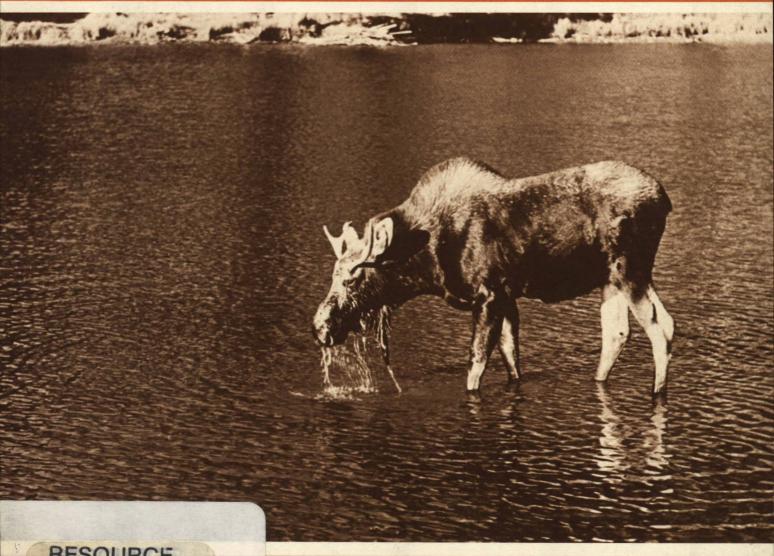


WATER QUALITY MONITORING DESIGN — **Proceedings of the Technology Transfer** Workshop

CONCEPTION DE LA SURVEILLANCE DE LA QUALITÉ DES EAUX —

Comptes rendus de l'atelier sur l'échange d'informations d'ordre technologique



RESOURCE CENTRE

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TECHNICAL WORKSHOP SERIES NO. 6 ÉTUDE Nº 6, SÉRIE DES ATELIERS TECHNIQUES

INLAND WATERS/LANDS DIRECTORATE OTTAWA, CANADA, 1987

DIRECTION GÉNÉRALE DES EAUX INTÉRIEURES ET DES TERRES OTTAWA, CANADA, 1987

PROCEEDINGS

of the

TECHNOLOGY TRANSFER WORKSHOP WATER QUALITY MONITORING DESIGN

Burlington, Ontario, April 29 to May 1, 1985
TECHNICAL WORKSHOP SERIES NO. 6

COMPTES RENDUS

de

L'ATELIER SUR L'ECHANGE D'INFORMATIONS D'ORDRE TECHNOLOGIQUE CONCEPTION DE LA SURVEILLANCE DE LA QUALITE DES EAUX

> Burlington (Ontario), 29 avril au 1 $^{\rm er}$ mai 1985 ETUDE N $^{\rm o}$ 6, SERIE DES ATELIERS TECHNIQUES

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FOREWORD

The Water Quality Monitoring Design Workshop was held in Burlington, Ontario, April 29 to May 1, 1985. The objective of the Workshop was to improve the ability, efficiency and effectiveness of the Inland Waters Directorate in fulfilling its responsibilities related to national water quality monitoring activities by:

- exchange of experience between regional personnel dealing with implementation of monitoring activities
- exchange of technical and research information among Inland Waters Directorate research and operational personnel involved in monitoring activities
- identification of gaps in knowledge requiring research, future study and/or detailed technical information transfer
- identification of improved methods for the transfer of research or technical information on a national basis.

The Workshop process was organized in three basic stages:

- (1) Regional representatives were identified to present an example of a monitoring activity within their region. Information on objectives, goals, station location, sample frequency, parameter list and monitoring activity outcome was supplied by each representative.
- (2) The Workshops broke into five working groups (one for each region). All participants were assigned to a specific working group, as was a secretary. Each group elected a chairperson. Each regional representative was required to expand on presentation, providing more detail to the working group, where appropriate, and highlighting problems and uncertainties. subsequent discussion, led by the chairperson, the problems and gaps in knowledge in water quality monitoring and recommendations for their solution for subsequent research or management action.
- (3) Day 3 of the Workshop consisted of a concluding plenary session. The chairpersons presented a report on the discussions and recommendations of their working groups. A general discussion followed.

The presentation of regional water quality monitoring activities, and the conclusions and recommendations generated by the participants make up these Proceedings.

Workshops may be considered as a learning experience for all participants, leading to a sharing of ideas and a better understanding of the position and views held by both the research and the operational components of IWD monitoring activities. Communication, an intangible output, often produces the most tangible result — better monitoring activities.

AVANT-PROPOS

L'atelier sur la conception de la surveillance de la qualité des eaux a eu lieu à Burlington, en Ontario, du 29 avril au l^{er} mai 1985. L'objectif de cet atelier était de permettre à la Direction générale des eaux intérieures d'assumer plus efficacement ses responsabilités nationales en matière de surveillance de la qualité des eaux par:

- des échanges entre les membres du personnel des régions sur leur expérience dans le domaine de l'application de la surveillance
- des échanges d'informations techniques et scientifiques entre les membres du personnel de recherche et des opérations de la Direction générale des eaux intérieures travaillant dans le domaine de la surveillance
- la détermination des lacunes dans les connaissances qui devront être comblées par des recherches, des études et des activités de transfert d'information technique détaillée
- la recherche de méthodes améliorées pour la diffusion des informations scientifiques et techniques à l'échelle nationale.

L'atelier a été divisé en trois parties:

- 1) Un représentant de chaque région a été chargé de présenter un exemple d'activité de surveillance dans sa région. Chaque représentant a donné des détails sur les objectifs, les buts, l'emplacement des stations, la fréquence d'échantillonnage, les paramètres mesurés et les résultats de la surveillance.
- 2) Les participants se sont divisés en cinq groupes de travail (un pour chaque région). Pour chaque groupe, un secrétaire a été désigné. Le président de chaque groupe a été élu par les membres. Le représentant de chaque région a été appelé à compléter son exposé en fournissant des données plus détaillées dans certains cas et en soulignant certains problèmes et certains sujets d'incertitude. Dans la discussion qui a suivi, animée par le président, on s'est penché sur les problèmes et les lacunes dans les connaissances en ce qui a trait à la surveillance de la qualité des eaux et on a élaboré des recommandations concernant la solution des problèmes et les mesures à prendre sur le plan de la recherche ou de la gestion.
- 3) Le troisième jour a eu lieu la séance plénière finale. Le président de chaque groupe de travail a alors présenté un rapport sur les discussions et les recommandations de son groupe. Une discussion générale a suivi.

Les exposés sur les activités régionales de surveillance de la qualité des eaux et les conclusions et recommandations formulées par les participants sont réunis dans le présent compte rendu.

Les ateliers peuvent être considérés comme des expériences enrichissantes pour tous les participants, permettant une mise en commun des idées en vue d'une meilleure connaissance des positions et points de vue des groupes de la recherche et des opérations dans le domaine de la surveillance à la DGEI. La communication, un résultat intangible, conduit souvent au résultat le plus tangible: une surveillance améliorée.

ACKNOWLEDGMENTS

The editor would like to thank all participants at the Workshop for their diligent, conscientious efforts. Thanks are also extended to the regional representatives who authored the presentations (T. Clair, H. Sloterdijk, R. McCrea, D. Munro and L. Churchland), the working group secretaries (P. Seidl, D. Bondy, L. Désilets, D. Haffner and K. Thibault), the working group chairpersons (M. Charlton, H. Vaughan, T. Pollock, D. Munro and R. Bukata), and A. Hamilton for leading the general discussion session. Special thanks go to D. Haffner, whose continued support throughout this project was greatly appreciated.

AGENDA

Monitoring Workshop April 29 - May 1 CCIW, Burlington

Monday, April 29	09:00 - 09:05	Welcome - W.J. Traversy, D.L. Egar
	09:05 - 09:10	Introductory Remarks, R. Kwiatkowski
Cafeteria	09:10 - 09:20	History of WQB monitoring, R. Kwiatkowski
Seminar room	09:20 - 09:30	Future role of monitoring, D. Haffner
	09:30 - 10:15	Annapolis Valley - Atlantic Region, T. Clair
	10:15 - 10:30	Coffee
	10:30 - 11:15	St. Lawrence River
		- Quebec Region, H. Sloterdijk
	11:15 - 12:00	Hudson Bay Lowlands
		- Ontario Region, R. McCrea
	12:00 - 13:30	Lunch
	13:30 - 14:15	Lake Diefenbaker - South Saskatchewan
		- Western and Northern Region, D. Munro
	14:15 - 15:00	Stikine River
		- Pacific and Yukon Region, L. Churchland
	15:00 - 15:05	Wrap-up, R. Kwiatkowski
	15:05 - 15:15	Film "Water Quality National Laboratory"
	15:15 - 15:30	Coffee
	15:30 - 16:30	Working groups - chairperson election
Tuesday, April 30	09:00 - 14:30	Working groups
	Room L701	Pacific and Yukon Region
		K. Thibault recorder
	Room L601	Western and Northern Region
		D. Haffner recorder
	Room L218	Ontario Region
		L. Désilets recorder

AGENDA (Cont.)

	Room L507	Québec Region D. Bondy recorder
	Room L401	Atlantic Region P. Seidl recorder
	14:30 - 15:30	Workshop chairpersons and recorders write up minutes
	15:30 - 16:30	Chairpersons present minutes to their respective work groups for approval
Wednesday, May 1	09:00 - 09:30 09:30 - 10:00	Working group - Pacific Region Working group - Western Northern
Cafeteria	10:00 - 10:30	Working group - Ontario Region
Seminar room	10:30 - 11:00	Coffee
	11:00 - 11:30	Working group - Québec Region
	11:30 - 12:00	Working group - Altantic Region
	13:30	General Discussion, A. Hamilton

The Future of Water Quality Assessment

by

D. Haffner

Water Quality Branch Inland Waters Directorate Environment Canada Ottawa, Ontario

THE FUTURE OF WATER QUALITY ASSESSMENT

The future of water quality assessment in Canada can be viewed from many perspectives. At one level it is possible to review what is presently occurring in water quality agencies across the country, and observe the provinces, such as British Columbia and Alberta, have greatly reduced their surface water quality monitoring activities over the past few years. Last summer Manitoba dropped much of its surface water quality program, and Quebec and New Brunswick are currently concerned about their continued level of support for such programs. Federally, water quality assessments are being reviewed with respect to their actual necessity and the possible effects of program reduction. Indeed, a research review questioned whether there were actually clients for basic research information on water quality! In such an atmosphere we cannot be overly optimistic about the future of quality assessments and future management of our aguatic resources.

Because of this apparent attitude in society or at least at political levels of our society, it might be prudent to speak of our future role only in scientific terms. Our basic purpose today is to determine how we might provide the best scientific advice on the plethora of water quality issues of today and tomorrow. What are the essential data sets required to ensure wise management decisions? How do we develop such data sets, and how do we enhance the awareness of the public concerning the present and future state of their water resources?

In the ECS Water Strategy paper it was asserted that historically we have managed water without regard to its life-supporting characteristics. It would seem appropriate then that we must change our perspective of the aquatic environment should we wish to manage the life-supporting characteristics of water for present and future generations of Canadians.

The Environmental Sensing Paper produced by EPS spoke of the capacity to predict, verify, assess and monitor impact and trends of toxic chemicals on environmental quality. Information gathered from these processes determines whether or not environmental quality criteria or guidelines are being met. Basically, these same information requirements can be applied to any environmental issue and not just toxics. Information is required to assess trends, compliance with guidelines and environmental impact. These three basic data sets are required for the future management of water quality particularly as related to the life-supporting characteristics of water.

There is also another future need for water quality concerns, that is, the close cooperation among the various agencies, whether operational or research, federal or provincial, fisheries, health or environmental, to recognize that although we have different mandates that tend to make us rather parochial, we share the same environment and we all have common environmental concerns. This is one part of the future that must be initiated in the next few days - a resolve to

work closely together at least at the scientific level. Keeping in mind what is happening to environmental agencies across Canada, it is good to remember the adage "United we stand, divided we fall!"

One thing is certain about the future of assessing the quality of the aquatic environment; much depends on our working together constructively, establishing links among the organizations represented here, and being able to develop an assessment framework from which we all can work. The task is large and much lies ahead. So welcome to our, and your, Monitoring Workshop.

Water Quality Branch Monitoring An Historical Review

by

R.E. Kwiatkowski

Water Quality Branch Inland Waters Directorate Environment Canada Ottawa, Ontario

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INTRODUCTION

Water represents one of Canada's most valuable resources. covering 7.6% of its surface. There is no substitute for water. The survival of all forms of life depends upon an adequate supply of water of acceptable quality. Thus, sound knowledge of water quality is essential to all levels of government for the management of Canada's present water uses and for the planning of future uses. While management responsibilities for water are shared between the provinces and the federal government, the federal government plays an important leadership role, particularly when addressing water quality level. national The Water Quality Branch (WQB), Inland Waters Directorate (IWD), Department of the Environment (DOE) is responsible for providing this leadership. This document outlines the evolution of the Branch's monitoring activities from its early conception in 1970, through its developmental years during the 1970s, to its present level, referred to in this document as the Agreement years. Throughout its development the Branch has collected and disseminated data, interpretive reports on water pollution problems within The purpose of the Water Quality Branch is to provide scientific and technical information and advice on water quality to promote the conservation and enhancement of the quality of Canada's inland water resources for the economic and social benefit of all Canadians (WQB 1985).

