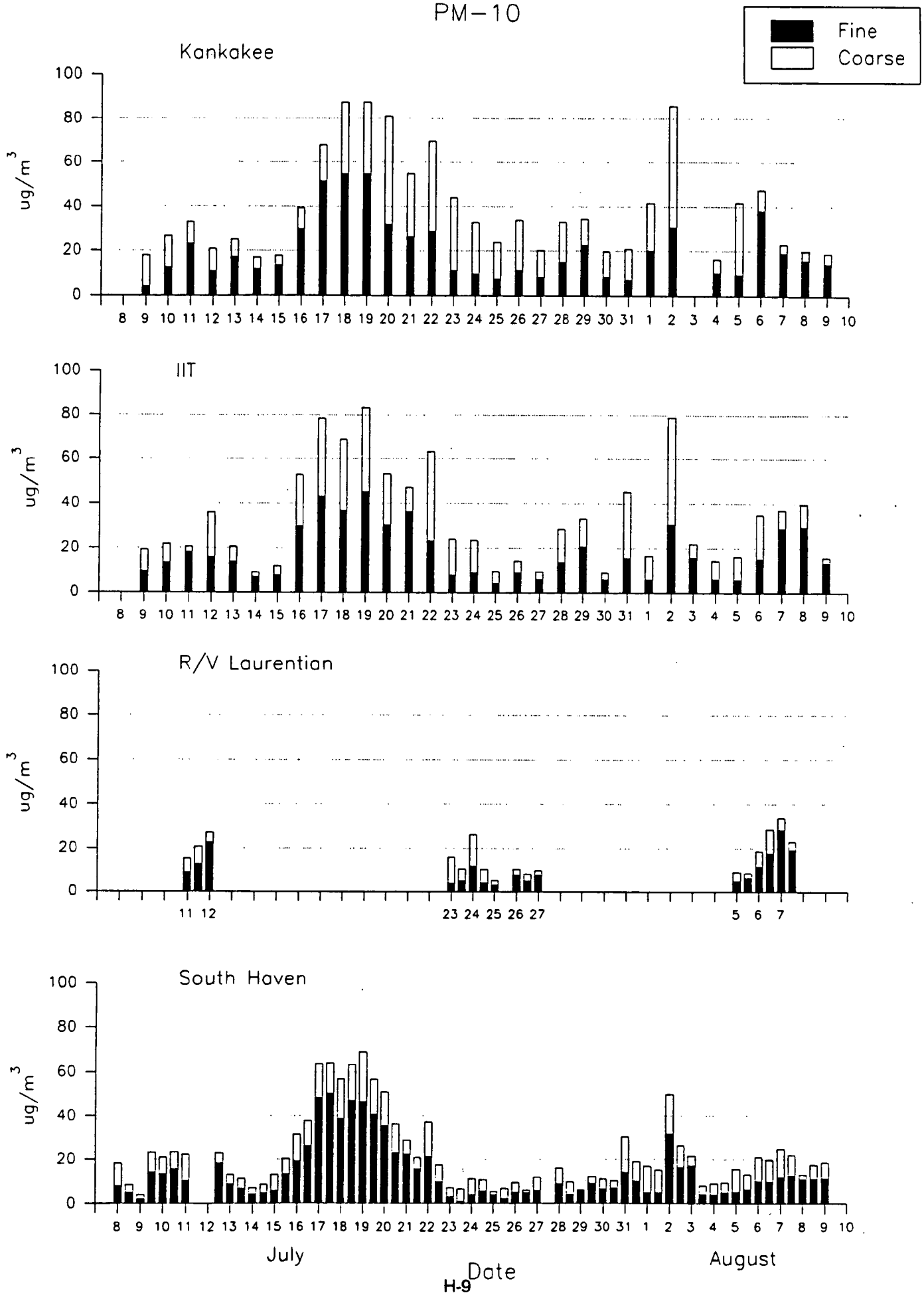


Figure 10(b). Same as (a), but using the combined GLAD/NADP data set.


PM−10
Fine
Coarse
Kankakee
IIT
R/V Laurentian
South Haven
ug/m3
0
20
40
60
80
100
8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 1 2 3 4 5 6 7 8 9 10
11 12
23 24 25 26 27
5 6 7
July
August
Date

GAS PHASE MERCURY RESULTS:

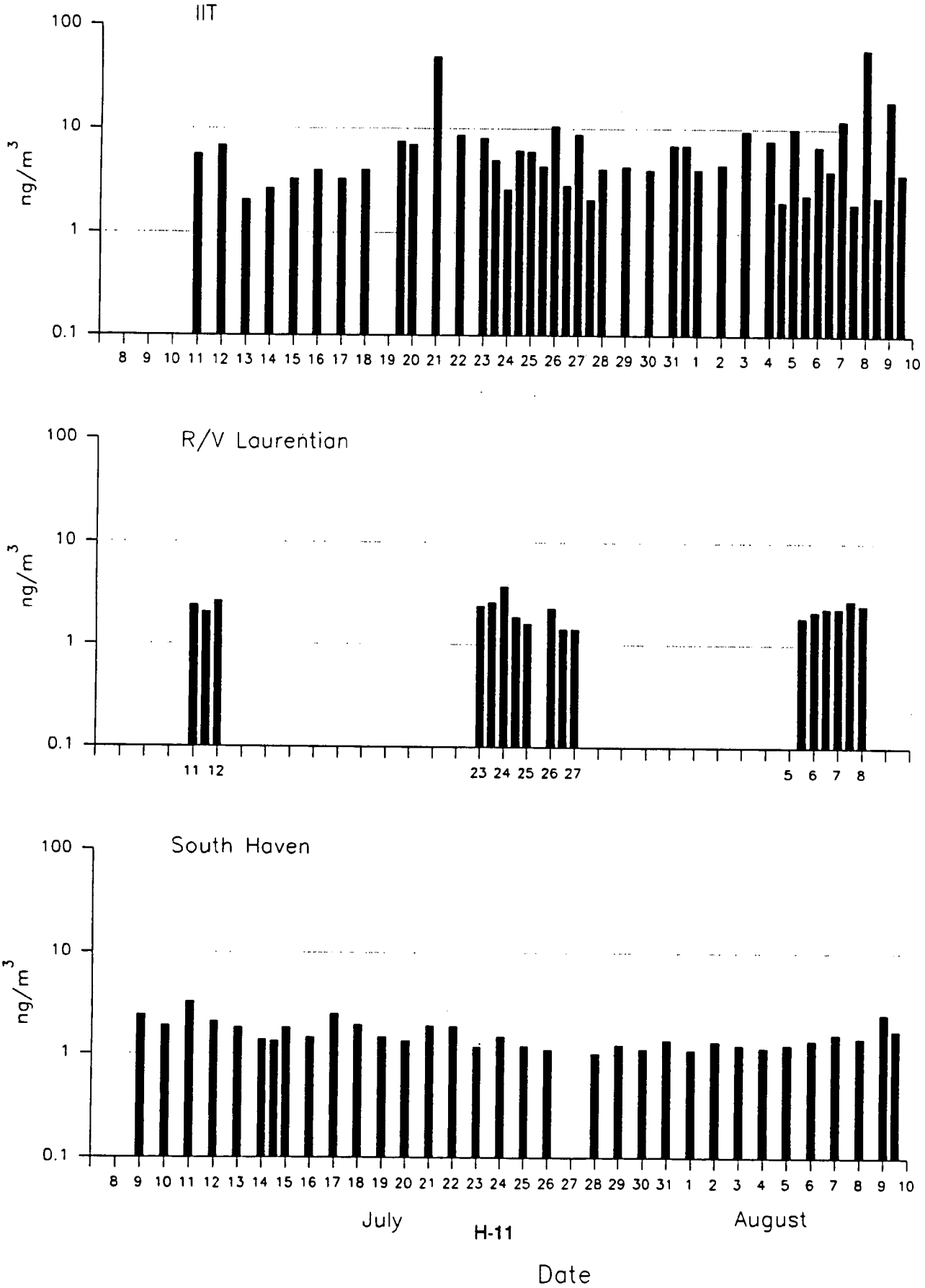
TOTAL VAPOR PHASE MERCURY COLLECTED ON GOLD-COATED SAND TRAPS

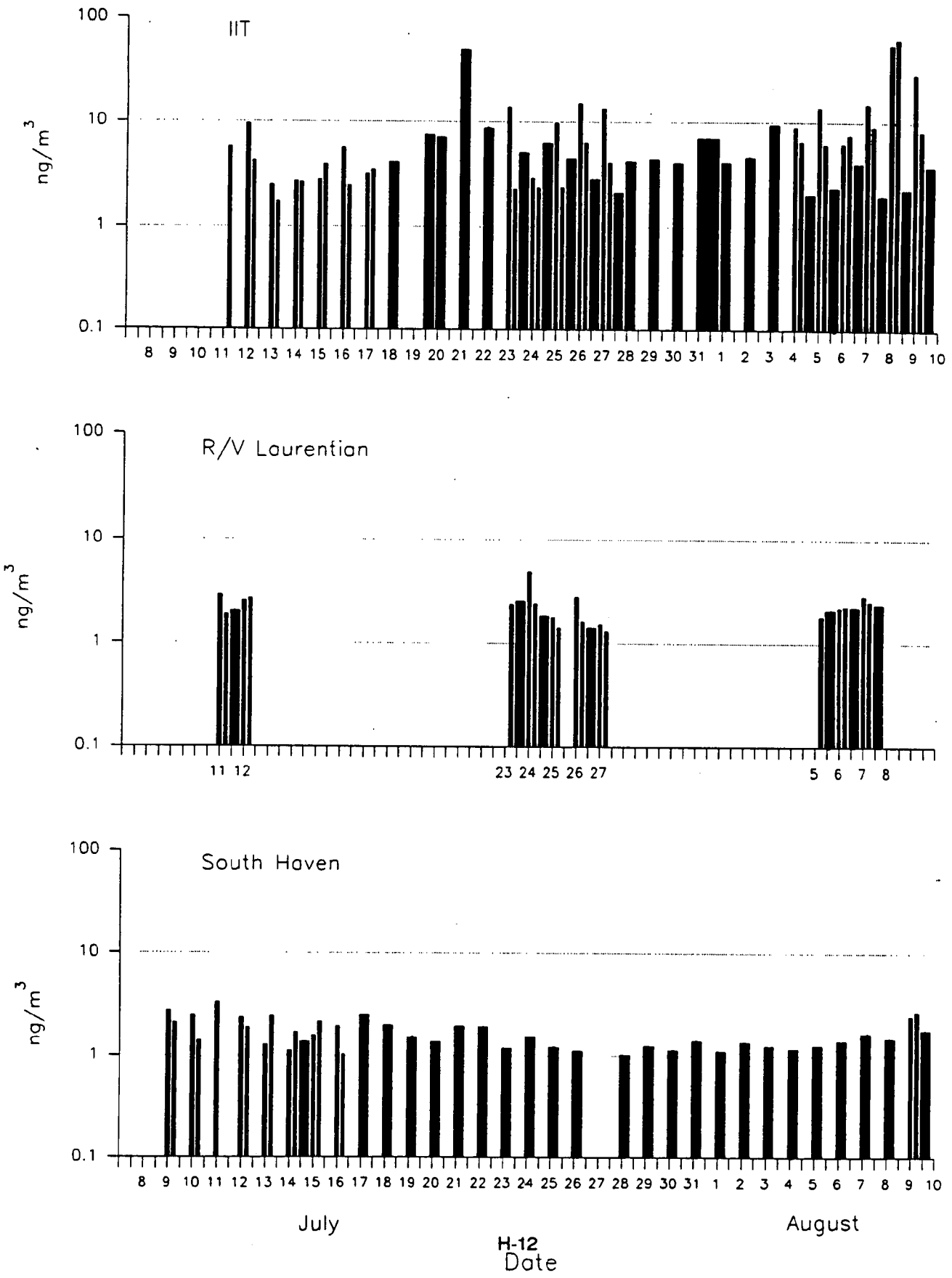
VALUES REPORTED IN UNITS OF NG MERCURY/M3

SITE	N	25%	50%	90%	MEAN	STD DEV	MAX
SHA	38	1.5	1.8	2.9	2.0	0.6	4.3
IIT	58	2.9	4.5	14.9	8.7	12.0	62.7
LAU*	25	1.8	2.2	2.9	2.3	0.7	4.9

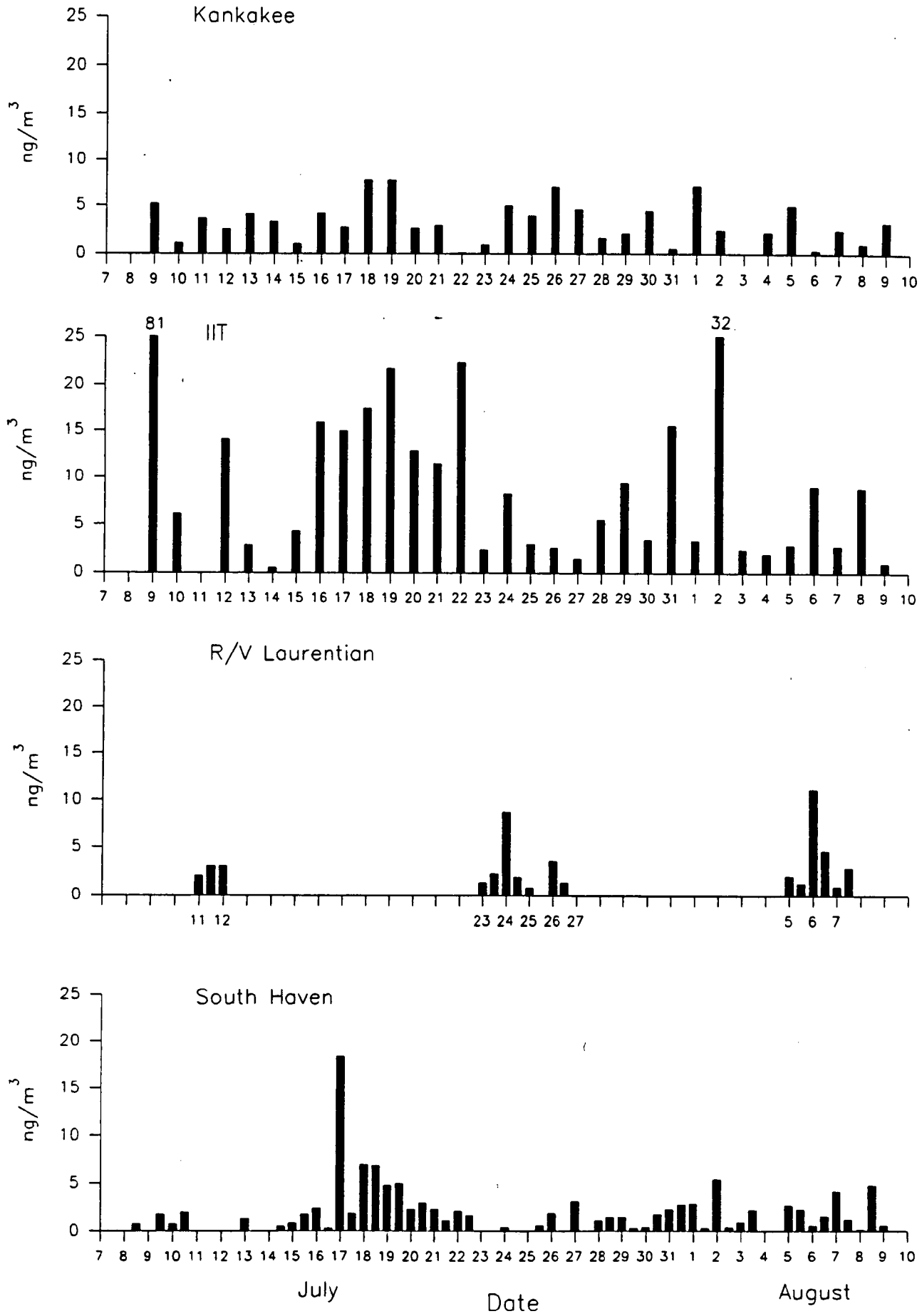
*DATES: 7/11-7/12, 7/25-7/27, 8/5-8/8

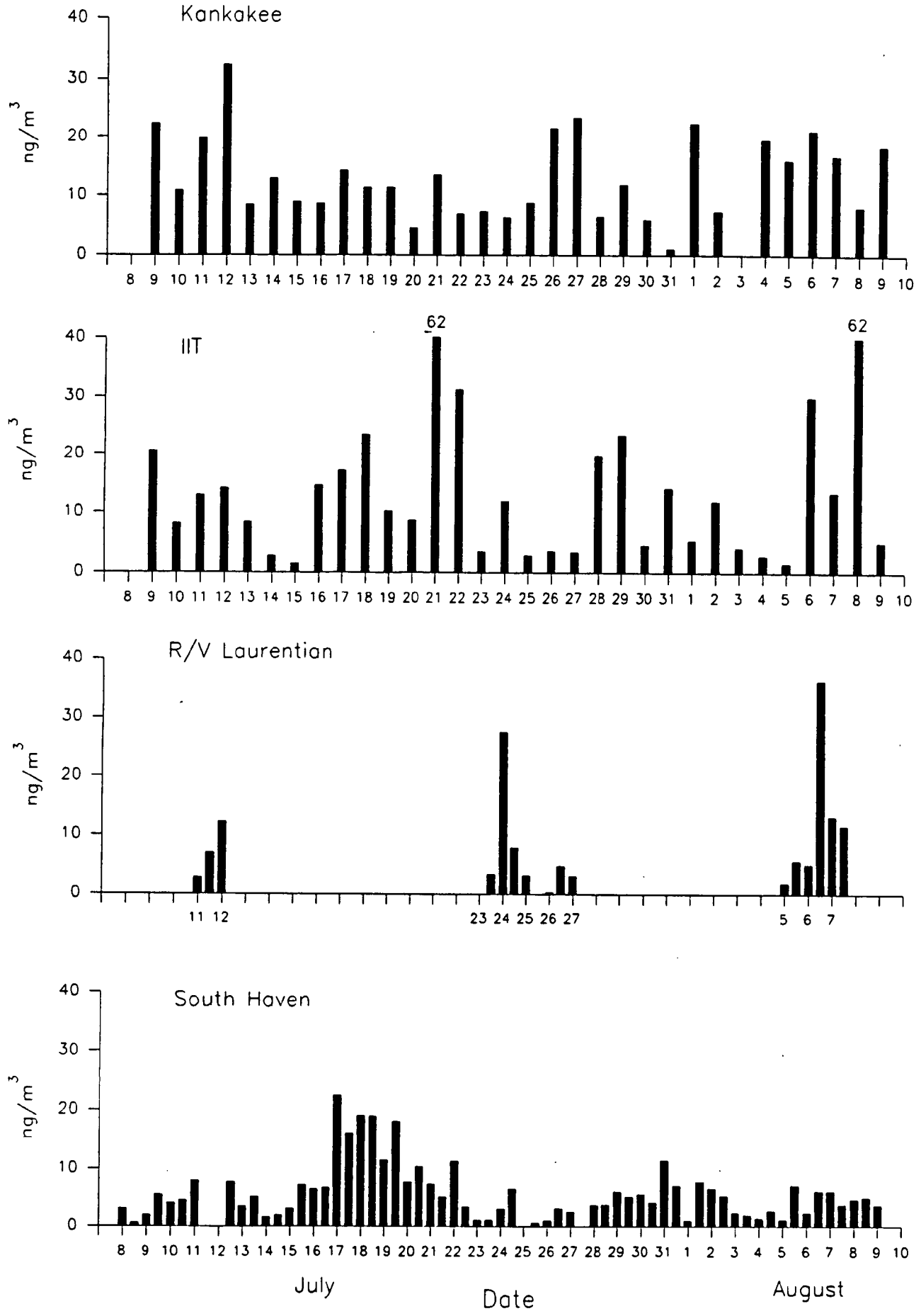
Vapor Phase Mercury
12 Hour Average




Vapor Phase Mercury
IIT
R/V Laurentian
South Haven
ng/m3
100
10
1
0.1
8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 1 2 3 4 5 6 7 8 9 10
11 12
23 24 25 26 27
5 6 7 8
July
August
Date

H-12


Kankakee
IIT
81
32
R/V Laurentian
South Haven
ng/m3
25
20
15
10
5
0
7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 1 2 3 4 5 6 7 8 9 10
11 12
23 24 25 26 27
5 6 7
July
Date
August


Kankakee
IIT
62
62
R/V Laurentian
South Haven
ng/m3
40
30
20
10
0
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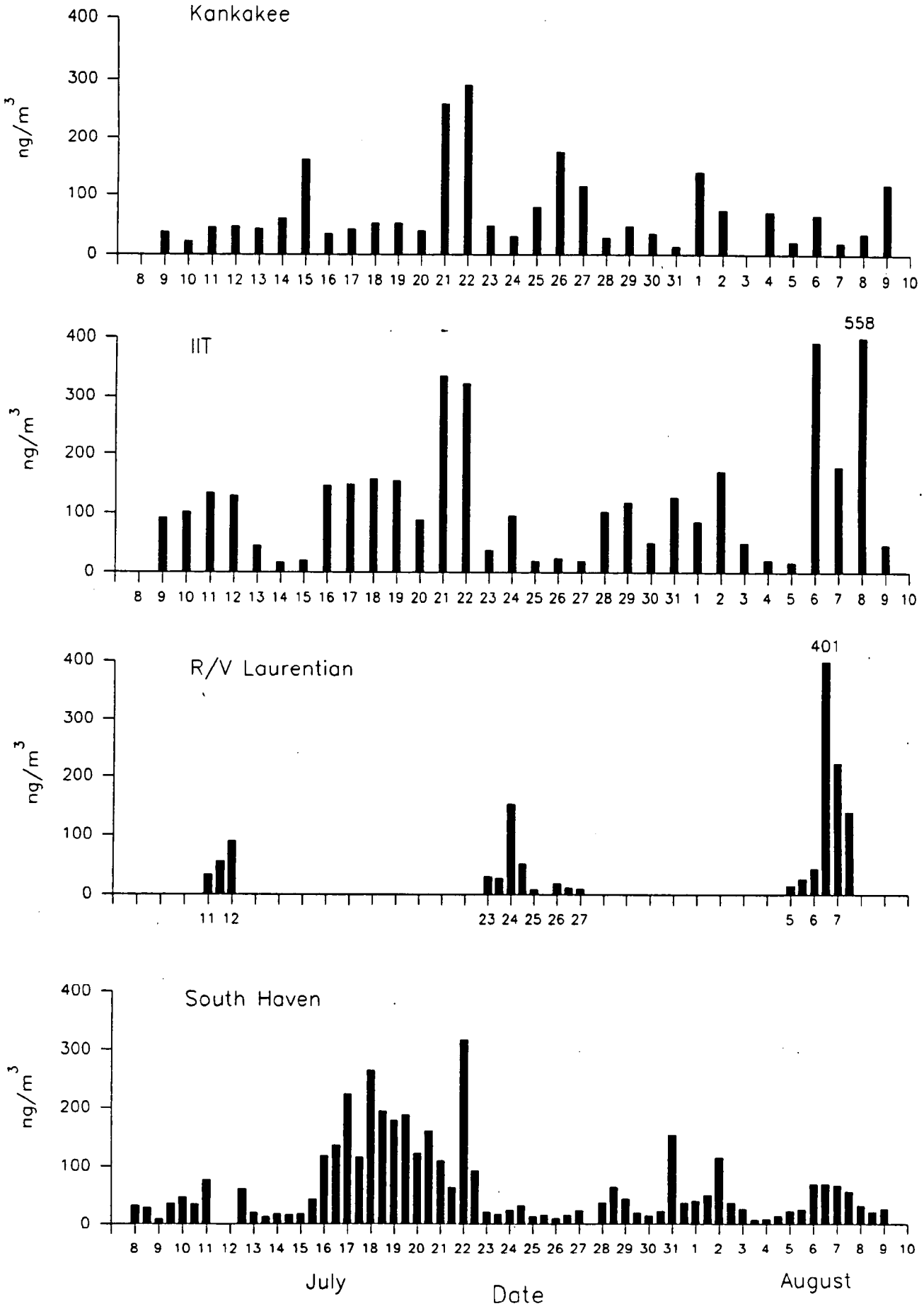
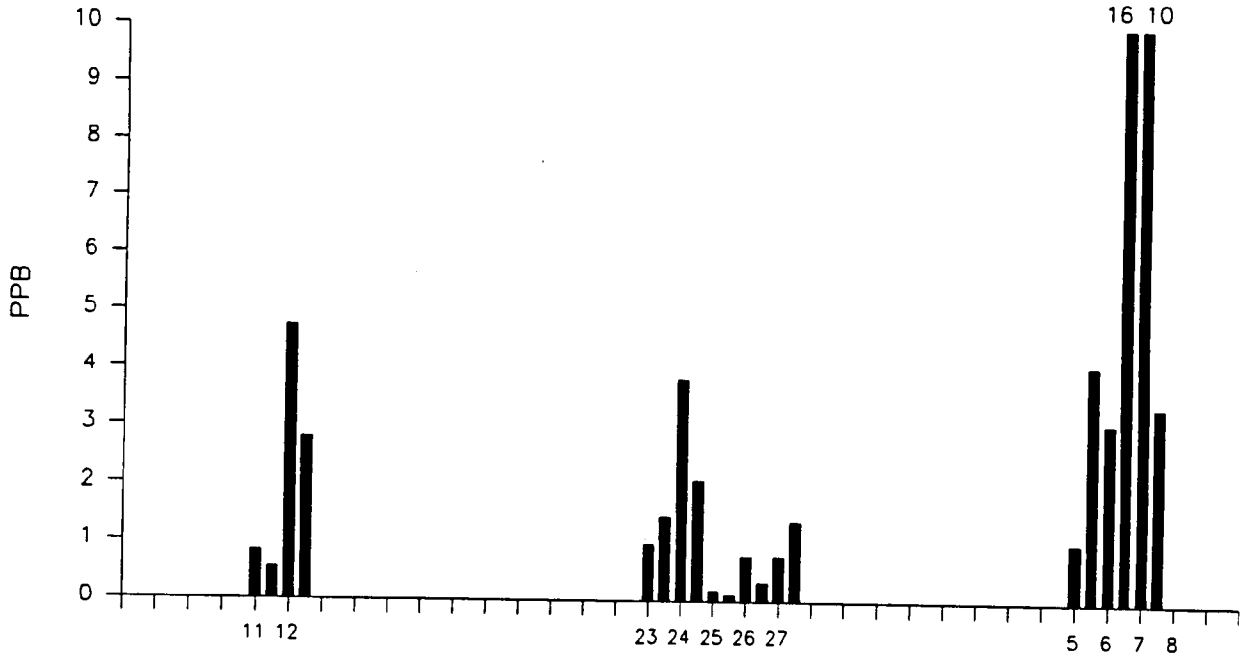
11 12
23 24 25 26 27
5 6 7
July
Date
August

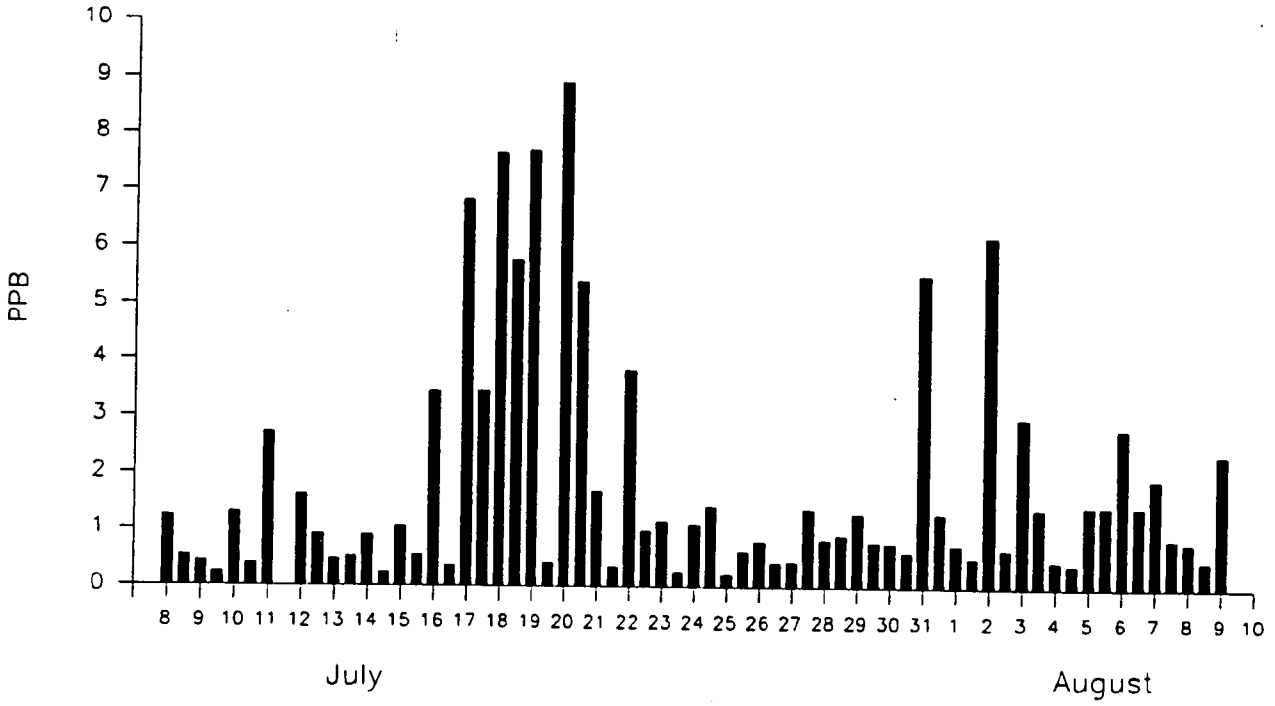

Kankakee
IIT
558
R/V Laurentian
401
South Haven
ng/m3
400
300
200
100
0
8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 1 2 3 4 5 6 7 8 9 10
11 12
23 24 25 26 27
5 6 7
July
August
Date

