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"Current Research"
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NATIONAL WATER RESEARCH INSTITUTE

Current Research '90

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CURRENT RESEARCH '90

A SYNOPSIS OF THE 1989-90 RESEARCH PROGRAM AT THE NATIONAL WATER RESEARCH INSTITUTE

National Water Research Institute
Inland Waters Directorate
Conservation and Protection
Environment Canada

Detailed information on the research projects at NWRI is available from the Research Branches or the Science Liaison Division. NWRI *Digest*, a quarterly newsletter on the activities of the Institute, is also available upon request. Please contact:

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INTRODUCTION

R.J. Daley
Executive Director
National Water Research Institute

I am pleased to present CURRENT RESEARCH '90, a summary of the research results and publications of the National Water Research Institute (NWRI) during 1989-90.

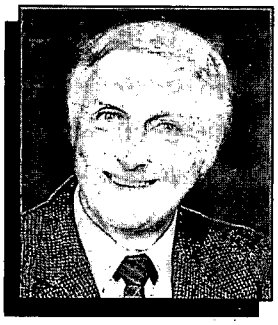
Our continuing goal at NWRI is to develop knowledge and expertise in the aquatic sciences in support of Environment Canada's responsibilities for water management. The current research program includes investigations into ecosystem interactions which control the fate and effects of pollutants, the physical dynamics of lakes and rivers affected by climate change, and the development of analytical protocols for assessing aquatic ecosystem health. The prediction of long-term impacts from physical, chemical and biological stresses has become a major component of our program. To these ends, the Institute's research is conducted within multidisciplinary project teams, each addressing the new knowledge requirements of a current or emerging water issue of national significance.

In 1989-90, NWRI was involved in a broad and challenging range of important issues. A new, five-year research program was initiated as part of the Great Lakes Action Plan, Canada's response to new commitments under the 1987 Protocol to the Great Lakes Water Quality Agreement. Research also continued on pesticides pollution, groundwater contamination, acid rain, toxic rain and global climate change. The aquatic impacts of toxic chemicals continued as a major research thrust, with field programs carried out from the Fraser and Athabaska rivers in the West, to the Hudson Bay lowlands, the Yamaska River (Quebec) and Prince Edward Island in the East. On the international front, the Institute strengthened its role in the GEMS/WATER program and initiated several new bilateral R&D agreements. In total, NWRI scientists published over 300 journal articles, research contributions and data reports on these and many other important issues.

The highlights reported in the following pages are necessarily brief, but I believe they show that our staff are committed to excellence and to the creation of practical new knowledge in support of Canada's water management needs. I hope this edition of CURRENT RESEARCH will provide our colleagues in the Canadian and international water research communities with a useful overview of our progress in the past year.

LAKES RESEARCH BRANCH

R.J. Allan, Director



The Lakes Research Branch undertakes applied research to provide effective management for the conservation and protection of Canada's lakes, man-made impoundments, and freshwater-dominated upper estuaries of major rivers. Emphasis is on the Laurentian Great Lakes, but study sites are located throughout the country.

Limnological processes, especially the chemical, biological and physical factors that affect their rates, are the primary focus of the Lakes Research Branch. Study areas of interest are primarily those which have been impacted by human activities, such as by petrochemical refining and manufacturing, pulp and paper mills, mining, steel production and urban development. Emphasis is placed on the sources, fate and effects of pollutants, such as toxic organic chemicals, metals, radionuclides and nutrients. The influence of lake trophic state on the fate and effect of toxic chemicals is a major area of interest. Depending on the nature of such influences, existing nutrient control programs may need to be integrated with toxic chemical control programs. Another important goal is to quantify the transfer of materials (toxic chemicals, nutrients, sediment, gases) across limnological interfaces, such as between sediments and water, air and water, and nearshore and offshore water masses. Investigations of methods to modify these transfer processes and their effects are a high priority. Some of the specific issues currently being studied include:

- long-term water quality trends;
- external and internal loadings of pollutants;
- sources, transport and movements of water masses and their particulate loads;
- partitioning of pollutants among media (water, sediment, biota, gas) in the water column;
- partitioning of pollutants between the water and the atmosphere;
- atmospheric inputs of contaminants and their fate;
- burial of contaminants in bottom sediments and their subsequent release;
- sedimentation/resuspension rates;
- biological mixing of sediments;
- degradation and biological uptake of pollutants;
- food chain transfer by benthic organisms of sediment-associated pollutants;
- evaluation of ecosystem health;
- water quality impacts due to climate change;
- role of wetlands in climate change;
- rehabilitation potential of lakes and reservoirs;
- in-lake restoration methods;
- manipulation of aquatic food chains.

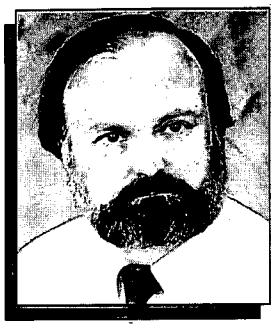
Comparisons between ecosystem impacts predicted by models and those observed in real ecosystems are an important test of research conducted in the Lakes Research Branch. Indeed, providing verified models for predicting the consequences of specific toxic chemical control programs is the ultimate goal of the research program.

The results of our research are used by national and provincial water management agencies throughout Canada as well as by agencies in other countries. The Branch also undertakes research and technology transfer for the development of Remedial Action Plans for the 17 Canadian and binational Areas of Concern within the Great Lakes. This work is in support of Canada's obligations under the Great Lakes Water Quality Agreement between Canada and the United States.

There are five multidisciplinary projects within the Lakes Research Branch: **Nutrient-Contaminant Interactions**; **Sediment-Water Interactions**; **Air-Water Interactions**; **Nearshore-Offshore Interactions**; and **Lakes Restoration**. Each of the five projects consist of several individual studies which are directed toward the goals of the project.

NUTRIENT-CONTAMINANT INTERACTIONS PROJECT

J.H. Carey, Project Chief



Introduction

The Nutrient-Contaminant Interactions Project is investigating the influence of lake trophic status on dynamics and impacts of atmospherically deposited contaminants in lakes. The first phase of the project, which is now complete, confirmed the general hypothesis that trophic status and contaminant dynamics in lakes are linked. Much of the work was conducted in a series of mostly headwater lakes centred around a field site near Bancroft, Ontario. This area is well away from point sources of contaminants and is in an area of geological transition between igneous and sedimentary bedrock so lakes with differing chemical compositions are available for study. Concentrations of atmospherically transported organochlorine contaminants in zooplankton from 33 lakes were examined. As expected, the relative proportions of contaminants in zooplankton from different lakes were constant but concentrations in zooplankton from oligotrophic, soft water lakes were higher than those in mesotrophic hard water lakes. Contaminant concentrations in zooplankton were inversely related to spring total phosphorus concentrations, i.e., the more oligotrophic the lake, the higher the contaminant concentrations.

Now that the general hypothesis behind the project has been confirmed, emphasis has switched to studies of the actual ways in which this linkage between nutrients and contaminants takes place.

Research Highlights

- A more detailed examination of the data from the series of headwater lakes near Bancroft, Ontario, revealed that a major factor controlling concentrations of atmospherically deposited contaminants in lake plankton was plankton biomass. Lakes with low plankton biomass had high concentrations of organochlorine contaminants in that biomass. Thus phosphorus control programs leading to a reduction in biomass would lead to higher contaminant concentrations in the remaining biomass, although other food web interactions could play a role in modifying this effect.

- Higher in the food chain, a different factor appears to control contaminant concentrations. A study of polychlorinated biphenyl (PCB) levels in lake trout flesh from Ontario lakes indicated that the complexity of the food chain itself was important. Lake trout PCB concentrations increased with length of the food chain. The most significant factor appeared to be the presence or absence of planktivores. Concentrations were highest in lakes with both *Mysis relicta* and forage fish such as smelt or coregonids, and lowest in lakes with no *Mysis* or offshore forage fish. These results have some apparent implications with respect to the impact on contaminant concentrations of stocking lakes with piscivorous fish.

- An examination of reductive dechlorination of a variety of chlorinated contaminants by sediments from lakes of different trophic and mictic character revealed a pattern of activity similar to that obtained from laboratory studies with reduced hematin. Compounds like lindane that react readily with reduced hematin also react readily in the sediments. Other compounds, such as PCBs and mirex, were not reactive in our experiments. These observations are consistent with what is known of the persistence of these compounds, and support the view that reductive dechlorination plays an important role in the degradation of chlorinated contaminants in sediments. Since these reactions occur under anoxic conditions that are more prevalent in lakes of higher productivity, trophic status may be important in determining site-specific degradation rates.

- Contaminant bioconcentration in organisms is known to be dependent on lipid content of the organism. In the past, lipids have been considered as a homogeneous non-polar phase and contaminant con-

centrations have been determined on a total lipid basis. Studies of the lipid production by phytoplankton and lipid content in zooplankton in lakes from the study region and Lake Ontario have revealed the composition and nature of the lipid pool can vary considerably. For example, in zooplankton whose total lipid varies from five to 35 percent, the fraction of non-polar lipid varied from zero to 25 percent. Thus some refinement of the lipid analysis into major classes may help explain some unresolved questions on bioaccumulation of contaminants in the environment.

- Indirect photochemical degradation of contaminants via reactive species, such as singlet oxygen, hydrogen peroxide and superoxide radicals, may be an important route of disappearance of certain contaminants from some aquatic systems. The most important factor controlling their significance is likely to be their steady-state concentrations, which are in turn controlled by rates of production and reaction. Rates of production of these reactive species have been shown to be dependent on light intensity and humic content of the water, but factors controlling the rates of reaction have not been studied. Recently, in a study of the rates of production and decay of hydrogen peroxide in lakes from the field site region, rates of decay were shown to be a function of bacterial abundance. Since bacterial abundance in lakes is likely related to productivity, the correlation between decay rates of photochemically produced reactive species and bacterial numbers may indicate a previously unexpected link between trophic status and contaminant pathways.

- While sedimentation rate is an important factor influencing the fate and distribution of persistent contaminants in lakes, the well known but variable decrease in planktonic hydrocarbons between sedimenting material and bottom sediment has indicated that remineralization of algae-derived particles and associated contaminants at the sediment interface needs to be evaluated. In a preliminary study of the composition of the saturated alkane fraction in bottom sediments in several lakes from the field site area, contributions from both algal and terrigenic sources were readily evident. However, the results showed that the relative importance of these sources varies from lake to lake. The relative contribution from algal sources, as determined by comparing the relative concentrations of the algal alkane n-C_{17} with the terrigenic alkane n-C_{25}, increases in the order Drag Lake < Hicks Lake < Jack Lake (Figure 1). This is the same order as the trophic status of these lakes. The results suggest that lake productivity could be an important factor in determining the amount of algal hydrocarbons in sediments. The processes controlling contaminant sedimentation are unlikely to be understood until diagenetic changes in sediment composition are taken into account.

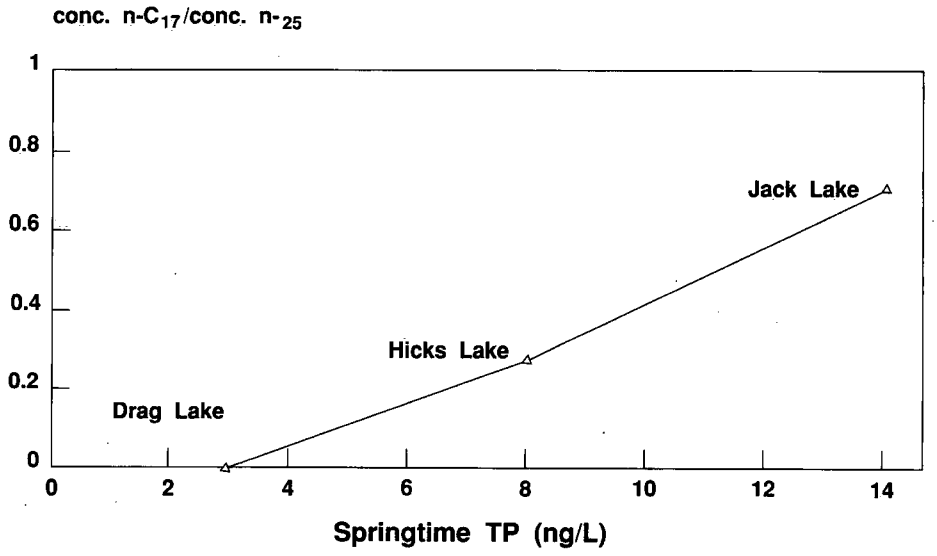


Figure 1. *Ratio of algal alkane (n-C_{17} and terrigenic alkane (n-C_{25}) in lake sediments versus phosphorus concentration at spring overturn, a measure of trophic status.*

SEDIMENT-WATER INTERACTIONS PROJECT

A. Mudroch, Project Chief

Introduction

Sediments which are contaminated with pollutants represent an environmental issue of major ecological and economic importance in both freshwater and marine environments. Contaminated sediments are a common problem in most of the 42 Canadian, U.S. and binational Areas of Concern in the Great Lakes, as well as at many other locations throughout Canada. Sediment-associated contaminants may migrate into pore water or the water column; they may also become available to aquatic organisms resulting in toxic effects or bioaccumulation in the food chain. Once in the food chain, higher organisms such as fish, wildlife and humans may be affected. Recognition of the severity and widespread occurrence of environmental effects from contaminated sediments has prompted federal and provincial agencies to initiate the development of management strategies for their regulation and remediation.