THE FORMATION YEARS

Water quality monitoring in Canada, which is mainly concerned with public health issues, has been carried out by various governmental agencies, universities and private firms since the late 1800s. Development of Canada's industrial base and rapid growth in agriculture throughout the twentieth century resulted in increased water quality concerns and, therefore, monitoring efforts. Reviews of pre-1970 water quality monitoring efforts can be found in Leverin (1947) and WQB In 1970, the water components of the Department of National Health and Welfare, and the Department of Energy, Mines and Resources, as well as the Fisheries Research Board of Canada were united as part of the Department of the Environment. The Water Quality Division of the Department of Energy, Mines and Resources was transferred to the Department of the Environment and later became the Water Quality The newly formed Branch was to promote the conservation and enhancement of the quality of Canada's inland water resources by providing scientific information and advice on water quality. this responsibility, the federal government enacted the Canada Water Act in 1970.

The Act provides for the management of Canada's water resources through research, planning and implementation, taking into consideration such factors as conservation, man-made developments, and water utilization. The Act covers three general areas in water resource management: the supply and demand of water, water quality management in critically polluted areas, and comprehensive water resource management programs.

ATLANTIC REGION

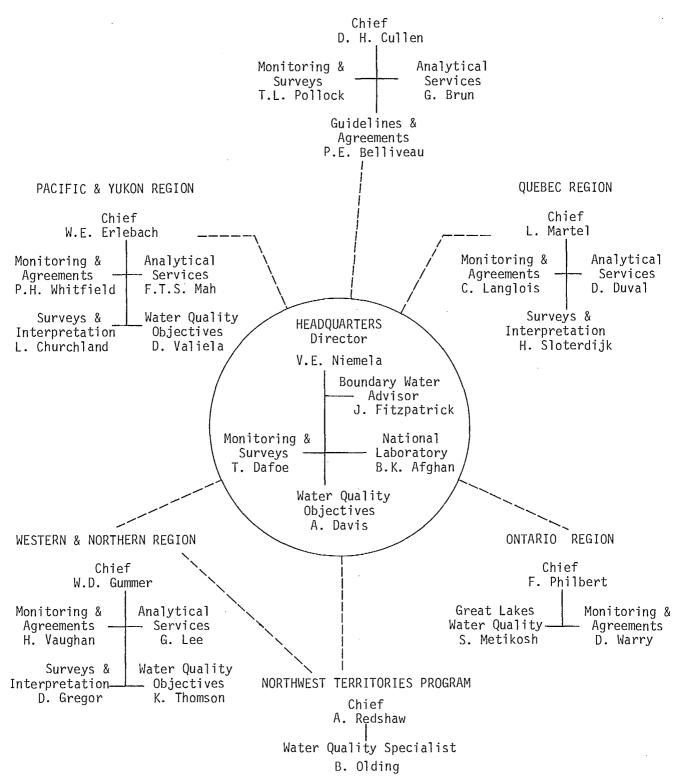


Figure 1. Water Quality Branch organization.

At its conception the Water Quality Branch consisted of 81 PYs, split between Ottawa, Moncton and Calgary. Each of these centres had a laboratory, where most of the staff were employed (Egar 1978). The Branch's first commitment to monitoring was within the International Hydrological Decade (IHD, 1964-1974), which had started six years prior to the Branch's conception. The main objective of the monitoring program carried out by WQB (WQB 1985) was to gather basic water quality data on surface waters across Canada. To meet this national objective, two new laboratories were established between 1970 and 1974 - one in Montreal and one in Vancouver, and the Ottawa laboratories were moved to a new regional office in Burlington. Thus by the mid-1970s the Branch, as today, consisted of a Headquarters (located in Ottawa) and five Regional Offices (Fig. 1).

During the Hydrological Decade the major water quality monitoring interests were with the physical and chemical measurements, such as major ions, specific conductance, pH, turbidity and colour. Since sample procedures were relatively simple, lay collectors (local residents paid to collect water samples at determined time intervals and ship them to Branch laboratories for analysis) were extensively used throughout the program (Egar 1978).

DEVELOPMENTAL STAGE

After the completion of the IHD in 1974, monitoring within the Branch moved from the establishment of baseline conditions of the physical and chemical measurements to one of monitoring broader management objectives, such as:

- (1) identification of pollution problems
- (2) trend assessments
- (3) surveillance of water quality objectives
- (4) assessment of the effectiveness of environmental regulatory measures.

The parameter list of routine measurements was expanded, new sampling procedures were developed, specialized equipment purchased, and lay collectors were replaced by professional field staff. Also by 1975, most of the provinces had developed their own water quality monitoring programs and the WQB began to concentrate its resources on areas of "significant national interest" which included, but were not limited to, areas of direct federal responsibility. Examples of cases of significant national interest included the management of boundary and international waters. interprovincial waters, waters in Indian Reserves, National Parks and the Territories; involving other federal waters. cases where jurisdictions, such as fisheries or navigation, were major concerns; or other such cases deemed by the Minister to be of sufficient importance to the people and the economy of Canada to require federal involvement.

By the late 1970s, an awareness had developed both within the scientific community and within the public at large of the susceptibility of the aquatic environment to degradation by deleterious substances in the environment. Program emphasis shifted from the study

of major ions and the characterization of general chemical quality to focus on specific pollutants, contaminants and nutrients, and the trends occurring in the quality of the aquatic environment (IWD 1977). Policy statements for the Inland Waters Directorate were prepared promoting joint, cost-shared, federal-provincial comprehensive river basin studies (IWD 1977). The studies were to include water quantity, water quality, water use and pollution control studies. Review of the historical WQB data sets (prior to 1976) for the purpose of issue identification and baseline river basin information identified a lack of both data confidence and data interpretability (IWD 1977). To ensure future confidence in the data set, monitoring programs were to develop comprehensive field and laboratory quality control components, and they were to address only specific, scientifically defensible questions, for which the data requirements could be identified prior to data collection.

The National Water Quality Branch's Monitoring Network identified in 1977 was composed of four sub-programs. The federal role (IWD 1977) of each sub-program was identified as:

Ambient Water Quality Monitoring Sub-Program Pollutant Specific Surveys Special Projects Trend Assessment Sub-Program

Each sub-program within the framework consisted of a set of projects rather than a network of stations. By focusing attention on project objectives it was felt a better definition of objectives, and in turn, a more critical evaluation of the monitoring activity carried out to meet the objectives would be realized. By emphasizing projects instead of networks, the framework would facilitate inter-agency cooperation and allow greater conceptual flexibility with respect to when, where and what to monitor.

Many of the environmental problems faced by the water managers during this period required holistic а view of the environment. Even though water was still the central focus of the Network, the concept of multimedia sampling (water, sediment and biota) identified as an essential component to any water monitoring program. A document entitled "The Role of the Water Quality Branch in Measuring and Assessing the Quality of the Inland Aquatic Environment" written 1978 defined the inland aquatic environment as including surface waters, ground waters, sediments and aquatic biota found within the confines of rivers, lakes, aquifers and estuaries. defined as including the flora. Aquatic biota was microorganisms existing in the waters and sediments of rivers, lakes, aquifers and estuaries (Gale 1980).

Two documents - "Report on the Use of Biological Monitoring in the Water Quality Branch Monitoring Program" (Clair <u>et al</u>. 1980) and "The Role of Biology in the Water Quality Branch Monitoring Program" (Shindler 1981) - provided the Branch with information on the use of aquatic biota measurements for the Water Quality Branch's measurement

and assessment programs, with emphasis on toxic substances and environmental assessment; which specific biological measurements should be immediately implemented; which specific biological measurements could be used but needed further research and development; and how the biological measurement program should be implemented.

It was felt (Clair et al. 1980) that through the incorporation of multimedia measurements into the WQB's assessment programs the Branch would be able to identify the presence of toxic compounds, hitherto undetected in water samples, and to determine their aerial extent and effect/impact on the aquatic community. No set biological techniques were presented by Clair et al. (1980) due to the knowledge that issues and therefore monitoring methods differed across Canada, and thus no hard and fast rules could be established with regard to which biological monitoring tool should be used by the Branch. However, the need for ongoing research into ways to implement and interpret biological data was established (Clair et al. 1980).

THE AGREEMENT YEARS

The WQB entered the 1980s in a state of transition. Implementation of the concepts outlined in the IWD policy statements and the WQB monitoring program, as detailed in IWD (1977), are still underway. Three major drawbacks have impeded the program's progress:

(1) The multimedia sampling (water, sediments and biota) to provide a holistic view of the aquatic environment has as yet not been successfully incorporated into the Branch's monitoring programs. Often it was only included as a separate component, requiring extra funds to implement, and when resources were restricted, was often However, with the myriad of issues the first component cut. (nutrients, metals, toxic organics) facing water quality managers today, the need to utilize the ecosystem or holistic approach to understand the aquatic resource properly is even more evident now than in the past. Water and sediment provide a transport mechanism for the pollutants of concern, while living organisms integrate the effects of low concentrations over long periods of time and provide an excellent means of detecting many pollutants and noting their One main objective of all environmental studies is to ensure the protection of the water for the most sensitive use: thus there is an inherent need to obtain information on the biotic component within each river basin. To achieve this, the WQB has had two biomonitoring workshops: one in Longueuil in 1983 to discuss which biomonitoring techniques were presently being used within the Branch, and one in Burlington in 1984 to discuss potential biomonitoring techniques in the various components within the biological community (bacteria, phytoplankton, zooplankton, The following Proceedings represent the benthos and fish). findings of a monitoring workshop, the purpose of which was to bring together the monitoring (WQB) and research (NWRI) components within IWD, to form a pool of expertise in all disciplines of the aquatic environment. Project leaders within each WQB Region will then be able to draw on this expert pool, as the need arises, to given environmental problem from a variety any perspectives and with a combination of approaches.

- (2) The WQB has historically been operational in nature. Research and support services are provided by the IWD research institutes, the National Water Research Institute and the National Hydrological Research Institute. The Branch, in turn, provides operational support to both institutes (WQB 1985). This division of research and monitoring, although adequate to meet the needs of the Branch in the past, now requires modification. Present-day pollutants are more difficult to monitor than those of a decade ago, encompassing a wide variety of elements and chemical compounds, some of which may be acutely toxic to fish or accumulate to unacceptable levels in sediments and in biological tissues. Evaluation of the effects of these toxic chemicals in the environment is a complex issue due to a large number of factors that can affect their toxicity. Some contaminants rapidly lose harmful effect through natural physical, chemical biological processes, whereas others break down to produce toxic by-products, thus requiring monitoring for the by-products, in addition to the parent compound. For many toxic chemicals, information on precise effects is unknown, and for others, the damages to biota have been assessed only for doses that are acutely toxic and the effects of small doses over long periods of time are generally unknown. Monitoring for these pollutants at extremely low concentrations (parts per trillion), from representative areas (both spatially and temporally), within a variety of media (water, requires research input. sediment and fish) IWD management presently strongly encourages the interaction of its research and operational components through the recent formation of working groups on monitoring, analytical methods and data storage, and water quality objectives.
- (3) The final drawback in the implementation of a holistic federal water quality monitoring network was the restriction of sampling almost exclusively to boundary stations or regions of national The acquisition of data from non-boundary waters within the provinces and territories was not considered to be within the Department's mandate. Consequently, the data collected by the Water Quality Branch lacked the spatial coverage needed to provide definitive information on location, severity, areal or volume extent, frequency and duration of deteriorated water quality conditions within the major river basins in Canada (WQB 1985). Water Quality Branch now promotes the collection of data on inputs from tributaries, point source discharges and the atmosphere to the necessary information for the development implementation of appropriate pollution control measures, or to identify emerging Also, issues. the Branch encourages standardization and quality assurance implementation on all sample collection, analytical analysis and data management, to ensure compatibility of data Canada-wide.

The basis for resolving these drawbacks was the 1982 Cabinet decision authorizing Environment Canada to negotiate federal-provincial water quality monitoring agreements (Table 1). The federal-provincial agreements represent a long-term commitment of the various agencies responsible for water quality monitoring for the acquisition of water

quality data on a river basin basis. Multimedia (water, sediment and biota) water quality information utilizing standardized methods with sufficient quality assurance to ensure data compatibility among agencies will be employed. Federal, provincial and external agency scientific personnel will be integrated into the monitoring program, from its conception to its final report.

Table 1. Federal-Provincial Water Quality Monitoring Agreements

		Sign	iìng
Province	Negotiations in progress	Signed	Projected
Newfoundland		April 1986	
Nova Scotia	Χ	r	
New Brunswick	χ		Mar. 1987
Prince Edward Island	χ		June 1987
Quebec		May 1984	
•	(effect	tîve Aprîl 1983	3)
Ontario	χÌ	•	Dec. 1987
Manitoba	Χ		Mar. 1987
Saskatchewan	Χ		Dec. 1987
Alberta	X		Jan. 1987
British Columbia	••	Oct. 1985	
Territories	Х		Submission to T.B.
	••		
			by Mar. 1987

In 1984, the Canadian Council of Resource and Environment Ministers (CCREM) decided to publish Canadian Guidelines for Water Quality. These guidelines are the first step toward the establishment Canada. site-specific water quality objectives across objectives represent limiting characteristics of water, sediment or biota that have been negotiated to support and protect designated water uses (WQB 1985). It is fully recognized that both provincial and federal governments have legislative responsibility for water. Provincial governments have legislative power over water pollution control, power generation and recreation, and the federal government is responsible for navigation and fisheries. As well, the federal government has an overriding jurisdiction on international waters and over the regulation of interprovincial waters. policies related to water management recognize the joint jurisdiction in water matters and are designed to encourage the bringing together of the powers of both governments to solve water management problems or plan management actions.

