Summary: A Plan for Assessing Atmospheric Deposition to the Great Lakes

Surveillance Work Group. Atmospheric Deposition Monitoring Task Force

International Joint Commission. Great Lakes Regional Office

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Report to the
Great Lakes Water Quality Board

Summary

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A Plan for Assessing Atmospheric Deposition to the Great Lakes

by the
Atmospheric Deposition Monitoring Task Force of the
Surveillance Work Group

International Joint Commission
Great Lakes Regional Office
Windsor, Ontario
July 1988
This report to the Water Quality Board was carried out as part of the activities of the Atmospheric Deposition Monitoring Task Force of the Surveillance Work Group. While the Board supported this work, the specific conclusions and/or recommendations do not necessarily represent the views or policies of the International Joint Commission, the Water Quality Board or its committees.
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I. EXECUTIVE SUMMARY

Deposition of chemicals from the atmosphere to the surfaces of the Great Lakes and catchment areas represents an important if not dominant mechanism by which toxic chemicals and nutrients enter that aquatic system. However, at present, it is not possible to provide accurate and precise estimates of the depositional loadings for a number of reasons, including the following factors: 1) wet deposition measurements made on land are not necessarily representative of over-water deposition; 2) particle deposition to the water surface cannot yet be measured or estimated with confidence; and 3) the process of vapor exchange between the atmosphere and water surface is not well known and 4) for many of the compounds, measurement and analytical procedures are not well established.

Goals and Objectives

The Water Quality Board of the IJC charged the Atmospheric Deposition Monitoring Task Force with development of a comprehensive plan to quantify the atmospheric input of selected contaminants to the Great Lakes and to identify, where possible, the sources of these contaminants so that corrective measures may be developed and implemented. Specific objectives of the plan include: 1) the determination of concentrations of selected chemical contaminants and nutrients in precipitation and the atmosphere; 2) the estimation of the annual deposition of these chemicals to each of the Great Lakes and basins; 3) the assessment of temporal and spatial trends in deposition of these chemical species; 4) the determination of the relative contribution of these species from major sources or source regions to deposition at receptor areas within the Great Lakes basin; 5) the provision of information on the occurrence of other toxic compounds in the atmosphere and precipitation within the Great Lakes basin, thus serving as an early warning of impending environmental problems.

In meeting these objectives, the Task Force plan tabled with the Surveillance Work Group of the Water Quality Board builds upon current information and ongoing monitoring activities and is structured to extend the knowledge so accrued over the entire Great Lakes basin.

Details of the Monitoring Plan

The recommended program consists of three phases encompassing research and monitoring (Table 1). The first two phases have a duration of two years each. Phase I outlines research required to resolve scientific questions relating to measurement and environmental processes and the development of interpretative models; the resolution of these questions should be provided in part through monitoring activities conducted at master (research) sites, one each in Canada and in the United States, located in the upper and lower basins. Deliverables at the end of Phase I include an assessment of atmospheric deposition methodology, including a design for the routine monitoring network, and updated estimates of atmospheric deposition to the Great Lakes. While monitoring capabilities are being enhanced, the task force strongly encourages the continuation of existing, albeit upgraded, monitoring
programs in the United States and Canada to provide the data for ongoing evaluation of temporal and spatial gradients.

Phase II incorporates information from Phase I to initiate an abbreviated monitoring network involving both master (research) and satellite (routine) monitoring sites. Scientific questions on measurement and deposition methodology will continue to be researched during Phase II. Anticipated deliverables at the conclusion of Phase II (anticipated within two years of its commencement) are a reassessment of atmospheric deposition methodology with a detailed design of a full-scale monitoring network, as well as updated estimates of atmospheric deposition to the Great Lakes.

Phase III, which will be extended indeterminately, calls for deployment of an integrated atmospheric monitoring network, with ongoing reports assessing the effectiveness of the network and providing more precise estimates of atmospheric deposition to the Great Lakes provided every two years.

The unique feature of this plan is the establishment of master (research) sites during Phase I which serves to focus scientific activities at particular loci. However, measurements to evaluate the effects of spatial heterogeneity on siting will be made at any appropriate site and additional discrete laboratory and field studies to gain more information on processes are envisaged. Necessary emphasis will be given to the development and testing of integrated models as well as process parameterization. Data bases for environmental measurements and atmospheric source emissions will also be established.

The chemical species of interest are those identified as having either a demonstrated or potential adverse influence on the aquatic ecosystem of the Great Lakes. A feature of this program is its flexibility, which should allow alterations in monitoring and measurement protocols as new pollutants are identified. At present, the focus is on organochlorine and other toxic organic compounds and selected trace metals such as lead and mercury. Reference is made to the IJC/Water Quality Board's list of Critical Pollutants, particularly as modified at the Scarborough Workshop on Atmospheric Deposition (Strachan and Eisenreich, 1987).