To manage contaminated sediments, the type of pollutants and the extent of contamination must be defined. In addition, standardized criteria with which to assess sediment quality must be developed. This requires detailed knowledge of the mobility, bioavailability, biological impact, and long-term ecological expression and interactions of contaminants in sediment. In support of these needs, the Sediment-Water Interactions Project includes specific research to identify and quantify the processes which control the pathways of sediment contaminants. The overall objective of the project is to develop a model which can be used in the long-term management of contaminated sediments within different areas of the aquatic environment.

Research Highlights

- Contaminated sediments are gradually isolated from the aquatic environment by natural processes of deposition and burial. Prior to burial, however, they pass through a dynamic cycle of deposition and resuspension which must be understood because the sediments may serve as a source of contaminants. Specific studies were designed to quantify the transport of fine-grained sediments using tracer techniques offshore of Port Hope Harbour (Lake Ontario) and in the upper estuary of the St. Lawrence River. At Port Hope, the dominant direction of transport was found to be offshore or towards the east. In the St. Lawrence study, zones of active sediment accumulation are being identified. Tracer studies will be undertaken in an attempt to determine the sources of contaminants. This study is being undertaken in collaboration with researchers at the Université du Québec (Montréal), and Université Laval. In another study, a cesium tracer was used to investigate the migration pathway of fine-grained sediment from a confined disposal facility located in Whitby Harbour. Monitoring will continue over the next year to determine whether fine particles migrate from the site.

- Lead isotope patterns in Lake Ontario sediments near the Niagara River have been compared with recent estimates of the sediment supply to Lake Ontario from the Niagara River. This comparison suggests that the annual lead loading from the river could be accounted for by the lead residing in 440 km^2 of annual sedimentation. In another study, analyses of radionuclides in bottom sediments of the Ottawa River indicate that one-half or more of the radioactivity currently in the river is the result of the historical fall-out of radionuclides from the atmosphere. The remainder of the activity is attributed to Chalk River sources. The current levels within the Ottawa River are well within the Canadian Water Quality Guidelines.

- The nepheloid layer in Lake Ontario developed over the stratified period and consists of particles of SiO_2, $CaCO_3$ and organic matter which settle slowly enough to build up significant concentrations. A

study of this layer indicated that the particles have high concentrations of contaminants and, hence, are considered to be an important medium for the transport of contaminants. Generally, the concentrations of zinc, lead, copper and PCBs were considerably higher on particles in the nepheloid layer than those in the upper portions of Lake Ontario bottom sediments. In addition, lower-chlorinated PCB isomers were more common, relative to higher-chlorinated compounds, in the nepheloid layer particles than in the sediments. Both these observations suggest biological interaction with the nepheloid layer could be affected more strongly by contaminants than by interaction with the sediments.

- Tubificid oligochaetes, a common variety of sediment-dwelling aquatic worm, were tested to investigate their potential as test organisms to determine the sediment toxicity. Measurements of reproductive success under different contaminant levels were tested for use as an assessment tool. The results indicate the test to be repeatable, sensitive, discriminatory and one that can be recommended as a standard method for sediment bioassay. Oligochaetes are common in temperate aquatic ecosystems and are an important component of the Great Lakes benthic community, particularly *T. tubifex* which can withstand certain levels of pollution.

- The quantification of the transport of sediments and associated contaminants during winter was carried out in all three basins of Lake Erie. The mean downward transport of material as well as the concentration of PCBs in all samples decreased from west to east (Figure 2). The concentration of PCBs in material collected within sediment traps was similar to that of surficial sediments at the same location. Concentrations of p,p,-DDE and p,p,-TDP showed a similar trend. The sediments in the central and eastern basins of Lake Erie were found to be continuously enriched with a loading of 3.1 $g/m^2/d$ of PCBs during the winter months.

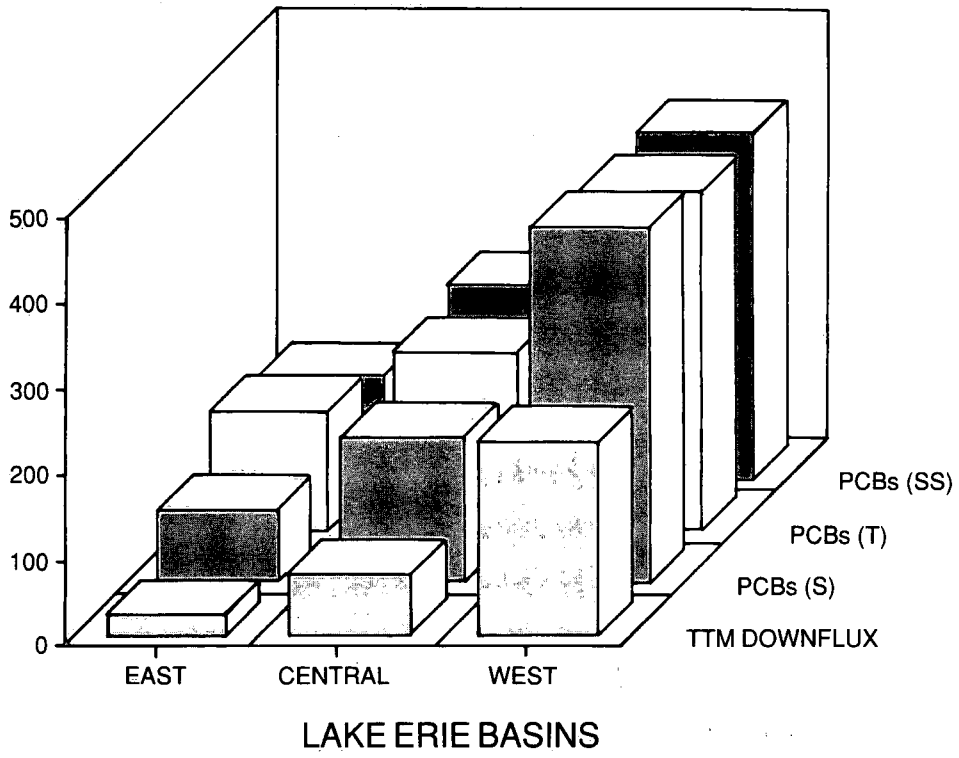
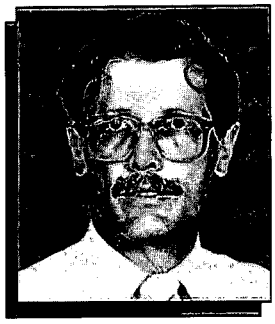


Figure 2. *Downward flux and PCB concentrations in Lake Erie suspended and bottom sediments.*

AIR-WATER INTERACTIONS PROJECT

W.M.J. Strachan, Project Chief



Introduction

Atmospheric input of airborne pollutants represents the major means whereby many metals and persistent organic contaminants reach the surface waters of Canada. Studies of the extent and mechanisms of relevant processes continue to be the major focus of the Air-Water Interactions Project. New ways of determining spatial and temporal patterns in such deposition are also included in these investigations. In addition, the project team is involved in preliminary efforts to establish a global monitoring network for measuring inputs from the atmosphere on a continental and hemispheric basis.

Research into air-water interactions affecting climate change is also a major focus of the project. Modelling of the relationships between various water quality parameters and those of air quality and climate is an ongoing activity. Recent interest has centred on the production of methane (CH_4) in the wetlands around Hudson Bay and the possible impact that changes there could have on global climate.

Research Highlights

- A co-operative venture between the University of Stockholm and the Air-Water Interactions Project has led to the discovery that needles of the Scots pine (*Pinus sylvestris*) are useful in monitoring persistent organic chemicals which are deposited from the atmosphere onto land and water surfaces. A survey of pine needles related to a DDT "event" in Europe demonstrated that the aerial transport, deposition and incorporation of this pesticide into the needles extended as far as 1500 km from the area of application (Figure 3). In contrast, PCBs showed a pattern appropriate for a globally distributed chemical uniformly dispersed in the atmosphere. The pattern for lindane and its isomer, α-HCH, on the other hand, indicated a source area south of France as well as an overlying global distribution. Differences in the yearly patterns were also apparent by examining pine needles up to five or six years old. Plans are under way for investigating the use of this technique in Canada.

- A northern wetlands multidisciplinary study has been preparing for an intensive field program in 1990-91. The objective of the work is to better understand the role of northern wetlands as sources and sinks for biogenic gases which may be involved in global climate change. Gases of interest include CH_4 and CO_2 in particular, but also N_2O, NO_x and several of the volatile organics. International co-operation among Canadian and U.S. government agencies along with Canadian universities is focused in the Hudson Bay Lowland where preliminary studies and reconnaissance took place during the past year. Field sites and sampling frequency have been identified in order to determine the gradients in CH_4 fluxes for several of the different types of wetlands. Preliminary flights have also been conducted to determine the above-ground gradients in CO_2 concentrations. Modelling requirements and sampling regimes to validate the models have also been described. Preliminary data will be used to better define investigations during the 1990 field season.

- The sources of pesticides observed in various parts of the Arctic and the processes that brought them there have only recently begun to be investigated. During 1989, lakes in the high Arctic were sampled as part of an effort to determine the fate of the contaminants in the snow. Data obtained from this sampling clearly show that much of the contaminant load enters the lakes along with snowmelt and remains in the water throughout subsequent winter periods. Concentrations of the hexachlorocyclohexanes (lindane and α-HCH) in Sophia Lake, for example, were higher than levels in the Great Lakes. Similarly, Lake Hazen, the most northerly lake studied, had concentrations and propor-

hexachlorocyclohexanes comparable to those of Lake Ontario.

- Trace metal studies are being undertaken to develop methodologies to determine true levels of these elements in surface waters using ultra-clean facilities. Present data on trace metals in the Great Lakes, for example, are unreliable due to contamination of samples during collection and/or analysis. Preliminary results with ultra-clean facilities and procedures indicate that average concentrations of lead in offshore waters of lakes Ontario and Erie are 30 and 77 picomol/kg respectively, values which are orders of magnitude lower than previously reported. Concentrations of copper, nickel and zinc are also several-fold lower than those reported elsewhere. These findings have major implications for present views on environmental cycling and bioaccumulation of trace metals in freshwaters.

- Models of lake circulation and surface energy fluxes were examined for their ability to mimic an anomalously warm period in Lake Erie (November 1982 to October 1983). The models underestimated temperature by 10 to 15 percent for the coldest part of the winter and the warmest part of the summer. This underestimation was ascribed to elevated dew point temperatures, elevated atmospheric pressure and reduced wind speed and cloudiness. The overall success of the models were considered as justification for accepting predictions about the consequences of global warming on the lake including the extent of winter ice cover, early disappearance of the thermal bar, depth of the seasonal thermocline and duration of the stratified period.

- Sediment cores from lakes in the Northwest Territories, Alberta, Saskatchewan, Manitoba and Ontario have been dated using Pb^{210} methods as well as *Ambrosia* sp. and Russian thistle pollen as marker horizons. The identification and enumeration of ostracod shells in these cores has allowed the determination of the water quality condition at different periods in time, and the corresponding climate for lakes with a predominantly atmospheric input. These interpretations extend back in time several thousand years and provide proxy data for use in global climate change models.

- The development of models on the role of air-water interactions in the concentrations of persistent organic contaminants in aquatic systems continues. A data set for a small, well-described watershed (Little Turkey Lake, north of Sault Ste. Marie, Ontario) has been collected and is being used to test a model which involves hydrological as well as chemical and meteorological components. A more ambitious data set for Lake Ontario is in preparation.

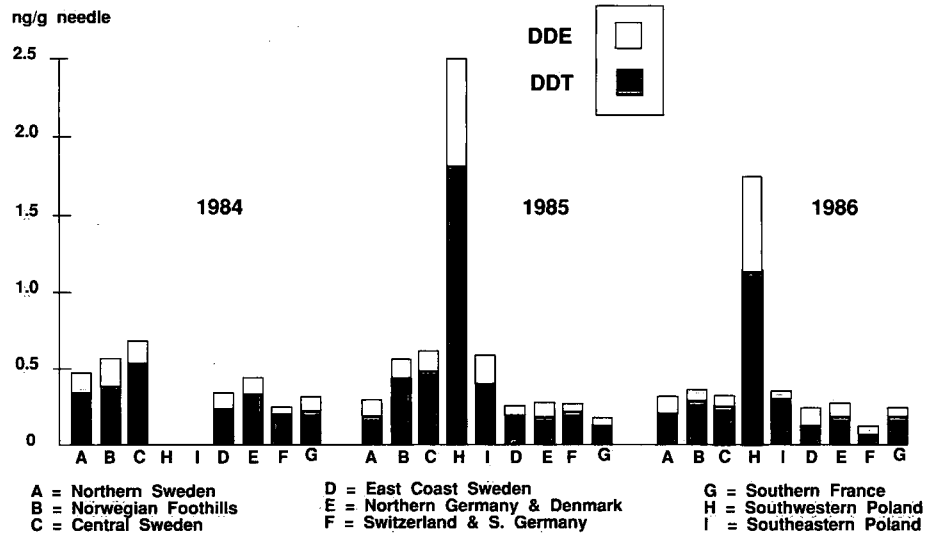


Figure 3. *Survey of Scots pine* (Pinus sylvestris) *needles related to a DDT "event" in Europe.*

NEARSHORE-OFFSHORE INTERACTIONS PROJECT

K.L.E. Kaiser, Project Chief

Introduction

Research under the Nearshore-Offshore Interactions Project is undertaken to investigate the pathways, fate and effects of contaminants in the Great Lakes as well as in major Canadian rivers and their estuaries. The project combines expertise in chemistry, physics, modelling, statistics and limnology.