The Canada Water Act (CWA) became the prime instrument for federal-provincial cooperation water matters on administered mainly by the Inland Waters Directorate. The Act calls for comprehensive river basin studies (monitoring and research) to be undertaken in jointly funded programs with the provinces, and for subsequent joint implementation of the study recommendations. studies are to encompass both quantity and quality considerations and seek to identify and recommend optimum use, allocation and management of the waters within a river basin to reduce or prevent pollution. Specific descriptive and parametric water quality objectives for the protection and enhancement of essential and desired uses, and for the protection of the aquatic ecosystem are inherent within the Act.

The Water Quality Branch Assessment Program (WQB 1984) was developed with the following specific objectives:

(1) to determine changes and long-term trends in water quality

(2) to detect emerging problems on a local, regional and national scale

(3) to determine the effectiveness of regulatory actions related to legislative controls (e.g., phosphorus limitation in detergents, bans on the importation, use and manufacture of PCBs)

(4) to determine compliance with water quality objectives (where these have been implemented)

(5) to determine the need for special (cause and effect) studies.

Before entering into the Agreement negotiations with the provinces, a large amount of preliminary work has been carried out by the Water Quality Branch to ensure that the Water Quality Branch Assessment Program is able to fulfill its objectives.

Assessment of water quality requires reliable data. Handbooks outlining agreed-upon methods for sample collection and handling have been, or are presently being prepared (Sampling for Water Quality - WQB, 1983; Field Quality Assurance - WQB, in press). Manuals on approved laboratory analytical methods (Analytical Methods Manual - Environment Canada, 1979) and laboratory quality control (Quality Assurance Methods Manual - WQB, in press) also exist. It is not expected that all regions be identical in their data collection and analysis techniques, but rather that certain approaches be agreed upon as being acceptable for providing data that would be comparable. The Branch presently devotes approximately 15% of its efforts to inter- and intralaboratory quality assurance to ensure reliable data.

Although regional laboratories in Moncton. Longueuil. Saskatoon and Vancouver provide direct support to field units, the Branch is in the process of consolidating its capability for complex and expensive analyses with the National Water Quality Laboratory (NWQL) located at the Canada Centre for Inland Waters in Burlington, The National Laboratory's primary purpose is to provide analytical services to support regional Branch programs. laboratory system was started in 1983 and completed in 1985. National Laboratory brings together teams of highly skilled analysts with the most sophisticated instruments, significantly improving the efficiency of the operational laboratory system and eliminating variability among laboratories so often found in large monitoring programs (WQB 1985).

The handling of thousands of data points annually by laboratories and data users requires an integrated computer network. Storage of all data collected under the Water Quality Assessment Program in a central data bank, NAQUADAT, will ensure that all agencies involved in the program will have quick and easy access to the data (Whitlow and Lamb 1983). Data management activities within the Branch fall into three broad categories (WQB 1985).

- (1) Laboratory Management The Automated Water Quality Laboratory System (AWQUALABS) is the primary data processing activity within the National Laboratory. The system accepts data directly from analytical instruments, performs quality control checks, and produces immediate reports on the status of any sample.
- (2) Data Management Verified data are transferred from AWQUALABS to regional computer systems and/or directly to NAQUADAT. NAQUADAT's storage and retrieval systems are designed to accommodate both federal and provincial data from stations across Canada.
- (3) Data Interpretation Increased emphasis on interpretative information has, in recent years, outpaced the capabilities of the Branch. In the past, interpretation consisted simply of providing descriptive statistics. Now, to be more useful to water managers, water quality interpretations are supported by more comprehensive data analysis and graphical presentations. More powerful tools are being applied and new approaches developed to understand water quality in both time and space dimensions.

Due to the varied backgrounds of the people involved in water quality monitoring, and the specific interests of the various agencies involved, statistical expertise differs greatly between agencies. assist all agencies involved in the Water Quality Branch Assessment Program in their treatment of the data, the Branch is presently preparing a statistical manual as well as a statistical course on statistical procedures applicable to water quality monitoring (Water Quality Data - Presentation and Analysis - WQB, in press). A Workshop on the Statistical Aspects of Water Quality Monitoring, cosponsored by the National Water Research Institute and the Water Quality Branch, was held on October 7-10, 1985. The Workshop provided an international scientists, statisticians users of statistical forum for and methodology in limnology, water quality regulations and control, design and aquatic environmental monitoring network modelling (El-Shaarawi and Kwiatkowski 1987).

CONCLUSIONS

The WQB monitoring program has undergone a series of changes in response to new demands. Demands have changed from the establishment of background levels of simple physical and chemical measurements, as done during the Hydrological Decade, to the measurement of the complex interaction of the biogeochemical components within the aquatic ecosystem. The present program is designed to determine the effect of man's activities on the quality of Canada's ecosystem. The federal-provincial agreements establish a national river basin water quality monitoring network designed to provide

information on the location, severity, areal or volume extent, frequency and duration of objectionable levels, as a basis for the establishment of environmental policy and remedial action. The program also supplies a mechanism for the evaluation of policy decisions or remedial action; determines aquatic ecosystem trends; identifies new or hitherto undetected problems; and supplies data for objective compliance monitoring. Water quality objectives, such as those already established through the Canada-United States Great Lakes Water Quality Agreement and other bilateral agreements, will provide a common basis for assessing water quality nationally.

The information obtained from the programs will reflect the state of the art knowledge of the aquatic environment. It will be based on information that already exists in the literature and that provided by federal and provincial networks. The first use of the data collected will be to evaluate whether the most cost-efficient network has been established. If not, modification of the program to incorporate the findings of the new information will be done. This evaluation of the network is seen as a necessary yearly process.

The following reports will be generated: National Assessments supplying federal provincial governments with trend-in-time and information, identification of new or hitherto unknown problems, and identification of the quality of the overall aquatic environment within the province or within Canada; Basin Networks reflecting the quality of the aquatic environment on a river basin basis with emphasis on integrating federal and provincial data to provide state of the art Studies knowledge of the basin: and Special supplying more comprehensive information on localized conditions and/or special issues of concern to the federal or provincial governments (WOB 1984).

The mandate of the Water Quality Branch is to supply the scientific information needed to address Canada's water quality problems. This can only be done in a cost-efficient manner through constant evaluation of existing programs and through the evolution of the Branch to meet the complex environmental problems facing Canada today and in the future.

ACKNOWLEDGMENTS

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ATLANTIC REGION

Selected Agricultural Pesticide Residues in Water, Sediment and Biota of Lakes and Rivers of the Annapolis Valley, Nova Scotia

by

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ABSTRACT

An overview of the levels of selected pesticides in water, sediment and aquatic biota was conducted in the Annapolis Valley of Nova Scotia, an area of important agricultural activity during 1984. Results showed that the herbicides 2,4-D and atrazine were at levels above detection limits in water, although below levels deemed to be deleterious to aquatic life. DDT, mancozeb and dichlone were found in sediments, although it was not possible to assess their potential toxic effect. Fish sampled at a number of sites showed measurable accumulations of DDT and mancozeb.

This study has identified a number of factors necessary in setting up studies of short-lived pesticides and identifies the need for methods to assess the toxicological effects of sediment pesticide concentrations. It also suggests that atmospheric transport of some pesticides affects their presence in the Annapolis Valley.

INTRODUCTION

Intensive use of agricultural pesticides is now a feature of modern farming practice. Although the benefits gained by their use are uncontested, the very nature of pesticides ensures that there is always a chance that they could have an impact in non-target areas due to their misuse or to unexpected environmental conditions.

There is abundant information on the toxicological effects of many pesticides in water, on aquatic organisms (U.S. EPA 1980), and of the probable chemical behaviour of pesticides in nature (Moore and Ramamoorthy 1984). Yet there is still a paucity of data on actual ambient levels of most short-lived chemicals. These data are necessary to test whether laboratory toxicity tests are relevant to natural conditions, to identify gaps in our understanding of pathways of pesticide residues in nature, and to provide information needed by water resource managers responsible for setting water quality objectives based on watershed uses.

A study was undertaken by the Water Quality Branch, Atlantic Region, on the distribution of agricultural pesticides in the Annapolis Valley of Nova Scotia to provide information on their levels in the aquatic ecosystems. This information would then be compared with toxicological information to assess the health of freshwater habitats in the area. The Annapolis Valley was chosen, as it is probably the basin with the most intensive agricultural activity in Nova Scotia, and perhaps in the Atlantic provinces. As with much of the Atlantic Region, the study area receives 1-1.5 m of precipitation (Department of Transport 1967) which could affect the dynamics of pesticide movement. Although there may be some use of surface waters for the irrigation of farms, the major use of the area's lakes and streams is as fish Parker and Doe (1981) report that 12 species of fish are known to inhabit the Annapolis River in the western end of the valley and that poor survival of the larvae of striped bass, Morone saxatilis (Walbaum), is an important concern. They concluded that two possible point sources of pollutants, a sewage lagoon and a plastic plant, were not responsible for the problem, nor could PCBs, 2,4-D and DDT in water and sediments be implicated (Parker 1984). The authors suggested that other pesticides could be partly responsible for the poor success of this population, and that this possibility should be explored.

The strategy chosen was to begin an overview of the lakes and streams of the Annapolis Valley area that receive various types and amounts of pesticides. The sampling effort was designed around a seasonal cycle so that a comparison of pesticide levels in aquatic ecosystems could be made during the spring, before pesticides were applied, during the summer, at the peak of chemical use, and in the late fall, after harvesting was complete.

AREA

The Annapolis Valley is located in the northwest corner of Nova Scotia. The study area chosen encompasses all of King's as well as the northern third of Annapolis County. Approximately 65 000 people

inhabit the study area, with two thirds of them in rural communities and the rest in small towns located on river banks (Statistics Canada 1981). The study area covered approximately 300 000 hectares (ha) of which one third was farmed. In 1981 the major crops, with a value of over \$100 million, included, in order of area used, grains and hay, apples, peas, beans and potatoes (Statistics Canada 1981). Of the 100 000 ha farmed, 11 500 were sprayed with herbicides and over 9000 ha, with insecticides and fungicides (ibid), although no published information is available on what products were used or in what quantities.

Four rivers drain into the Bay of Fundy from the study area: the Annapolis with a basin size of 102 000 ha, emptying the western least inhabited section, and the Cornwallis, Canard and Habitant rivers, draining the eastern end (Fig. 1). A number of small lakes or ponds often surrounded by farmland are found on the Valley floor. The study area is bordered on the north and south by two mountains called the North and South mountains, which shelter the Valley from the cooling influences of the Bay of Fundy and the Atlantic Ocean, respectively.

Seven lotic and two lentic sites were chosen on the Valley floor, based on accessibility and on coverage of the major farming areas (Table 1, Fig. 1). Two other sites, a river and a lake located in wooded areas of the South and North mountains, respectively, were chosen as controls, since no agricultural activity occurred in their basins.

METHODS

Although no published information existed on the types and amounts of pesticides used in the Annapolis Valley, the Nova Scotia Departments of Agriculture and Environment had identified a number of products for which they needed further information (D. Waugh, N.S. Department of Environment, pers. comm.). These were reviewed and a list was made of those for which analytical methods were available in-house (Table 2). A literature search was made to identify some of the physical, chemical, and toxicological characteristics of the identified pesticides, and these are reported in Table 3.

All pesticide analyses were done according to NAQUADAT (1985) except for mancozeb, dichlone, and captan, which were analyzed by electron capture gas chromatography under contract and those parameters whose codes begin with 88 or 89. Descriptions of these methods are in Appendix A.

To complement the pesticide data, a number of other parameters were also analyzed in water, sediments, and biota. Major ions, physical parameters, metals, and nutrients were analyzed in water, using standard Water Quality Branch methods (NAQUADAT 1985); percent carbon was analyzed in sediments and percent lipid content was measured in biota samples.