The major scientific questions to be investigated may be separated into those necessary for the establishment, operation and maintenance of a monitoring network (measurement), and those which pertain to the estimation of over-lake deposition based on shoreline measurements (process). Questions to be addressed for measurement purposes are:

1. inland vs shoreline vs open lake siting;
2. local site selection criteria;
3. spatial variability;
4. temporal variability;
5. quality assurance and quality control;
6. meteorological method development;
7. analytical method development;
8. sampler method development;
9. indirect indicators of atmospheric input;
10. source apportionment and emissions; and,
11. activities in surface water in support of the deposition monitoring plan.
To estimate the magnitude of atmospheric deposition, the following scientific issues and concerns should be addressed further:

1. vapor/particle partitioning;
2. particle deposition velocity as a function of particle size, receptor site and meteorology;
3. mass transfer across the air-water interface;
4. solute partitioning between dissolved and particulate forms in surface waters;
5. rain and snow scavenging of vapors and particles from the atmosphere and;
6. extension of point measurement to lake and basin wide averages and totals.

**Estimated Costs**

The master sites described in this plan will be equipped with both atmospheric sampling and meteorological measurement instrumentation. The meteorological equipment should provide continuous measurement of temperature, wind speed and direction, humidity and rainfall. Atmospheric samplers should characterize atmospheric and precipitation concentrations of selected constituents and surrogate measures of air quality such as Total Suspended Particulate (TSP) and Polycyclic Organic Compounds (POC). The cost of instrumentation for a master station is estimated to be $55K US; operational costs are estimated as $30K per annum. Associated chemical analysis and interpretation costs are estimated to be $125K per annum. Given the establishment of two master sites under Phase I of the Plan, the cost of this phase is estimated to be $850K US over the two years of operation. These costs do not include support of necessary research on measurement and process questions or the development of integrated models. The cost of the research program in support of the monitoring network is anticipated to be comparable to the Phase I master station monitoring costs. Support of both the research and monitoring components is essential to the success of the Plan.

A satellite monitoring station is estimated to cost $35K for instrumentation, $13K per annum for operation and $40K per annum for chemical analysis and data interpretation. Thus, the estimated total cost of a satellite site implemented in Phase II or Phase III is $88K per annum.

At this time, geographic distribution and the precise number of the master and satellite sites for full implementation of the Plan cannot be determined. Locations selected for sampling sites should consider climatological and pollution gradients (cold vs. moderate regions; upper lakes vs lower lakes). However, assuming implementation of an atmospheric monitoring network consisting of four (4) master sites and twenty (20) satellite sites divided equally between the two countries, the estimated costs of a Phase III network would be $920K for equipment and $1680K per annum for operation and analysis. These costs do not include research in support of measurement and process questions.
II. INTRODUCTION

The atmosphere is now recognized as an important contributor of anthropogenic organic compounds and toxic metals to the ecosystem burden of the Great Lakes (e.g. Murphy and Rzeszutko, 1977; Strachan and Huneault, 1979; Eisenreich et al. 1981; Doskey and Andren, 1981; Murphy 1984; Strachan 1985; Strachan and Eisenreich, 1986, 1987). Among other topics, these studies support the hypothesis that wet and dry deposition of PCBs to the upper Great Lakes dominate total inputs from all sources, and the lower lakes receive at least a significant fraction of total inputs via the atmosphere. As an example, Strachan and Eisenreich (1987), using mass balance calculations, show that the approximate percentage of total PCB inputs deposited via the atmosphere is: Lake Superior, 90; Lake Michigan, 58; Lake Huron, 78; Lake Erie, 13; Lake Ontario, 7. Corresponding estimated percentages for benzo(a)pyrene are: Lake Superior, 96; Lake Michigan, 86; Lake Huron, 80; Lake Erie, 79; Lake Ontario, 72. The low percentages of atmospheric inputs of PCBs to the lower lakes indicate the presence of significant loadings to the Detroit and Niagara Rivers from discrete or point sources and hazardous chemical disposal sites.

For most of the other compounds of interest, insufficient data are available to construct mass balances. For those compounds which have adequate data available, a poor understanding of transport terms is one of the principal sources of uncertainty in the mass balance.

Atmospheric inputs, combined with inputs from connecting channel and tributary flows and river and industrial discharges, have resulted in the accumulation of anthropogenic, toxic organic chemicals in fish, wildlife and in humans in the basin.

Organic and inorganic chemicals are deposited in the Great Lakes from the atmosphere (directly onto the lake surface) by precipitation (rain and snow), dry deposition (particle) and vapor exchange at the air-water interface, as illustrated in Figure 1. Other sources include ground water, tributary and connecting channel inputs, and direct municipal and industrial discharges. These contaminants are lost from the water column of individual lake systems by connecting channel or riverine outflows, sedimentation, volatilization and in situ degradation (e.g. biodegradation, hydrolysis, photolysis, photochemical degradation).