Many of today's pollution problems exist in zones of physical and biological complexity such as the harbours and bays of the Great Lakes and the large rivers of Canada with their associated riverine lake sections and estuaries. To assess the impact of pollution in these zones, multidisciplinary research programs, which include intensive field experiments as well as laboratory and computer modelling experiments, have to be devised. Last year, the Nearshore-Offshore Interactions Project has brought a critical mass of expertise to bear on assessing contaminant issues along the Toronto waterfront, the outlet of Lake Ontario, the entire St. Lawrence River, and the Fraser estuary. Along with these site-specific studies, the project has maintained an analysis of Great Lakes water quality changes that are reflected in the whole lake data sets collected by the Water Quality Branch. Advances were also made in techniques to measure sediment flux in quantitative structure-activities relationships for classes of chemicals and in statistical analyses of data sets obtained with various methods and detection limits.

Research Highlights

- The contaminant fate model TOXFATE was coupled with the hydrodynamic model RAND to describe the fate of contaminants entering Lake Ontario from sources at the Toronto waterfront. Based on data for the late 1980s, inputs of organic contaminants from the Toronto area represent between 0.5 and 25 percent of the loading from the Niagara River. However, as controls and abatement programs for the Niagara River are implemented, loadings to the lake from other sources will become relatively more important.

- The movement of water in the Kingston basin of Lake Ontario is dominated by the hydraulic flow towards the St. Lawrence River; however, there is also a superimposed, wind-induced movement. Lagrangian drifter trajectories indicate that of the total flow past Wolfe Island, approximately 55 percent is in the south channel. Loading estimates of selected chemicals to the St. Lawrence River were made by combining the transport data with contaminant concentration data for this area.

- Long-term water quality records for Lake Ontario were updated for the 1986 to 1989 seasons. The results indicate a continued drop in soluble reactive phosphate levels to approximately 3 µg/L in March/April 1989 (Figure 4). This value is approximately five times lower than the levels recorded in the mid-1970s. This low concentration may influence primary production and food web composition to the extent that contaminant cycling and fisheries could be altered.

- PCB residues in biota and sediment constitute one of the largest organochlorine contaminant concentrations in the St. Lawrence River. Approximately 50 percent of the PCB burden enters the river from Lake Ontario with the remainder originating in the river basin. Significant PCB source areas occur in the vicinities of Cornwall, Massena, Montréal, and Trois-Rivières, as well as within lakes Saint-Louis and Saint-Pierre.

- In collaboration with Université Laval researchers, the PCB contamination of three of the most abundant forage fish species in the upper St. Lawrence estuary was studied. Smelt, tomcod and capelin were found to contain PCB levels in excess of the 0.1 ppm water quality objective for the protection of fish-eating wildlife in the Great Lakes basin. A preferential bioaccumulation of certain

cumulation pattern was similar to the PCB contamination known to occur in beluga whales in the estuary, but at much higher concentrations in the whales.

- A simple method of modelling the Fraser River salt wedge was developed using the theory of internal gravity wave propagation. A comparison of observed and predicted maximum salt wedge intrusions indicates varying degrees of accuracy. The model results are good for high and medium flow conditions, but underestimate the excursions under low-flow conditions in the Fraser main arm. Future work will attempt to integrate this model with a one-dimensional tidal model developed at the Institute of Ocean Sciences, Sidney, B.C.

- A standard current meter was modified with the addition of a pressure sensor, a high-speed thermometer, an optical transmissometer and a conductivity meter. This device permits the measurement of horizontal sediment flux and its variability in estuaries. It is referred to as the profiler for estuarine sediment transport (PEST). Data from PEST will assist with the determination of the pathways and fluxes of lipophilic contaminants which are predominantly adsorbed to the particulate matter in the water column.

- Inter-species correlations of the toxicity of single chemicals to a variety of aquatic and non-aquatic species, including bacteria, algae, zooplankton, fish and mammals, indicate significant co-linearity over a molar toxicity range of up to eight orders of magnitude. These results will be useful for the prediction of the effects of new chemicals and for the development of standards and guidelines for known contaminants.

- Improvements were made on the statistical analyses of river monitoring data, specifically with regard to improved precision, separation of the effects of analytical method changes, seasonal variability, and trend analysis.

- Work continued on the statistical analyses of Niagara River contaminant data. Previous procedures of replacing non-detectable values with arbitrarily chosen values between zero and the detection limit were shown to produce biased results. Our research now allows the calculation of such biases and, hence, improves the accuracy of data interpretations.

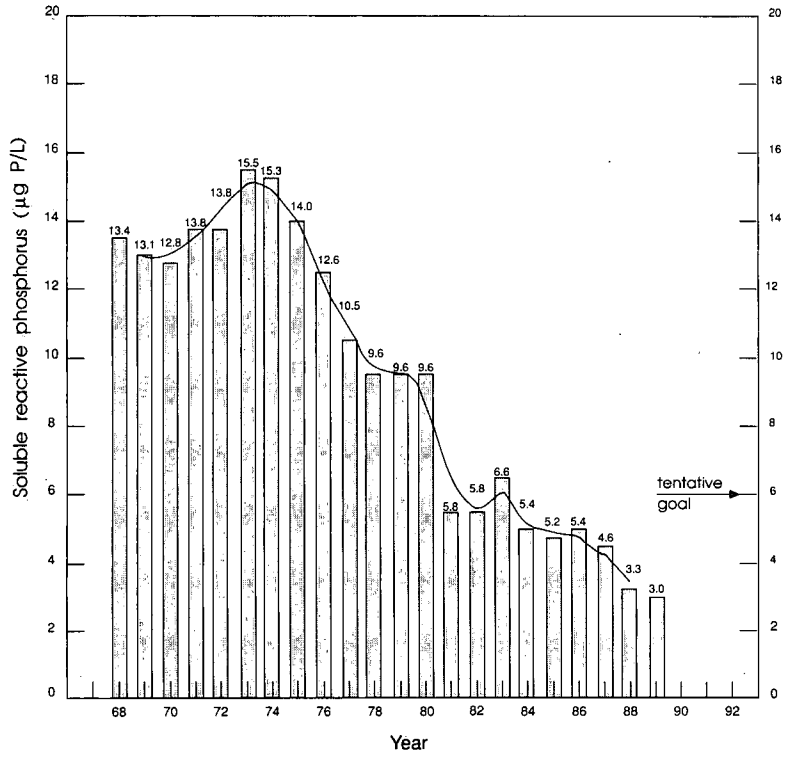


Figure 4. *Mean values of soluble reactive phosphate (concentrations as µg/L phosphorus) in the upper 20 m of offshore waters in Lake Ontario. Data are for the March to April periods between 1968 and 1989, with a smoothed trend curve. A steep decline from the 1973 peak through to 1989 is apparent.*

LAKES RESTORATION PROJECT

M. N. Charlton, Project Chief

Introduction

The Lakes Restoration Project provides practical expertise, advice, data and methods for the remediation of lakes and the management of pollutants. In 1989-90, investigations centred on supporting the Great Lakes Water Quality Agreement, specifically, the development of Remedial Actions Plans being prepared for the "Areas of Concern" identified by the International Joint Commission, and assessing the effects of contaminated sediments and potential remedial options.

Research Highlights

- The assessment of a 50 percent nutrient abatement at the Hamilton Sewage Treatment Plant (STP) indicated that summer concentrations of phosphorus, oxygen and ammonia in Hamilton Harbour had scarcely changed, but that algae and transparency may be improving (Figure 5). The overall reduction of phosphorus concentrations in the harbour will likely require loading reductions from other sources including the Dundas and Skyway STPs. Water clarity in Cootes Paradise has not responded to reduced loadings of suspended solids from the Dundas STP. This is due to the high load of suspended solids contributed by tributaries as well as resuspension of bottom sediments within the shallow embayment. A Geographic Information System (GIS) identified the potential for improving fish habitat in Hamilton Harbour by re-colonizing deeper areas with aquatic weeds which have dried out due to suspended sediment shading. Bathymetric information was combined with data on transparency increases expected in response to nutrient loading reductions to predict a 70 percent increase in fish habitat.

- Studies of coal tar contamination in Hamilton Harbour have shown that the contaminated area contains more than 70,000 m^3 of material with PAH concentrations in excess of 200 µg/g. These sediments contain visible amounts of tar and were found to be acutely toxic to zooplankton, mayflies, bacteria and fish. Work concentrated on delineating the contaminated area and developing criteria to guide removal operations.

- The role of elevated iron concentrations in the precipitation and retention of phosphorus in Hamilton Harbour was studied by comparing the total and soluble phosphorus concentrations in the intake and effluent streams of a steel mill. There was no significant change between them, which suggests that the forms of iron in steel mill effluents (wustite and hematite) may not be very active in precipitation reactions.

- A survey of PCB contamination in Hamilton Harbour revealed no significant point sources, including STPs. This finding is surprising because STPs are considered to act as collection systems for PCBs delivered to urban areas from the atmosphere as well as from industrial sources within the urban drainage. Levels of PCBs in the harbour as well as tributaries and STPs are around 20 ng/L, which is 5 to 10 times higher than in Lake Ontario. The maintenance of PCB concentrations in the harbour may be due to sediment resuspension.

- Preliminary work on denitrification in Hamilton Harbour sediments was started in 1989 in collaboration with McGill University. There are indications that denitrification rates, a measure of sediment microbial activity, are decreased in sediments with high levels of metals and organic pollutants. This work may lead to a direct sediment toxicity index which would replace the current indirect tests using pore water on organisms.

- Research in the Bay of Quinte (another Area of Concern) concentrated on accumulated nutrients and organic chemicals in sediments. The anthropogenic portion of stored phosphorus was quantified from these studies. From this information it was determined that within the upper bay, most

these studies. From this information it was determined that within the upper bay, most of the phosphorus contributed by ongoing discharges from STPs is rapidly recycled. On the other hand, stored phosphorus on sediments in the same area was not released at comparable rates, suggesting more phosphorus control may be required at the STPs.

- Nearshore sediment information is required for planning purposes relating to shoreline erosion and the effect of fluctuating lake levels. Several studies, including a refinement of coastal sediment budgets using GIS and the effect of bedrock geology on shoreline erosion on the north shore of Lake Erie, were completed during 1989-90.

- Sediment traps were used at stations in the eastern part of Lake Ontario and in several locations in the St. Lawrence River as far downstream as Lake Saint-François to collect samples for PCB analysis. The highest sediment PCB concentrations in the river were found offshore of Massena, N.Y., and downstream in Lake Saint-François. Concentrations were higher than in the eastern portion of Lake Ontario but were similar to some samples from the middle of Lake Ontario.

- Investigations of restoration technology in small lakes continued. The oxygenation equipment at Amisk Lake, Alberta, was refined resulting in the maintenance of an 8 mg/L oxygen concentration. Prior to oxygenation, concentrations frequently dipped to zero. Teams from the University of Alberta and the Alberta Ministry of Energy and Natural Resources are determining system responses. In another restoration project, a small cost-efficient dredging apparatus was developed for use at Chain Lake, B.C. The apparatus removes up to 16 m^3 of material per hour (28 percent sediment) and has a capital cost of $10,000.

- Methodology development for the dating and mapping of sediments was undertaken as part of the Lakes Restoration Project. Preliminary results from a cooperative study with McMaster University indicate that magnetic susceptibility may be useful for the non-destructive dating of sediment cores. An acoustic means of mapping sediment stratigraphy was developed that allows remote measurement of the thickness of recently deposited contaminated sediments.

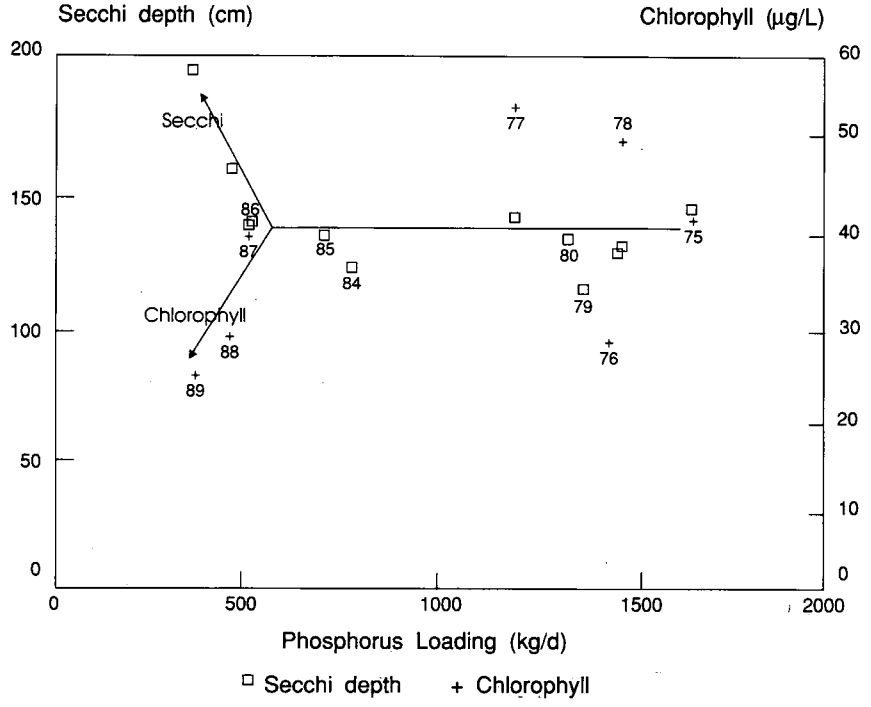


Figure 5. *The effect of phosphorus loading on Secchi depth and chlorophyll concentrations in Hamilton Harbour.*

RIVERS RESEARCH BRANCH

E.D. Ongley, Director

The Rivers Research Branch conducts applied research and provides policy advice on a wide range of water resource issues associated with rivers and river basins in Canada. The management of water resources in Canada is carried out within the framework of land-water interactions. Rivers receive and integrate the effects of a multitude of anthropogenic activities associated with point sources such as effluents from municipal and industrial facilities, and non-point sources such as atmospheric deposition, groundwater, agricultural chemicals and urban runoff. Rivers are the primary means by which impacts from these sources are transferred to large lakes and oceans.