Water samples were collected in pre-cleaned 4-L glass bottles. Organochlorines (OC), polychlorinated biphenyls (PCBs), and organophosphate (OP) water samples were preserved with 100 mL of

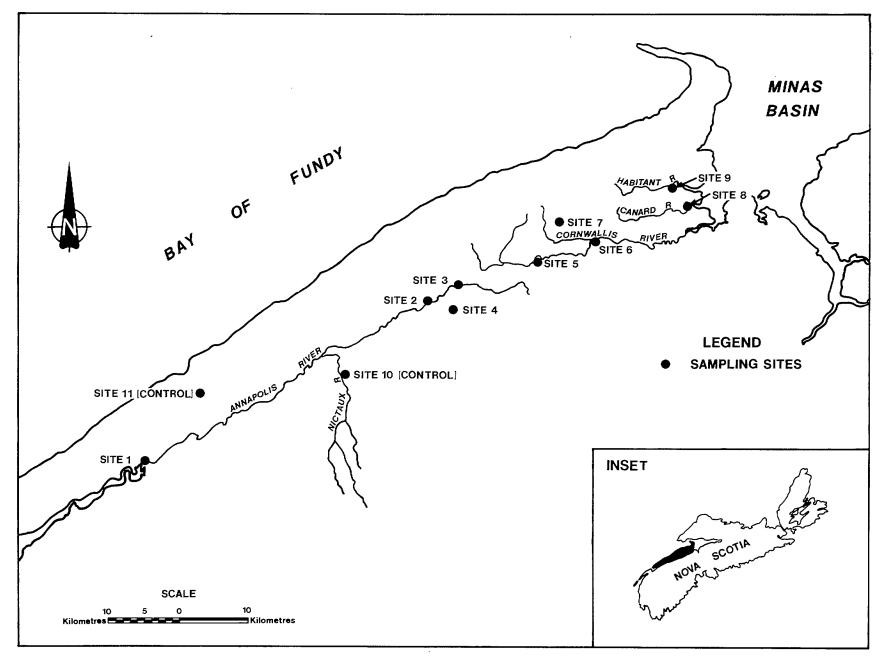


Figure 1. Location of stations.

hexane. Carbamates and triazine herbicides were preserved with concentrated sulphuric acid ($\rm H_2SO_4$) to pH 3.5. All bottles were kept cool until extracted. Major ion and metal samples were also kept cool until analysis. All sediment and biota samples were frozen immediately after collection and brought to the lab. Spiking of both water and sediments with known concentrations of nine pesticides representing the main pesticide groups was done on every field trip, and percent recovery was calculated.

Table 1. Station NAQUADAT Numbers and Locations for the Annapolis River Survey of 1984

Station No.	NAQUADA No.	ΛT	Location
1	02NS01DC0004 52NS01DC0004		Annapolis River near Mochelle
2	00NS07DC0091 50NS07DC0097		Annapolis River at Palmer Road, Auburn
3	00NS01DC0084	(water)	Annapolis River at Hwy bridge 2 km East of Aylesford
4	01NS01DC0009 51NS01DC0009 90NS01DC0009	(sediment)	Pond at Klahanie Campground, Aylesford
5	00NS01DD0038 50NS01DD0038		Cornwallis River at Waterville
6	00NS01DD0036 50NS01DD0036		Cornwallis River at Lovett Road Bridge
7	01NS01DD0006 51NS01DD0006 90NS01DD0D06	(sediment)	Silver Lake at centre, Lakeville
8	00NS01DD0039 50NS01DD0039		Canard River 200 m above The Aboiteau
9	00NS01DD0037 50NS01DD0037		Habitant Creek, 50 m above secondary road bridge, Hillaton
10	01NS01DC0010 51NS01DC0010		Nictaux River at dam, Nictaux Falls (control)
11	01NS01DC0008 51NS01DC0008 90NS01DC0008	(sediment)	Ramsey Lake at centre (control)

Table 2. Organic Contaminants Analyzed from the Annapolis Valley, N.S.

		<u>Detection Limit</u> Water NAOUADAT Sediment			NAQUADAT parameter code*	
Pesticide	Use	(ng·L ⁻¹)	NAQUADAT parameter	Sediment and Fish (µg·kg ⁻¹)	Sediment	Fish
p,p-DDT	Insecticide	1	18000L	7	18009L	18602L
o,p-DDT	Insecticide	1	18005L	7	18008L	18606L
p,p-DDD	Insecticide	1	18010L	1	18012L	89551L
p,p-DDE	Insecticide	٦	18020L	7	18026L	18621L
p,p-Methoxychlor	Insecticide	10	18030L	50	18034L	18631L
Heptachlor	Insecticide	1	18040L	7	18043L	18631L
Heptachlor epoxide	Insecticide	7	18045L	7	18048L	18646L
Alpha-endosulfant	Insecticide	10	18050L	10	18054L	18651L
Beta-endosulfan†	Insecticide	10	18055L	10	18058L	18656L
Alpha-chlordane	Insecticide	5	18060L	5	18063L	18661L
Gamma-chlordane	Insecticide	5	18065L	5	18068L	18666L
Gamma-BHC	Insecticide	٦	18070L	1	18079L	18671L
Alpha-BHC	Insecticide	7	18075L	1	18074L	18676L
Mirex	Insecticide	7	18125L	1	18128L	18629L
Aldrin	Insecticide	1	18130L	7	18133L	18632L
Endrin	Insecticide	10	18140L	10	18143L	18642L
Dieldrin	Insecticide	7	18150L	N.D.	N.D.	N.D.
Malathion†	Insecticide	5	18250L	5	89052L	89053L
Guthiont	Insecticide	10	18190L	10	89045L	89044L
Phorate†	Insecticide	5	18300L	5	89048L	89049L
2,4-D†	Herbicide	4	18500L	4	18501L	89482L
2,4,5-T	Herbicide	2	18510L	2	18511L	89484L
Carbofuran†	Insecticide	10	89271L	100	89272L	89347L
Carbary1†	Insecticide	5	18400L	50	88401L	88402L
Atrazine†	Herbicide	20	89802L	5	89803L	89840L
Captan†	Fungicide	N.D.		1		
Dichlonet	Fungicide	N.D.		1		
Mancozeb†	Fungicide	N.D.		1		
% Carbon		N.D.		!	06076L	N.D.
% Lipid		N.D.		?	N.D.	89990L

^{*}Codes beginning with 89 and 88 or left blank are described in Appendix A.

[†]Identified by N.S. Department of Agriculture as being of importance.

[!] Sediments only.

[?] Biota only.

N.D.= Not done.

Table 3. Selected Chemical Properties of Pesticides Currently Used and Found in the Annapolis Valley Sites

Chemical	Vapour []] pressure (mm Hg)	Solubility ^l in water	Soil ² adsorption coefficient	Bioconcentration ² factor	Persistence ³ in water or sediments	Comments on the toxicity ³ to aquatic life
DDT	1.9 x 10 ⁻⁷ at 20°	Insoluble	238 000	61 600 ⁴	Several years	LC ₅₀ 0.07 ppm (mosquito larvae)
Endosulfar	n 1.0 x 10 ⁻⁵ at 25°	Insoluble	No data	No data	3-7 days in water, longer in sediments	LC_{50} 0.01 mg·L $^{-1}$ for <u>Gammarus</u> (lower for fish)
Alpha-BHC	0.06 at 40°	10 mg·L ⁻¹ at 25°	911	3254	Several years	No data
Malathion	4.0 x 10 ⁻⁵ at 30°	145 mg·L ⁻¹ at 25°	No data	05	Several days	LC_{50} 0.1 mg· L^{-1} catfish
Guthion	Negligible at 25°	33 mg·L $^{-1}$ at 25°	No data	No data	1-3 weeks	Highly toxic to fish
Phorate	2.4 x 10 ⁻⁴ at 20°	50 mg·L ⁻¹ at 25°	3200	No data	4-12 weeks	No data, although OP's can be very toxic
2,4-D	1.1 x 10 ⁻² at 25°	620 mg·L ⁻¹ at 25°	20	₀ 5	A few weeks	LC ₅₀ 1.0 to 250 mg·L ⁻¹ on fish, depending on ester
Atrazine	3.0 x 10 ⁻⁷ at 20°	30 mg·L ^{-]} at 20°	149	05	3-4 months	Low
Carbofuran	n 2 x 10 ⁻⁵ at 33°	700 mg·L ⁻¹ at 25°	No data	05	1-2 months	LC_{50} 0.28 mg·L $^{-1}$ to trout
Carbaryl	<4 x 10 ⁻⁵ at 25°	3.3 mg·L ⁻¹ at 25°	230	<15	2-6 weeks	LC_{50} 0.02 mg·L $^{-1}$ to <u>Gammarus</u>
Captan	1 x 10 ⁻⁵ at 25°	3.3 mg·L ^{−1} at 25°	No data	No data	1-7 hours	LC_{50} 0.028-0.07 mg·L ⁻¹ to fish
Dichlone	No data	0.1 mg·L ⁻¹ at 25°	No data	No data	No data	Very toxic to fish at 1 ppm, 0.01 will immobilize <u>Daphnia</u>
Mancozeb	No data	Insoluble	No data	No data	4-6 weeks	Low

l From Worthing (1979). 2 From Kenaga and Goring (1979). 3 From Seatech (1982). 4 In running water. 5 In standing water.

Sites were visited on the weeks of May 14, July 2 and October 15 in 1984. At each site, water and sediment samples were taken. Water samples were taken directly into bottles from the middle of the water body, following Water Quality Branch, Atlantic Region field methods described by Arseneault et al. (1984). Three sediment samples were collected using a 23 x 23 cm 2 Ekman grab at each site. Only the top 1 cm of the grab sample was taken, using a metal scraper. Samples were immediately frozen in aluminum pie plates precleaned with acetone and hexane.

During the May sampling, attempts were made to drag river and pond bottoms with a clam dredge. As insufficient numbers of mussels were recovered at any site, this part of the study was dropped. At each site for all sampling trips field crews wearing waders swept the shore with a 0.5-mm mesh seine, 10 m long, to capture forage fish. All captured fish were identified, placed in washed aluminum containers, and immediately frozen. Samples were then brought to the laboratory within four days of collection and were subsequently analyzed.

RESULTS AND DISCUSSION

Table 4 demonstrates the range of recoveries from spiked samples measured during this project. They are deemed satisfactory, since they encompass errors from matrix effects, analytical variability and sampling variability for spiking levels at the low range of instrument capability. The values indicate that the reported results will tend to be biased low.

Table 5 gives the ranges of important major ion parameters at the sampling sites over the three field trips. The Annapolis River at Mochelle, the Cornwallis River at Waterville, and the Canard River were affected by tidal influence as shown by the high specific conductance levels. These sites also tended to have high turbidity levels due to the stirring up of bottom sediments by tidal action. Also noted are the high levels of nitrate-nitrite at the Cornwallis Basin sites, which indicate the influence of crop fertilization in the eastern section of the Valley. Apart from showing tidal influence or high levels of fertilizers, the major ion data show the Annapolis Valley sites to have relatively high pH and major ion levels compared with much of the Atlantic Provinces due to high limestone levels in soils and bedrock. None of the metals measured (Cu, Pb, Zn, Fe, Mn, Al, Cd) exceeded guidelines for human intake or use by aquatic life.

Table 6 shows the levels of the only three organic contaminants which were measured in surface waters. Alpha-BHC, a lindane isomer, was ubiquitous, being found at all sites, although at levels near the detection limit. Lindane is used for seed treatment and livestock insect control as well as against soil dwelling and phytophagous insects (Seatech 1982), although little is known of the actual quantities used in Nova Scotia. It is quite persistent, fairly volatile (Table 3), and has been consistently measured in precipitation at nearby Kejimkujik National Park (Brun 1984). The levels measured in this study are probably only background levels due to long range transport effects and not to local use.

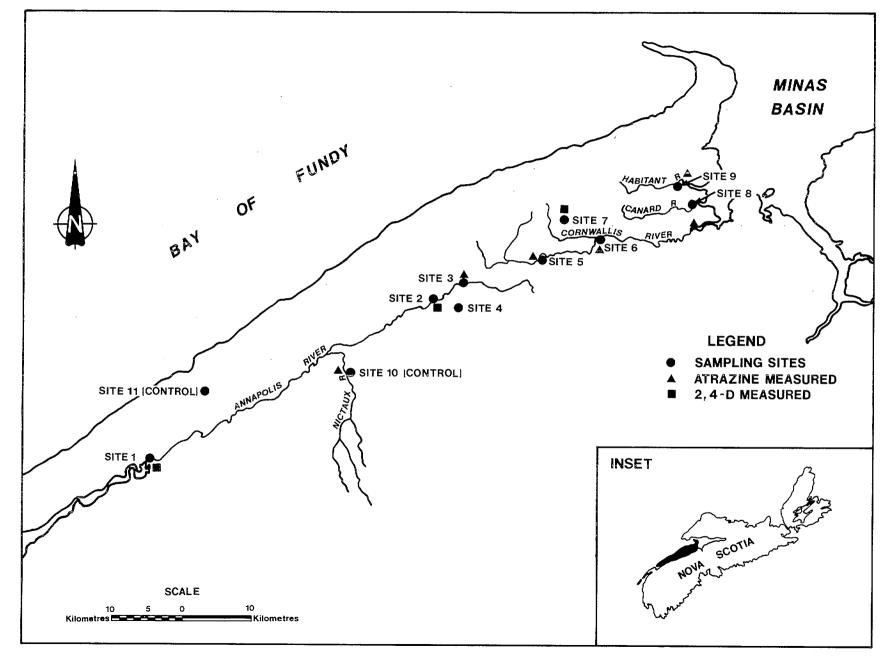


Figure 2. Location of stations where herbicides were measured.