Recent studies (Murphy 1984; Mackay et al. 1986; Eisenreich 1987; Swackhamer and Armstrong, 1986) indicate that water to air transport is a major loss process for previously deposited PCBs and perhaps many other chemicals. Inorganic contaminants such as lead are lost by sedimentation and eventual burial. Atmospheric transport and deposition of specific chemical contaminants depend in part on the distribution of the chemical between the particle and vapor phases in the atmosphere, the size distribution of the chemical-laden particle phase, the relative removal efficiencies of each chemical via wet and dry deposition, and the distribution of the chemical between the dissolved and particle phase in surface water.
Since many toxic chemicals are persistent and have relatively long atmospheric half-lives, sources beyond as well as within the Great Lakes basin may be of importance. Presently, information on the physical and chemical properties, processes, pollutant sources and environmental concentrations is insufficient to construct comprehensive models or budgets for the evaluation of the current state of the ecosystem and to predict its response to future changes in source strengths (Strachan and Eisenreich, 1986, 1987). To reduce uncertainty in atmospheric deposition estimates, field measurements, combined with laboratory experimentation and theoretical studies, must be conducted.

The Atmospheric Deposition Monitoring Task Force was established under the Surveillance Work Group, Water Quality Board, in February of 1986 to prepare the atmospheric component of the Great Lakes Surveillance Plan. This component was to outline, in a scientifically defensible fashion, how the atmospheric input of toxic chemicals to the Great Lakes basin could be determined and to describe a network that would also serve as an early warning system for emerging contamination of the Great Lakes ecosystem.

This report is divided hereafter into a number of sections. Section III provides the background for establishment of the Task Force. Section IV lists the goal and objectives of the Task Force to derive an atmospheric deposition monitoring plan. Section V provides the details of the plan and its estimated costs. Section VI provides recommendations of the Task Force for support of the measurement, research and modeling aspects of the plan. The rationale for the plan is discussed in a companion background document("A Plan for Assessing Atmospheric Deposition to the Great Lakes: Scientific Background") (IJC, 1987).
III. BACKGROUND

In February 1986 the Great Lakes International Surveillance Plan (GLISP) was published by the International Joint Commission (IJC). The plan, prepared by the Surveillance Work Group of the Great Lakes Water Quality Board, is required under the 1978 Great Lakes Water Quality Agreement. It represents an updated and expanded version of the Great Lakes International Surveillance Plan (GLISP) of 1980 (IJC 1980). The most recent plan embraces the protection of the entire Great Lakes Basin Ecosystem rather than a narrower focus on water quality per se. More emphasis has also been given to detection and identification of emerging problems and to the quality, compatibility and interpretation of collected data.

Since for many inorganic and organic pollutants, the atmosphere provides an important, if not dominant, route of entry to the Great Lakes basin, the surveillance plan requires a comprehensive atmospheric component. Evidence of the importance of the atmospheric pathway is summarized in a report to the Science Advisory Board in 1980 (Eisenreich et al. 1980) and in the pre- and post workshop reports based on the IJC-sponsored workshop on atmospheric loadings of toxic chemicals to the Great Lakes basin (Strachan and Eisenreich, 1986; 1987).

The objectives of the atmospheric component of the plan are to estimate the net contribution from atmospheric sources to the chemical loading of the lakes, to quantify trends in deposition, and to provide information on the presence/absence of toxic chemicals in the atmosphere within the entire basin. This latter objective, when fulfilled, would serve as an early warning of emerging atmospheric and ecosystem concerns within the Great Lakes Basin Ecosystem. The current GLISP, which relied on measurements from the United States Great Lakes Atmospheric Deposition (GLAD) network and from the Canadian Great Lakes Precipitation (GLP) network, is inadequate to meet the objectives of the Surveillance Work Group as determined in both a peer review requested by the Work Group and presentations at the IJC Biennial Meeting in July 1985.

The adequacy of each of the GLAD sites with respect to precipitation network siting criteria was reviewed during the summer of 1985 (Murphy, 1987). This review resulted in a recommended upgrading and reconstitution of the network. In March 1985, the Ad Hoc Advisory Group on Atmospheric Monitoring were established under the Surveillance Work Group to develop the atmospheric component. The Group prepared a three stage plan containing a monitoring as well as research and integration component. The plan was presented to the Great Lakes Water Quality Board in September, 1985. In January 1986, the Ad Hoc Advisory Group formed the nucleus of the newly established Atmospheric Deposition Monitoring Task Force of the IJC, and its membership and terms of reference were expanded. Its major task is to refine and augment the atmospheric monitoring plan in the GLISP.