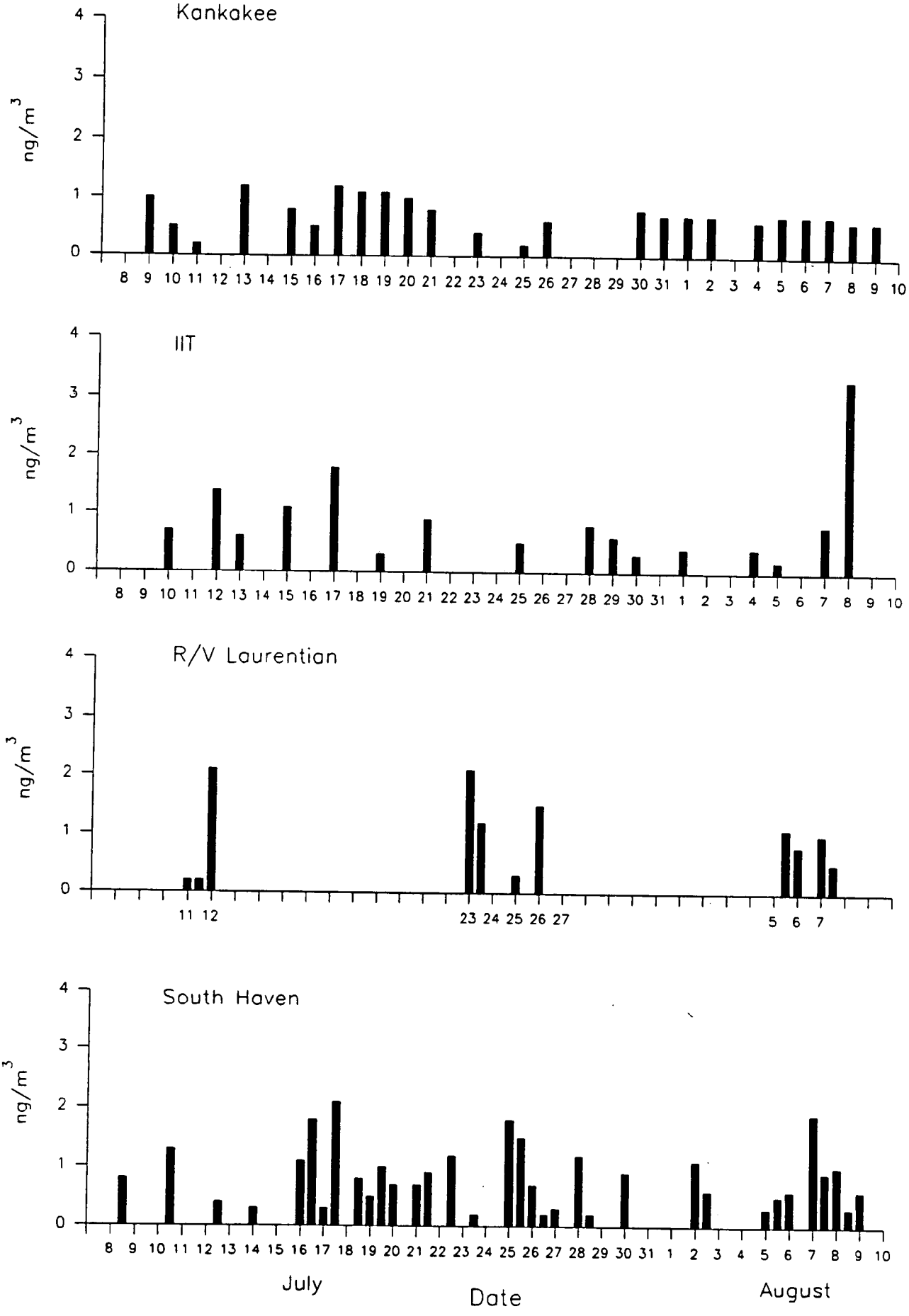
R/V Laurentian

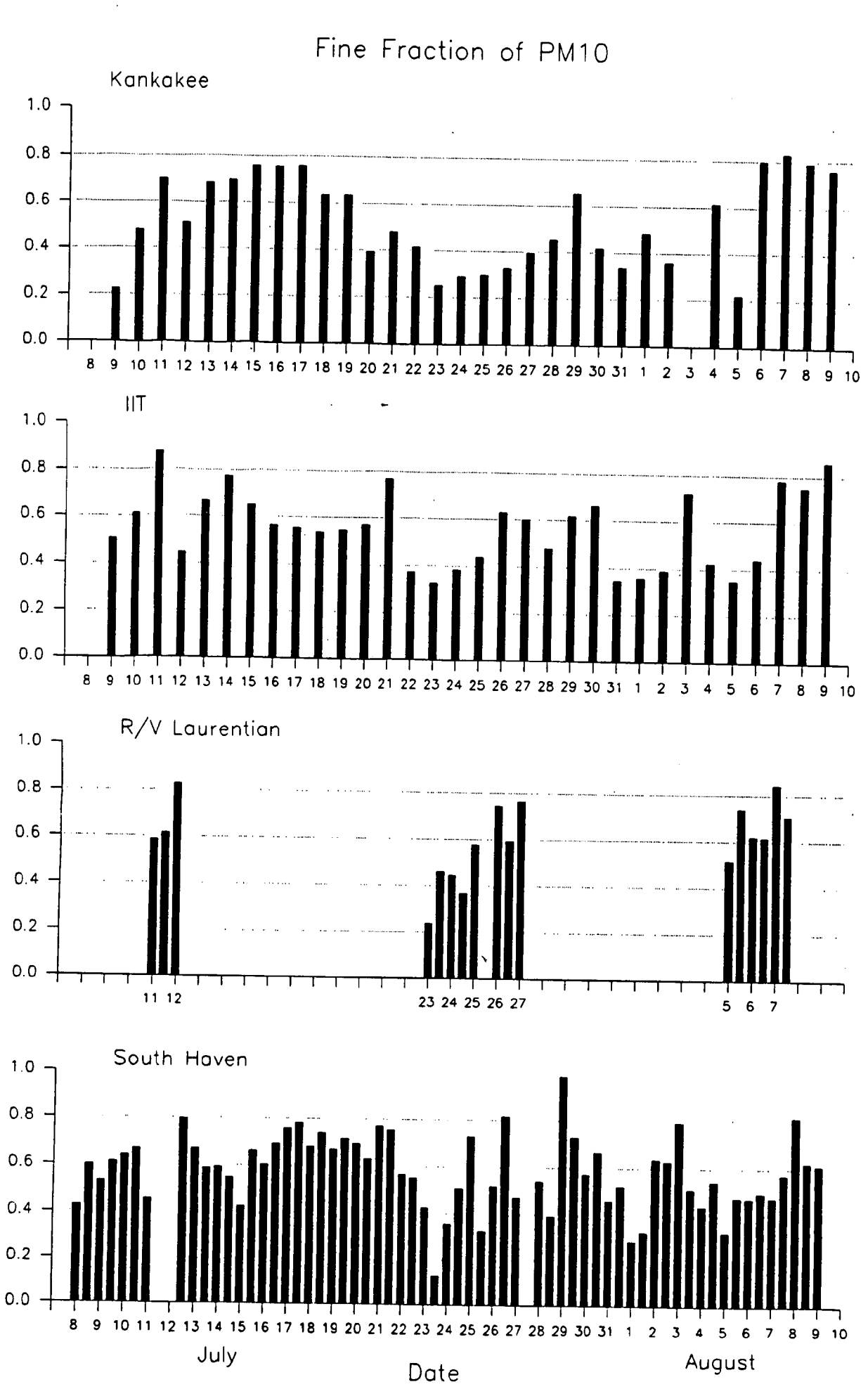
SO_2



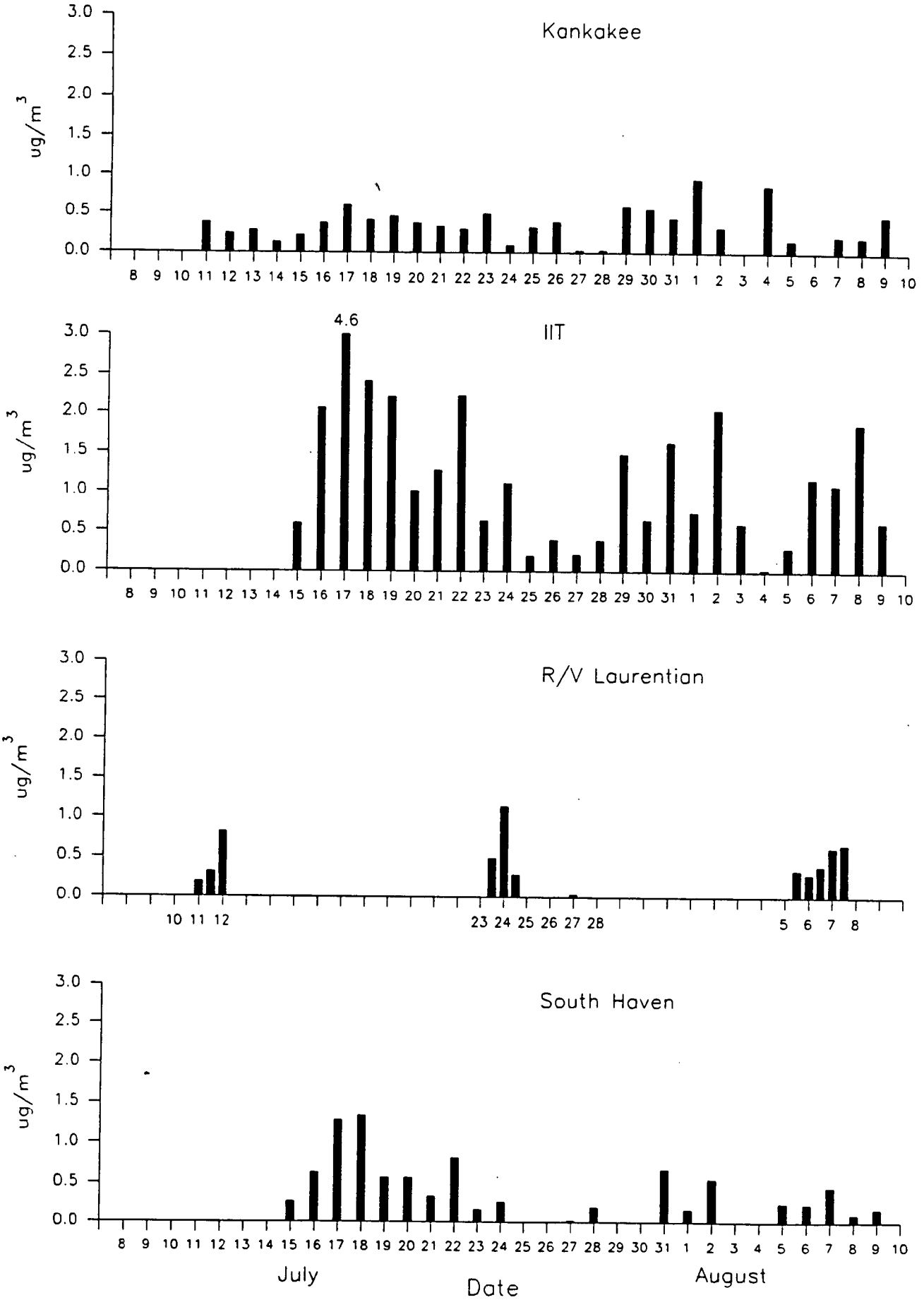
South Haven



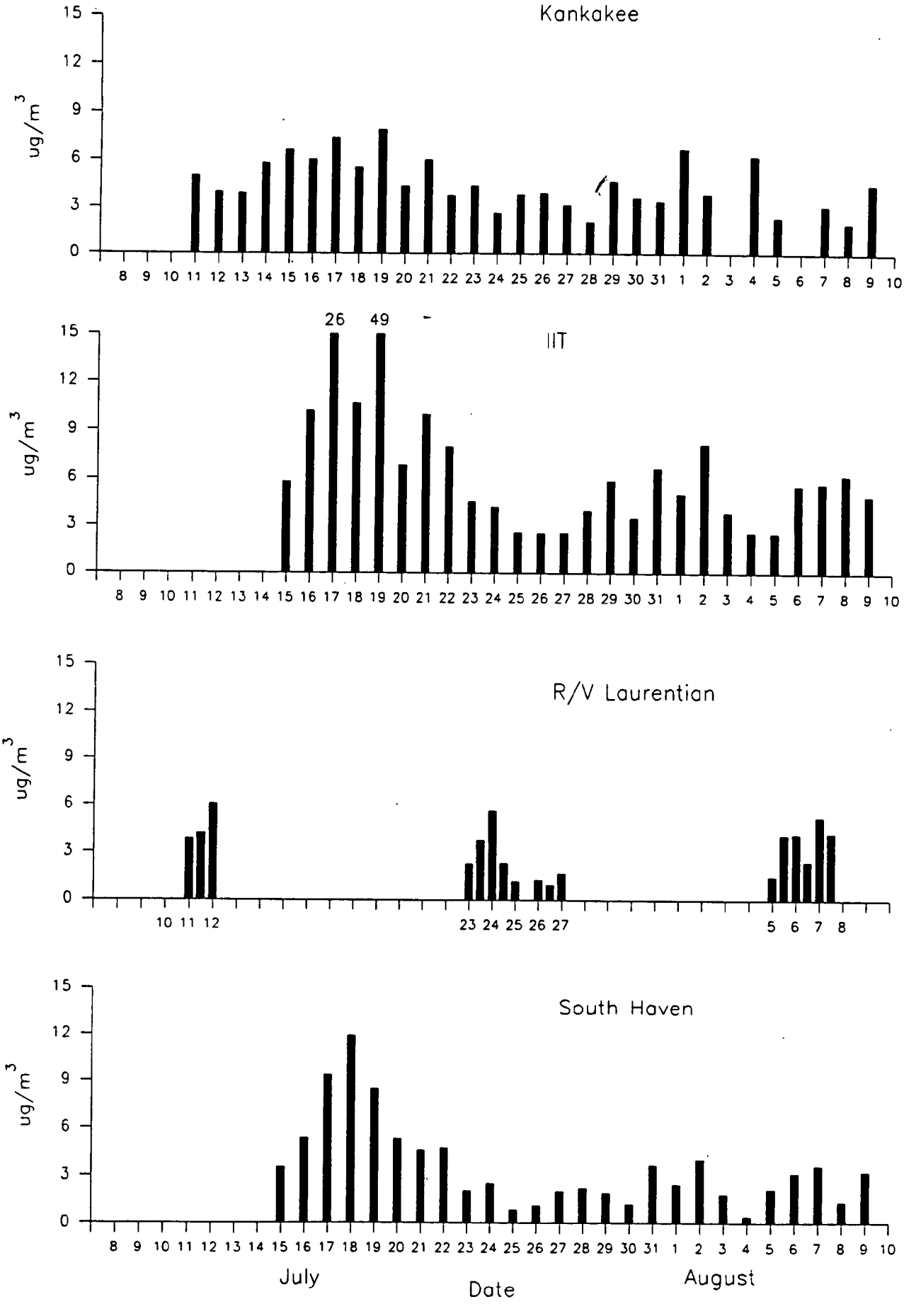

Kankakee
IIT
R/V Laurentian
South Haven
ng/m3
0
1
2
3
4
8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 1 2 3 4 5 6 7 8 9 10
11 12
23 24 25 26 27
5 6 7
July
August
Date


Fine Fraction of PM10
Kankakee
1.0
0.8
0.6
0.4
0.2
0.0
8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 1 2 3 4 5 6 7 8 9 10
IIT
1.0
0.8
0.6
0.4
0.2
0.0
8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 1 2 3 4 5 6 7 8 9 10
R/V Laurentian
1.0
0.8
0.6
0.4
0.2
0.0
11 12
23 24 25 26 27
5 6 7
South Haven
1.0
0.8
0.6
0.4
0.2
0.0
8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 1 2 3 4 5 6 7 8 9 10
July
Date
August

Elemental Carbon

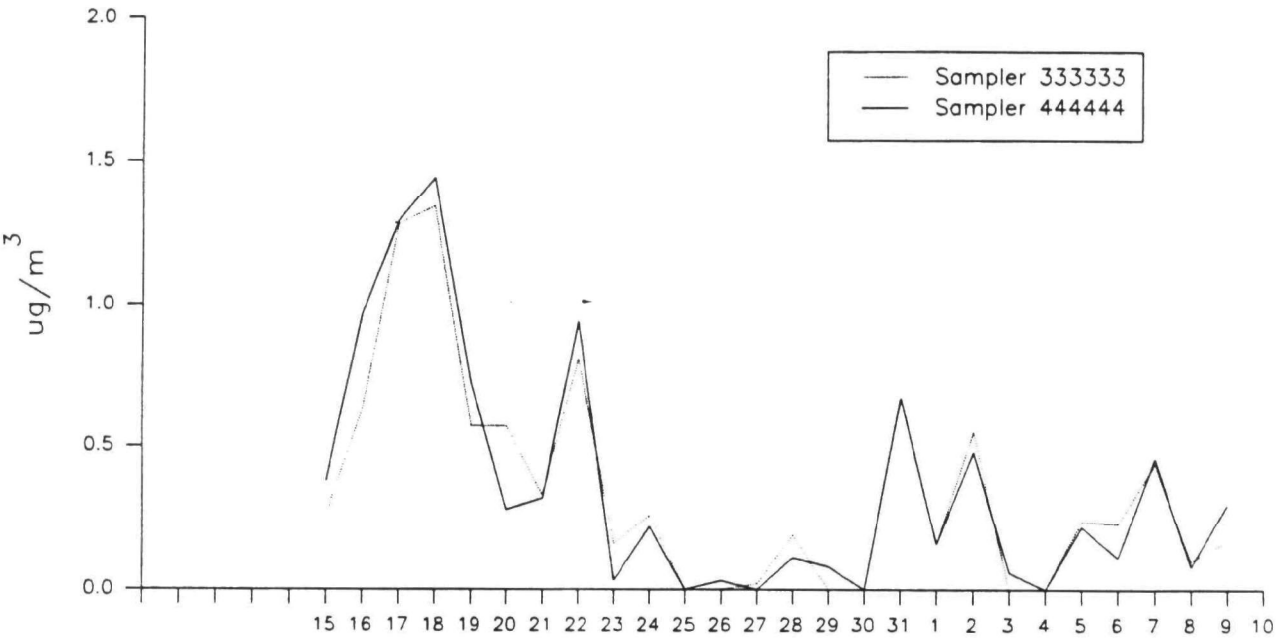


Organic Carbon

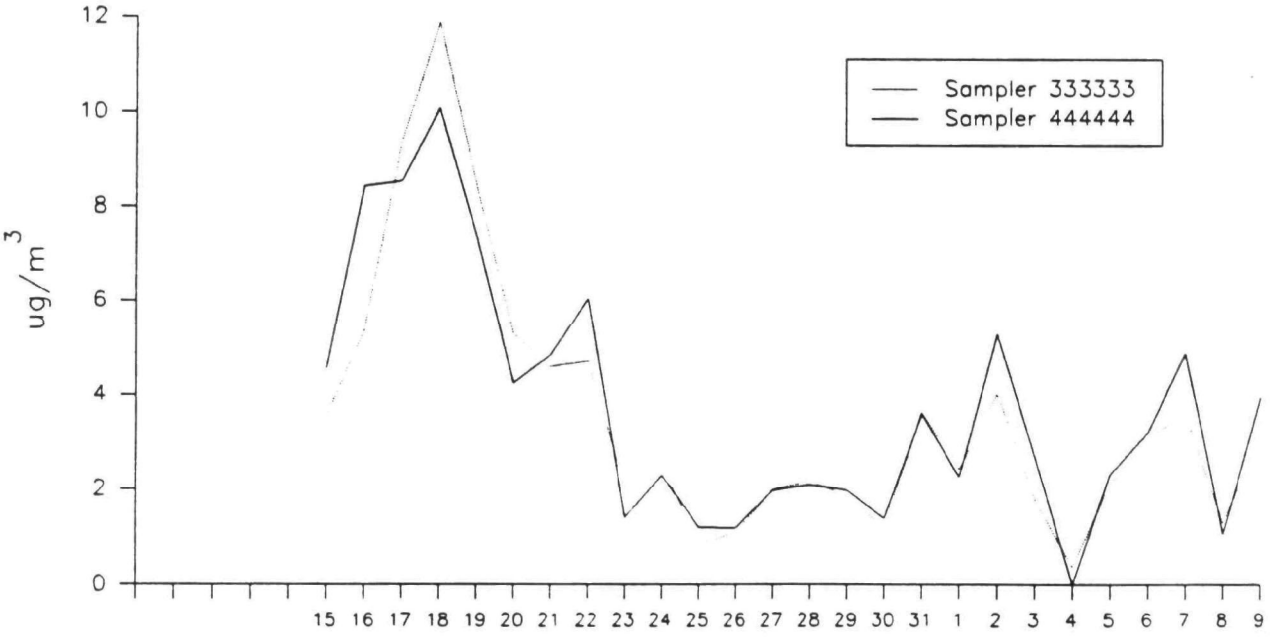


Comparison of two samplers at South Haven

Elemental Carbon



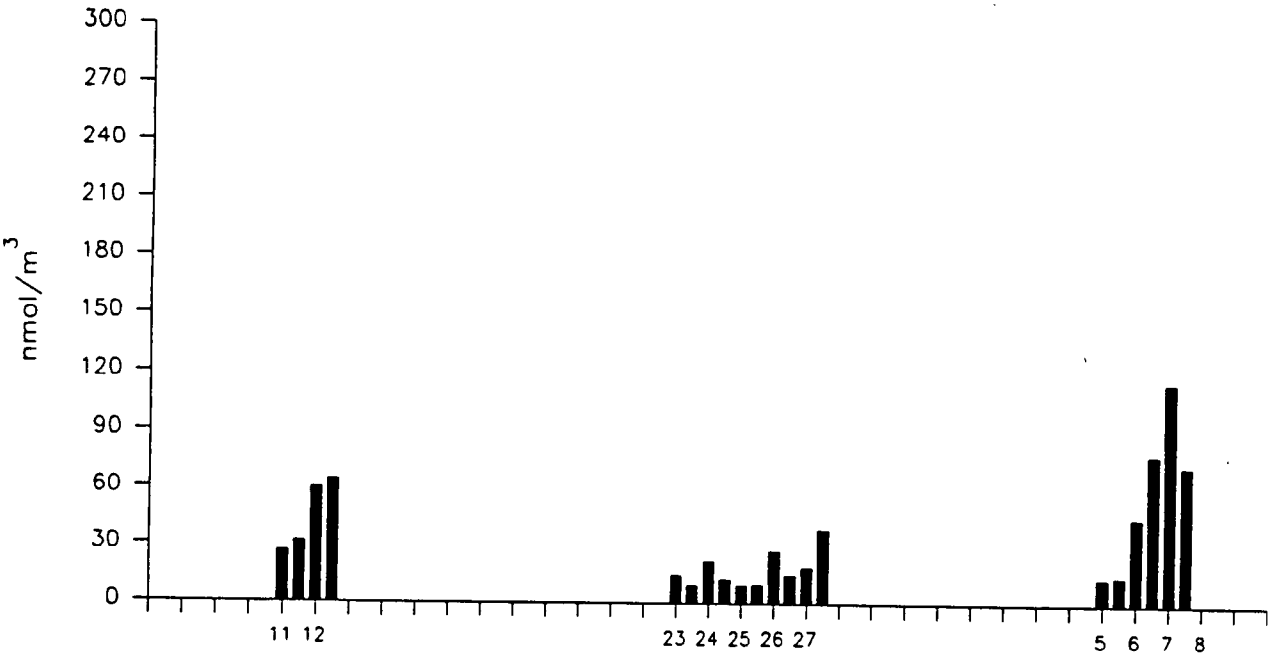
Organic Carbon



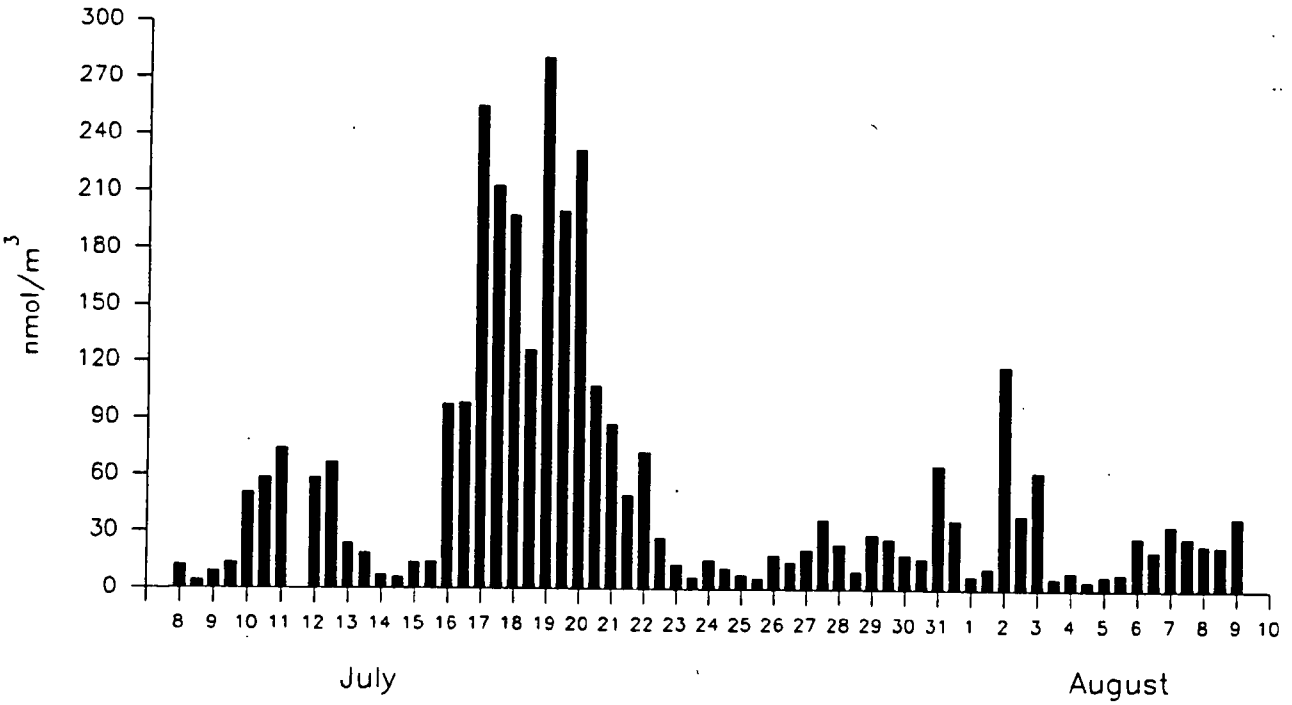
H-21 Date

R/V Laurentian

SO_4^-

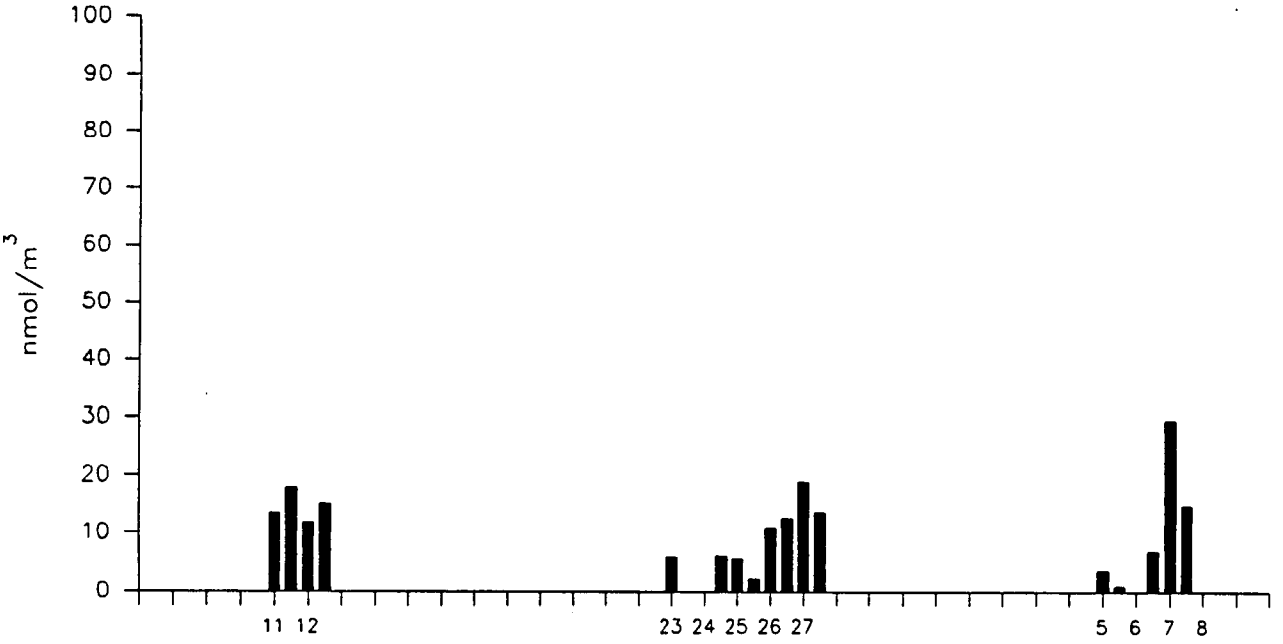


South Haven

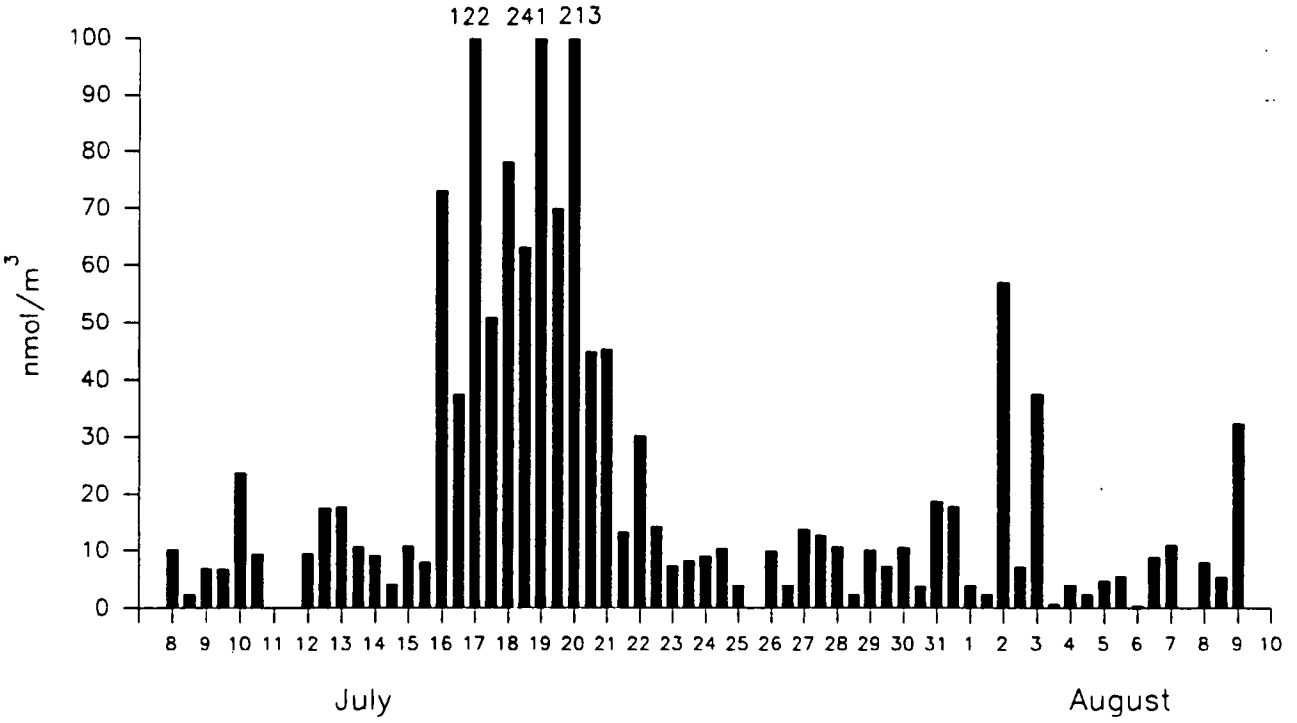


H^+

R/V Laurentian



South Haven



APPENDIX I

INTERFACE OF ATMOSPHERIC AND AQUATIC MODELS IN DESIGN OF MASS-BALANCE STUDIES

PRESENTATION

DR. WILLIAM BENJEY

TOXIC EMISSION INVENTORIES

FOR REGIONAL DISPERSION AND

DEPOSITION MODELING

CLEAN AIR ACT AMENDMENTS

TITLE III

- SECTION 112(c)
- SECTION 112(k)
- SECTION 112(m)

COMPOSITE TOXIC EMISSIONS
INVENTORY ASSEMBLY

COMPILATION OF EXISTING INVENTORIES,
DUPLICATE CHECKING AND QUALITY CONTROL

NAPAP——> NESHAP——> TRIS

SUPPLEMENTAL DATA
(I.E. CORRECTED OR TYPICAL STACK DATA)

APPLICATION OF EMISSION FACTORS
o UNINVENTORIED SOURCES
o UNSPECIATED TOXICS
o NATURAL BACKGROUND

==========

EXAMPLE
RFF PESTICIDE APPLICATIONS
DATA BASE

INTERIM TOXIC EMISSION INVENTORY

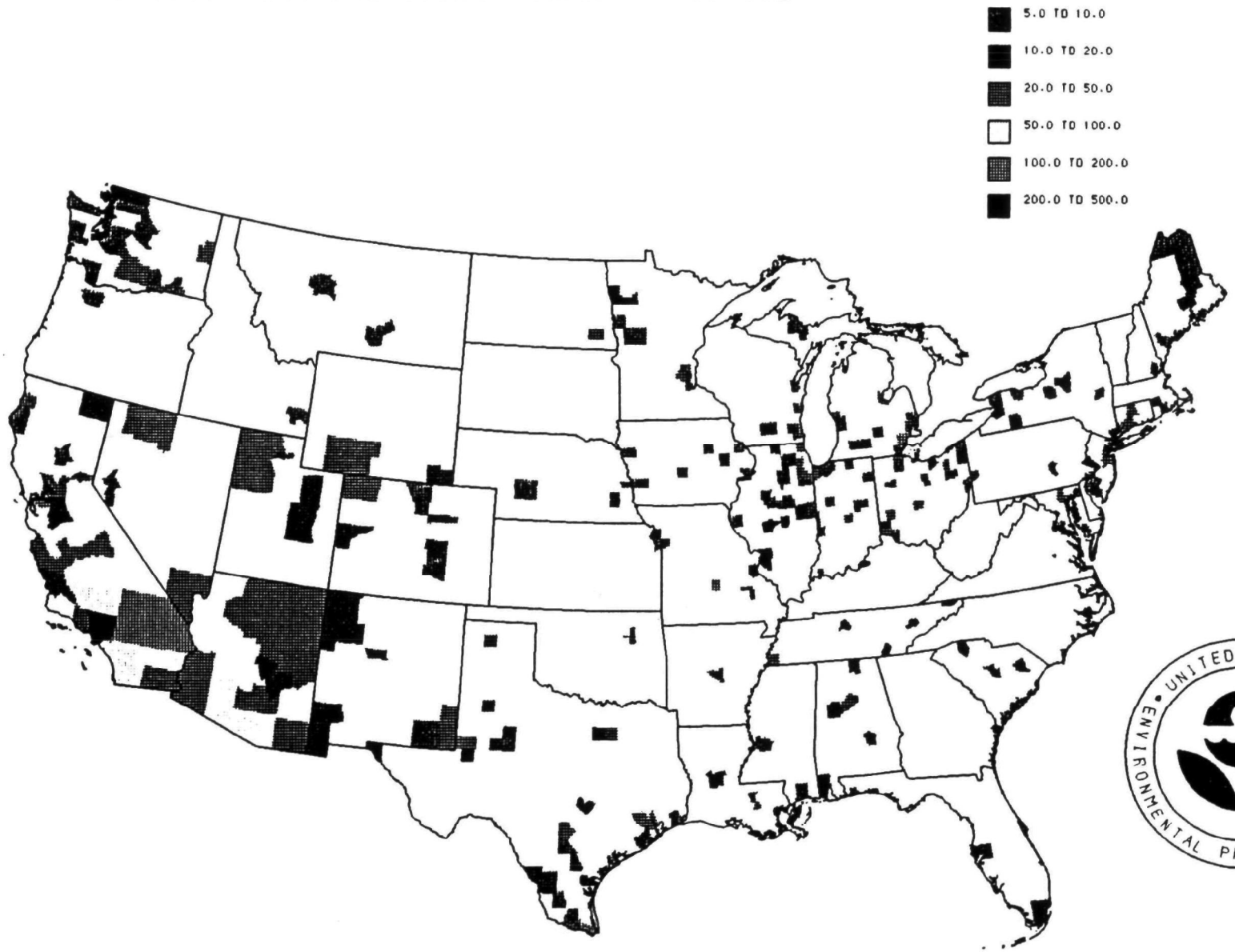
- o PURPOSE
  - INITIAL GENERAL ASSESSMENT
  - DISPERSION MODELING
- o CURRENT STATUS
  - QUALITY CONTROL OF INPUT DATA
  - MERGING OF EMISSIONS DATA
    - REGIONAL
    - STATE AND LOCAL
- o MODELING APPLICATION PROCEDURES
  - GRIDDING FOR GEOGRAPHIC DISTRIBUTION
  - ANALYSIS BY SOURCE TYPE (SCC)

INTERIM TOXIC EMISSION INVENTORY CONTENTS AS OF MARCH 1992

*MERCURY	*CADMIUM
*LEAD	STYRENE
ETHYLENE DIBROMIDE	METHYL CHLORIDE
CARBON TETRACHLOR.	SELENIUM
*1,3-BUTADIENE	*BENZENE
*CHROMIUM	TRICHLROETHYLENE
PERCHLOROETHYLENE	EPICHLOROHYDRIN
CHRYSENE	DINBUTYLPHTHALATE
ACRYLONITRILE	*CHLOROFORM
BERYLLIUM	VINYL CHLORIDE
PHENANTHRENE	FLUORANTHRENE
*BENZO(A)PYRENE	*NICKEL
1,2 DICHLOROETHANE	*ARSENIC
ETHYLENE OXIDE	ETHYL ACRYLATE
METHYLENE CHLORIDE	*FORMALDEHYDE

V2

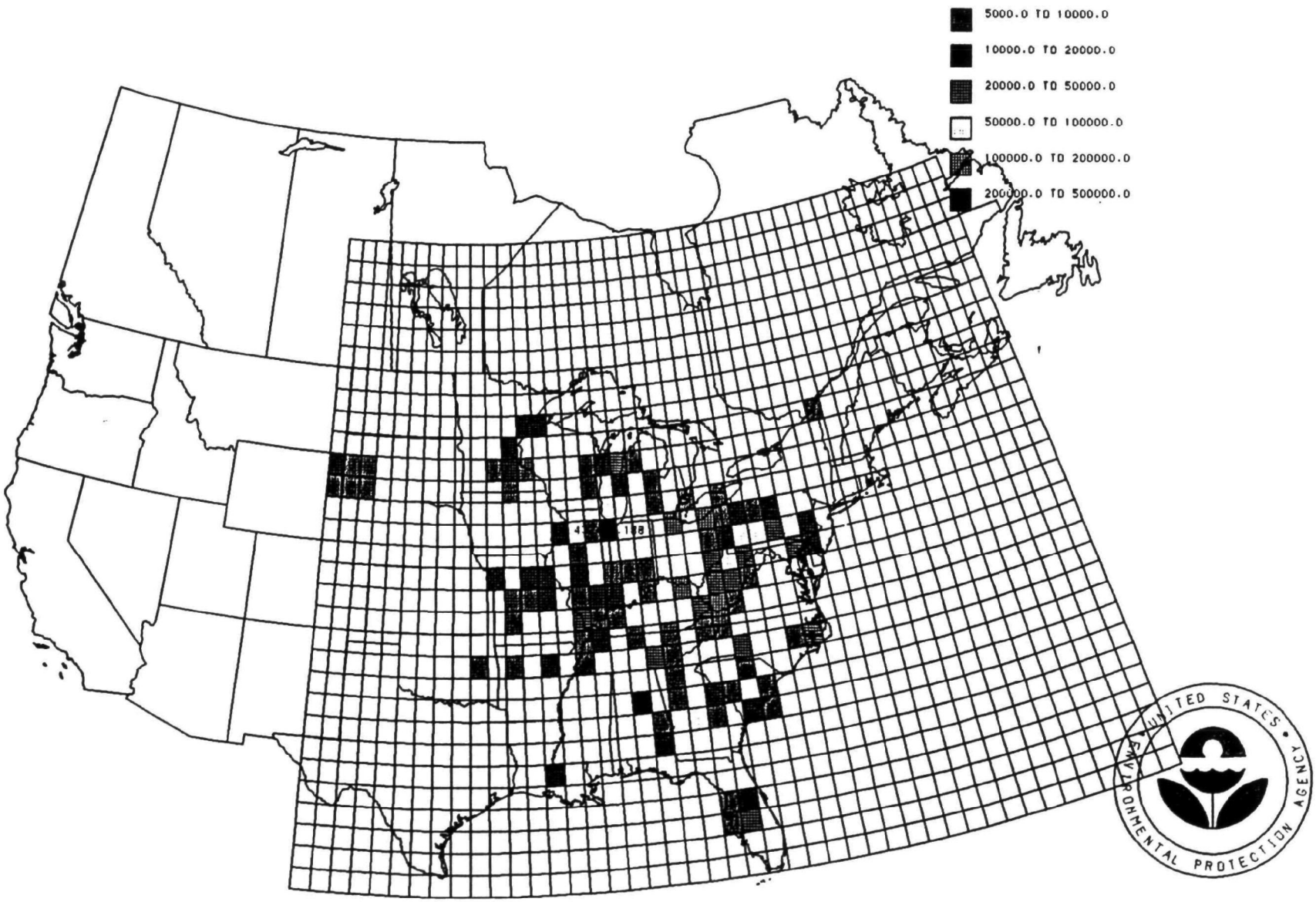
MERCURY EMISSIONS IN TONS/YEAR
MAX IS 428.99 TONS/YEAR AND MEAN IS 4.30 TONS/YEAR
WITHOUT 305 SCC CODES. JANUARY 10,1992



AREAL RTP, N.C.