The Branch seeks to understand the complex relationships involving physical, biological and chemical interactions in rivers and river basins. This knowledge is required to meet federal objectives for contemporary and emerging water resource management concerns that have national and international implications. The Branch also seeks opportunities to improve the competitive position of Canadian environmental industries, through both the transfer of research and development results and the utilization of international contacts to identify commercial opportunities for Canadian industry. Research and technology transfer activities extend from coast to coast and include such diverse topics as:

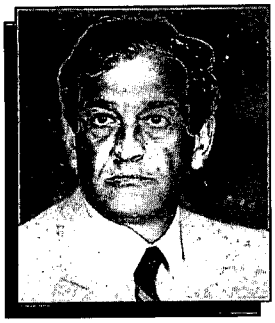
- contamination of groundwater in Atlantic Canada;
- hydrocarbon contamination in northern rivers;
- evaluation of pesticide contamination;
- acid rain effects and evaluation of mitigation options in Quebec and Atlantic Canada;
- expert systems applications to contaminant pathways in rivers in Ontario and British Columbia;
- protocols for monitoring water quality in the Prairie provinces;
- hydraulic and sediment transport issues at several locations;
- ecotoxicological R&D and public health issues.

Branch scientists serve on a variety of national and international commissions, associations and committees, and participate in national and international policy negotiations. They travel internationally on collaborative and consultative missions for Canadian and international development agencies and scientific organizations. They also serve as editors, conference chairpersons and organizers for a wide range of international activities. Many hold adjunct faculty positions in universities in Canada and abroad.

The Rivers Research Branch is structured around five research projects: **River Modelling**; **Contaminants/Pesticides**; **Long Range Transport of Airborne Pollutants (LRTAP)**; **Ecotoxicology** and **Groundwater Contamination.** While these projects facilitate multidisciplinary research, they also seek to preserve a critical mass of disciplinary expertise. Individuals often contribute to more than one project and any one project may provide disciplinary expertise to another project.

RIVER MODELLING PROJECT

S. Beltaos, Project Chief



Introduction

Physical processes within rivers and river basins, interactions with water quality, and implications regarding resource issues are the main areas of research for the River Modelling Project. Particular emphasis is placed on runoff processes, the transport of contaminants in rivers, remote sensing of water quality, and river ice phenomena. Interdisciplinary research is common, usually carried out in collaboration with other projects.

Research Highlights

- Agricultural runoff is a major non-point source of pollution. This type of pollution is characterized by the transport of sediment and chemical residues from agricultural areas by surface runoff and subsurface flow. A study of agricultural runoff was initiated in 1989 in the Nissouri (Ontario) catchment. The basin was instrumented to collect water samples for chemical analyses and to measure hydrologic parameters. Preliminary results indicate that one-third of the phosphorus in runoff is associated with particulate matter.

- The fate of many river contaminants is governed by the transport and fate of fine-grained sediments, a process complicated by flocculation which alters the erosional and depositional properties of the sediment in ways that remain poorly understood. This problem is being addressed by several ongoing studies. To measure the size of sediment flocs, sophisticated laser equipment (Malvern particle size analyzer) has been acquired and adapted for both laboratory and field applications. The Malvern uses optical techniques to determine the *in situ* particle size distribution within a control volume of fluid in a non-disturbing manner (Figure 6). Moreover, this year saw the completion, delivery and installation of a five-metre diameter annular flume specifically designed for studies of processes associated with fine-grained sediment. The large diameter will help minimize the secondary currents that typically develop in the flow around bends and, thus, better approximate conditions in a very long, straight channel. In a concurrent study, experiments in a smaller annular flume (2 m) suggest that the settling rate of fine sediments decreases when water temperature increases, possibly due to changing floc properties.

- The latest in a series of water quality monitoring devices, under the general acronym MOMS (multi-spectral optical monitoring system), has been fabricated and field testing has been initiated. This instrument is capable of unattended continuous monitoring of sediment concentration as the flow moves past a fixed point in a river. Limited field testing has confirmed the feasibility of this method and has prompted some revisions in instrument design and sampling strategy.

- A major activity within the Rivers Research Branch pertains to the transport and fate of hydrocarbons in the lower Athabasca River and further downstream (i.e., Lake Athabasca, Peace River and Slave River). Two companies, Suncor and Syncrude, currently mine, extract and upgrade bitumen from the Athabasca Tar Sands. A third plant (OSLO) has been proposed. Participation in this five-year study, supported by the federal Panel on Energy Research and Development (PERD), consisted mainly of two reconnaissance surveys (August 1989 and March 1990). Chemical analysis of water samples is currently in progress. Fish samples did not reveal any compounds or metabolites that were attributable to the tar sands operations.

- Ice jamming and subsequent flooding is common during winter thaws and spring freshets, but little is known about how to forecast, prevent or mitigate such events. This problem is being addressed by an ongoing study comprising field data collection and laboratory investigations. A mathematical model (RIVJAM) has been developed to

predict the shape of ice jams and associated water levels in natural streams. Application to field data from the Restigouche River, obtained with the collaboration of the New Brunswick Department of Environment, indicated good model performance under conditions of severe grounding, a situation that has not previously been quantifiable.

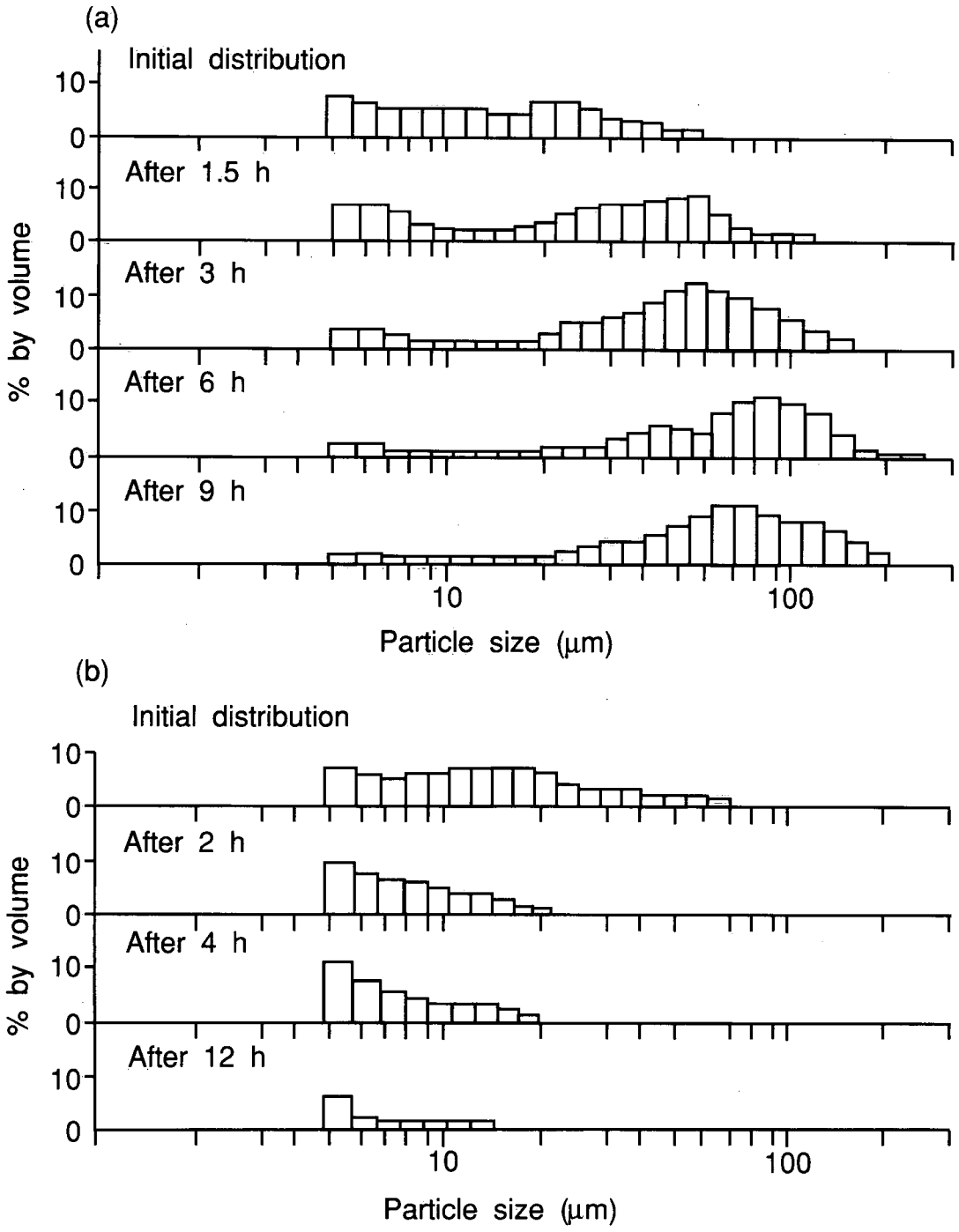


Figure 6. *Size distributions determined from the Malvern particle size analyzer: (a) during floc-settling; and (b) during single-grain settling.*

CONTAMINANTS/PESTICIDES PROJECT

R.J. Maguire, Project Chief

Introduction

The general objective of the Contaminants/Pesticides Project is to develop knowledge to help Environment Canada assess the hazard posed by toxic chemicals released to aquatic environments. The hazard of a given chemical to organisms in water or sediment is a function of its concentration, toxicity and persistence. Research topics are chosen in a variety of ways. They may be gaps in the scientific literature on a particular phenomenon (e.g., the formation of apparently unextractable pesticide residues in sediments, which are nevertheless available to bottom-feeding organisms, and the utility of fish bile analysis as an indicator of exposure to relatively water-soluble pesticides). Chemicals may already be identified in priority lists for risk assessment (e.g., under the *Canadian Environmental Protection Act* or the *Pest Control Products Act*), or there may be regional concerns about the heavy use of a chemical or the production of certain wastes.

Research Highlights

● The powerful insecticide deltamethrin is registered for use on a variety of crops in Canada. Contamination of streams and ponds near sprayed fields is undesirable because of the high toxicity of deltamethrin to aquatic organisms. Earlier studies on the aquatic persistence and fate of deltamethrin had not distinguished among its isomers. There are eight possible stereoisomers of deltamethrin. A complete description of the persistence and fate of this pesticide in natural waters must include an analysis of its isomerization behaviour. Optically active high-performance liquid chromatographic analyses have shown that deltamethrin, in natural waters, is subject to cis/trans-isomerization yielding the 2′-deltamethrin isomer, which is inactive against water fleas (*Daphnia magna*), houseflies and mice. However, sunlight irradiation of deltamethrin in natural waters produced the inactive 2′ and 4′ isomers as well as the active 3-isomer. Thus, isomerization of deltamethrin in natural waters is only a partial detoxification step.

● A differential pulse polarographic method has been developed for the determination of metallothionein in mussel tissues. The detection limit of 1 ng/g is suitable for the study of induced production due to metal stress in contaminated rivers. Laboratory experiments have shown good correlations between metallothionein induction and exposure to cadmium, copper and zinc.

● A study of the microbial degradation of 2,4-dinitrotoluene has shed light on the discrepancy between short-term *in vitro* and long-term *in vivo* toxicity results for this chemical. Short-term bioassays indicate that 2,4-dinitrotoluene has low toxicity, while long-term bioassays reveal high toxicity. The difference can be explained by different degradation and metabolic pathways. The chemical is fairly stable under aerobic conditions. Under anaerobic conditions, however, 2-nitroso-4-nitrotoluene is formed, which is highly toxic, albeit unstable. This finding illustrates the need for both long- and short-term toxicity tests in assessing potential hazards.

● Dissolved organic carbon (DOC), especially humic acid, in natural waters can form stable complexes with lipophilic organic chemicals, thus decreasing their bioavailability to aquatic biota. This may occur through formation of a DOC chemical complex which is too large or too polar to penetrate biological membranes. A reduction in the bioavailability of a chemical to aquatic biota should also result in a reduction in toxicity. The effects of DOC on the accumulation and acute toxicities of three synthetic pyrethroid pesticides to *Daphnia magna* were studied (Figure 7). Concentrations of DOC as low as 2.6 mg/L, which is within the usual range in natural waters, resulted in a significant decrease in bioaccumulation of all three pesticides. In addi-

tion, the acute toxicities of all three pesticides decreased as DOC increased. For example, the acute toxicity of fenvalerate to *Daphnia magna* decreased by a factor of 17 as the DOC concentration increased from 2.6 to 15.5 mg/L. These results may at least partially explain why the impact of synthetic pyrethroid insecticides on aquatic biota is generally less than expected on the basis of laboratory bioassays.