In the Task Force review of the atmospheric component, conclusions and recommendations from three workshops in which selected members of the task force played a role have been considered: 1) Atmospheric Deposition Workshop
on Organic Contaminant Deposition to the Great Lakes Basin, held in November 1985 in Minneapolis, Minnesota; 2) Atmospheric Loadings of Toxic Chemicals to the Great Lakes Basin, held in Scarborough, Ontario, October, 1986 under the auspices of the IJC (Strachan and Eisenreich, 1987); 3) Siting of Atmospheric Monitoring Stations, held in Toronto, Ontario in March, 1987 under the auspices of the IJC.
IV. OBJECTIVES

The overall objective of the Task Force is to develop a comprehensive plan to quantify the net atmospheric input of selected chemical contaminants to the Great Lakes. Specific objectives are:

- To determine the concentrations of selected chemical contaminants and nutrients in the atmosphere and precipitation.
- To determine the annual deposition of these chemicals to each of the lakes and their associated watersheds.
- To determine temporal and spatial trends in the deposition of selected chemical contaminants.
- To determine source/receptor relationships, that is the relative contribution from major sources or source regions of these contaminants to deposition at receptor areas within the Great Lakes region.
- To provide timely information on other toxic compounds in the atmosphere or precipitation within the vicinity of the Great Lakes basin.
The Plan

A limiting constraint to determining atmospheric loadings to the lakes is the inability to make measurements of deposition to the Great Lakes directly. The desired assessment of pollutant fluxes from the air to the water surface of the lakes must necessarily be obtained indirectly; a program that combines field and laboratory experimentation with theoretical development is thus required. The experimental part will provide basic information on the characteristics of the atmosphere to which the Great Lakes are exposed, on the processes controlling deposition to the lakes, and on related temporal trends with time. The theoretical component is required to construct the necessary integration, and to provide the predictive capability needed to assess the consequences of various control strategies on inputs to the lakes.

The program developed by the Task Force consists of three phases encompassing research and monitoring (Table 1). The first two phases have a duration of two years each. Phase I outlines research designed to resolve scientific questions relating to measurement and environmental processes and the development of interpretative models; the resolution of these questions should provide the scientific basis for monitoring activities at master (research) sites, one each in Canada and in the United States, located in the upper and lower basins. Deliverables at the end of Phase I should include an assessment of atmospheric deposition methodology, including a design for the routine monitoring network, and updated estimates of atmospheric deposition to the Great Lakes. While monitoring capabilities are being enhanced, the Task Force strongly encourages the continuation of existing, albeit upgraded, monitoring programs in the United States and Canada to provide the data for ongoing evaluation of temporal and spatial gradients.

Phase II incorporates information from Phase I to initiate an abbreviated monitoring network involving both master (research) and satellite (routine) monitoring sites. Scientific questions on measurement and deposition methodology will continue to be researched during Phase II. Deliverables at the end of Phase II would include a reassessment of atmospheric deposition methodology with a design for implementation of a full scale monitoring network and updated estimates of atmospheric deposition to the Great Lakes.

Phase III would mark the establishment of an ongoing routine and indeterminate integrated atmospheric monitoring network, with reports assessing the effectiveness of the network and updated estimates of atmospheric deposition to the Great Lakes provided every two years.

The proposed plan will focus initial attention on the need to provide adequate responses to a number of questions, each of which arises from existing uncertainties which prohibit immediate design of an optimal measurement approach. These are rooted in the objectives presented earlier.
To quantify the wet deposition, it is presently necessary to extrapolate from data obtained on shore or inland. Research is needed to quantify the errors associated with such extrapolations and determine a strategy to minimize them.

To quantify the deposition loading due to dry deposition of particles, it is necessary to measure the concentration in air \( C_{ap} \), and to specify the appropriate deposition velocity \( V_d \), as a function of particle size from which the desired flux to the surface can be computed as the product \( C_{ap} \cdot V_d \). Work is needed to improve the ability to measure concentrations and the capability to specify \( V_d \).

To determine the gas exchange with the surface, the concentration of the same species must be measured both in the air \( C_{ag} \) and under the surface of the water \( C_{1w} \) and an appropriate transfer velocity applied so as to derive the surface exchange rate as the product \( C_{ag} - H \cdot C_{1w} + k \). Of the terms of this equation, \( H \) is a constant that can be measured in the laboratory; however, capabilities to measure \( C_{ag} \) and \( C_{1w} \) must be improved and expanded. Information about \( k \) is presently rudimentary, and field measurements are required. Laboratory evaluations of \( H \) need to be tested for their applicability to field conditions.

The discussion in the Appendix (IJC, 1987) emphasizes the lack of well-accepted methodologies; the state of the science is not yet such that monitoring can be initiated with confidence for either wet or dry deposition. Moreover, the design of an appropriate initial network cannot yet be specified with assurance. Existing networks are therefore regarded as exploratory field tests of alternative sampling technologies and as initial probes of spatial and temporal variability. In recognition of the significance of these concerns and of the need to defend both the scientific credibility and the geographical distribution of the monitoring and surveillance activity that is desired, a three phase approach has been recommended.

The plan as outlined involves an evolutionary development of a monitoring network based on sound scientific information beginning with the present state of the art and incorporating changes and improvements based on the research components of the plan. The result should be the efficient development of an Atmospheric Deposition Monitoring Network. The evolution of the network in three phases is described below.