I-7

RELMAP MERCURY EMISSIONS IN TONS/YEAR
WITH THE 305 SCC CODES. JANUARY 23,1993



AREAL RTP, N.C.

8-1

VINYL CHLORIDE TOTALS FOR REGION V STATES

	POINT	AREA	TOTAL
OHIO	513.926	956.249	1470.175
INDIANA	499.355	612.507	1111.861
MICHIGAN	143.555	665.165	808.720
ILLINOIS	25589.973	1130.704	26720.676
WISCONSIN	87.224	328.185	415.409
MINNESOTA	100.976	398.575	499.551

MERCURY TOTALS FOR REGION V STATES

	POINT	AREA	TOTAL
OHIO	17.598	496.798	514.396
INDIANA	16.301	246.854	263.155
MICHIGAN	12.512	413.592	426.104
ILLINOIS	31.149	434.602	465.751
WISCONSIN	13.406	243.692	257.098
MINNESOTA	14.811	203.966	218.777

EMISSIONS OF MERCURY IN REGION V BY PROCESS

NO 305 SCC CODES

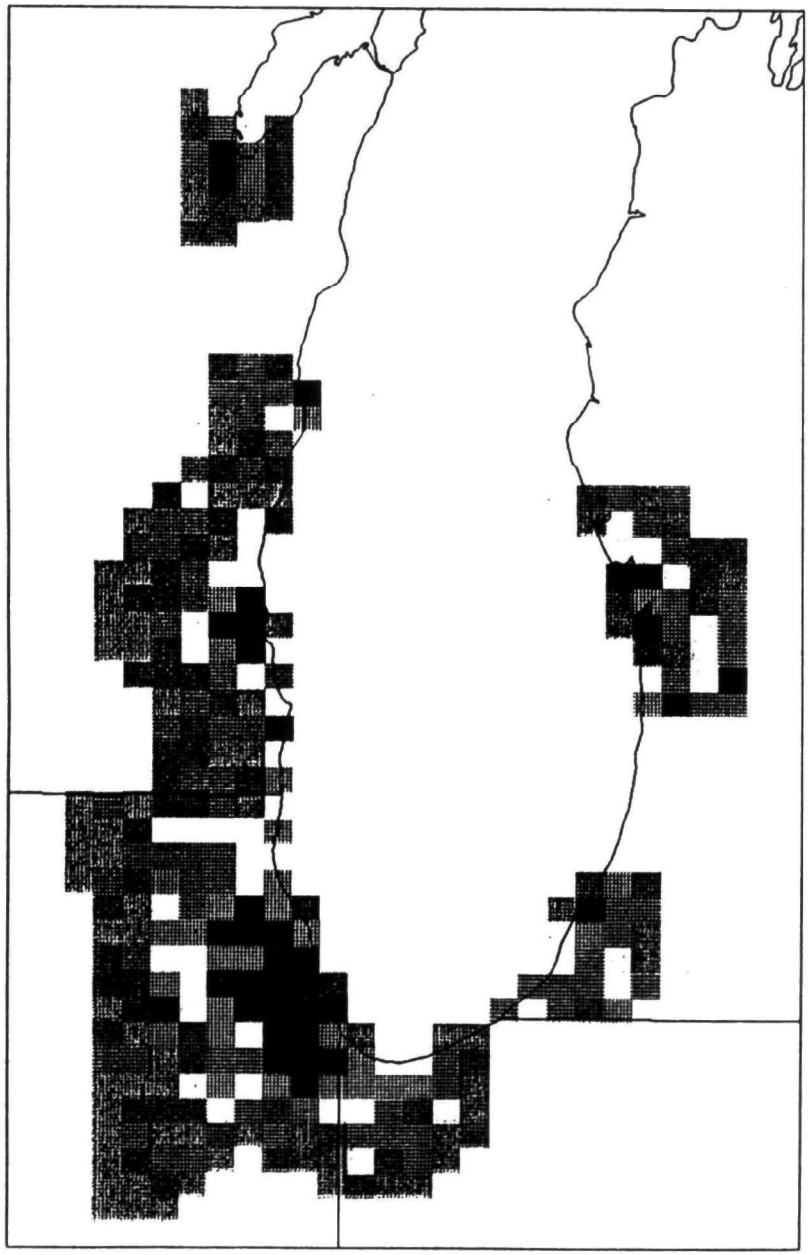
SCC	EMISSIONS
21	1691.907
23	218.462
902	95.162
5010	25.747
22	20.151
1010	15.794
5020	15.537
3020	15.301
3030	8.734
1020	8.193
5030	6.917
30	4.768
3040	4.222
27	3.608
28	1.990
3010	1.580
46	1.528
3900	1.385
99	0.880
3038	0.670
3060	0.548
3090	0.326
48	0.283
35	0.243
38	0.201
47	0.183
3070	0.174
3999	0.164
3080	0.161
36	0.138
1030	0.091
3140	0.059
3039	0.046
3099	0.036
4058	0.027
4020	0.020
4010	0.012
3079	0.011
4909	0.010
4050	0.006
4030	0.004
3089	0.001
3098	0.001
3600	0.000

- RESIDENTIAL INCINERATION
- COMMERCIAL INCINERATION
- WIND EROSION & AGRICULTURE
- SOLID WASTE INCINERATION

Annual Emissions of Nickel

Gridded on Relmap Grid

Tons/year



Annual Emissions of P.O.M.

Gridded on Lake-Michigan Grid

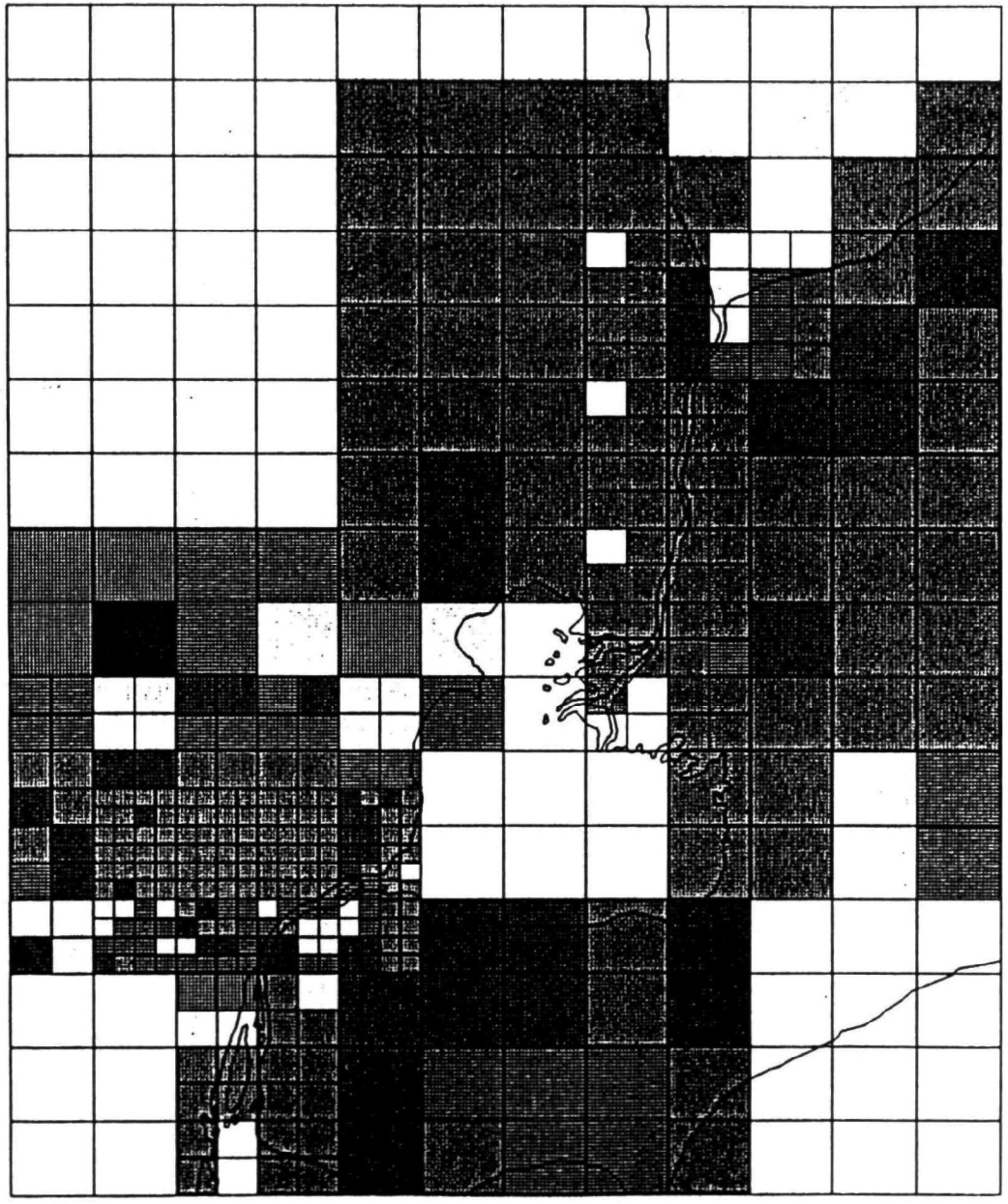
Tons/year

- 0 TO 0.1
- 0.1 TO 0.2
- 0.2 TO 0.5
- 0.5 TO 1.0
- 1.0 TO 2.0
- 2.0 TO 5.0

Max = 5.4 Sum = 223.8

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

AREAL RTP, N.C.



Annual Emissions of

Perchloroethylene

Gridded on Grid:

Local Detroit Grid

Tons/Year

Area Sources
Annual

- 0 TO 5
- 5 TO 10
- 10 TO 20
- 20 TO 50
- 50 TO 100
- 100 TO 200

Max = 147.8' Sum = 3028.6

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

AREAL RTP, N.C.

TOXIC EMISSIONS INFORMATION NEEDS FOR MODELING

IDENTIFICATION OF UNKNOWN TOXICS SOURCES

NEW (AND REVISED) EMISSIONS FACTORS

NEW AND REVISED SPECIATION PROFILES

ACTIVITY INDICATORS TO ESTIMATE EMISSIONS INVENTORIES

PROJECTION METHODOLOGIES

EPA/AREAL/wgb

TOXIC EMISSION INVENTORY NEEDS

ATMOSPHERIC CHEMISTRY

SPATIAL AND TEMPORAL VARIABILITY OF NATURAL TOXIC EMISSIONS

BACKGROUND CONCENTRATIONS OF ANTHROPOGENIC TOXIC EMISSIONS

IMPLICATIONS OF ATMOSPHERIC TRANSFORMATIONS ON TOXIC EMISSIONS INVENTORIES

APPENDIX J

INTERFACE OF ATMOSPHERIC AND AQUATIC MODELS IN DESIGN OF MASS-BALANCE STUDIES

PRESENTATION (CONTINUED)

MR. TERRY CLARK

Terry L. Clark
USEPA/ORD/AREAL
Lake Michigan Mass Balance Study
March 1992

UTILITY OF ATMOSPHERIC MODELS FOR MASS BALANCE CALCULATIONS

(1) Estimates of dry/wet deposition to 40-km cells

(2) Attribution of source categories and geographic areas

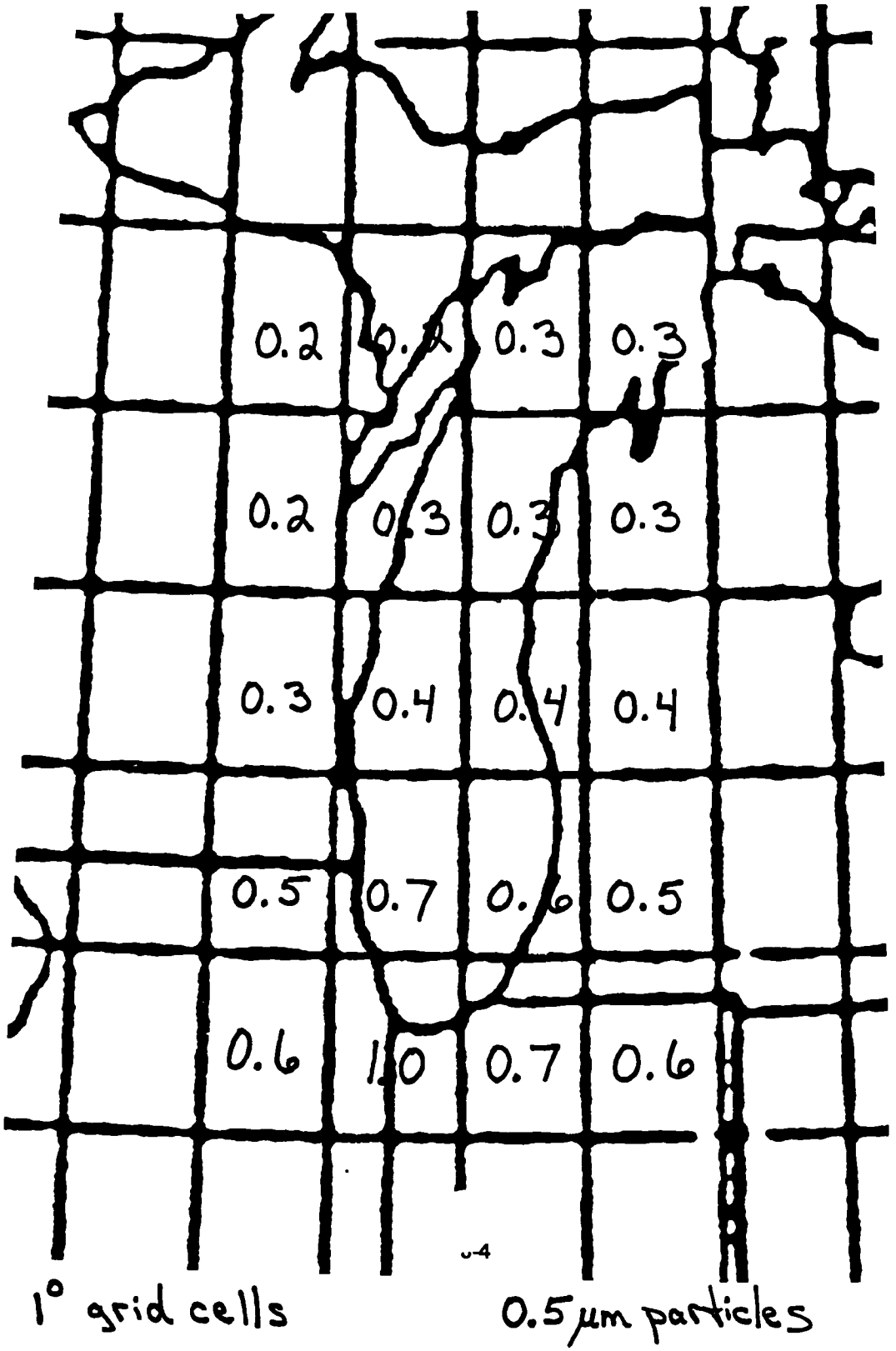
(3) Seasonal variability of dry/wet deposition

(4) Optimization of surface monitoring network

INPUT REQUIREMENTS FOR ATMOSPHERIC DEPOSITION MODELS

	MINIMUM	PREFERRED
Characterization of Air Flow Patterns	Routine hourly land-based and 12-h upper air meteor. data	Gridded wind fields produced by diag. meteor. model
Concurrent Air/Water Temperatures	Climatological water temperatures and land-based air temperatures near shorelines	Daily measurements at various distances from shorelines
Air Emission Rates	Assume no daily variability in annual emissions	Daily estimates of factors used to calculate emissions
Precipitation Amounts	Routine hourly amounts at land-based sites interpolated to lake	Minimum plus hourly radar images to assist in the interpolations

ANNUAL MEAN AIR CONCENTRATIONS OF LEAD RELATIVE TO MAXIMUM



ANNUAL DEPOSITION TO LAKE MICHIGAN
--- LEAD ---
(kg/year)

	Dry Deposition	Wet Deposition	Total
RELMAP (1992)			
0.5 micron	62,500 (9.1%)	627,300 (91.3%)	689,800
5.0 micron	254,200 (37.7%)	420,800 (62.3%)	675,000
Strachan & Eisenreich (1988)			
	120,000 (22.2%)	420,000 (77.8%)	540,000
	90,000 (16.7%)	450,000 (83.3%)	540,000

APPENDIX K

ESTIMATION OF DRY DEPOSITION FOR MASS-BALANCE STUDIES

PRESENTATION

DR. THOMAS HOLSEN

ESTIMATION OF DRY DEPOSITION FOR MASS BALANCE STUDIES

Thomas M. Holsen

Illinois Institute of Technology

Acknowledgments

Kenneth E. Noll

Guor-Cheng Fang, Jui-Min Lin, Wen-Jhy Lee, Shi-Ping Liu

Talk Overview

Objectives

Instruments

Comparison of Measured and Modeled Dry Deposition

Recent Metals and PCB Data

Implications for Mass Balance Studies

Talk Summary

1. Realistic estimates of dry deposition can be made with existing dry deposition models if complete airborne size distributions are known.

2. Results obtained from dry deposition measurements with smooth surrogate surfaces with sharp leading edges are comparable to modeled fluxes.

Sampling Techniques for Complete Size Distributions (WRAC)

Two sampler system

Cascade Impactor - particles < 10 μm

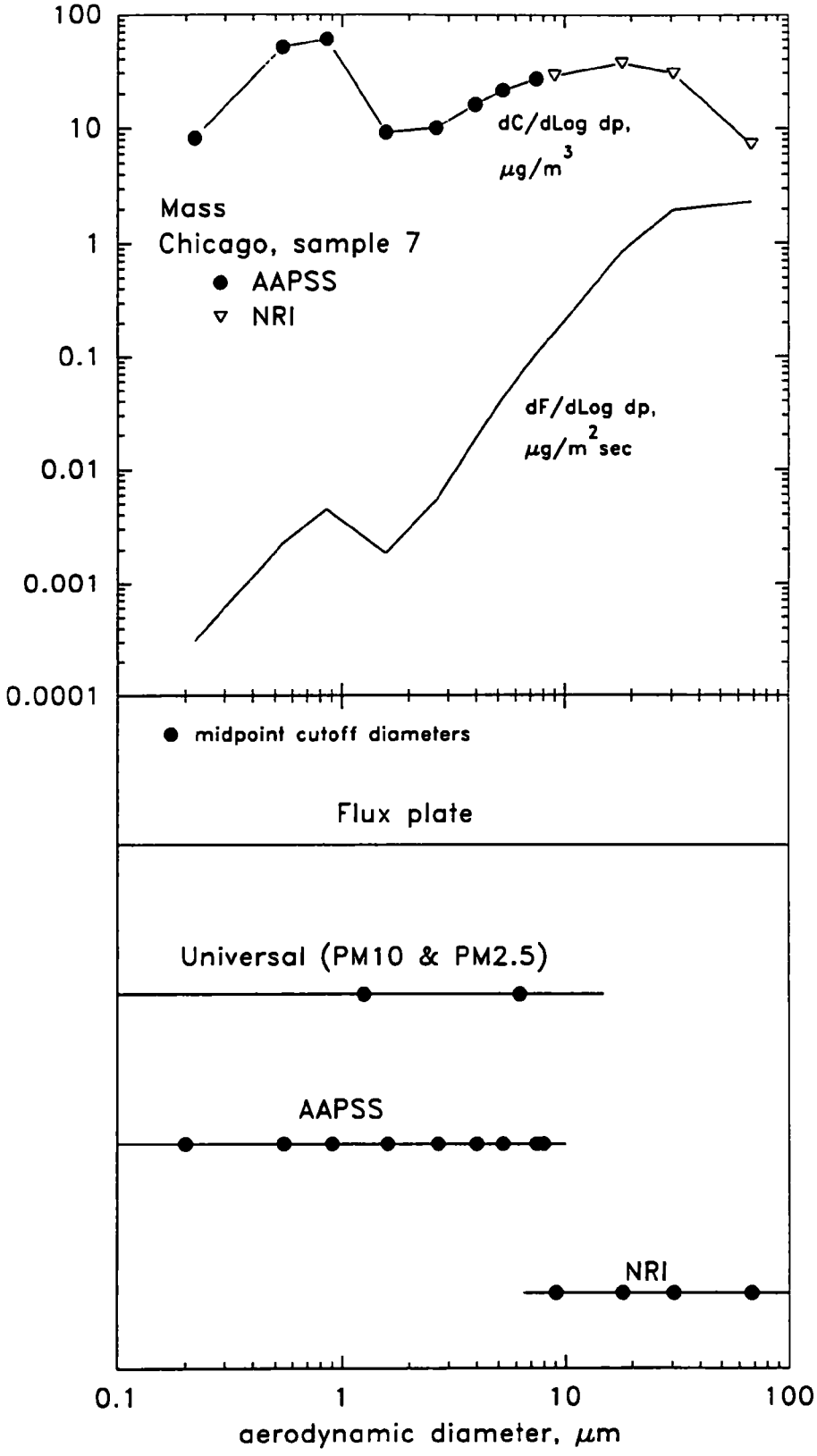
Noll Rotary Impactor (NRI) - coarse particles

- multi-stage rotary inertial impactor
- rectangular stages
- greased mylar strips weighed before and after sampling
- strips can be extracted and analyzed
- typical cut diameters of 6.5 μm, 11.5 μm, 24.7 μm and 36.5 μm

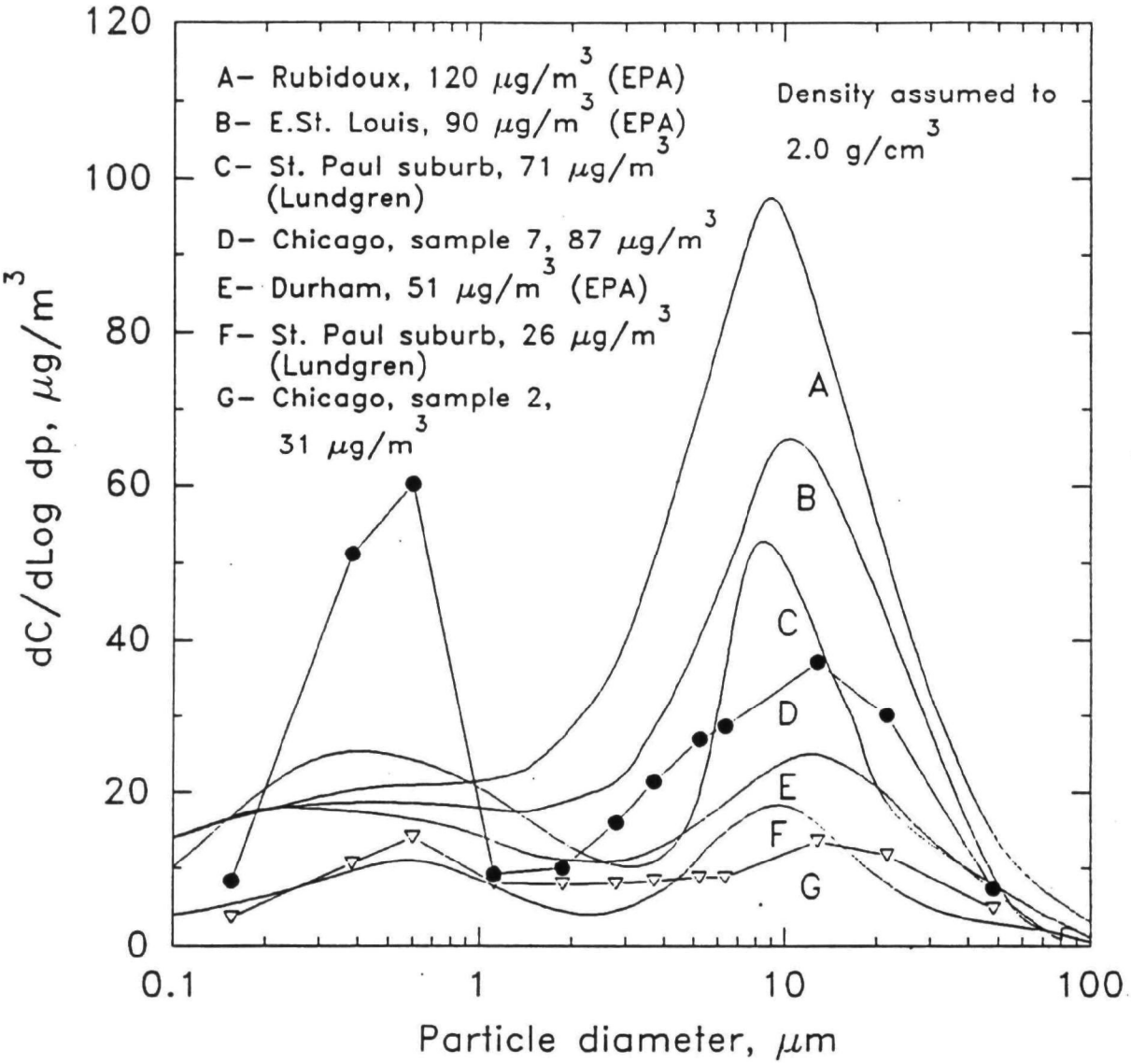
Deposition Plate -

- PVC plates with a sharp leading edge
- pointed into the wind by a wind vane
- greased mylar strips
- weighed before and after sampling
- strips can be extracted and analyzed

- Smooth surrogate surfaces produce minimum deposition velocities - deposition velocities measured with other collectors changes with collector geometry



Range of particle sizes measured with various instruments are compared to mass and flux distributions.

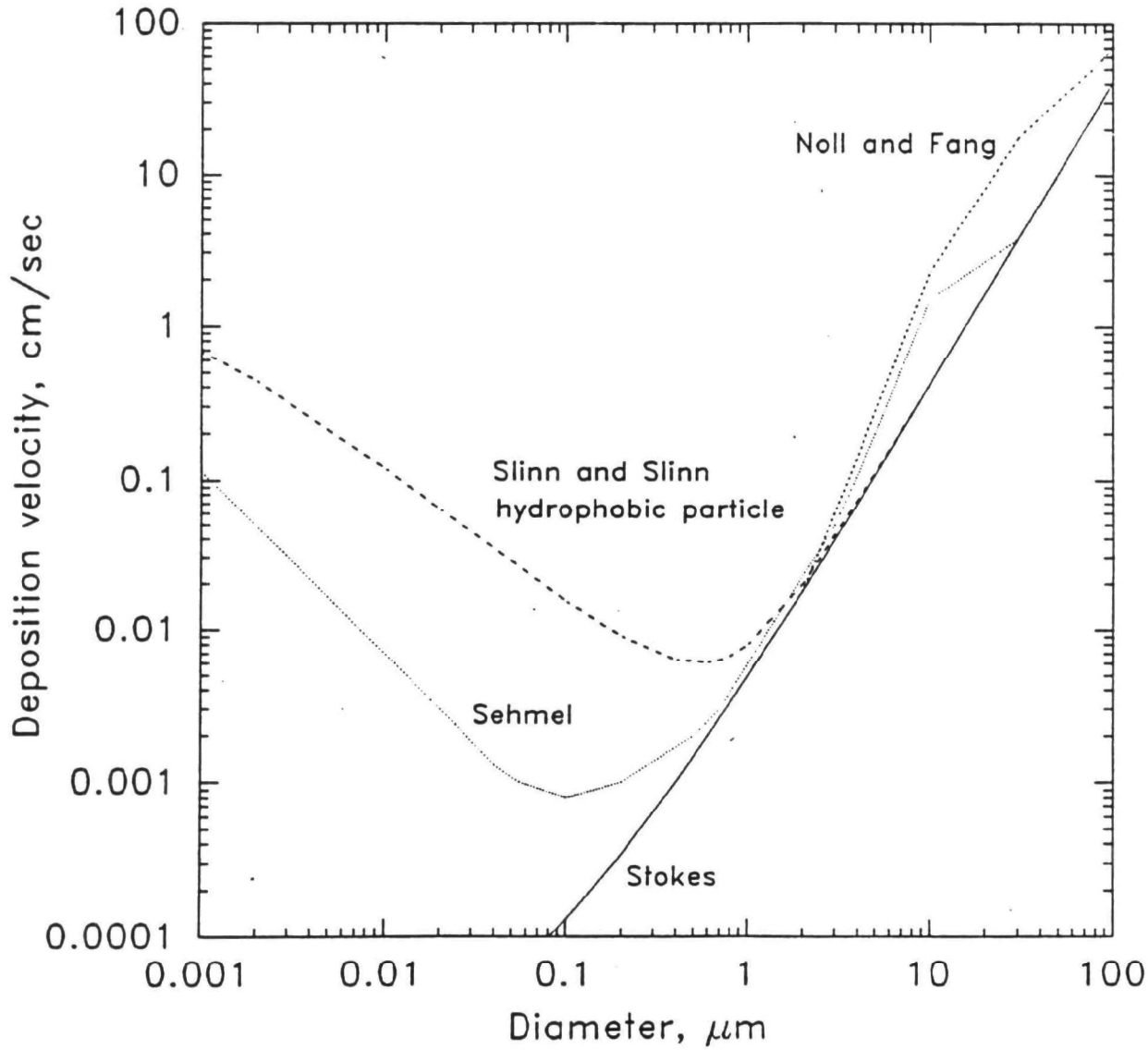


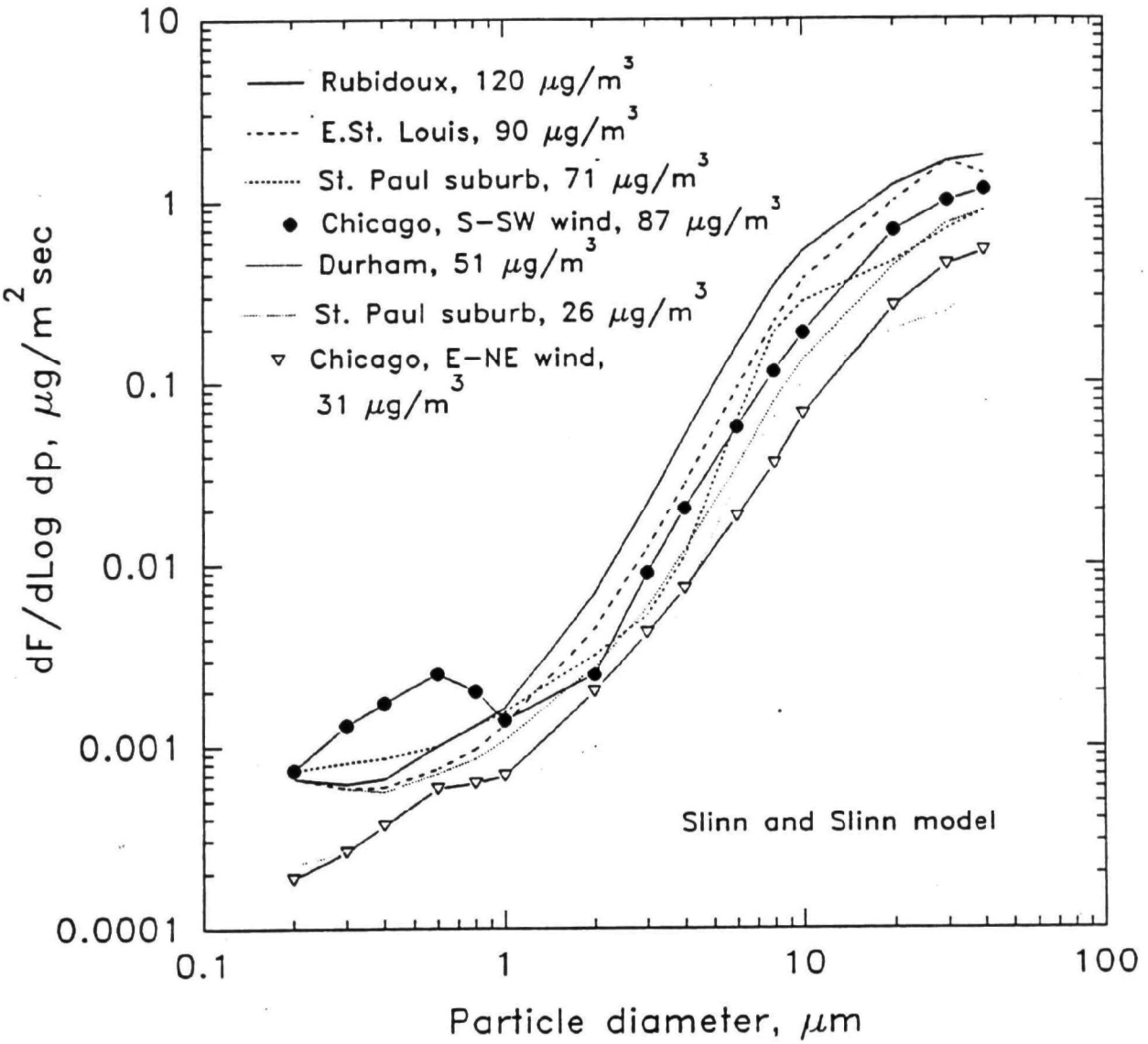
Measured particle size distributions obtained from 3 different studies at 5 different locations in the U.S.. The size distributions labeled "EPA" are from a study by Rodes et al. (1985) and those labeled "Lundgren" are from a study by Lundgren and Paulus (1975). The size distributions labeled "Chicago" are 2 of the 9 five day samples collected in 1991.

