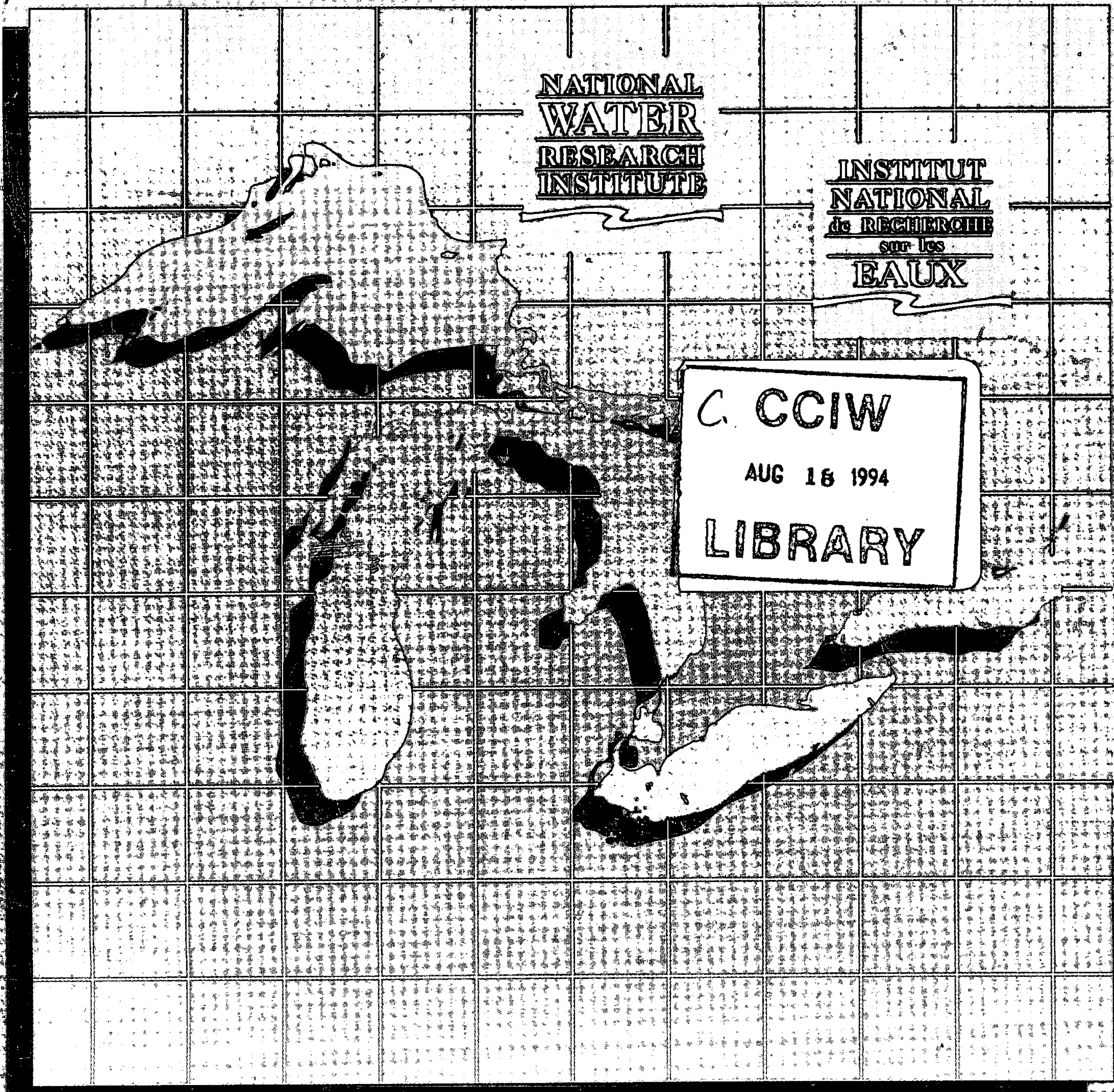

NATIONAL WATER RESEARCH INSTITUTE

INSTITUT NATIONAL de RECHERCHE sur les EAUX

Research Results Under GLAP I

Compiled and Edited
by
M. Zarull and R.J. Allan
N.W.R.I. Contribution No: 94-1

AN OVERVIEW OF RESEARCH CONDUCTED BY THE NATIONAL WATER RESEARCH INSTITUTE IN SUPPORT OF THE GREAT LAKES ACTION PLAN

1989-1994

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MANAGEMENT PERSPECTIVE

The National Water Research Institute received financial assistance from the preservation fund to conduct research in support of Canada's Great Lakes Action Plan (GLAP). This research was guided by Canada's joint Great Lakes commitments and management requirements described in Annexes 1, 2, 11, 12, 13, 14, 15 and 16 of the 1987 Protocol amending the 1978 Great Lakes Water Quality Agreement.

A great deal of the research was performed in Areas of Concern or in support of the formulation and implementation of Remedial Action Plans through the development of key techniques and technologies. Other major research areas included the procurement of information supporting: the development of Lakewide Management Plans, fate, effects and mass balance modelling of critical pollutants; determining trends and loadings of atmospherically transported toxic substances; assessing the extent, origin and remediation potential of contaminated groundwater; quantifying and evaluating non-point source pollution from urban and agricultural sources and; understanding the role and significance of sediments for Great Lakes contaminant processes.

This report highlights the applied research conducted at the institute over the five-year period 1989-1990 to 1993-1994 under GLAP. It also provides a list of publications that resulted from this work.

SOMMAIRE À L'INTENTION DE LA DIRECTION

L'Institut national de recherche sur les eaux a reçu de l'aide financière du Fonds de préservation pour réaliser des études dans le cadre du Plan d'action des Grands Lacs (PAGL). Pour orienter ces études, l'Institut s'est reporté aux engagements et aux exigences de gestion du Canada définis dans les annexes 1, 2, 11, 12, 13, 14, 15 et 16 du Protocole de 1987 sur l'Accord de 1978 relatif à la qualité de l'eau dans les Grands Lacs.

De nombreux travaux de recherche ont été réalisés dans les zones critiques pour faciliter l'élaboration de plans d'assainissement et leur mise en oeuvre au moyen de technologies clés. D'autres travaux de recherche visaient à accroître l'information requise dans les domaines suivants : l'élaboration de plans d'aménagement lacustre; le devenir, les effets et la modélisation du bilan massique des pollutants critiques; les tendances et les charges des substances toxiques aéroportées; l'évaluation des causes, de l'étendue et des possibilités d'assainissement des eaux souterraines contaminées; l'établissement des sources diffuses urbaines et agricoles et l'évaluation de la pollution causée par ces sources; la compréhension du rôle et de l'importance des sédiments dans les processus des contamination des Grands Lacs.

Ce rapport met en relief les travaux de recherche appliquée réalisés à l'Institut de 1989-1990 à 1993-1994 dans le cadre du PAGL. Il contient aussi une liste des publications produites à la suite de ces travaux.

TABLE OF CONTENTS

FIGURES AND TABLES

Figures

Tables

INTRODUCTION

The Laurentian Great Lakes represent the largest body of freshwater on earth. They contain over 24,000 km^3 of water, which is roughly 20% of the liquid, surface freshwater on the planet. This region has long been considered the heartland of North America because of its natural resources and its role in the history and development of both Canada and the United States. Today, some 36 million people live within the drainage basin and there are 28 cities whose populations exceed 50,000. These lakes, along with their tributary waters and connecting channels, are used for drinking water, transportation, power generation, industrial processes and waste disposal.

As a result of these ever-increasing and sometimes conflicting demands, population growth and land-use practices, the lakes have become degraded. In response to a series of study references on water quality and land use given to the International Joint Commission by both national governments, research scientists documented environmental problems and, in conjunction with resource managers, made a series of recommendations for action. Recognizing the severity of the problems and their responsibility for the stewardship of the lakes, Canada and the United States signed the Great Lakes Water Quality Agreement in 1972. While providing a binational basis for managing their common resource, this Agreement focussed on the control of eutrophication by reducing phosphorus inputs.

Research results and social awareness provided the impetus for revising the Agreement in 1978. This new Agreement recognized the need to understand and effectively manage the discharge of toxic substances into the Great Lakes basin. As well, the Agreement adopted an ecosystem approach to managing the resource. This approach attempts to account for the interrelationships among water, air, land and all living things, including humans and aims to provide a holistic approach to research, planning and management.

In 1987, the two countries signed a protocol amending the 1978 Agreement. This protocol recognized the significance of the atmospheric pathway in the loading of toxic substances, as well as groundwater and non-point sources of contamination, the need to address contaminated sediments and to develop and implement both Remedial Action Plans (RAPs) for Areas of Concern (AOCs) and Lakewide Management Plans (LAMPs). In addition, the protocol established specific research needs that were integrated with management goals and requirements throughout the existing and new annexes. The creation of a separate research annex recognized the significant historical and continuing role of research in managing the lakes.

In response to the challenges and demands posed by the 1987 Protocol, the Canadian federal government launched a five-year, $125 million Great Lakes Action Plan (GLAP). GLAP 1 was comprised of three major components: the Preservation Program, the Cleanup Fund and the Great Lakes Health Effects Program. While these components are managed separately, there remains strong integration and support among them.

The $50 million Preservation Program was designed to address the wide spread contamination of the Great Lakes Ecosystem by toxic chemicals in a comprehensive manner. In addition to providing resources for the development of RAPs and LAMPs, the program consists of five components that address the major aspects of Great Lakes pollution: ecosystem health, land-based pollution, pollution associated with shipping, contaminated sediments and atmospheric deposition of pollutants.

The National Water Research Institute (NWRI) received funding to conduct research in support of management goals under Annexes 1 (chemical and ecosystem objectives), 2 (RAPs and LAMPs), 11 (surveillance), 12 (persistent toxic substances), 13 (non-point source pollution), 14 (contaminated sediments), 15 (atmospheric toxic substances) and 16 (groundwater). In addition, NWRI along with Canada's National Science and Engineering Research Council and the Great Lakes Environment Office jointly sponsored the Great Lakes University Research Fund. This fund was designed to support University based research that would assist Environment Canada in fulfilling its commitments under Annex 17 of the GLWQA.

The major role of government research on the Great Lakes is to investigate and assess ecosystem function and health. This work is usually initiated in response to identified or suspected problems. Investigations of underlying causes often leads to the discovery of more complex problems. However, this represents only the initial phase of applied research. The first imperative of research conducted by NWRI under GLAP was to develop sufficient understanding of ecosystem function under anthropogenic stress to: adequately define impacts and causes; propose achievable ecosystem goals, targets or objectives; formulate and evaluate corrective management actions and; develop programs to measure ecosystem recovery in response to management actions. To accomplish this requires the development of tools, techniques and technology, leading to a greater understanding of the physical, chemical and biological processes affecting the Great Lakes ecosystem. The acquisition of this knowledge is the critical first step in the management of the resource. The development of regulations on resource use and the implementation of remedial measures without this information could have disastrous and expensive consequences for both the natural environment and the economic functioning of our society.

Scientists at NWRI have published a large number of papers in technical journals and made many presentations at national and international conferences based on the research conducted under GLAP 1. These activities are essential not only for the maintenance of the individual's and the institute's professional credibility and authority, but also for the critical evaluation of the validity of the work itself. However, along with these activities, institute scientists have provided significant public and educational material on the Great Lakes. Several scientists are continuing members of RAP writing teams, while many more have made presentations and provided reports to RAP stakeholders, public advisory groups and the general public. In addition to being members on other technical groups advising Great Lakes resource managers, many of the scientists have given talks to service organizations, educational institutions and teachers' groups. These talks, reports and interviews all provide information on the results of Great Lakes scientific research and its implications for the management of one of Canada's most important natural resources.

This report provides a summary of the research conducted by NWRI under GLAP 1. The information is organized according to the GLWQA Annexes, since funding was provided specifically to acquire knowledge necessary to meet the objectives stated in each Annex. The report includes a list of publications associated with the work. National Water Research Institute authors are indicated in **bold face.**

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ANNEX 1

SPECIFIC OBJECTIVES

Annex 1 of the Great Lakes Water Quality Agreement provides specific chemical objectives (in water and biota) for use by both Canada and the United States to protect the Great Lakes. The annex also provides the principles and requirements for the development and adoption of new chemical-specific objectives and lake ecosystem objectives.

The development of either chemical or ecosystem objectives requires considerable background research. In the case of chemical objectives this begins with drawing-up a list of substances that are known to be, or could be present and, singly or in combination with other substances have acute or chronic toxic effects on aquatic, animal or human life. Next, analytical methods to test for the presence of specific chemicals in sediment, water or biota are required. Then, methods to evaluate effects need to be developed and/or employed. All of this needs to be done before publicly proposing a safe or (in the case of persistent toxic substances) interim level. Lake ecosystem objectives require considerable knowledge of structure, function, stability and stress response of the ecosystem, as well as the factors that affect each of these properties.

Lake ecosystem objectives represent a new approach to goal setting and managing the Great Lakes. Ecosystem objectives and their indicators refer to the desired conditions to be attained and maintained to protect the health and integrity of the system. Ecosystem objectives are a set of narrative statements that describe a desired state of the ecosystem. The indicators are the variables that reflect the attributes of the objectives. Each indicator requires the establishment of an independent target or reference value.

Chemical Objectives

Reliable analytical measurements are the basis of all water quality management programs, including research, ambient and trend monitoring, remedial measures or regulatory compliance. Suitable analytical methods that provide meaningful data are a fundamental prerequisite to these programs. Therefore, progress mandates accurate, cost effective, sensitive and selective methods and techniques for the identification and quantification of contaminants in aquatic ecosystems.

The Analytical Chemistry Research Project (ACRP) team, at NWRI, has conducted research leading to the development of new and improved analytical methods, sampling, preconcentration and screening procedures for the measurement of chemical and biochemical parameters in Great Lakes substrates. Activities have been focused on the problems and needs related to GLAP and in support of other research studies of this program. The ACRP research goals were to develop methodologies and techniques to: better understand the aquatic ecosystem, assess impairment and assist the implementation of remedial and regulatory actions. This included the development of sensitive and selective methods capable of the unambiguous detection and accurate determination of toxic substances of the aquatic ecosystem at ultratrace levels. Screening (immunoassay), preconcentration (liquid-liquid, solid-liquid, supercritical fluid and microwave extraction) and separation (electrophoresis, gas and liquid chromatography) together with the high technology instrumentation (atomic, molecular and mass spectroscopy and electrochemistry) represent the basic components of the research.

The ACRP team is responsible for the operation and maintenance of a clean and hazardous chemicals laboratory, where facilities are available to prepare appropriate standards for the analyses of highly toxic (e.g., dioxins, furans and toxaphenes) contaminants. The laboratory offers maximum protection to users and minimal contamination of samples. A large number of Great Lakes water samples have been processed in this laboratory.

The ACRP has also designed user and environmentally friendly techniques, including *in situ* measurements; including the development of cost-effective automated, computerized and robotized systems capable of analyzing large numbers of samples and minimizing human errors (e.g., flow injection analysis).

Under GLAP Annex 1, seven analytical methods related to were developed and evaluated for ammonia, cyanide, inorganic and organic acids, lead, dissolved oxygen, sodium and potassium.

The development of Laser Excited Fluorescence Spectrophotometer (LEAFS) has significantly improved our ability to measure the concentration and distribution of metals in the Great Lakes. Due to its extreme sensitivity, metal concentrations are measured directly, without preconcentration and separation steps. This reduces the problems of sample contamination and human error. Study results comparing the conventional method (graphite furnace atomic spectroscopy) and LEAFS on Great Lakes water samples show lead concentrations have been consistently overestimated in the past by 20 to 100%. These new, accurate values are important for mass balance calculations, for example, to quantify atmospheric inputs of metals such as lead, cadmium and mercury.

Ammonia

A flow injection analysis method for testing ammonia in water, effluents and Kjeldahl digests at the sub µg/L level, was developed. The method is based on the combination of a gas diffusion technique with a continuous flow system interfaced with a conductivity detector. Ammonia diffuses through a hydrophobic membrane from an alkaline medium to a dilute acid solution, which is monitored for changes in conductance. The method is suitable for a wide range of ammonia concentrations (sub µg/L to high mg/L), and overcomes the interference and sensitivity problems of the time-consuming, commonly used spectrophotometric and electrochemical methods. It is simple, sensitive, selective, fast and reliable.

Cyanide

The flow injection analysis method was also developed for testing cyanide in water, at a detection limit of 10 ng/L. The method utilizes the iso-thermal distillation of hydrogen cyanide gas as a separation and preconcentration step in a continuous flow system with amperometric detection. The distinction between the various forms of cyanide is made by measuring the amperometric response at pH 6, then at pH 1, and finally after in-line UV irradiation of the sample. This automated method is rapid, sensitive, selective and virtually interference-free, as well as capable of measuring cyanide concentrations ranging from 0.1 µg/L to mg/L levels.

Inorganic Acids and Organic Acids

Isocratic ion chromatography was used to measure inorganic acids (hydrochloric, nitric, nitrous, phosphoric, sulphuric) and organic acids (hydroxymethylsufonic, methanesulphonic, oxalic) in precipitation at the 10 to 40 µg/L level for inorganic acids and at the 50 to 250 µg/L level for organic acids. Isocratic anion chromatography with conductivity detection is used for the simultaneous analysis of 8 inorganic and organic acids. The 8 acids (methanesulfonic, hydrochloric, nitrous, phosphoric, nitric, hydroxymethylulfonic, sulphuric and oxalic) are resolved in 10 minutes. The method is accurate and precise but provides mainly data for inorganic acids.

Lead

Flameless atomic absorption was used ot measure lead in water at a detection limit of 1 µg/L. The method is based on the application of atomic absorption spectrophotometry using a Zeeman modulated tungsten ribbon furnace. Analytical interferences are eliminated by the addition of ammonium tartrate-nickel (II) nitrate to the sample as a matrix modifier and for pH adjustment. The nickel-ammonium-tartrate modifier also enhances the accuracy and precision of the analytical data. The method requires simple instrumentation and is economical and efficient for the determination of trace levels of lead in a variety of water samples.

In addition, laser-excited atomic fluorescence was also used to measure lead in water at a detection limit of 0.4 ng/L. A laser-excited atomic fluorescence spectrometer is used to measure lead directly in natural water samples without any sample pretreatment or preconcentration. This high-tech method is simple, reduces analysis time to minutes and avoids the contamination problem inherent in the preconcentration steps of other methods.

Dissolved Oxygen

Flow injection analysis was used to measure dissolved oxygen in water at a detection limit of 0.1 mg/L. A continuous flow injection system based on "Winkler Chemistry" using the spectrophotometric detection of iodine is employed for the determination of dissolved oxygen in fresh water. The method is suitable for the automated analyses of large numbers of samples, as well as for continuous monitoring. Turbidity and colour do not interfere with the method. The equipment required is inexpensive and the consumption of reagents is low.

Sodium and Potassium

Flow injection analysis was also employed to measure sodium and potassium in water at a detection limit of 0.1 mg/L for sodium and 0.02 mg/L for potassium. The automated method is based on the application of flow injection analysis to atomic absorption spectroscopy (AAS) for the determination of sodium and potassium. The method requires only 500 to 1000 µL of sample and is optimized at a throughput rate of 120 to 180 samples per hour with high accuracy and precision. It is superior to direct aspiration AAS and automated flame photometric procedures for routine environmental analytical laboratory application.

Ecosystem Objectives

The development of ecosystem objectives and their indicators is a two-stage process. The first, development of the objectives themselves, is a consensual process requiring input from all potential ecosystem users. Because the objectives describe desirable conditions, they reflect societal values and long-term visions for the state of the ecosystem. The process, therefore, is largely political rather than technical, although technical input is necessary to ensure that elements of the vision are achievable and sustainable.

Once agreement has been reached on the objectives, then measurable indicators can be considered and targets set that will describe ecological conditions when the objectives have been achieved. The selection of indicators and target values is largely a technical process, requiring expert review of historic and current data, and translation of the objectives into quantifiable measurements.

NWRI has co-chaired and administered the Canadian participation in the parties Ecosystem Objectives Work Group (EOWG) from 1990-1993. EOWG has been responsible to the Parties for the development of ecosystem objectives for Lake Ontario. A public workshop was organized in early 1990 at Buffalo, New York, from this and other discussions five ecosystem objectives were submitted to the Lake Ontario Toxics Management Plan Secretariat and subsequently approved and adopted. These objectives are: aquatic communities, wildlife, human health, habitat and stewardship.

Aquatic Communities

The waters of Lake Ontario shall support diverse healthy, reproducing and self-sustaining communities in dynamic equilibrium, with an emphasis on native species. This objective will be measured by the selection of attributes for a population of a large predator fish species or community assemblage and components of a benthic community. Separate targets for the nearshore and offshore will be established.

Wildlife

The perpetuation of a healthy, diverse and self-sustaining wildlife community that utilizes the lake for habitat and/or food shall be ensured by attaining and sustaining the waters, coastal wetlands and upland habitats of the Lake Ontario basin in sufficient quality and quantity. Candidate indicators for this objective are bald eagle, osprey, cormorant, gull, and mink populations.

Human Health

The waters, plants and animals of Lake Ontario shall be free from contaminants and organisms resulting from human activities at levels that affect human health or aesthetic factors such as tainting, odour and turbidity.

Habitat

Lake Ontario offshore and nearshore zones and surrounding tributary, wetland and upland habitats shall be of sufficient quality and quantity to support ecosystem objectives for health, productivity and distribution of plants and animals in and adjacent to Lake Ontario. Development of indicators will be to specific a minimum number of acres of suitable habitat such as wetlands. this will require an initial and continuing inventory.

Stewardship

Human activities and decisions shall embrace environmental ethics and a commitment to responsible stewardship. This, perhaps, is the most difficult, tenuous, and novel of the proposed objectives. Quantifiable indicators such as the proportion of profit/budget of a company spent on effluent control, the number of courses offered on the environment in schools, or the enrollment in environmental studies could be employed.

Benthic Communities

Due to their importance in food web processes and contaminant dynamics, the benthic community is one of several components of the aquatic community being considered for the derivation of structural and functional indicators in support of this objective. Scientists at NWRI have been working on the development of specific quantitative indicators for benthic invertebrates. The structural approach was previously used to develop a benthic invertebrate objective for mesotrophic Great Lakes waters. The approach employs the use of multivariate techniques to define reference communities that are expected to occur over a wide range of healthy environmental conditions. These conditions include chemical and physical factors unrelated to pollution such as pH, alkalinity, slope, depth, temperature, current, substrate, etc., which determine community type. The reference communities then become targets for restoration of the various ecoregions in the lake. The benefits of this approach are that benthic community structure is a well-established bioassessment tool and historical data are usually available for determining the reference communities. Alternative structural approaches, including functional feeding groups and size spectra, were also considered but none have been adequately tested. A disadvantage of structural indicators is that they provide "after the fact" information.

Functional indicators, including bioassays, biochemical indicators, scope for growth and bioaccumulation were also considered. While most functional indicators are still in the research phase, they have important benefits. General indicators such as scope for growth, condition factors and reproductive impairment integrate stresses and provide early warning of bioeffects, while specific indicators such as MFOs and metallothioneins are stressor-specific and provide information on causality.

To date all available benthic community datasets for Lake Ontario have been identified through contacts with Canadian and American government agencies, universities, etc., as well as literature and on-line database searches. Datasets on all distinct ecoregions of the Lake were to be sought. These ecoregions were identified by workshop participants as: Kingston basin, the main Lake (Rochester, Mississauga and Niagara basins), the North shore, the South shore, embayments, river mouths and the Bay of Quinte. In addition, permission has been obtained to use the datasets; all relevant details about the datasets (date, location, sampling technique, etc.) has been acquired and; the databases have been evaluated as to quality and potential usefulness of each dataset. Maps indicating the locations of study sites for each dataset have been prepared and a bibliography of all Lake Ontario benthic studies identified in the search is available. In conjunction with Dr. R.C. Bailey, Department of Zoology, University of Western Ontario, various multivariate techniques for data analysis have been assessed. A test dataset will be analysed using different multivariate techniques, and the results will be used to select the method to be applied to the entire database.

We anticipate that the final report on benthic community indicators for Lake Ontario will be available by April 1, 1994.

Publications

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ANNEX 2

REMEDIAL ACTION PLANS AND LAKEWIDE MANAGEMENT PLANS

Under the 1987 Protocol, Remedial Action Plans (RAPs) and Lakewide Management Plans (LAMPS) are required to be developed and implemented for all identified Areas of Concern (AOCs) and the five Great Lakes. These plans must embody a systematic and comprehensive ecosystem approach to restoring and protecting beneficial uses, aid in the virtual elimination of persistent toxic substances and assist in restoring and maintaining the physical, chemical and biological integrity of the Great Lakes Basin Ecosystem. These plans are required to address 14 use impairments when considering the need for remedial and preventative actions. These use impairments include: restrictions on fish and wildlife consumption; tainting of fish and wildlife flavour; degradation of fish and wildlife populations; fish tumours or other deformities; bird or animal deformities or reproductive problems; degradation of benthos; restrictions on dredging activities; eutrophication or undesirable algae; restrictions on drinking water consumption, or taste and odour problems; beach closings; degradation of aesthetics; added costs to agriculture and industry; degradation of phytoplankton and zooplankton populations; or loss of fish and wildlife habitat.

Remedial Action Plans are to be submitted to the International Joint Commission (IJC) for review and comment at three stages: when the problems have been defined; when remedial and regulatory measures are selected and; when monitoring indicates that the impaired beneficial uses have been restored. Similarly, Lakewide Management Plans must also be submitted to the IJC for review and comment, but at four stages: when a definition of the problem has been completed; when the schedule of load reductions for Critical Pollutants is determined; when remedial measures are selected and; when monitoring indicates that the contributions of the Critical Pollutants to impairment of beneficial uses has been eliminated.

Remedial Action Plans

Scientists at NWRI are participating directly in writing RAP documents for the Spanish River, Severn Sound and Hamilton Harbour (Figure 1). They are also providing essential information to define environmental problems, develop and evaluate remedial options and, develop and demonstrate remediation techniques and technology.

Environmental conditions, in the Areas of Concern are strongly influenced by land use throughout their respective drainage basins, as well as present and historical water uses. Due to the breadth of the environmental problems and their fundamental causes, research conducted under other Annexes (e.g., 13 -- Pollution from Non-Point Sources, 14 -- Contaminated Sediment, etc.,) is directly and immediately applicable to restoring beneficial uses in the Areas of Concern. As a result, considerably more resources were expended and greater knowledge gained for the RAP program through issue related research than appears in this brief synopsis of results.

Hamilton Harbour

Hamilton Harbour is located at the western end of Lake Ontario. At one end, the harbour is connected to the lake via a narrow shipping canal, and at the other, to a large wetland complex, Cootes Paradise (Figure 2). Environmental conditions within the harbour were described in the Stage 1 RAP document published in 1989. Two of the identified impaired uses (fish habitat and water quality) were affected by poor water clarity. The relative importance of pollutant sources were investigated and recommendations were made on the reductions necessary to improve water clarity. These recommendations were incorporated into the Hamilton Harbour Stage 2 document as the targets or goals for nutrient, chlorophyll and suspended solids concentrations to be achieved through future abatement actions.

A research study of water quality in the harbour at the time of loading changes showed that ammonia responds immediately to improved treatment at the Hamilton Sewage Treatment Plant (STP). The winter build up of ammonia was reduced through an experimental treatment at the STP and harbour spring

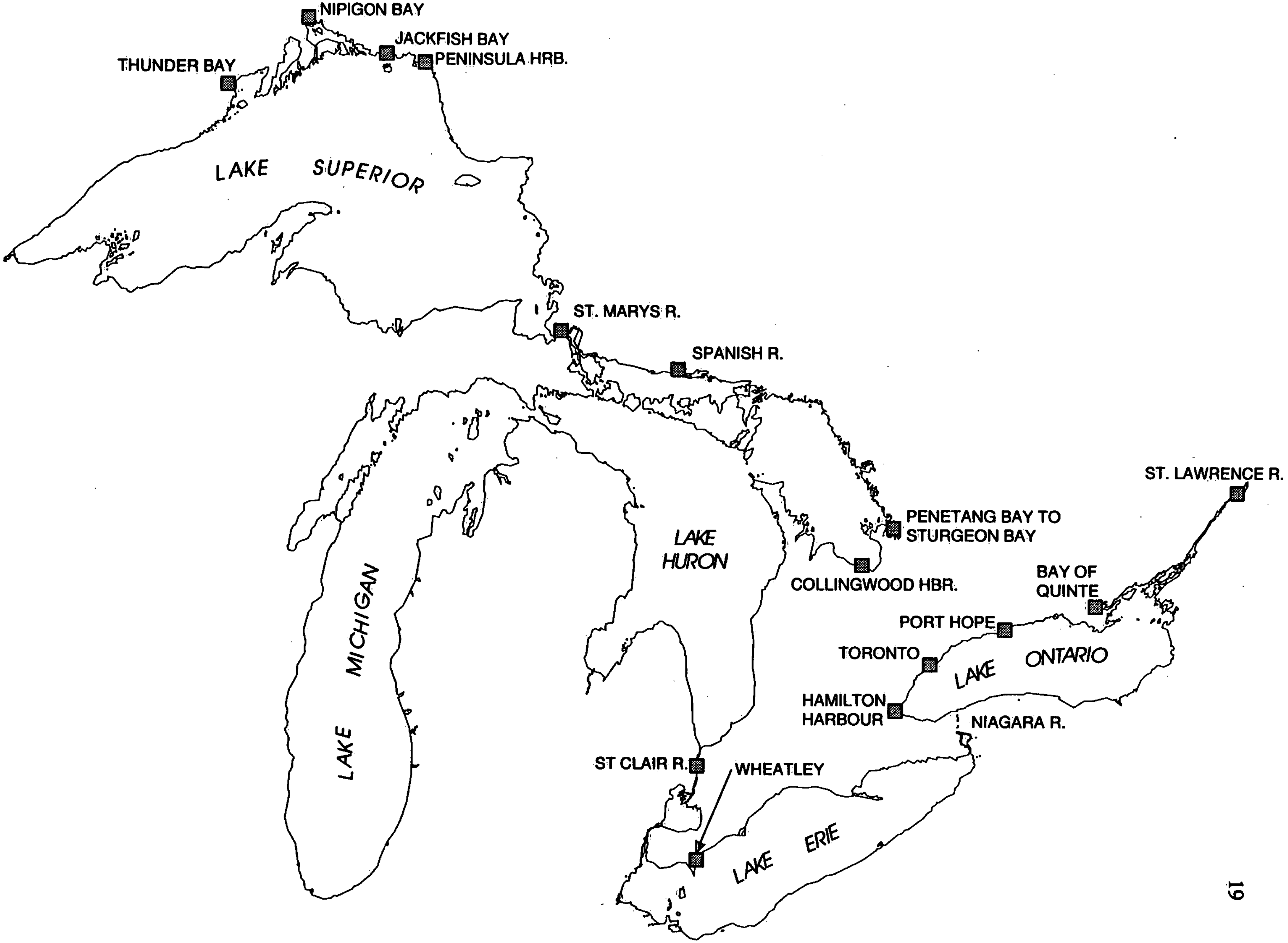

Figure 1. Great Lakes showing Canadian and binational Areas of Concern.