Table 4. Recoveries of Selected Spiked Pesticides from Water and Sediments in the Annapolis Valley

		Percent recovery	
Pärameter	May (2 spikes)		October (1 spike)
<u>Water</u>			
p,p-DDE	84,32	125	
Alpha-endosulfan	97,52	100,104	155
Beta-endosulfan	128,52	160,138	152
Malathion	50,48	74	
Guthion	88,100	136	-
2,4-D	84,90	89,92	83
Carbofuran	72,82	65,108	101
Carbaryl	27,64	100,80	88
Atrazine	78,81	88,80	128
<u>Sediment</u>			
p,p-DDE	80	134,62	-
Alpha-endosulfan	100,100	100,100	46
Beta-endosulfan	20,20	40,20	_
PCBs	79,139	100,72	108
Malathion	43,60	75,16	112
Guthion	91,74	100,78	-
2,4-D	40		vien
Dichlone	78	84	73
Captan	82	77	71
Mancozeb	72	76	69

Two relatively water soluble herbicides, atrazine and 2,4-D, were also measured in water: atrazine was measured mostly in the eastern end of the Valley and on all three sampling dates; 2.4-D was measured at the two most westerly sites, plus Silver Lake, only during the spring and summer samplings (Fig. 2). An exception to this pattern occurred when atrazine was measured at the Nictaux River control site Local usage probably explains the distribution of these In Nova Scotia, atrazine is mostly used to control weeds in corn fields and broadleaf plants in forestry applications, and 2,4-D is generally used to protect grain crops from weeds. Much of the eastern Annapolis Valley was seen to contain corn acreage, and the western end was dominated mainly by orchards, grains and cattle pasture. Moreover, logging activities were noted in the Nictaux Basin, suggesting that atrazine was perhaps used in a non-agricultural operation. Some correlation between crop type and herbicide use and distribution can thus be suggested. Of the two herbicides, atrazine has the greater persistence and the lower volatility (Seatech 1982),

Table 5. Range of Selected Parameters in Water of the Annapolis Valley over the Study Period

Site No.	Site	Нq	Colour (rel. Units)	Turbidity (JTU)	Spec. Cond. (μs·cm ⁻¹)	DOC (mg·L ^{-l})	NO ₂ -NO ₃ (mg·L-1)
1	Annapolis River at Mochelle	6.6-7.1	90	0.1-1.5	3900-7450	5.3-5.4	0.14-35
2	Annapolis River at Auburn	6.5-7.4	35-55	0.7-2.0	78-141	5.4-5.9	0.22-66
3	Annapolis River at Aylesford	6.6-7.4	30–125	0.7-1.3	70-109	3.5-16	0.3-1.3
4	Pond at Klahanie	6.5-7.0	140-200	0.5-1.4	76-89	1418	0.11
5	Cornwallis River at Waterville	6.8-7.5	15-100	1.6-41.0	289-2050	3.7-4.6	1.6-2.5
6	Cornwallis River at Lovett Road	6.7-7.4	15-50	0.5-0.8	193-194	3.3-8.0	1.3-1.5
7	Silver Lake	5.8-6.2	<5	0.5-0.8	42-44	4.0-4.7	<0.01
В	Canard River at Dam	7.0-7.6	_	33–210	428-830	7.0-8.7	1.2-2.1
9	Habitant Creek at Hillaton	6.9-7.7	15-20	1.2-1.9	310-380	3.7-3.8	2.0-2.1
10	Nictaux River at Falls	5.9-6.3	55-100	0.5	29-37	7.6-10	<0.01
11	Ramsey Lake	6.2-6.5	<5	0.3	36	2.0-2.7	<0.01-0.02

Table 6. Organic Contaminants in Waters of the Annapolis Valley ($ng \cdot L^{-1}$)

		1pha-B			,4-D			razine	
Site	May	July	Oct.	May	July	Oct.	May	July	Oct.
Annapolis River at Mochelle (1)*	2	5	5	BDL	81	BDL	BDL	BD1.	BDL
Annapolis River at Auburn (2)	1	2	1	BDL	94	BDL	BDL	BDL	BDL
Annapolis River at Aylesford (3)	1	2	1	BDL	BDL	BDL	BDL	135	BDL
Pond at Klahanie (4)	BDL	3	3	BDL.	BDL	BDL	BDL	BDL	BDL
Cornwallis River at Waterville (5)	1	2	BDL	BDL	BDL	BDL	50	BDL	30
Cornwallis River at Lovett Road (6)	1	2	1	BDI.	BDL	BDL	BDL	345	BDL
Silver Lake† at Centreville (7)	10	7	7	230	230	BDL	BDL	BDL	BDL
Canard River at Dam (8)	2	2	2	BDL	BDL	BDL	49	66	40
Habitant Creek at Hillaton (9)	1	2	1	BDL	BDL	BDL	33	55	30
Nictaux River† at Falls (10)	2	2	1	BDL	BDL	BDL	127	BDL	BDL
Ramsey Laket (11)	4	5	9	BDL	BDL	BDL	BDL	BDL	BDL

^{*} Site number is given in parentheses.

BDL = Below detection limit.

which is confirmed by its continued presence into the fall at three of the five sites where it was found. At the concentration levels measured in these samples, neither of the two herbicides nor alpha-BHC would present a threat to aquatic fauna (Table 3). As there was no overlap between herbicides at any site, and alpha-BHC was at a very low level, these data show that the pesticides that we examined in the water column did not potentially compromise aquatic life at the time of sampling.

[†] Control.

A suite of pesticides different from those measured in water was found in sediments. The only organochlorine contaminant measured was DDT and its degradation by-products (Table 7), although trace levels of alpha-BHC and aldrin were measured in May and July at Klahanie Pond and Habitant Creek, respectively. All four DDT breakdown products -p,p-DDT, o,p-DDT, p,p-DDD and p,p-DDE - were found at most of the sites in the same general proportions and levels as they have been found in the upper Saint John River valley (Bailey 1985).

The presence of DDT in samples comes as no surprise. Although its use in Canada was banned in the 1960s, its persistence and its high soil absorption coefficient ensure that it will be found in sediments for years to come. The only place where DDT was not found in samples collected was at the Nictaux River site. The continued scouring of the site because of the steep river bed probably keeps sediments from accumulating, so that fresh material is constantly being deposited. Little variability between replicate samples and between sampling times was noted for DDT except at Silver Lake, where spring values were considerably lower than the remaining two times, which was probably a reflection of spatial variability within the lake.

Two other compounds, the fungicides dichlone and mancozeb, were measured in sediments. As with DDT, they are insoluble in water (Table 3), and so probably have a pronounced affinity for sediments (Kenaga and Goring 1980). Unlike DDT, they are in current use, as both chemicals are sprayed on potatoes and/or orchards (Agriculture Canada pers. comm.) and have relatively short half-lives (Seatech 1982). Because of the suggested affinity for sediments, a major pathway of contaminants to lake bottoms should thus be soil particles running off from fields into lakes and rivers, as has been measured elsewhere for other chemicals (Blachford and Ongley 1984). Other studies have also shown some correlation between the organic fraction of sediments and DDT and other pesticides (Hague et al. 1977). significant No correlations, however, could be drawn between any pesticide and percent carbon of sediments. The lack of correlation could be due to the small sample size used in the calculations.

Dichlone was measured at seven sites, including both control sites, and mancozeb was found at six, including Ramsey Lake (Table 7). Both chemicals were found sporadically at most sampling sites, although in some cases, they were found all three times. Unlike herbicides in water, there were no east-west differences in fungicide distribution (Fig. 3). There was also poor reproducibility in replicate samples, probably due to heterogeneity of the substrate, as the fungicides, with their relatively short half-lives, may not be as well distributed in sediments as DDT, which has been around for a much longer period and has probably been subjected to more homogenizing influences such as physical and biological mixing of the sediments.

The presence of fungicides in sediments at the control sites raises a number of interpretation problems. One possibility is that sample contamination had occurred, but only an indirect argument could counter this claim. Quality control in the field was as strict as could be done, with immediate freezing of samples <u>in</u> <u>situ</u>. Also, laboratory

Table 7. Organic Contaminants in Sediments of the Annapolis Valley ($\mu g \cdot kg^{-1}$) (mean and S.D. of 3 values)

		DDT		Ma	ncozeb		Di	chlone		Perc	ent ca	rbon
Site	May	July	Oct.	May	July	Oct.	May	July	Oct.	May	July	
Annapolis River at Auburn	12 <u>+</u> 6	6.3 <u>+</u> 2.3	6.0 <u>+</u> 0	3.7 <u>+</u> 0.7	BDL	1.0 <u>+</u> 0.1	BDL	6.0 <u>+</u> 8.0	60 <u>+</u> 100	3.1 <u>+</u> 1.0	5.1 <u>+</u> 1.0	4.8 <u>+</u> 0.1
Annapolis River at Mochelle	3.0 <u>+</u> 0	3.0 <u>+</u> 0	BDL	Trace	BDL	BDL	BDL	BDL	BDL	4.5 <u>+</u> 1.4	2.6 <u>+</u> 0.3	9.3 <u>+</u> 1.4
Pond at Klahanie	310 <u>+</u> 45	280 <u>+</u> 51	200 <u>+</u> 25	BDL	BDL	BDL	Trace	4 <u>+</u> 7	11 <u>+</u> 17	27 <u>+</u> 4	69 <u>+</u> 5	36 <u>+</u> 5
Silver Lake at Centreville	65 <u>+</u> 40	330 <u>+</u> 240	360 <u>+</u> 130	BDL	BDL	7.4 <u>+</u> 2.7	10.0 <u>+</u> 15	58 <u>+</u> 52	10 <u>+</u> 10	33 <u>+</u> 0.7	35 <u>+</u> 1	45 <u>+</u> 12
Cornwallis River at Brooklin Corner	10 <u>+</u> 4	Not done	5.0 <u>+</u> 0	BDL	Not done	Not done	Trace	Not done	Not done	11 <u>+</u> 3	Not done	3.5 <u>+</u> 0.7
Cornwallis River at Waterville	10 <u>+</u> 4	4.3 <u>+</u> 1.5	13.0 +10	3.7 <u>+</u> 3.1	3.0 <u>+</u> 3.0	19 <u>+</u> 9	30 <u>+</u> 52	BDL	BDL	7.0 <u>+</u> 2.1	6.8 <u>+</u> 0.8	13 <u>+</u> 2
Habitant River	13 <u>+</u> 6	4.7 <u>+</u> 10	20 <u>+</u> 2	BDL	2.8 <u>+</u> 1.8	BDL	BDL	32 <u>+</u> 3	BDL	12 <u>+</u> 7	7.1 <u>+</u> 1.9	8.0 <u>+</u> 2.4
Canard River	17 <u>+</u> 2	9.7 <u>+</u> 4	26 <u>+</u> 6	1.5 <u>+</u> 4	5.8 <u>+</u> 3.4	9.4 <u>+</u> 7.3	BDL	BDL	BDL	3.4 <u>+</u> 1.1	4.3 <u>+</u> 0.2	3.0 <u>+</u> 0.3
Nictaux River at Falls	BDL	BDL	BDL	BDL	BDL	BDL	BDL	20 <u>+</u> 24	5.0 <u>+</u> 7.0	4.3 <u>+</u> 1.6	6.7 <u>+</u> 0.7	11.8 <u>+</u> 0.3
Ramsey Lake	4.0 <u>+</u> 0	3.0 <u>+</u> 0	3.3 <u>+</u> 0.6	5.3 ±2.5	2.0 <u>+</u> 1.6	3.1 <u>+</u> 2.0	15 <u>+</u> 25	54 <u>+</u> 46	56 <u>+</u> 69	8.9 <u>+</u> 1.1	15 <u>+</u> 1	15 <u>+</u> 2

BDL = Below detection limit.

analyses were done blind, so that the constant levels measured for both pesticides at Ramsey Lake and at Nictaux could only be due to random laboratory analytical errors, an unlikely occurrence.

Examination of topographic maps offers a possible explanation for the presence of fungicides at the control site. Ramsey Lake was only 1.5 km from the valley floor, with a 200 m elevation difference. whereas the Nictaux site was approximately 4 km from the nearest orchards and only 150 m higher. Ground spray application of both fungicides can cause the drift of droplets away from the target area, to sites up to 35 km away, depending on wind speed at application time, type of equipment used, and size of the spray droplets. Moreover. volatilization and entrainment as dust are also known to transport pesticides from treated fields (Lewis and Lee 1976). Because of the short distances from Ramsay Lake and the Nictaux River to orchards, short range transport of fungicides and not sample contamination is the more likely the source of detected values in the control lakes. The patterns of distribution of the two fungicides in sediments of the Annapolis Valley are very complex and cannot be predicted very accurately without more information on use patterns, climate and spraying equipment.

The contaminant levels found in sediments may be more of a concern to aquatic health than those measured in water. Few toxicity studies are available showing pesticide effects on sediment dwelling biota, although both DDT and dichlone are known to be toxic to animals (Seatech 1982). Their presence, especially in the case of dichlone which was at levels up to 65 ppb, could cause stress on benthic populations or even on fish eggs deposited on lake or stream bottoms. As benthic invertebrates are a major food source for fish, reductions in their populations from pesticide stress could also indirectly impact on fish and other higher consumers. More information, however, is needed before potential impacts of these levels of pesticides in sediments can be understood.