Dry deposition models

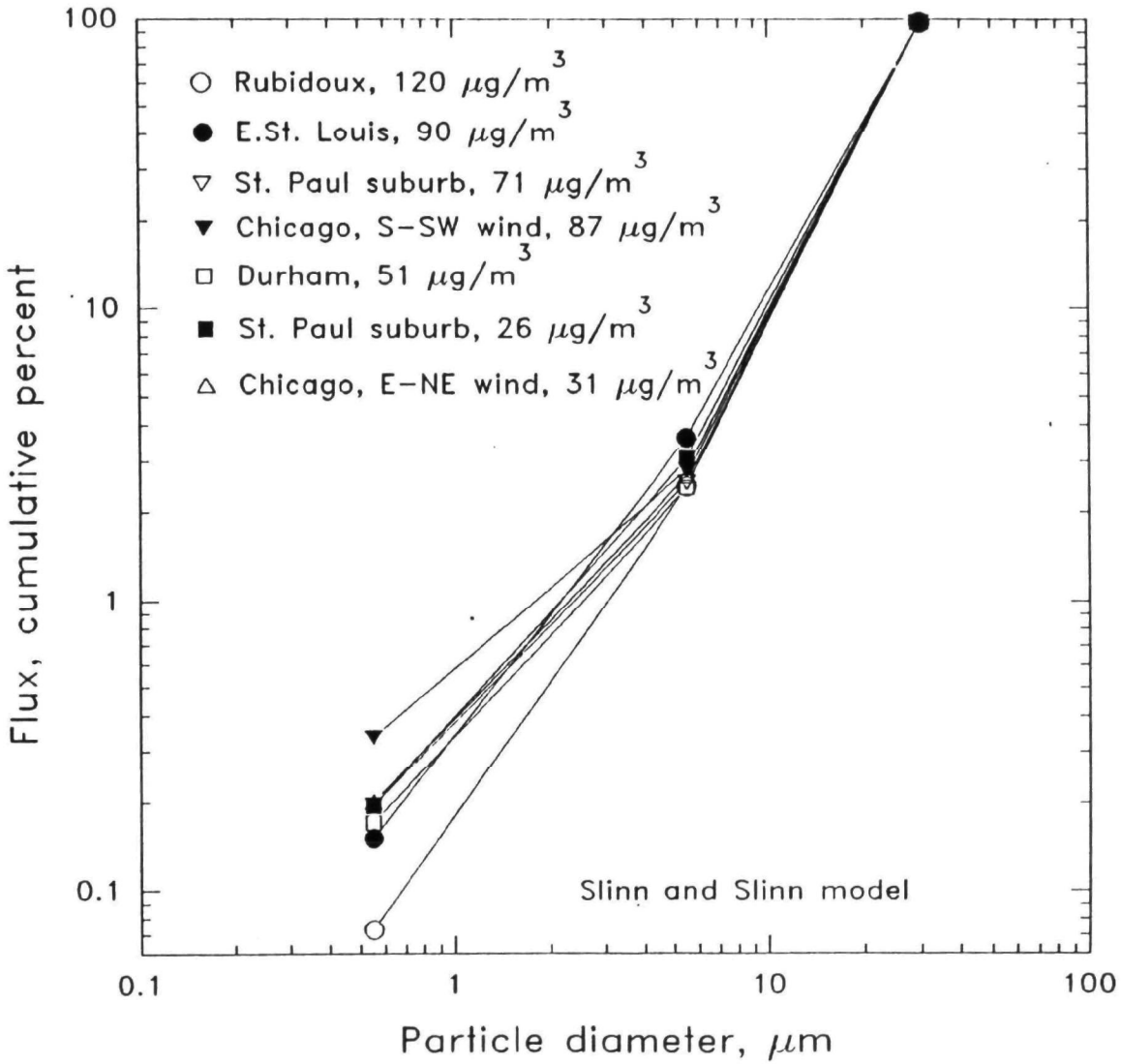
Sehmel (1973), Slinn and Slinn (1980), Noll and Fang (1989) + others

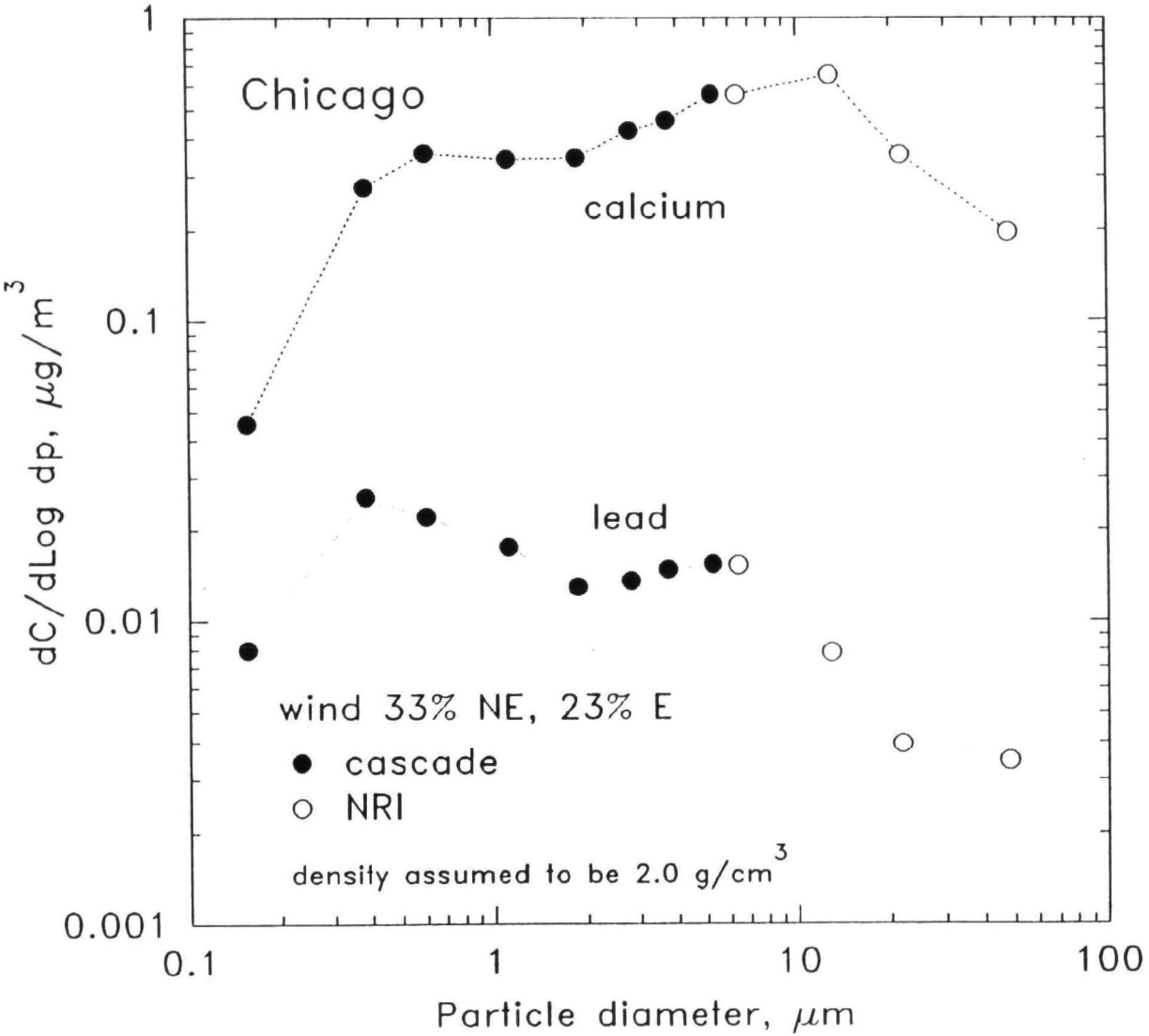
Predict deposition velocities as a function of particle diameter for a variety of environmental and particle characteristics. In this example a particle density of 1.5 g/cm, wind velocity of 6.7 m/sec and U* of 34.1 were used.





dF/dLog dp = dC/dLog dp · V_d where F is the flux in $\mu g/m^2 sec$, Vd from Slinn and Slinn (1980).


Rubidoux, 120 μg/m3
E.St. Louis, 90 μg/m3
St. Paul suburb, 71 μg/m3
Chicago, S–SW wind, 87 μg/m3
Durham, 51 μg/m3
St. Paul suburb, 26 μg/m3
Chicago, E–NE wind, 31 μg/m3
Slinn and Slinn model
Flux, cumulative percent
Particle diameter, μm
100
10
1
0.1
0.1
1
10
100


Chicago
calcium
lead
wind 33% NE, 23% E
cascade
NRI
density assumed to be 2.0 g/cm3
dC/dLog dp, μg/m3
Particle diameter, μm
1
0.1
0.01
0.001
0.1
1
10
100

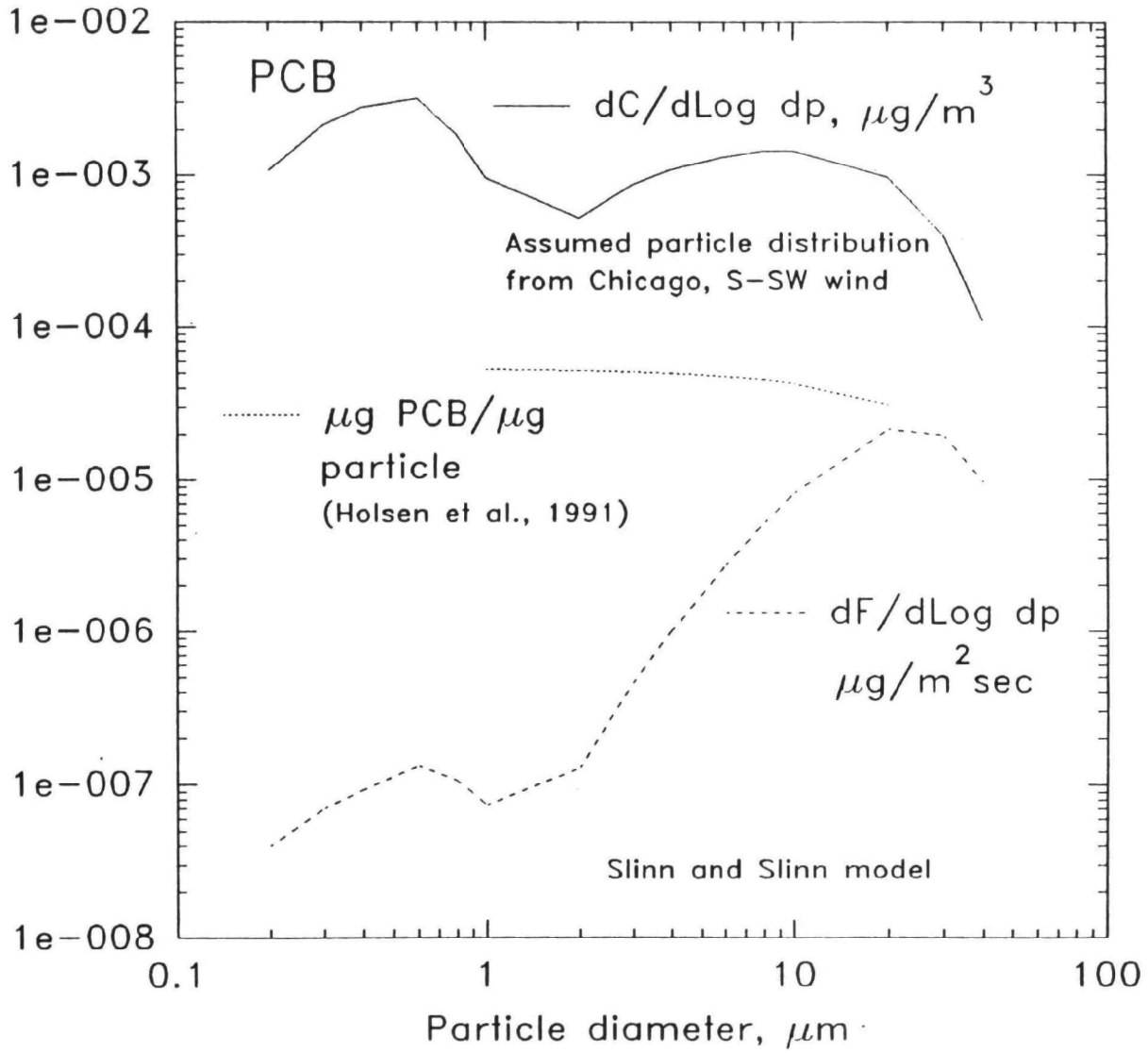
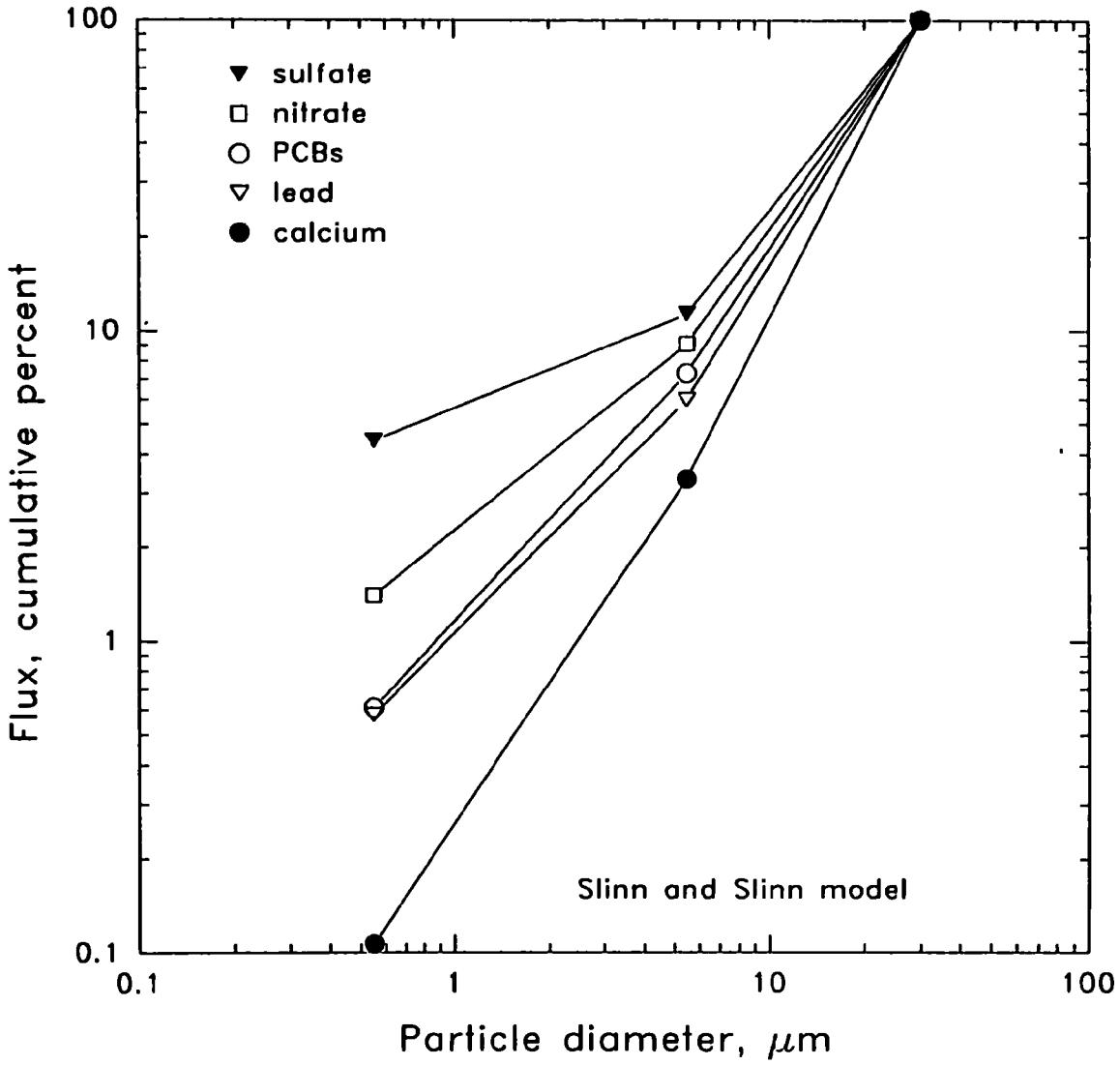
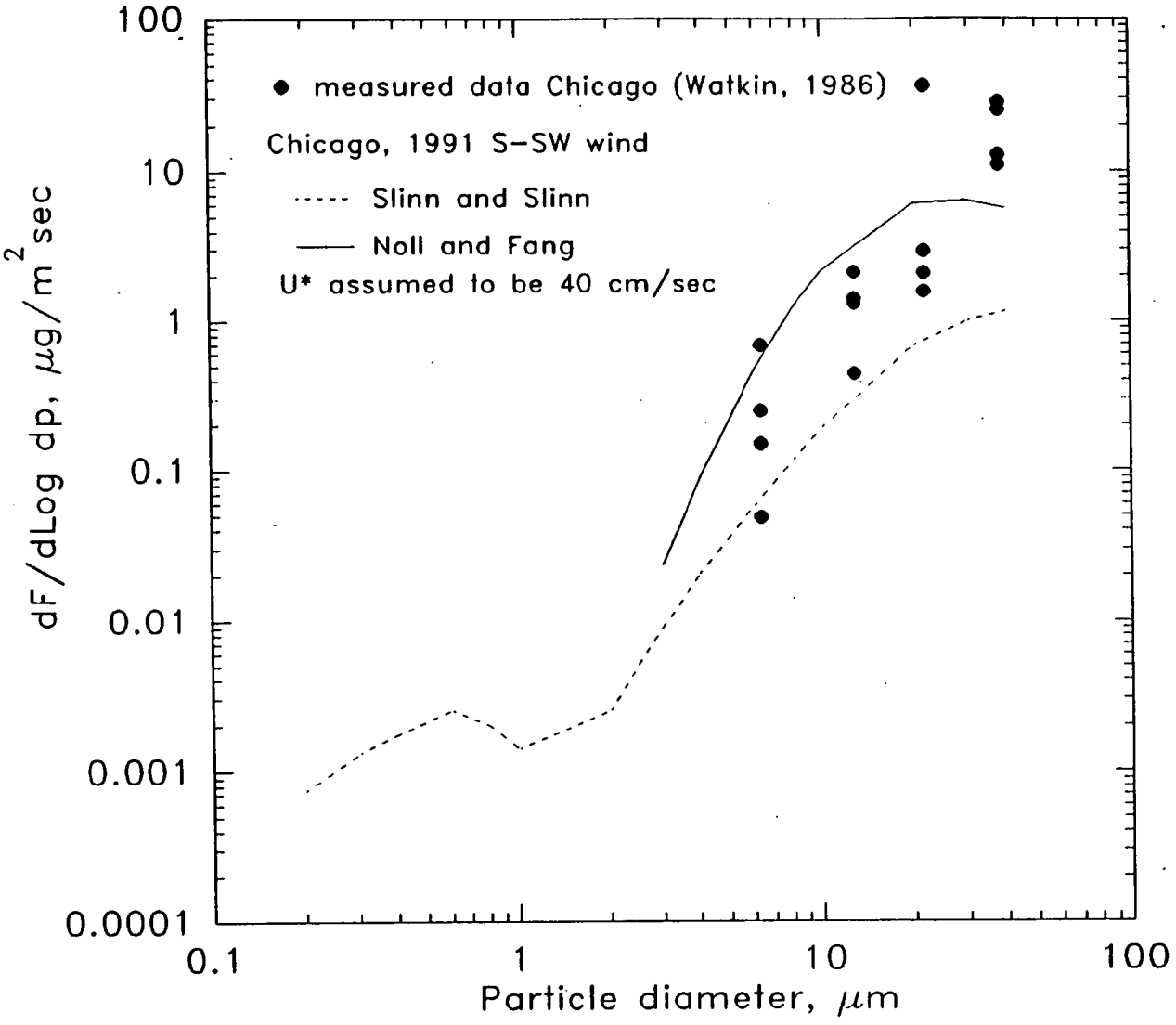

PCB
dC/dLog dp, μg/m3
Assumed particle distribution
from Chicago, S-SW wind
μg PCB/μg
particle
(Holsen et al., 1991)
dF/dLog dp
μg/m2 sec
Slinn and Slinn model
1e-002
1e-003
1e-004
1e-005
1e-006
1e-007
1e-008
0.1
1
10
100
Particle diameter, μm

Table I. Chicago sample information.

Sample No.	Sampling date, 1991	% of time exposed	% of time wind was from land	Ave wind speed, m/s	Fine particle conc., $\mu g/m^3$	Coarse particle conc., $\mu g/m^3$
1 - mass	6/21-6/27	75	41	4.7	20.6	21.5
2 - mass	7/8 - 7/16	85	25	3.6	13.7	17.4
2 - lead					0.032	0.015
2 - calcium					0.33	0.73
3 - mass	7/23-7/29	88	53	4.0	21.8	16.5
4 - mass	7/30-8/6	81	46	4.2	18.5	37.9
5 - mass	8/9-8/15	94	38	3.2	19.5	20.1
6 - mass	8/16-8/24	72	46	4.0	28.1	24.9
7 - mass	8/25 - 8/29	100	92	3.5	47.3	39.9
8 - mass	8/31-9/8	87	59	4.0	26.2	28.4
9 - mass	9/17-9/29	69	69	4.2	24.6	25.5


100
10
1
0.1
0.1
1
10
100
Flux, cumulative percent
Particle diameter, μm
sulfate
nitrate
PCBs
lead
calcium
Slinn and Slinn model


100
10
1
0.1
0.01
0.001
0.0001
0.1
1
10
100
dF/dLog dp, μg/m² sec
Particle diameter, μm
● measured data Chicago (Watkin, 1986)
Chicago, 1991 S-SW wind
----- Slinn and Slinn
—— Noll and Fang
U* assumed to be 40 cm/sec

Comparison of Measured and Modeled Dry Deposition

Models

Product Model: $C_i\ Vd(MMD_i)$ where i is either the fine or coarse particle phase.

Slinn and Slinn
modification of Noll and Fang.

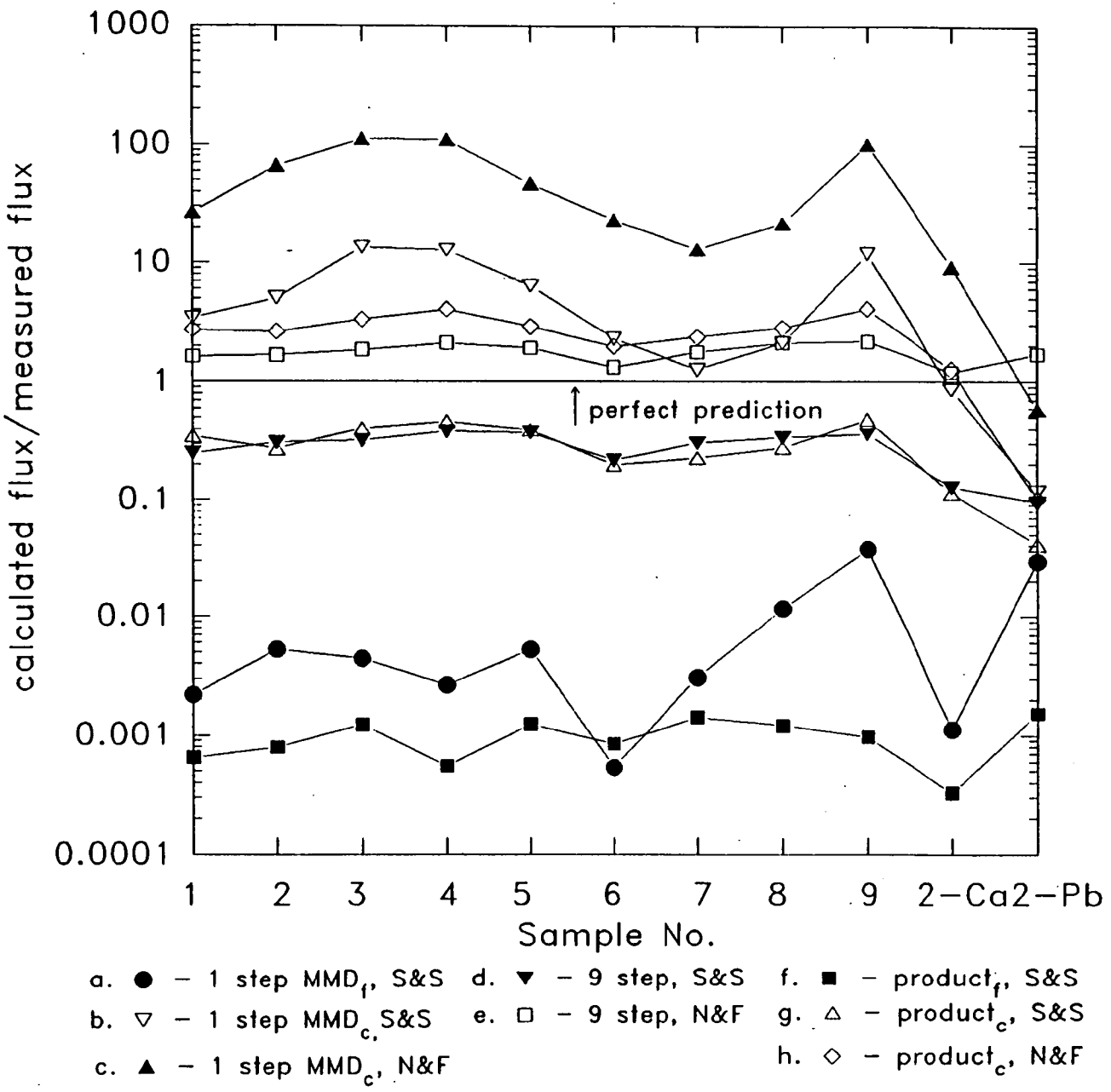
1-step method (Slinn and Slinn, 1980): $F_1 = C\ K(\sigma_g)\ V_d(MMD)$

C is the mass concentration
σ_g is the geometric standard deviation
V_d is the deposition velocity
MMD is the mass median diameter
$K(\sigma_g) = \exp\{2(\ln \sigma_g)^2\}$
$K(\sigma)V_d(MMD)$ is the flux mean deposition velocity

fine and coarse particle mode - Slinn and Slinn
coarse particle mode with the modification of Noll and Fang

9-step method: $F_9 = \sum_{i=1}^{9} C_i\ V_d(D_i)$ where D_i = the is the midpoint cut-off diameter of each impactor stage.

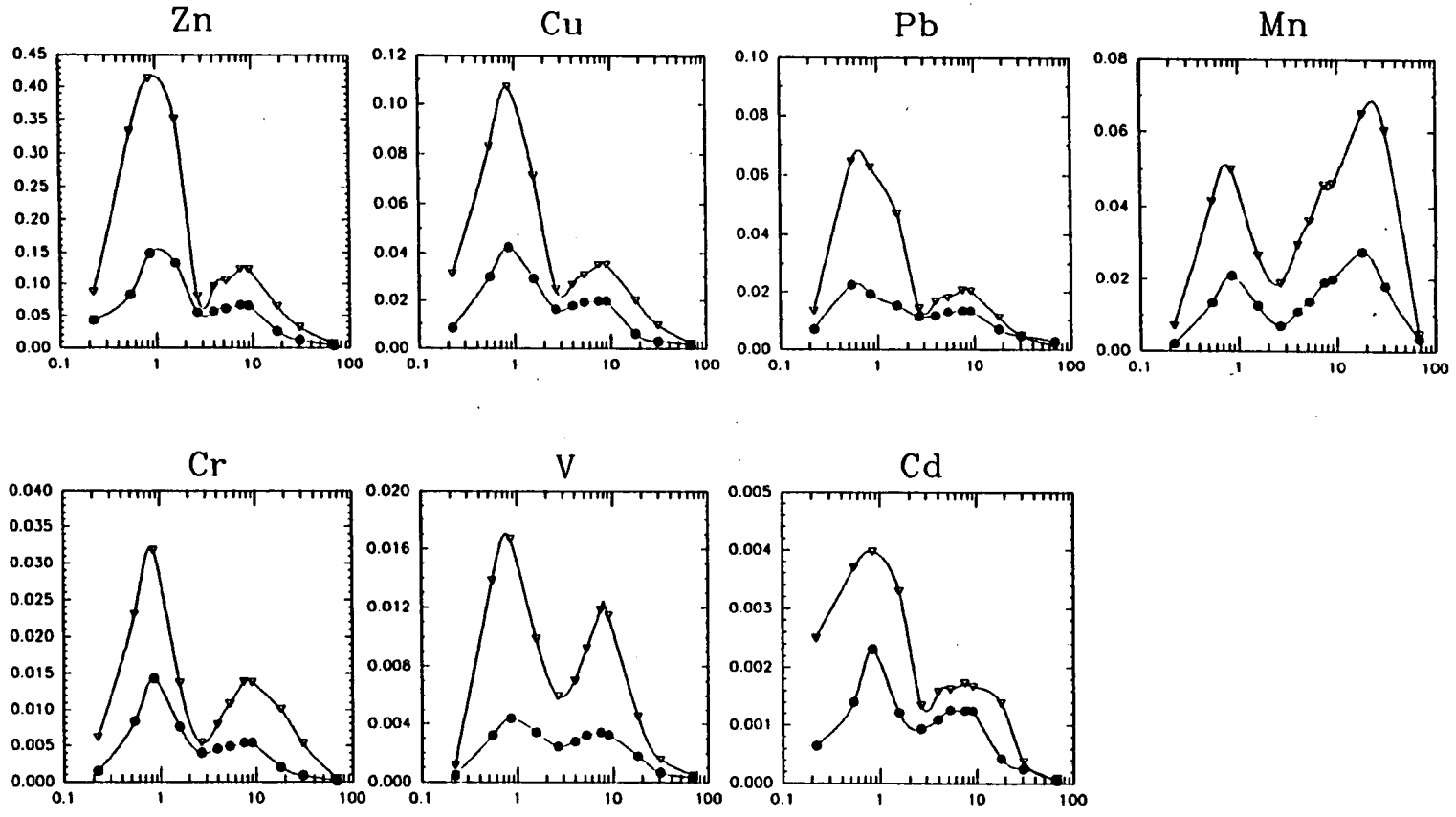
Slinn and Slinn
modification of Noll and Fang.