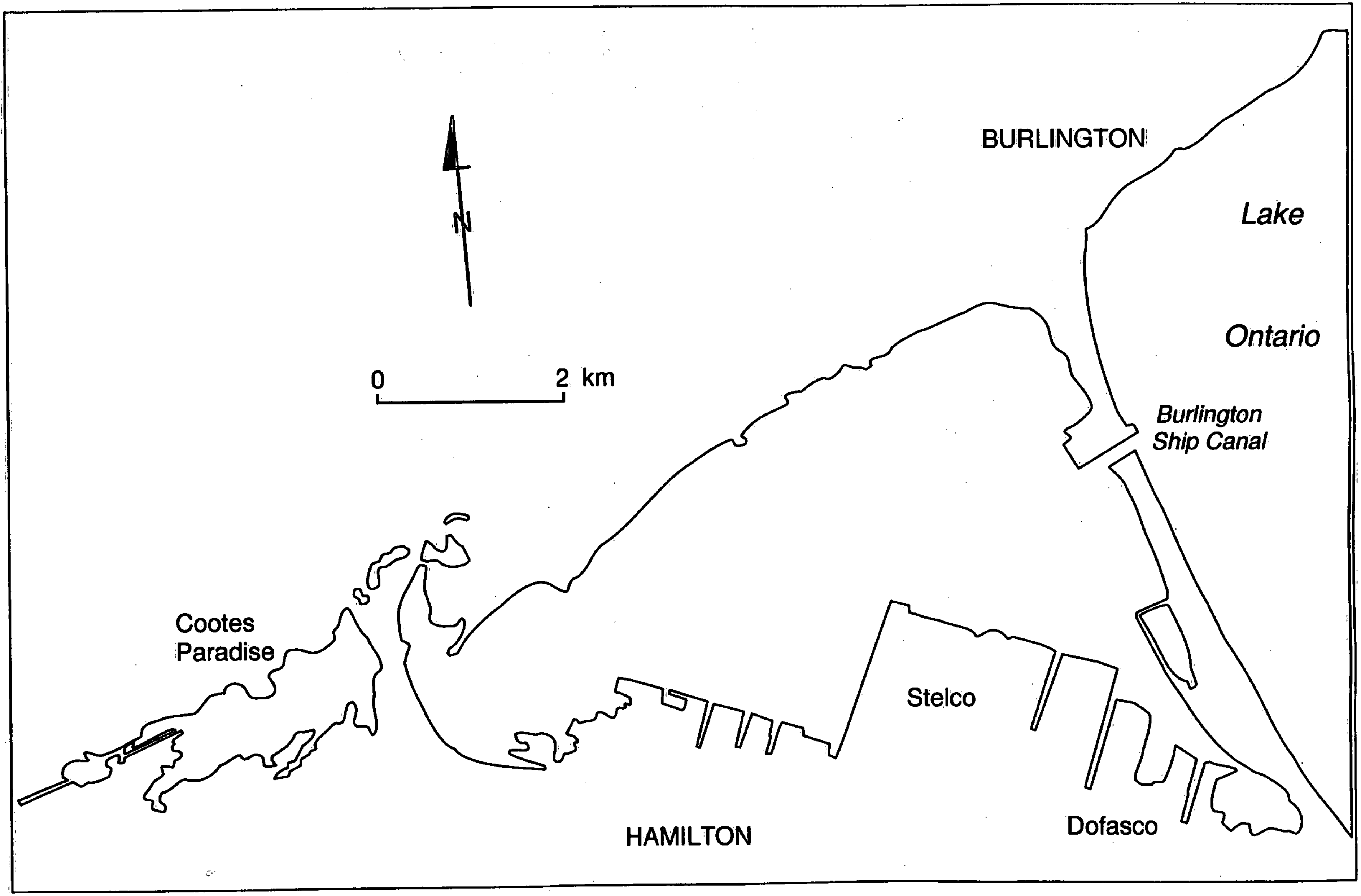

Figure 2. Hamilton Harbour/The Bay

maximum concentrations were cut in half. This shows the harbour will respond quickly to major loading changes. However, nutrient load reductions were insufficient to prevent periodic alga blooms during the summer. Regular monitoring of 23 sites in the harbour provided details on layers of lake water entering the harbour throughout the summer. The study showed that on occasion, low oxygen water is pushed within a few meters of the surface due to rippling effects in the thermal structure. This means that fish are sometimes forced to vacate favoured areas of the harbour in order to survive.

An analysis of the oxygen problem, in response to an artificial aeration proposal was completed. A report for a lay audience was completed that explained the relationship of eutrophication and lake depth on the oxygen problem. A model for predicting oxygen concentrations in response to nutrient load was developed and used to show the degree of nutrient removal required. Massive reductions in the nutrient loads as well as reductions in ammonia are needed to bring back acceptable oxygen levels. These findings indicate that the aeration proposal would be ineffective in solving the problems and impractical to install. Nutrient loads must be reduced to much lower levels in Hamilton Harbour than are currently required at other sites.

Although ammonia and subsequent nitrification processes consume oxygen and produce the nutrient nitrate, little is known about the suite of processes that affect the fate of nitrogenous nutrients in the harbour. In partnership with McGill University and funded by Environment Canada's Great Lakes University Research Fund (GLURF), a study of denitrification and methane production was conducted at 21 sites in Hamilton Harbour. The study found that ammonia producing, denitrifying bacteria are dependent on carbon sources, which are produced to excess as a result of the highly eutrophic conditions in the harbour. Thus, the oxygen problem is exacerbated by ammonia released through these microorganisms in the sediment as well as the decompostion of algal carbon. Again, this points to the need for more stringent nutrient controls. More importantly, the study found that the variability between sites was explained by simple physical and chemical factors. Microbe metabolism was not strongly affected by metal gradients. Observations of sediment organism metabolism showed little toxicity of in-place contaminants.

During the microbial metabolism study the distribution of ammonia in sediment pore waters was mapped. Over much of the harbour values of about 20 mg/L were found. These levels are known to be indicative of eutrophic lakes. The concentrations are also of concern since they can result in toxic concentrations of un-ionized ammonia under certain pH and temperature conditions. Near the Burlington STP outfall, however, concentrations of 200 mg/L ammonia were found in porewater. These are probably caused by decomposing particles from the STP. A subsequent survey in 1993 showed that this area is persistent from year to year. As yet the size of the deposit is unknown but indications are that it is relatively small. The outfall area receives the full wave action from west winds and this tends to remove lighter particles that may otherwise accumulate. Therefore, particles from the STP may be contributing to water quality problems and oxygen depletion throughout the harbour.

The time and space scales of physical processes such as resuspension, transport, mixing and settling mediate the vigour and distribution of biological and chemical processes. Therefore the interpretation of observed biogeochemical variability, as well as contaminant fate and impact, requires an assessment of the physical processes operating at the time. The physical behaviour can be viewed as the context in which the other processes act.

The interlocking of physical and biogeochemical processes may be viewed in the simplest possible terms as the interplay among three time scales. These are: (1) the flushing time of the harbour (Tf), the time taken for the water within the harbour to be "replaced" by precipitation, runoff and lake/harbour exchanges; (2) the horizontal mixing time of the harbour (Tm), the time taken, on the average, for a blob of a conservative contaminant introduced at a point within the Harbour to be mixed uniformly throughout the basin; (3) the removal time scale (particular to the contaminant) (Tr), the time taken for a contaminant to be altered or removed by biogeochemical processes acting within the harbour.

An assessment of the present state of knowledge concerning physical processes in the harbour identified five (5) questions whose answers would define the physical context for contaminant distributions and impacts.

What are the time scales of flushing of the different compartments of the harbour in different seasons of the year?

What are the time scales of horizontal mixing of different compartments of the harbour in different seasons of the year?

What is the climatology of episodes of sediment resuspension and transport in the harbour? Can this knowledge be combined with the answers to Question 1 and Question 2 above to estimate the export of suspended material from the harbour?

Does the export of contaminants to the open lake from the harbour depend in any significant way on the location of the source of such contaminants to the ship canal (phenomenon of short-circuiting)?

What are the impact zones of point sources of contaminants such as storm sewers? Will the various berms, dykes, enclosures proposed as habitat rehabilitation measures have significant effects on nearby water quality?

As opportunities have arisen, and in response to the needs of biological and chemical studies in the harbour, physical data has been collected. For example, the 1993 experimental program now in progress concentrates on water movements in the northeast sector of the harbour with the intent of providing information for the construction and calibration of numerical hydrodynamic models (joint program with McMaster University) for the nearshore zone, and to provide a physical context for a study of the effects of the Burlington STP on the harbour. An adjoint study aims at extending the "library" of longitudinal temperature cross-sections of the harbour (together with supporting meteorological information) in order to develop models of lake-harbour exchanges.

Failure of Hamilton Harbour sediments to meet guidelines for dredgeate disposal is a use impairment that must be redressed prior to delisting the harbour as an Area of Concern. A study of contaminated suspended particles was conducted using sediment traps. These particles can be transported out of the harbour to the lake or settle to the bottom of the harbour. The rates of particle accumulation are very high, compared to Lake Ontario, indicating large loadings. Resuspension of these contaminated particles seems to be relatively weak and most resuspension occurs in shallow sediments that are minimally contaminated. Contaminant concentrations increase near industrial areas. Concentrations of polynuclear aromatic hydrocarbons (PAHs) in the traps can reach 5000 ng/g, which is 2-3 times higher than in most of the bottom sediments. Metal concentrations in these particles routinely exceed their guidelines for the open water disposal of dredge spoils. Most contaminants of interest are highly correlated in the trap materials, indicating a common source. PAHs, not on priority lists, have been found in a joint study at with researchers from McMaster University. The source of these PAHs, which do not seem to emanate from toxic tar deposits, is the subject of an investigation by the University and NWRI under the TRICERP funding to McMaster. The sediment trap data appear to indicate that formation of new sediments, sufficiently clean to meet the dredging guidelines, is hampered by existing discharges, even though these discharges satisfy regulations.

In another study, temporal trends in sediment deposition in the harbour were investigated using long (>8.5 m) sediment cores. In cooperation with scientists at University of Waterloo, the paleoecology of the Hamilton Harbour area in the context of its postglacial evolution, was interpreted.

Spatial transport and dispersal of contaminated sediments were also investigated using chemical markers for sewage effluents as tracers. A range of such markers, including fecal sterols, C- and N-isotope ratios, and physical sediment properties were used to trace the dispersal of the effluent from the Burlington Skyway STP, in the northeast corner of the harbour. The plume for coprostanol showed a dominant, shore-parallel dispersion in both directions, apparently in response to the prevailing SW-W wind regime. This research was conducted in collaboration with McMaster University.

Degraded benthos populations are another of the use impairments listed in the Hamilton Harbour RAP. Just how degraded are the populations after many years of industrial and municipal pollution abatement? The benthic invertebrate communities from 13 sites along a nearshore-offshore transect on the north shore of Hamilton Harbour were sampled four times between June and August 1989. Species distributions were documented to evaluate the community's response to past remedial actions and also to enable future assessments of changes in the benthic invertebrate community. Although the benthic invertebrate community in Hamilton Harbour is still indicative of a highly eutrophic environment, substantial improvements have occurred. The most noticeable sign of improvement is the significant increase in species diversity. The total number of species increased from 13 to over 31, while the number of oligochaete species decreased from 9 to 5. Similarly, community composition has shifted away from pollution tolerant species towards slightly more pollution sensitive species. Detailed analysis of the physico-chemical variables will allow us to establish the relationships between benthic invertebrate community structures and contaminants and how these relationships are affected by physico-chemical variables. The results show that there is a fairly diverse nearshore fauna and pollution control has had a beneficial effect, but greater improvement is necessary.

The harbour receives high inputs of phosphorus from the sewage treatment plants of Burlington and Hamilton. It also receives heavy loadings of iron from the steel industry; consequently, concentrations of iron are elevated in the sediments. The interaction between phosphate ion and ferric iron was studied over two summers to determine (a) the role of iron in reducing the availability of phosphorus and (b) the export of metal contaminants to Lake Ontario. Field work was based around the collection of bottom sediments and suspended particulates from several stations at different times of the year, emphasizing the periods of thermal stratification. Sediments and particulate matter were analysed for different forms of phosphorus and iron, and for Pb, Cd, Cu, Ni, and Zn. Correlations between elements were assessed statistically.

Ferric iron, as poorly crystalline oxides (hematite and wustite) are the main industrial forms of iron. Hematite and wustite are relatively inert and are useful in tracking plumes of industrial effluent. Hydrated ferric oxide is a strong adsorber of phosphorus, Pb, Zn and other contaminants. This property is beneficial in binding these ions and lowering their bioavailability. In addition, it was found that although iron and manganese are released from the bottom sediments during bottom anoxia, no phosphorus is released. Further analyses showed that metal loadings from the harbour to Lake Ontario are negligible when compared with the loadings from the Niagara River.

Bay of Quinte

Eutrophication remains a major problem in the Bay of Quinte, Lake Ontario (Figure 3) in spite of major and expensive reductions in the loadings of phosphorus from the sewage treatment plants (STPs). This study has attempted to answer such questions as "Have these cut-backs been justified?" and "What other remedial actions might be invoked?" To answer these questions, the summer loadings of bioavailable phosphorus to the Upper Bay of Quinte from each of the main sources (the STPs, the rivers and the in-place sediments) were measured.

Field work over the past five years has included activities such as the extensive coring of bottom sediments in the Bay of Quinte, the placement of porewater

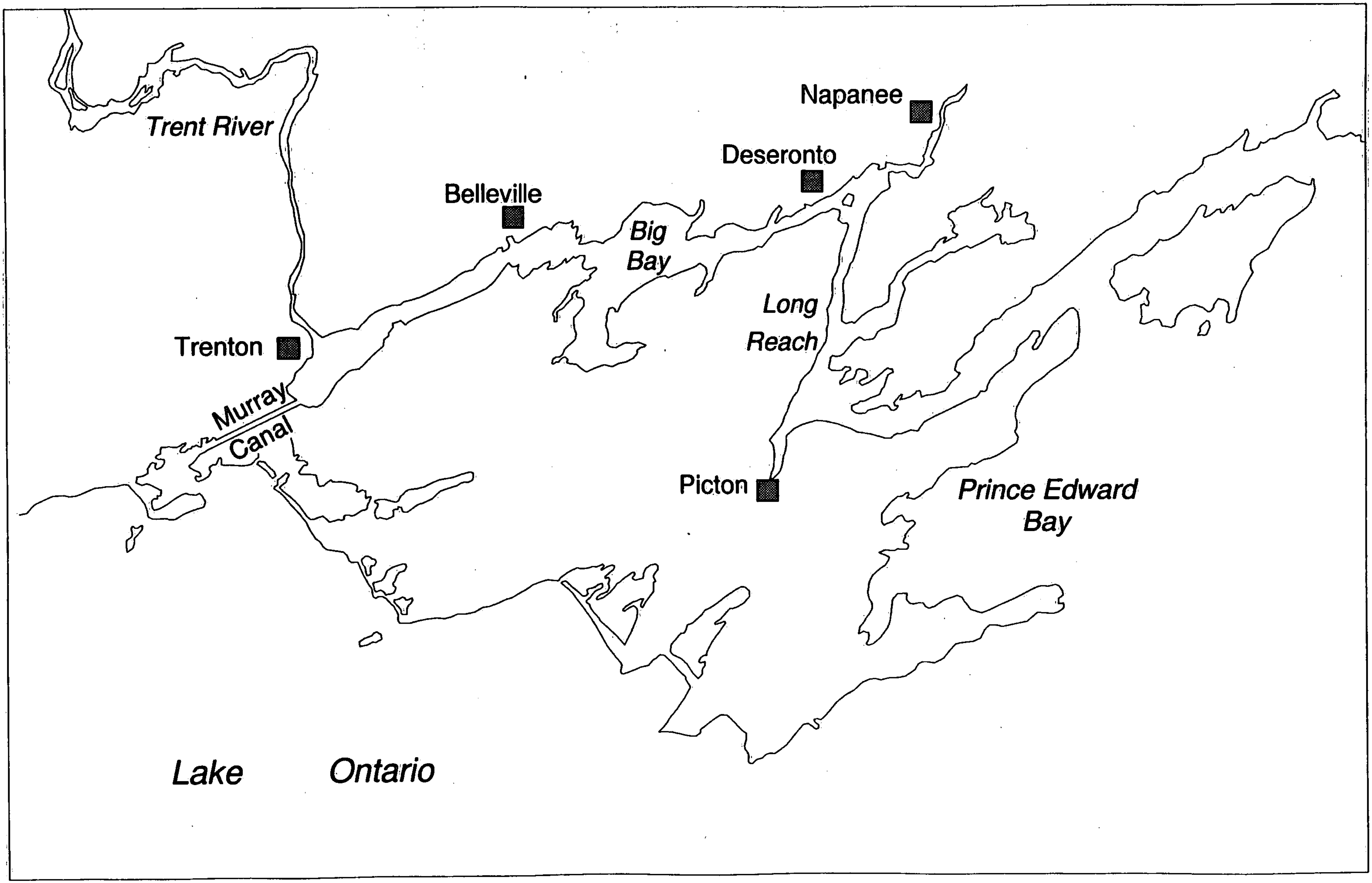

Figure 3. Bay of Quinte

"peeper" samplers, and the collection of suspended particulates in the Trent and Moira Rivers. Analyses have been directed at the definition of the chemical forms of iron and inorganic phosphorus in the river particulates, the in-place sediments and the water, in order to understand the geochemical processes underlying the availability of phosphorus.

The results indicate that as summer progresses, loadings of inorganic phosphorus from the rivers decrease (in response to lower flow rates); whereas, phosphorus loads from the in-place sediments increase (in response to rising water temperatures and higher rates of diffusion of phosphate ion). Consequently, by July, the loadings of bioavailable phosphorus from the in-place sediments become dominant. Much of this sediment phosphorus is probably derived from the STPs. Hence, eutrophication in the Bay of Quinte has been driven directly and indirectly by the STPs. Additional reductions in the rate of sedimentation of phosphorus in Upper Bay are essential to improving water quality. These reductions are likely best achieved through more controls on the loadings of the STPs (from March through October) and improved erosion control in the watershed.

Jackfish Bay

Bleaching methods for pulp and paper frequently use elemental chlorine, which leads to the formation of chlorinated materials. The volatile compounds formed are mostly low molecular weight chloro-methane/ethane products such as chloroform, and their higher molecular weight precursors. Jackfish Bay on the north shore of Lake Superior (Figure 4) receives on average, 94,000 m^3/day of bleached kraft mill effluent which constitutes 65 to 90% of the flow of Blackbird Creek and originates near Terrace Bay, Ontario, some 14 km from the creek's discharge into Moberly Bay. The objective of this work was to examine chloroform and other halocarbon emissions into the bay as they originate from the bleached kraft mill (BKM) effluent.

Chloroform has been shown to be a useful tracer of pulp effluent into oceans. In addition, our previous studies have demonstrated the sensitivity and application of volatile halocarbon fingerprints to determine contaminant sources and differentiate water masses and plume dispersions into lakes. It is thought that such techniques may also be useful in addressing certain aspects of the proposed

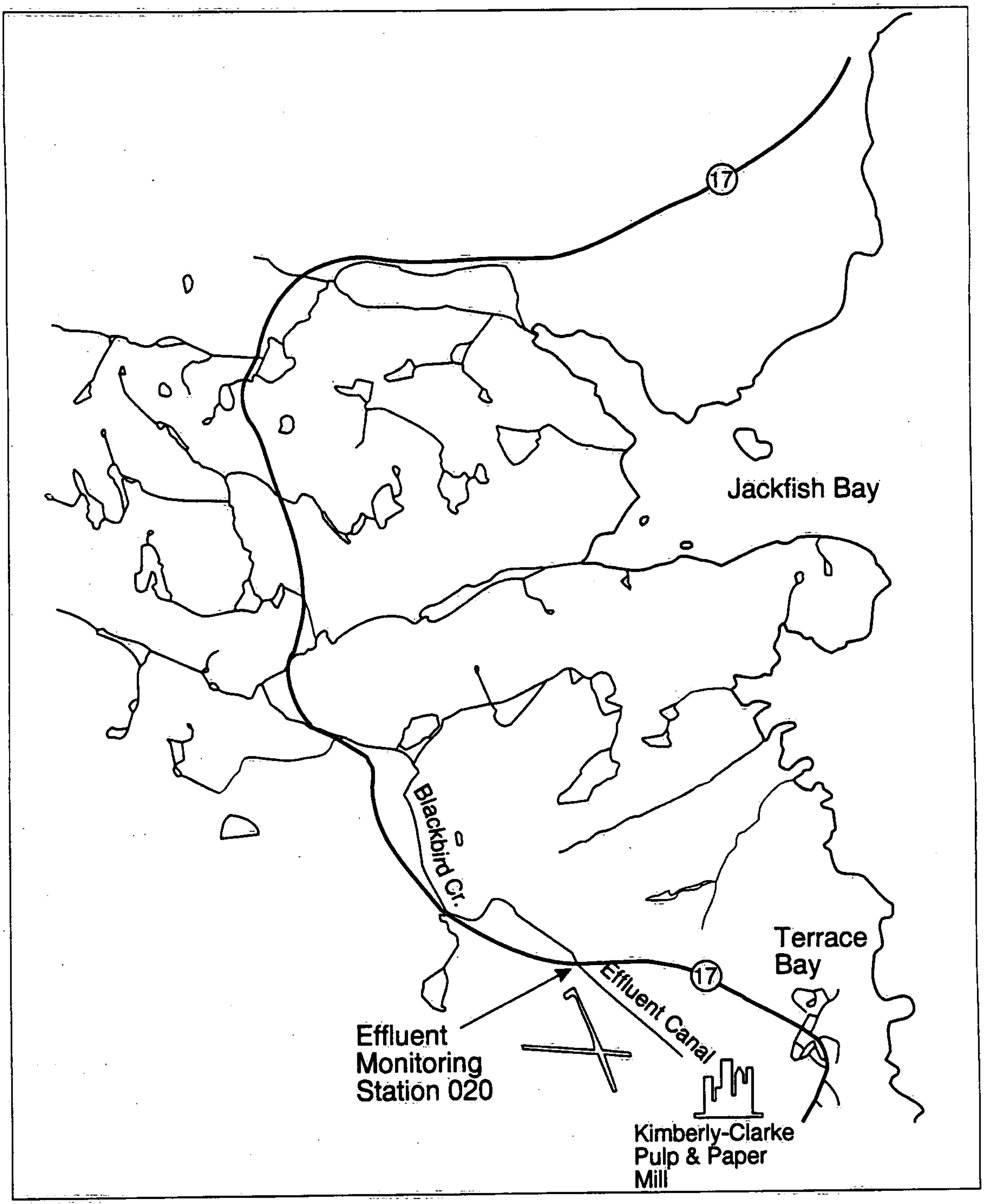

Figure 4. Jackfish Bay

federal Environmental Effects Monitoring (EEM) strategy as they apply to pulp and paper discharges.

Our findings indicate that the volatile halocarbon contaminant distribution patterns in Jackfish Bay appear to be primarily governed by the thermal regime of the receiving water in the bay and secondarily by wind driven currents. The chloroform (CFM) and bromodichloromethane (BDCM) concentrations and their ratios suggest that sediments may be secondary sources of these compounds. Figure 5 shows the distribution of effluent in Jackfish bottom water in October, 1991, as determined from the CFM/BDCM ratios. It indicates the highest concentrations of effluent in the central part of the bay's bottom water.

The CFM/BDCM ratios further allow the determination of source stream content in the receiving waters. The observed variations in volatile contaminant concentrations and percentage source values suggest that some discharges are intermittent, and therefore contaminant levels and source stream concentrations do not correlate very well. We observed that conductivity was only weakly correlated with chloroform values and not correlated with the other volatile halocarbons. Therefore, we conclude that conductance measurements appear to be of limited use for determining areas of contamination. However, the volatile halocarbon profiles provided greater resolution, sensitivity and differentiated lake and effluent water masses, their movement and level of contamination.

Port Hope Harbour

Port Hope Harbour is located on the north shore of Lake Ontario (Figure 6), approximately 100 km east of Toronto. Harbour sediments are contaminated by uranium and thorium series radionuclides, heavy metals and PCBs. Dredging has been considered as a remedial action for contaminated sediments in Port Hope Harbour. Dredging will involve the removal and disposal of 90,000 m^3 of sediments, which are contaminated mainly by radionuclides..

As part of a Remedial Action Plan study, the National Water Research Institute was requested to determine the present contaminant loading rates to harbour sediments.

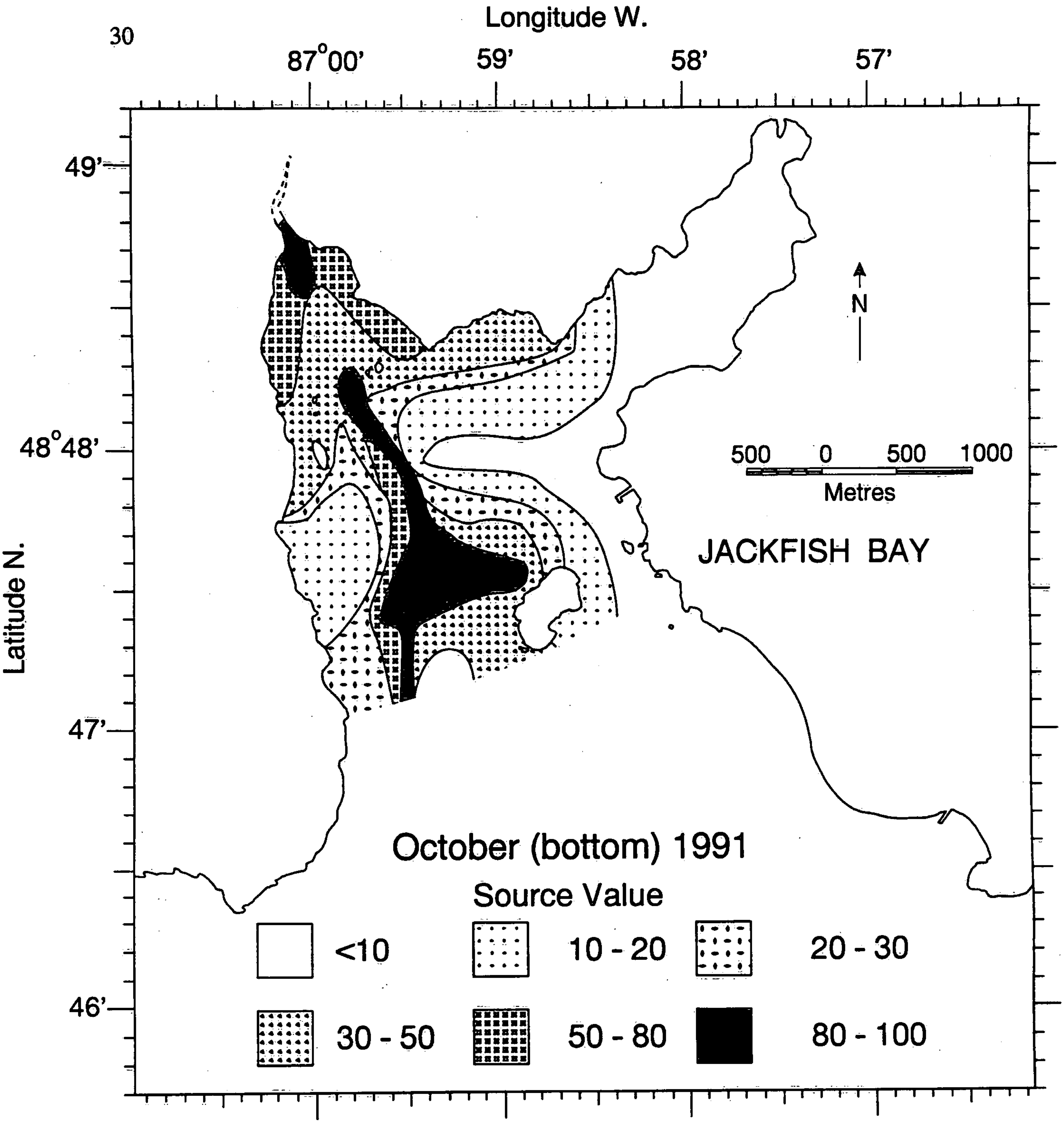

Figure 5. Distribution of pulp mill effluent as determined from the chloroform/bromodichloronethane ratios in Jackfish Bay, Lake Superior, during October, 1991.