The direct impact of pesticide usage on the biota was only measured by studying contaminant levels in forage fish. Although freshwater mussels were to be sampled, empty shells were noted, and none could be collected at any site. Nor were forage fish found in numbers suitable for organic analysis at more than the three lake sites. The major species found was the banded killifish (Fundulus diaphanus), and some threespine sticklebacks (<u>Gasterosteus</u> <u>aculeatus</u>). Due to the small numbers captured, the two species were combined to provide enough material for pesticide analyses, results of which are shown in DDT was found at higher levels in fish of two lakes located Table 8. in agricultural areas than in the control lake. The only other pesticide measured in the fish was mancozeb found at the Klahanie Pond in May and July, and at a control site, Ramsey Lake in July. Unlike results from a number of other studies, no relationship between fish sample lipid content and either DDT or mancozeb levels could be measured, but there seems to be some relationship between percent carbon of lake sediments and DDT levels in the fish. As with the lack of relationship between pesticides in sediment and percent organic content, the small sample size is probably responsible for the lack of correlation.

Table 8. Organic Contaminants in Forage Fish of the Annapolis Valley $(\mu g \cdot kg^{-1})$

	Kla	hanie	Pond	Sil	ver La	ke	Ram	sey La	ke
Parameter	May	July	Oct.	May	July	Oct.	May	July	
DDT	53	25	26	68	48	NS	2	5	NS
Mancozeb	70	60	NS	<0.01	NS	NS	<0.01	35	NS
Percent lipid	2.5	1.8	2.2	1.6	1.8	NS	1.6	1.4	NS

NS = No sample.

The presence of DDT in the fish comes as no surprise, as it has also been measured in Labrador (Lockerbie and Clair 1983), having been transported there through long range weather systems (Rapport et al. 1985). The lakes in farmed areas probably are subjected to greater input of soils from fields where DDT was formerly used, so that their fish populations have higher body burdens than in Ramsey Lake. levels are probably due to past local use is partially confirmed by noting that p,p-DDT, o,p-DDT, p,p-DDD and p,p-DDE were all found in the Annapolis Valley, whereas only p,p-DDE and some o,p-DDT were measured near those levels in Labrador (Lockerbie and Clair 1983). levels in the fish had no relationship to either their lipid content or sediment levels. No residues were detected in Klahanie Pond sediments, yet May and July fish contained measurable levels. No further data were generated by this work which would help explain this discrepancy. This pesticide is not thought to be toxic to fish or other aquatic biota (Table 3), so that its presence does not indicate difficulties for aquatic life.

CONCLUSIONS

This study was only partially successful in producing information for evaluating the freshwater system of the Annapolis Valley as an environment for fish and other biota. The study found that the herbicides and OC's measured in water did not pose a danger to aquatic flora and fauna, as their levels were well below LD $_{50}$ levels. No OP levels were measured in water, although quality control tests showed poor recovery of these compounds from spiked samples. Based on studies elsewhere (Brun 1984), we can conclude that alpha-BHC originated in precipitation. However, we can only suggest that based on their water solubilities and locations found, 2,4-D and atrazine probably enter the system in runoff.

Other data showed that water insoluble compounds such as DDT, dichlone and mancozeb are found in sediments. DDT levels are most likely due to past local use and inputs through runoff, whereas the distribution of the fungicides suggests that short range atmospheric

transport may be a factor in their transport, as is runoff of sediment particles in heavy use basins. No information was found in a thorough reference search to allow an assessment of the toxicological properties of the compounds found in sediments, so that we could not determine their probable effect on biota. DDT and mancozeb were found in the tissues of forage fish, although the low levels of DDT and the low toxicity of mancozeb did not cause alarm. The absence of dichlone from fish, however, could either indicate that no transfer from sediments is occurring or that it is having toxic effects on aquatic populations which are then not sampled.

This study has thus identified a number of agricultural pesticides found in measurable quantities in the Annapolis Valley and has also identified some potential pathways for their transfer through the Due to inadequate toxicological and use information, environment. however, we were unable to place our results in a perspective useful for quantitative assessment of the aquatic health of lakes and rivers area, or chemical pathways. This suggests that agricultural pesticide surveys should be limited to smaller basins where amounts and periodicity of pesticides used could be more easily assessed in the light of their usually short life spans, of their potential impact to aquatic life, and of basin hydrological regimes. Also, this work suggests that more information is needed on the toxicological effects of pesticides on sediment-dwelling plants and animals, as most water insoluble compounds will undoubtedly be found there, at levels the effects of which are impossible to evaluate.

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APPENDIX A

SUMMARY OF ANALYTICAL METHODS

This Appendix contains a summary of the analytical methods used in this study but not listed in NAQUADAT (1985).

(a) Organophosphate Pesticides in bottom sediments or fish: malathion (Codes 89052L, 89053L), guthion (89045L, 89044L), phorate (89048L, 89049L) (from Bailey 1985).

A 20-g portion of the sample was extracted with a 1:1 acetone-hexane mixture in an ultrasonic homogenizer (for sediment) or a Polytron homogenizer (for fish). The extract was reduced in volume and put on a florisil column. The species of interest were then eluted from the column with petroleum ether and mixtures of diethylether in petroleum ether. The solvent of each fraction was changed to iso-octane by evaporating off the ethers on a rotary evaporator; the fractions were then diluted to volume. Analysis for the OP's was carried out on a gas chromatograph using a TS detector.

(b) Phenoxyalkanoic herbicides in fish: 2,4-D (89482L), 2,4,5-T (89484L).

Same as for sediments (codes 18501L and 18511L) except using a Polytron homogenizer during the extraction procedure.

(c) Carbamate insecticides in bottom sediments and fish: carbofuran (89272L, 89347L), carbaryl (88401L, 88402L) (from Bailey 1985).

Twenty-gram portions of the sample were extracted with a 3 x 100 mL volumes of ethyl/acetate using an ultrasonic (for sediment) or Polytron (for fish) homogenizer. The extracts were cleaned using coagulation/filtration and liquid partitioning. They were then dried over Na $_2$ SO $_4$ and reduced to a final volume of 2 mL with hexane. Analysis was carried out by GLC using an NP detector.

(d) Atrazine herbicide in water (89802L).

A 4-L sample was extracted by XAD resin and analyzed using GLC with NP detector.

(e) Atrazine in sediments (89803L) and fish (89840L) (from Bailey 1985).

A 20-g portion of sample was extracted with methanol in an ultrasonic (for sediment) or Polytron (for fish) homogenizer. The methanol extract was filtered, diluted with water, and back extracted with methylene chloride. This solution was dried over Na_2SO_4 , then evaporated to dryness under reduced pressure. The residue was taken up in ethyl acetate, diluted to volume, and analyzed on a GLC using a TS detector.

(f) Captan Analytical Protocol - Sediments and Tissues (from Oceanchem 1985).

To a 35-g sample, 100 mL of acetone is added and the mixture homogenzied in a 250-mL centrifuge bottle. 2. After centrifugation, the extract is decanted through a glass wool plug into a 500-mL separatory funnel. (The glass wool plug is placed in a filter The solids left behind are re-extracted with 100 mL of funnel.) dichloromethane, and without centrifuging, are decanted into the same separatory funnel through the glass wool plug and filter funnel 4. 100 mL of hexane is added through the glass wool and assembly. funnel into the separatory funnel. 5. The extract is shaken for 2 and the lower (aqueous) phase is drawn off into a 250-mL separatory funnel containing 10 g of solid sodium chloride. 6. The remaining phase (organic) is poured through a small column (approx. 15 cm length x 25 mm i.d.) containing a glass wool plug and approximately 30-40 mm of anhydrous sodium sulphate into a 1000-mL round-bottomed flask. 7. The aqueous phase from step (5) is extracted with 2 x 70 mL of dichloromethane, shaking for 1 min each time, and the dichloromethane phase is added through the drying column in step (6) into the 1000-mL round-bottomed flask. 8. The extract collected in the 1000-mL flask is evaporated to near dryness (approx. 1 mL) on a rotary evaporator, 10-20 mL of acetone is added, and the extract is evaporated to near dryness again. 9. The procedure in step (8) is repeated with hexane being added each time, to replace the acetone with The extract is made up in 10 mL of hexane prior to florisil clean-up.

Each batch of florisil must be cleaned and calibrated prior to clean-up of extracts. Florisil should be heated in a Pyrex round-bottomed flask to 300° C for 24 h, allowed to cool in the oven to approximately 100° C, the stoppered and allowed to cool to room temperature prior to deactivation. The florisil clean-up column topped with 1-2 cm of anhydrous sodium sulphate is calibrated using a captan standard, and should be deactivated to allow consistently high recovery of captan in the third elution (florisil under these conditions is usually deactivated to 3% to 3.5%).

The 10-mL hexane extract from step (10) in the procedure is added to the florisil column and is eluted with the following elution solvents:

1st elution: 120 mL of 5% dichloromethane in hexane 2nd elution: 120 mL of 30% dichloromethane in hexane

3rd elution: 120 mL of 15% acetone in hexane.

Under these conditions, captan will be eluted in the third elution.

The cleaned extract is evaporated on a rotary evaporator and made up to a suitable volume prior to quantification by electron capture gas chromatography.

- (g) Dichlone Analytical Protocol Sediment (from Oceanchem 1985).
- 1. A suitable portion of the seiment sample is allowed to dry in a vacuum desiccator. 2. 50 g of the dried sample is partially pulverized to break up large lumps and added to a chromatography

column, containing a Pyrex glass wool plug. 3. Three 100-mL portions of benzene are allowed to percolate slowly through the sample and are collected in a 500-m round-bottomed flask. (Each 100-mL portion is separately.) 4. The benzene extract İs evaporated approximately 2-3 mL and applied to a florisil column previously calibrated to allow a rapid clean up of the extract and consistent, high recovery of spiked dichlone. (The florisil column will be topped with a suitable portion of anhydrous sodium sulphate to remove moisture.) The cleaned-up extract is evaporated to a suitable 5. volume and quantified by electron capture gas chromatography by the usual procedures. After extraction, solutions of dichlone residues must be protected from light and analyzed as soon as possible to prevent photodegradation of the dichlone. A dichlone spiked "blank" should be carried through the extraction and clean-up procedure to quantify the degree of photodegradation.

- (h) Dichlone Analytical Protocol Fish (from Oceanchem 1985).
- 1. A suitable sample portion is blended with benzene. (Sample size will depend on availability and tissue type. Relatively larger samples of low lipid material, e.g. muscle, will be extracted compared with relatively high lipid content tissues, e.g. liver.) 2. The extract is centrifuged and the benzene extract removed. 3. This is repeated twice more with additional portions of benzene. 4. Continue at step (4) under Sediment protocol.
- (i) Mancozeb (Dikar) Analytical Protocol Sediment and Fish (from Oceanchem 1985).
- Suitable sample sizes (50 g for sediments, 10 g for high lipid tissues, 25 g for low lipid tissues) are weighed into a 250-mL round-bottomed flask. 2. Freshly prepared SnCl₂·2H₂O in 1 N HCl (1 mg·mL⁻¹) is added to the flask (150 mL for sediments, 50 m \overline{L} for high lipid tissues, 100 mL for low lipid tissues) and the mixture refluxed for 60 min. 3. After cooling, the digest vacuum-filtered through a Buchner funnel and filter appropriate porosity (dependent on sample type and appearance of digest). 4. The filtered digest is applied to a previously prepared ion exchange column (see following section for preparation of cation exchange resin) and the ethylene diamine adsorbed at a flow rate of 25-30 $mL \cdot h^{-1}$. 5. Following adsorption, the column is eluted with 15 mL of 1.0 \underline{N} NaCl. When the surface of the NaCl solution reaches the top of the resin bed, flow is stopped and a suitable reservoir is placed to receive any further eluant (e.g. 5-mL calibrated centrifuge tube, 5-mL volumetric flask). 6. Small portions (2-3 mL at a time) of saturated NaHCO3 are then added to the column to elute the ethylene Additional small portions of saturated NaHCO3 are added as required until 5.0 mL of eluant is collected. 7. 200 μL of the eluate is added to a 5-mL centrifuge tube, fitted with a Teflon-lined screw cap, containing 50 μL concentrated HCl. 8. The acidified solution is evaporated to dryness over NaOH pellets in a vacuum desiccator. A reference standard of ethylene diamine dihydrochloride dissolved in saturated NaHCO3 is also acidified and simultaneously with the actual samples. 9. 100 μL

trifuloroacetic anhydride is added and the centrifuge tube is capped. 10. After 1 h at room temperature the excess trifluoroacetic anhydride is evaporated in a vacuum desiccator and 50 μL of NaHCO3 is added. 11. The contents of the centrifuge tube are thoroughly mixed and the trifluoroacetylated ethylenediamine is extracted into 400 μL of benzene by vigorous agitation on a vortex mixer. 12. Suitable portions are taken for electron capture gas chromatographic analysis using standard procedures.

Preparation of ion exchange column for Mancozeb: 1. Dowex 50W-X8, 100-200 mesh, cation exchange resin (Sigma Chemical Co., St. Louis, M0.) is washed by suspension in sufficient 2 \underline{N} NaOH to produce a strongly alkaline pH. 2. After the resin has settled, the fines and supernatant liquid are removed. 3. This procedure (steps (1) and (2) above) is repeated with 1 \underline{N} NaOH and distilled water. 4. The resin is then converted to the H+ form with 1 \underline{N} HCl. 5. After removal of the HCl the resin is converted to the Na+ form with 1 \underline{N} NaOH and allowed to stand overnight. 6. The 1 \underline{N} NaOH is then removed, and the resin washed with distilled water and twice with 0.2 \underline{N} NaOH. 7. A volume of 0.2 \underline{N} NaOH equal to the settled volume of the resin is then added. 8. A suitable glass column fitted with a Teflon stopcock and a plug of glass wool above the stopcock is packed by adding 6.0 mL of the 50 % (v/v) resin suspension in 0.2 \underline{N} NaOH to the column approximately half-filled with distilled water. 9. After the resin is allowed to settle, the column is eluted before use at a flow rate of 30 mL·m-1, with the following solutions:

- (i) 15 mL of 1 N HC1
- (ii) 15 mL of $1 \overline{N}$ NaOH
- (iii) 15 mL of 1 N HCl.