1000
100
10
1
0.1
0.01
0.001
0.0001
calculated flux/measured flux
perfect prediction
1
2
3
4
5
6
7
8
9
2-Ca2-Pb
Sample No.
a. ● – 1 step MMD$_f$, S&S
b. ▽ – 1 step MMD$_c$, S&S
c. ▲ – 1 step MMD$_c$, N&F
d. ▼ – 9 step, S&S
e. □ – 9 step, N&F
f. ■ – product$_f$, S&S
g. △ – product$_c$, S&S
h. ◇ – product$_c$, N&F

Particle Size Distribution for Anthropogenic Elements

Lake vs. Land

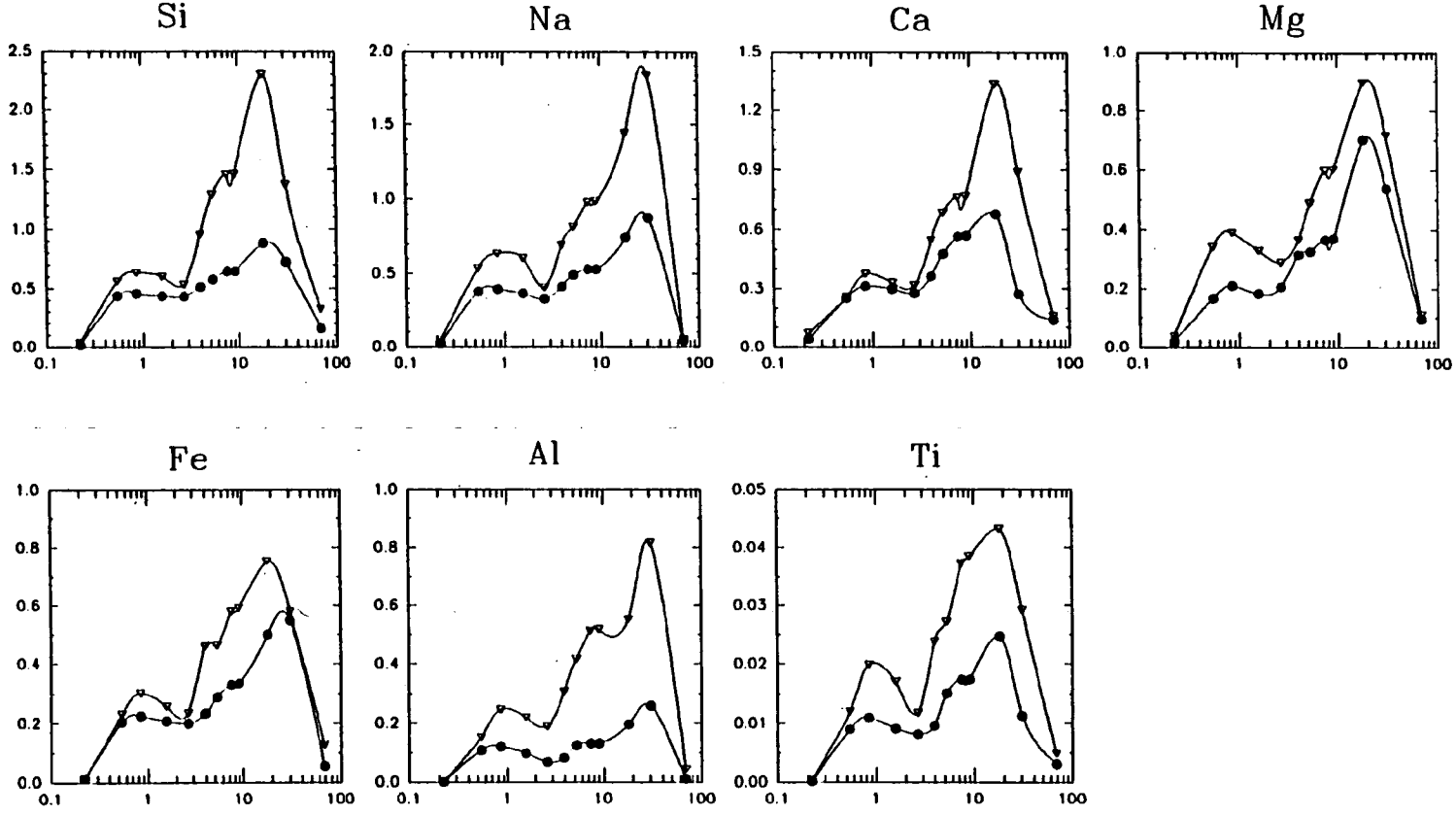
• Lake ▿ Land

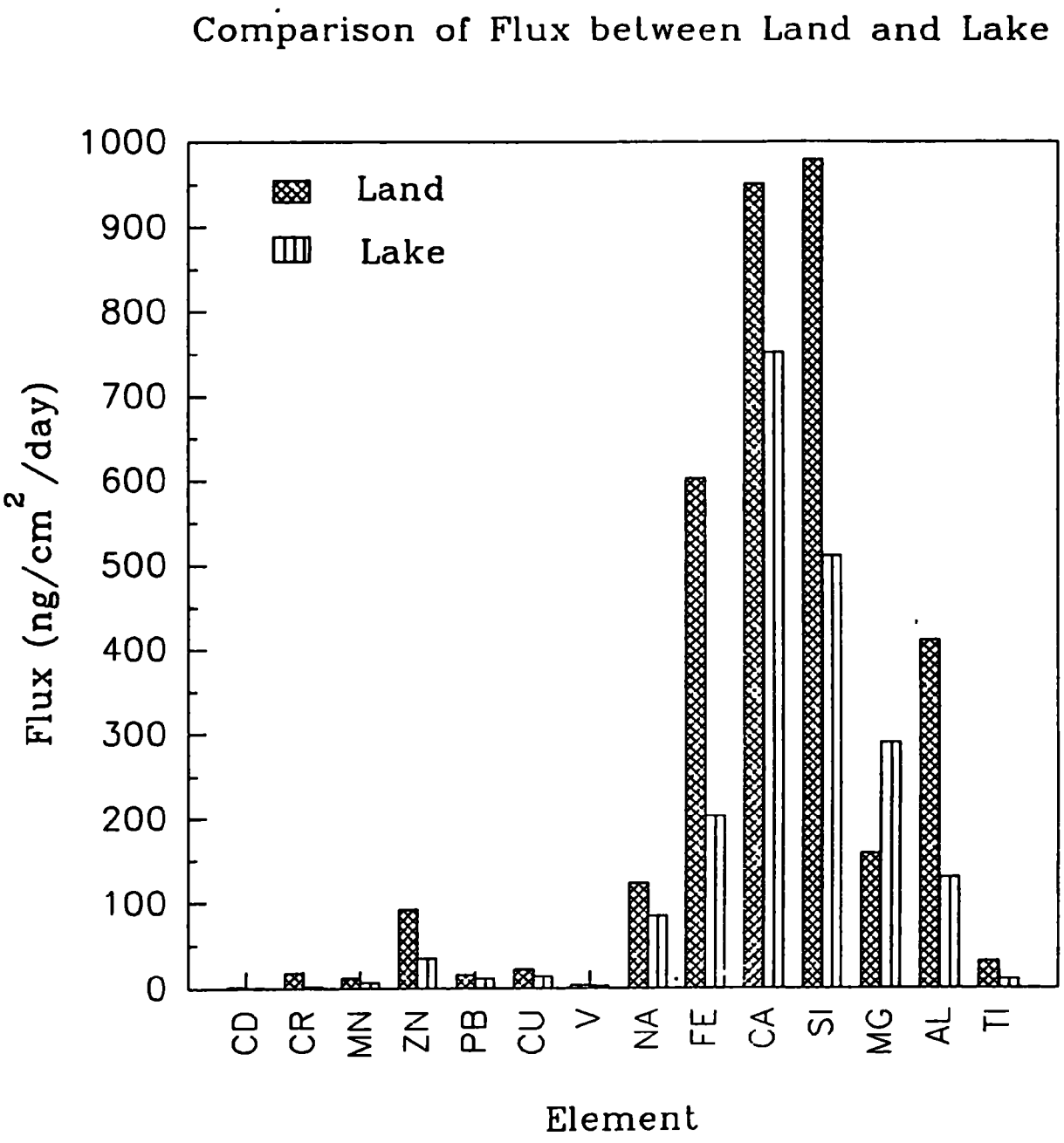


Particle Size Distribution for Crustal Elements

Lake vs. Land

• Lake ▿ Land

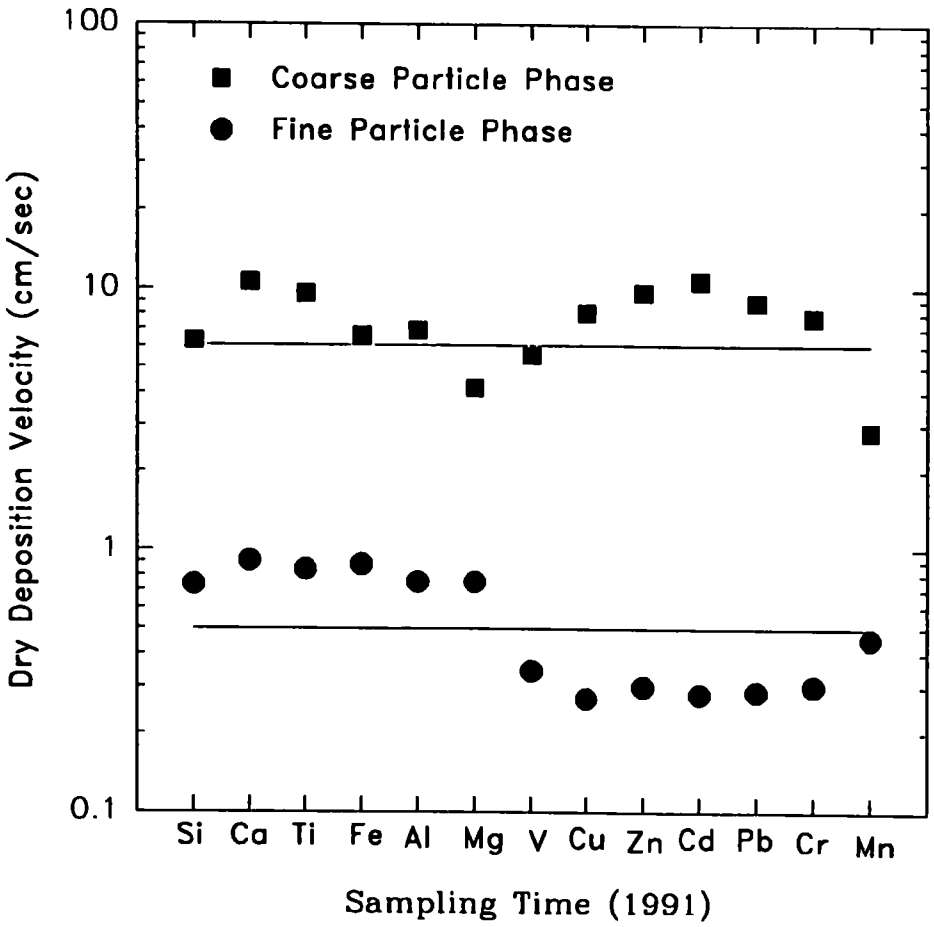



Comparison of Flux between Land and Lake
Land
Lake
Flux (ng/cm^2/day)
1000
900
800
700
600
500
400
300
200
100
0
CD
CR
MN
ZN
PB
CU
V
NA
FE
CA
SI
MG
AL
TI
Element

For Each Metal:

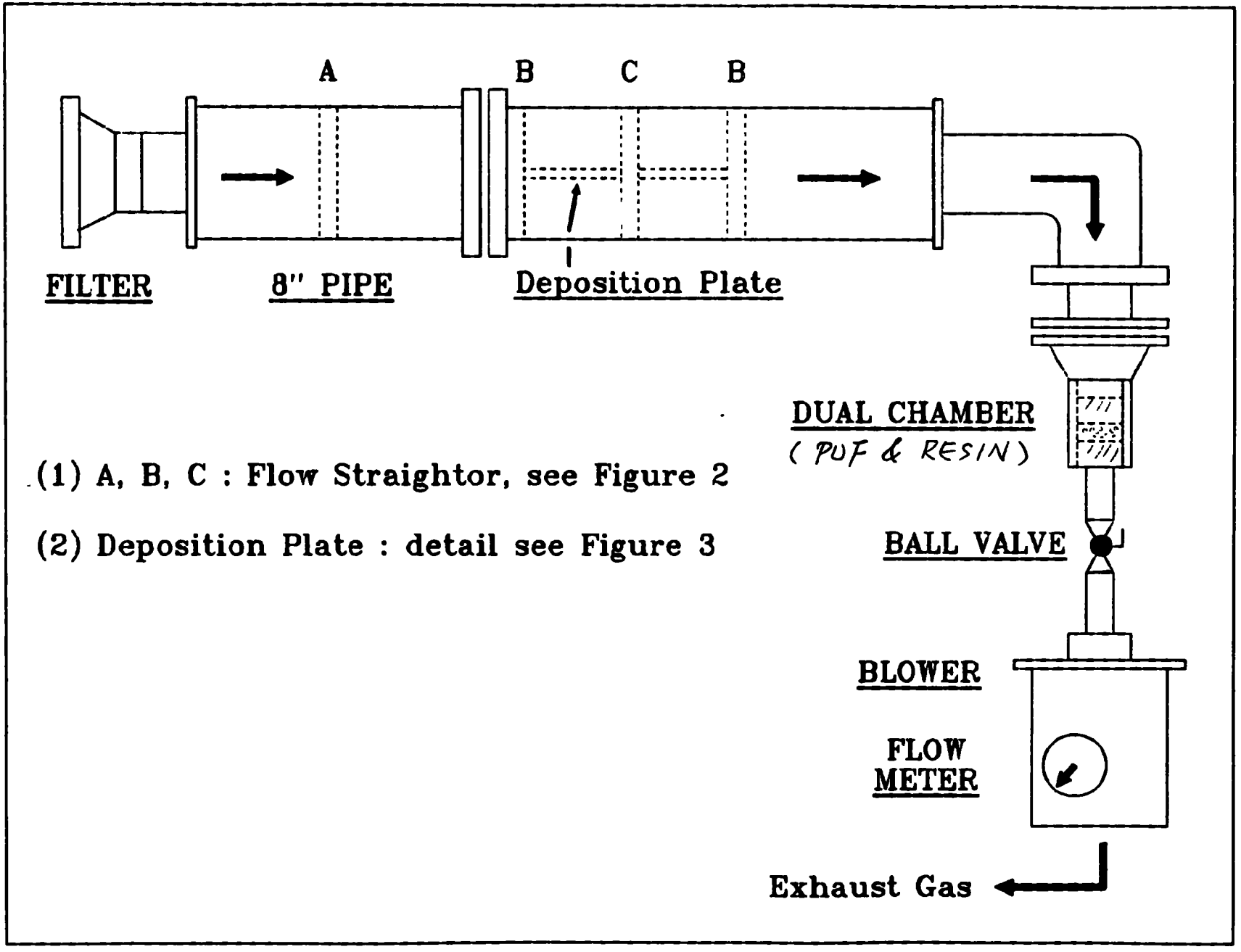
Total Flux = $V_{df} \cdot C_f + V_{dc} \cdot C_c$

Total flux = measured (n= 9)
C_f = fine particle concentration (n=9)
C_c = coarse particle concentration (n=9)
V_d = deposition velocities for fine and coarse particles - obtained by multiple regression (9 equations , 2 unknowns)


100
10
1
0.1
Dry Deposition Velocity (cm/sec)
Coarse Particle Phase
Fine Particle Phase
Si Ca Ti Fe Al Mg V Cu Zn Cd Pb Cr Mn
Sampling Time (1991)

Coarse Particle Flux
Fine Particle Flux
Percent %
100
90
80
70
60
50
40
30
20
10
0
Cd
Cr
Mn
Zn
Pb
Cu
V
Na
Fe
Ca
Si
Mg
Al
Ti
Mass

Fig 1

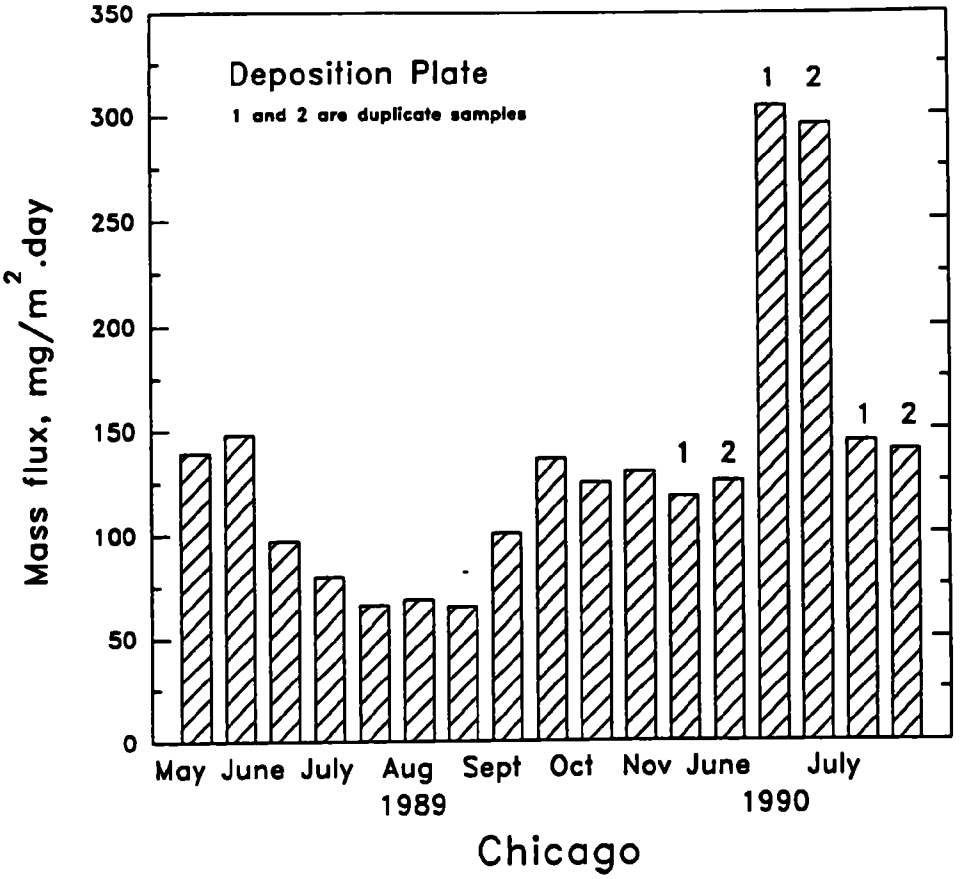


(1) A, B, C : Flow Straightor, see Figure 2

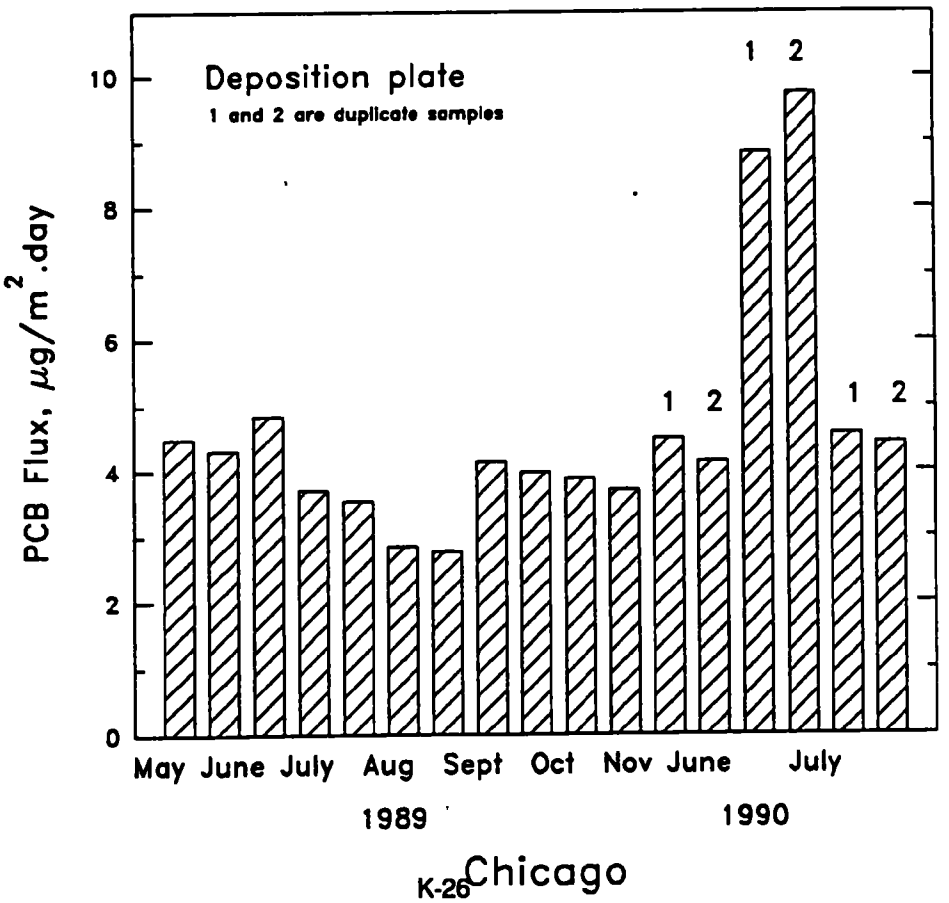
(2) Deposition Plate : detail see Figure 3

Deposition of Semi-Volatile Compounds (compounds with both a gas and particle phase)

Experiments in which deposition plates were exposed to filtered, PAH and PCB containing air for periods up to 30 days continuously collected these compounds. Calculated deposition velocities for these compounds remained constant and in the range of expected values (0.01-0.02 cm/sec).



Chicago



Chicago

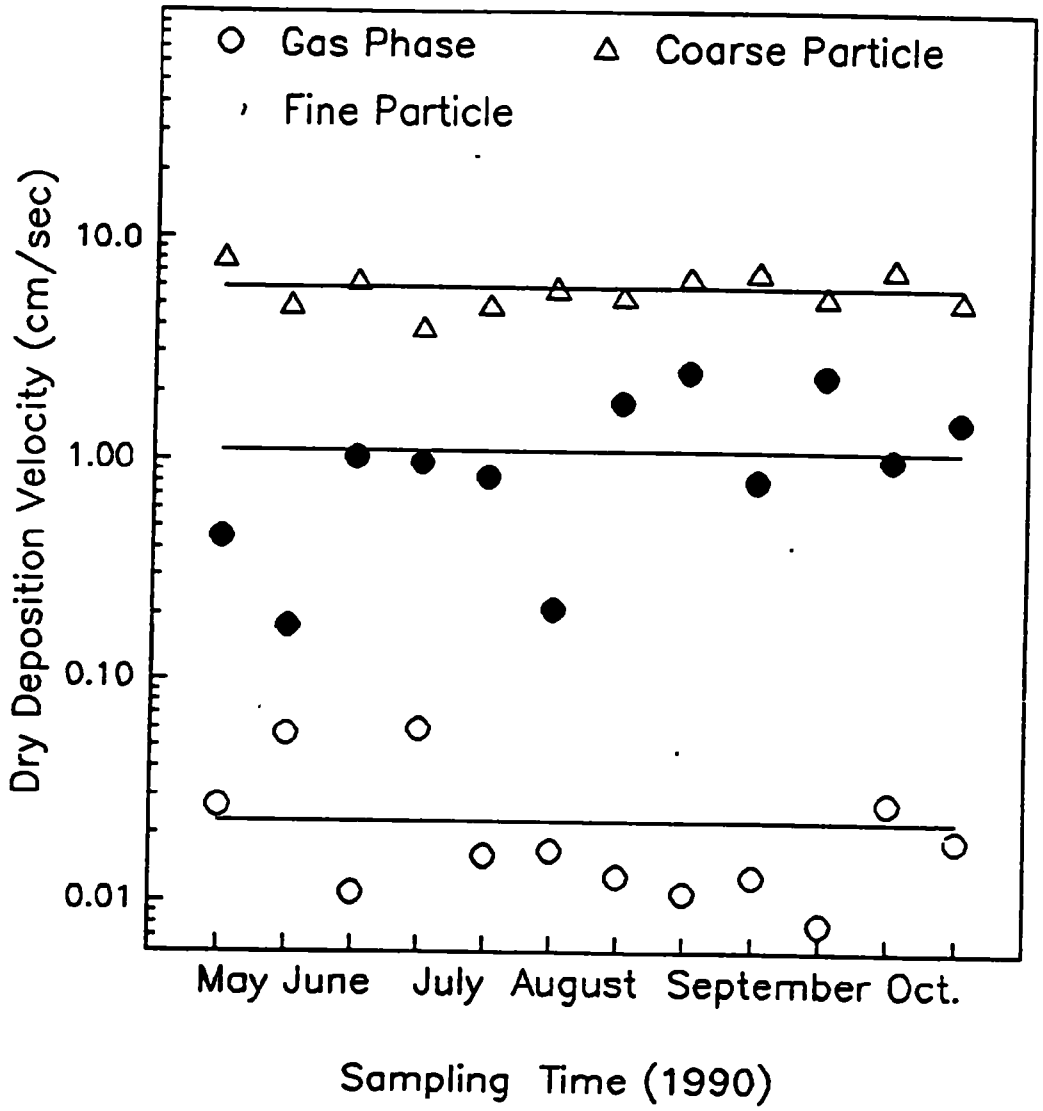
Deposition Velocities

By phase: Flux = $V_gC_g + V_fC_f + V_cC_c$

where : V - deposition velocity
C - concentration
g - gas phase
f - fine particle phase
c - coarse particle phase

Fluxes and concentrations measured - deposition velocities solved for using multiple regression (24 equations and 3 unknowns)

Problems - poor definition of fine particle phase → new instrument
- filter artifact formation (gas and fine particle phase) → denuder


Gas Phase
Coarse Particle
Fine Particle
Dry Deposition Velocity (cm/sec)
10.0
1.00
0.10
0.01
May
June
July
August
September
Oct.
Sampling Time (1990)

Particle vs. gas phase deposition

Total PCB Flux = $V_{dg} \cdot C_g + V_{df} \cdot C_f + V_{dc} \cdot C_c$

where the measured values are:

Total PCB flux = 6.04 $\mu g/m^2 \cdot day$
C_g = gas phase PCB concentration = 10.4 ng/m^3
C_f = fine particle PCB concentration = 3.2 ng/m^3
C_c = coarse particle PCB concentration = 0.9 ng/m^3
and the literature values are:
V_{dg} = PCB gas phase deposition velocity to a smooth surface = 0.01-0.1 cm/sec
V_{df} = PCB fine particle deposition velocity to a smooth surface = 0.1-0.5 cm/sec

Comparison of gas phase, fine particle phase and coarse particle phase PCB flux to a smooth surrogate surface with a sharp leading edge.

V_{dg}, cm/s	V_{df}, cm/s	V_{dc}, cm/s	Gas phase flux, $ng/cm^2 \cdot s$	Fine particle flux, $ng/cm^2 \cdot s$	Coarse particle flux, $ng/cm^2 \cdot s$	Total flux, $ng/cm^2 \cdot s$
0.01	0.1	7.3	1.04E-7 (1.5%)	3.2E-7 (4.6%)	6.6E-6 (94%)	7.0E-6
0.01	0.5	5.9	1.04E-7 (1.5%)	1.6E-6 (23%)	5.3E-6 (76%)	7.0E-6
0.10	0.1	6.3	1.0E-6 (15%)	3.2E-7 (4.6%)	5.7E-6 (81%)	7.0E-6
0.10	0.5	4.8	1.0E-6 (15%)	1.6E-6 (23%)	4.3E-6 (62%)	7.0E-6

Large Particles Control Flux

- Davidson and Friedlander (1978) - Pb in LA
- Murphy (1984) - PCBs near Lake Huron
- Davidson et al. (1985) - sulfate
- Dulac et al. (1989) - metals and mass in Mediterranean
- Injuk et al. (1990) - metals in North Sea

Conclusions

1. Realistic estimates of dry deposition can be made with existing dry deposition models if complete airborne size distributions are known.

2. Results obtained from dry deposition measurements with smooth surrogate surfaces with sharp leading edges are comparable to modeled fluxes.

3. Coarse particles are responsible for the majority of dry deposition flux.

Future Work

- Determine the effect of variations in particle size distribution and turbulence on indirect and direct fluxes using short-term urban data
- Compare indirect and direct fluxes in low concentration/flux environments (non-urban data)
- Compare indirect and direct fluxes on a size distribution basis by counting particles on the deposition plate
- Compare data collected simultaneously with the NRI and PM10 sampler to see if a relationship can be developed that would allow PM10 data to be utilized in indirect flux modeling studies
- Compare urban and non-urban data so that global transport and fates of atmospheric particles and pollutants associated with them can be determined.

Implications for Mass Balance Studies

To quantify dry deposition either measure the flux directly with a smooth surrogate surface or measure the total size distribution of ambient particles and the gas phase and apply deposition velocity models (or both).

Using partial size distributions (PM2.5 or PM10) and effective or average deposition velocities has little physical meaning.

Using complete size distributions (WRAC)

Advantages

- linked with meteorological models
- used with models which account for deposition on natural water surfaces (waves, spray, particle growth)
- simulate changes in size distribution and flux with changes in env. factors

Disadvantages

- short term samplers (12-24 h for NRI)
- difficult to measure and expensive to obtain
- not a direct measurement of flux

Eagle (II) Automated Flux Measurement

Advantages

- Simple and easy to use
- directly measures flux of mass, metals, or organics
- compares to modeled data
- can operate unattended long or short term

Disadvantages

- Is not a natural surface
- collected particles need to be counted to obtain mass-size distributions
- can not do chemistry by size

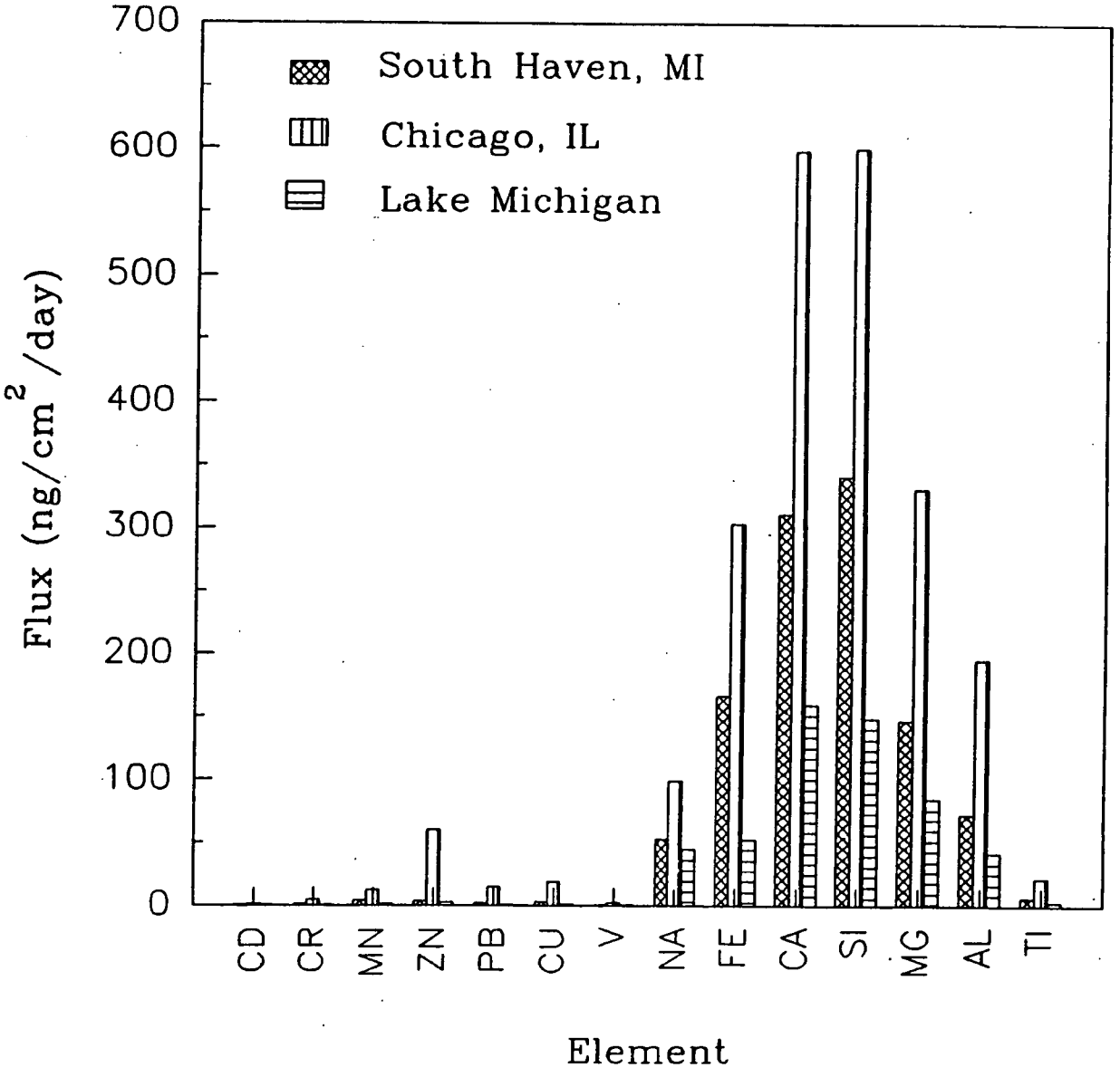
Days needed to obtain measurable samples with various instruments in urban and non-urban areas.