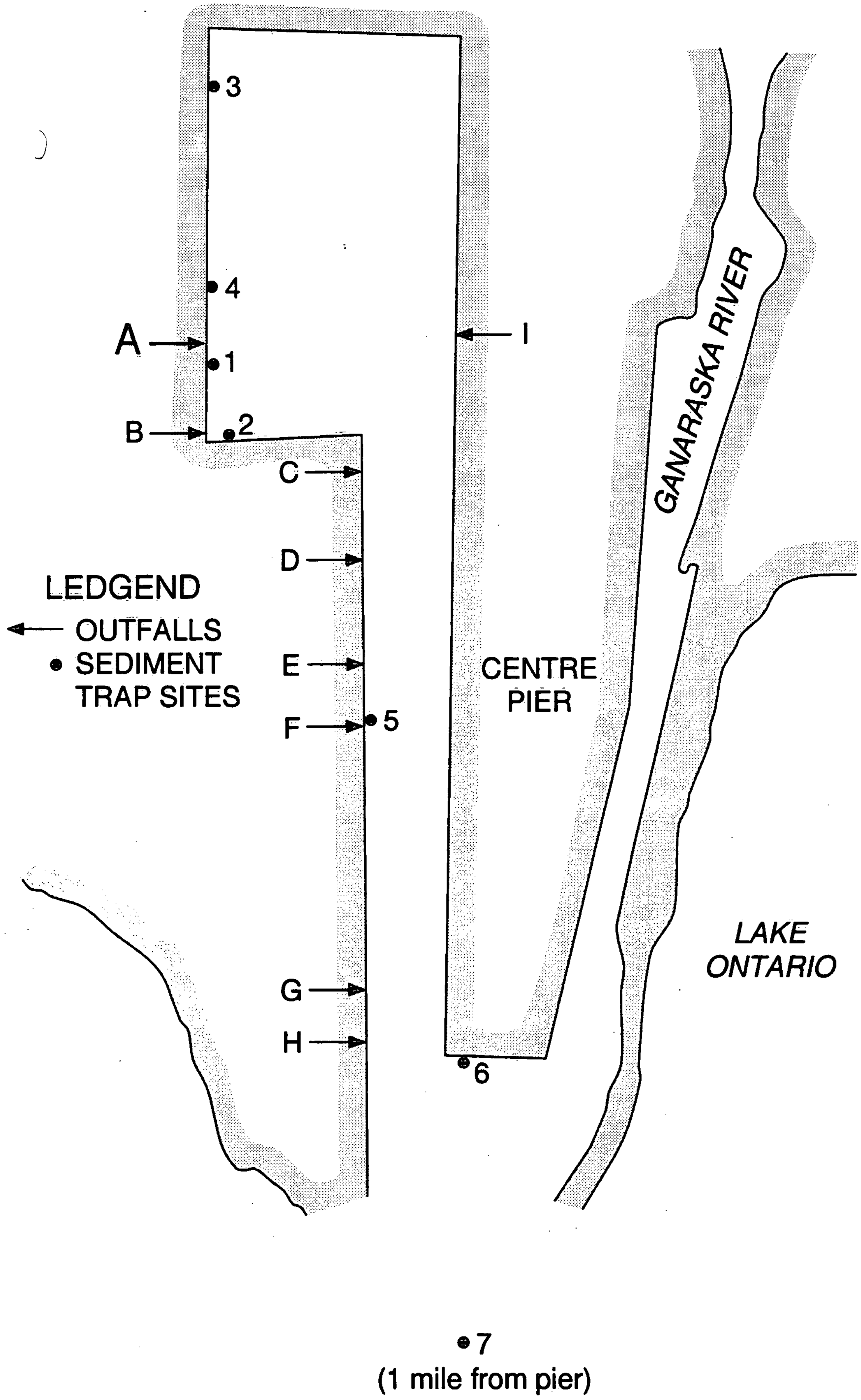

Figure 6. PORT HOPE HARBOUR

Sediment traps were deployed at strategic sites inside and outside of the harbour. Bottom sediments were sampled at four stations in the harbour, and sediment and associated contaminant concentrations in the effluent at the main outfall (UO_2/UO_3 plant, "A") were measured. The trap content was freeze-dried and weighed to determine the accumulation rate ($g{\cdot}m^{-2}{\cdot}d^{-1}$) in the traps at each site. The total trapped matter (TTM), particulate matter collected from the effluent, and bottom sediment samples were analysed for different organic and inorganic contaminants (nutrients, metals and TPCBs) and seven radionuclides (^{210}Pb, ^{226}Ra, ^{238}U, ^{228}Th, ^{228}Ra, ^{137}Cs, ^{7}Be). Particulate matter in the traps and in the effluent was also analysed for trace elements, to be used later as tracers for sediment transport.

The uranium refinery operated by CAMECO Ltd. discharges directly into the harbour (turning basin and west slip) at a mean rate of $\approx 20.5 \times 10^3$ m^3 per day. Based on the effluent information 37×10^6 µg or 37 g of ^{238}U are being discharged into the harbour each day. The accumulation rates of TTM and ^{238}U, as measured by sediment traps, show some differences within the harbour, but there is a distinct decreasing trend as distance increases from the source, "A". All other contaminants showed a similar trend. The mean concentration of ^{238}U (207 ± 22 $\mu g{\cdot}g^{-1}$) in the trapped matter for sites near the source was lower than the concentration of ^{238}U (237 $\mu g{\cdot}g^{-1}$) in particulate matter collected from the effluent.

Study results indicate that bottom sediment recontamination is likely by all compounds analysed (nutrients, metals, and radionuclides and some PCB congeners).

Toronto Harbour

The IJC has identified Toronto Harbour and Waterfront, Lake Ontario (Figure 7) as an Area of Concern in the Great Lakes and this has lead to a combined federal and provincial effort to draw up a Remedial Action Plan (RAP). At the same time the Ontario Ministry of the Environment and Energy (OMOEE) initiated its Municipal and Industrial Strategy for Abatement (MISA) program. The former activity examined conditions in the harbour and along the eastern and western waterfront while the latter program has focused on the assessment and control of pollution sources on land. There are four Sewage Treatment Plant STP) effluent outfalls along the study area which are being evaluated by the MISA program. The study described in this report was co-funded by NWRI and OMOEE to assess

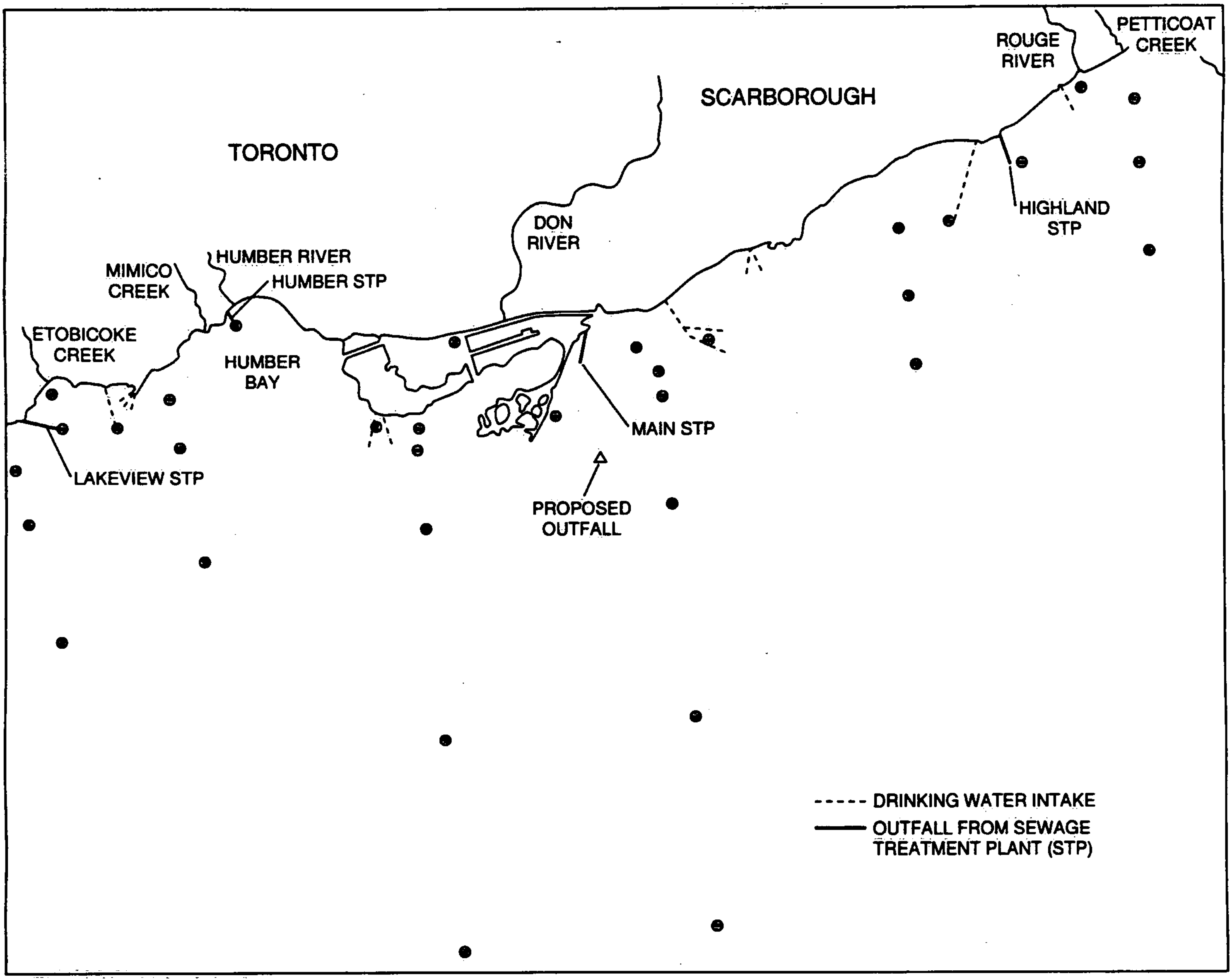

Figure 7. Station locations off the Toronto Waterfront

the present extent of contamination of the nearshore zone by selected organochlorine compounds found in the STP effluents. These data will also serve as a baseline for evaluating the effectiveness of controls on chemical discharges to be promulgated by MISA in the near future.

This study produced concentration maps of 89 chlorinated organic chemicals found in samples collected in the lake along the Toronto waterfront area in spring, summer and fall. A novel ranking technique is used to analyse the overall pattern of chemical contamination. This ranking does not translate to an absolute risk scale for exposure to organochlorine compounds, but it identifies a number of contamination levels relative to this data set. Results show that the western waterfront, Humber Bay, the Inner Harbour, and areas near the Toronto Main STP discharge have the highest pollution rankings.

On several occasions, however, high rankings occurred offshore, which indicate that other sources as well as the Toronto area could be contributing contaminants to the waterfront.

The pollution ranking technique used here could be applied to assess the effectiveness of pollution prevention initiatives in the Toronto area and assist in the Lake Ontario Toxics Management Plan.

Severn Sound

Penetang Bay is located in Severn Sound, in the south-eastern portion of Georgian Bay, Lake Huron, Ontario (Figure 8). The bay shows evidence of noticeably impaired water quality, having a significant algae problem, declining fish populations and elevated concentrations of nutrients.

The RAP Committee, in the process of information gathering, defined areas where further research would help make an accurate environmental assessment to achieve their goal of having swimmable waters virtually everywhere in the area. In calculating a nutrient budget for the area, it was noted that an internal loading estimate was required in order to later establish appropriate loading requirements from controllable sources, as well as determining whether an oxygen depletion occurred during summer stratification or under ice in winter, and whether it contributed to eutrophication of the bay. Minimizing these sources would lead to

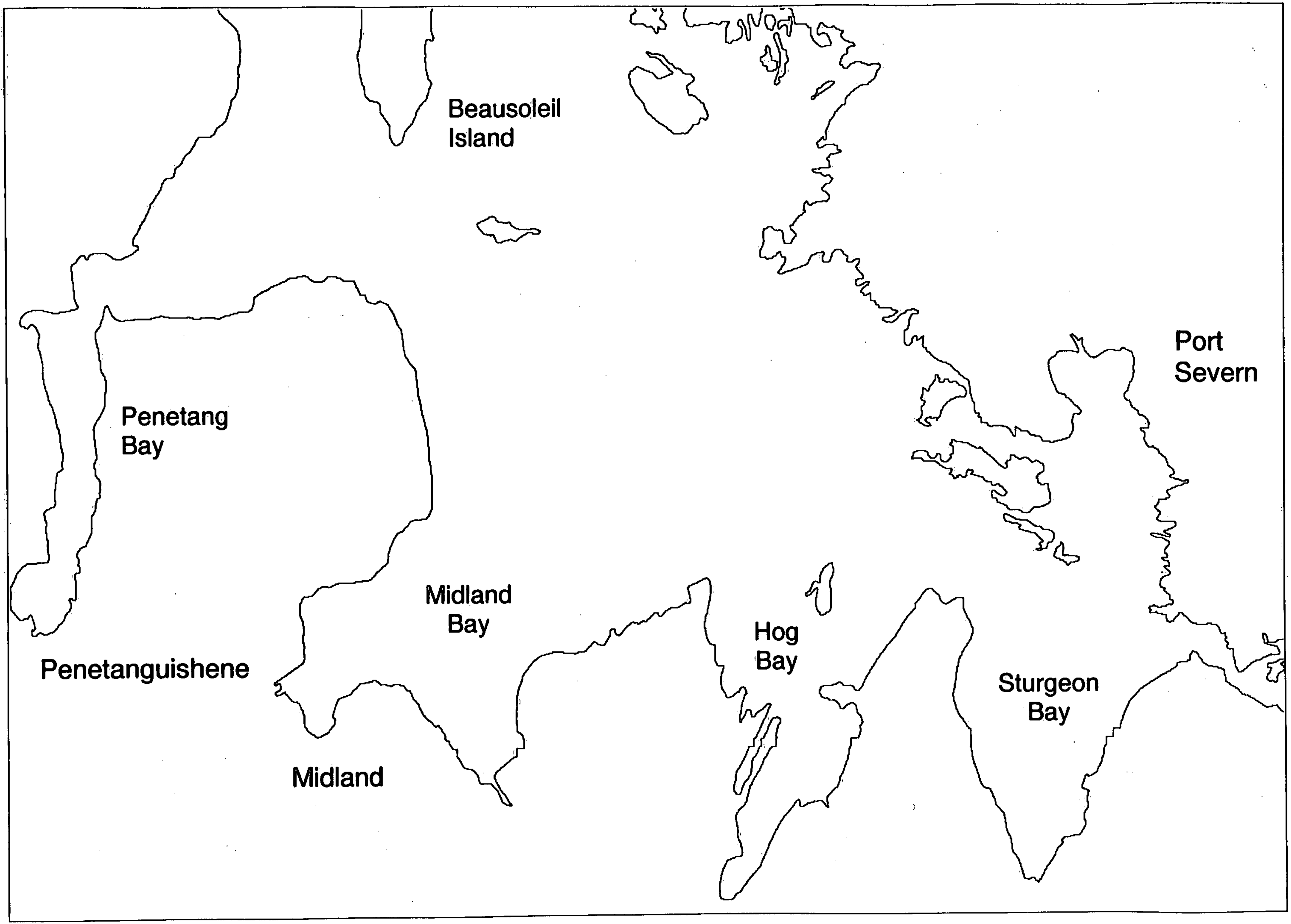

Figure 8: Severn Sound

the control of nuisance algal growth, ameliorate fish rehabilitation, and improve recreational usage of the area.

Penetang Bay receives inputs from two Water Pollution Control Plants (WPCPs). In order to provide an estimate of the internal loads, sites in Penetang Bay were examined. Interstitial (pore) water samplers (dialysis chambers or peepers) were used to measure bottom sediment pore water profiles over a one year study period. Water quality data for lake water were also collected from various sites in the sound. Peepers were deployed at two locations in Penetang Bay and at a reference station off the south-east shores of Beausoleil Island.

Representative ammonia and soluble reactive phosphorus data were used to derive a conservative estimate of the internal loading of these nutrients. The sediments of Penetang Bay act as a source of nutrients to the overlying water. Thus molecular diffusion is responsible for an internal load of 751 and 3078 kg/yr for SRP and NH_3, respectively. External inputs (1663 kg/yr) contribute the remainder of the phosphorus load to the bay. The internal load of SRP represents 31% of the total loading to Penetang Bay. These results are further supported by an examination of the water chemistry data for the Bay and surrounding area, which showed that soluble reactive phosphorus, total phosphorus, and ammonia have consistently higher concentrations near the surface waters, rather than in the bottom waters, as would be expected if the internal loads were the major contributing factor. Oxygen depletion was not noted in the water column to any great extent, though a decrease was noted during a brief period in the summer.

Spanish River

Another Canadian AOC is the Spanish River, located in the North Channel of Lake Huron (Figure 9). Preliminary survey data provided an indication of impairment to the benthic communities in a large part of the Whalesback Channel, adjacent to the river mouth. There was also some indication that these effects were due to high metal levels rather than pulp and paper effluents originating upstream. A more detailed investigation of this and the transport of contaminated harbour sediments into the North Channel proper was subsequently conducted. The new study included measures of sediment toxicity, chemistry and physics, as well as benthic community structure.

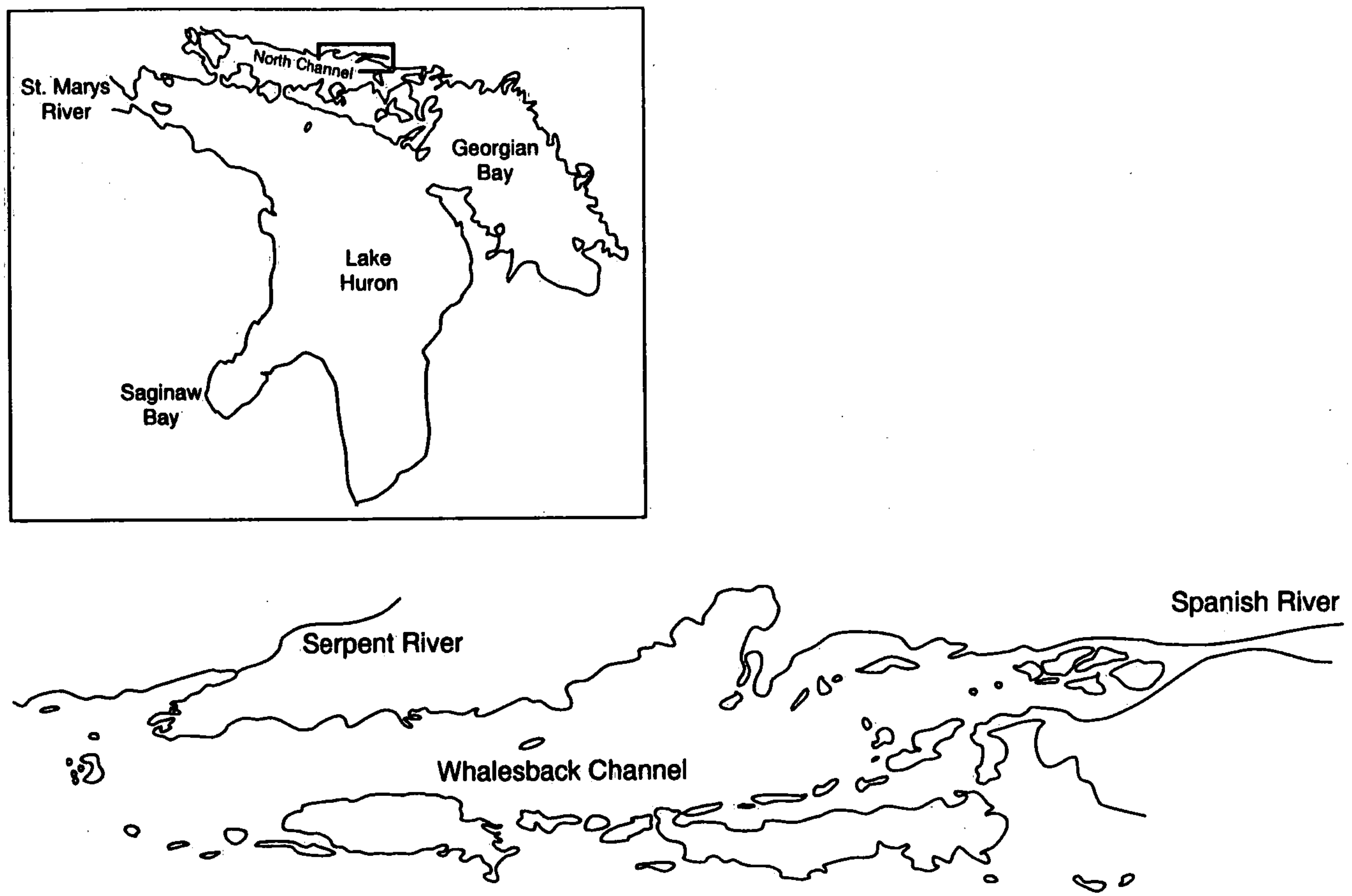

Figure 9. North Channel Study Area

Results of the study indicate that at least during the summer months, metal transport from the Spanish River to the North Channel is occurring, predominantly through surface waters. The benthic enumeration work found the community in the Whalesback area to be extremely depauperate and have the lowest numbers of all the major taxonomic groups. Subsequent analysis of community data and sediment toxicity tests confirmed that the high levels of zinc, nickel and copper in the sediments of the Whalesback Channel have had a significant detrimental impact on that entire area.

St. Marys River

The St. Marys River is actually a channel connecting Lake Superior and Lake Huron (Figure 10). It is also an Area of Concern. Pollution from power generation, shipping, and the discharge of nutrients and organic and inorganic contaminants from industrial and municipal point sources and different urban non-point sources in the past 40 years has contributed to the degradation of river water and fish habitat.

During the past 20 years, different studies have indicated an impaired benthic community, contaminated sediments, and elevated concentrations of organic and inorganic compounds in the water of the St. Marys River. In addition, more recent studies indicated elevated concentrations of PAHs in some fish species in the North Channel of Lake Huron, near the outlet of the St. Marys River.

Many of the Areas of Concern are harbours or embayments, with limited water and suspended material circulation and transport out of the area. However, contaminants originating along the St. Marys River can be transported by water, suspended matter, or by resuspension of bottom sediments, and can affect the environment in the lower part of the river and Lake Huron.

The objectives of this study were:

(a) to determine the geochemistry and concentration of trace elements in bottom sediments and to compare these with concentrations in suspended sediments in the river;

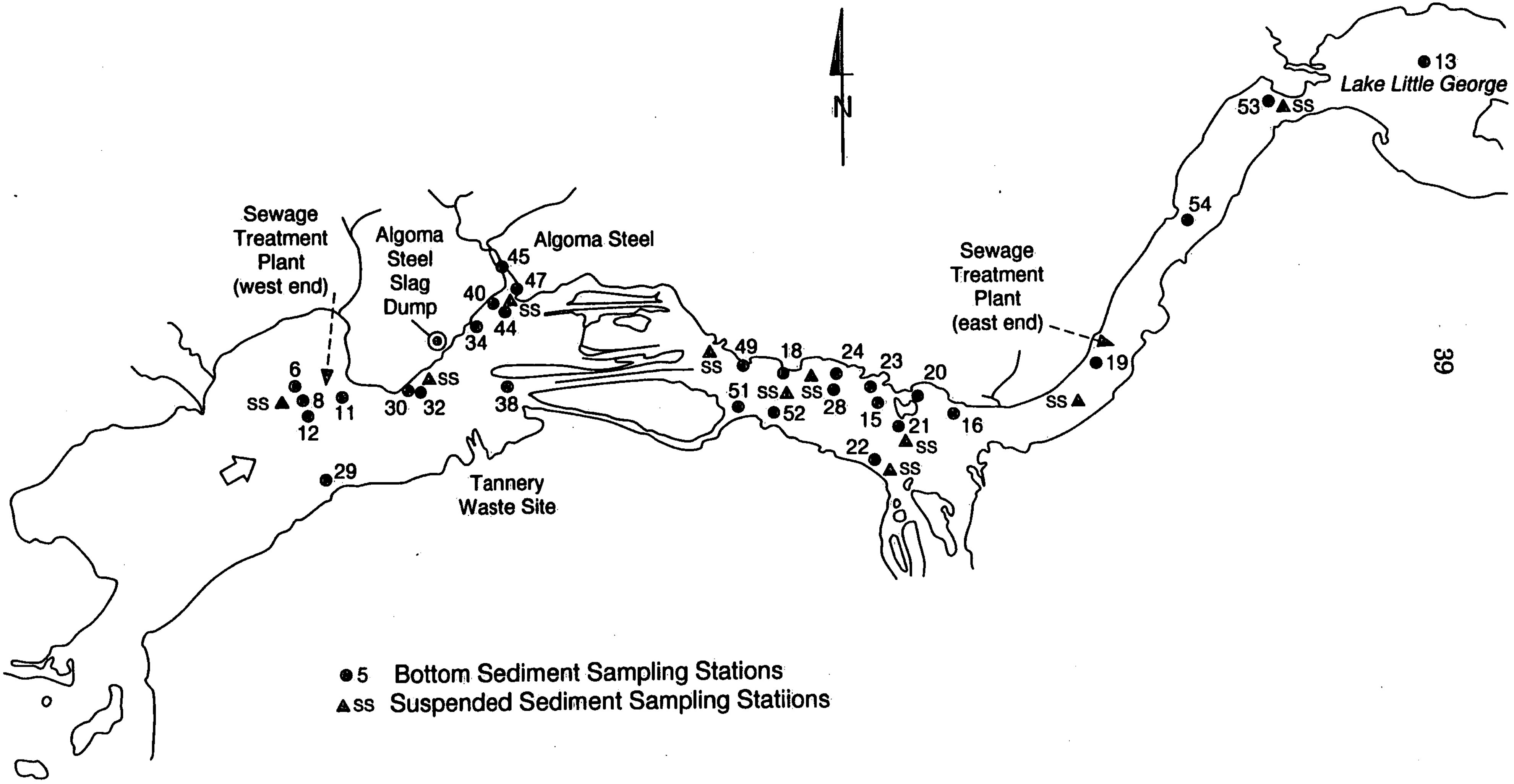

Figure 10. St. Marys River, Ontario

(b) to assess the deposition and transport of particle-associated contaminants through the St. Marys River system; and

(c) to identify the areas with the most contaminated bottom sediments within the river.

Concentrations of Fe, Mg, Ca, Mn, Pb, Sn, and As in suspended and bottom sediments, above background, were observed along the Canadian shore in the vicinity of the Algoma Steel slag dump. A further increase in the concentrations of these elements, particularly bottom sediment, existed near the Algoma Steel slip. In this area, the concentrations of Pb, Zn and As in bottom sediments (1965, 4600 and 92 µg/g, respectively) were many times greater than in the other sections of the river. However, the concentrations of Cr, Cu and Ni in suspended and bottom sediment increased at several locations along the St. Marys River indicating several different sources of these trace elements. The maximum concentrations of Cr, Cu and Ni in the bottom sediments were 1004, 102, and 53 µg/g, respectively. Generally, the concentrations of trace elements were considerably lower in the suspended sediments than in the bottom sediments. However, sediments are resuspended in the upper river and transported, along with their contaminant burdens, downstream, where they are again deposited. Concentration profiles of Cr, Zn and Pb and dating of sediment cores for Lake George in the lower St. Marys River system showed that metal contamination peaked between 1957 and 1965.

General

Contaminated sediments are an issue in 16 of the 17 Canadian AOCs in the Great Lakes. RAP teams have been struggling with the assessment of what is contaminated and what is not, as well as the biological significance of the contaminants within the sediment. A geo-referenced database of contaminated sediment data in each of the AOCs was created. The database was used to determine the area within each AOC that exceeded the Ontario Ministry of Environment and Energy's Sediment Quality Objectives. The database has been used many times to describe the sediment issue in the Canadian AOCs, explore remedial options, and assist in additional sampling programs to fill in data gaps or better delineate a "hot spot".

Another geo-referenced database of background sediment chemistry from the datafiles of the Geological Survey of Canada was also created. The Geological Survey of Canada data was used to illustrate the background concentrations for various metals in sediments from lakes within the watershed of an AOC, for example Thunder Bay. The comparison between what was naturally present in the watershed and the sediment data within the AOC itself helped the RAP team delineate what was anthropogenically enriched. The sediment information within the watershed also could be used as clean-up criteria.

Lakewide Management Plans

Under the 1987 Protocol, Lakewide Management Plans are to be developed for the open waters of each lake to reduce loadings of Critical Pollutants and restore beneficial uses. Initially, plan development has been restricted to Critical Pollutants; however, more recently, the basis or focus of these plans is being broadened to better embody an ecosystem approach.

NWRI has been one of the major research groups collecting information on the health of the Great Lakes since the late 1960s.

In addition to their work on the Lower and Upper Lakes Reference studies and PLUARG, NWRI scientists have continued to investigate ecosystem stress impacts, whole-lake process changes, sources and pathways of contaminants and, the effectiveness of management approaches throughout the Great Lakes. This section provides a synopsis of the research conducted under GLAP, most of which was focussed on the lower lakes, including the St. Lawrence River.

Lake Erie

Over twenty years ago the Lake Erie "Project Hypo" study articulated many of the pollution problems in Lake Erie. At that time relatively little was known about the Great Lakes. It was, however, clear that quick action needed to be taken to reverse the impacts from uncontrolled nutrient loads. This setting has provided a natural laboratory to learn more about the response of large lakes to nutrient loads. A series of research cruises took place in the mid 1980s and in 1990, twenty years after both Project Hypo and the initiation of nutrient controls. The work focused mainly on the central basin, which was of greatest interest due to the GLWQA goal of "restoring year round oxygen" in the hypolimnion. Some sampling took place in both the west and east basins as well. Data obtained using an NWRI developed vertical profiler showed that investigators in the 1930s were likely unable to sample oxygen properly in the thin hypolimnion. Thus, the degree to which the oxygen situation had become worse due to increased nutrient loads (the foundation of the GLWQA goal) was questioned. The surveys showed that offshore water, representing most of the central basin, was of good quality. The persisting low oxygen problem is consistent with resiliency phenomena that slow down and reduce both damage and recovery in the huge offshore areas of the lake. Greatest impacts from eutrophication were manifested in the shallow west basin and southern nearshore areas, with the offshore waters being rather less affected. The water quality in the offshore area was probably acceptable even in 1970 and certainly has been exemplary since our studies in 1979. This work shows that the eutrophication issue represents an ongoing lake management challenge. As the population grows the fiscal pressure to relax nutrient controls may increase and/or loads may gradually increase if treatment standards are not improved. Understanding the response of lakes is critical to their future management.

An understanding of the pathways and fate of nutrients and contaminants in aquatic ecosystems is critical for assessing their potential impacts on the environment. Research studies, conducted at the institute, have examined nutrient inputs from major river sources, agriculturally derived herbicides and pesticides, and contaminated sediment settling and redistribution in Lake Erie.