10. The column is then eluted with distilled water until the effluent is neutral.

The ion exchange column is now ready for use. Due to difficulties in regeneration, the resin is discarded after each run.

(j) Lipid content in fish (89990L) (from Bailey 1985).

Ten grams of sample was extracted with a 2 x 100 mL portions of acetonitrile using an ultrasonic homogenizer. The extract is filtered through a three-layer glass microfibre filter into a tarred, round-bottomed flask. The solvent is removed on a rotary evaporator at reduced pressure and weight of the residue determined as lipid.

ATLANTIC WORKING GROUP SESSION

Attendees

M. Charlton (Chairman) Aquatic Ecology Division (NWRI)

P. Seidl (Recorder) Headquarters (WQB)
T. Clair (Presenter) Atlantic (WQB)

J. CarrieJ. DermottEnvironmental Contaminants Division (NWRI)Great Lakes Fisheries Research Branch (DFO)

B. Dutka Analytical Methods Division (NWRI)

A. Fraser Aquatic Physics and Systems Division (NWRI)

J. Jerome Aquatic Physics and Systems Division (NWRI)

L. Kalas Aquatic Ecology Division (NWRI)

R. Lemieux Water Planning and Management (IWD-Quebec)

E. Ongley Western and Northern Region (NWRI)

P. Wong Great Lakes Fisheries Research Branch (DFO)

NWRI - National Water Research Institute, Department of the Environment

WQB - Water Quality Branch

DFO - Department of Fisheries and Oceans

IWD - Inland Waters Directorate

The working group decided to develop a generic work plan for the monitoring of agricultural pesticides, with the Atlantic Region's presentation on the Annapolis Valley to be used as a case example, supplying the group with a real-life situation.

The issue identified in this monitoring program was seen as a perceived or unconfirmed issue. The use of agricultural pesticides for the various crops (potatoes, corn, apple orchards) within one of the most intensive agricultural areas of Nova Scotia was a known fact. However, no sampling by the WQB had yet been carried out, and thus the proposed monitoring was to be regarded as a baseline/pilot study. The objectives of the monitoring program were set as the identification of the presence, area/extent of, and ecological effect of agricultural pesticides within the Annapolis Valley River basin.

The working group agreed that the first step required was for a historical review of all pertinent data to be carried out. Significant events, such as the description of the hydrological cycle within the basin, needed to be determined. Due to their importance to the discharge regime, the presence of any control structures should be documented. entire group identified the need for a basin inventory of potential pesticides expected to be within the river basin as mandatory, prior to collection. The group stressed the need for effective communication between the various departments, services, branches, etc., within federal and provincial governments. Due to the involvement of various jurisdictions, a great deal of information often exists but may not necessarily be on any central data bank. Also, interaction with universities, companies (those responsible for the manufacture and distribution of the pesticides) and the general public (specifically local farmers or co-ops) can provide valuable information and thereby reduce needless sampling. Because ground water is heavily used in the

Atlantic provinces and can act as a potential sink for many pollutants, any information on ground-water sampling (site location, parameter list, frequency, etc.) should be sought. Background biological data (i.e., fish species, information on aquatic communities and productivity) is mandatory for the determination of aquatic health. Analysis of aquatic health in an already contaminated system is difficult without information on the pre-contaminated aquatic community.

the background information has been gathered assimilated, a statistically sound monitoring design must be developed. which will address the stated question/hypothesis of the monitoring program. Station density, parameter list and sample frequency should all reflect the diffuse and point source inputs in the basin, bearing in mind the land use activities (i.e., which chemicals are used, timing of spraying, quantities used). Sampling should occur upstream and downstream from the major identified point source inputs, as well as one station at the exit point of the river system. In the case of the Annapolis Valley, the station should be located above the salt water wedge (e.g., upstream from the tidal effect). The establishment of controls for the determination of impact assessment received a great deal of attention within the group. The difficulty with the present study was that all the tributaries within the study basin were ground-water fed and the potential for ground-water contamination of the control sites was identified. If a suitable head water control could not be found. sampling outside the immediate river basin was suggested.

Discussions then revolved around which analytical components were to be sampled. A GC-MS scan of water samples to identify which chemicals were present was identified as a valuable monitoring tool. Thorough examination of the chromatograms, although time and labour extensive, was highly recommended, while the use of a national menu, or list of pollutants to look for, was discouraged. A list of potential pesticides present, generated by a literature review of application rates (amount and frequency), was considered as a key to an effect pesticide Difficulties with laboratory method limitations, monitoring program. turn around times on analysis and the cost limitations of contracting out were all identified. Interaction, with research, was identified as a possible solution to many of these problems. Method development could be carried out for the routine identification of unknown peaks on the GC-MS scans while the monitoring program was underway. Biotoxicity tests (e.g., Ames test) could be used to identify priority sampling sites and thereby reduce the number of sampling locations.

It was also recognized that even though agricultural pesticide usage was the main issue identified within the river basin, other issues (mining in particular) could also cause deleterious environmental effects and therefore should be taken into account when the monitoring design is established. Monitoring design must be dynamic. Sampling should not be restricted solely to surface water; the influence of ground water must be considered.

The importance of monitoring sediments, both bottom and suspended, was then discussed. Bottom sediment sampling should occur in depositional zones (e.g., areas such as reservoirs with a high residency

time). Suspended sediment sampling should occur during high flow (e.g., spring peak) when suspended sediment concentrations are at a maximum. The use of sediment traps, with a 10:1 ratio of length to diameter, for integrated sampling over time, and the continuous flow through centrifuge for short time (synoptic) sampling were identified as two important sampling tools. The need to determine the toxic effects of contaminants associated with sediments was also discussed. It was felt that the bioassay approach could provide valuable information on the toxic nature of the contaminated sediments.

It was agreed that fish, because of their high lipid content, often better to sample than sediments or other biological components, such as invertebrates, if concentration (presence/absence of a particular chemical) is the sole purpose of the study. In Nova Scotia, very little information on fish species and habitat is available. Seining has proved to be ineffective on the coarse bottom and therefore electrofishing was suggested as a viable alternative. The commercial aspect of the fish was identified as important. Fish caught and consumed by the general public should be monitored. A sound biomonitoring program was considered desirable because it not only answers the question whether or not the compound was present within the system but also supplies information on bioaccumulation and impact as related to the biota of the river basin (e.g. effects). This aspect would be complemented by research to answer or define the effects of agricultural activities on the aquatic environment.

The species of biota used in any given study will depend on the study area and the issues. Certain biota are better for bioaccumulation studies, while effects monitoring may require sampling of sentinel species. Some reaches within a river may not provide suitable habitat for the biota. Control structures can restrict movement or migration of fish; too much suspended sediment or too little bottom sediment can restrict the kinds or numbers of benthic organisms. Conversion of biological data into knowledge on aquatic health received a great deal of attention from the working group. Discussion concerned the determination of aquatic health of the entire ecosystem versus detecting subtle changes within a group or groups of organisms. It was decided that whole system responses would only occur with gross pollution, and this gross pollution would already be known or more easily sampled in subtle other ways. The alterations community in structure. identification of tumours, backbone defects, altered genetic makeup, etc., would be most valuable as an early warning system. natural sampling variance can make interpretation of the data difficult.

The basic objective of all monitoring programs was assumed to be the protection of the aquatic environment for the most sensitive water user. The aquatic organisms were considered by the group to be the most sensitive user. The group agreed that water quality guidelines should be established specifically for the Annapolis Valley, based on the uses within the watershed.

Gaps in information identified by the WQB for either the monitoring design or the establishment of guidelines could be addressed by either NWRI or DFO. Communication at the management level between

regions, as well as agencies, was identified as being critical to ensure that a cooperative effort was put into place. Depending on the issues identified and the need for further research and resource availability, monitoring program could be updated from baseline to identification, to trend assessment, to ecological effects monitoring in a logical evolutionary manner. However, this would require many years. Movement from one level to another should only occur after the full and complete interpretation of the data from the previous level. baseline study was simply seen as a means to generate ambient levels data so that a consensus could be reached on environmental effects. would require that a scientifically defensible study be done, generating credible data for either further baseline investigation, research or trend development. The group felt periodic peer review of the scientific content of the monitoring program was needed. Also, the establishment of a standard set of protocols in each regional program, based on knowledge the critical pathway, would produce a standardized or perspective to the various monitoring programs carred out by the Branch. Finally, the group agreed that storage of all generated data, within a reasonable length of time to allow for publication, in a national data bank such as NAQUADAT was necessary.

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Use of Young-Of-The-Year Fish as Bioindicators of Toxic Chemicals to Complement the Water Quality Network in the St. Lawrence River,

Quebec Province

bу

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ABSTRACT

Some historical aspects and the evolution of the water quality network in the St. Lawrence River are presented, and the use of forage fish as bioindicators is also discussed. Even though the surveillance of toxic chemicals was one of the main goals of the network, the analysis of water samples provided little quantitative information on presence of contaminants. The orientation of the network, therefore, was changed; water samples were taken to provide general information on the water quality of the river, while special studies on sediments and adult fish were carried out for the monitoring of toxic chemicals. Nevertheless, a monitor tool was needed to complement the quality network in order to establish a long-term trend assessment program on toxic chemicals. A pilot study was carried out in 1984. evaluating the use of young-of-the-year forage fish, Notropis hudsonius (spottail shiner) and Perca flavescens (yellow perch). results of this study show that these young-of-the-year are good quantitative indicators of persistent lipophilic substances such as PCBs, DDE, and HCB as well as some metals such as Hg. Following the recommendations of this study, the Quebec Region has established a forage fish program for the monitoring of toxic chemicals in the St. Lawrence River.

RESUME

Nous présentons quelques aspects historiques du réseau de qualité de l'eau et son évolution dans le fleuve Saint-Laurent; l'utilisation des poissons fourrage comme bioindicateurs est aussi discutée. Bien que la surveillance des substances toxiques fût un des réseau, l'analyse des échantillons buts du fournissait peu d'information quantitative sur la présence des contaminants. Par conséquent, nous avons changé l'orientation du échantillons d'eau pour réseau: prélèvement des fournir l'information générale sur la qualité de l'eau du fleuve. études spéciales sur les sédiments et les poissons adultes pour surveillance des substances toxiques. Néanmoins, il nous fallait un outil de surveillance additionnel au réseau de qualité de l'eau afin d'établir un programme d'évaluation des tendances à long terme des substances toxiques. Une étude pilote fut effectuée en 1984 pour évaluer l'utilisation des jeunes de l'année (poissons fourrage). hudsonius (Oueue à tache noire) et Perca (Perchaude). Les résultats de cette étude démontrent que ces jeunes de l'année sont de bons indicateurs quantitatifs de substances lipophiles persistantes telles que les BPC, DDE, et HCB, ainsi que de certains métaux tels que le Hg. Suite aux recommandations de cette étude, la région du Québec a établi un programme de poissons fourrage pour la surveillance des substances toxiques dans le fleuve Saint-Laurent.

INTRODUCTION

The St. Lawrence River (Fig. 1) is one of the major rivers of this continent, flowing about 1000 km between Lake Ontario and the Gulf. It is complex in its hydrological and geological characteristics, rich in biological resources, and important for navigation and recreational activities. It also receives the full impact of industrial and agricultural activities, and untreated domestic sewer discharges.

Government (federal and provincial) and private agencies (universities, industry) have carried out various studies on the biological resources, the hydrology and geomorphology of the river, as well as monitoring of the river's water quality.

In 1971, a joint federal-provincial committee (Comité consultatif Canada-Québec) was formed to study the environmental quality of the river. In 1972, this joint committee recommended the formation of a multi-disciplinary interdepartmental Canada-Quebec St. Lawrence River working group, which was consequently formed in 1973 and called the St. Lawrence River Study Committee (Comité d'étude sur le fleuve Saint-Laurent).

At the end of a five-year period, this study committee completed its mandate with the publication of about 16 final technical reports, including 14 annexes, on such diverse subjects as hydrology, sedimentology, water quality, biological resources, toxic chemicals and socio-economic aspects, as well as a summary report and a small booklet for the general public (Anon. 1978a).

The Study Committee identified the major types of deterioration within the river system, of which the dissemination of toxic chemicals was identified as the most important.

Environment Canada, and specifically the Inland Waters Directorate, Quebec Region (IWD-Q), has continued operating a water quality network since 1978. In response to the major findings of the Study Committee, the primary objective of the network was to monitor toxic substances in the river. However, since toxic chemicals in water samples, especially organics, are often below or close to detection limits, the IWD-Q developed programs to use substrates other than water, such as sediments and biota.

This presentation deals with the evolution of IWD-Q's toxic chemicals program regarding the monitoring of contaminants in the St. Lawrence River. The focus will be on the fish program, since it is most directly related to the water quality network. The use of sediments will not be discussed here, although it is an important aspect of the ongoing toxic chemicals program within IWD-Q.