- Polynuclear aromatic hydrocarbons (PAHs) are priority chemicals for assessment under the *Canadian Environmental Protection Act*. Work is being carried out on the biological degradation of selected PAHs. Using a substrate-supercharging technique, a mixed culture of PAH-degrading bacteria was obtained which could degrade naphthalene, phenanthrene and anthracene. This degradation was accomplished without an exogenous carbon or energy source. An advantage of working at such high concentrations is that higher concentrations of metabolites may be produced, thereby facilitating identification by gas chromatography/mass spectrometry. The identification of major metabolites so far has shown 1-naphthol from naphthalene, 1-hydroxy-2-methylnaphthoate from phenanthrene, and 2-naphthalenecarboxylic acid, 3-hydroxymethyl ester from anthracene.

- Two project staff members are currently serving as assessment team leaders for two priority chemicals which are being assessed under the *Canadian Environmental Protection Act*. The chemicals are nickel and non-pesticidal organotin compounds.

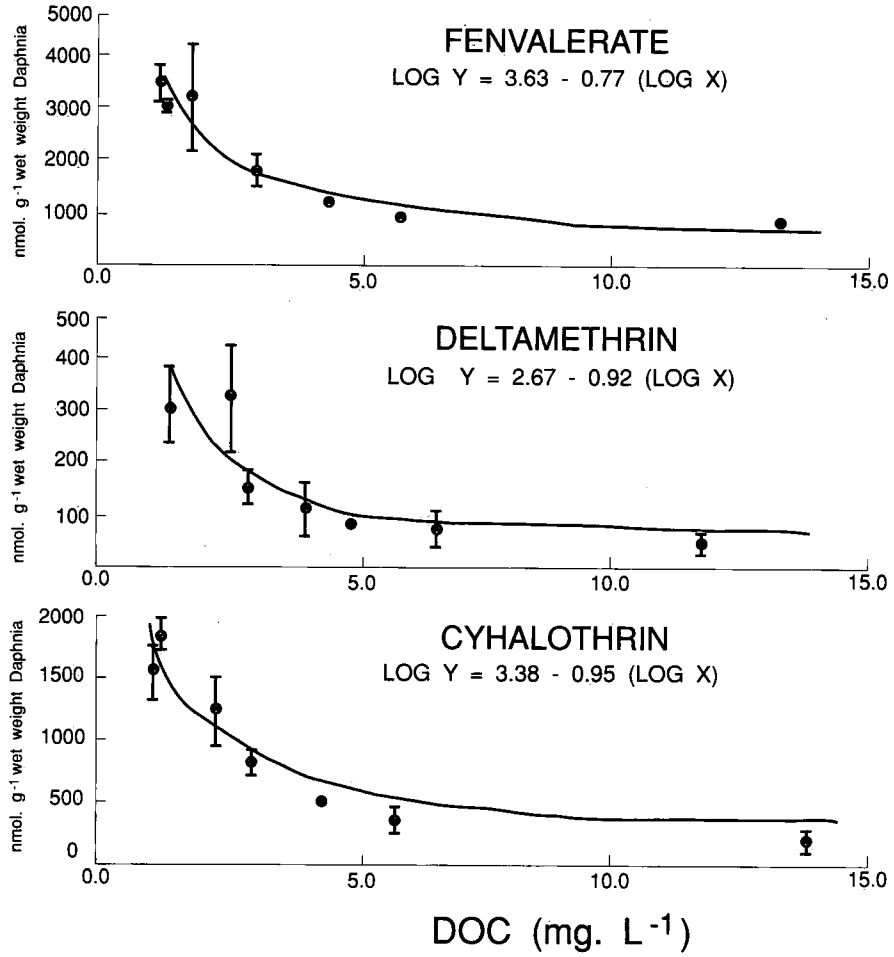


Figure 7. *Influence of dissolved organic carbon concentration on the accumulation of three synthetic pyrethroid insecticides by* Daphnia magna.

LONG RANGE TRANSPORT OF AIRBORNE POLLUTANTS PROJECT

D.C.L. Lam, Project Chief

Introduction

The objective of the Long Range Transport of Airborne Pollutants (LRTAP) Project is to provide scientific support for Environment Canada to develop and implement acid rain control strategies. Specifically, work is directed towards: the prediction of surface water acidification and recovery under various emission reduction scenarios; the development of new scientific concepts relating to the LRTAP issue; and the preparation of the 1990 national LRTAP assessment report to be coordinated by the federal-provincial Research and Monitoring Coordination Committee (RMCC).

Research Highlights

- An expert systems approach was developed to predict the number of lakes in Eastern Canada that would have a pH≤6 given various wet sulphate deposition rates. The results of this modelling provided the main contribution to the 1990 national LRTAP assessment report. This modelling approach required both quantitative and qualitative judgement for the selection of the proper model in the expert system for each lake or watershed. The model uncertainties generally decreased when the loading was decreased. Based on a comparison of predicted and observed alkalinities for over 2000 lakes, relative errors ranged from 19 to 31 percent. Due to these uncertainties as well as to data limitations, the threshold criterion for the critical load for wet sulphate deposition has been conservatively chosen. The criterion identifies the load which is predicted to put more than 10 percent of a region's lakes in the pH≤6 category, not including those lakes which would have been acidified with naturally occurring organic acids. Figure 8 shows that with a deposition of 20 kg/ha/y wet sulphate, only four out of 22 subregions in Eastern Canada will meet the threshold criterion (i.e., by checking along the vertical line corresponding to ten percent). These four subregions all have terrain factors that render the surface waters less sensitive to acidic deposition. Subregions in the Atlantic provinces, Labrador and eastern Quebec are more sensitive and require critical loads which are close to background (≤8 kg/ha/y).

- The RMCC also provided four deposition scenarios and requested the NWRI modelling team to predict corresponding aquatic effects. As examples, Figure 8 shows the outcomes of the first scenario (the current deposition based on an average over the period 1982-86) and scenario 4 (scheduled Canadian plus U.S. reduction programs). The predicted damages (i.e., excess percentage of lakes with pH≤6) are plotted as solid lines. According to the models, the implementation of scenario 4 will result in a large part of Eastern Canada, mainly in Ontario and Quebec, attaining the threshold criterion, with substantial improvement from the current condition (compare the two solid lines with the ten percent vertical line). However, the reduction programs will only slightly improve the condition for the Atlantic provinces. This is due to relatively smaller changes in the amount of wet sulphate deposition between the two scenarios in combination with highly sensitive terrain.

- A long-term time dependent watershed acidification model (MAGIC) has been applied to Batchawana Lake in the Turkey Lakes watershed in order to evaluate long-term trends based on a constant SO_4 load of 27.8 kg/ha/y and variable loading according to the scheduled reduction in Canadian and U.S. emissions. Constant sulphate deposition results in a depression in pH of 1.2 units whereas the variable deposition results in a depression of only 0.4 units. In both cases, approximately 100 years are required for equilibrium to be reached.

- Evidence of regional differences is also manifested in the observed water chemistry data. After screening, data were available for approximately 8500 lakes in Eastern Canada. Median SO_4^{2-} values (μeq/L) in

lakes, aggregated by region, were found to reflect the influence of the deposition plume which was highest over southern and central Ontario, declining toward the east into Quebec, and lowest in the Atlantic provinces.

- A statistical approach was used to test the adequacy of the three-parameter, log-normal model. This model is commonly used for determining regional acidification by defining a family of probability models using the power transformation of Box and Cox which includes the log-normal as a special case. The results show that the log-normal model is inadequate for representing lake alkalinity in New Brunswick, Newfoundland and Nova Scotia, while only the Quebec data set supports the use of this model.

- Snowpack sampling has continued in the Turkey Lakes watershed to provide measurements of water volume and major ions available at spring melt, and to characterize the chemistry of atmospheric deposition over the winter months. The annual mean (11 sites) water equivalence of the pre-melt snowpack ranged from 159 to 377 mm over the period 1981 to 1988. The annual trend in the equivalent ratios of SO_4/NO_3, H/SO_4 and H/HO_3 supported the hypothesis that the H^+ and NO_3 levels in snowfall have increased relative to SO_4 since 1980.

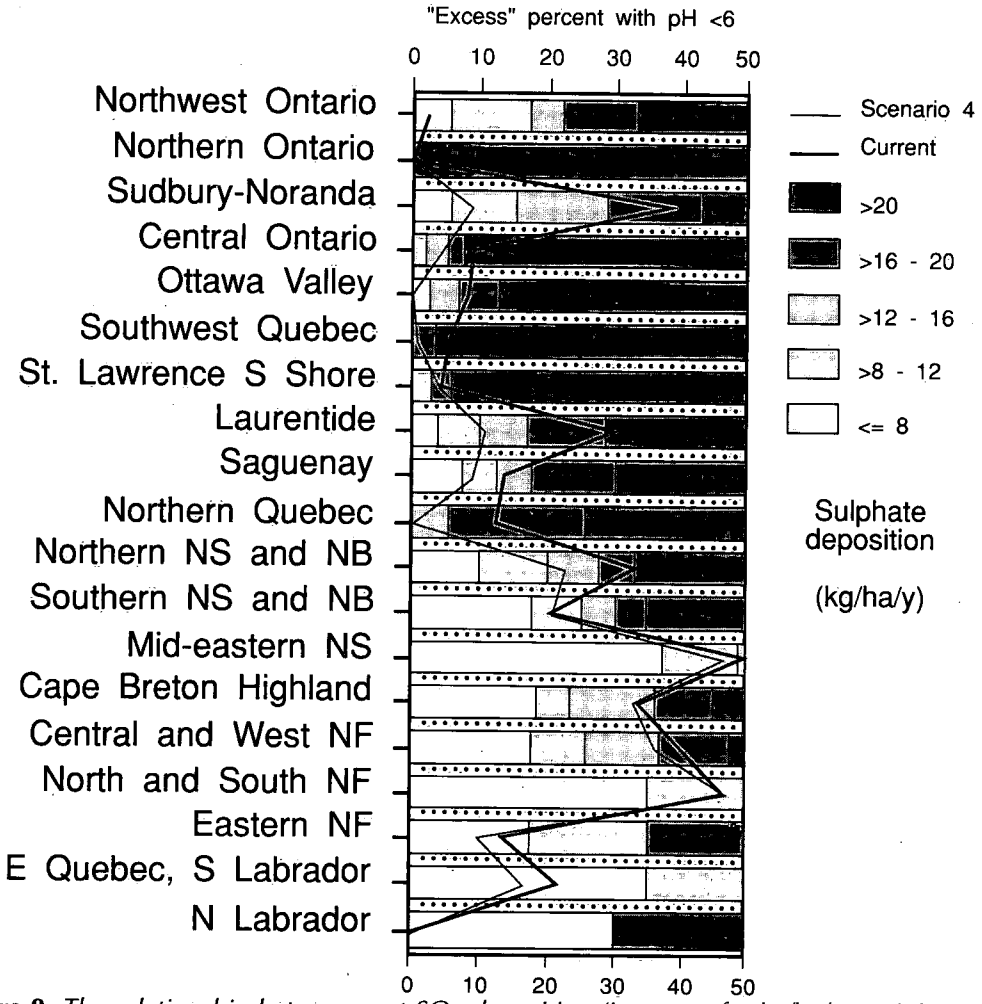
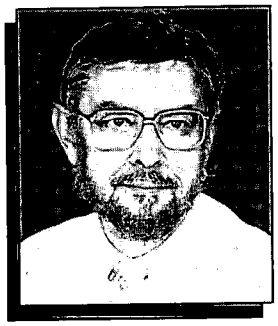


Figure 8. *The relationship between wet SO_4 deposition (in steps of 4 kg/ha/y) and the excess percent of lakes having pH≤6 for identified regions of Eastern Canada. The damage level associated with the current deposition scenario and a scenario combining U.S. and Canadian sulphate reduction programs (scenario 4) is also shown.*

ECOTOXICOLOGY PROJECT

B.J. Dutka, Project Chief



Introduction

The main objectives of the Ecotoxicology Project are to identify biological indicators with which to predict contaminant stresses on the aquatic ecosystem, and establish the extent and degree of their impact. The project is developing an appropriate battery of tests which will be applicable in a wide range of aquatic ecosystems. Study efforts have been directed toward developing, modifying and evaluating a variety of toxicological, mutagenic, biochemical and microbiological procedures for potential inclusion into universally applied screening tests.

Ancillary objectives of the project team are to use the screening tests approach to determine the geographical extent and the ecological impact of contaminants entering our rivers and lakes, and develop an understanding of the role of suspended particulates in the downstream transport of pollutants. The expertise of the project team members is also used to provide advice and guidance to national and international agencies and industries on microbiological and ecotoxicological problems.