Sediment traps, deployed over winter in the central basin of Lake Erie were used to measure year-to-year differences in the winter particulate downflux and the concentration of total PCBs in the trapped material. Previous research has shown that the central basin sediments continue to be laden with PCBs translocated from the west basin. Differences in the downflux are primarily the result of hydrodynamic effects caused by variable meterological conditions, including sediment resuspension. The variability observed in the total trapped material (TTM) downflux (Figure 11) is typical of other limnological variables.

The material downflux ranges form 40 to 61 $g{\cdot}m^{-2}{\cdot}d^{-1}$, with a mean of 51 $g{\cdot}m^{-2}{\cdot}d^{-1}$, and a coefficient of variation (CV) of 18%. The concentration of total PCBs over the same time period ranges from 90 to 400 $ng{\cdot}g^{-1}$ with a CV of 57%. The variability shown by the PCBs is quite large compared to the TTM downflux and

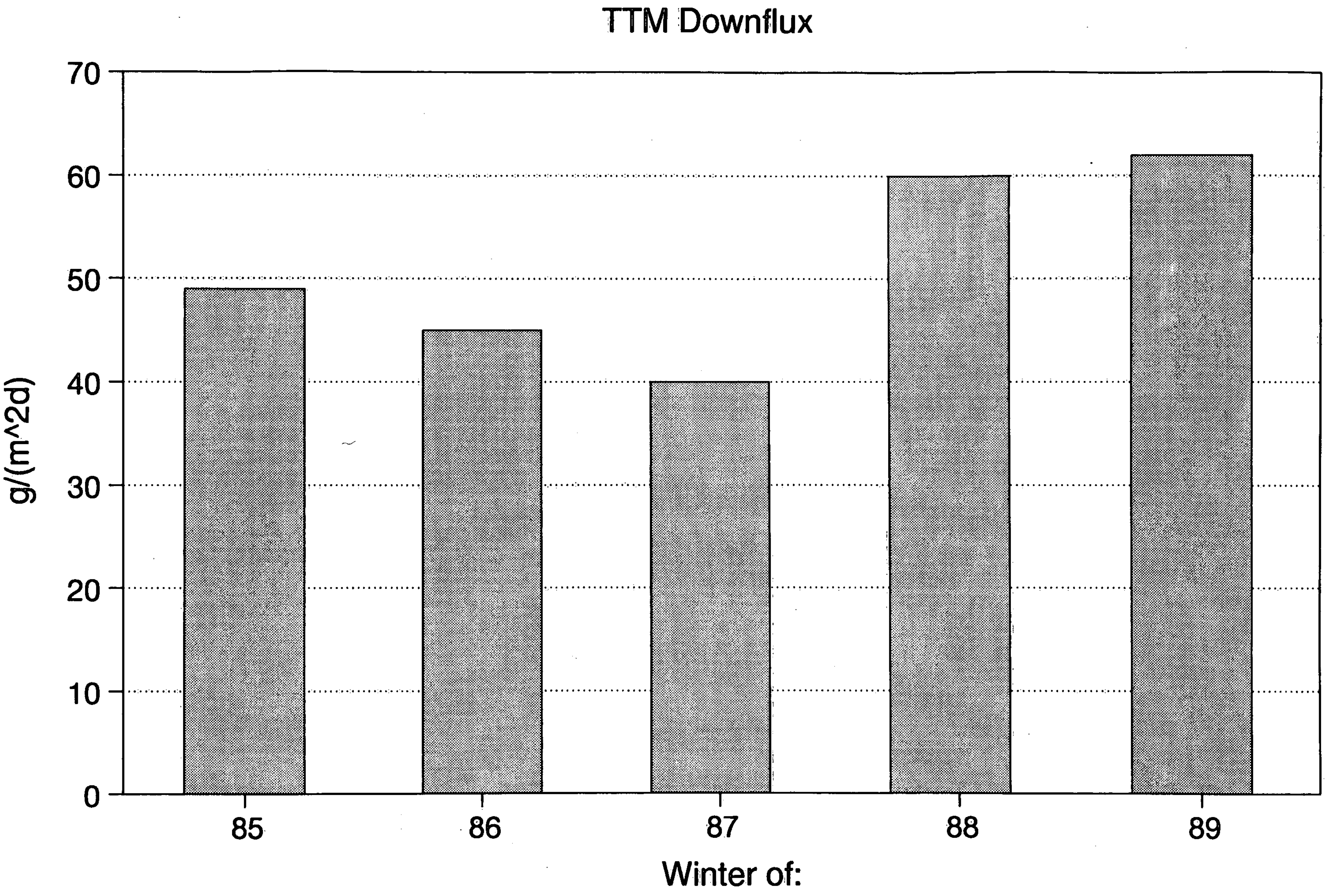

Figure 11. Year to year differences in the winter downflux of total trapped material CTTM.

seems to show a trend with time. Regression analysis shows an increasing concentration trend from 1985 to 1989 (Figure 12) of 55 $ng \cdot g^{-1} yr^{-1}$ ($n=5$, $r=0.74$, $P<0.1$). The mean sediment accumulation (as measured by traps) during the five-year period was 9180 $g \cdot m^{-2} \cdot yr^{-1}$. Thus an average of 0.51±0.1 $mg \cdot m^{-2} \cdot yr^{-1}$ of total PCBs continue to be deposited in the central basin of Lake Erie during the winter period.

Changes in wildlife habitat have been observed in Lake Erie coastal marshes. In particular, macrophyte communities adjacent to creeks flowing through some marshes have been altered. A study was conducted to collect information on the transport of pesticides and herbicides from agricultural activities through some of the north shore marshes, and to evaluate the potential effects of these compounds on the marsh environment. The study sites were Hillman Creek, Malden Creek and Wheatley Harbour, Ontario. From 17 selected compounds tested, only trifluralin, metribuzin, metolachlor and atrazine were detected in the suspended matter in concentrations up to about 250 mg/g (dry weight). Atrazine and metolachlor were found in all water samples with concentrations up to 1230 and 1590 mg/L, respectively. Other compounds found in collected water samples were trifluralin, simazine, metribuzin, carbofuran and alachlor. Trifluralin and metolachlor were the only compounds detected in concentrations up to about 12 ng/g (dry weight) in bottom sediments. Several bioassays based on the growth of different macrophytes using water collected at the sampling sites indicated some toxicity to the tested species, particularly to *Lemna gibba*. The concentrations of trifluralin and metolachlor were considerably greater in the marsh water collected in May, June and/or September than those in the water collected in July. However, the greatest concentrations of dissolved organic carbon were observed in the water samples collected in July. This suggests more intensive degradation of the herbicides in the summer during high primary production and microbial activity in the marsh than in the spring and fall. The results of the study indicated a continuous transport of herbicide and pesticides, mainly by the aqueous phase, through Lake Erie coastal marshes.

Some of the impacts of phosphorus from the Grand River, Ontario, on the nearshore area of Lake Erie were investigated. A study looked at the various chemical forms of iron and phosphorus in suspended particulates collected at different distances from the river mouth and at different water depths. Results indicate that the zone of influence of the river is less than 4 km offshore and that

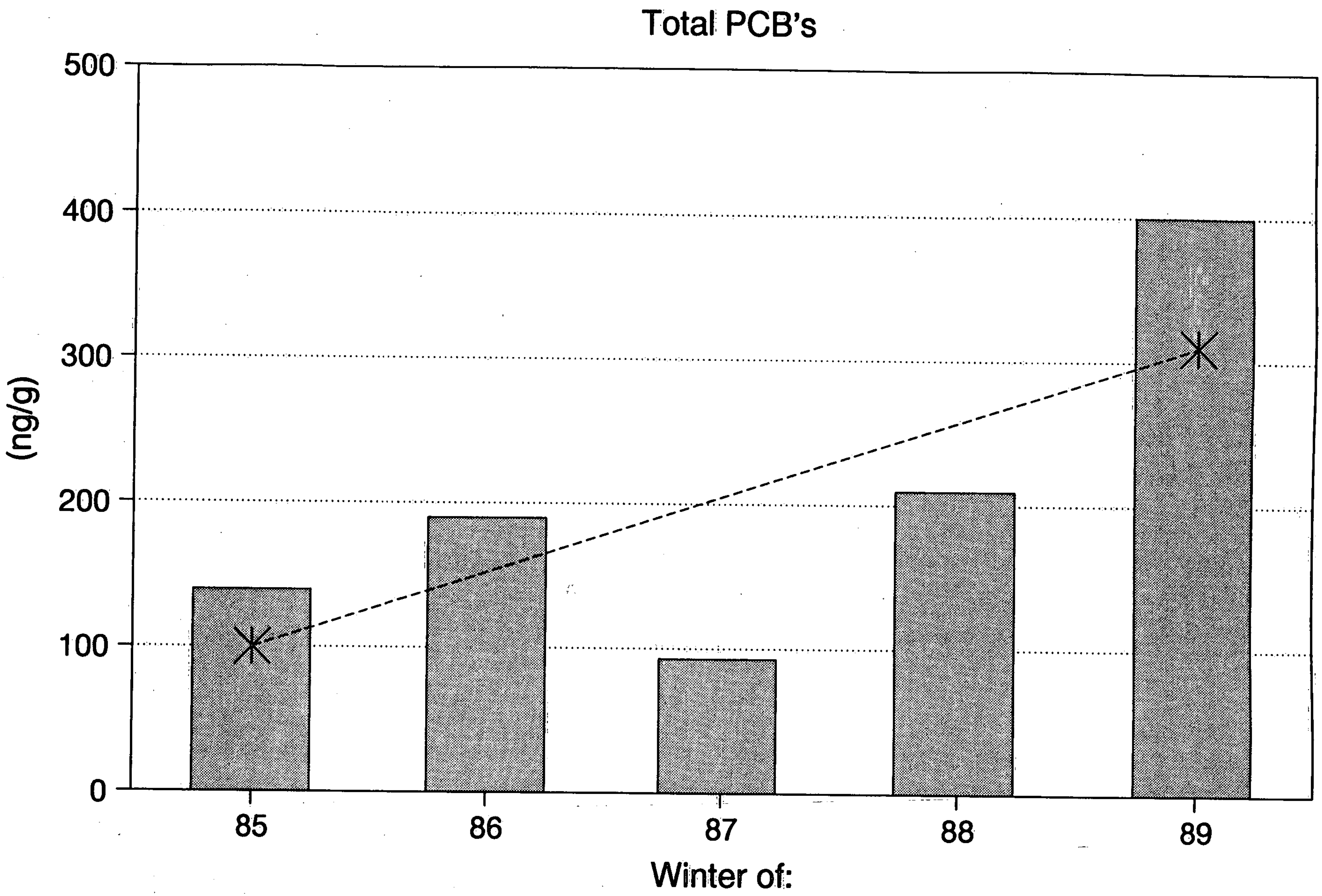

Figure 12. Year to year differences in the downflux of particulate-associated PCB.

resuspension of bottom sediment is the dominant process controlling the phosphorus availability.

Research conducted in 1990 showed some of the first evidence of water clearing in the west basin thought to be due to the zebra mussel invasion. These data are important since they show that the clearing phenomenon occurred only in certain areas; the majority of recorded secchi depths are as expected from the historical data shown in Figure 13. This means that in order to determine the importance of the mussels to the rest of the food chain the full extent of the mussels and their water clearing action must be carefully surveyed in all areas not just where the mussels are prevalent.

Lake Ontario

In preparing a management plan for Lake Ontario, knowledge of the processes that control the transport and partitioning of contaminants is equally important to information on quantities of contaminants entering the lake from different external sources. In the early 1980s, the presence of a nepheloid layer in Lake Ontario was reported. It was suggested that the nepheloid layer may be important in the transport of different contaminants across the lake. A comprehensive study was carried out to investigate the origin and character of the nepheloid layer in Lake Ontario, and to evaluate its role in contaminants transport.

Nepheloid layer formation usually commences in July, gradually increasing in thickness up to a maximum, of about 40 m in September. During the lake's fall turnover, the suspended matter in the nepheloid layer becomes mixed throughout the water column. Silica, calcite and organic matter are the major components of the suspended matter in the nepheloid layer, particularly in the central and eastern basins. The suspended matter in the nepheloid layer in the western basin contained more sediment particles than that in the central and eastern basins. Light transmission profiles and the goechemistry of the particles suggests that the nepheloid layer contents in the central and eastern basins originate mainly from primary production and the precipitation of calcite in surficial waters during the summer. Results also indicate that sediment particles in the nepheloid layer in the western basin originate from the resuspension of bottom sediments by currents generated through vertical mixing of warmer water transported from Lake Erie at the Niagara River mouth in early spring. The concentrations of Pb, Zn and Cu in

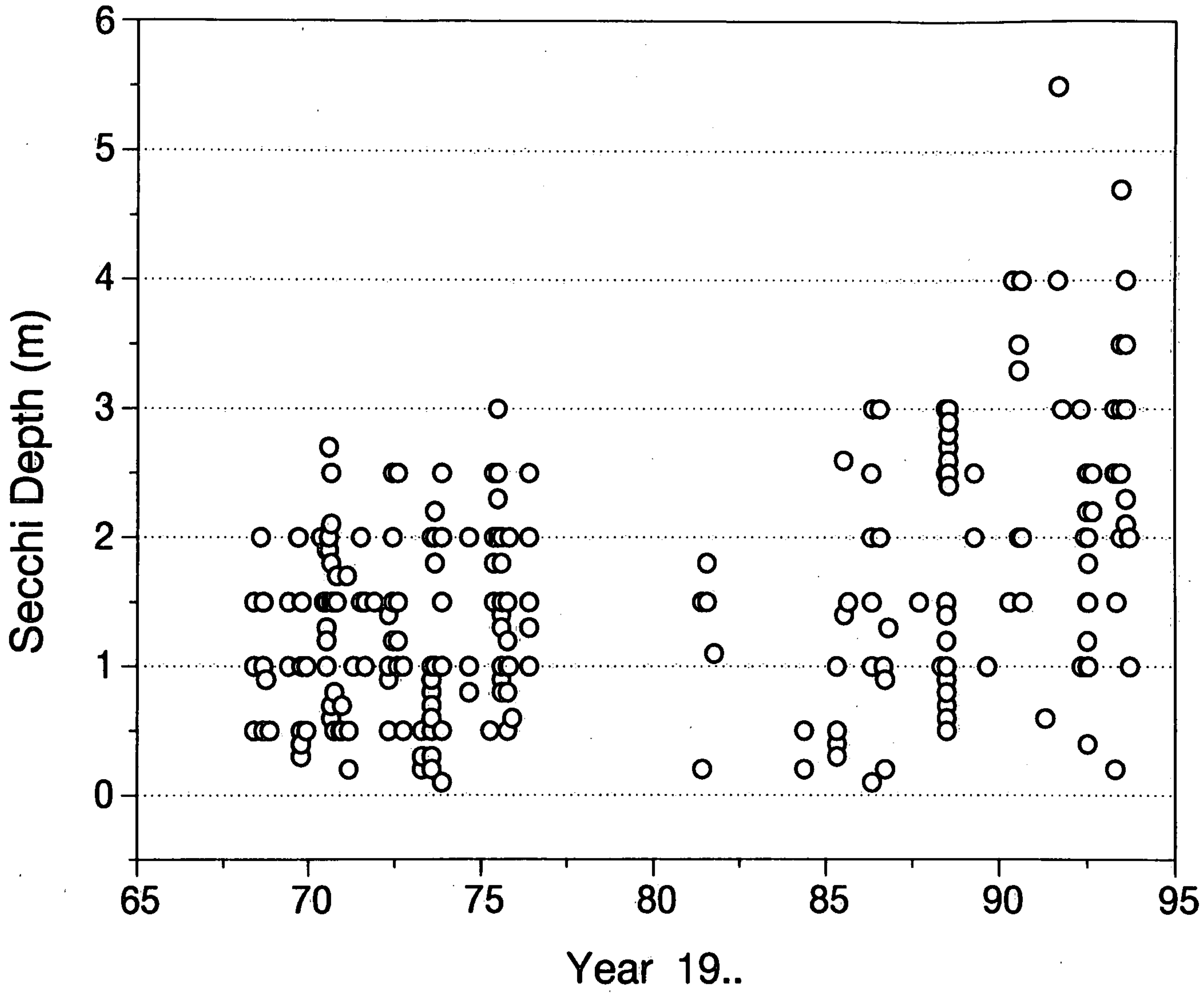

Figure 13. Water clarity in the west basin of Lake Erie.

the suspended matter in the nepheloid layer (up to 683, 1180 and 396 μg/g, respectively) were greater than those in the bottom sediments (up to 203, 665 and 298, respectively). However, the concentrations of As, Co, Ni, Cr, V and Hg were similar or lower than those in the sediments. The concentrations of PCBs in the suspended matter in the nepheloid layer ranged from 151 to 728 ng/g, and were greater than those in most of the sediments. Further, the suspended matter in the nepheloid layer contained more lower chlorinated biphenyls, particularly tetra- and pentachlorobiphenyls, than the bottom sediments.

The results of the study indicate that the suspended matter in the nepheloid layer is an important medium for the accumulation, recycling and transport of contaminants in Lake Ontario. Lower chlorinated PCB congeners appear to be stripped from the sediments and subsequently accumulate in the suspended matter of the nepheloid layer. Particles transported into Lake Ontario from Lake Erie and the Niagara River, as well as those particles that originate from primary production in Lake Ontario, become enriched by trace elements and organic contaminants while in the water column. These particles accumulate in the nepheloid layer prior to settling on the lake bottom. The dissolution of some particles and the decomposition of organic matter in this suspended matter would result in the release of contaminants that were associated with these particles.

These processes lengthen the time that the Lake Ontario ecosystem takes to respond fully to any reduction in contaminant loading and must be factored into the models used to predict the results of the Lake Ontario Toxics Management Plan and the LAMP.

Ontario-St. Lawrence

Most aquatic use impairments occur in the nearshore, where they are more visible and of great concern to the public. Several physical factors combine to make the hydrodynamics of the nearshore zone quite unique and complex. The practical importance of this recognition is obvious for waste disposal, nearshore erosion, recreation, navigation and many other uses. The physical factors that govern nearshore water movement are wind stress, bathymetry, stratification of the water column, the Coriolis force (due to earth's rotation) and frictional forces. All of these physical factors contribute to create a nearshore flow field that is much more complex than the offshore flow field. These properties play a profound role in the biogeochemical processes in the nearshore zone. The fate of riverborne nutrients and contaminants released into this zone is just one such example. Their residence time and their degree of accumulation in the sediments are determined partly by physical exchange processes of transport and dispersion and partly by biotic processes active in the nearshore/offshore region. In fact, these processes are well identified and their importance is recognized in maintaining nearshore water quality in the Great Lakes. Under GLAP research was conducted to delineate the coastal exchange processes relevant to contaminant transport and pathways in the nearshore waters, biota and the sediments.

During the 1988-1993 GLAP period, major field experiments and modelling activities were undertaken at the Niagara River mouth, the St. Lawrence River and the Kingston Basin, Lake Ontario. Additional work was done on the north shore of Lake Ontario, where the Pickering and Darlington nuclear generating stations are located. These experiments combine a network of fixed point current meter moorings, fixed temperature profilers, meteorological stations, satellite and GPS tracked Lagrangian drifters, remote sensing and detailed hydrographic surveys of temperature structure. The data from these experiments are analysed to delineate the nearshore and offshore exchange processes and to develop and validate water quality models. The data base was used to develop statistical and climatological summaries of physical transport in these coastal areas, interpret toxic contaminant information and, develop and validate coastal transport and pathway models in Lake Ontario.

Fine-grained sediments comprise the bulk of the sediment entering the Great Lakes and St.Lawrence River ecosystem. These sediments have become contaminated to a greater or lesser degree by man-introduced chemicals through industrial, agricultural and municipal activities. Although contaminated sediments are gradually removed from the system by deposition and burial, they first pass through a dynamic cycle of deposition and resuspension during which they could serve as a contaminant source for aquatic organisms. Therefore, their net pathway through the physical environment, and the rate at which they are transported and buried (i.e., their overall dynamic behaviour is of considerable importance).

One way of studying the dynamics of contaminated fine sediments in the aquatic environment is through the use of various tracers either natural or artificial.

Tracer experiments have now been carried out at four sites in Lake Ontario: Humber Bay, Port Hope, Whitby Harbour, and Hamilton Harbour.

In Humber Bay, distribution patterns were examined for the bottom sediment concentrations of the naturally-occurring elements thorium, cobalt, and scandium, as well as for the cesium-based artificial tracer. Initial testing was also successfully carried out on organic contaminants (n-alkanes, vitamin-E acetate, PAH's) as sediment tracers. The long-term sediment transport trend was inferred to be southward along the west shore of Humber Bay, then curving westward parallel to the shore.

An investigation was conducted at the mouth of Port Hope Harbour, using the above-mentioned cesium artificial tracer, as well as a variety of incidentally-introduced elements believed to be entering the lake at this point. Concentration of uranium, thorium, and cobalt were relatively high throughout the nearshore zone between Port Hope and Port Granby, indicating that sources of these contaminants exist in the area other than Port Hope Harbour. Despite normal variability, the dominant transport trends at Port Hope were clearly offshore or toward the east, with a minor amount of transport into the harbour.

The Great Lakes, especially Lake Ontario, are recipients of radioactive releases from various nuclear installations as well as waste management facilities. During 1988-1993, several studies were conducted to assess the levels, modes of association and routes of environmental transport of various radionuclides. The impact of such releases on the receiving waters and biota was also assessed.

A comprehensive study of the influence of West Valley-delivered radionuclides on Lake Ontario was conducted. Study results clearly showed that the pattern of radionuclide deposition, recorded in western Lake Ontario sediment cores, is consistent with the pattern of West Valley discharges to the local aquatic system. This work demonstrated that any accidental release of radioactivity at this site will quickly reach the Niagara River/Lake Ontario system.

In another study, the partitioning of radionuclides across natural interfaces was investigated. Results showed that radionuclides such as ^{137}Cs and ^{226}Ra are efficiently collected by the foam accumulating in the pool just below Niagara Falls.

The potential for leaching of uranium refinery waste radionuclides from the Port Granby site to Lake Ontario was investigated and modelled. The results from this extensive investigation showed that low-level leaching of radionuclides, via groundwater, will continue to take place for many years even after the waste is removed from this site.

The model TOXFATE, developed at NWRI, was coupled with the hydrodynamical model, RAND, developed at OMOEE, to assess the consequence of reducing contaminant loadings to Lake Ontario from the Toronto Waterfront. A computer graphics program enabled managers to view the effect of reducing some or all local sources of three contaminants, 1,2-dichlorobenzene, hexachlorobenzene and total PCBs. These three chemicals represent different categories of contaminants. The most significant findings were that the concentrations of toxic organic pollutants in Lake Ontario water along the Toronto Waterfront, depend mostly on loadings from sources other than Toronto, mainly the Niagara River and the atmosphere. The waters along the Toronto Waterfront are replenished every 10 to 15 days. Thus, local loadings are diluted fairly rapidly. Only in specific areas, for example Humber Bay and the outfall of the Toronto Main sewage treatment plants, were concentrations of toxic contaminants found to be higher than the rest of the lake. Inputs of toxic contaminants to Lake Ontario from the Toronto area were about 0.5 to 25% of the loadings from the Niagara River.

As part of an international modelling study on Lake Ontario, a contaminants fate model was developed and validated. Research teams from EPA in Grosse Isle and from Manhattan College were also involved. The dynamical fate model, TOXFATE (version 3.0), was run to steady state, i.e., for 75 years, and results compared with simulations performed by U.S. EPA as part of the simulation exercise funded by the Lake Ontario Fate of Toxics Committee. Simulations with TOXFATE show that burial is an important process for chemicals with high K_{ow}. Volatilization is an important removal process for chemicals with low K_{ow}. Dieldrin is a notable exception. At present, TOXFATE has been updated to version 3.6.

In addition, a mass balance model of the food web in Lake Ontario was also developed. This was used to examine the transfer of persistent toxic contaminants in the food chain. The trophic status of Lake Ontario was studied in energy terms, and the information summarized as a food web. The underlining assumptions of the model were described along with the research needed to fully test these assumptions. The lack of essential data on the food web did not permit balanced the development of an energy balanced model; therefore, a mathematical model was used to logically integrate the data and to produce a balanced food web. This procedure provides generality and stability to the hypothesized energy flow through the Lake Ontario food web.

In another research study, biological variables were measured in Lake Ontario to quantify the importance of suspended matter in the pathways of contaminant mobilization. Phytoplankton contaminant uptake is highly variable. Uptake rates are affected by variations in concentration and composition of suspended matter, algal growth rates and total biomass, as well as species differences. Suspended matter concentrations were found to be lower and less variable (temporally and spatially) in Lake Ontario (0.8 to 3.1 mg/L), than in a smaller more eutrophic lake.

General

The effect of sampling protocol on estimating mean phosphorus and chlorophyll concentrations in lakes were studied in order to optimize sampling procedures and to evaluate the effect of this variation on phosphorus-chlorophyll (P/Chl) regression models. All protocols were found to be similarly precise, even though they yielded significantly different values. Greater variability is found between lakes and sampling date, while the effect of sampling site is negligible. Differences in sampling protocol and depth seem unlikely to contribute to the high uncertainty in existing P/Chl models. From this work, a recommendation for more accurate and efficient sampling was developed to provide more accurate water quality measurements and thereby assist resource managers.

Computer models of the fate and effects of contaminants rely on assumptions about the relationships between lake physics and biology. As knowledge develops, these assumptions need to be tested and updated. The predictive power of 17 empirical models that relate mixing depth to morphometric variables was evaluated on data from 123 temperate lakes. An improved model using the best single morphometric predictor of the mixing depth of temperate lakes, maximum effective length (MEL), was formulated. The effect of plankton biomass on mixing depth was also tested. Even though morphometry and an index of lake trophy (secchi disc depth) were significantly correlated morphometry was by far the most powerful predictor of mixing depth. This empirical model provides a quick tool for more efficient management decisions regarding nutrient control measures, land use, etc.

Recurring questions in water quality monitoring and research include; how to detect and to estimate trend or differences between locations and; how to estimate mean levels and relationships between variables. Because of the inherent variability in the data collected, the magnitude of the trend, difference, or mean level must be compared to residual variability if a quantitative estimate is to be obtained. Statistical methodology provides the means of doing this.

Trend assessment methodology for individual locations such as those found in water quality monitoring or surveillance, has been evaluated and demonstrated on river data, including Niagara River phosphorous concentrations. These data have also been used to investigate the importance of adequately modelling the seasonality and the form of the trend. Methods to compare water quality variables between sampling stations were also investigated. In addition to the components of seasonality and time trends lake data also have the complexity of spatial variation in three dimensions. Methodology for defining a set of homogeneous seasonal regions to follow over time is being developed.

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ANNEX 11

SURVEILLANCE AND MONITORING

NWRI's role, under Annex 11, has been one of support through the development and testing of tools and techniques for surveillance, monitoring and research activities. The Canadian federal government is responsible for a major portion of the Great Lakes International Surveillance Plan (GLISP) and a series of other programs under binational agreements and the Canada-Ontario Agreement (COA). These enterprises all require state-of-the-art ship-board and laboratory equipment, as well as quality assurance and quality control programs.

Increasing Measurement Capabilities

NWRI activities under Annex 11 have included the specification, development and testing of state-of-the-art water quality profiling systems and flow measurement devices. These activities are designed to increase the efficiency of the various vessel-based measurement programs, while at the same time improve the precision and accuracy of the data gathered. GLAP funding has provided some of the resources necessary to begin the automation of the basic field monitoring capability of the various agencies undertaking GLWQA surveillance, monitoring and research. In particular, there were two initiatives: (i) an Acoustic Doppler Profiling system was purchased and made operationally available to researchers and, (ii) the major research vessels used by NWRI in support of the Great Lakes programs were equipped with state-of-the-art water quality profiling systems. The former involved the purchase of commercial equipment and implementation for our particular needs while the latter involved system definition, component specification, procurement, acceptance testing and implementation.

The water quality profiling systems have completed the testing against specification phase and one system is presently operational aboard the MV Limnos. A second system, also operational, is ready for service aboard the MV Lauzier as required. A third system, scaled in depth and speed capability is now available for use aboard smaller vessels such as the MV Shark or MV Advent. These systems provide a continuous profile of DO, pH, and conductivity, temperature and light transmission with depth. The data are collected by a system computer that also controls the speed at which the sensor package is lowered. Data collected in this manner are highly automated, continuous in depth, and synoptic within the sensor set. Comparisons between this and the traditional, discrete bottle cost method show that significant variations of the profile near the surface, at the thermocline, and near the bottom are often missed when utilizing bottle casts, causing erroneous estimates of the measurement parameter (Figure 1). The water quality profiling systems give the Great Lakes research community a measurement tool that is flexible in sampling scheme, state-of-the-art in capability, increases the confidence in interpretation of results and is highly automated for ease of use and data base management.

An Acoustic Doppler Profiler (ADP) has been used to collect measurements for numerous research projects in the Great Lakes. This device gives researchers the capability to collect time-series of current profiles at a given location, or to collect moving boat profiles across rivers and shallow areas. The particular advantage of this device is it's non-intrusive capability. The acoustic technology permits the device to be set on the lake bottom directed upward into the water column to take measurements of current speeds at intervals of 1 meter or greater. The ADP essentially replaces a string of up to 40 conventional current meters when used in a standard mooring configuration. Since each conventional meter costs approximately $20,000.00, this represents a considerable saving. However, for areas of heavy ship traffic where buoys and floats are not practical, the ADP gives researchers the capability to make flow measurement that could not be previously made In addition to saving money, the ADP has much better resolution and can be used to take moving vessel profiles. This allows cross-sectional river and canal flow measurements to be made. The improved spatial and temporal resolution make it ideal for use in complex layered and flow reversal systems. The ADP has been employed in Hamilton Harbour (in support of RAP work), in Lake Ontario (in support of LAMP work) and in the St. Lawrence River (in support of the SLAP program).

Quality Assurance Activities

NWRI's Quality Assurance (QA) Group is providing support to different programs within Environment Canada, including the Great Lakes Action Plan (GLAP). The key activities are: 1) the interlaboratory comparison studies and inherent performance evaluation reports to laboratories and 2) the parallel development of highly characterized reference materials such as (i) waters for major ions, nutrients, and physical properties, (ii) waters for trace metals, (iii) sediments for toxic organics including dioxins and furans, and (iv) sediments for toxic metals.