PHASE I, estimated to require two years, consists of research to resolve scientific questions relating to measurement and environmental processes and the development of interpretative models. The resolution of these questions should be provided in part through monitoring activities at master (research) sites, one each in Canada and in the United States. Deliverables at the end of Phase I should include an assessment of atmospheric deposition methodology, including a design for the routine monitoring network, the development of related QA/QC procedures and recommendations for routine sampling instrumentation. A research program should be initiated to characterize the spatial variability in air and precipitation across the Great Lakes for toxic chemicals of interest; updated estimates of atmospheric deposition to the Great Lakes will also be provided. As noted previously, while Phase I is
underway, the Task Force strongly encourages the continuation of existing, albeit upgraded, monitoring programs in the United States and Canada.

A key feature of PHASE I is the establishment of master (research) sites which will focus scientific activities at particular basin locations. However, measurements to evaluate the effects of spatial heterogeneity on siting will be made at any appropriate site, and further field studies to gain more information on processes are envisaged. Emphasis will be given to the development and testing of integrated models as well as process parameterization. Data bases for environmental measurements and atmospheric source emissions will be established also. The major scientific questions to be investigated may be separated into those necessary for the establishment, operation and maintenance of a monitoring network (measurement) and those which pertain to estimating over-lake deposition based on shoreline measurements (process).

Questions to be addressed for measurement purposes are site selection criteria including a consideration of: 1) site selection criteria, including a consideration of inland vs. shoreline vs. open lake siting; 2) spatial variability; 3) temporal variability; 4) quality assurance and quality control; 5) meteorological method development; 6) analytical method development; 7) sampler method development; 8) use of indirect indicators of atmospheric input; 9) source identification; and 10) studies of surface water phenomena in support of an atmospheric deposition plan.

Specific questions to be addressed to estimate the magnitude of atmospheric deposition include: 1) vapor/particle partitioning; 2) particle deposition velocity as a function of particle size, receptor and meteorology; 3) mass transfer across the air/water interface; 4) solute partitioning between dissolved and particulate forms in surface water; 5) rain and snow scavenging of vapors and particles from the atmosphere; and 6) extension of point measurements to lake and basin wide averages and totals.

PHASE II incorporates information available at the end of PHASE I to initiate an abbreviated monitoring network involving 4 master (research) and 10 satellite (routine) monitoring sites. Scientific questions on measurement and deposition methodology will continue to be researched as required during PHASE II. Deliverables at the end of PHASE II should include a reassessment of atmospheric deposition methodology with a design for full-scale implementation of a monitoring network and updated estimates of atmospheric deposition to the Great Lakes. Two years of intensive effort should provide much of the required output from this phase.

PHASE III calls for full-scale implementation of an integrated atmospheric monitoring network on an ongoing basis, with reports assessing the effectiveness of the network and updated estimates of atmospheric deposition to the Great Lakes provided every two years. At this time, four (4) master and approximately twenty (20) satellite sites are envisaged.

Master and Satellite Sites

Both sampler development and intensive research investigations have need for the use of special sites, where measurements can be made at a level of detail greater than that at routine monitoring locations. The research and
monitoring strategy is therefore based on a nested network philosophy, in which sophisticated ‘Master’ sites operate in close collaboration with simpler ‘Satellite’ sites where routine measurements are made. In the context of sensor development, the master sites are centers of speciality, where specific questions are addressed with the intent of providing the scientific basis for interpreting measurements made elsewhere.

It is assumed that all existing, albeit upgraded, monitoring programs measuring toxic chemicals and trace metals in air and precipitation within the basin will continue without interruption, and that the experiences gained in these ground-breaking monitoring activities will be available to guide the subsequent phases of the program presented here. These initial monitoring activities constitute a critical component of the Phase I endeavour.

For the process related research activities, master sites should provide locations for the development of capabilities to extrapolate from routine measurement locations to over-water situations.

Two master sites should be established in Phase I of the Plan; one each in Canada and the United States. Location of the master sites should take into account climatological and pollution gradients present in the Great Lakes basin. Master sites should be equipped with instrumentation to characterize and quantify the concentrations of selected components in the atmosphere and precipitation.

Instrumentation will include samplers capable of characterizing the distribution of chemical species between the vapor and particle phase in the atmosphere and dissolved and particle phases in wet-only integrated precipitation samples retrieved approximately every two weeks. Meteorological instruments should be available to monitor wind speed and direction, temperature, humidity and rainfall intensity on a continuous basis. Organic and inorganic contaminants to be analyzed at the master site should reflect the composition of several lists of critical pollutants and those crucial to the support of the research component.

Cost of the Plan

Phase I of the plan calls for the establishment of two (2) master sites, one each in Canada and the United States. The master site, will be equipped with meteorological and atmospheric sampling instrumentation. The atmospheric samplers should characterize atmospheric and precipitation concentrations of selected organic constituents as well as surrogate measures of air quality, e.g. Total Suspended Particulates (TSP) and Poly Cyclic Organic Compounds (POC).