Research Highlights

- The Yamaska River Basin (Quebec) has many point and non-point sources of contaminants. This basin was surveyed to evaluate, under field conditions, the efficacy of various ecotoxicological tests and processes. For example, the Mutatox test for genotoxicants, in the first ever field evaluation of the procedure, was found to be a very responsive test in all three sample types (e.g., water, Milli-Q water-extracted sediments and solvent-extracted sediments). This test indicated that chemicals with genotoxic activity were distributed throughout the Yamaska River basin and that there appeared to be an increasing accumulation of these chemicals in sediments in the downstream direction. The information will be used to develop a better understanding of the spatial and temporal distribution of toxicants in river water and sediments.

- Procedures for the extraction of sediments or suspended sediments for toxicity and genotoxicity studies are becoming increasingly complicated as well as being time-consuming and expensive. The original concept of using short-term bioassays was to test water, suspended particulates and/or sediment samples in a quick and efficient manner, such that only responsive samples could be selected for the more costly and time-consuming chemical analyses. To this end, three simple, quick and inexpensive sediment-extracting media procedures were tested. These included Milli-Q water, DMSO and methanol extracts, each of which was tested individually for sediments and suspended particulates. Each extract was thoroughly mixed with the sediment and then separated by centrifugation. The three extracts were tested for the presence of toxicity and genotoxicity using the Microtox™, Toxi-Chromotest™ and Mutatox procedures. Results of this study indicated that the Mutatox genotoxicity screening test was an extremely sensitive procedure responding to chemicals using all three types of extracts. Methanol was found to be slightly more efficient than DMSO or Milli-Q water for extracting toxic and genotoxic chemicals from some of the samples. In addition, each extracting procedure was found to have an affinity for extracting certain toxicants and genotoxicants.

- To gain a better understanding of contaminant partitioning between suspended particles and the dissolved phase in fluvial systems, laboratory studies were initiated using suspended aggregates obtained from several Canadian rivers. These river samples were subjected to particle size distribution analysis using a laser particle size analyzer. A modified cascade fractionation technique (Figure 9) was used to isolate the various aggregate fractions. Each fraction was sub-

and toxicant analyses, as well as to contaminant/particle interaction tests to establish the nature and efficiency of contaminant binding by suspended aggregates and bacteria. Data indicate that aggregates in the 20-40 micron fraction were the dominant size class in these rivers. They also contained the greatest microbial, toxicant and nutrient loads. It is essential to establish the size distribution pattern and composition of these suspended aggregates in riverine systems before accurate contaminant transport models can be developed.

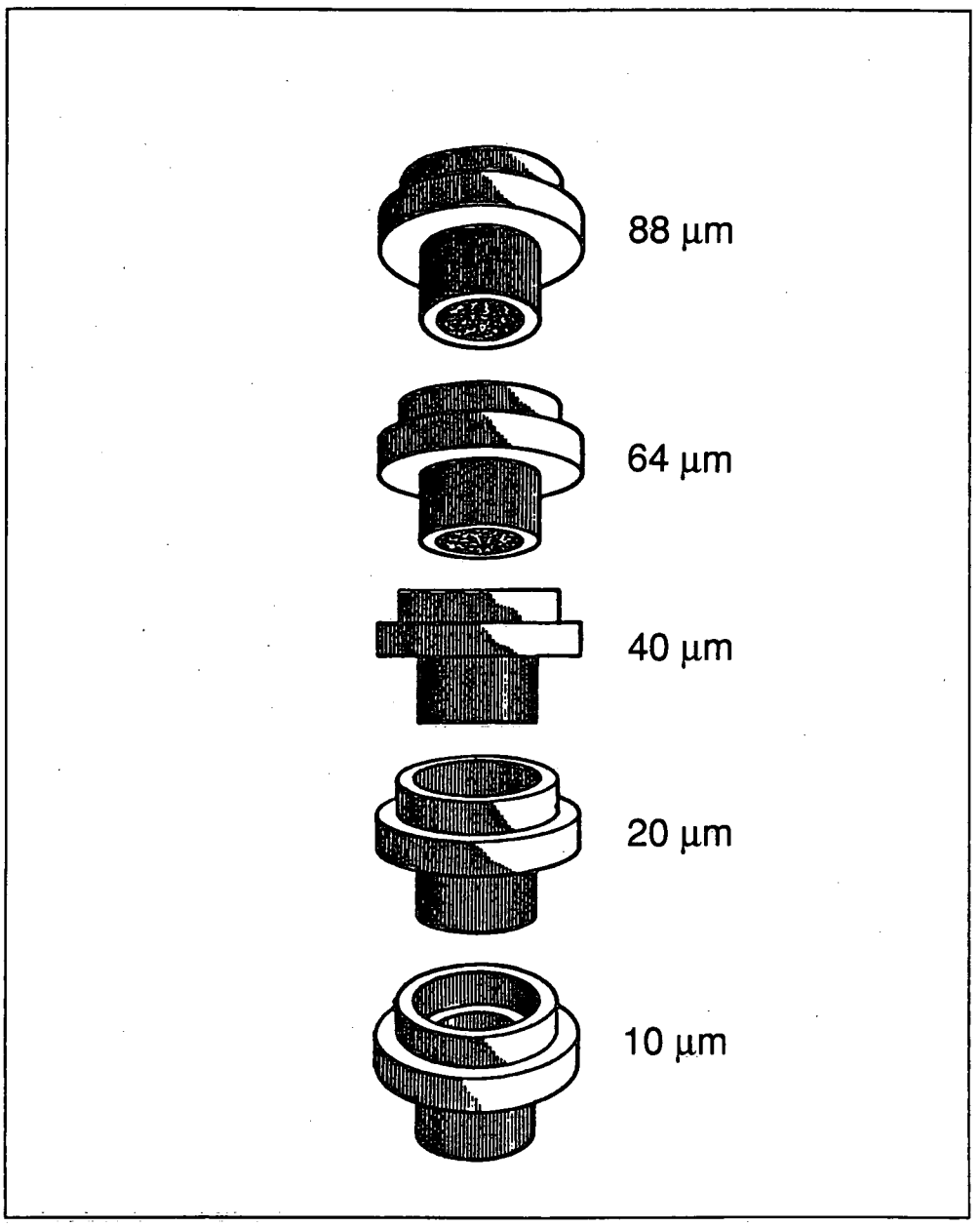


Figure 9. *Illustration of a cascade filtration system.*

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GROUNDWATER CONTAMINATION PROJECT

K.S. Novakowski, Project Chief

Introduction

The major objective of the Groundwater Contamination Project is to determine the movement and fate of toxic contaminants in groundwater environments. Field research is carried out at a variety of sites in Eastern Canada, including a large site in Niagara Falls, several sites on Prince Edward Island (PEI), the Gloucester Landfill near Ottawa, and a field site in the town of Clarkson, Ontario. In addition, laboratory experiments and computer simulations are employed to conduct research into a variety of contaminant transport processes. Recent evidence suggests that a particular type of contaminant within the groundwater regime, referred to as non-aqueous phase liquid (NAPL), is very resistant to groundwater remediation efforts. Consequently, the focus of current and future work is shifting towards developing an understanding of the behaviour of NAPL in complex groundwater environments. Scientists from the project frequently provide advice to federal and provincial agencies and the private sector on matters related to the pollution of groundwater by NAPLs and other contaminants.

Research Highlights

- Contaminated leachate seeping from waste sites in Niagara Falls, N.Y., threatens the water quality of both the Niagara River and Lake Ontario. During the summer of 1989, a study was conducted in cooperation with the U.S. Geological Survey to evaluate standard hydrogeological and geophysical methods for determining contaminant pathways in the sedimentary rock underlying Niagara Falls. The results show that the standard methods of hydraulic and geophysical testing provide information only about the pathways controlled by the highest permeability and often miss those associated with features of lower permeability which, in total, may play an equally important role in contaminant transport.

- A cooperative program between the Groundwater Contamination Project and the University of New Brunswick has been established to foster groundwater research in the Maritime provinces. The collaborative studies included: the development of a numerical model to simulate the consumptive use of the Fredericton aquifer; a study of the controls on manganese concentrations in the groundwater of the Fredericton aquifer; and an investigation of the chemical and physical processes controlling the attenuation, migration and degradation of the pesticide aldicarb in PEI.

- Research continued at the field site of the Petro-Canada oil refinery near Clarkson, Ontario. The objective of the study is to determine the rate of contaminant dispersion and groundwater velocity in a single fracture located within shale bedrock which underlays the site. The results obtained to date show that the coefficient of dispersion for the fracture is large relative to equally spaced porous media. In addition, a large percentage of the fracture was found to be closed, suggesting that a significant amount of channelling of groundwater flow must take place. Current methods for estimating groundwater velocity and contaminant dispersion in such environments will thus yield unreliable results.

- The development of an expert system to evaluate the potential impact from agricultural pesticides on typical Canadian groundwater environments commenced during the past year. The expert system incorporates existing numerical models which can be used to simulate the transport and transformation of pesticides in the unsaturated zone, coupled with a knowledge-based system which directs the simulation. The knowledge-based system guides the user through the selection of all the necessary information for characterizing the geological, physical, climatic, hydrogeological, pedological and agricultural settings of typical agricultural areas across Canada. The expert system is designed to be

used as a management tool to aid in the policy-decision process and the regulation of new agricultural chemicals.

● Groundwater contaminated by the Gloucester Landfill near Ottawa is migrating off-site towards a light industrial area. In order to prevent off-site migration of contaminants, methods of restoring groundwater quality at the site are being investigated. Transport Canada, the site owner, is funding the project to study the "pump-and-treat" method of groundwater remediation. In order to minimize the length of time required to decontaminate the aquifer, and thus minimize costs, the placement of pumping and re-injection wells as well as the pumping rates and schedules must be optimized. The optimization procedure is undertaken using a combination of numerical groundwater flow models and contaminant transport models with optimization codes executed in sequence.

● Leachates from landfills and industrial sites often contain many organic compounds that undergo a degradation or transformation process under anaerobic conditions. A laboratory study to investigate the transformation of the chlorofluorocarbon CFC-113 under anaerobic conditions was initiated. This chemical is a solvent used as a degreasing agent in the electronics industry. The results show that CFC-113 is reductively dechlorinated to CFC-123a. CFC-113 is also transformed to chlorotrifloroetylene, a chemical which has much greater toxicity than the parent. This latter compound is the product of abiotic transformation and found to be unstable in the presence of sulphide, but stable in landfill leachate.

● Analysis of heavily contaminated groundwater for base-neutral extractable and water-miscible compounds is a time-consuming and expensive task. As a means of expediting the analysis of this type of sample, a new analytical method was developed whereby on-line thermal desorption is used to prepare the sample for GC/MS analysis. Results were compared to conventional solvent-extraction GC/MS for both base-neutral extractable and water-miscible compounds. Comparable to superior performance was observed.

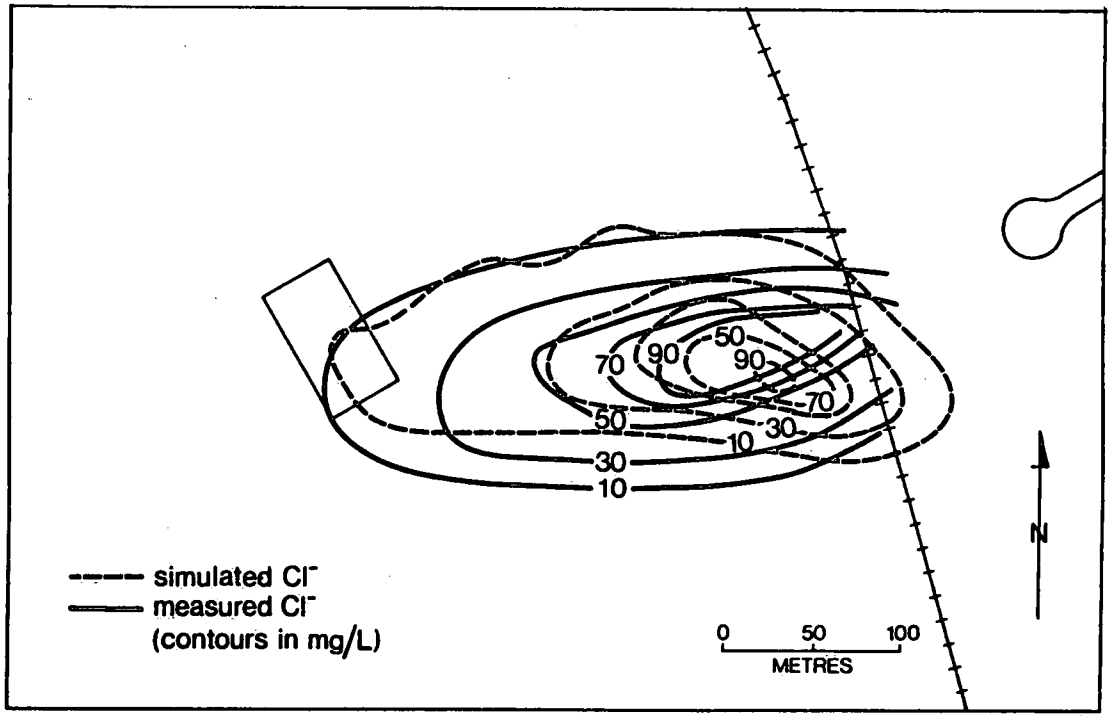
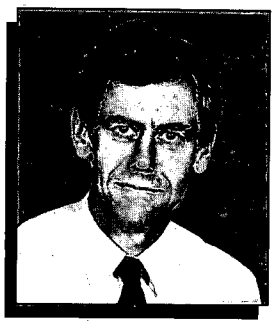


Figure 10. *Simulated and measured chloride concentrations in the contaminant plume at the Gloucester Landfill (May 1989).*

RESEARCH AND APPLICATIONS BRANCH

J. Lawrence, Director



The Research and Applications Branch conducts mission-oriented basic and applied research in areas of analytical chemistry and hydraulics. It is also responsible for transferring research results and technology to the operational sectors of Environment Canada and for providing technical and scientific services, such as current meter calibration, sedimentology and geotechnical services, and analytical quality assurance. The work addresses priority issues identified by Inland Waters and other agencies of Environment Canada. The Branch also has corporate responsibility for third party, cost-recovery work with universities and the private sector.