Interlaboratory QA Studies

As part of GLAP, interlaboratory studies are conducted to compare, evaluate and follow the long term performance of the Great Lakes laboratories analyzing surface and sewage waters, and sediment samples. Additionally, interlaboratory studies on rain water samples, many of which come from the Great Lakes basin, are conducted through various funding sources. The studies provide an assessment of the laboratory measurement bias (systematic error) and results that deviate significantly from target values. These studies ensure that analytical problems are detected quickly, and corrective measures taken.

Each interlaboratory study involves between 15 and 75 different laboratories. The main laboratories that are involved in the Great Lakes Program, include the National Laboratory for Environmental Testing (NLET), the five Ontario Ministry of Environment laboratories, and several Ontario based commercial laboratories.

Over the past five years (1988 to 1993), the QA group has offered interlaboratory performance studies for the following substrates and parameter groups:

- major ions, nutrients, metals and physical properties in hard waters
- major ions, nutrients and physical properties in soft waters (acid rain studies)
- total phosphorus at ambient concentrations (low level range, 0.2 to 150 ppb P)
- total phosphorus in sewage plant effluents (0.1 to 2 ppm P)
- mercury in water (ambient range)
- arsenic, selenium, antimony and bismuth in water (ambient range)
- pesticides in water, sediments and sediment extracts

- PCBs in water and sediments
- herbicides in water, sediments and sediment extracts
- chlorobenzenes in water and in sediments
- polynuclear aromatic hydrocarbons in water and in sediments
- octochlorostyrene in sediments
- butyltin in sediments
- chlorophenols in sediment extracts
- dioxins in sediments and sediment extracts.

All of these studies have included laboratories contributing data to GLAP programs or data users. The QA data of most studies are currently processed and archived in a database management system, enabling easy long-term follow-up of individual laboratory performance.

Total Phosphorus in Sewage Studies

A large ten-sample interlaboratory study on total phosphorus in sewage plant effluents was completed in conjunction with the Ontario MISA program and the Canadian Association for Environmental Analytical Laboratories (CAEAL). The results confirmed the findings of two earlier studies provided to the Great Lakes Surveillance Work Group, of the IJC's Water Quality Board, in the early 1980s. As many as 15% to 20% of the sewage plant laboratories still have serious problems in accurately or precisely estimating phosphorus concentrations in effluents. This situation may increase the uncertainty of phosphorus loading estimates to the Great Lakes.

Major Ions, Nutrients and Physical Properties in Soft Waters

The acid rain QA program, referred to as the LRTAP, delivers three large QA studies each year. Each study involves ten water samples that are sent to about 65 different laboratories in Canada and the United States. These studies include the key network laboratories in Canada (CapMon) and in the US (the NADP network), as well as the principal laboratories generating data for the Canadian Great Lakes Precipitations Network and the American Great Lakes Atmospheric Deposition Network (GLAD). Over the last 10 years, the performance of these laboratories has ranged from satisfactory to excellent for inorganic constituents in rainfall. Toxic organic constituents have not been addressed through this program.

Major Ions, Nutrients, Metals and Physical Properties in Hard Waters

For major ions, nutrients, metals and physical properties in hard waters, the studies show that the overall performance (precision and accuracy) of the participants is considered satisfactory, including the two major laboratories involved in the open lake and nearshore Great Lakes surveillance programs.

Occasionally, through these studies, problems are identified. In all cases, the issue was reviewed and corrective actions were taken and confirmed through follow up studies. These ongoing interlaboratory audits have proven highly valuable to the Great Lakes programs as they allow for an independent check on the effectiveness of intra-laboratory quality control.

Toxic Organics Studies

Studies on toxic organics (PCBs, PAHs, chlorobenzenes, pesticides, phenolics etc.) clearly demonstrate the lack of agreement among laboratories. Results between laboratories may differ by as much as an order of magnitude. Many of the laboratories have either different in-house analytical reference standards or lack in internal quality control procedures. There is definitely a need for increased harmonization and increased QA/QC to monitor laboratory performance on a routine basis.

National Dioxin QA Program

This program examined the quality and comparability of data generated by Canadian government and commercial laboratories for the analysis of dioxins and furans in naturally contaminated Great Lakes sediments. Each of the studies to date has revealed extreme outlying results, strong biases and erratic surrogate recoveries in the data sets submitted by several of the participants. At the same time, the studies have identified a core of laboratories that have the capability to provide sensitive, accurate and comparable analyses for dioxin and furans.

This program will continue to identify common trends and problems experienced by many of the participants and will highlight individual biases and inaccuracy. This program is also contributing to the development of a naturally-contaminated reference sediment for dioxins and furans in sediments. Such a standard will enhance the measurement capability and the reliability of the information base on these important toxics.

Reference and Certified Reference Materials

Large intercomparison studies produce samples that are highly characterized, e.g., aqueous reference samples, sediment reference materials and organic standards in ampoules. Such samples can be developed as certified standards. Several Great Lakes' sediments have now been certified for PCBs, PAHs, chlorobenzenes and trace metals.

Many different water samples for major ions, nutrients and physical properties, and trace metals have been routinely used in several Great Lakes laboratories and are highly characterized. These reference materials enable laboratories to calibrate their entire measurement process, and provide data users with a useful tool to compare different sets of data.

The following reference materials are available from National Water Research Institute:

- trace metals in sediments

- PCBs, PAHs, and chlorobenzenes in sediments

- inorganics in water (major ions, nutrients, physical parameters and trace metals)
- toxic organics in rainwater (a rainwater extract is under development)
- dioxin and furans in sediment (reference values for homologue totals only).

Benefits and Relevance of the Great Lakes QA Program

For most inorganic analyses, the performance of GLAP laboratories has improved over the years. Bias and the occurrence of flagged data are infrequent. Because interlaboratory comparison studies were conducted frequently during the last 10 years, the performance of each individual laboratories over time is well established. This provides valuable information on data quality to the users. Monitoring of the laboratories' capabilities should continue to maintain the performance, and in certain areas, to enhance it (e.g., low-level trace metals, and some of the nutrients).

For GLAP laboratories, the performance appraisal on toxic organics is not as well defined as that for inorganics. The toxic organics QA program lacks the resources to deliver frequent studies for the numerous classes of organic parameters. However, the studies conducted clearly demonstrate the need for better harmonization and more stringent QA procedures for organic analyses in the Great Lakes basin.

The creation of reference and certified reference materials (RMs and CRMs) from natural Great Lakes' water and sediment is an important activity of the QA group. The availability of Great Lakes RMs and CRMs allows laboratory managers to validate their internal quality control procedures with a reference material that closely resembles the samples they analyse.

The importance of QA is now recognized by governmental and private laboratories within the Great Lakes basin. Many of the GLAP laboratories have applied for certification and accreditation by national agencies. This process provides general information on the capabilities, competence of the personnel and QC procedures of the laboratories. The program-specific GLAP QA activities are an essential complement to accreditation and certification programs. The GLAP QA activities (interlaboratory comparisons and reference materials) provide a continuous monitoring of specific laboratory performance and the means to quickly identify and correct problems as they arise. It also promotes increased harmonization among GLAP laboratories, and provides an independent assessment of the adequacy of the data to meet the data quality objectives of the GLAP programs.

Recommendations

As a result of the studies conducted in conjunction with GLAP, the QA Group recommends the following:

- all Great Lakes laboratories that analyse toxic organics (in water, sediments, tissues) should be monitored routinely through interlaboratory comparison studies that employ natural samples and standard solutions, at a frequency of two per year per constituent group
- program specific reference samples and certified reference materials should be developed by NWRI and made available to laboratories generating data as part of GLAP
- current interlaboratory comparison studies for inorganics in hard and soft waters should be maintained to monitor performance of GLAP laboratories
- a repository of ampoule standards should be developed and maintained to allow intercalibration of organic standards in GLAP laboratories
- the electronic archiving of all QA data should be maintained and improved for the benefit of GLAP data users
- a management work group should be created to harmonize QA practices and requirements for the atmospheric, aquatic, biota and terrestrial elements of GLAP.

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ANNEX 12

PERSISTENT TOXIC SUBSTANCES

Annex 12 of the GLWQA requires research to be conducted on the pathways, fate and effects of toxic substances for the protection of human health, fishery resources and wildlife of the Great Lakes Basin Ecosystem. A prerequisite for assessing the fate and effect of persistent toxic substances is the development of standard, multimedia laboratory analytical techniques and methods. Research on the effects of toxic substances includes both laboratory and field toxicology, as well as studies on impacts to indigenous species. Also, the prediction of likely effects of compounds that are either present in the Great Lakes or could be released to the lakes is essential. At NWRI, research on the predictive technique -- quantitative structure-activity relationships (QSARs), has been a major component of Annex 12 work.

Analytical Methods Development

Conventional methods for the analysis of trace organic contaminants in environmental samples are generally time consuming and expensive. Many samples that have undergone extraction and clean-up procedures prior to gas chromatography or gas chromatography and mass spectrograph analysis are found to be contaminant free. The inclusion of screening steps in analytical protocols can greatly reduce costs through the early elimination of samples that have no contaminants present. Research at NWRI has shown that immunoassays (IAs) are among the most promising screening tests available. Based on the classical antigen-antibody reaction, IAs are relatively simple, inexpensive, powerful and adaptable techniques for the rapid detection of trace levels of organic compounds. Radioimmunoassay (RIA) is one of the techniques that has been studied and developed at the institute. This technique has been examined for trace organic contaminants in a variety of environmental matrices.

In all, nine analytical methods were developed and evaluated for the identification of nine compounds or families of compounds in water, sediment, biological tissue and complex solid waste. The methods employ a series of existing and new techniques including: enzyme immunoassay, gas chromatography, microwave extraction, supercritical fluid extraction and radioimmunoassay.

Atrazine and Other Triazine Herbicides

Enzyme-immunoassay was used to measure atrazine and other triazine herbicides in water with detection limits of 62 ng/L (in lake water) and 180 n/gL (in river water). The method is a tube based enzyme-immunoassay (EIA) for the detection of atrazine and other triazine herbicides. It is a direct competitive assay that employs the spectrophotometric measurement of atrazine bound peroxidase enzyme activity. The method provides an inexpensive screening technique for large sample sets and is ideal for field use for the identification of contaminated sites. It requires no extraction or cleanup of the water samples and is repeatable, rapid and sensitive.

Acid Herbicides

Gas chromatography was used to measure acid herbicides; 4-CPA, MCPP, Dicamba, MCPA, 2,4-DP, 2,3,6-TBA, 2,4-D, bromoxynil, Silvex, 2,4,5-T, MCPB, 2,4-DB and picloram in water with detection limits of 50 ng/L (using electron capture detection) and 20 ng/L (using negative ion chemical ionization mass spectrometry). This improved method reduces the interference of fatty acids with the electron capture detection of the acid herbicides. Water samples are acidified to pH <2 and the analytes extracted with dichloromethane. The herbicides are converted into their pentafluorobenzyl (PFB) derivatives and cleaned up on a silica gel column. A gel permeation chromatography cleanup step is included to remove PFB esters of fatty acids which interfere with the electron capture detection of the herbicide PFB derivatives during the gas chromatographic analysis. Negative ion chemical ionization mass spectrometry is used for confirmation. Recoveries range from 45% to 90%.

Butyltin

Gas chromatography was also used to measure butyltin in fish and sediment extracts with a detection limit of 6 pg tin. An atomic emission detector coupled to a capillary column gas chromatograph is used for the speciation and quantification of trace levels of organotins. The method has an absolute detection limit which is lower than that of ion spray mass spectrometry/mass spectrometry. The technique is element specific and the presence of tin compounds can be confirmed by examining the emission spectra of chromatograph peaks.

Organochlorine Insecticides

Microwave extraction was used to measure organochlorine insecticides; hexachlorobenzene, α-chlordane, γ-chlordane, dieldrin, p,p'-DDE, endrin, p,p'-DDD, o,p'-DDT, p,p'-DDT, methoxychlor and Mirex in sediment at µg/kg levels. The method is based on the use of microwave energy to extract pesticides from sediment samples by applying 30-second bursts of energy rapidly up to 5 or 6 times. The extracted sample is centrifuged and the supernatant filtered prior to analysis by capillary column gas chromatography with electron capture detection. Organochlorine pesticide residues are quantitatively extracted from sediment faster, more reliably and cheaper than by conventional techniques. The microwave extraction procedure significantly reduces analysis time and the amount of organic solvents required.

Pentachlorophenol and Related Compounds

Supercritical fluid extraction was used to measure pentachlorophenol and related compounds; pentachlorophenol and di-, tri-, tetra, chlorophenols (2,6-dichloro-, 2,4,-dichloro-, 3,5-dichloro-, 2,3-dichloro, 3,4-dichloro-, 2,4,6 -trichlor-, 2,3,6-trichloro-, 2,3,5-trichloro-, 2,4,5-trichloro-, 3,4,5-trichloro-, 2,3,5,6-tetrachloro-, 2,3,4,6-tetrachloro, 2,3,4,5-trachloro-, phenols) in soil and sediment with a detection limit of 0.1 mg/kg. On-line supercritical fluid extraction and derivatization provides a rapid quantitative method for the gas chromatographic determination of pentachlorophenol and related compounds in soil contaminated by wood preserving chemicals. Chlorinated phenolics are extracted from soil and acetylated *in situ* with supercritical carbon dioxide in the presence of triethylamine and acetic anhydride at 80°C and 365 bar. The derivatized extract is partitioned with potassium carbonate solution, dried and cleaned up on a deactivated silica gel micro-column before gas chromatography analysis with electron capture detection. The method is applicable to a wide range of concentrations (µg/kg to mg/kg) and is as quantitative and precise as the established steam distillation procedure. The method is faster and consumes far less solvents and chemicals than existing derivatization methodologies and has the potential of being automated.

Chlorinated Compounds

Supercritical fluid extraction was also used to measure chlorinated phenolics; chlorinated catechols, chlorinated guaiacols, chlorinated syringols, chlorinated vanillins in sediment at µg/kg levels. The method is based on a single step *in situ* derivatization in conjunction with supercritical carbon dioxide extraction. Chlorinated phenolics in air dried sediment samples are extracted at 110°C and 385 bar, and simultaneously acetylated under static conditions with acetic anhydride in the presence of triethylamine. The derivatives are removed from the matrix in a dynamic extraction step and cleaned up on a deactivated silica gel micro-column prior to analysis by capillary column gas chromatography using both electron capture and mass selective detectors. The method is extremely efficient and requires only 10% of the time of conventional solvent extraction techniques. Recovery is quantitative.

Chlorobenzenes

Supercritical fluid extraction was employed to measure chlorobenzenes; di-, tri-, tetra-, penta-, hexa-, chlorobenzene isomers and hexachloro-1,3-butadiene in sediment with a detection limit of µg/kg. The method is based on the extraction of chlorobenzenes and hexachlorobutadiene from sediment samples using supercritical carbon dioxide at 80°C and 168 bar with a mixture of methanol and dichloromethane as modifier. Extracts are cleaned up on an activated Florisil micro-column and treated with mercury prior to capillary column gas chromatography using both electron capture and mass selective detectors. Only 25 minutes is required to obtain recoveries which are comparable to 7 hours Soxhlet extraction, and the method uses a minimal amount of organic solvents.

Resin and Fatty Acids

Gas chromatography was used to measure resin acids (pimaric, sandaracompimaric, isopimaric, abietic, dehydroabietic, 12-chlorodehydroabietic, 14-chlorodehydroabietic, 12,14-dichlorodehydroabietic) and fatty acids (lauric, myristic, palmitic, stearic, oleic, linoleic, linolenic, arachidic, behenic) in sediment at a detection limit of 0.1 mg/kg. The sediment sample is air dried and Soxhlet extracted for 7 hours with an acetone/methanol mixture in the presence of hydrochloric acid. The extracted acids are converted into pentafluorobenzyl esters and cleaned up on a deactivated silica gel column. The derivatized acids are determined using capillary column gas chromatography with an electron capture detector. Peak identity is confirmed by electron capture detector. Peak identity is confirmed by electron impact mass spectrometry or by negative ion chemical ionization mass spectrometry. Quantitative recovery is obtained.

A supercritical fluid extraction was, also developed to measure resin acids (pimaric, sandaracopimaric, isopimaric, palustric, abietic, dehydroabietic, neoabietic, 12-chlorodehydroabietic, 14-chlorodehydroabietic, 12,14-dichlorodehydroabietic) and fatty acids (lauric, myristic, palmitic, stearic, oleic, linoleic, linolenic, eicisanoic) in sediment at sub mg/kg levels. The method is based on the rapid extraction of resin and fatty acids from wet sediments using supercritical carbon dioxide with a 1:1 mixture of methanol and formic acid as modifiers. Quantitative recovery is obtained for all acids except for palustric and neoabietic acids employing a 5-minute static and 10-minute dynamic extraction at 365 bar and 80°C. Recoveries for palustric and neoabietic acids are at least 250% better than those obtained using the classical Soxhlet technique. The supercritical fluid extraction requires less organic solvents and is much faster than Soxhlet extraction. It also produces cleaner extracts which require less stringent cleanup.

Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans

A radioimmunoassay technique was developed to measure polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans; 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and related compounds (2,7-dichloro-, 1,2,3,4-tetrachloro-, 1,2,7,8-tetrachloro-, 1,3,7,8-tetrachloro-, 1,2,3,7,8-pentachloro-, 1,2,3,4,7,8-hexachloro-, 1,2,3,4,6,7,8-heptachloro-, dibenzo-p-dioxins and 2,3,6,8-tetrachloro-, 2,3,7,8-tetrachloro-, 1,2,7,8-tetrachloro-, 2,3,4,7,8-pentachloro-, 2,3,4,6,8-pentachloro-, 1,2,3,4,7,8-hexachloro-, 2,3,4,6,7,8-hexachloro-, 1,2,3,4,6,7,8-heptachloro-, pentachloro-, dibenzofurans) in fish tissue at a detection limit of 3.9 pg 2,3,7,8-TCDD. The method is an improved [^{3}H] based radioimmunoassay screening test for the rapid detection of polychlorinated dibenzo-p-dioxins in environmental samples. The assay uses a stable [^{3}H] - 2,3,7,8-TCDD radio-ligand that has the advantages of greater similarity to the target molecule and longer shelf life than the previously used iodinated radio-ligand. The use of [^{3}H] - 2,3,7,8-TCDD improves the performance and reliability of the assay. The speed, sensitivity, detection limit and precision of the [^{3}H] based assay are superior to the [^{125}I] based version.

A gas-chromatography method ws also developed to measure polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans; tetrachloro-, pentachloro-, hexachloro-, heptachloro-, octachloro-, dibenzo-p-dioxin and dibenzofuran congeners in fish at a detection limit range of 2-15 ng/kg for dioxin congeners. The method is a streamlined extraction and cleanup procedure for the detection of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans in fish samples using gas chromatography with mass selective detection. Ground samples, blended with anhydrous sodium sulfate are packed into a column and extracted with dichloromethane. The bulk of the fish lipids is removed by size exclusion chromatography, with residual lipids and biogenic material removed by chromatography on combination acid/base silica micro-columns. The extract is further enriched by high pressure liquid chromatography on basic alumina and activated carbon, and then analysed by high resolution gas chromatography. The method is faster and more efficient than those based on liquid phase extraction and cleanup steps, and provides a cost-effective technique for screening fish samples for the presence of chlorinated dioxins and furans.

Polychlorinated Dibenzofurans

A supercritical fluid extraction method was developed to measure polychlorinated dibenzofurans; tetrachloro-, pentachloro-, hexachloro-, heptachloro-, octachloro-, dibenzofuran congeners in municipal fly ash at low mg/kg levels. Polychlorinated dibenzofuran congeners are extracted from municipal fly ash samples using an optimized multi-residue supercritical fluid extraction (SFE) technique. Sample extracts are cleaned up on both a Florisil column and a basic alumina column, and then analysed using high resolution gas chromatography with low resolution mass spectrometry. The optimized SFE procedure is more efficient than a conventional Soxhlet extraction and provides higher recoveries and more precise data. The method is quantitative and significantly shortens the analysis time.

Structure-Activity Relationships

Quantitative Structure-Activity Relationships (QSAR) have been recognized as a promising tool for estimating environmental properties and fate of chemicals. Of some 60,000 to 100,000 chemicals in commerce, only a small fraction have measured physico-chemical data of environmental significance, such as soil/water partitioning constants, rates and products of degradation, volatilisation, much less toxicological information, such as acute or chronic toxicity to important fish species. This enormous data gap cannot be filled by measuring all missing data since the cost and time requirements are far beyond the available means. Therefore, it was recognized that reliable estimation methods had to be developed to undertake this task. The use of QSAR, which is widely used in the field of pharmaceutical drug development, has greatly enhanced our ability to correlate existing information and hence predict missing data on the basis of chemical similarities.

One premise for quantitative data comparison is data compatibility. While many biological tests are described in the literature, only a few have been employed using a significant number of chemicals. Furthermore, variations between laboratory conditions, water hardness, temperature, pH, acclimatization of species, and other variables, frequently prevents a quantitative comparison of test data between laboratories. We have therefore embarked on an ambitious toxicity testing program, using a standardized bacterial bioassay, to determine the acute effects of individual chemicals.

This database on *Photobacterium phosphoreum*, commonly known as the Microtox™ test, has been extended significantly and now includes approximately 1300 individual chemicals of many different classes and properties. The strong expansion of the database spawned new developments in the field of quantitative relationships between the toxicity of chemicals and different aquatic species. For example, it was shown that there are strong parallels between the Microtox™ test results and fathead minnow (*Pimephales promelas*) tests for most types of compounds; however, certain chemical groups, such as the vicinal -CR=CR2 group

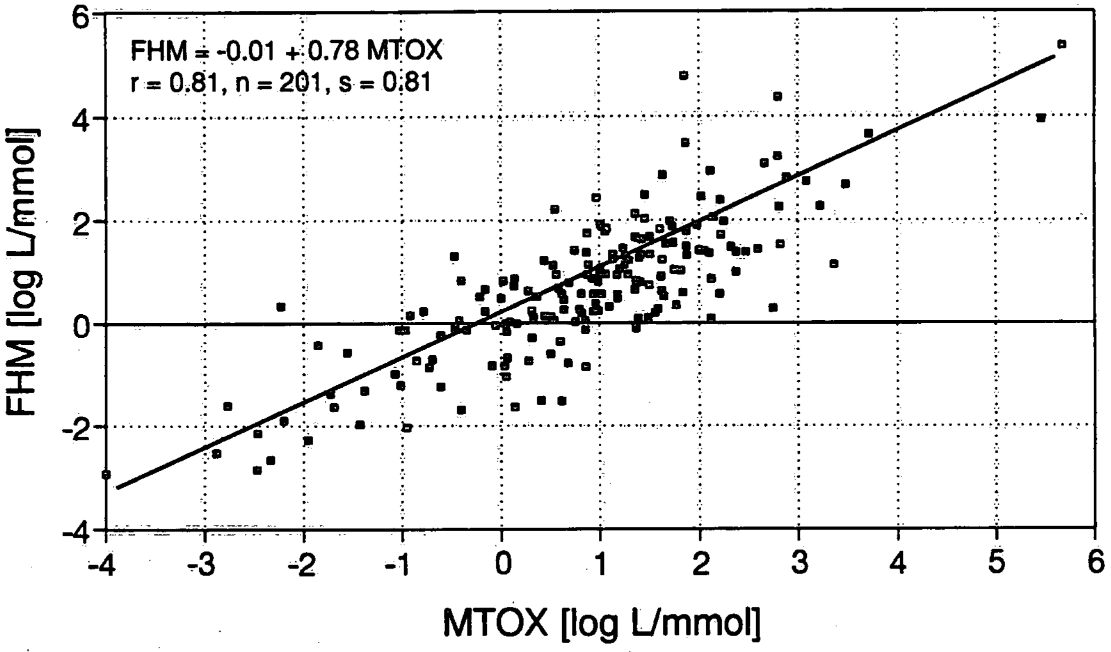

Figure 14. Plot of the acute toxicities of over 200 individual organic chemicals in the fathead minnow 96-hr LC_{50} test (FHM) versus the luminescent bacteria 5-min to 30-min EC_{50} test (MTOX).

(where R=H, Cl, or possibly similar atoms), the fish is more sensitive than the bacterium. This relationship is highly significant and Figure 14 shows a plot of toxicities over 10 orders of magnitude, i.e., from the least toxic compound (methanol) to the most toxic organotin derivatives, together with the regression data.

A "by-product" of the *Photobacterium phosphoreum* toxicity database is the development of a novel type of scientific database system for desktop computers. This approach utilizes commercial computer spreadsheets to store and manipulate the data for mathematical and graphical applications. This development, in turn, has led to an investigation of the toxicological effects of chemicals on terrestrial species, primarily the rat and mouse. Since there is a very large number of toxicity values to rat and mouse available from the literature, quantitative correlations and predictions may also be possible. This work is ongoing together with research into the applicability of advanced statistical methods, such as neural networks.

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ANNEX 13

POLLUTION FROM NON-POINT SOURCES

Annex 13 requires management and surveillance programs, as well as demonstration projects and research activities to be implemented on non-point sources of pollution from land-use activities. These activities should address biological, as well as chemical pollutants and, both urban and agricultural sources.

At NWRI, research activities on non-point source pollution under GLAP, included: the identification and characterization of urban and agricultural sources; the investigation of pollutant transport in riverine systems; the measurement of pollutant fluxes in tributaries; chemical losses in rivers through biofilm uptake; and urban stormwater pollution control using stormwater ponds.

Agricultural Sources

General

A comprehensive methodology for tributary monitoring was developed. This methodology accounts for seven main attributes of the loading regime - load response, spatial variability, seasonal variability, transport modes, load distribution with particle size, load mixing and concentrations versus discharge relationships. Monitoring programs based on these findings will produce superior estimates of pollutant fluxes in rivers.

Uptake of toxic chemicals by biofilms has been studied using two identical outdoor flumes and different flow velocities, sheer stresses and bottom materials. A fast build-up of biofilm was observed, which corresponded to rapid decreases in tributyltin concentrations in the overlying water. These results should lead to the development of predictive methods for chemical uptake by biofilms and an exploration of their potential enhancement and application as a remediation technique for contaminant removal.

Nissouri Creek

A 1988 survey of agricultural pesticide use showed that herbicides accounted for 76% of the 6200 metric tons applied to field crops. This represents a significant increase since 1973 when herbicides accounted for 59% of the 4500 metric tons of pesticides used on field crops. In addition, a significant shift in the herbicide types applied to field crops was also noted.

Studies of pesticide movement from agricultural land have shown that most atrazine herbicide loss occurs in the water phase while a greater portion of metolachlor appears to be transported by sediment. An NWRI study examined the residue levels of five herbicides in storm runoff from a small agricultural watershed.

The Nissouri Creek agricultural watershed, located within Oxford county in southwestern Ontario (Figure 15), was selected for this work. The watershed covers about 3500 hectares and contains about 55 active farms using both conventional and no-till procedures with crop rotation. The creek drains a portion of the Oxford till plain and joins the Thames River upstream of the town of Thamesford. More than 50% of the area is planted with corn and 30% with hay, soyabeans, cereals, cash crops and fruits. The remaining area is comprised of forests, feed lots, roadways and residences. Almost all the cultivated acreage of the area has a subsurface drainage system.

Water samples were collected from the creek during runoff events using an automatic sampler. The time-composited samples were analysed for alachlor, atrazine, cyanazine, deethylatrazine and metolachlor. These chemicals were commonly applied to the corn fields and other crops for weed control over the past few years.

Atrazine and deethylatrazine were present in all samples. Alachlor and cyanazine were not detected at all. The absence of alachlor residues was not surprising since registered use was cancelled in 1985; however, the absence of cyanazine may have been due either to a lack of use in the study area, at that time, or because the chemical has a rather short half life. Metolachlor occurred in about 40% of the samples. The majority of these occurrences were in May and July, with no detectable amounts being found after early October. The concentrations of atrazine, deethylatrazine and metolachlor rose during the periods of pre-planting

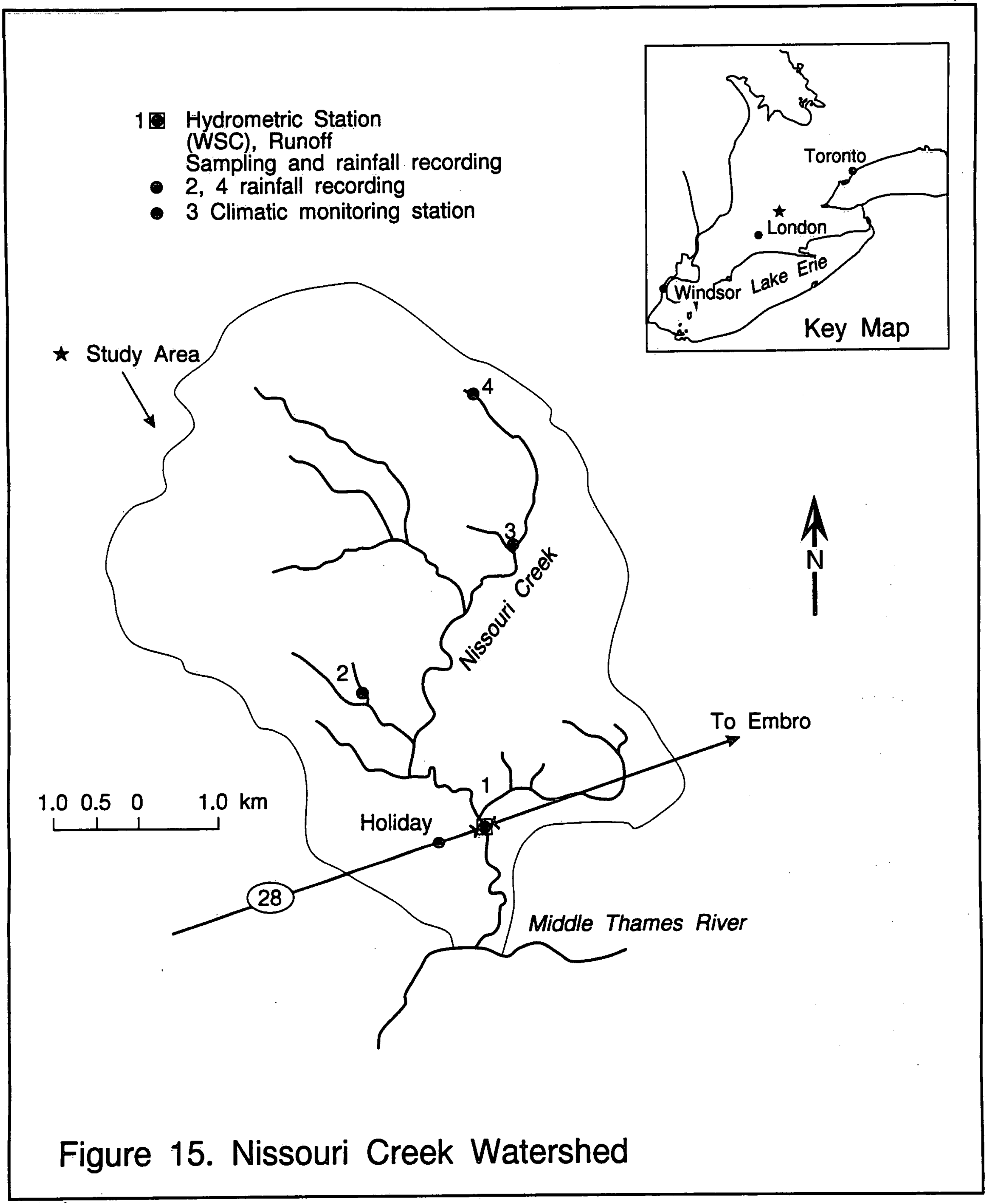

Figure 15. Nissouri Creek Watershed

and post-planting treatments, but declined almost exponentially shortly thereafter. Atrazine and deethylatrazine were consistently detected in the creek during baseflow conditions, but metolachlor was not.