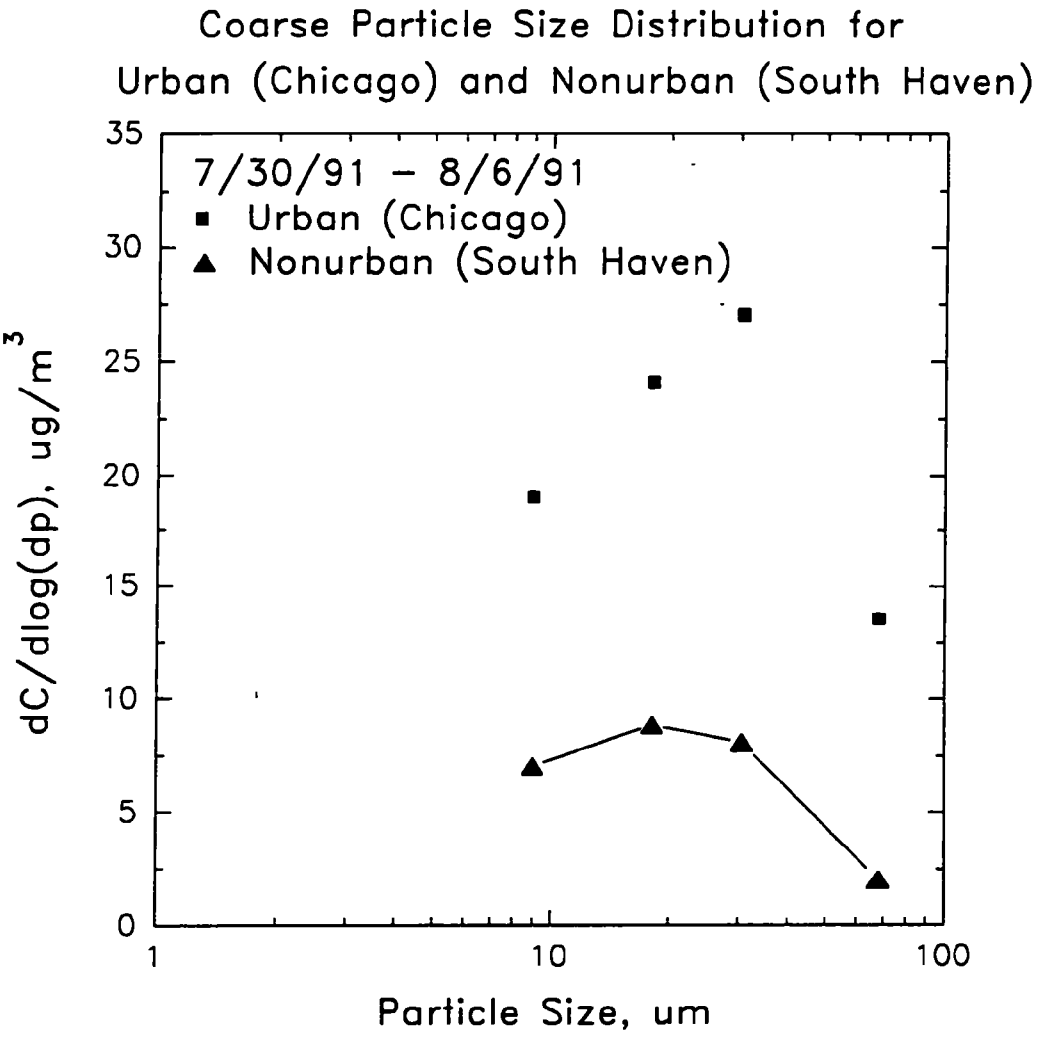
	Urban			Non-urban		
	mass	metals	semi-volatile organics	mass	metals	semi-volatile organics
Flux plate	0.5	0.5	15	1-2	3-5	15-30
UAS	0.5	0.5	1-2	1-2	2-4	2-4
AAPSS	1-3	3-5	5-10*	3-5	5-10	10-30*
NRI	0.5	0.5	5-10	1-2	2-4	10-20

* - collects particle phase only UAS - Universal Air Sampler
AAPSS - Anderson 1 ACFM non-viable ambient particle sizing sampler
NRI - Noll Rotary Impactor

Flux ($mg/m^2.d$)		
Chicago	South Haven	Lake
98.2	36.2	
102.9	44.1	27.2
195.4	37.9	24.9

7/30/91-8/6/91


South Haven, MI
Chicago, IL
Lake Michigan
Flux (ng/cm 2 /day)
700
600
500
400
300
200
100
0
CD
CR
MN
ZN
PB
CU
V
NA
FE
CA
SI
MG
AL
TI
Element

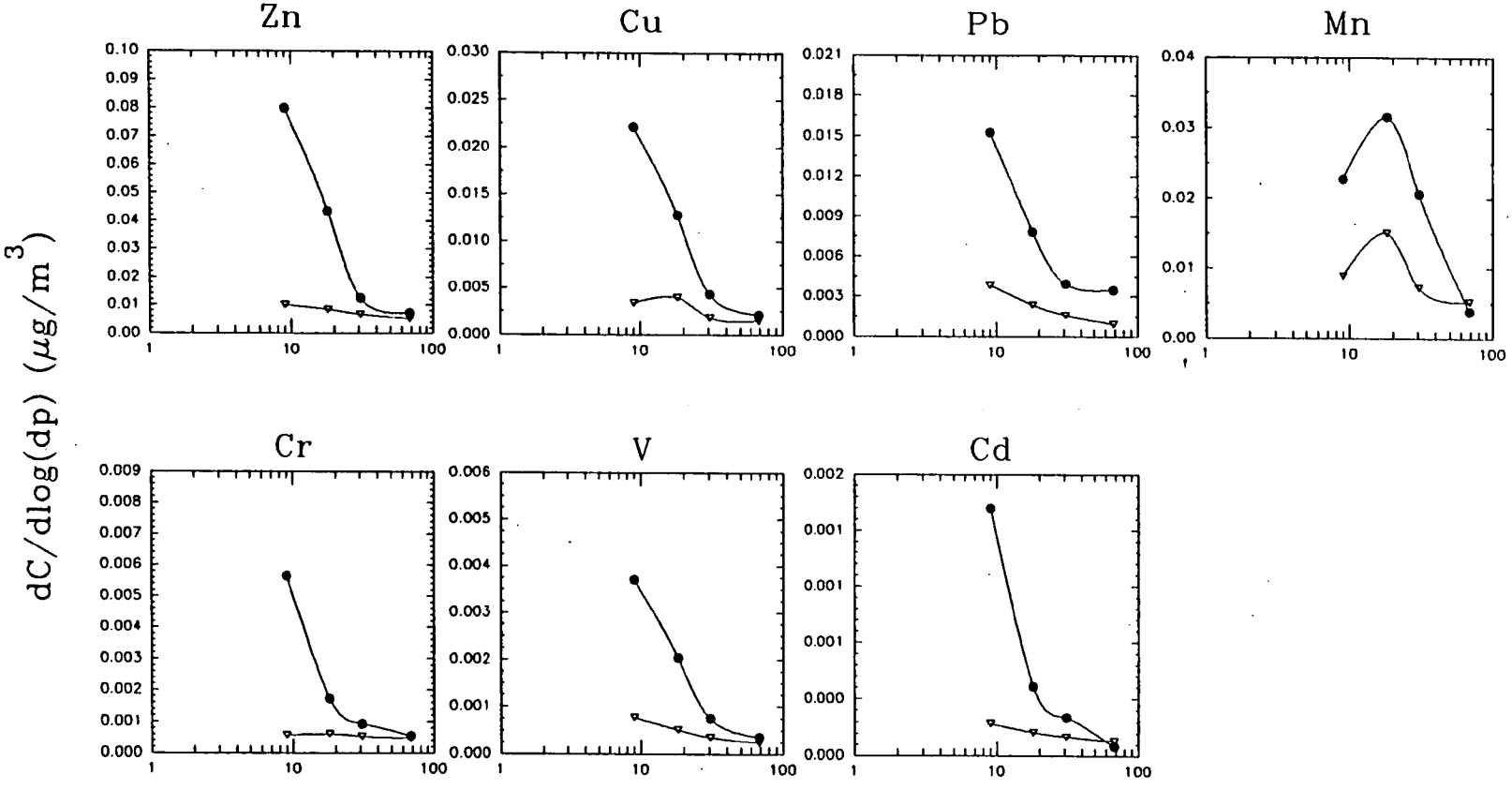

Coarse Particle Size Distribution for
Urban (Chicago) and Nonurban (South Haven)
7/30/91 – 8/6/91
Urban (Chicago)
Nonurban (South Haven)
dC/dlog(dp), ug/m3
Particle Size, um
0
5
10
15
20
25
30
35
1
10
100

7/30/91 - 8/06/91

Coarse Particle Size Distribution for Anthropogenic Elements

Nonurban vs. Urban

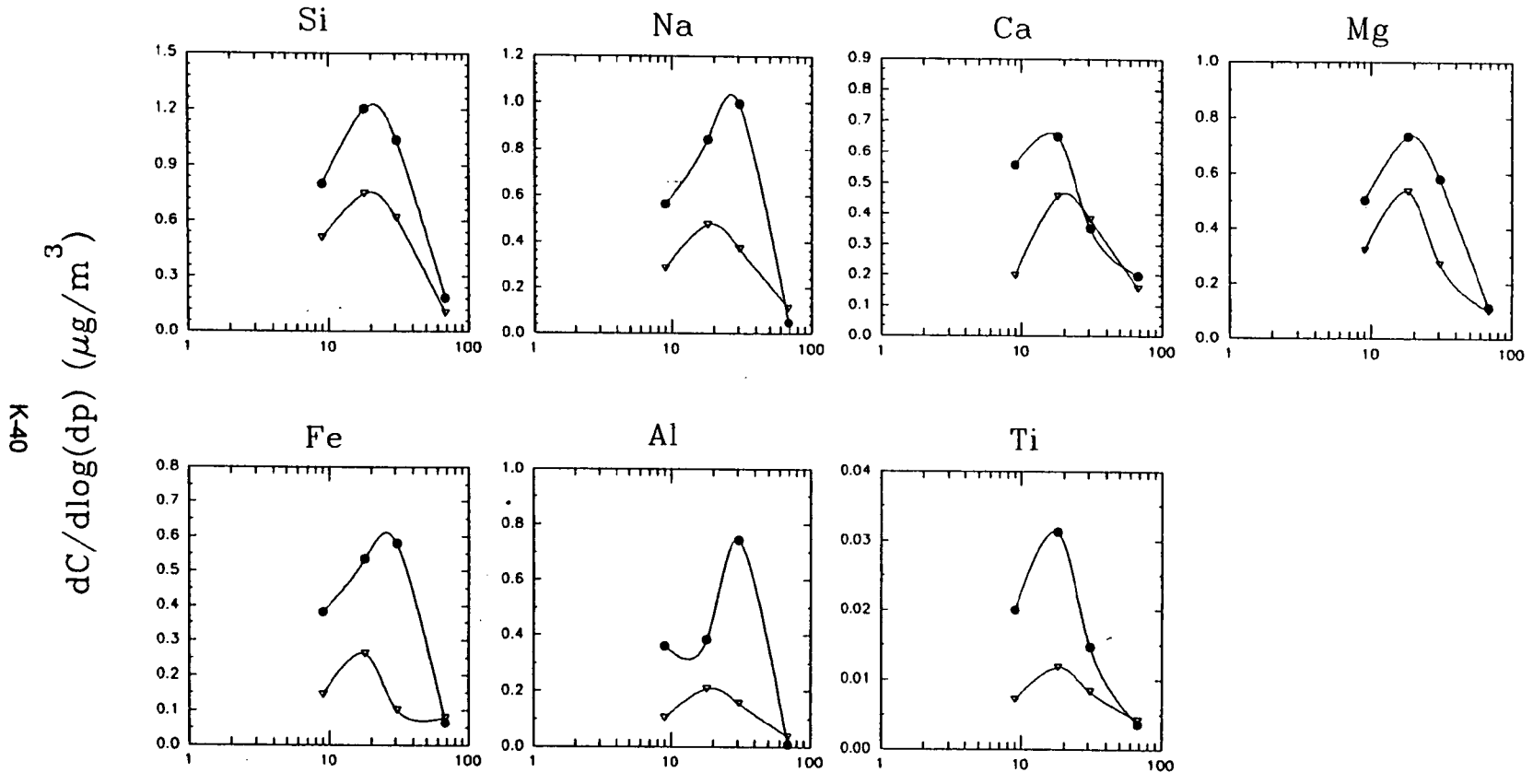
• Urban ▿ Nonurban



Coarse Particle Size Distribution for Crustal Elements

Nonurban vs. Urban

• Urban ▿ Nonurban



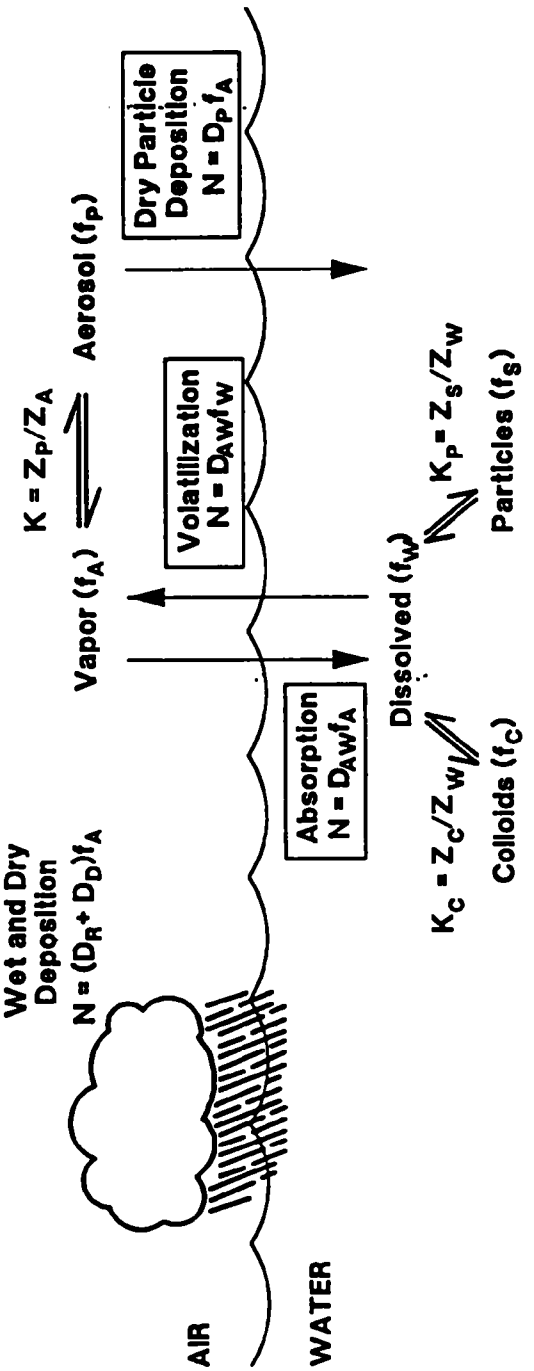
We have not succeeded in answering all your questions. The answers we have found only serve to raise a whole new set of questions. In some ways, we feel as confused as ever, but we believe we are confused on a higher level about more important things.

APPENDIX L

ESTIMATION OF WET DEPOSITION FOR MASS-BALANCE STUDIES

PRESENTATION

DR. JOEL BAKER


Dry Particle Deposition N = $D_P f_A$
Aerosol (f_P)
$K = Z_P/Z_A$
Volatilization N = $D_{AW} f_W$
Vapor (f_A)
Absorption N = $D_{AW} f_A$
Wet and Dry Deposition N = $(D_R + D_D) f_A$
Dissolved (f_W)
$K_P = Z_S/Z_W$
Particles (f_S)
$K_C = Z_C/Z_W$
Colloids (f_C)
AIR
WATER

WET DEPOSITION MEASUREMENTS IN SUPPORT OF A MASS BALANCE

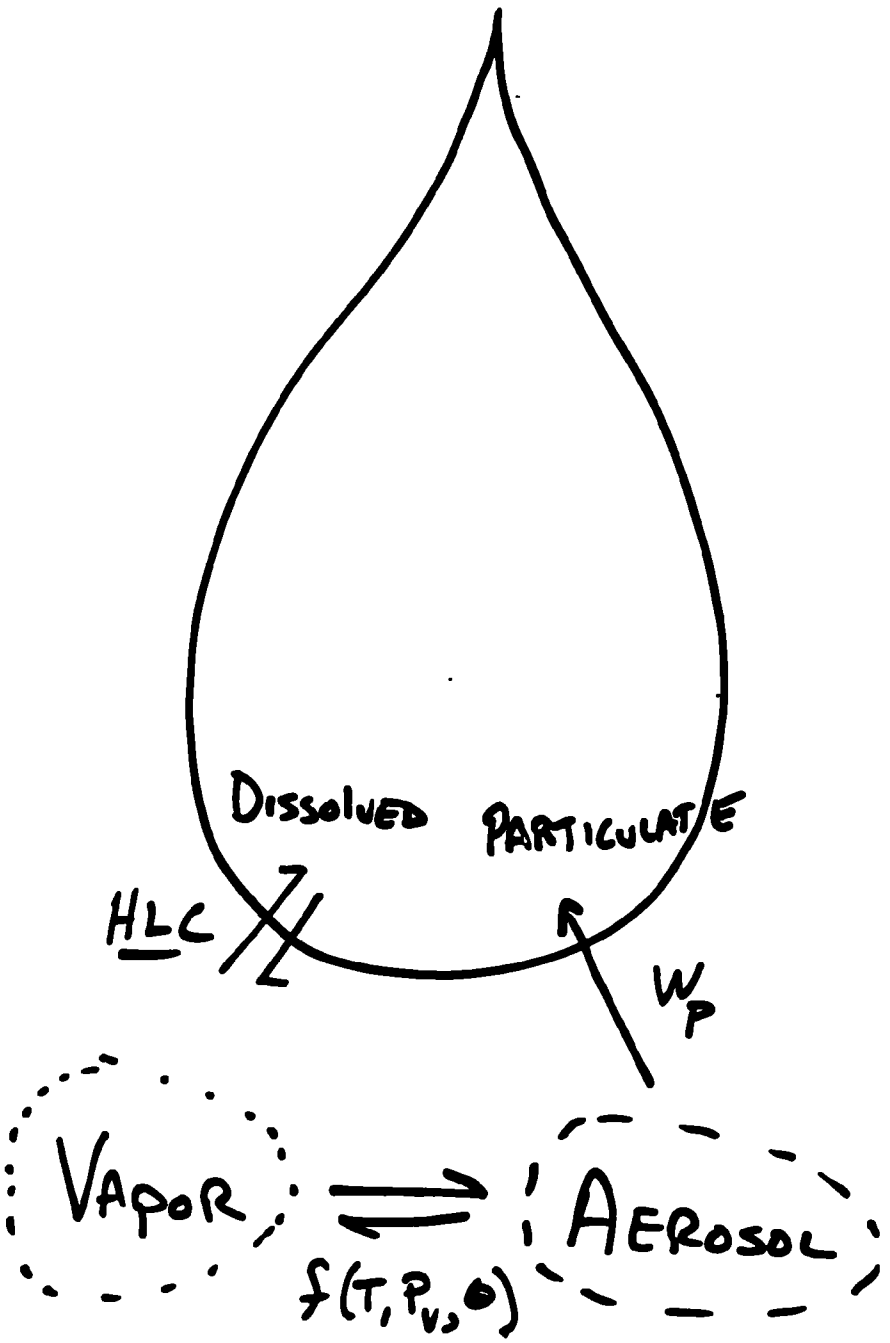
? WHAT IS THE QUESTION?

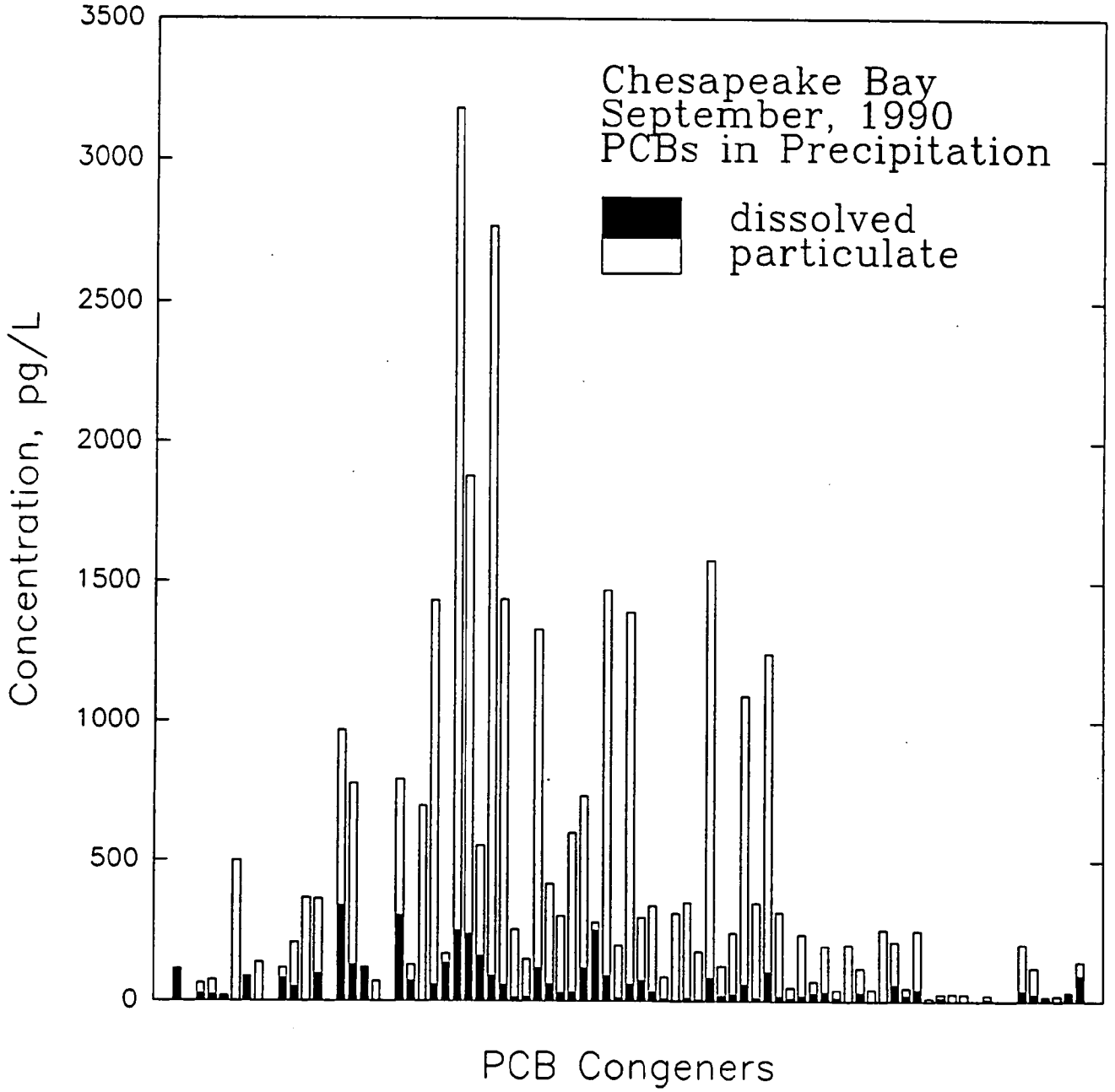
1. GROSS LOADINGS ONLY
   - moderate site density
   - monthly integrated sampling
2. SCAVENGING / SOURCE ATTRIBUTION / SPECIATION
   - EVENT-BASED
   - HIGH SITE DENSITY ?

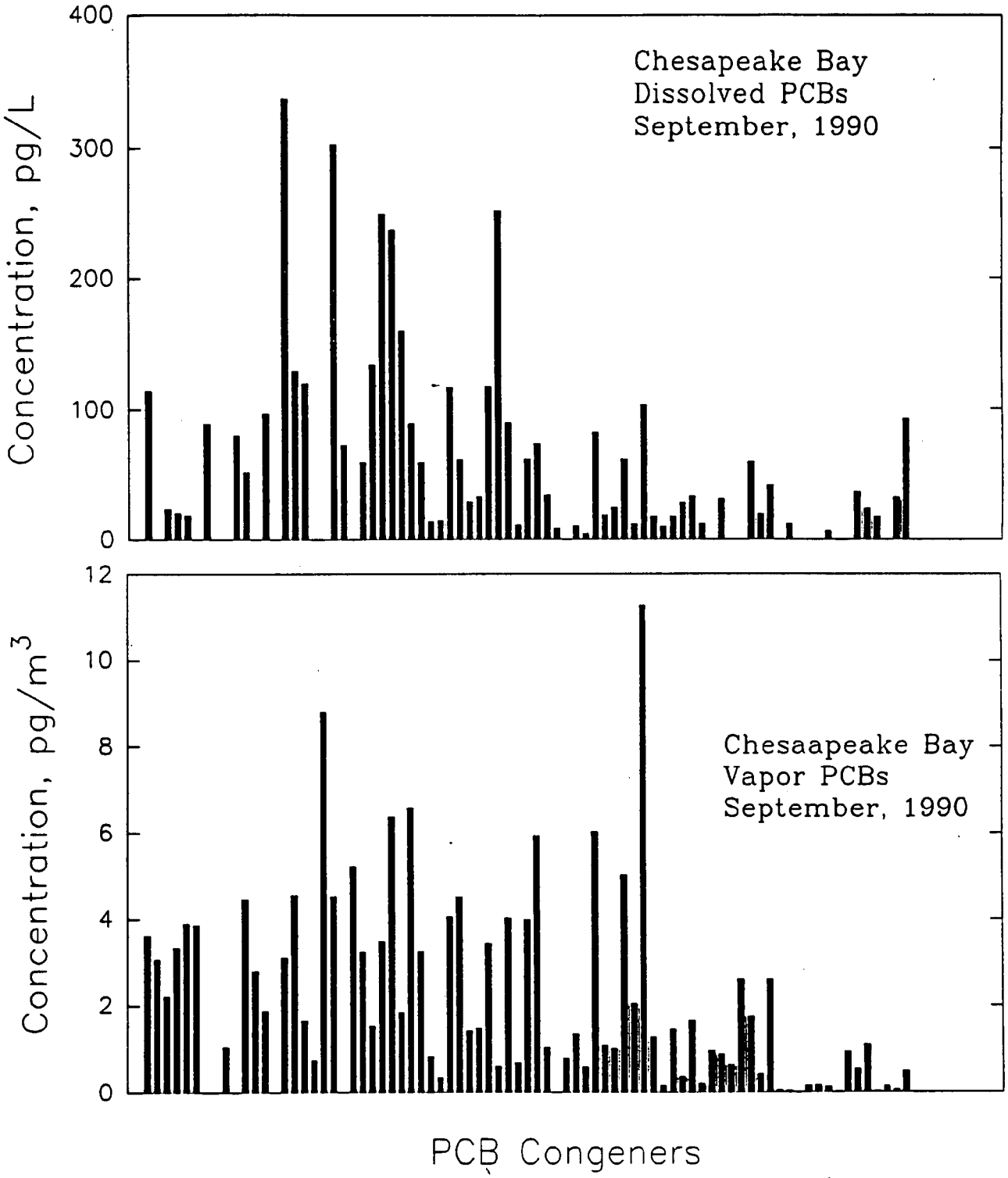
t-PCB (ng)

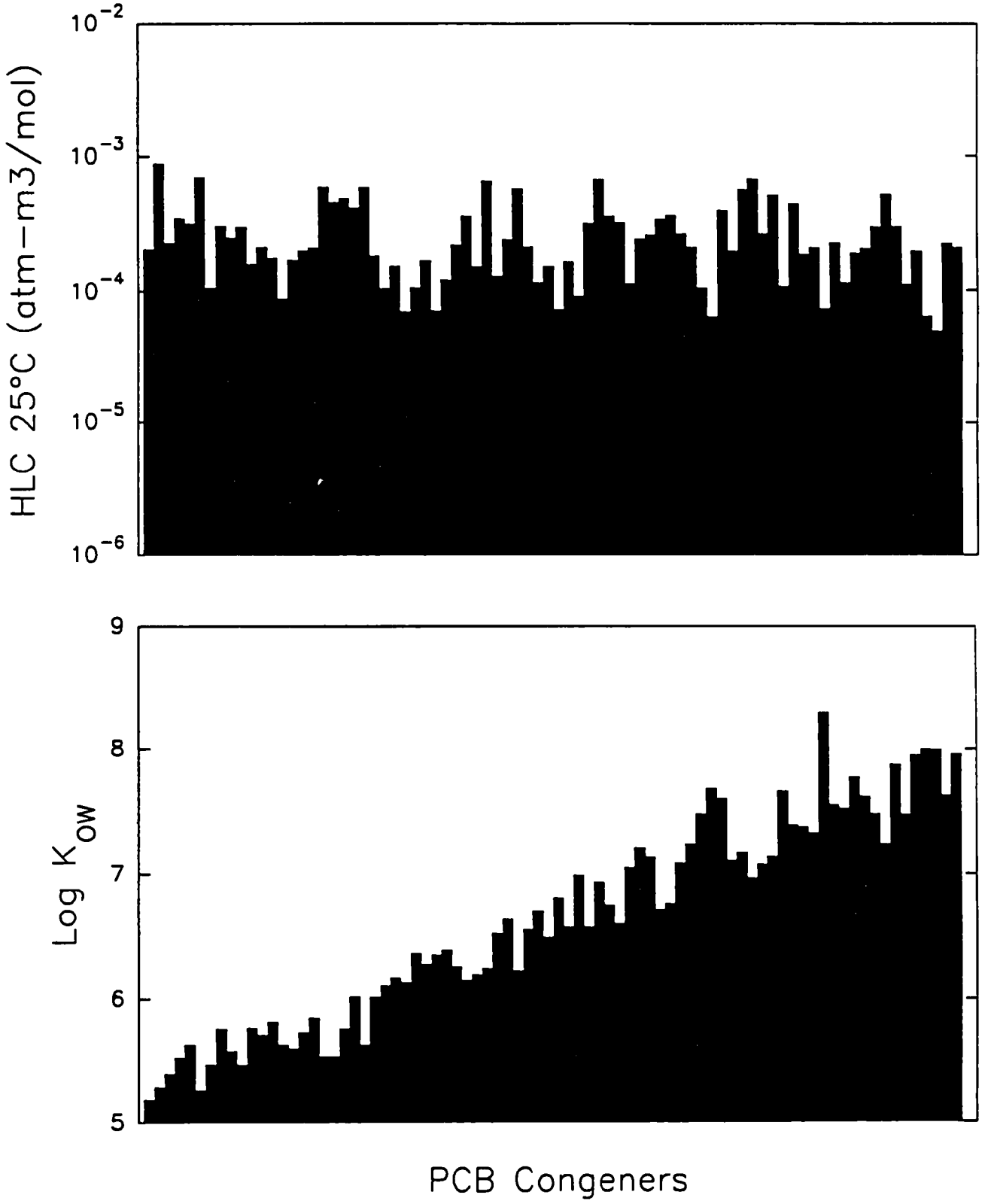
	EVENT(?)	WEEKLY(52)	MONTHLY(12)
0.2 m^2	4	5.8	25
1 m^2	20	29	125

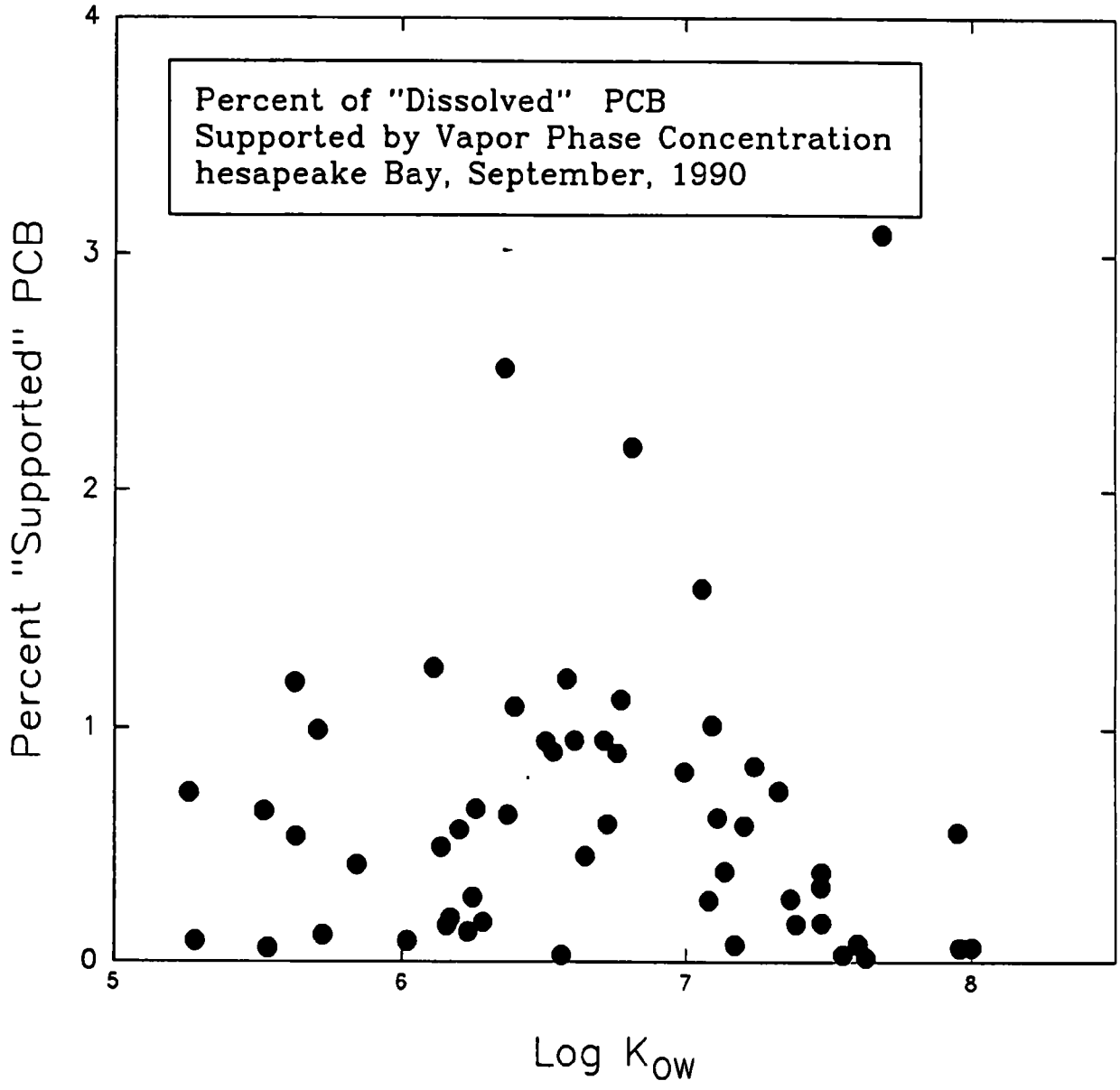
WET DEPOSITION MECHANISMS




Chesapeake Bay
September, 1990
PCBs in Precipitation
dissolved
particulate
Concentration, pg/L
3500
3000
2500
2000
1500
1000
500
0
PCB Congeners


Chesapeake Bay
Dissolved PCBs
September, 1990
Concentration, pg/L
400
300
200
100
0
Chesaapeake Bay
Vapor PCBs
September, 1990
Concentration, pg/m3
12
10
8
6
4
2
0
PCB Congeners


HLC 25°C (atm-m3/mol)
10-2
10-3
10-4
10-5
10-6
Log KOW
9
8
7
6
5
PCB Congeners


Percent of "Dissolved" PCB
Supported by Vapor Phase Concentration
hesapeake Bay, September, 1990
Percent "Supported" PCB
Log K_{OW}
0
1
2
3
4
5
6
7
8

Wet Deposition

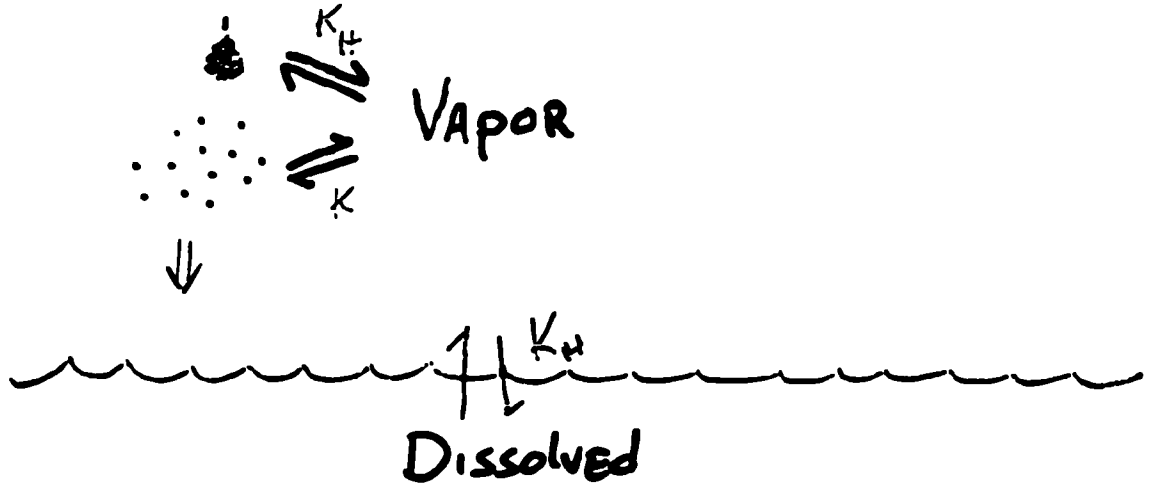
⇒ Measurements

1. Vapor absorption supports only <1-20% of PCBs, etc. in rain
2. Rain is enriched in more hydrophobic compounds relative to air.