New, improved, and more cost effective analytical techniques (including laboratory automation) are developed and evaluated for the measurement of priority chemicals and biochemical parameters in environmental matrices. The Branch also has lead responsibility for analytical quality assurance for most of Conservation and Protection's chemical monitoring programs. The major recipients for this analytical work include NWRI, the national and regional laboratories of Conservation and Protection, federal-provincial water quality agreements, the Long Range Transport of Atmospheric Pollutants Program, the Prairie Provinces Water Board and the Great Lakes Water Quality Agreement.

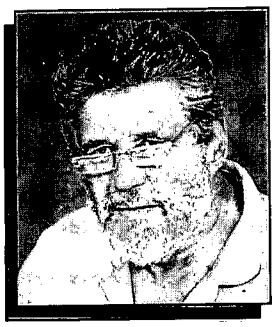
Knowledge of the dynamics of water is sought to provide a framework for the management of water resources and for research into aquatic biology and chemistry. The interfaces among water, the atmosphere, bottom sediments and the shore are studied to explain the mechanisms controlling the transport of pollutants and erosion. Advances are made in river metrology to improve management of that resource. The major clients are Environment Canada's Water Resources Branch, Water Planning and Management Branch, Environmental Protection, and Atmospheric Environment Service as well as the Great Lakes Water Quality Program.

Universities and private industry are encouraged to make use of the facilities and expertise of the Branch either through collaborative studies with the professional staff or the leasing of in-house facilities with or without technical support. The Branch maintains a well-equipped hydraulics laboratory, sedimentology and geotechnical laboratories, a special "Clean and Hazardous Chemical Laboratory", and conventional chemical laboratories. Costs associated with all direct requests for services from external agencies are charged to the client, in full or in part, in accordance with the Treasury Board Cost Recovery Policy.

The activities of the Branch are organized into three projects: **Analytical Chemistry**; **Hydraulics**; and **Quality Assurance.**

ANALYTICAL CHEMISTRY PROJECT

I. Sekerka, Project Chief



Introduction

The objective of the Analytical Chemistry Project is to advance knowledge and provide expertise on analytical chemistry requirements for environmental applications. New analytical protocols, instrumentation and methods are essential for the assessment and management of water resources and for water pollution research, especially the identification of emerging problems. Specific activities of the project include: the development of new analytical methods as well as screening and sampling procedures, which are accurate, cost-effective, sensitive and unambiguous, for the identification and quantification of contaminants in aquatic ecosystems; the documentation, validation and standardization of analytical methodologies for ensuring the accuracy and reliability of analytical data; the provision, maintenance and continued updating of sophisticated instrumentation and facilities for NWRI; and the transfer of methods and technologies which are developed in the Analytical Chemistry Project to the national and regional laboratories of Inland Waters and a wide variety of other users.

Research Highlights

- A simple method has been developed for the direct coupling of supercritical fluid extraction (SFE) with high resolution gas chromatography (HRGC) having an electron capture detection. SFE conditions relating to mobile phase, entrainer, pressure, temperature, and mass flow through the extractor have been investigated for the quantitation of polychlorinated biphenyls (PCBs) and dioxins. Extraction efficiencies of up to 100 percent in less than 15 minutes have been obtained for PCBs, and in 30 minutes for 2,3,7,8-TCDD. Tandem SFE-HRGC provides the possibility to combine sample preparation and determination steps and results in a significant improvement for the analysis of organic compounds as compared to conventional methods in terms of rapidity, efficiency and safety.

- The assembly of a prototype large-sample extractor, with solvent recovery, has been completed and will be tested under field conditions (Figure 11). The commercial production of this version of the Goulden large-sample extractor was initiated through a marketing arrangement with La-Salle Scientific Inc., Guelph, Ontario. The technology is expected to be of interest to many water management organizations. A commercial unit of the extractor was exhibited at the GLOBE '90 Trade Fair, held in Vancouver, B.C., in March 1990.

- Methods for the determination of ammonia (NH^{4+}) and cyanide (CN^-) by flow-injection analysis have been developed. In a continuous-flow system, the species of interest is converted to the gaseous state for diffusion across a hydrophobic gas permeable membrane into a stationary solution for reconversion to the ionic form. After a preselected time, the solution is pumped to the detector cell for amperometric (CN^-) or conductometric (NH^{4+}) analysis. The interface of the procedure with a computer system allows automation of the operation as well as the handling, evaluation and storage of data. The methods are based on the isothermal distillation principle and thus are interference-free.

- The robotic system developed previously under this project has been integrated within the operations of the National Water Quality Laboratory for performance evaluation purposes. When coupled to a FIA-ICAP analytical system, good results and dependable performance have been obtained for the determination of a variety of parameters, including successful interfacing with a computer system.

- The draft versions of an analytical protocol for the determination of polychlorodibenzo-*p*-dioxins (PCDDs) and polychlorodibenzofurans (PCDFs) were prepared at the request of Environment

Canada's Industrial Programs Branch. This protocol is proposed as a reference method for analyses of PCDDs and PCDFs in the monitoring and control of effluents from the pulp and paper industry.

- An effective and efficient extraction and cleanup method for use in the analysis of PCDDs by radioimmunoassay or conventional methods has been developed using tritiated 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) as the tracer. Preliminary results indicate that the assay allows detection at 5 pg of 2,3,7,8-TCDD, and it has been shown to overcome problems encountered earlier in the study, such as the presence of inseparable hapten impurities and the instability of the hapten. The method also incorporated a novel separation step using activated charcoal which reduces the separation time by two orders of magnitude.

- A system combining gas chromatography and atomic emission spectroscopy has been applied successfully to the screening of environmental samples for organic compounds containing phosphorus, sulphur and nitrogen. The analytical approach proved particularly valuable during the special programs organized as part of the departmental response to environmental incidents, such as the alleged importation into Ontario of tainted fuels and the Hagersville tire fire.

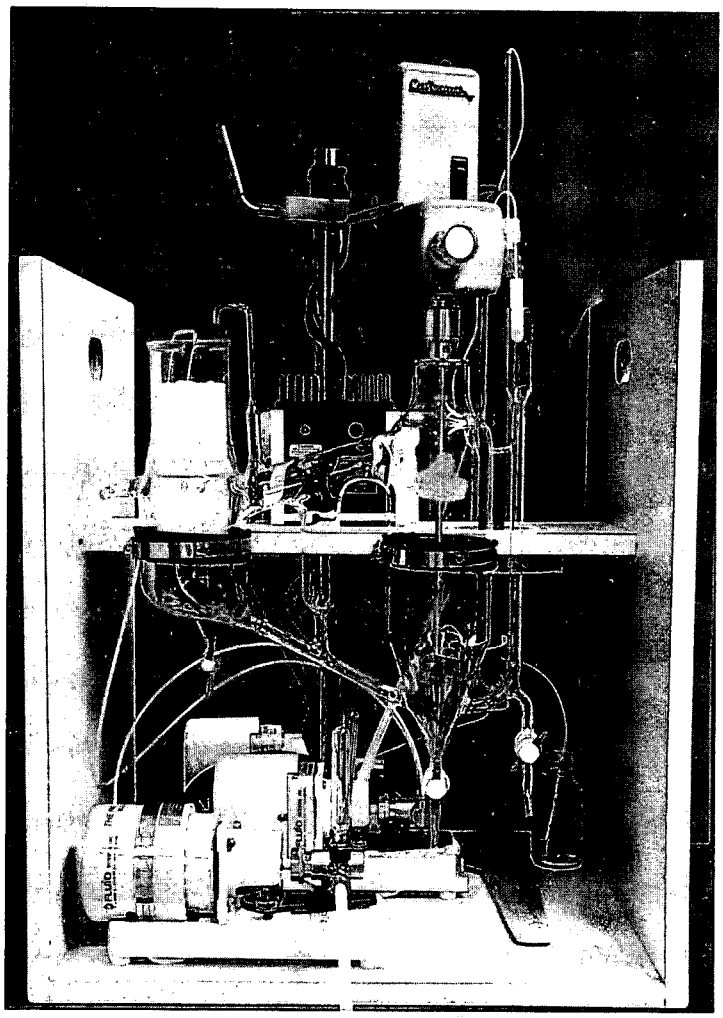


Figure 11. *The Goulden large-sample extractor.*

HYDRAULICS PROJECT

M.G. Skafel, Project Chief

Introduction

Research undertaken within the Hydraulics Project focuses on the physical dynamics of water and its interaction with air, sediments, shores and man-made structures. Studies on wave mechanics, river flow and sediment transport provide new knowledge for use by water resource managers and engineers in Environment Canada and elsewhere. Special attention is given to understanding hydraulic processes that could lead to structural failure with serious environmental consequences.

Wave mechanics studies create new knowledge to advance the understanding of toxic gas transfer, diffusion of pollutants, wave prediction, lake circulation, seasonal thermocline development, weather forecasting and climatic change. Coastal engineering studies address interactions between the lake and the lake bottom/shoreline to determine sediment resuspension, shoreline evolution and interactions between waves and shoreline structures. Fluvial engineering research is directed at improved understanding of fluid mechanics and sediment transport in rivers, the development of new and improved techniques for monitoring river processes, and interactions between flow and structures.

Research Highlights

- In support of the Water Resources Branch of Environment Canada, the project is conducting applied research studies addressing a variety of specific issues. Recent work includes: evaluation of an acoustic current meter; development of a new calibration equation for the Price current meter which improves the measurement accuracy at low flows; the development of a calibration strategy for suspended sediment samplers as well as the design and construction of a suspended sediment nozzle test facility; and assistance in the development of a research program to measure flows under ice.

- In order to minimize the chance of oil spills from submarine pipelines in the Beaufort Sea, pipelines will be laid in trenches to avoid scour due to ice flows. Model tests completed in the hydraulics laboratory have indicated that forces due to waves on a pipeline in a trench can be approximated by forces on a pipe on a flat bottom at the same total depth. This finding means that in developing designs to protect pipelines from wave forces, the extensive literature available for flat bottom situations can be utilized.

- A monitoring program was undertaken by Transport Canada to determine the effects of a breakwater extension on water depths in an adjacent river mouth and marina. The hydrographic data were examined by the project scientists and no adverse effect was found. However, unexpectedly, the results indicated that the harbour area was undergoing subsidence due to a salt mine under the area. Transport Canada and Public works Canada have been advised on the implications for ongoing maintenance of the harbour structures.

- Gas transfer at the air-water interface plays an important role in global biogeochemical cycles. Recent experiments in the new air-tight recirculating gas transfer flume have examined the influence of small-scale wave breaking on the transfer of a liquid phase controlled compound (chlorobenzene). Small-scale wave breaking is pervasive in open waters, in contrast to white-capping which is intermittent. It was found that the transfer rate increased dramatically under conditions where small-scale wave breaking began. While other studies have reported the enhancement of the mass transfer velocity only in terms of wind speed, this study characterizes the mass transfer velocity in terms of wind and wave properties. Initially, the results of this study will be used to calculate mass balances for volatile contaminants in the Great Lakes.

● Preparation for the surface waves dynamics experiment (SWADE), sponsored by the U.S. Office of Naval Research, has proceeded as planned with the first intensive experiments carried out in the autumn of 1990. A multi-agency team, led by staff from the Hydraulics Project, has been developing instrumentation systems for five meteorological and wave direction buoys, as well as a wave direction system to be integrated onto a large spar buoy (Figure 12). A prototype wave direction and flux buoy was tested in the Gulf of Mexico. The main objectives of the experiment are to understand the dynamics of the evolution of the wave field in the open ocean and to determine the effect of waves on the air-sea transfer of momentum, heat and mass. The results of these studies are applicable to both ocean and lake situations.