The data gathered in this study characterize the movement of these five pesticides from their area of application to the receiving water. This information is useful for modelling application rates, residue runoff and resultant receiving water concentrations, which can be used to adjust management practices and investigate environmental impacts.

The importance of phosphorus to the enrichment of water bodies has been well documented and was addressed in the Great Lakes Water Quality Agreement. For practical reasons, the Agreement deals only with total phosphorus (TP) loads and their reduction; however, phosphorus loads vary widely in bioavailability and their resultant impacts on receiving waters. For example, most of the phosphorus in sewage treatment plant effluents is in the dissolved form, which is considered the most readily bioavailable form of phosphorus. However, phosphorus in agricultural runoff is largely associated with sediment and 40% to 80% of the TP load is particulate, which is considered to be much less bioavailable. Therefore, the development and implementation of phosphorus control programs requires information on the forms of the loads and their bioavailability. Under GLAP, a study was conducted to examine phosphorus partitioning in runoff from a small agricultural watershed. The study investigated the temporal variation in phosphorus forms and attempted to relate them to catchment hydrology. The study site chosen was Nissouri Creek (Figure 15).

Project results indicate that about 54% of the TP in runoff is associated with sediment particles. The remaining 46% was transported in the dissolved form as soluble phosphorus. The mode of phosphorus transport was very similar to that observed in the Nith River, which drains an agricultural watershed in southern Ontario. Significant correlations were found between total particulate phosphorus and the inorganic fraction of suspended sediments and, between soluble phosphorus and the concentration of organic matter in suspended sediments. Although none of the forms of phosphorus were well correlated with runoff volumes, the highest concentrations of both total and soluble phosphorus were found in the spring and autumn when plant cover was low or absent. These results will assist in the development and refinement of models to adjust the time, methods and rates of phosphorus application to minimize losses and improve use efficiency.

Grand River

Selected pollutants in agricultural runoff were characterized at sites in the Grand River. These studies focused on the various forms of phosphorus and selected herbicides in both water and suspended sediment. Export rates for these herbicides were determined and can be used in the predictive mode. The field data were used in conjunction with the agricultural runoff model AGNPS to simulate agricultural runoff quality. Experience gained with this model can be used elsewhere in assessing agricultural runoff pollution. Further work is continuing in cooperation with Agriculture Canada.

Pollutant transport was also studied in the Grand River system. Field observations at three river cross-sections served to establish the roles of various transport mechanisms in pollutant transport. Close correlations among the various metals were found and their concentrations were directly related to the suspended sediment concentrations. Channel scouring and bank erosion was an important source of metals and phosphorus, particularly during the high flows, indicating a significant contribution of erosion-derived P to the total load, during wet years. It is during wet years that the P loads exceed the target loads stipulated by the GLWQA, and the tributary loads constitute a significant portion of the total P loads to the Great Lakes. Other work continued on flocculation of fine grained sediment and the role of flocs in pollutant transport. This new knowledge will be helpful in improving riverine transport models providing detailed assessments of nutrient and contaminant management and developing management plans.

Nith River

Pollutant transport in the Nith River during various flow regimes was investigated. The Nith River, a tributary of the Grand River, drains an agricultural watershed in southern Ontario. The mode of P transport in the Nith River was remarkable similar to that observed in the Nissouri Creek, with 54% of the TP load being transported in dissolved form, the form most readily available for biological utilization. Assessment of particulate P forms showed that about 19% of particulate P is biologically inert apatite-P. Analysis of bed sediments showed that the river bed is one of the sources of this P form during high flows.

Although no significant spatial differences were observed in P and metals concentrations over the investigated reaches of the river, seasonal differences were apparent in particulate P forms, revealing seasonal effects on the sediment availability, source characteristics and delivery processes. Co-precipitation and bioaccumulation of manganese with P in biological materials was evident from the seasonal differences in particulate manganese concentrations.

Contaminant Studies

The main focus of this work was to examine pollutant transport characteristics of representative rivers within the Great Lakes basin and to evaluate their impact on contaminant sampling design. Seven transport characteristics have been examined; load response, spatial variability, seasonal variability, transport modes, load distribution with particle size, load mixing and concentration versus discharge relationships. At present many of the monitoring programs within the Great Lakes basin lack continuity and compatibility with one another as the data generated are generally sampled, analyzed and reported differently from one program to another. In addition quality and quantity monitoring programs have traditionally been segregated form one another. Successful integration and standardization will require two sets of activities. The first is to resolve the fundamental scientific questions such as in-stream variance and down stream transport of contaminants; and the second is a management exercise in standardization of field and analytical methods relative to the level of accuracy realistically required to address water quality management issues.

Results have demonstrated that a river's transport characteristics can have a profound effect on sampling design and, therefore, loading estimate error. The degree to which transport characteristics can affect loading estimates is site and contaminant specific and is dependent on the original objectives of the program and on the desired level of accuracy.

The primary study site was located on the Nith River (the largest tributary of the Grand River) using dissolved and particulate metals as indicator contaminants for sampling. This work has demonstrated that the significance of contaminant variability in a cross-section to loading estimates is highly dependent on the dominant mode of transport (dissolved or particulate). The impact of variability on loading estimation at the study site was minimal as the highest degree of variability generally occurred in the transport mode which was least significant at the time of transport. The cross-sectional variability which was observed demonstrated no systematic temporal or spatial pattern, suggesting that the variation may be related to random temporal variations in concentrations rather than to morphological or sedimentological conditions. The number of samples to be taken is strictly determined by the river's load response, level of loading accuracy required and by the relative cost of each sample. Maximum benefit from a sampling program will be obtained if both the dissolved and fractionated (<63 µm and >63 µm) particulate loads are calculated. This will better allow the manager to interpret the source, fate and effect of contaminant(s).

Flocculation Studies

While flocculated particles in river systems have been known to exist for some time, only recently have we begun to understand the complex interactions of the physical, chemical and biological factors which influence their formation. Flocculation of cohesive sediment in freshwater riverine systems may have significant practical consequences for sediment and contaminant modelling as flocs possess settling characteristics that are significantly different from primary particles. For six south-eastern Great Lake basin rivers flowing to the Great Lakes, the floc was found to be the dominant form of sediment transport. The flocculation of fine-grained suspended sediment is believed to be the dominant mechanism for the formation of surficial fine-grained laminae on river beds during low flow conditions. These laminae represent temporary contaminant sinks as they are resuspended during high flow events and transported along with the associated contaminants downstream. Field data suggests that suspended solid concentration, particulate organic carbon and attached bacteria may play an integral role in the flocculation of fine-grain sediment. The association of bacteria with flocs is believed important not only for floc building through extracellular exudate production but also for the biochemical alteration of adsorbed contaminants.

Urban Sources

Toxic Contaminants

Urban runoff represents a non-point source of many pollutants, including toxic chemicals to adjacent receiving water bodies. Loadings can be estimated using many methods including direct monitoring, regression modelling, and runoff quality simulation using sophisticated hydrodynamic models. Runoff monitoring is the most accurate and expensive procedure to determine the loads; however, the collected data cannot be used to quantify the likely effects of control measures on contaminant fluxes. The use of runoff quality simulation models requires site-specific information to calibrate the model parameters, which may not be transferable to other sites. Very little improvement in model accuracy will be achieved without a considerable increase in the resources applied to the study. Therefore, the better approach for planning-level evaluations of pollutant loads from urban areas is to use characteristic runoff quality data, which have been collected at some previous time, and apply these to unmonitored sites with similar characteristics.

A user friendly, planning-level, computer model to estimate pollutant loadings was developed at NWRI. The model is menu driven and allows more than 60 pollutant constituents to be selected for study. The model was applied to three major urban centres in the Niagara River area: Fort Erie, Niagara Falls and Welland Ontario. Data were obtained from previous work and used to provide loading estimates of several contaminants. The model results, for the 10 metal contaminants used, compared extremely well with existing loading estimates based on monitoring data. However, additional data input and calibration are necessary to increase its applicability.

Bacterial Pollution

In conjunction with the Ontario Ministry of the Environment and Energy, the University of Windsor and other groups in Environment Canada, NWRI conducted studies of bacterial contamination along the Windsor waterfront of the Detroit River and the Sault Ste. Marie waterfront of the St. Marys River. The studies were intended to establish data bases for statistical descriptions of indicator bacteria during wet and dry weather, calibrate land-based loading and receiving

water models for bacteria, examine the sources and extent of contamination and the feasibility of various remedial options.

Observations of fecal pollution indicator bacteria and coliphage were used to assess the faecal contamination of the St. Marys River in the vicinity of Sault Ste. Marie, Ontario. Concentrations of four indicators, faecal coliform, *P. aeruginosa, E. coli* and coliphage indicate minimal faecal contamination. Impacts are mainly found during summer wet-weather conditions. Faecal bacterial sources included stormwater runoff, urban creeks, sanitary sewers, urban garbage and litter, and catchment surface wash. Similarly, bacteria counts on the Windsor side of the Detroit river were statistically related to rainfall events. The highest bacterial counts were observed at the beginning of the runoff period, followed by rapid dilution.

Combined Sewer Overflows

Urban runoff has been identified by the International Joint Commission as one of the contributing sources to use impairments in the Areas of Concern, including Hamilton Harbour. The harbour receives stormwater from several urban and suburban areas including; Waterdown, Dundas, Ancaster, Hamilton and a portion of West Burlington (Aldershot, Tyandaga and Maple Community). Urban runoff enters the harbour either from separate storm sewers or from combined sewer overflows. The development of an effective remedial strategy for control of these sources requires a characterization and quantification of their significance. A modelling study, using both previously collected and current monitoring data was conducted on the urban stormwater discharges from the City of Hamilton to Hamilton Harbour.

About 75% of the city area is served by a complex combined sanitary and storm sewer network (Figure 16). During periods of dry weather, the sanitary discharges are conveyed cross-town to deep trunk collector sewers and delivered to the Woodward Avenue Wastewater Treatment Plant (WWTP). During wet weather, the combined sewer flows exceed the capacity of the treatment plant and it is necessary to divert the excess flows directly to receiving streams and the harbour.

A sewer separation program has been in place for some time, and will likely continue in conjunction with the redevelopment or replacement of old combined

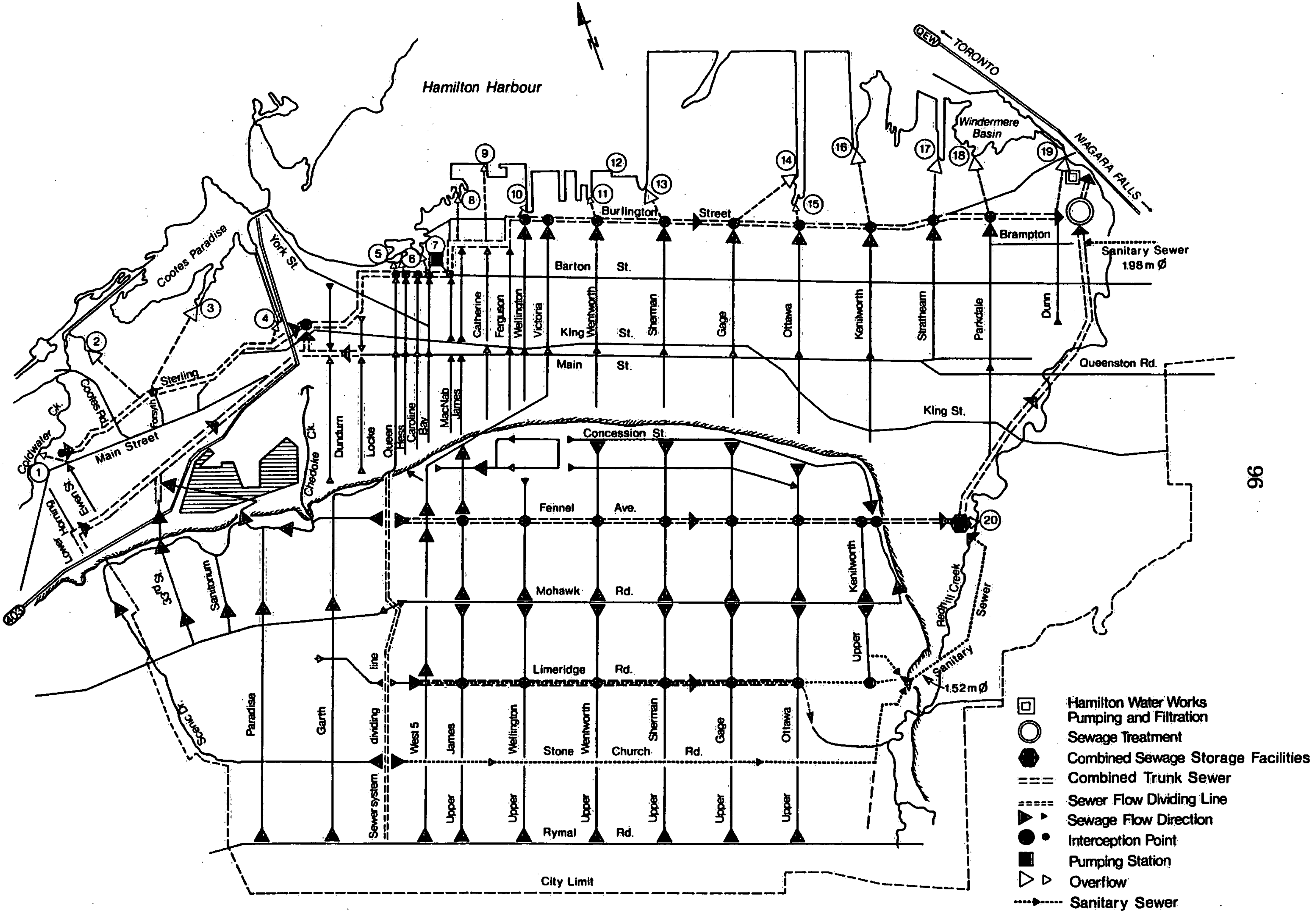

FIGURE 16. SCHEMATIC DRAINAGE NETWORK OF COMBINED SEWERS AND INTERCEPTORS IN HAMILTON, ONTARIO

sewers. Recently, a storm water storage tank, approximately 60,000 m^3 capacity, was built to alleviate hydraulic overloads during storm events and allow for later treatment.

Stormwater discharges, dry weather flows and combined sewer overflows were simulated for that part of the City of Hamilton that is served by combined sewers. The results indicate that for the entire basin and the treatment capacity that existed in the mid-to-late 1980s, about one third of the annual wet-weather flow, representing a mixture of stormwater and municipal sewage may be diverted in the form of combined sewer overflows to the harbour. The added storage tank reduces the simulated overflow volumes to about one quarter of the annual volume and in conjunction with the improved treatment capacity of the WWTP (recently instituted), the simulated overflow volumes further reduce to about one seventh of the annual wet-weather flow. Due to uncertainties inherent in the simulation process, these results are more useful for the comparison of control alternatives rather than the establishment of exact overflow volumes. In addition, these results apply only to the land-use conditions and sewer network at the time of the study;however, it is possible to use the model and these results to examine the likely impacts of such changes on the wet-weather inputs to the harbour.

Stormwater Ponds

Stormwater ponds are used extensively throughout the urban centres in Canada. These ponds are designed for use as storage systems to reduce stormwater runoff peaks and reduce the risk of downstream flooding. One of the current challenges in urban water management is the retrofitting of existing stormwater ponds to better protect the quality of the receiving waters. NWRI, in conjunction with MOEE and Queen's University is engaged in an ongoing program to review the mechanisms used in ponds to control stormwater quantity and quality, analyse specific retrofit measures and examine their feasibility for wide-scale use.

Information collected thus far indicates that before addressing pond retrofitting, measures should be introduced to reduce both the quantity of stormwater entering the system and its associated contamination. Such measures, also referred to as best management practices include the redirection of roof leaders and the removal of illicit storm sewer connections. A number of pond retrofitting measures can be employed either singly, or in some cases they can be combined (Figure 17). Some

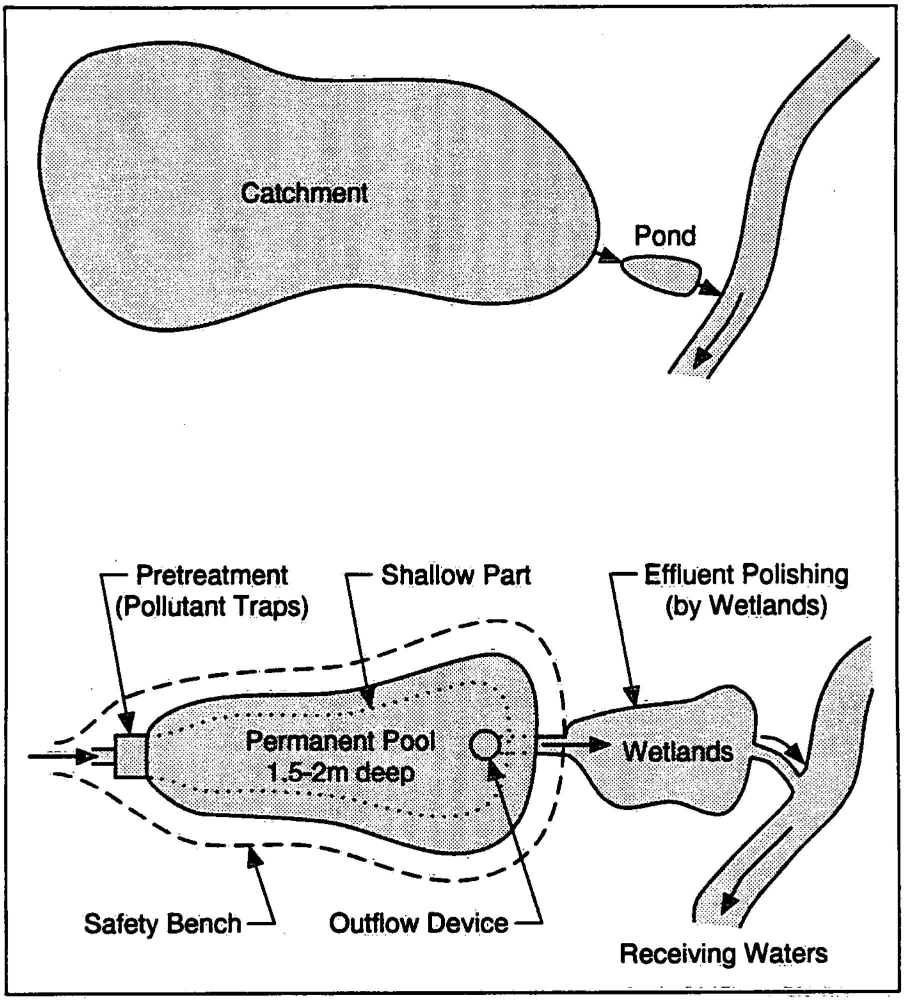

Figure 17. Catchment-Stormwater Pond-Receiving Water System

of these measures are: pretreatment using filter strips, oil booms and sedimentation basins, increasing the size of the pond, modifying the layout and depth of the pond, placement of internal baffles, establishing rooted plants in shallow parts of the pond, installing submerged pods containing macrophytes, and installing disinfection systems. Additional pollutant removal can be achieved through various downstream measures. These measures may include effluent polishing by routing pond outflow through wetlands and effluent treatment. Significant environmental benefits can be realized by auditing the water quality protection performance of older stormwater ponds and where feasible, employing the most recent knowledge to improve this performance through retrofitting.

Urban Drainage Controls of PAHs

Anthropogenic sources of polyaromatic hydrocarbons (PAHs) are ubiquitous in urban areas and require some degree of control due to their persistence and biological impacts. Source controls, preventing the release of PAHs to the environment, are best; however, these may be very costly and difficult to implement, particularly residential and vehicular sources. Where source controls are not feasible , clean-up efforts should be directed at PAHs deposited on impermeable surfaces (e.g., roads). On pervious surfaces, such as grassy areas, accumulations are mitigated by natural processes like biodegradation or photolysis. PAHs, which are deposited on impervious surfaces, are usually picked-up during precipitation events and deposited in nearby surface waters where they may bioaccumulate.

A study of PAH behaviour and potential remedial measures for contaminated runoff was conducted in Sault Ste. Marie, Ontario. Urban drainage for the city is provided by storm sewers that discharge either directly into the St. Marys River or into several creeks draining into the river. Emission sources of PAHs include; a large steel company, residential heating and wood burning and, vehicular traffic. During dry weather, PAHs are adsorbed onto sediment particles on urban impervious surfaces and are washed off during rain events. The accumulation rates do not depend solely on surrounding land use due to atmospheric transport. Consequently, accumulations of PAHs on urban surfaces are difficult to measure. Accumulation rates for various sources were established through dispersion-deposition modelling, direct measures of concentrations in snowpack and the effectiveness of PAH removal from impervious surfaces was examined. The remedial options studied include; more frequent street cleaning, storage facilities for runoff settling and snow removal.

The study showed that street cleaning, snow removal, dry ponds and wet ponds were all effective methods for reducing urban surface PAH accumulation and subsequent transport to nearby receiving waters. Street cleaning was most cost-effective on a five-day cycle but, its efficiency never exceeded 25% accumulation removal. The maximum removal efficiencies of the other mitigative measures were; snow removal, 27%; dry pond detention, 56%; wet pond detention, 88%.

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ANNEX 14

CONTAMINATED SEDIMENT

Sediments play an important role in the physical movement, chemical partitioning and biological fate of metals, organics and nutrients. Fine-grained sediments have the potential for collecting the highest concentrations of contaminants. These sediments initially accumulate in low energy areas such as nearshore embayments in lakes, river mouths and harbours. Many of these areas also receive urban, industrial and agricultural inputs of contaminants. Although bottom sediments are the primary sink for materials in aquatic environments, physical resuspension, biological and geochemical processes at the sediment-water interface can substantially prolong the time that contaminants remain bioavailable and accumulate in the food chain.

Annex 14, of the GLWQA, requires the nature and extent of sediment pollution in the Great Lakes be identified. Furthermore, based on these findings, methods to evaluate both the impact of polluted sediments and the technological capabilities of programs to remedy such pollution are to be developed. The knowledge gained through research in these areas is to be used to guide the development of Remedial Action Plans and Lakewide Management Plans.

Research activities at NWRI included studies of physico-chemical and biological processes involved in the release and bioavalability of sediment contaminants. In addition, methods have been developed for a comprehensive assessment of sediment quality. Different techniques have been developed for *in situ* treatment of contaminated sediments. Some of these techniques have been tested through demonstration projects, in Areas of Concern. Other areas of investigation provided recommendations for the long-term management of contaminated sediments including material dredged from navigation channels and harbours.

Assessment

Traditionally, contaminated sediments have been addressed only in the context of navigational dredging and disposal projects. However, the extensive contamination of sediments in Great Lakes' Areas of Concern has become a major consideration in the development of Remedial Action Plans. Managing contaminated sediment, for both navigational purposes and ecosystem remediation, requires a set of compatible guidelines. This objective has formed the basis of a large, ongoing research program at NWRI.

A number of approaches have been used to assess sediment contamination; however, they all employ either chemical or biological measures, or in some cases, both. Once the chemical concentration, biological response or state has been ascertained, the results are compared to some predetermined objective, criteria or standard. Chemical analyses are most frequently performed on the bulk sediment for total compound concentration (e.g., total PCBs). Analyses are done less often on pore water. Also, chemical species or congeners are measured infrequently in either bulk sediments or pore water. These chemical concentrations are then compared to background concentrations, water quality criteria or to known biological effects levels. These methods all infer biological impact rather than demonstrating effects. While these approaches should provide a reasonable degree of protection to the aquatic ecosystem when managing navigationally dredged material, they are unlikely to prove adequate in justifying expensive removal, treatment or mitigation of in-place pollutants as part of the RAP program. In response to these needs, a research program was initiated at NWRI in 1991.

This program is designed to provide essential information for the development of biological sediment guidelines, combining both structural and functional bioassessments (i.e., benthic invertebrate community structure and sediment toxicity tests). The fundamental assumption of this work is that the ultimate objective of a sediment management strategy is the maintenance and recovery of sustainable populations. Therefore, the final consideration must be given to measuring impacts on the biological organization of the aquatic ecosystem. This can be determined by the occurrence through time of an assemblage of species that is self-maintaining and resilient to environmental fluctuations and by a suite of appropriate toxicity tests.

Recent developments in multivariate statistical analysis have shown that it is possible to predict community assemblages at reference stations from a few physico-chemical variables. Such predictable communities, or key species within a community assemblage, can be used to form site-specific guidelines that can be compared with an existing community to determine whether a target has been met.

The study objectives were to: develop a system of classification of unpolluted nearshore sites in the Great Lakes based on benthic invertebrate fauna and selected toxicity endpoints; determine the degree to which site classifications can be predicted from physico-chemical variables; establish the relationship between community structure and toxicity assessments of sediment conditions; develop procedures for prediction of key elements of the fauna expected at a site from its environmental features that have not been modified by human activity; select key species and toxicity tests that show the most robust predictive response for the purpose of developing guidelines; and to propose a framework for numerical biological sediment guidelines for determining the need for sediment remediation and or dredge material disposal based on the invertebrate fauna and toxicity response.

Over 300 stations, in the nearshore of all five lakes have been sampled over the three years of the project (Figure 18). Several sites were resampled regularly to provide estimates of seasonal and interannual variability. In addition to benthic community structure analysis, several physical and chemical variables were measured in the overlaying water, the sediment and pore water. Four organisms, indigenous to the Great Lakes, were used in whole sediment toxicity tests with multiple endpoints: *Hyalella azteca, Chironomus tentans, Tubifex tubifex* and *Hexagenia limbata*. The endpoints used in the assays are survival, growth and reproduction.

Preliminary analyses of the data demonstrate the ability to define distinct community assemblages with a strong spatial signal and that community type can be predicted very accurately. The acquisition of larger data sets and greater taxonomic resolution are expected to improve this capability significantly. Analysis of the toxicity data indicates that the two most important endpoints for distinguishing the response groups are *Hexagenia* growth and *Tubifex* reproduction. The other endpoints showed no significant spatial differences. The low spatial variability of the toxicity endpoints implies that single criteria, independent of the physical and chemical characteristics of the sediment matrix can be developed for most endpoints.

In other research studies, different methods for mapping the distribution of contaminated fine-grained sediments in Hamilton Harbour and the St. Lawrence River have been examined. Acoustic techniques used in Hamilton Harbour

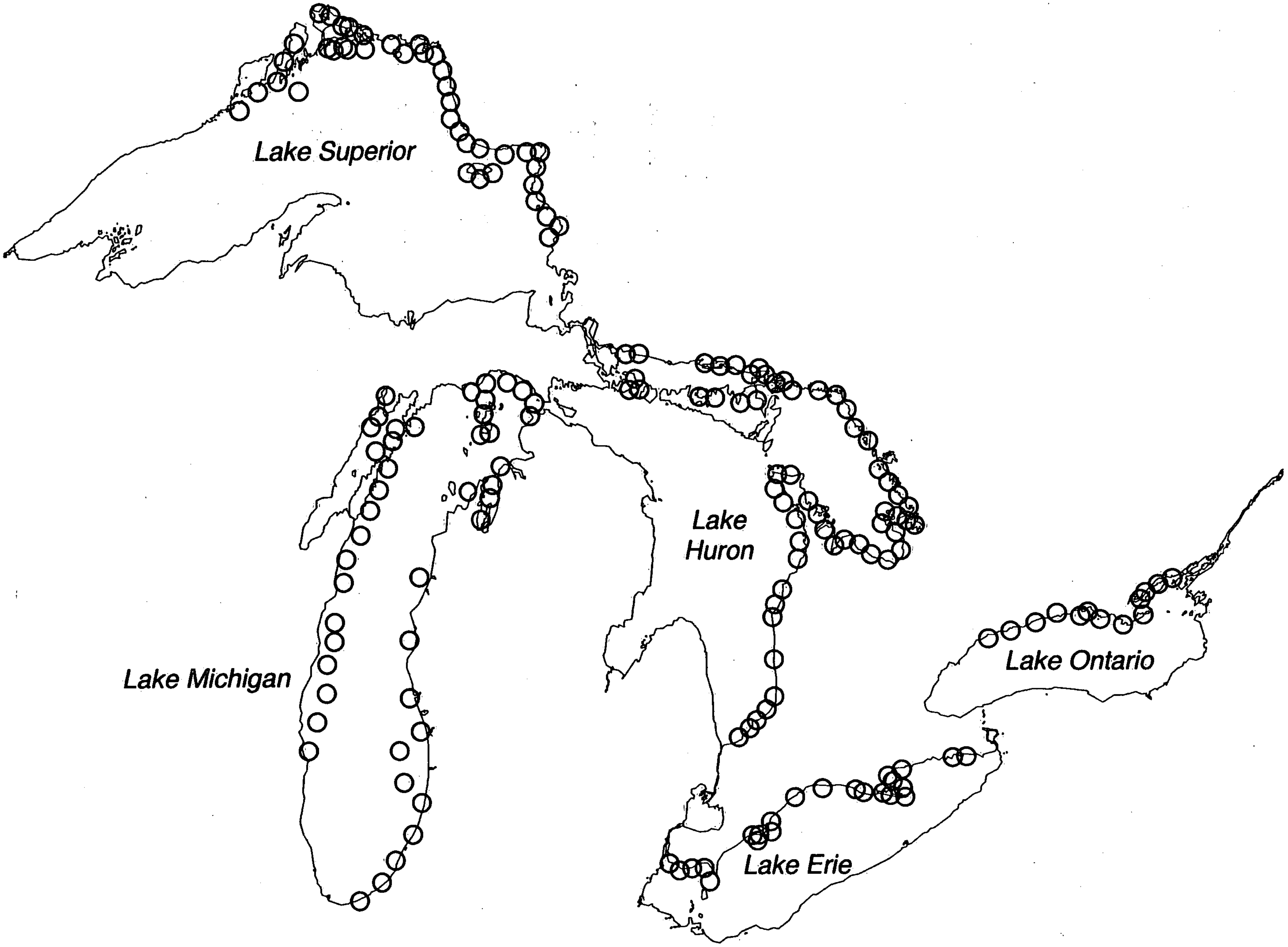

Figure 18. Reference stations for sediment criteria.

revealed considerable areal and spatial variability in sediment physical properties that are most likely due to industrial discharges. This information is essential for collecting and interpreting chemical and biological data on the sediments and for planning remedial actions. Sediment data collected in Lac Saint-Louis and Lac Saint-Pierre, St. Lawrence River, have been analysed with a SPANS geographic information system to determine the volumes of contaminated sediments. This information, combined with existing data on sediment contamination, has allowed preliminary estimates to be made on the volumes of contaminated material present (Figure 19). These data are also being used to plan additional survey work in the St. Lawrence River.