Possible Scavenging Mechanisms

1. Efficient aerosol washout
2. Temperature-driven vapor absorption
3. Adsorption to droplet surfaces
4. Complexation by Organic Matter in droplets

Aerosol Washout by Precipitation



Pros: 1. Matches congener distributions in rain
2. Meteorological evidence

Cons: At system equilibrium (fast partitioning)
Aerosol washout does not
create a fugacity gradient;
∴ No "Bounce" & Large loadings
(Gross ≈ Net)

Submicron aerosols?

TEMPERATURE-DRIVEN DISEQUILIBRA

ENRICHMENT IN RAIN RESULTS FROM VAPOR (& AEROSOL) SCAVENGING AT LOW T

Settling rapid relative to WATER WARMING & degassing

PROS: 1. METEOROLOGICAL EVIDENCE

2. CREATES fugacity gradient ACROSS AIR-WATER INTERFACE

CONS: 1. REQUIRES slow kinetics (complexation?)

2. CONGENER profiles?

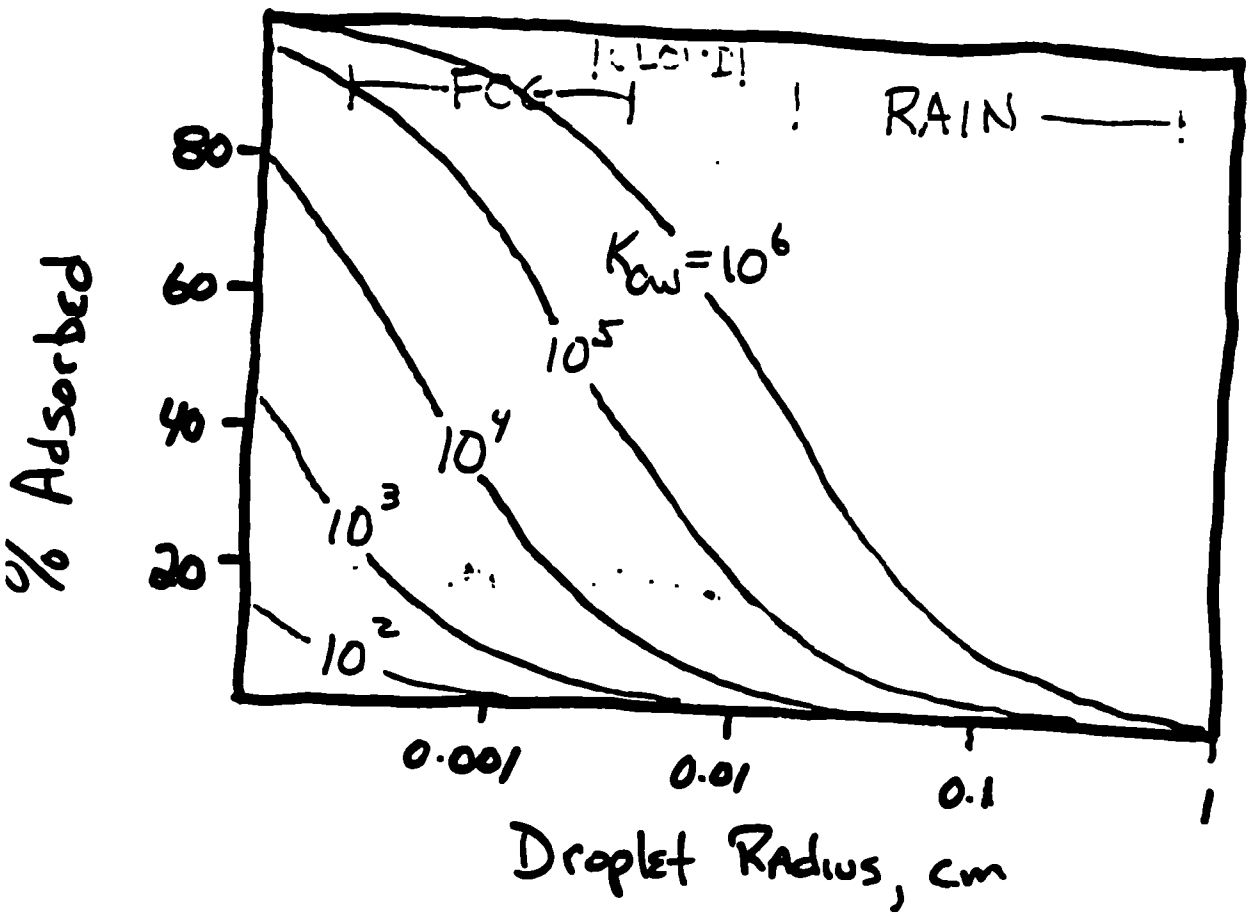
VERTICAL [ ] profiles?

Adsorption at the Air-Water Interface

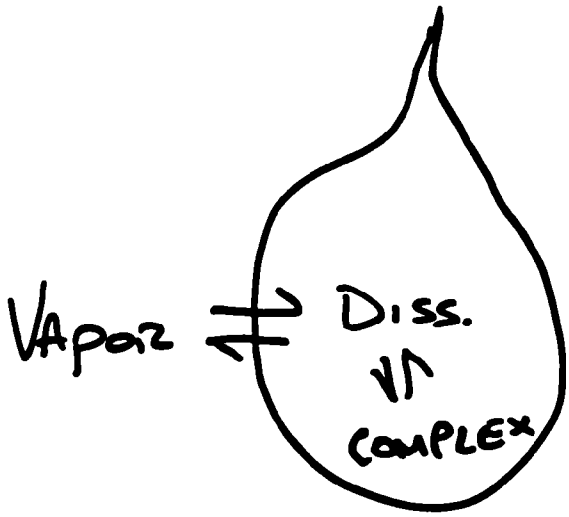
→ $K_a = \frac{\text{ADSORBED, mol/cm}^2}{\text{DISSOLVED, mol/cm}^3}$

→ $\text{Log } K_a = 0.71 \text{ Log } K_{ow} - 6.68$

(KRIGER ET AL, 1971-72)



Complexation By Organic Matter



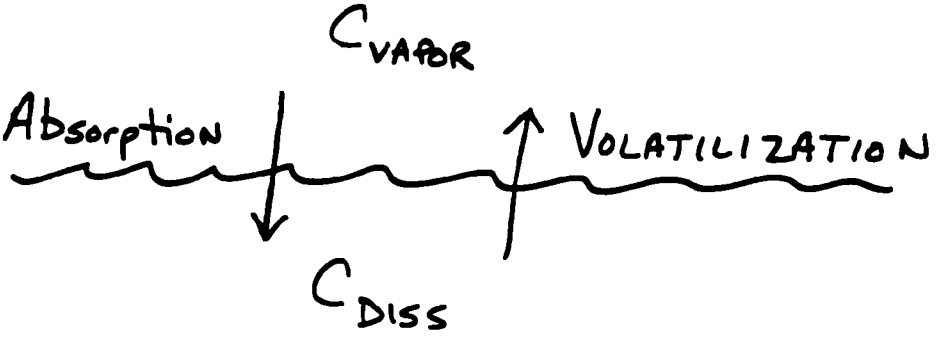
Evidence

1. High OC in fogwater
2. Surface films

Implications

1. Lability of complex?
2. Source of OM?

VAPOR EXCHANGE ACROSS THE AIR-WATER INTERFACE



$$F_V = \frac{K_{OL}}{M.T.C}\underbrace{\left(C_{DISS} - P_V/H\right)}_{GRADIENT}$$

$$\frac{1}{K_{OL}} = \underbrace{\frac{1}{k_l}}_{\substack{\text{Liquid}\\\text{Film}}} + \underbrace{\frac{RT}{H k_g}}_{\substack{\text{Gas}\\\text{Film}}}$$

"Two Film Resistance"

MACKAY & YEUN (1983)

$$k_g = 10^{-3} + 4.62\times10^{-2}\, U^* (Sc_g)^{-0.67}$$

$$k_l = 10^{-6} + 3.41\times10^{-3}\, U^* (Sc_l) \quad U^* > 0.3 \text{ m/s}$$
$$= 10^{-6} + 14.4\times10^{-3} (U^*)^{2.2} (Sc_l)^{-0.5} \quad U^* < 0.3 \text{ m/s}$$

Fluxes of PCBs Across the Air-Water Interface of the Great Lakes.

	ng/m² ·d	Reference
Volatilization	19	(1)
	15	(2)
	23	(3)
	63	(4)
Deposition	18	
Wet	10	(4)
Dry	8	(4)

1. Lake Superior, Baker and Eisenreich, 1989
2. Lake Michigan, Swackhamer and Armstrong, 1986
3. Siskiwit Lake, Swackhamer et al., 1988
4. Lake Superior, Strachan and Eisenreich, 1988

GREEN BAY (ACHMAN, Hornbuckle & Eisenreich)

	t-PCB (ng/m².d)	
Southern (4)	21-41	252-346
mid-Bay (18)	4-62	28-101
	STILL AIR	WIND ENHANCED

LIQUID-FILM MASS TRANSFER COEFFICIENT
(Liss and Merlivat, 1986)

$k_l = 0.17u$	$u < 3.6$ m/s	smooth surface
$k_l = 2.85u - 9.65$	3.6 m/s $< u < 13$	capillary waves
$k_l = 5.9u - 49.3$	$u > 13$	bubble breaking

$$\frac{k_{l(CO_2)}}{k_{l(PCB)}} = \frac{Sc^n_{(CO_2)}}{Sc^n_{(PCB)}}$$

TEMPERATURE INFLUENCES

- Henry's Law Constants

$$\log H = 7.91 - \frac{3414}{T}$$

Tateya, et al (1988)

- Vapor-Aerosol Distribution

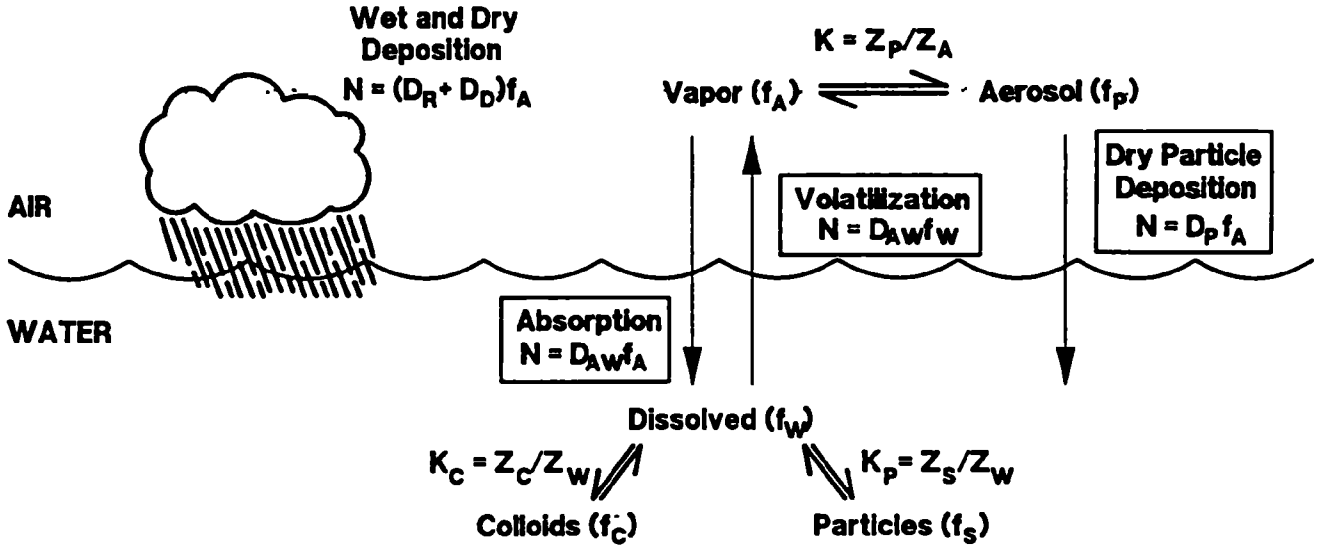
$$\log \frac{A(TSP)}{F} = \frac{-m}{T} + b$$

Bidleman and Foreman (1987)

m: 2755-5870
b: 14.3-22.8

- Mass Transfer Coefficient

$$D \propto T$$



Steady-State, Non-Equilibrium Exchange (Mackay et al., 1986)

→ Exchange is diffusive UP AND DOWN BUT Advective DOWN ONLY

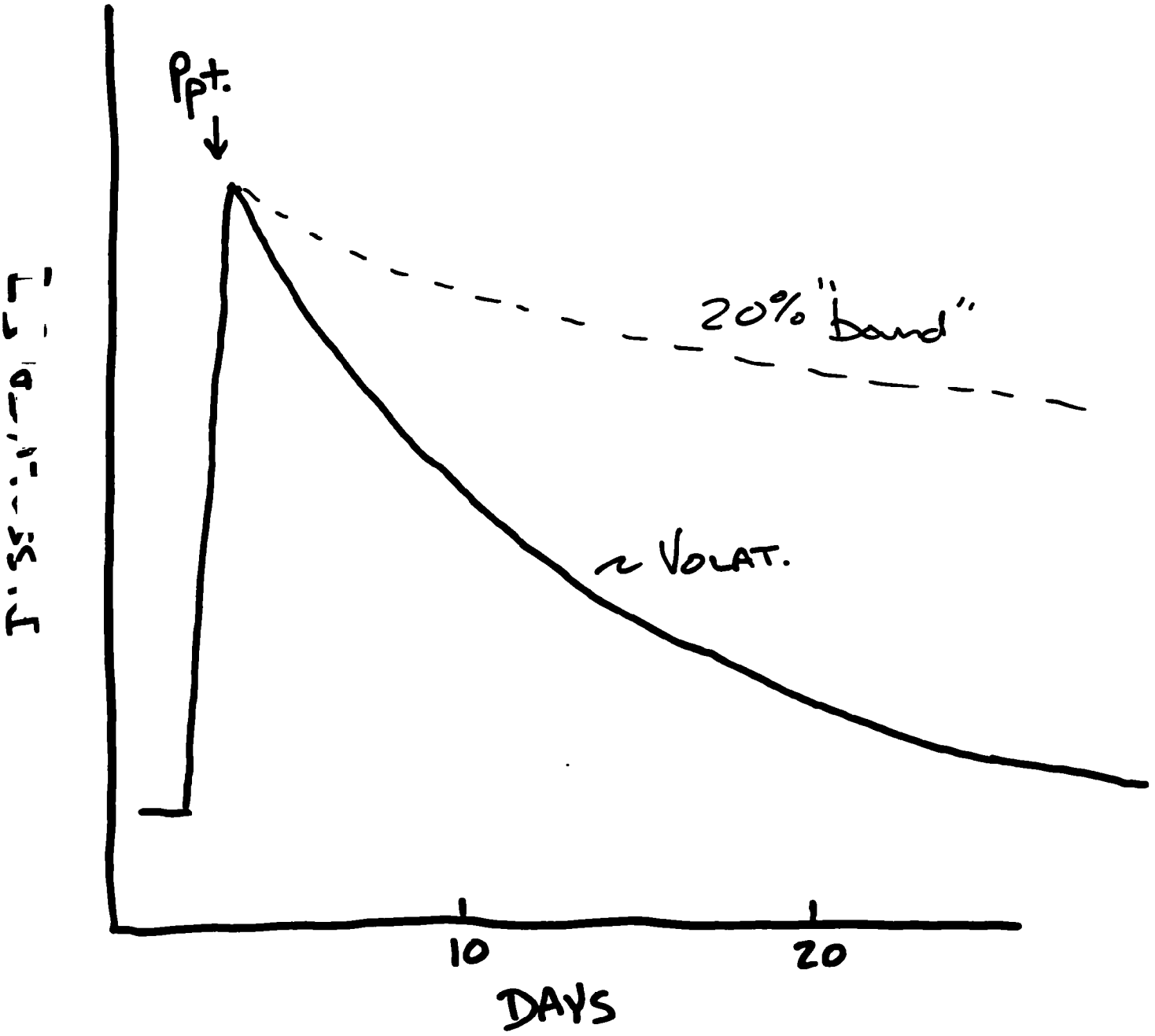
→ With no net flux (i.e. Steady State)

$$[D_{AW} + D_R + D_D + D_P]\, f_A = D_{AW} f_W$$

— TRANSPORT PARAM. - fugacity

$$f_W / f_A = \frac{D_{AW} + D_R + D_D + D_P}{D_{AW}} = 1 + \frac{D_R + D_D + D_P}{D_{AW}}$$

$f_W / f_A \geq 1$: Surface waters release PCBs to Atmosphere during dry periods



MTC
MIXING
TEMP - Hoff ET AL. 1992 Environ. Sci. Technol.
Speciation

Summary and Opportunities

1. Volatilization

- Good evidence for summer fluxes in Great Lakes
- Mass balance for PCBs requires volatilization to offset Deposition
- Seasonal fluxes?
- Improved dissolved measurements
- Mass transfer coefficients; wind, bubbles

2. Wet Deposition

- Reliable measurements of total gross flux
- Washout mechanism(s) unresolved
  - Speciation in rainfall
  - Incorporation of meteorology into models
  - Cloud/fog studies

3. Recommendations for L. Michigan

- Wet Deposition
  1. Monthly - integrated @ 2-3 remote sites
  2. Event-based "intensives" in urban areas.

- Mass Balance
  1. Gaseous Flux (LARGE? Uncertain!)
     - intensive field work (monitoring program)
     - coupled meteorology
  2. Speciation in Precipitation
     - scavenging mechanisms (RADM)
     - fate of deposited material

Consider the Whole Picture!

APPENDIX M

OVERVIEW OF PRESENT TRANSPORT/FATE, FOOD CHAIN MODELS FOR THE GREAT LAKES PRESENTATION

MR. WILLIAM RICHARDSON

DE

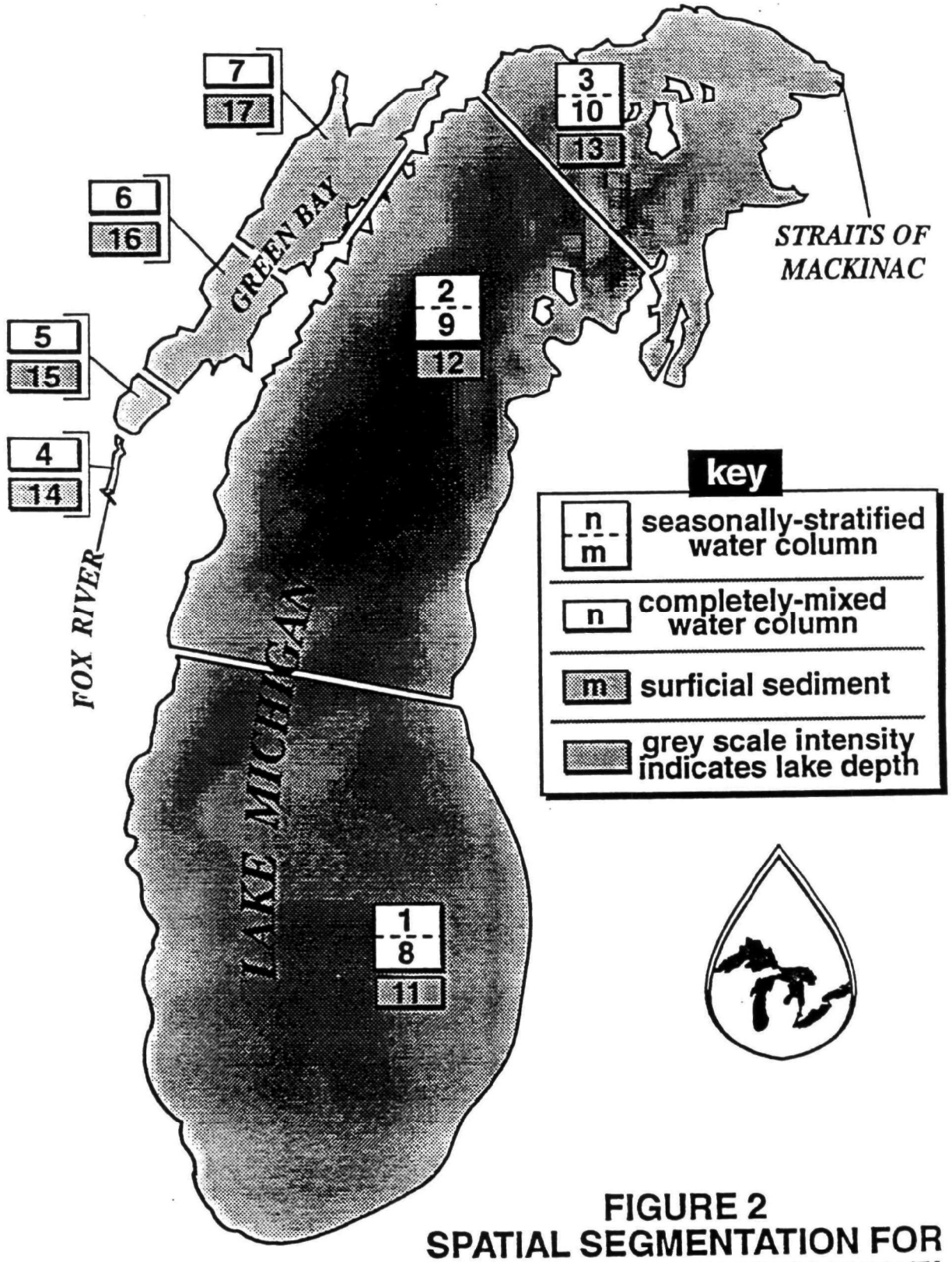
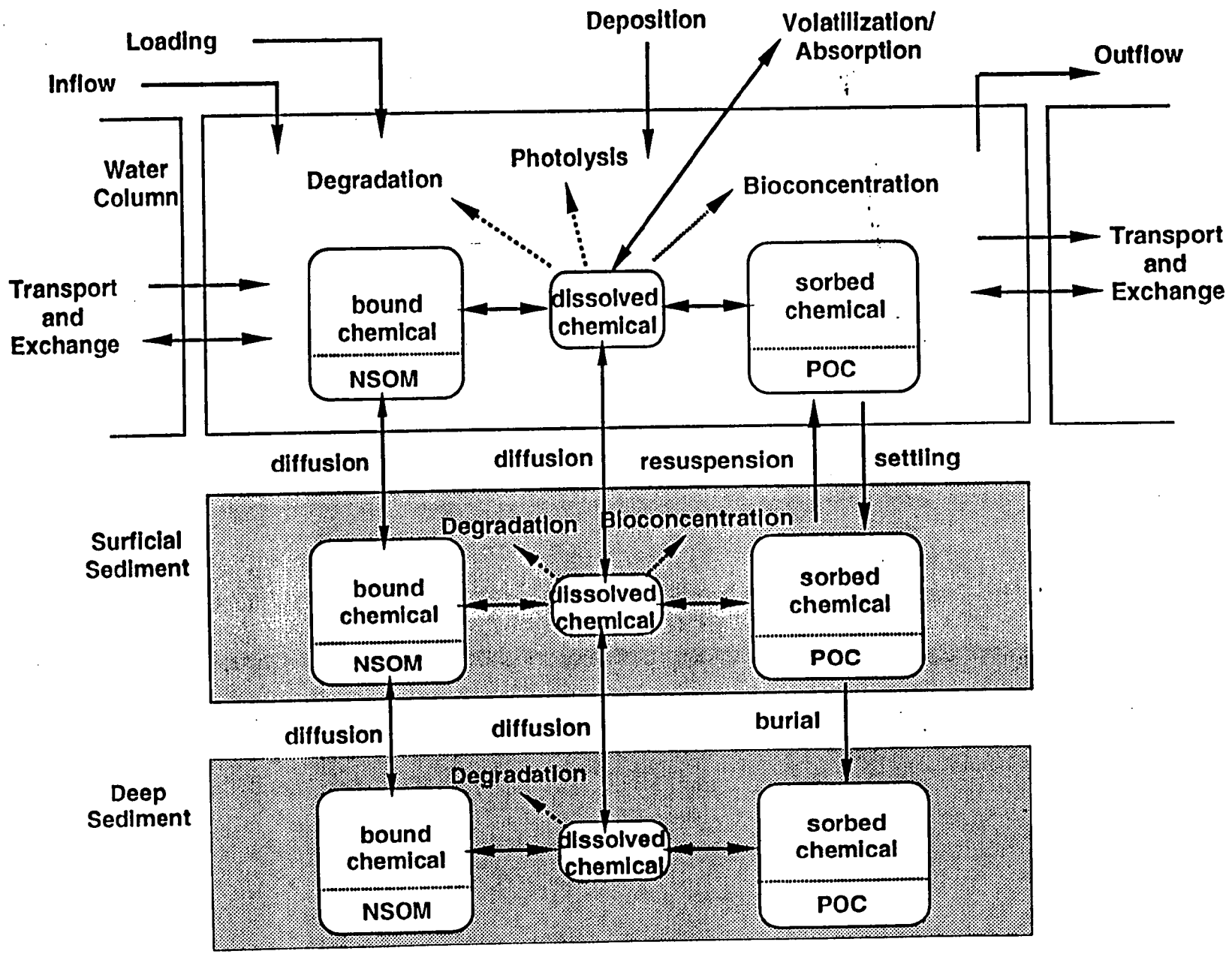


FIGURE 2
SPATIAL SEGMENTATION FOR 17-SEGMENT MICHTOX MODEL

Toxic Chemical Model Schematic

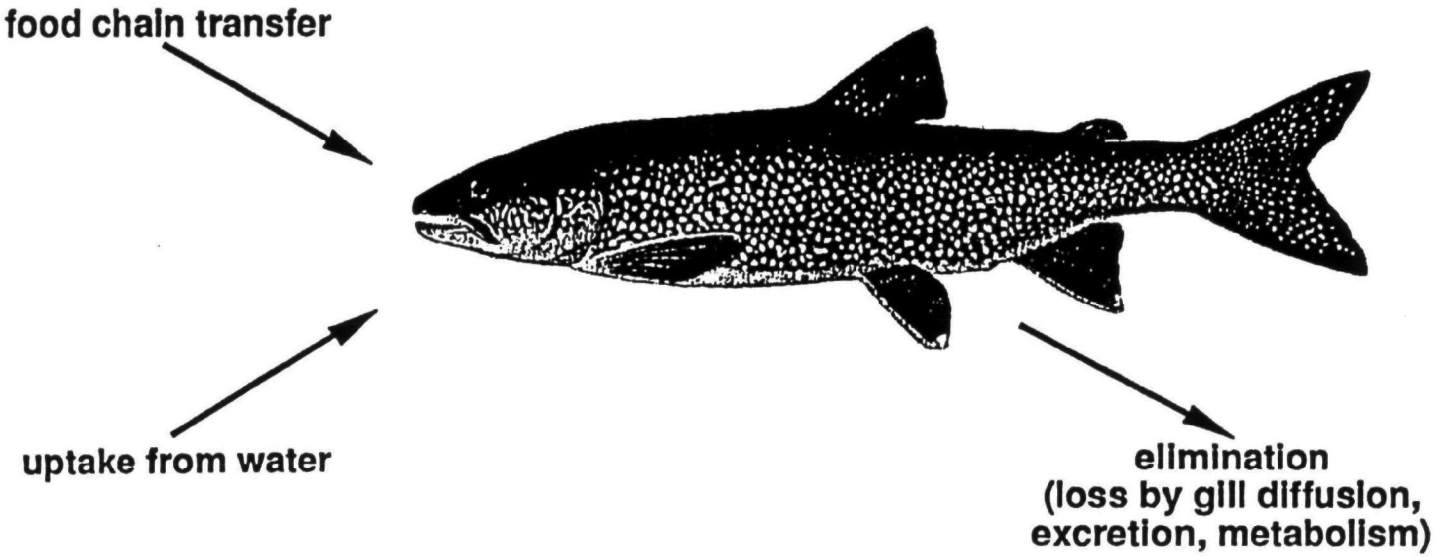


Lake Ontario (level 1) Toxics Model Parameters

water column volume
surficial sediment volume
air-water cross-section area
water-sediment cross-section area
outflow
suspended solids concentration
surficial sediment porosity
sediment particle density
settling flux
resuspension flux
deposition flux
sediment-water diffusive exchange coefficient
water column NSOM (non-settling organic matter)
sediment pore water NSOM
suspended solids foc
sedimented solids foc
octanol-water partition coefficient
organic carbon partition coefficient
water column NSOM binding coefficient
sediment NSOM binding coefficient
liquid film transfer coefficient
gas film transfer coefficient
henry's constant
transformation (photolysis) rate
load
dissolved oxygen concentration
phytoplankton BCF
lipid fraction (mysis, alewife and lake trout)
dry weight fraction (" ")
chemical assimilation efficiency (" ")
chemical transfer efficiency (" ")
food assimilation efficiency (" ")
growth rate (" ")
respiration rate (" ")

Total number of parameters = 48 (16 chemical-specific)

Bioaccumulation Model Processes

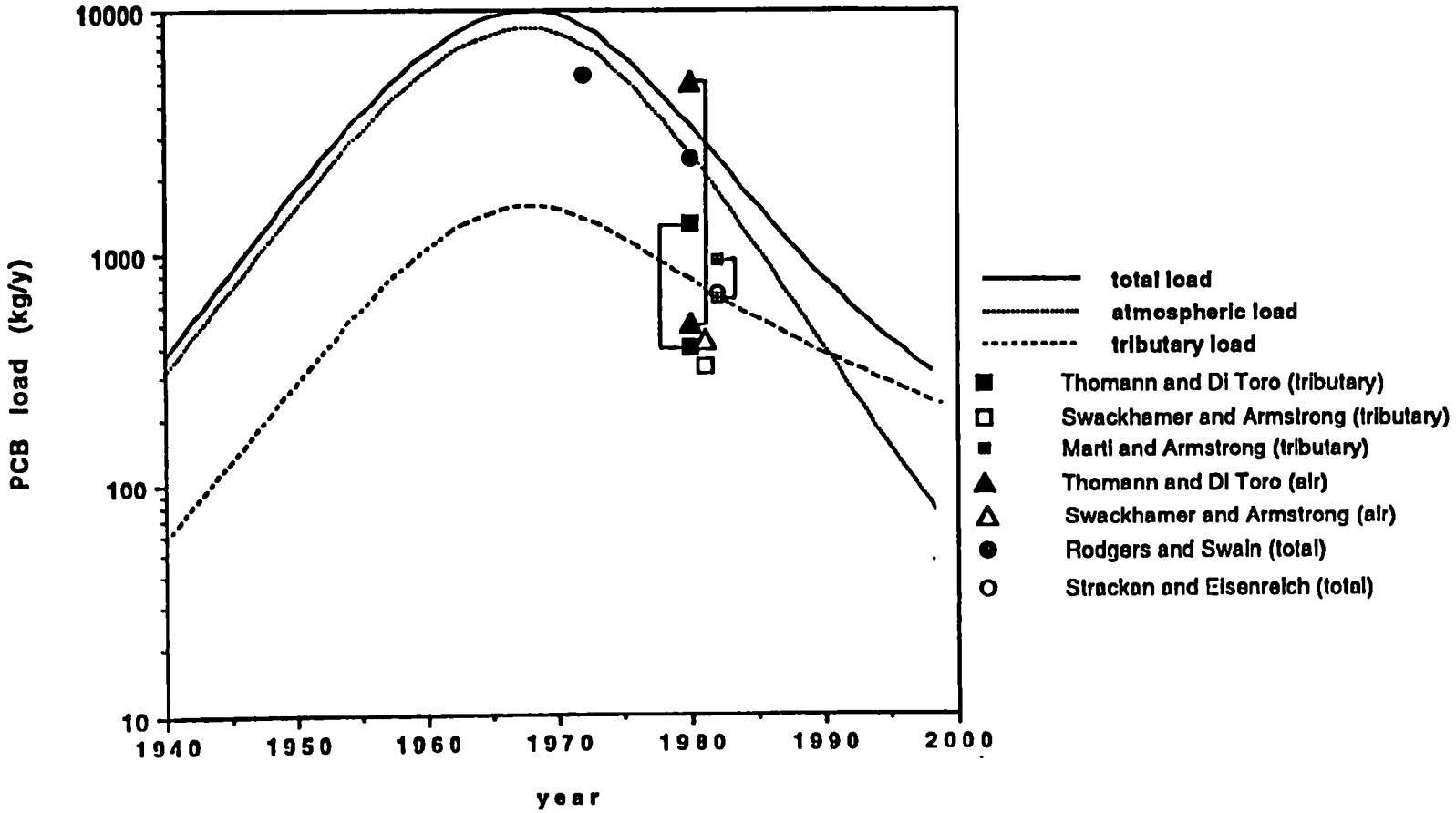


chemical mass balance in fish:

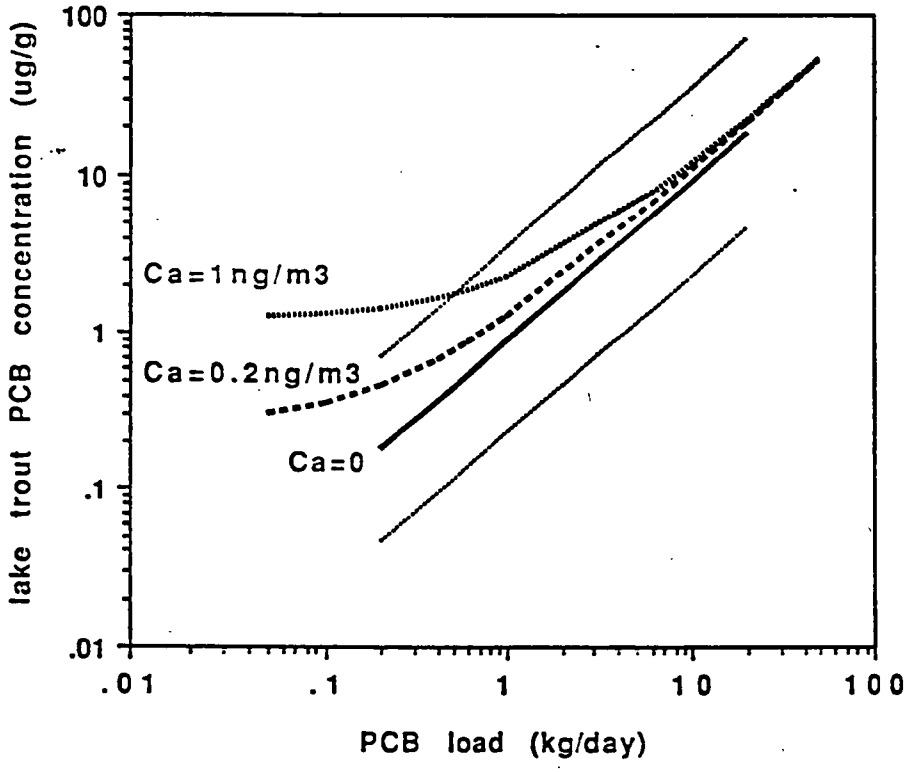
bioaccumulation	=	uptake from water	+	food chain transfer	-	elimination

Lake Trout
1 - 2
3 - 12
Bloater
1
2 - 4
5 - 7
Diporeia spp.
1
2
3
Mysids
1 - 2
3
4
Detritus
Phytoplankton

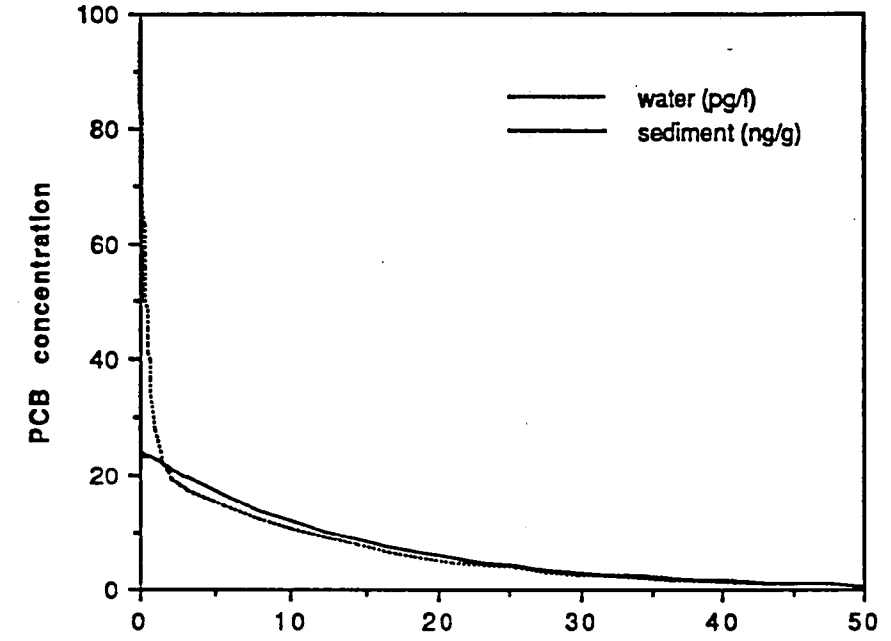
PCB loading time function used in MICHTOX and reported PCB load estimates



Load-Concentration Relationships for PCBs in Lake Ontario lake trout Sensitivity to PCB Air Concentration (Ca)



Lake Ontario model response to PCB loading cutoff



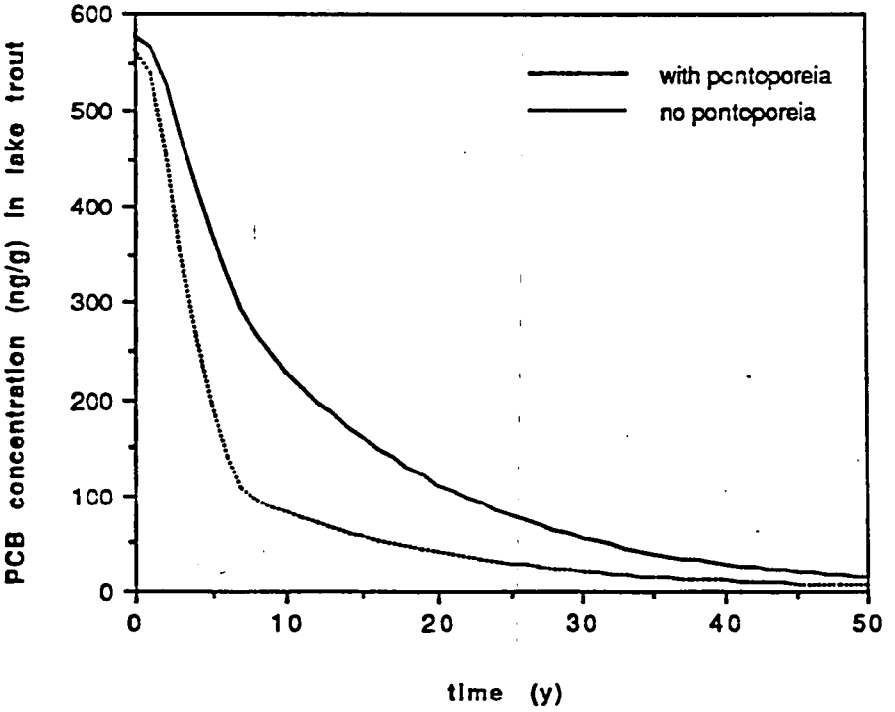


Figure 24. **Sources of Uncertainty in Lake Trout Concentration Predictions**
(Lake Ontario)

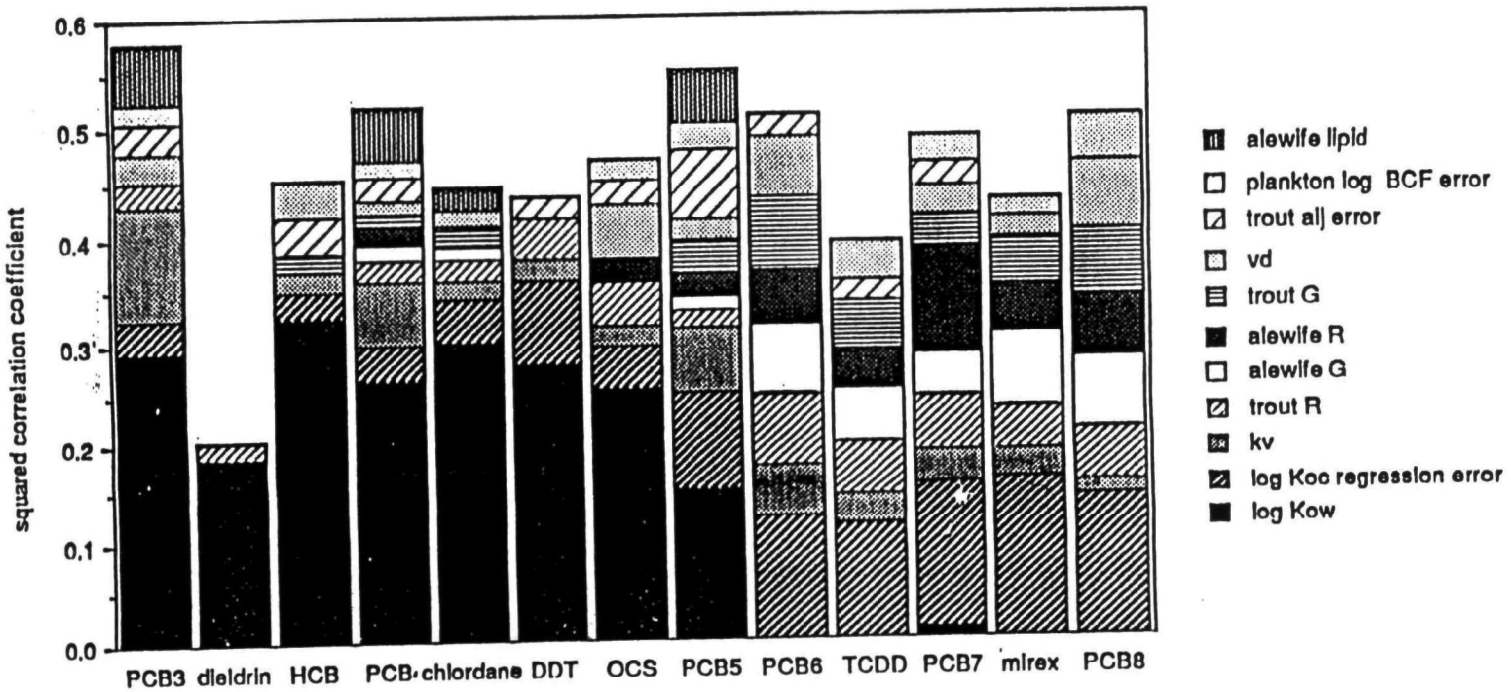


Figure 20. Results of Monte Carlo Analysis for Lake Ontario Toxics

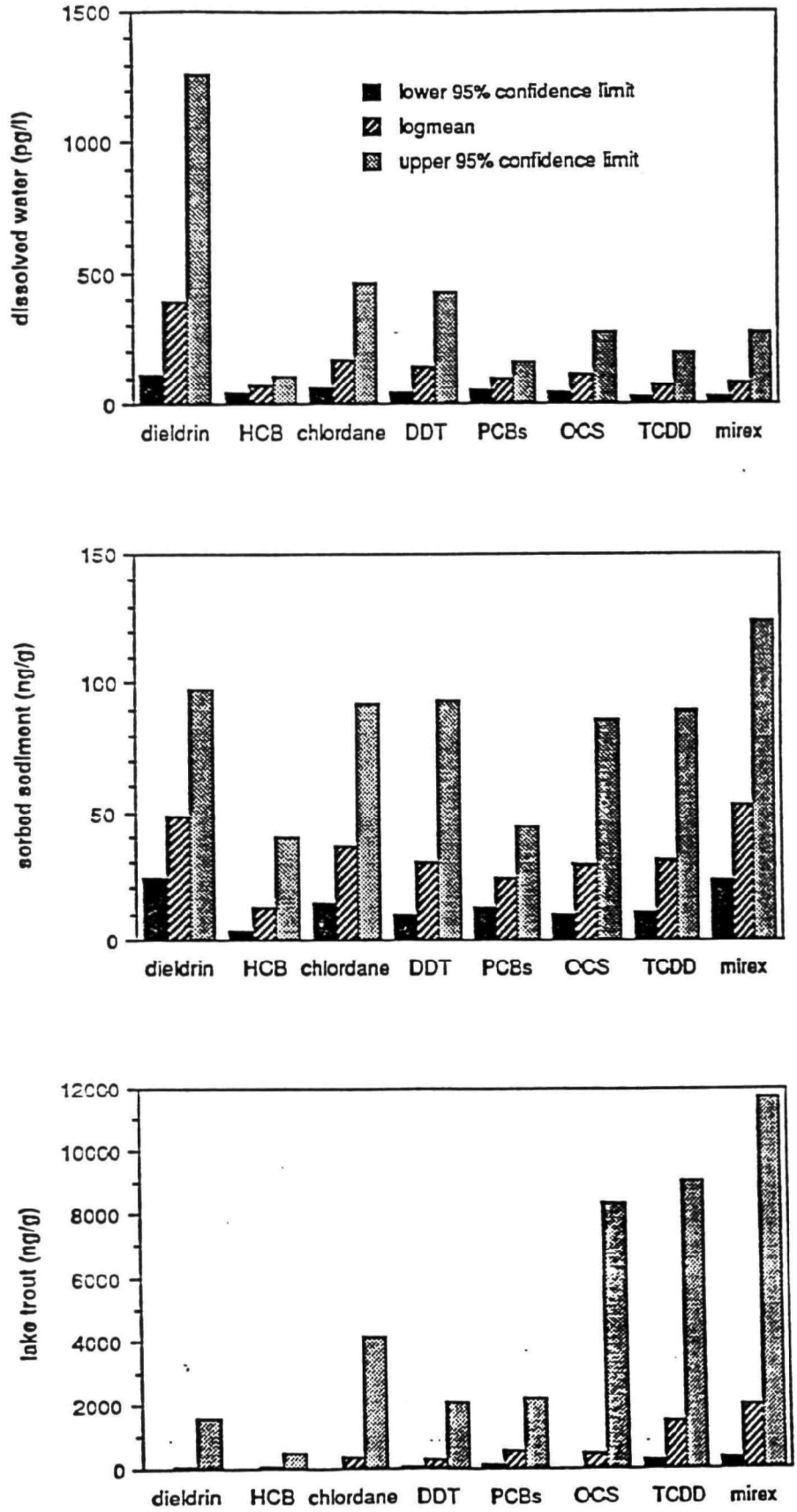
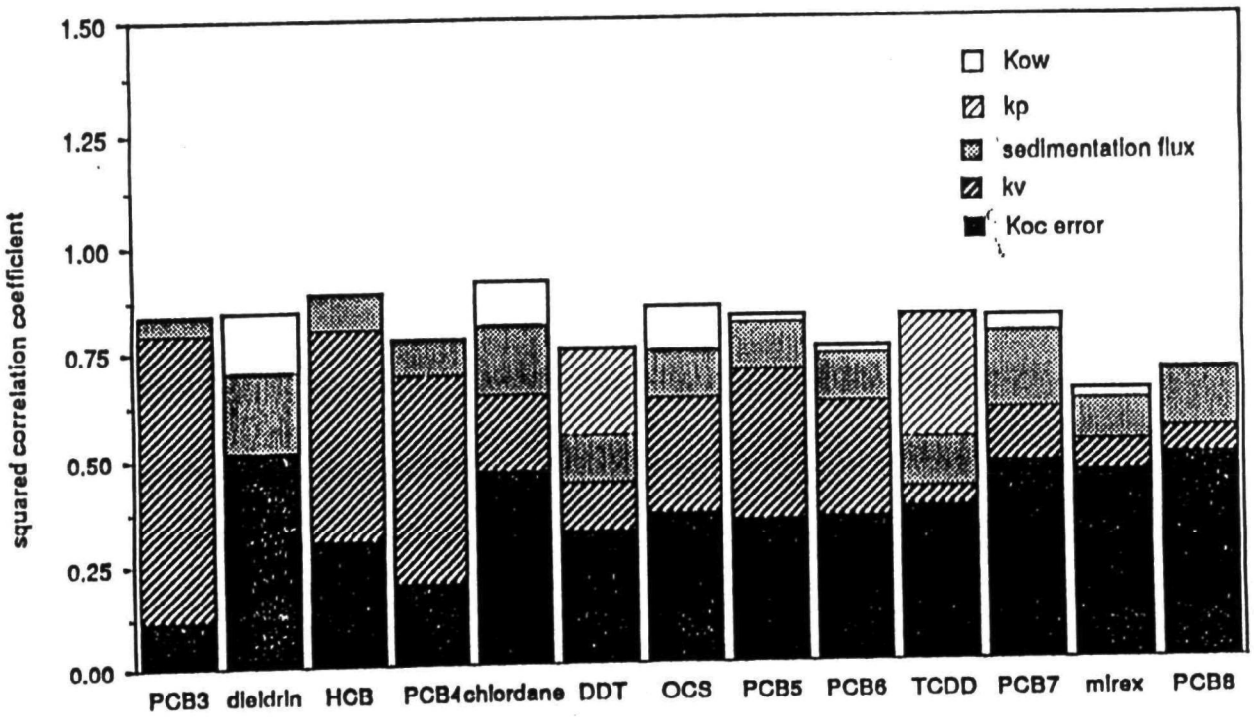
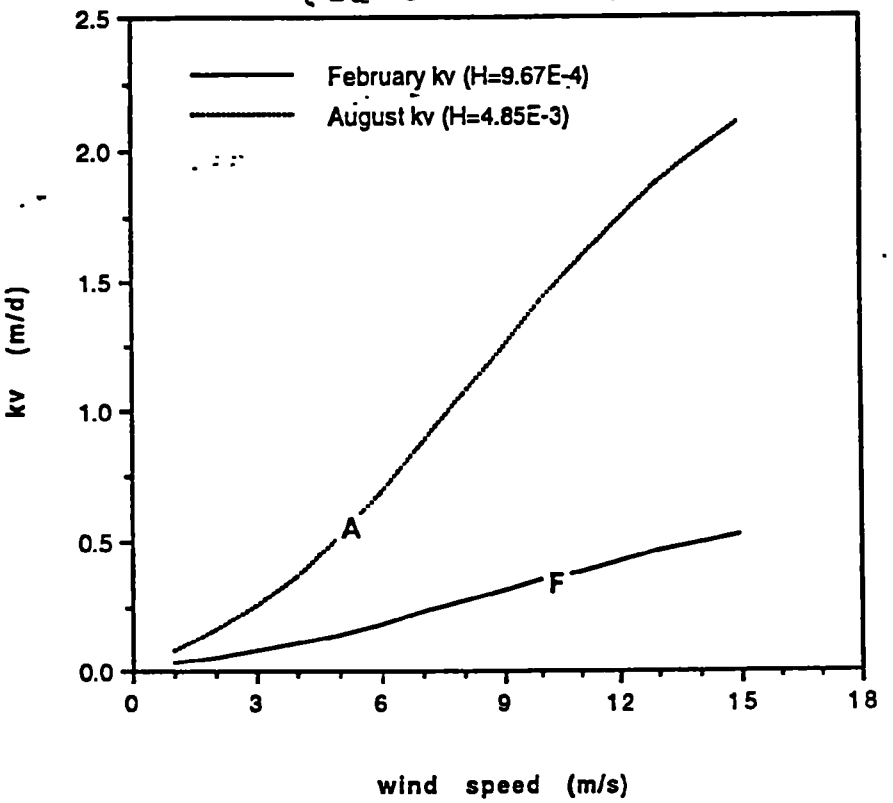


Figure 23. Sources of Uncertainty in Water Concentration Predictions
(Lake Ontario)



Sensitivity of Computed Volatilization Rate to Wind and Temperature

(Lake Ontario)



APPENDIX N

PRELIMINARY OBJECTIVES FOR LAKE MICHIGAN MASS-BALANCE MODEL

PRESENTATION

MR. DAVID DEVAULT

LAKE MICHIGAN

Mass Balance

WHAT IS IT?

INPUT - ACCUMULATION - CONSUMPTION = OUTPUT

N-3

PARAMETERS and TARGETS

Target Parameters:

PCBs
Trans Nonachlor
Dieldrin
Lead

Target Fish:

Lake Trout
Coho Salmon
Bloater Chubs

WHAT DO WE GET?

- Mass Budget Quantifying Sources and Sinks of Contaminants.

- Fully Calibrated Model Predicting Concentrations in Fish From Loadings. This will allow:

  1. Prediction of Environmental Response to Regulatory/ Remedial Activities.

  2. Reduction in Future Monitoring Efforts.

- Coordination and Focusing of research and Monitoring Activities of Several Govermental and Academic Institutions.

POSSIBLE APPROACH

USE CALIBRATED MODEL DEVELOPED FOR GREEN BAY

FOCUS 1992 DATA COLLECTION ON:

- Loadings
- Process Rates
- Relativly Small ~~Verification~~ Calibration Data Set for Open Lake

CONTAMINANT MASS and LOADINGS WILL BE MEASURED IN

- Lake Water
- Bottom Sediments
- Atmosphere
- Phytoplankton
- Forage Fish
- Tributaries
- Suspended Sediments
- Nonpoint Sources
- Zooplankton
- Target Fish

LAKE MICHIGAN MASS BALANCE

WORK PLAN

D. De Vault and J. Giattina, Co-chairs
Lake Michigan Mass Balance Technical Coordinating Committee

DRAFT - APRIL 24, 1991

Study Purpose

Significant progress has been made on control and reduction of pollution in the Great Lakes. However, accumulation of toxic substances remains a serious problem in each of the lakes, as well as, in many of the 28 areas of concern. In 1983, the Water Quality Board reported to the IJC that 900 chemicals and heavy metals, potentially dangerous to human health and the biota, have been identified in the Great Lakes.

Concern about the potential effects of these chemicals has increased with growing evidence of links between the presence of contaminants and carcinogenicity in fish, genetic defects in fish eating birds, and reproductive disorders in biota. Further, possible links have been reported between developmental disorders in human infants and prenatal exposure to contaminants through consumption of certain Great Lakes fish by their mothers.

Traditionally, the management of water quality has focused on control of direct releases of pollutants. Such sources were the easiest to identify, characterize and control. The regulatory laws to control sources of pollutants are media specific with air, water and land as separate, compartmentalized media. For these reasons, restoration and maintenance of water quality were largely tied to control of point sources from which contaminants were discharged directly into the nations waterways.

With recognition that pollutants are also introduced indirectly from contaminated air, soil and sediments, the entire approach to management of Great Lakes water quality had to be reassessed. The reassessment led to the conclusion that adequate management of contaminants requires that the total contribution of pollutants from all media be quantified and a mass balance approach be employed. This approach was successfully applied to the regulation of nutrient loadings during the past decade.

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 prioritization, allocation of resources 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 budget has been established for each pollutant of concern, the long term effects on water quality can be simulated by mathematical modeling. The model will provide water quality managers the ability to evaluate the impact (at various levels of the ecosystem) of potential regulatory or remedial actions, and to determine the reductions in amount and types of loadings that will result in criteria being met.

Study Goal

In Green Bay, a modeling and monitoring framework was established and tested to provide greater understanding of the sources, transport and fate of toxic substances and to ultimately guide and support regulatory activity. In Lake Michigan the lessons learned on Green Bay will be employed on a whole lake basis to develop mathematical models and monitoring tools to predict the response of Lake Michigan and Lake Michigan fish to proposed regulatory actions. To accomplish this goal, the transfer of contaminants from sources to important fish species will

be modeled. To allow predictive capacity able to cope with the complex interactions occurring in the environment the toxicant model will be coupled with existing nutrient and solids models. Due to the high analytical costs associated with development of a calibration data base for contaminants, compounds which are themselves problematic and are representative of larger groups of compounds have been selected for modeling.

Parameters to be modeled are:

- PCB congeners (all for nonplanar, subset for planer)
- Dieldrin
- Trans Nonachlor
- Lead

Additional parameters required for model calibration include:

- Organic Carbon (dissolved and particulate)
- Nutrients (P,N,Si)
- Chlorophyll
- Alkalinity
- Water Temperature
- Suspended Solids
- pH
- Conductivity
- Dissolved Oxygen
- Chloride
- Incident Light
- Wind Speed and Direction
- Length, Weight, Age of Target Fish

The model will predict concentrations of target chemicals in whole Lake Michigan fish. The species chosen are important to the Lake Michigan sport or commercial fisheries and represent differing exposure routes and histories. They include:

- Lake Trout
- Coho Salmon
- Bloater Chubs

(Additional biota and forge species will be analyzed to support the food chain model)

It is anticipated that a fully calibrated toxicant model will be produced. To accomplish this, the mass of target contaminants will be monitored in each significant environmental compartment and, to the extent possible the rates of contaminant exchange between compartments. Monitoring

and research efforts will be directed at measuring target contaminant mass in and exchange between:

- Lake Water (dissolved and particulate phases)
- Tributary Loadings (dissolved and particulate phases)
- Bottom Sediments (multiple layers, mass, loadings, and sedimentation rates)
- Suspended Sediments
- Atmospheric Loadings (wet and dry participation, gas phase fluxes both into and out of the lake)
- Significant Nonpoint Loadings
- Phytoplankton
- Zooplankton
- Forage Fish
- Target Fish Species

The modeling effort will focus on Lake Michigan with the Green Bay interface treated as a source function. As a result the majority of the calibration data base will be collected from Lake Michigan and tributaries to Lake Michigan. To the extent possible, tributaries will be considered as point sources to the Lake. Limited sampling in Green Bay may be required to characterize the Bay-Lake exchange for compounds not included in the Green Bay Mass Balance Study.

Data Quality Objective and Quality Assurance

The final data quality objectives (DQO) can not be developed until detailed the study planning is underway. However, the study will be designed to produce a final modeling output that produces predictions accurate to within a factor of five. This will allow the use of modeling output to make risk assessment based management decisions. As modern risk assessment is accurate to no better than a factor of ten, we believe that modeling output accurate to a factor of five is sufficient.

Because of the extremely low concentrations of organic and metal contaminants in the waters of Lake Michigan, tributaries, and the atmosphere, and of the necessity for an internally consistent data base across several media and laboratories, very stringent quality assurance procedures will be required. The following approach will be used to achieve this.

An independent Lake Michigan Mass Balance Quality Assurance Coordinator will be appointed. This individual will be a highly respected , recognized expert in trace level analysis, and interpretation, of organic contaminants in environmental media. The individual will not be an employee of an agency or laboratory participating in routine data collection. The responsibilities of this individual will include:

- Preparation of a generic "Mass Balance Quality Assurance Management Plan" in conjunction with the Sampling and Analysis Committee (see section VII). This

document will describe the minimum QA requirements such as blanks, duplicates, spikes and detection limits (both analytical and environmental) for the study, as well as, procedures for identification, quantitation, surrogate correction etc for organic and metal contaminants. Each participating laboratory and principal investigator will formally agree to follow the procedures outlined in this document.

- Conducting a laboratory round robin and certifying laboratory performance on round robin samples prior to actual sample analysis.

- Trouble shooting analytical problems at participating laboratories and, if problems can not be solved, recommending appropriate actions (including that a laboratory be dropped from the study) to the Technical Coordinating Committee.

- Review and approve organics, metals, solids, and carbon data bases prior to their inclusion in the study data base and release to modelers or others.

In addition to the above, each participating organization will be required to prepare and follow a Quality Assurance Project Plan (QAPP) specific to their activities. This QAPP will be approved by the Project Officer, Region V Quality Assurance Office and Lake Michigan Mass Balance Quality Assurance Coordinator prior to collection or analysis of samples.

Organization and Study Management

A Three level management structure will be employed.

Management Committee:

Decision makers in organizations with responsibilities for water quality monitoring and management in the Lake Michigan watershed. To assure consistency with the Lake Michigan Lake Wide Management Plan (LaMP), which the model will support, the Mass Balance Management Committee will be synonymous with the Lake Michigan LaMP Management Committee.

Responsibilities: Approval of final study plan (including compounds to be modeled and level of model accuracy), commitment of resources to conduct necessary planning, monitoring and modeling activities.

Technical Coordinating Committee:

Chairs of the Technical Committees, Study Quality Assurance Coordinator and selected technical experts.

Responsibilities: Preparation of the Study Plan, recommendation of funding commitments to the Management Committee, study coordination and resolution of technical conflicts.

Technical Committees:

Several technical committees, as outlined below, will be required for study planning and design. It is anticipated that the majority of the technical committee activity will occur during the planning stages. Once the Study Plan and the Mass Balance Quality Assurance Plans are completed, and the individual components of the study are funded and underway, the study will be managed by the Technical Coordinating Committee with Technical Committees being consulted as necessary.

- Modeling Committee (MC) - Government and funded academic modelers.

  Responsibilities: Development of Modeling Plan, identification of modeling data needs.

- Sampling and Analysis Committee (SAC) - Mass Balance Quality Assurance Coordinator (Chair), EPA Region V Quality Assurance Office, and leads from participating analytical laboratories.

  Responsibilities: Preparation of Mass Balance Quality Assurance Management Plan. Decisions and recommendations on analytical methods, practicality of parameter list, sample collection, extraction and analytical methods.

- Biota Committee (BC) - lead fisheries and biological staff from participating organizations.

  Responsibilities: In cooperation with SAC and MC prepare biological sampling Plan.

- Tributary Loadings Committee(TLC) - Lead state, federal, and university staff with tributary monitoring expertise.

  Responsibilities: In cooperation with MC and SAC develop tributary monitoring plan.

- Atmospheric Loadings Committee - Lead State, Federal and University staff with expertise in atmospheric loading estimation.

Responsibilities: In cooperation with MC and SAC Prepare atmospheric monitoring/modeling plan to provide atmospheric fluxes as defined by the modeling committee.

Critical (Fast Track) Planning Activities

Successful completion of the Lake Michigan Mass Balance Study will require the cooperation and coordination of several Federal Agencies and offices, multiple agencies and offices from the Lake Michigan States, as well as, universities and contractors. This coupled with the high cost involved with collection and analysis of trace level organics samples argues for substantial up front planning. The above described committee structure is designed to conduct the majority of this planning and to produce the final study plan. However, the compressed time schedule in effect for the Lake Michigan study requires the some planning activities begin prior to full implementation of the committee process. These include:

- Formation of Modeling Committee and begin planning.
- Evaluation of existing data on fish and sediments to develop a preliminary list of tributaries for load monitoring.
- Evaluation of existing open lake data for contaminants or surrogate compounds to determine numbers and locations of stations, and number and timing of surveys required to describe open lake conditions at differing levels of accuracy.
- Fund the Mass Balance Quality Assurance Coordinator and begin preparations for the analytical laboratory round robin.
- Determine number of atmospheric monitoring stations required and select sites and sampling methods.
- Fund study for determination of short range urban atmospheric loadings.

Major Work Activities

March 1991:
1. Prepare draft Work Plan
2. Decisions on FY91 planning activities
3. Evaluate existing tributary mouth data.

April-May 1991:
1. Establish Management and Technical Committees.
2. Management Committee agrees on

	parameter list and level of modeling. 3. Fund FY91 projects. 4. Technical Committees meet/planning begins.
June-July 1991	1. Planning continues.
Aug.-Sept. 1991	1. Modeling Com. identifies data requirements.
Oct.-Dec. 1991	1. Draft Study Plan Complete. 2. Draft Quality Assurance Management Plan complete. 3. Train tributary monitoring teams/ field shake down. 4. Atmospheric sites constructed. 5. Lab QA evaluation underway. 6. Sampling shakedown for open water.
Jan.-Feb. 1992	1. Final Study Plan Complete. 2. Supply procurement continues. 3. Funding complete for grants/contracts. 4. Atmospheric sites fully operational. 5. Final Quality Assurance Management Plan complete.
Mar.-April 1992	1. Begin Field season.
May-Dec. 1992	1. Continue field work. 2. Sample analysis underway.
Jan.-Mar. 1993	1. Sample analysis continues 2. Winter survey(if required) 3. Atmospheric and tributary monitoring continues
April-May 1993	1. Final spring survey (if required) 2. Sample analysis continues

Major Products

1. Work Plan	draft	March 91
	final	April 91
2. Quality Assurance Management Plan	draft	Oct 91
	final	Jan 92
3. Study Plan	draft	Oct 91
	final	Jan 92
4. Sampling SOPs	draft	Dec 91
	final	Feb 92
5. Initial mass budget		Dec 93
6. Final Report		Dec 94

Relationship to Other Lake Michigan and Great Lakes Activities

There are several monitoring and planning activities underway on Lake Michigan and the other Great Lakes. In order to avoid competition between these activities, we are taking this opportunity to present our vision of how the Lake Michigan Mass Balance Study, the Lake Michigan LaMP, and the Great Lakes Monitoring Review complement each other.

Monitoring Review

The Great Lakes Monitoring Review is a review and revision of Great Lakes monitoring activities to address specific management questions identified by Great Lakes water quality managers. Among the questions identified are several relating to loadings and ambient conditions. Thus it is likely that the programs developed will provide loadings from at least generalized (tributaries, atmosphere) sources, as well as, possibly, processes for determining specific sources.

Lake Michigan LaMP

The Lake Michigan LaMP is an action oriented effort that will, among other activities, describe a program to monitor loads, ambient conditions, locate sources, and devise and implement load reduction programs. Because of the action orientation of the LaMP, it is likely that the monitoring program will include a process to locate and quantify specific sources once a generalized source (tributary, atmospheric etc.) has been identified.

Mass Balance

The Lake Michigan Mass Balance will result in a one year intense effort to monitor loads and ambient concentrations with a very high level of accuracy. This data base will then be used to calibrate toxic chemical models for Lake Michigan. This effort will, to the extent possible, consider tributaries as point sources. Thus, limited effort will be expended on location or quantification of specific sources to tributaries or the atmosphere. However, the estimates of ambient concentrations, tributary and atmospheric loads will probably be much more precise than those required for either of the above (longer term) monitoring efforts.

The Management Questions that the Great Lakes Monitoring Review will address are those identified by Great Lakes water quality managers, including those involved in the LaMP process. The programs developed through the review should, therefore, meet most, if not all, of the LaMP monitoring requirements. The Mass Balance Study will, through intensive monitoring, provide actual data that may be used to design longer term monitoring efforts so that the desired level of precision is achieved without costly over-sampling. The development of calibrated models for Lake Michigan will further reduce the amount of sampling required for known contaminants, allowing more resources to be directed at locating specific sources and identifying and preventing future problems. Through the involvement of State and other Federal agencies, the Mass Balance will also provide an arena for transferring monitoring technology and assuring comparable collection and analytical methods in four of the Great Lakes states.