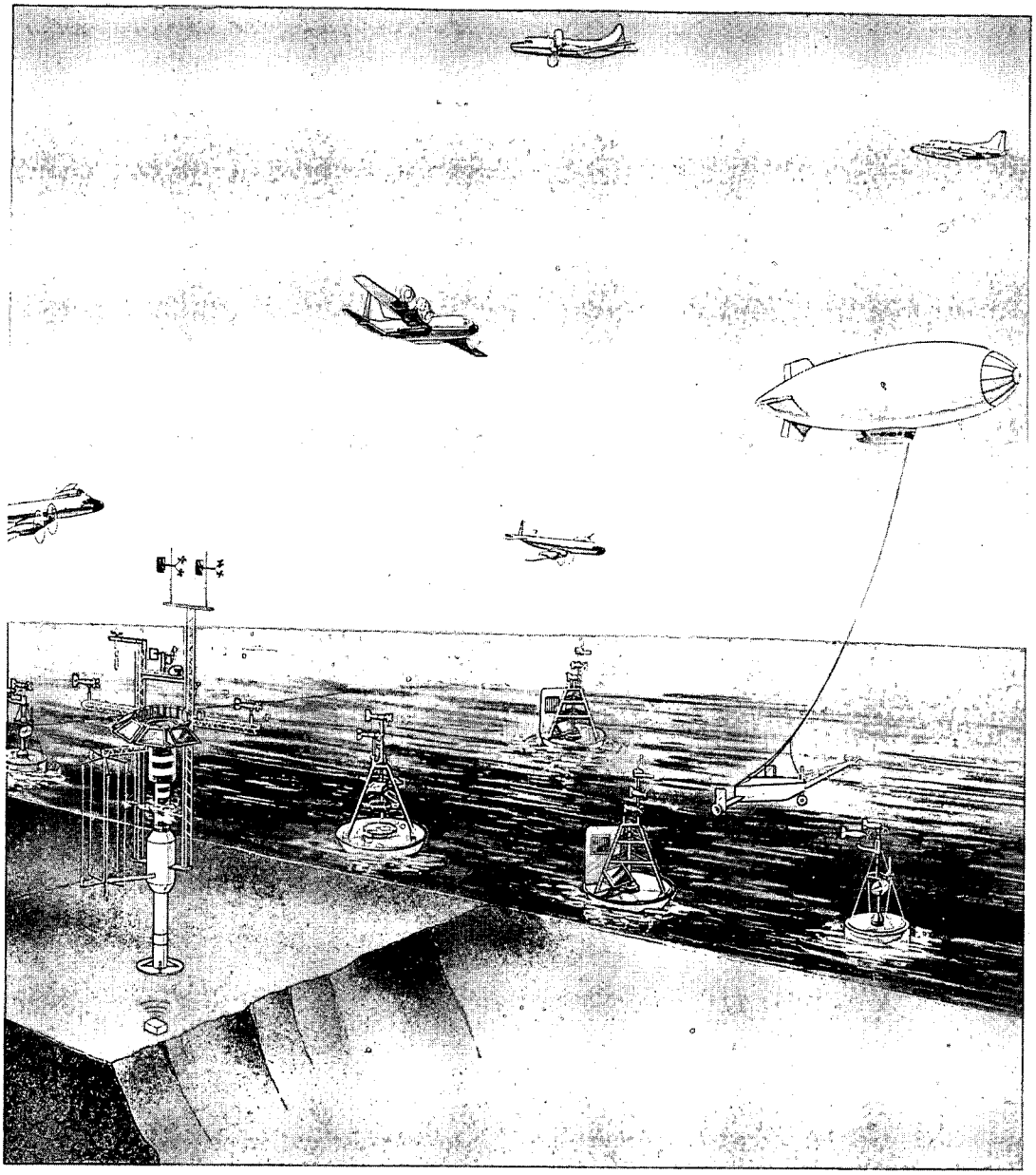
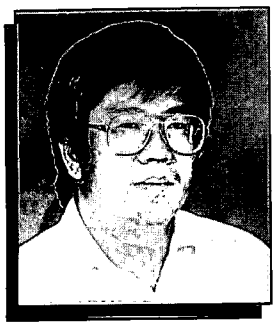


Figure 12. *Schematic representation of the data-capture instrumentation that has been planned for deployment during the field work portion of SWADE.*

QUALITY ASSURANCE PROJECT

A.S.Y. Chau, Project Chief



Introduction

Reliable chemical data are essential for environmental research, monitoring and assessment programs. Not only have these programs become more complex in recent years, but there has also been a dramatic increase in the number of compounds which need to be measured. Also, many of these compounds occur in the environment at extremely low concentrations. In addition to multi-agency and binational co-operative studies, global aspects of many environmental issues are requiring concerted international, co-operative efforts in the generation of scientific information.

All the above factors have increased the need to ensure the quality and comparability of data. Biased data can lead to errors in assessment and in subsequent enforcement/control actions. In addition, the generation and interpretation of data is extremely expensive and this increases the requirement for accurate, defensible data.

The main objective of the Quality Assurance (QA) Project is to coordinate and undertake quality assurance programs for Environment Canada to ensure that analytical data are consistently accurate and comparable in all its laboratories. Assurance of data quality enables Environment Canada to provide authoritative, credible scientific advice on control and remediation strategies derived from the interpretation of scientific data. Studies are also conducted for federal, provincial, university and private laboratories which produce analytical data for the Department's programs.

The long-term goal of the QA Project is to assist with the development of comprehensive analytical quality assurance programs. This includes the production of reference materials (RMs) and certified reference materials (CRMs) that are representative of typical environmental samples of water, sediment and biota.

Research Highlights

- A number of RMs for water analysis and CRMs for sediment analysis have been developed. RMs and CRMs are similar except the latter are more rigorously tested. The lake sediment CRMs include several of the world's first to be developed for polynuclear aromatic hydrocarbons (PAHs), chlorobenzenes, PCBs and selenium. An active program to market these products has been initiated, including the production of a bilingual brochure describing the RMs and CRMs developed at NWRI. These initiatives have resulted in many inquiries and considerable attention from national and international agencies, notably the International Reference Material Committee of the International Standards Organization (ISO), and coverage in the scientific and technical literature. Sediment CRMs and RMs currently available include PCBs, PAHs and chlorobenzenes for sediments from various Great Lakes Basin sources; arsenic, selenium, mercury and trace metals for sediments from Lake Ontario sources; and trace metals for sediment from a variety of sources.

- Upon request from the Environment Canada's Dioxin Task Force, a member of the QA Project formed and chaired a Quality Assurance Committee to support the Canadian Pulp and Paper Association's national pulp and paper mill dioxin sampling program. The Quality Assurance Committee has received several hundred analytical data points and has generated an interlaboratory QA protocol for dioxin and furan analyses. The same protocol will be adopted under the national Ocean Dumping Program.

- An interlaboratory QA program was initiated in 1989 in support of the activities associated with the assessment of organic compounds listed as priority substances under the *Canadian Environmental Protec-*

tion Act. These substances included dioxins, organotin and chlorophenols. Work is under way for the development of RMs for levels of dioxin and organotin, with plans to select some of these RMs for further development as CRMs.

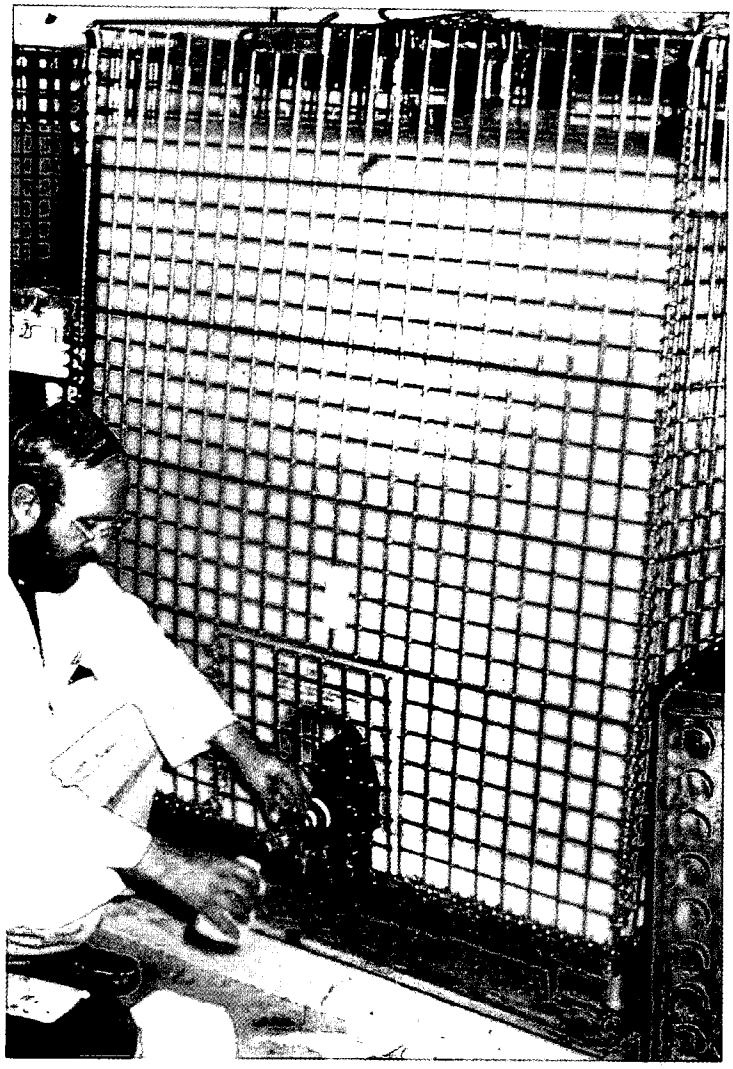
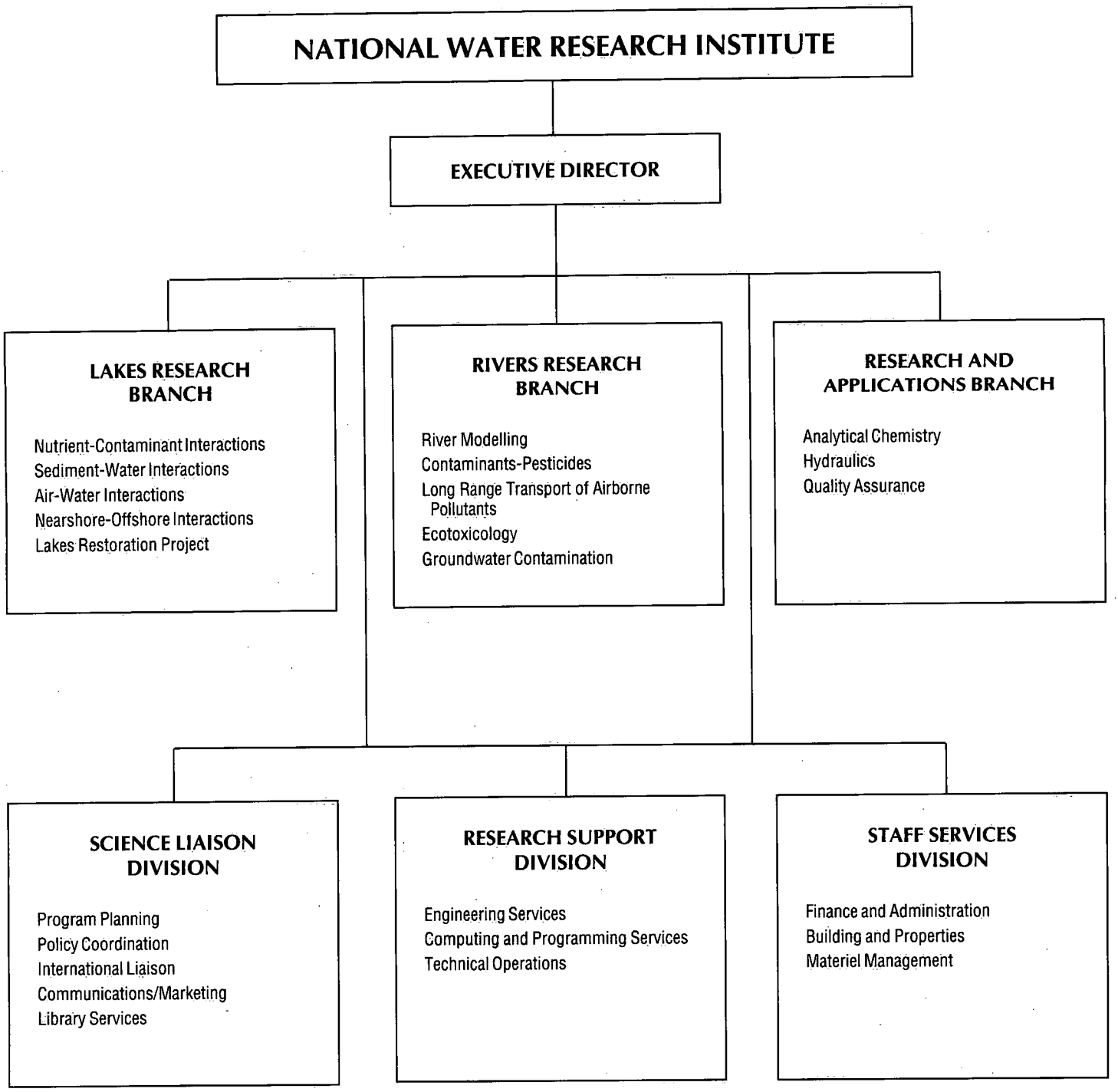


Figure 13. *Subsampling test from stock water reference materials for use in interlaboratory QA studies.*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Air-Water Interactions

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PUBLICATIONS

Boyce, F.M., M.A. Donelan, **P.F. Hamblin**, **C.R. Murthy** and T.J. Simons. 1989. Thermal structure and circulation in the Great Lakes. Atmosphere-Ocean 27: 607-642.

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PUBLICATIONS

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PUBLICATIONS

Carey, J.H., **E.D. Ongley** and E. Nagy. 1990. Hydrocarbon transport in the Mackenzie River, Canada. Sci. Tot. Env.97/98: 69-88.

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River Modelling

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PUBLICATIONS

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Contaminants/Pesticides

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PUBLICATIONS

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