The cost of a Phase I master site can be separated into instrumentation, operation, and chemical analysis/data interpretation (Table 2). The cost of instrumentation is estimated to be $55K per annum. Operational costs of a single master site are estimated to be $30K per annum. Chemical analysis/data interpretation costs are estimated to be $125K per annum. Given the establishment of two master sites in Phase I of the Plan, the cost of phase I is estimated to be $850K over the two years of operation (Table 3). These costs do not include support of necessary research on measurement and process questions and development of integrated models. The cost of the
research program in support of the monitoring network is anticipated to be comparable to the Phase I master site costs. The success of the plan requires support of both the research and monitoring components. An example of the equipment which might be deployed is given in Tables 4 and 5.

At this time, the number and geographical distribution of master and satellite sites for full implementation of the plan is not known. The instrumentation for the satellite monitoring site is estimated to be $35K, $13K per annum for operation and $40K per annum for chemical analysis and data interpretation. These sites will be equipped with somewhat less instrumentation than the master site, will collect samples at a lower frequency and will not generally provide a location for expanded research. The estimated cost of a satellite site implemented in Phase II or III is $88K per annum.

Assuming full implementation of an atmospheric monitoring network consisting of four (4) master sites and twenty (20) satellite sites, the costs of a Phase III network are $920K for equipment and $1680K per annum for operation and analysis. These cost do not include research in support of measurement and process questions. The integrated, bi-national atmospheric network will consist of two master sites and ten satellite sites in both Canada and the United States. The specific siting criteria will be described in detail in the Scientific Background document.
For the research described above, MWG is planning to provide locations near the current site of the measurement of atmospheric aerosol. With the next site to be located closer to the current site, the aerosol will be more representative and continuous measurements will be possible. The current aerosol will be analyzed and compared with the aerosol at the new site to provide a more comprehensive understanding of atmospheric processes.

Instrumentation will include sensors capable of characterizing the concentration of aerosol particles and particles that are relevant to the development of precipitation. The instruments will sample and analyze aerosol and particles in a way that is representative of precipitation. The data will be retrieved approximately every two weeks. Meteorological instruments should be available to monitor wind speed and direction, temperature, humidity, and rainfall intensity on a continuous basis. Dynamic and static contaminant sources in the vicinity of the site should reflect the composition of aerosol from different pollutants and those crucial to the success of the research component.

Cost of the Plan

The cost of the plan calls for the establishment of the aerosol sites in Canada and the United States. The costs will be determined with integrated and atmospheric-sampling instrumentation. The Canadian sites will require monitoring stations and precipitation collectors of soil type measurement employed, as well as surrogate measures of air quality, such as metal analysis of air samples (US EPA and Cyclic Organic Compounds - COCs).

The cost of the aerosol site can be separated into instrumentation, operation, and maintenance. The cost of instrumentation is expected to be $50,000 per year. The annual costs of a single site is the average for the two years of operation (Table 3). These costs do not include capital and necessary research on measurement and processing equipment and development of integral models. The cost of the
VI. RECOMMENDATIONS

For the success of the Plan it is essential that the recommendations are acted upon in Phase I. The background document provides a discussion of the recommendations (IJC, 1987).

Measurement

1. The air quality and movement affecting the Great Lakes basin are largely ill-defined. Existing networks, albeit upgraded, should continue operations even as new measurement and estimation techniques evolve.

2. The horizontal gradients of pollutant concentrations in ambient air and wet deposition across the Great Lakes basin need to be quantified.

3. The concentrations and fluxes of toxic chemicals in precipitation need to be determined, especially in precipitation over the lakes.

4. Sites for measurement stations must be carefully selected to correspond to existing guidelines of Canadian and U.S. networks.

5. Samplers for the collection of samples of atmosphere and precipitation need to be further developed and calibrated to allow precise assessments of concentrations and fluxes.

6. Analytical techniques to precisely and accurately detect and quantify trace levels of toxic chemicals in atmosphere and precipitation should be developed.

7. Atmospheric sampling at over-lake sites (islands, ships, floating platforms) must be secured for comparison to shoreline or land-derived data.

8. Measurements of the distribution of toxic chemicals between particle and vapor phases in the atmosphere and particle and dissolved phases in rain should be made at both master and satellite sites.

9. Development and field testing of snow collectors and all-weather collectors should be continued. The possibility of using biological indicators of deposition should be explored.

10. A uniform QA/QC procedure should be adopted and applied to all measurement programs contributing data to the proposed network.

11. A concerted effort to interpret network data on a continual basis must be maintained.
Research

1. The necessary theory to define toxic chemical distribution between vapor and particle phases in the atmosphere must be developed and applied to the sampling technology.