Since the early 1970s about 56% of sediments dredged from Great Lakes harbours and navigational channels have been placed in confined disposal facilities (CDFs). The present management of CDFs in Ontario usually results in the development of aquatic (i.e., marsh) habitat that gradually changes into terrestrial habitat as the sediment dewaters. Once the disposed sediment has dried out, it should be considered soil, which the Ontario Ministry of the Environment has soil guidelines for comparison. Consequently, contaminated dredged sediments, which have been confined with all precautionary measures to eliminate contaminant mobility, become terrestrial soils that could be acceptable for agricultural, parkland or residential land use because the concentrations of contaminants in the soil guidelines are 3 to 40 times greater than those for the open water disposal of material.

An environmental audit of present confined disposal facilities has been performed to determine if plants and wildlife colonizing the new habitat are at risk. Sediments/soils at most CDFs were determined to be no more contaminated than urban soils elsewhere in Ontario. Some CDFs, however, were determined to be highly contaminated, most notable the one in Hamilton Harbour. Vegetation growing on the sediments/soils accumulated cadmium, copper and zinc to a larger degree than other metals. Generally, contaminants in vegetation were found at acceptable concentrations. Accumulation of contaminants in grasses and clover was less than in sedges suggesting that manipulating the vegetative cover and the depth of cap which isolates the contaminated sediments/soils, could minimize contaminant mobility.

Most significant, however, is the comparison between the sediment/soil and the provincial soil guidelines. Only three of the 12 CDFs had soils unsuitable for

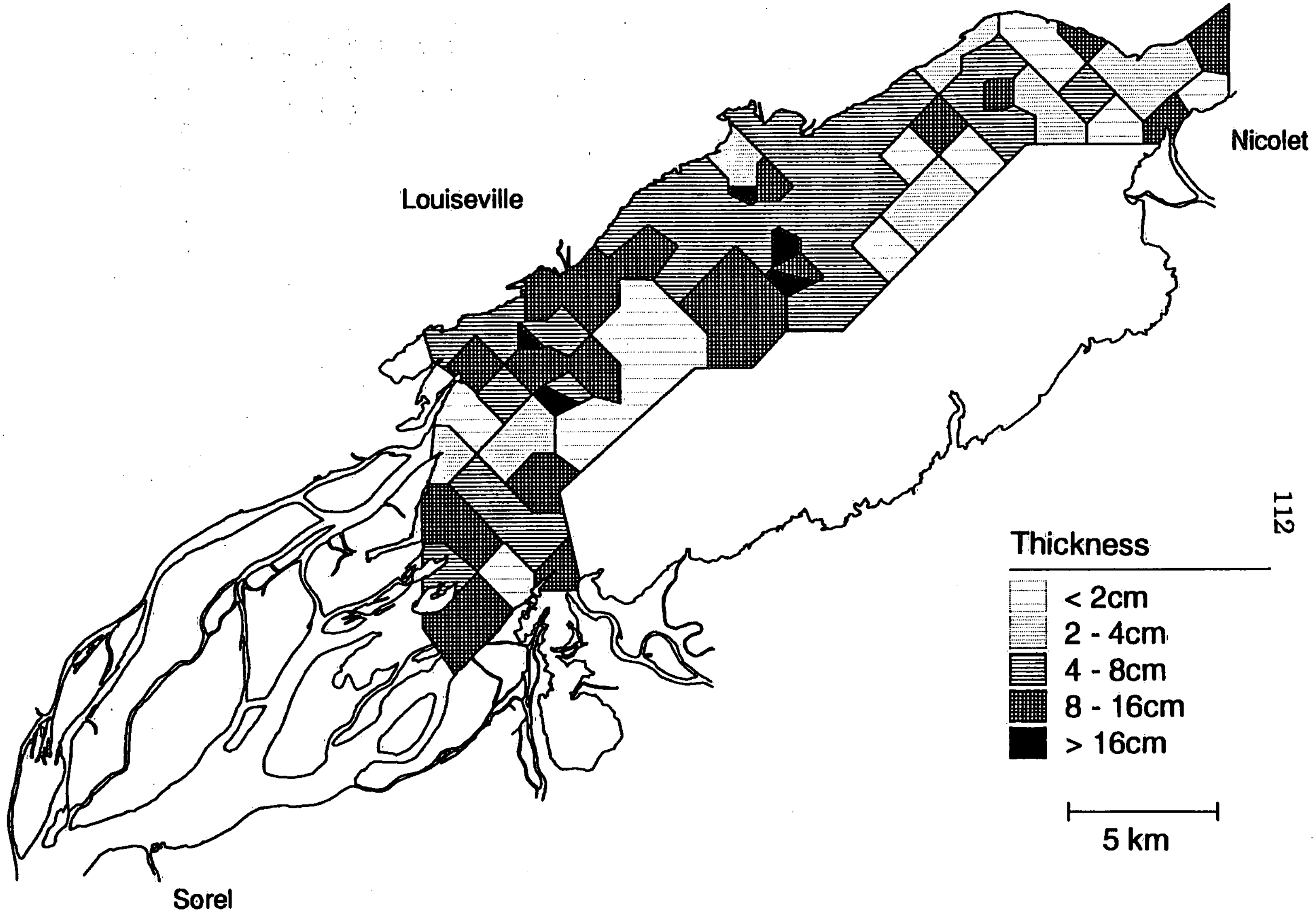

Figure 19. Modern-sediment thickness, Lac Saint-Pierre.

agricultural, parkland or residential land use. In two of the three, the soils were suitable for commercial/industrial land use and in the remaining one, at Hamilton Harbour, the soil was unsuitable for any land use due to excessively high zinc concentrations.

Metal concentrations in shrews, voles and ducks from the Thunder Bay CDF were comparable to the control sites and to other reported studies. Bioaccumulation of mercury in waterfowl muscle was examined. The bioaccumulation factor determined, when applied to other Canadian CDFs, suggests that mercury would not accumulate to hazardous concentrations elsewhere.

Bioaccumulation of priority PCB congeners was observed in waterfowl, shrews and voles. Extrapolating our data to other Canadian CDFs in the Great Lakes, waterfowl at the Hamilton Harbour CDF would accumulate PCBs to concentrations greater than the U.S. FDA poultry consumption guideline. The U.S. FDA poultry consumption guideline, which is being applied to waterfowl in several U.S. states, would be exceeded if the sediment had a total PCB concentration of 300 µg/kg. Bioaccumulation factors for total PCBs from sediments to shrews and voles would suggest that a 1 kg predator could experience reproductive failure by consuming one to two shrews or voles per day from the Hamilton CDF.

Generally, the creation of confined disposal facilities for dredged sediments and the creation of terrestrial habitat for parkland is an acceptable option for all Canadian Great Lakes CDFs except Hamilton Harbour. In the near future, the confined disposal option will be evaluated for the remediation of contaminated sediment problems in the Areas of Concern. In light of this report, this option should be evaluated using sediment guidelines during the first phase after the CDF is created and the soil guidelines during the next phase after the sediment is dry and partly consolidated. If the contaminant concentrations in the sediment of interest are significantly higher than the sediment guidelines but below the soil guidelines, every effort should be made to minimize the length of time of the first aquatic phase and reach the second terrestrial phase as quickly as possible.

Remediation

In situ treatment represents a nonremoval alternative for remediating contaminated sediment. These techniques have recently received some attention in the Great Lakes' AOCs that have large areas of contaminated sediments or areas that do not require navigational dredging. These treatments include physical capping and the enhancement of chemical or biological processes that will lower or eliminate contaminant toxicity and availability.

Many organic contaminants such as polynuclear aromatic hydrocarbons (PAHs) cannot be biodegraded in anoxic environments, while others such as polychlorinated biphenyls (PCBs) and oils can be biodegraded only very slowly. In addition, much of the sediment toxicity in Hamilton Harbour and the St. Marys River appears to be related to low redox potential and the products of anoxic decay, such as hydrogen sulphide.

An ongoing series of laboratory and field studies examined the enhanced biodegradation of some organic contaminants, such as naphthalene, by sediment treatment with ferric chloride or calcium nitrate. Pilot scale treatments of contaminated sediments were conducted in the St. Marys River and in Hamilton Harbour in conjunction with the Cleanup fund (Figure 20). The injection of ferric chloride reduced acute toxicity of the sediments by about 75% as measured by the ATP-tox bioassay. In laboratory incubations, the addition of ferric chloride stimulated biodegradation of organic contaminants. In other laboratory trials, the addition of calcium nitrate stimulated faster biodegradation. In six weeks, some compounds, such as naphthalene and toluene, were completely biodegraded. Some compounds were persistent and with six week incubations of sediment samples from the deep basin of Hamilton Harbour about 25% of the oil and grease was biodegraded. Biodegradation has also been observed in sediment samples from the Randle Reef coal tar hotspot in Hamilton Harbour. Development of a design and construction of a system for injection of calcium nitrate into five hectares of sediments in Hamilton Harbour and St. Marys River was completed.

Additional post-treatment analysis of an area in Hamilton Harbour showed that the oxidation of the sediments decreased the iron concentration of the porewater by a factor of 50 in the top 15 cm of sediment. Manganese also precipitated, but the concentration of other trace metals remained unchanged. In addition, phosphorus concentrations were reduced by a factor of three leading to the conclusion that nutrient binding can be affected in the sediments, keeping them from being reintroduced into the water column and slowing the recovery of eutrophic areas.

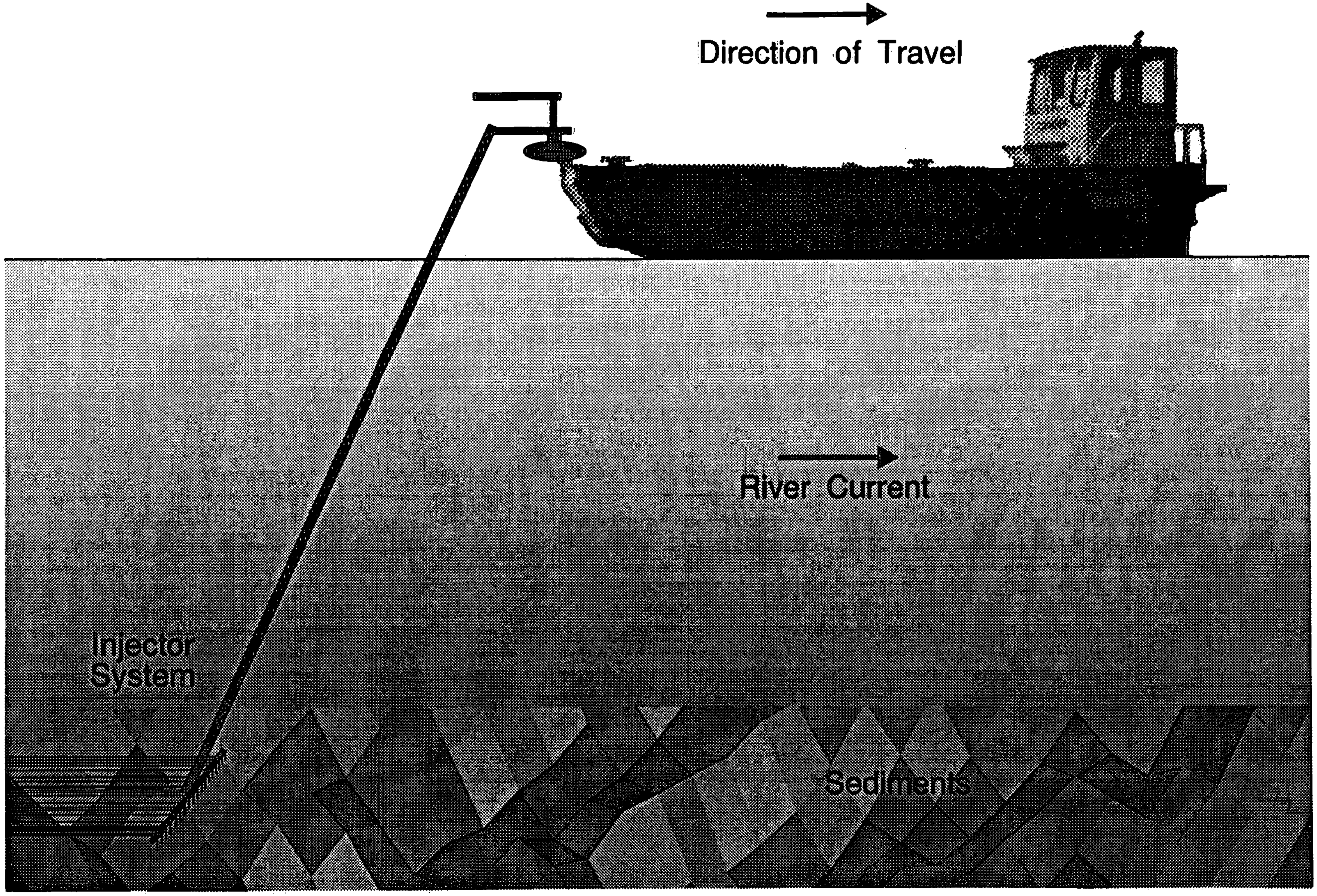

Figure 20. System for injecting chemicals into sediment

Although sediment contaminant concentration reduction resulting from *in situ* treatment is slower than removal, it is considerably less expensive than the confined disposal, land farming and *ex situ* treatment that is ultimately required to safely dispose of the contaminated material.

The consolidation behaviour of sediments has been investigated for two sites in Hamilton Harbour in preparation for a demonstration of subaqueous capping. Results of the investigation allowed predictions of particle settling and consolidation post application of a 0.5 m thick sand cap. Impact velocities of the sand material in various slug and grain sizes released from different heights above the harbour bottom were examined. Results of the studies and the model predictions are to be used in the selection of equipment and deciding on the sand cap thickness for the demonstration project. Subsequent laboratory tests conducted in a large observation tank confirmed earlier theoretical predictions of post capping consolidation and penetration. Tests of equipment that are to be used for the capping demonstration project have also been completed.

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ANNEX 15

AIRBORNE TOXIC SUBSTANCES

Many chemicals are transported to and deposited into aquatic and terrestrial ecosystems by the atmosphere. In the Great Lakes, the atmosphere represents the most important single source of some of the most persistent organochlorine chemicals and a number of metals. It is also an important sink for some of the same substances. The atmosphere serves as a medium for a continuous cycle of deposition and volatilization of persistent organic contaminants. Quantification of this cycle is essential to understanding the impacts associated with atmospheric contaminants and their management.

Annex 15 addresses the need for specific research to determine the pathways, fate and effects of atmospherically transported toxic substances. Research is required to be conducted to: understand the processes of wet and dry deposition, and those associated with the vapour exchange of toxic substances; understand the effects of atmospherically transported persistent toxic substances; develop models of the intermediate and long-range movement and transformation of toxic substances. In addition, an Integrated Atmospheric Deposition Network (IADN) is to be instituted to: identify toxic substances and their significant sources, which are being introduced to the Great Lakes via the atmosphere; determine the atmospheric loadings of these substances; define the temporal and spatial trends in their deposition; develop RAPs and LAMPs.

Atmospheric Deposition and Contaminant Chemistry

NWRI, working with the Atmospheric Environment Service (AES) of Environment Canada, has established two master stations as part of the IADN. These stations are located at Point Petre, Lake Ontario and Burnt Island (near Manitoulin Island), Lake Huron. Biweekly air and precipitation sampling at these stations has provided improved estimates of organic and metal contaminant loadings to the lakes from the atmosphere. Early in 1992, a workshop of U.S. and Canadian researchers convened to: review the most recent measurements of toxic organic chemicals and trace elements in the atmosphere and wet deposition; select consensus concentrations of toxic substances in air and rain applicable to each of the Great Lakes; and calculate updated estimates of atmospheric deposition of as many toxic organic chemicals and trace elements as the data permit. The compounds considered included; organochlorine pesticides and industrial by-products, including PCBs; chlorinated dioxins and furans; combustion related polycyclic aromatic hydrocarbons (PAHs); and the trace elements Hg, Pb, Cd and As. Estimates of dry deposition were dramatically improved by incorporating seasonal atmospheric concentrations of toxic organic chemicals and seasonal variations in the fraction of organic chemical in the particle phase.

As a result of the workshop, revised atmospheric deposition values for several compounds were reported (Table 1). These represent the best loading estimates for the Great Lakes so far produced and demonstrate that significant progress has been made in the collection of seasonal air concentrations. The estimates of loadings to the Great Lakes have been considerably improved, at least partly, as a result of increased information on some of the process parameters, which are essential for the loading calculations. This topic, however, remains the largest single difficulty in developing reliable estimates of overall atmospheric loading to the Great Lakes. Under monitoring, improvements in wet and dry deposition determinations are noted; exchange of some of the same chemicals in the gas phase, is still largely unknown and the magnitude of this contribution to (or removal from) the Great Lakes is largely a conjecture. Research at NWRIs gas-transfer flume and at its field site at Turkey Lake in northern Ontario has demonstrated the feasibility of experimental determination of the mass transfer coefficients needed to make these estimates. The 1992 estimates for atmospheric wet deposition are generally one-half to one-third those reported in 1988. These differences are a result of real reductions in concentrations, better estimates of wet sample concentrations (for some chemicals) and the use of seasonal variations in air concentration and gas-particle distributions to calculate dry deposition. The B[a]P loading estimates for Lake Superior are higher in 1992 as a result of assigning a higher concentration to both air and rain. Overall, these improved data are also supported by evidence from accumulation measurements taken in peatlands and in Great Lakes sediment cores. These estimates suggest that atmospheric loadings to the Great Lakes are decreasing; however, there is other convincing evidence that suggests atmospheric concentrations for some chemicals (e.g., Σ PCBs) have not substantially decreased. It will likely be some time before trends in atmospheric concentrations and deposition can verify this hypothesis. In addition, the workshop provided some definite research needs such as air-water exchange of persistent organic chemicals, for improving both our understanding of certain processes and the quantification of their effects on atmospheric loads.

Trace metal research has also experienced significant advances at NWRI. Studies published in the late 1980s clearly show that most of the available data on low concentrations of trace metals in the Great Lakes waters were biased by contamination artifacts that were introduced during the collection, handling and analysis of samples. These problems require special measures to reduce and eliminate contamination from sampling equipment, labware, reagents and even the air in contact with the samples. NWRI has adapted, modified and added novel features to published methods to provide very accurate, benchmark measurements of metals in the open waters of the Great Lakes and in precipitation samples.

TABLE 1: Comparison of atmospheric loading estimates (after Strachan and Eisenreich 1992).

Lake	Σ-PCBs	Σ-DDT (kg/yr)	B[a]P	Pb (x 10^3)
Superior				
1988	548	90	69	234
1992	157	34	116	67
Michigan				
1988	394	64	179	540
1992	114	25	83	138
Huron				
1988	399	61	183	404
1992	124	25	84	105
Erie				
1988	182	33	81	225
1992	53	12	40	97
Ontario				
1988	143	26	62	216
1992	43	9.5	31	48

1988 = Strachan and Eisenreich (1988);
1992 = Eisenreich and Strachan (1992).

One of the first, and most expensive steps was to construct a Class-100 clean laboratory. This facility, constructed at CCIW, is comprised of two self-contained handling and analytical laboratories with a separate clothing change area. The labs have filtered air supplies, which are maintained at sequentially higher positive pressures in relation to each other and the exterior environment. All metal surfaces have either been eliminated or epoxy resin coated along with protective Teflon overlays on the counter tops. Other special features have been included in the lab along with several protective clothing innovations.

Special sampling and filtration techniques are followed, along with the decontamination of bottles and labware. Great care has been taken to provide ultrapure water along with uncontaminated acids and other reagents. A new methodology, for the analysis of lead and other metals, with improved sensitivity, has been developed and implemented. In addition, a portable clean lab was constructed for all sample handling and field procedures.

Preliminary results, obtained using these methods and facilities, suggest that most of the published data on trace metal concentrations in the Great Lakes are inaccurate. The profiles of dissolved metal concentrations in the water column of Lake Ontario show very distinctive, source-dependent features, which were previously obscured by poor data quality.

Modelling, and the development of several input parameters essential to this activity, formed a major part of the NWRI efforts in assessing atmospheric toxic chemicals. Coefficients for vapour phase contaminant movement of some compounds were made using a specially constructed gas transfer flume (Figure 21). Some of the more volatile persistent and bioaccumulating compounds (e.g., the chlorobenzenes) have been investigated and present efforts are focussed on lindane and specific PCB isomers. Initial parameterization of a mass flux model has been succcessfully completed for lindane in Little Turkey Lake and the experience is being applied to model the movement of chemials within the Lake Ontario system.

In order to identify the factors that influence the accumulation of atmospherically derived organic contaminants in aquatic food chains in the Great Lakes ecosystem, contaminant patterns observed in inland lakes were compared with those observed in Lake Ontario. The fundamental questions asked were:

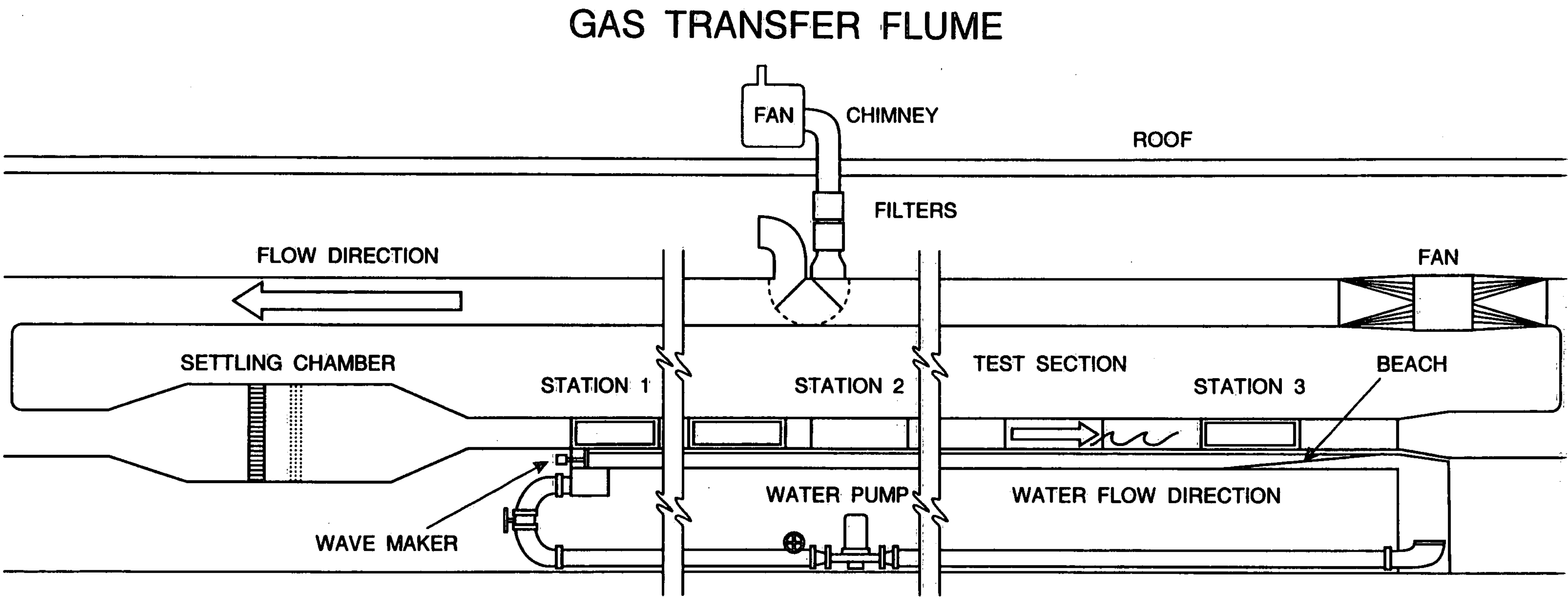

Figure 21. Gas transfer flume used in experimental studies of the transfer of toxic chemicals across the air-water interface.

1. Are the fish in Lake Ontario contaminated because the water is more contaminated, or

2. Is the water of similar concentration in all lakes but the bioconcentration pathways different?

Biological Accumulation

From sampling zooplankton from 33 lakes between Kingston and Bracebridge a correlation with total phosphorus was found. Lakes with high phosphorus generally had zooplankton with less contamination than those where phosphorus was low. Since then, a more careful analysis of the data showed that a better correlation exists with zooplankton abundance. Principal component analysis was used, but the trend fits for individual pollutants quite well. An example of this relationship is given on Figure 22 for PCB congener 153. When plotted against lipid content (Figure 23) no relationship was found. Nevertheless, if the most abundant contaminants in zooplankton from one lake are plotted against that in another lake, they are highly correlated indicating a common source.

At the same time, using summary data from the Ontario Ministry of the Environment Guide to eating fish in Ontario, it was noticed that lakes with smelt, alewife or other similar planktivorous fish contained lake trout that were much more contaminated that those lakes with simpler food chains. Furthermore, when the freshwater shrimp *Mysis relicta* was present the lake trout were even more contaminated. In some lakes the level of PCB and DDT contamination was similar to that of Lake Ontario. A simple regression model which required only presence or absence of planktivorous fish and/or *Mysis,* lake trout lipid level and latitude, was developed. It was also found that DDT and its metabolites are highly correlated with total PCBs in inland lakes that receive no point source pollution. Such data have now been used to predict that at least 40% of the contamination of Lake Ontario lake trout can be explained by atmospheric contribution.

More recent work has been focused on food chain determinants that lead to highly contaminated sport fish, such as those in Lake Ontario. Ecosystem scale research is expensive and labour intensive. GLAP funding has been used along with cooperative work by GLURF recipients at the University of Waterloo, Trent University, and University of Ottawa. In total, 25 inland lakes and 5 stations in

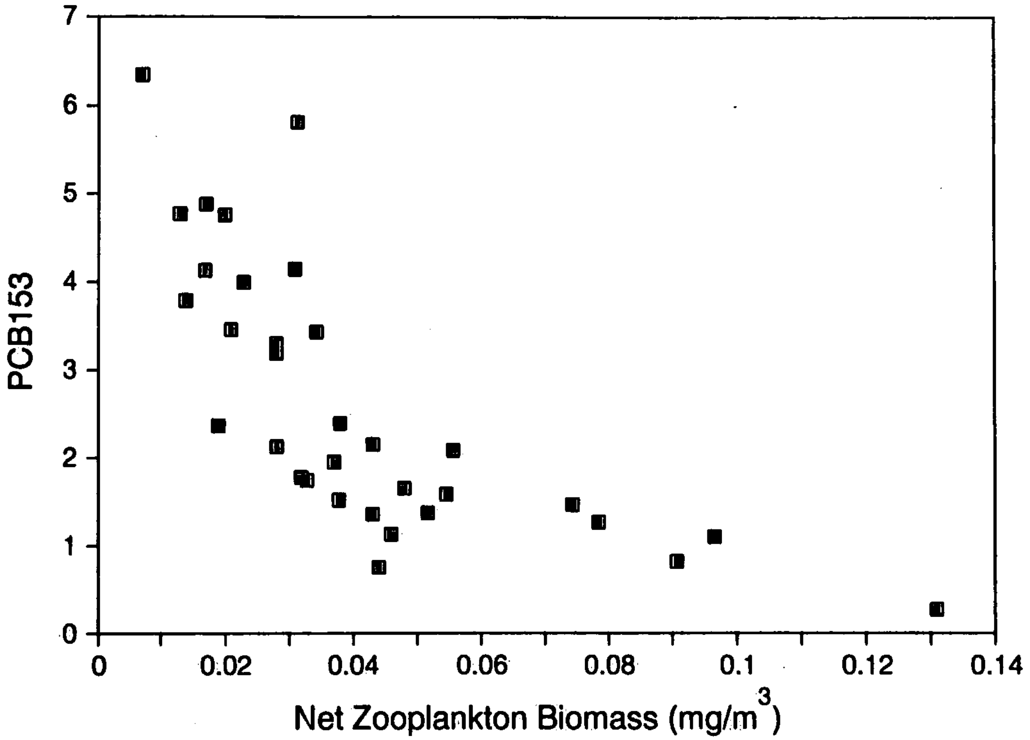

Figure 22. Relationship between the biomass of zooplankton and their content of PCB153.

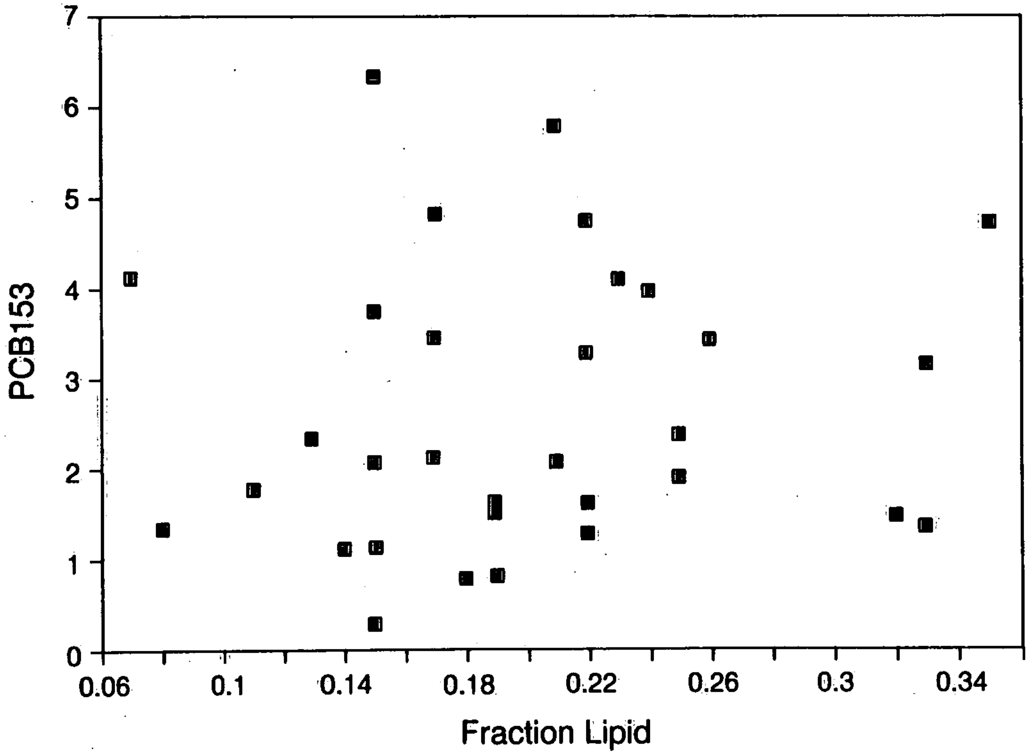

Figure 23. Lack of relationship between lipid content of zooplankton and their content of PCB153.

Lake Ontario (including Hamilton Harbour and the Bay of Quinte) were studied in 1992, with additional data being obtained in 1993. Results from these data reveal that there are some lakes where the fish are less contaminated than predicted. These anomalies are being used to try to identify significant variables and potential remedial actions. For example, if there were no point source pollution sources in Lake Ontario, the lake trout would only be about half as contaminated.

The influence of planktivores on lipid production and accumulation on plankton size structure and sedimentation rates have been examined also. Preliminary analysis indicates that in low density zooplankton lakes, such as Lake Ontario (Figure 23), a fish that eats zooplankton will allocate a greater amount of energy in maintaining itself and catching its prey. As a result, planktivores will increase in contamination even faster than their prey. Therefore, the restoration of a balanced zooplankton community is a prerequisite to a low contaminant fish community.

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ANNEX 16

POLLUTION FROM CONTAMINATED GROUNDWATER

Introduction

The contribution of groundwater to the regional hydrologic cycle in the Great Lakes basin occurs through a variety of mechanisms including direct groundwater discharge along the shorelines of the Great Lakes, deep regional discharge of groundwater into lake bottoms and groundwater discharge into the streams and rivers within the basin which ultimately reach the lakes. In addition, approximately 40% of the residents of the Great Lakes basin utilize groundwater as their primary source of potable water. Thus the quality of groundwater within the basin is of critical importance to the overall health of the Great Lakes and of the population that resides nearby.

There are numerous distributed sources of groundwater contamination within the basin such as nitrate, agricultural chemicals and pathogens. However, contamination emanating from waste and industrial sites on or near Great Lakes shorelines or tributary rivers provide for concentrated sources of toxic chemicals that tend to receive much public attention. The intent of Annex 16 in the 1987 Revised Great Lakes Water Quality Agreement reached in 1988 was to promote investigation of both distributed and point sources of groundwater contamination affecting the Great Lakes. In addition, methods for the control and remediation of the groundwater contamination were to be developed.

Groundwater research conducted at the National Water Research Institute in support of Annex 16 focussed on groundwater contamination issues related to the connecting channels of the Great Lakes, regional sources of poor-quality groundwater in the basin and on the development of new methods for the clean-up of groundwater contaminated by chlorinated solvents. In particular, groundwater investigations in the Niagara and Sarnia regions of southern Ontario were focussed on general interpretations of regional groundwater flow and on the development of new field, laboratory and modelling techniques for the investigation of contaminated groundwater that might be applied in these areas. Groundwater pollution from more distributed sources such as agricultural chemicals was investigated using modelling techniques coupled with an "expert system" approach. In the following, a brief synopsis of several of the research projects is provided.

Regional Groundwater Mapping

During the period 1989 to 1990, research into the factors influencing the migration of groundwater contamination which occurs at Niagara Falls continued. During this time, a regional study of groundwater flow in the Niagara Falls area was completed. The results of the study show that there are primarily two groundwater flow regimes in Niagara Falls, one at shallow depth confined to the Lockport and Guelph Dolostones, and a second at greater depth in the Cataract Group of shales and sandstones. The upper flow regime is characterized by active groundwater flow in regionally extensive sheeting fractures. Conversely, groundwater flow in the lower flow regime is virtually non existent with little groundwater movement in recent geological history. The water quality in both regimes is highly variable although the water in the upper regime generally has less dissolved constituents than that in the lower regime. Subsequent work focussed on developing new methods to investigate the hydraulic and contaminant transport properties of large scale sheeting fractures. This work has been conducted with the cooperation of the U.S. Geological Survey (USGS) using several boreholes drilled by the USGS in Niagara Falls, NY. The results of the study show that standard methods of testing usually employed to determine the permeability of fractured rock will lead to an incorrect interpretation of the distribution of fractures in the type of bedrock common in Niagara Falls. In addition, the use of the standard method failed to give an accurate determination of the permeability of the bulk rock matrix. Knowledge of the matrix permeability is crucial in formulating accurate predictions of contaminant migration.

During the same period, groundwater investigations continued in the Sarnia, Ontario, region. The objective of the study was to assess the possible impact of the deep well disposal of industrial wastes on a local aquifer. A monitoring well network of 29 piezometers was installed in the Sarnia area adjacent to the St. Clair River. Numerous samples of groundwater were obtained from this network and from a nearby deep monitoring well for geochemical analysis. Many of the volatile organics observed to be present in the deep well are not detected in the shallow network. It is concluded that the migration of contaminants from depth towards the shallow aquifer is not widespread. Furthermore, the localized presence of chloride contamination observed in the shallow aquifer is likely due to the upwelling of deeper, chloride rich formation water. One of the difficulties encountered in this study is related to the differentiation between chemicals of natural and anthropogenic origin. A new multivariate plotting technique was developed to address this issue. The method was employed with some success to fingerprint fluids from the disposal wells and natural formation waters in the Sarnia area.

During the period of 1990 to present, a detailed analysis of groundwater flow in the Sarnia region was conducted. The objective of the exercise was twofold: 1) to provide insight into the regional groundwater flow system as background to site-specific studies of groundwater contamination, and 2) to develop a novel calibration technique for large-scale groundwater models. Analysis of physiographic and groundwater data from across Lambton County revealed a strong correlation between ground surface topography and groundwater levels within the thin, unconsolidated aquifer that occurs at the base of the glacial overburden. This relation was used to construct a model of groundwater flow within the aquifer in which recharge is expressed as a function of topography. Determination of the spatial variation of recharge was performed using an inverse analysis implementation of the well-known SUTRA model of groundwater flow and transport. Inverse analysis of the data returned the pattern of recharge that best replicates known groundwater levels. Figure 24 compares the known and computed groundwater levels. The known and computed results are quite similar and this suggests that the numerical model developed through the analysis accurately reflects the hydrogeological processes acting on the aquifer. The modelling results revealed an area of elevated groundwater recharge that is coincident with the Wyoming moraine, a glacial topographic feature that extends across the county. Identification of the topographic features that control groundwater flow is very useful in developing a program of sustainable groundwater resource development for the region and in assessing the potential for groundwater contamination by past and present waste disposal practices and by the naturally occurring sources of hydrocarbon that underlie the region. The methodology applied in the Sarnia region is generic in the sense that it can be applied wherever adequate data exist to define the form and state of a subsurface hydrologic system.

In many locations throughout the Great Lakes basin, the groundwater in near-surface aquifers is of naturally poor quality. Assuming that the source of the poor

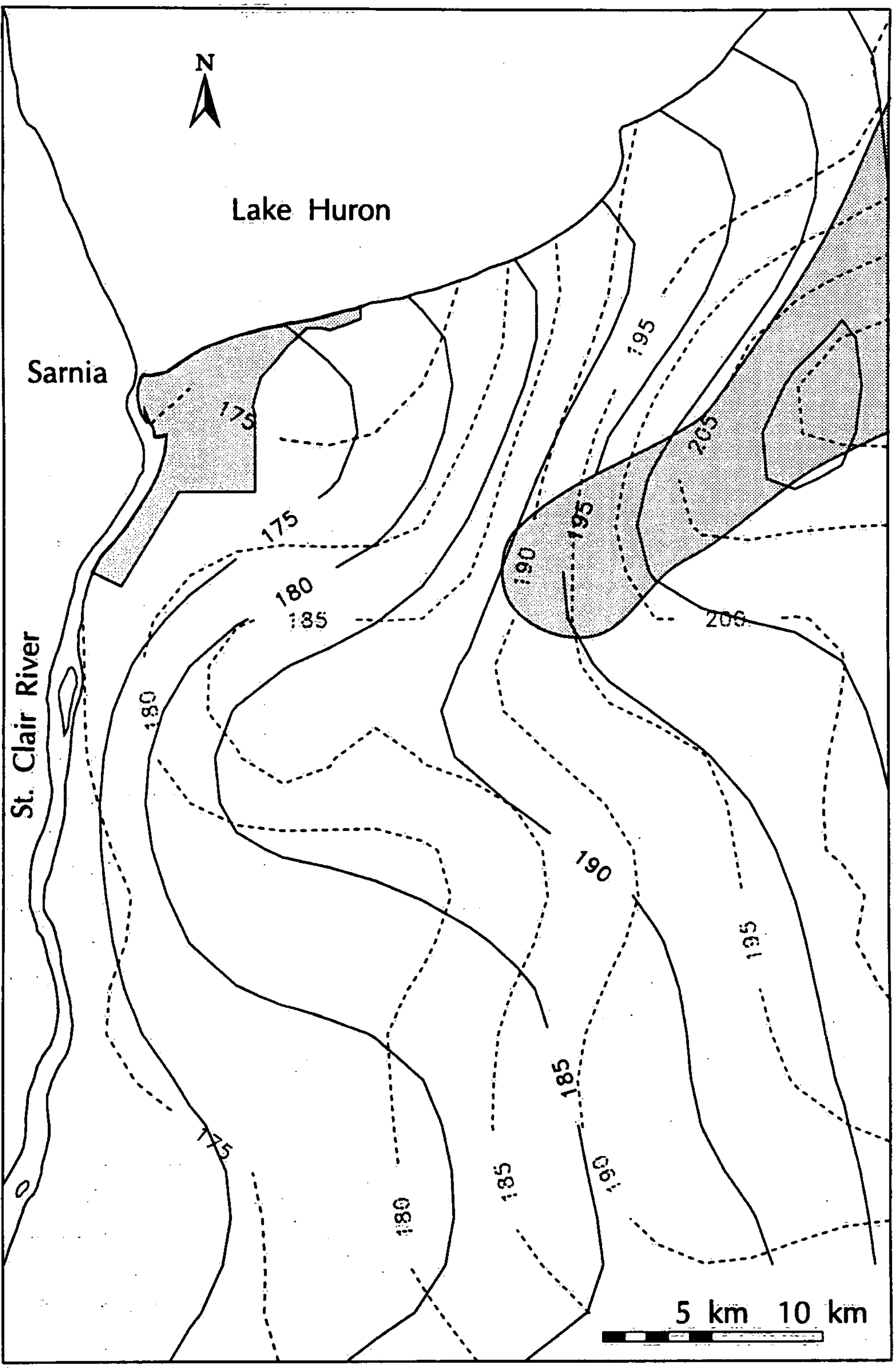

Figure 24. Comparison of known and computed groundwater levels within Lambton County. The contour interval is 5m where the dashed contours denote known groundwater levels and the solid contours denote computed results. The shaded area extending inward from the eastern boundary of the region is the recognized extent of the Wyoming moraine.

quality water is deep, regional groundwater carrying natural hydrocarbons, a study of the near-ground-surface impact of vertical thermal gas and BTEX (benzene, toluene, ethylbenzenes and xylenes) migration was undertaken. Results indicate that soil gas surveys show significant promise in determining the location of regional geological structure and associated shallow groundwater impacts. Two studies were conducted over the 1991 and 1992 field seasons, one in the area of the Dawn Fault in Lambton County and one focussed on a north-south trending fault in the Niagara-Toronto region known as the Niagara-Pickering Linear Zone (NPLZ). Approximately 250 soil gas samples were collected and analysed for methane concentration and many of these were also analysed for the higher C_2-C_4 hydrocarbons. At several locations along the NPLZ, groundwater samples were obtained and analysed for BTEX content. Based on the distribution of the hydrocarbon concentrations, a conceptual model was developed to explain the process of methane (and BTEX) accumulation in the shallow subsurface. Research is continuing on this problem, to develop methods for distinguishing between these naturally-occurring hydrocarbons and those of local anthropogenic origin.

Agricultural chemicals such as pesticides and nitrate are likely the most significant groundwater pollutants from non-point sources within the Great Lakes basin. An expert system, known as EXPRES (Figure 25), was developed to model the migration of pesticides in typical agricultural settings across Canada. EXPRES was recently coupled to RAISON, a package of environmental software which acts as the basic system for manipulation of both data and models, and applied to the Great Lakes "Ecoregion". It is anticipated that regulatory and monitoring bodies such as the State of the Environment Reporting, will use the system to map the potential for individual chemicals to contaminate groundwater in agricultural areas throughout the Great Lakes basin.

Freshwater wetlands in the Great Lakes region, such as coastal marshes, swamps, bogs, ponds and small lakes, have recently been recognized as an integral component of the aquatic environment. Specifically, wetlands influence the hydrological balance of a region, filter contaminants and nutrients, and are an important wildlife habitat. Recent investigations into quantifying the contribution of groundwater to the hydrological and chemical balance of wetlands was initiated in two directions. First, field investigations were undertaken with the objective of developing a conceptual model of the hydrogeological regime in a wetlands environment at a coastal marsh (Point Pelee National Park) and a local bog (The Sifton Bog in London, Ontario). Secondly, a numerical model of groundwater flow

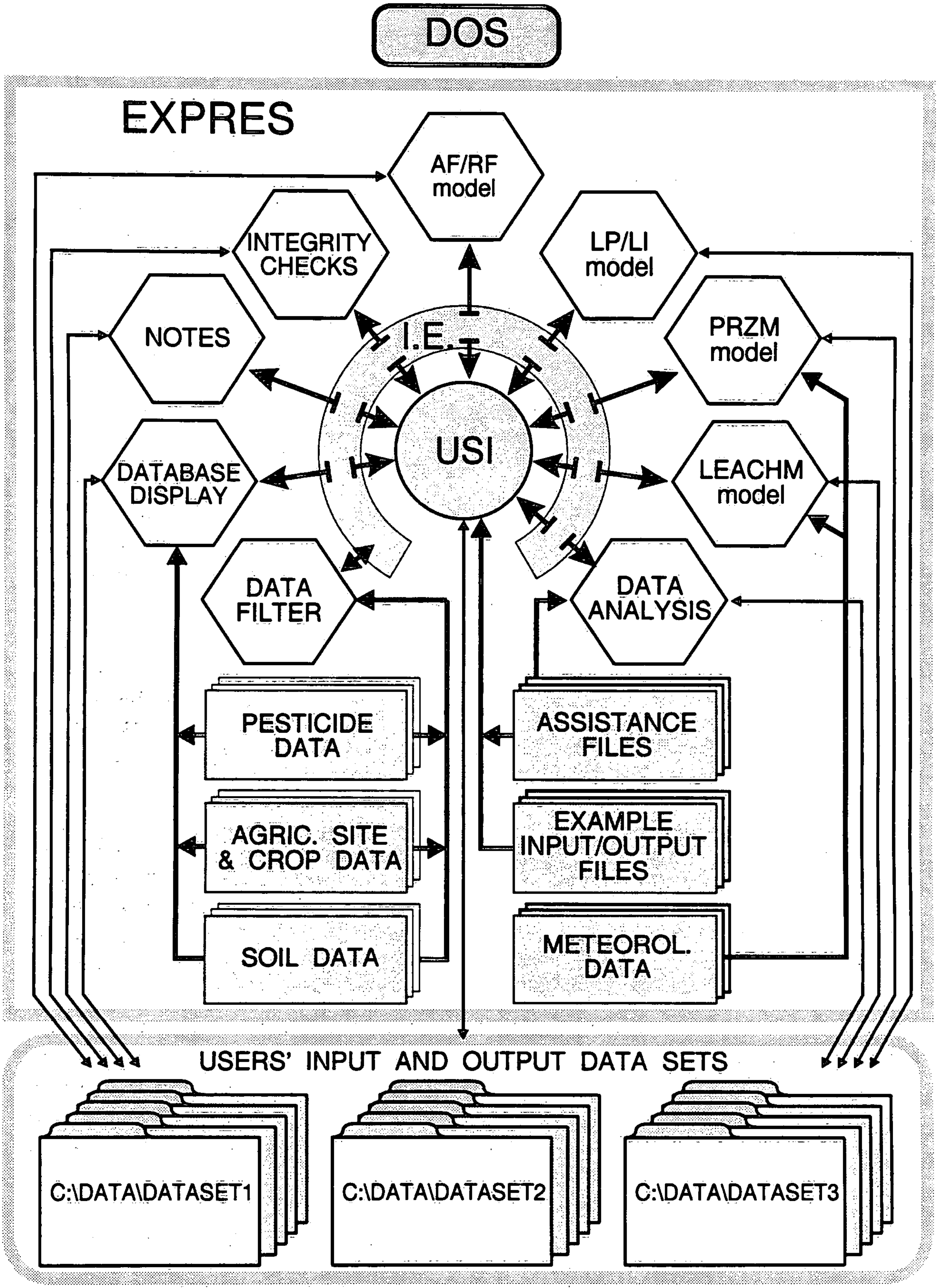

Figure 25. Schematic diagram showing the major components, structure and operation of the EXPRES expert system. The user enters the User System Interface (USI) of EXPRES from DOS. The USI controls the operation of EXPRES, including access to all models, data bases and modules. Input data sets for, and output from, an assessment is stored as individual DOS subdirectories.

and solute transport within a wetlands environment is being developed and will be used to predict changes to the system (e.g., changes due to global climate change, increase usage of septic systems, impact of contaminant spills, etc.). A preliminary model which accounts for global climate change, was tested on a known set of data obtained from a shallow lake in western Canada.

Control of Groundwater Contamination

One of the major concerns in many groundwater environments is the presence of solvents that occur as dense non-aqueous phase liquids (DNAPL). These solutions dissolve slowly in groundwater and act as a continuous source of contamination. Most research has focussed on petroleum products and very little information is available on mixed wastes. Thus, a laboratory experiment was conducted to observe the behaviour of a mixture of chlorinated and aromatic, dense and light solvents during dissolution. It was shown that these mixtures do not dissolve in an ideal fashion and their behaviour cannot be predicted using simple mathematical models. This is primarily due to non-linear interactions between the compounds during dissolution. These results indicate that more research is required to gain a better understanding of these mixtures so that proper design of remedial solutions and techniques can be undertaken.

More recently, attention has been devoted to direct remediation of the DNAPLs. Because most chlorinated solvents are toxic to bacteria, bioremediation cannot be effective in the presence of the non-aqueous phase. The potential role of porphyrins as biochemical catalysts was investigated. The most effective catalyst was not a porphyrin, but rather a corrin, which is chemically related. Vitamin B12, which is a cobalt containing tetrapyrrole derivative, is a very effective catalyst of the process of reductive dechlorination under reducing conditions. Using laboratory columns, it was found that a solution of vitamin B12 in titanium citrate could totally dissolve and dechlorinate tetrachloroethylene to ethylene in only a few days. Normal degradation in the absence of a catalyst may be in the order of years. Thus, injection of this solution *in situ* has very good potential for the treatment of contaminated soil and groundwater.

Investigation into the fundamental processes of contaminant transport in fractured rock has continued. This issue is of special importance to those who manage contaminated sites in the Niagara area and elsewhere in the Great Lakes basin where DNAPLs have penetrated the bedrock. Several hundreds of millions of dollars have been spent to remediate these sites with an uncertain degree of success. Several laboratory and field studies have been conducted which show that contaminants travel in fractured rocks at a rate less than predicted by the results of hydraulic tests. Results also show that dilution processes which occur during transport, are minimal. Although, a significant amount of contaminant is lost from the fracture to the surrounding matrix through the process of diffusion. This means that contaminants arriving at bodies of surface water will have high concentrations when the surface water is located close to the contaminant source. At greater distances, the amount of contaminant lost through diffusion significantly diminishes the potential impact on surface water quality.

Thorough characterization of groundwater samples, during site investigation, led to the discovery of biodegradation products of CFC-113. This fostered fundamental research into the conditions that lead to the biodegradation of CFCs and of other organic contaminants in landfill leachate. Both laboratory microcosms and field investigations using mesocosm were used to study the rate of degradation of aromatic and chlorinated solvents leaching from landfills. The anaerobic transformations occur under a variety of conditions where either sulphate reducing bacteria or methanogens can flourish. The products of transformation are, in many cases, the same in bacteria and in mammals. Cytochromes, which are porphyrin-containing enzymes, appear to be involved in the catalysis.

Analytical Methods and Protocols

The identification of the chemicals in groundwater at the Uniroyal Chemicals site in Elmira, Ontario, was the subject of investigation. The mixture was very complex and many of the compounds present were water-miscible, which meant that they could not be extracted efficiently with solvents. The results of a new analytical technique, whereby the samples were adsorbed on Carbotrap and then thermally desorbed, were compared to conventional analyses. The new method was found to be very effective for the rapid assessment of a complex mixture and suitable for highly soluble compounds such as dioxane and aniline.

The problem of distinguishing natural and anthropogenic sources of aromatic hydrocarbons in areas throughout the Great Lakes basin, led to the search for other environmental indicators of petroleum. Petroporphyrins were assessed as potential marker compounds. Petroporphyrins are a group of compounds that are present in all crude oils and are derived from chlorophyll. The petroporphyrin composition varies, depending on the source of the crude. A new, simplified, analytical method was developed that produces a characteristic fingerprint. The fingerprint was found to be recognizable in soils contaminated with crude oil or heavy fuel oil, even years after a spill, where other hydrocarbon indicators have been biodegraded. Because petroporphyrins are poorly soluble in water, they remain associated only with soils or bottom sediments.

In addition to the development of methods already described above, a method for the analysis of oxygenated solvents such as dioxane, acetone and tetrahydrofuran was developed using dynamic thermal stripping. During research into the control of groundwater contamination, a special flow cell to conduct dynamic headspace analysis was designed (Figure 26) and a patent application was filed. The cell, which allows the totally automated measurement of volatile organic solvent in a flowing stream, has potential applications for field monitoring as well as laboratory studies.

As part of the process of standardization of groundwater sampling techniques and the development of analytical protocols, a review of the commonly used methods for the analysis of hazardous wastes in groundwater was conducted. The results indicate that although a broad range of analysis techniques are available, some of which are rapidly evolving, most field practitioners rely on relatively old technology which often leaves a considerable portion of the contaminant suite unidentified. Therefore, the development of protocols for the sampling and analysis of groundwater contaminants may be premature and unnecessarily restrictive to those field practitioners who wish to pursue the most up-to-date technology.

Development of a new analytical/conceptual model for vertical groundwater flow in rocks of the Niagara region was recently completed. Over 300 constant-head tests were conducted to provide for a detailed hydrogeological description of a field site adjacent to the Fletcher Creek Quarry near Freelton, Ontario. The field site is employed as the test case for the conceptual model. Further characterization was completed using a detailed pumping test method. Interpretation of the pumping test results was conducted using analytical models originally intended for interpretation of pumping tests conducted in porous media. The results show that these analytical models underestimate the vertical hydraulic properties of the rock. This is because the individual vertical fractures, which are the primary

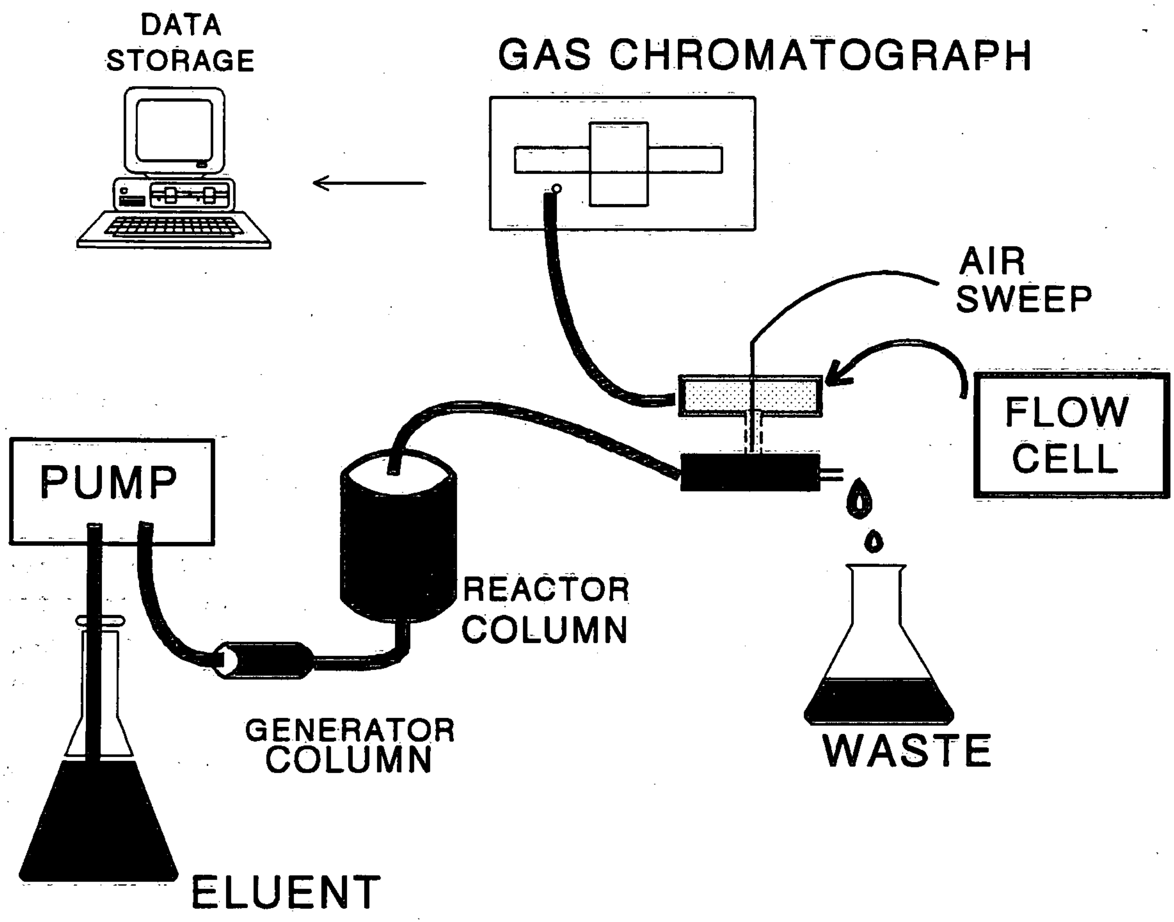

Figure 26. This experimental configuration was used to evaluate the dissolution of NAPL solvent mixtures. It is also used with soil columns to test potential remediation treatments. The flow cell (Pat. pending) provides totally automated on-line analysis of column effluent.

groundwater flow pathways, are not explicitly incorporated in these models. The degree of underestimation is significant enough to warrant consideration when designing a waste disposal site or investigating an existing site. Development of a new analytical method is continuing.

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ANNEX 17

RESEARCH AND DEVELOPMENT

The federal government maintains goal oriented research programs in the Great Lakes Basin to: improve our understanding of fundamental ecosystem processes; assess impacts due to anthropogenic stress; and develop techniques and technologies to remediate, protect and preserve our natural resources. These research programs have been driven, for the most part, by the Great Lakes Water Quality Agreement and, by the responsibilities and mandates of the various federal agencies. In an attempt to enhance collaborative research with the academic community and enlist its assistance in providing essential fundamental knowledge to manage the Great Lakes, the federal government created the Great Lakes University Research Fund (GLURF).

Introduction

GLURF was established by Environment Canada in partnership with the Natural Sciences and Engineering Research Council (NSERC) of Canada to promote and finance research within Canadian universities that will assist Canada in meeting its obligations under the Canada-U.S. Great Lakes Water Quality Agreement. The Fund is also intended to promote multidisciplinary ecosystem research, develop research partnerships among universities, government agencies and the private sector, and to promote the training and development of new scientists. The Fund has provided a total of $4 million over four years in support of Great Lakes' research on: the sources, pathways, fate and effects of pollutants; the responsiveness of the Great Lakes ecosystem to stress, other than pollutants (e.g., climate change, habitat alteration, exotic species invasions); restoration and remediation technologies; and, social and economic factors and policies associated with sustainability.

In year three of GLURF, 41 applications, totalling $4,524,455, were submitted for possible funding, and of these, 16 received partial funding. While most applications originated from universities located within and around the Great Lakes basin, proposals were drawn from across the country, from as far away as British Columbia and Newfoundland. As in previous years, the proposals were drawn from a wide range of disciplines, but in 1993, for the first time, the collection of applications contained in a representative number which included a socio-economic perspective.

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