2. The validity of current methods to infer concentrations and fluxes over the lakes from land-based or shore-based measurements must be evaluated.

3. Theory and methods for estimating dry deposition of particles to the lakes must be developed.

4. Theory and methods for estimating gas exchanges at the air/water interface under varying environmental conditions must be developed.

Modeling/Synthesis

1. Numerical simulations should be developed to evaluate the influence of lake breeze and topographically-induced circulations on patterns of concentration and fluxes in the vicinity of urban centers and point sources.

2. Models/transfer functions need to be developed to relate land-based chemical fluxes to over-lake deposition, and to define a minimum network to accomplish this goal.

3. Development of mesoscale and long range transport models for the estimation of concentration and deposition over the Great Lakes region and for interpretation of source/receptor relationships must be continued.

4. A common data base should be established to process and store data from the evolving network.

5. Emission inventories of toxic chemicals of concern to the Great Lakes should be developed.
VII. FIGURES

\[ \text{FIGURE 1: Surface and subsurface fluxes, respectively.} \]

\[ \text{FIGURE 2: Wet, dry particle and vapor fluxes, respectively.} \]

\[ \text{FIGURE 3: Total dissolved and particulate concentrations in water, respectively.} \]

\[ \text{FIGURE 4: Net uptake fluxes in a biogeochemical cycle.} \]

\[ \text{FIGURE 5: Fluxes due to respiration, incident and net accumulation in sediments, respectively.} \]
1. The necessary theory to define tracer concept; distribution between vapor and particulate phases in the atmosphere must be developed and applied to the sampling technology.

2. The validity of current methods to total concentrations and fluxes over the lakes from land-based and water-based measurements must be evaluated.

3. A theory and method for estimation of deposition of particles to the lakes must be developed.

4. Theory and method for estimation of exchange at the air/water interface under varying wind conditions and water temperatures must be evaluated.

5. Model-based analysis would be essential to evaluate the influence of the land-use on the lakes. A modeling strategy to be followed of the transport and transformation of pollutants in the environment must be presented.

6. Development of accurate and long-range transport models for the estimation of concentration and deposition over the Great Lakes region for interpretation of source/receptor relationships must be continued.

7. A common data base should be established to process and store data from the evolving network.

8. A listing inventory of toxic chemicals of concern to the Great Lakes should be developed.
**MASS BALANCE PARADIGM**

**NET ATMOSPHERIC DEPOSITION**

\[
Q_i, Q_o = \text{surface and subsurface fluxes, respectively.}
\]

\[
F_w, F_d, F_{gas} = \text{wet, dry particle and vapor fluxes, respectively.}
\]

\[
C_T, C_D, C_P = \text{total, dissolved and particulate concentrations in water, respectively.}
\]

\[
F_{Bio} = \text{biological fluxes (e.g. biodegradation).}
\]

\[
F_{res}, F_{sed}, F_{accum} = \text{fluxes due to resuspension, sediment and net accumulation in sediment, respectively.}
\]
### VIII. TABLES

<table>
<thead>
<tr>
<th>Phase</th>
<th>Table 1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Table 2</td>
</tr>
</tbody>
</table>

**DELIBERABLES**

Phase II

- Development of Atmospheric Deposition Methodology (incl. Network Plan)
- Improved Estimates of Atmospheric Deposition

### RESEARCH & PROCESS QUESTIONS

**MEASUREMENT**

1. Site selection criteria
2. Incident vs. Echelable vs. Open lake sites
3. Regional spatial variability
4. Temporal variability
5. Quality assurance/control

**PROCESS**

1. Vapor/particle partitioning
2. Fertilizer deposition ecology
3. Data transfer accuracy at water interface
4. Solution partitioning in water
5. Heat and mass exchange
6. Extent of local measurement and average and total

**SOURCE IDENTIFICATION**

- Surface water measurements
TABLE: 1: A PLAN FOR ASSESSING ATMOSPHERIC DEPOSITION TO THE GREAT LAKES: STRATEGY AND TIME LINES

<table>
<thead>
<tr>
<th>Yrs</th>
<th>PHASE I</th>
<th>PHASE II</th>
<th>PHASE III</th>
<th>Ongoing</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Provide Scientific Basis for Monitoring Activities</td>
<td>Initiate Monitoring Network</td>
<td>Implementation of Full-scale Network</td>
<td>Monitoring</td>
</tr>
<tr>
<td>2</td>
<td>Establish 2 Master Stations</td>
<td>Establish 2 Master Stations and 10 Satellite stations</td>
<td>Establish 10 additional satellite stations</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Continue Research</td>
<td>Continue Research</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**DELIVERABLES**

**Phase I**
- Assessment of Atmospheric Deposition Methodology (incl. Network Plan)
- Improved Estimates of Atmospheric Deposition

**Phase II & III**
- Reassessment of Atmospheric Deposition Methodology
- Updated Estimates of Atmospheric Deposition

**MEASUREMENT & PROCESS QUESTIONS**

**MEASUREMENT**
1. Site selection criteria
2. Inland vs. shoreline vs. open lake sites
3. Regional spatial variability
4. Temporal variability
5. Quality assurance/control
6. Meteorological factors
7. Analytical methods development
8. Sampler method development
9. Indirect indicators of atmospheric input
10. Source Identification
11. Surface water measurements

**PROCESS**
1. Vapor/particle partitioning
2. Particle deposition velocity
3. Mass transfer across air-water interface
4. Solute partitioning in water
5. Rain and snow scavenging
6. Extension of local measurements to lake and basin-wide averages and totals
### TABLE: 2: COST ESTIMATES FOR MASTER AND SATELLITE STATIONS IN THE ORGANIC ATMOSPHERIC MONITORING NETWORK

<table>
<thead>
<tr>
<th>Type of Station</th>
<th>Cost Instrumentation ($1,000 U.S.)</th>
<th>Cost Replacement ($1,000 U.S.)</th>
<th>Cost Operation</th>
<th>Chemical Analysis</th>
<th>Data Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Master</td>
<td>55</td>
<td>5</td>
<td>30</td>
<td>100-125</td>
<td>50</td>
</tr>
<tr>
<td>Satellite</td>
<td>35</td>
<td>4</td>
<td>13</td>
<td>30</td>
<td>50</td>
</tr>
</tbody>
</table>

### TABLE: 3: COST ESTIMATES FOR THE ORGANIC ATMOSPHERIC MONITORING NETWORK IN PHASE I TO PHASE III

<table>
<thead>
<tr>
<th>Phase</th>
<th>Master Stations #</th>
<th>Satellite Stations #</th>
<th>Cost U.S. $1000</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Year 1</td>
</tr>
<tr>
<td>I</td>
<td>2</td>
<td></td>
<td>480</td>
</tr>
<tr>
<td>II</td>
<td>4</td>
<td>10</td>
<td>1670</td>
</tr>
<tr>
<td>III</td>
<td>4</td>
<td>20</td>
<td>2030</td>
</tr>
</tbody>
</table>

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### TABLE 4: EXAMPLE OF EQUIPMENT TO BE DEPLOYED AT THE MASTER SITES

<table>
<thead>
<tr>
<th>Number of Samplers</th>
<th>Sampling Interval</th>
<th>Description of Equipment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Weekly</td>
<td>Aerochem Metrics automatic sensing wet/dry precipitation collector (with standard Belfort rain gauge) for the collection of nutrients and trace metals</td>
</tr>
<tr>
<td>2</td>
<td>Biweekly</td>
<td>Wet-only integrating precipitation samplers with resin* extraction cartridges for the collection of organic compounds</td>
</tr>
<tr>
<td>1</td>
<td>Event</td>
<td>Wet-only event precipitation sampler with a resin extraction cartridge for the collection of organic compounds</td>
</tr>
<tr>
<td>3</td>
<td>24 hours**</td>
<td>Hi-volume air samplers with filters and backup adsorbent* and wind sector controllers for the collection of organic compounds</td>
</tr>
<tr>
<td>1</td>
<td>24 hours</td>
<td>Anderson four-stage cascade impactor with backup adsorbent for the collection of organic compounds</td>
</tr>
<tr>
<td>1</td>
<td>24 hours</td>
<td>Hi-volume sampler for the determination of total suspended particles (TSP) and organic carbon (OC)</td>
</tr>
<tr>
<td>1</td>
<td>Continuous</td>
<td>Meteorological equipment for continuous recording of rain intensity and amount, temperature, relative humidity, wind direction and velocity.</td>
</tr>
</tbody>
</table>

*Resins and adsorbents will be either XAD-2, XAD-5, or Tenax.

**Air samples will be collected every sixth day.
TABLE 5: EXAMPLE OF EQUIPMENT TO BE DEPLOYED AT THE SATELLITE SITES

<table>
<thead>
<tr>
<th>Number of Samplers</th>
<th>Sampling Interval</th>
<th>Description of Equipment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Weekly</td>
<td>Aerochem Metrics automatic sensing wet/dry precipitation collector (with standard Belfort rain gauge) for collection of nutrients and trace metals</td>
</tr>
<tr>
<td>2</td>
<td>Biweekly</td>
<td>Wet-only integrating precipitation samplers with resin* extraction cartridges for the collection of organic compounds</td>
</tr>
<tr>
<td>2</td>
<td>24 hours**</td>
<td>Hi-volume air samplers with filters and backup adsorbent* and wind sector controllers for collection of organic compounds</td>
</tr>
<tr>
<td>1</td>
<td>24 hours**</td>
<td>Anderson four-stage cascade impactor with backup adsorbent for collection of organic compounds</td>
</tr>
</tbody>
</table>

*Resins and adsorbents will be either XAD-2, XAD-5, or Tenax.
**Air samples will be collected every third day.
IX. REFERENCES


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