THE TERRITORY

The following description of the study area was taken from Germain and Janson (1984). The St. Lawrence River drains one of the most developed hydrographic basins of the world, the Great Lakes basin.

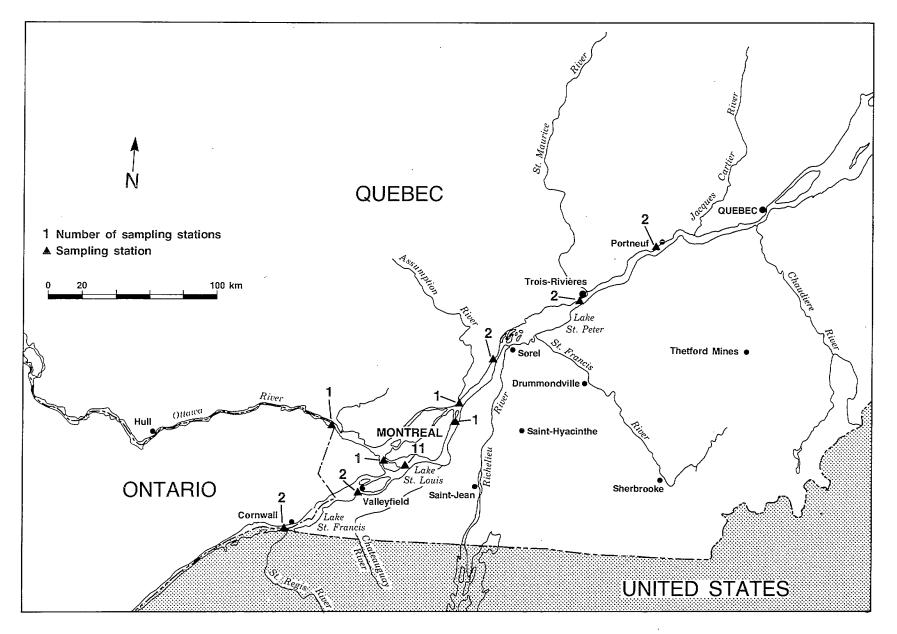


Figure 1. The St. Lawrence River, Quebec Province, station locations of the forage fish pilot study.

Although the river drains the whole of the Great Lakes basin (almost $800\ 000\ km^2$), representing the industrial heartland of North America, its water quality is impacted mainly by Lake Ontario. This means that toxic chemicals identified in Lake Ontario, such as PCBs, mirex, and dioxins, present a potential threat to the St. Lawrence River system.

The St. Lawrence River enters the Province of Quebec at Cornwall, where a widening of the river forms Lake St. Francis (lac Saint-François). The river runs for about 380 km to Quebec City, representing the stretch of the river being monitored by the Water Quality Branch (WQB) of IWD-Q. After Quebec City, it opens up into the estuary and gradually becomes marine (Fig. 1).

The river is of prime importance to the people of Quebec. More than half of its population (53%) live on its shores, most of whom obtain their drinking water from the river. Industrial activities are important on the Montreal-Sorel stretch, while most of its tributaries drain semi-industrial and agricultural areas.

In the Montreal area, the Ottawa River joins with the St. Lawrence River. The drainage basin of the Ottawa River (about 15 000 km²) consists mainly of Canadian Shield country. The river forms the border between Ontario and Quebec. Downstream from Pembroke, on the Ontario side, there is agricultural development. Except for pulp and paper plants, there is very little industrial activity on the river.

The confluence of the Ottawa and St. Lawrence rivers forms Lake St. Louis. There is little cross-sectional mixing, so the two types of can be easily distinguished as far downstream as The water from the Ottawa River is higher in colour, St. Pierre. turbidity, organic matter and nutrients, but lower in conductivity, alkalinity and hardness, than the water originating from the Great This duality of the St. Lawrence River is an important and Pollution coming from the Montreal significant aspect. (specifically the Montreal urban community sewage discharges) confined to the brown, turbid Ottawa River waters, whereas pollution originating from Lake Ontario and the international section of the river (Kingston-Cornwall) is confined to the clearer blue-green Great Lakes waters.

THE WATER QUALITY NETWORK

Since 1978, the Inland Waters Directorate has been operating a water quality network on the St. Lawrence River between Cornwall and Quebec City. Despite the importance of the river, very little was done beyond this network. Resources were minimal (Survey and Monitoring staff 1978-1983: one scientist and one technician), and priority was given to transboundary waters. It is only since 1983 that the St. Lawrence River has increased in priority as its importance was recognized by the Regional Director General's office. The signing of the federal-provincial agreement made official Environment Canada's mandate to monitor the St. Lawrence River. Although there is some effort to increase the toxic chemicals program in the St. Lawrence, new resources (one section head and two scientists) received under the

federal-provincial agreements are being used to operate the various water quality networks (e.g. St. Lawrence River and transboundary rivers), and the administration of the Agreement. However, toxic chemical programs may become an integral part of the Agreement.

The original network, initiated in 1978, was based on the concept of homogenous zones, developed by Lachance <u>et al</u>. (1979). Correspondence and cluster analyses, applied to data on turbidity, inorganic nitrogen and inorganic phosphorus, collected at 112 stations, led to the definition of 26 homogeneous zones in the St. Lawrence River between Cornwall and Quebec. Parameters such as heavy metals and other toxic chemicals were not taken into account, and this particular concept of homogenous zones has been abandoned now.

In the beginning this network was called a "Contaminants Network"; it replaced the "National Network," which was in effect from 1969 to 1974 and operated by the Water Quality Branch in Ottawa, with field assistance from the Water Survey of Canada.

This new Contaminants Network followed the recommendations of the St. Lawrence River Study Committee (Anon. 1978b). Analyses for toxic chemicals were limited to PCB/OC and heavy metals.

PROBLEM IDENTIFICATION

It soon became evident that the Contaminants Network did not give any useful information on the presence of toxic chemicals: concentrations were often below detection limits, especially the organics and the more toxic metals such as Cd, Hg and Pb (Table 1); even when detected, values were usually so close to detection limits that any useful statistical analysis and interpretation was virtually Furthermore, grab samples such as the traditional water sample have been found to contain so much variation that it is difficult to make any meaningful spatio-temporal comparison (Ongley 1984).

For these reasons, the IWD-Q decided on the use of fish as indicators of the presence of toxic chemicals. In general, fish are excellent organisms to study toxic chemicals in the aquatic environment, especially lipophilic and persistent substances. They provide information on bioavailability, bioconcentration, ambient contamination, and trend assessment (temporal and spatial).

Even though adult fish provided useful information on substances such as PCBs and Hg, they proved to be very poor indicators of heavy metal pollution, especially when muscle tissue was analyzed (Sloterdijk 1977). Mercury is an exception, since it is bioaccumulated in its organic form, methyl mercury. Most of the other metals remain in their inorganic form, and biological uptake is much less than that for the organic compounds.

Many metals (Cu, Zn, etc.) are biologically active and essential to living organisms. Therefore, fish are able to regulate, to a large degree, the uptake and excretion of these metals. Sloterdijk (1978)

Table 1. Detection Frequency (%) of Organochlorinated Compounds and Heavy Metals for Various River Sections in the St. Lawrence River Water Quality Network, 1978-81*

Parameter	Lake St. Francis	Lake St. Louis	Lac des Deux Montagnes	Montreal- Lanoraie	Lake St. Pierre	Trois-Rivières- Québec
PCBs	25	19	0	21	25	18
α-BHC	82	63	56	66	67	55
β-ВНС	24	31	-	21	8	9
γ-BHC	85	56	11	36	50	27
&-BHC	3	6	-	29	29	9
p,p¹-DDT `	69	31	11	50	33	27
o,p'-DDT	84	81	100	79	83	55
p,p¹-DDE	81	81	78	86	91	55
Endrin	1	0	_	7	8	9
α-Chlordane	41	31	22	21	25	18
НСВ	12	0	-	21	8	0
Hg	44	48	50	54	54	54
Cd	4	6	2	1	6	3
Cu	75	83	98	97	99	97
Ni	64	65	71	73	79	76
Pb	4	13	29	26	43	34
Zn	91	76	72	84	76	82

^{*} Adapted from Germain et Janson (1984).

has shown that fish from polluted and unpolluted areas of the St. Lawrence were equally "contaminated." Mollusks from the same areas, however, showed great differences in heavy metal concentrations, those from polluted environments being much more contaminated than those from less or unpolluted areas (Table 2). It is interesting to note that Hg behaves differently, as do PCBs; their levels in fish do reflect the differences between the two areas (river vs. estuary = polluted vs. unpolluted; the term "unpolluted" is not meant in its absolute sense).

Table 2. Some Comparative Data (range with mean in parentheses) on Metals in Fish (F) and Mollusks (M) from Polluted (river) and "Unpolluted" (estuary) Areas*

Contaminant	Organism	St. Lawrer	nce River	St. Lawrence Estuary		
Cadmium	F	0.04- 0.1	(0.04)	0.04		
	М	3- 8	(4.7)	0.04-0.45	(0.17)	
Copper	F	0.1- 3.0	(0.7)	0.05-1.5	(0.7)	
	М	6-33	(14)	0.05-11.2	(4.0)	
Lead	F	0.05- 0.5	(0.3)	0.05-0.5	(0.2)	
	М	0.05-12	(2.5)	0.05-0.5	(0.2)	
Manganese	F	0.1 - 8.8	(1.7)	0.1 -8.0	(0.9)	
	M	1360 - 8330	(4200)	0.3 -11.6	(1.7)	
Zinc	F	2 -75	(15)	1 -24	(10)	
	М	109 –591	(246)	2 -28	(12)	
Mercury	F	0.1 - 3.5	(0.9)	0.01-1.6	(0.13)	
	M	0.01- 2.6	(0.3)	0.01-0.3	(0.07)	
PCB's	F	0.05-15.0		0.05-2.5	(0.07)	
	М			0.05-0.2	(0.07)	

^{*}Adapted from Sloterdijk (1978).

Although adult fish have proven to be good indicators of Hg and PCB pollution, some major problems remain. Fish caught at certain locations may not be representative of that particular area. They tend to move around, the extent of which depends on the species; therefore, exposure to contaminants will vary according to the area through which the fish moves.

It must be realized that in addition to mobility, food chain effects, change in diet, reproductive cycle, and the general life history of the species, including size and age, also complicate the interpretation of fish contaminant data. As elaborated in the next section, the use of young-of-the-year forage fish avoids all of these problems.

Indeed, young-of-the-year forage fish have proven to be excellent bioindicators of environmental contaminants, especially with regard to trend assessment (temporal or spatial). In general, they are very site-specific, with a simple life history, uniform in age, subject to little or no foodchain effects, and representative of the year of capture (Suns and Rees 1978).

In general, the use of adult fish should be limited to the detection of new substances and where the level of bioconcentration may become an health hazard, either human or for the ecosystem itself. In certain cases, it is desirable to have temporal or spatial integration of environmental contamination, in which case adult fish should be used.

FORAGE FISH PILOT STUDY

Background

As discussed earlier, the water quality network, as such, proved to be inadequate in monitoring the presence of toxic chemicals in the St. Lawrence River. Notwithstanding the value of the study of sediments and adult fish, a monitoring tool was needed that accurately reflected the levels of toxic chemicals in the water column at key locations related to the water quality network stations. Since the use of sediments, bivalves or adult fish had not met those objectives, a study on the feasibility of using young-of-the-year forage fish was initiated.

The choice of using forage fish as a bioindicator was based on the work of Karl Suns of the Ontario Ministry of Environment (MOE) (Suns and Rees 1978). The IWD-Q carried out a very limited study in 1979 in Lake St. Francis and Lake St. Louis of the St. Lawrence River system. It was found that the species proposed and used by Suns, Notropis hudsonius (spottail shiner; queue à tache noire), is distributed throughout these lakes, although not necessarily at all localities (Guay 1979). Analytical results showed that local variations in contamination patterns (known from point sources, sediment studies, etc.) were reflected by levels in forage fish (Sloterdijk 1984).

In the early 1980s, it was recommended that the Water Quality Branch consider the use of biological organisms or biomonitoring in the study of water quality and toxic chemicals (Shindler 1981). This was

re-emphasized by a Water Quality Branch internal workshop on biomonitoring held in Longueuil, Quebec, in August 1983. At this workshop the use of forage fish was discussed, and Karl Suns of MOE informed the attendees of his work on N. hudsonius in the Great Lakes. The workshop culminated in the proposal, and the subsequent decision to initiate forage fish programs in all the WQB regions.

This decision gave the needed impetus to carry out a pilot study in the Quebec Region. The consulting agency, "Environment Illimitée," which had done the fieldwork for the previous study for the WQB-QR (Guay 1979) became aware of the renewed interest in forage fish, and initiated in 1984 an unsolicited proposal (PS-E-181) with the help of Novalab Ltée to carry out a feasibility study. This unsolicited proposal was accepted and sponsored by the WQB-QR and WQB-Headquarters, with the Department of Supply and Services (DSS) providing the major part of the funding. The final report of the study has been completed (Guay et Dandurand 1986). Here, we will highlight some of its findings.

Study Description

The pilot study in question evaluates the possibility of using \underline{N} . $\underline{hudsonius}$ 0+ (0+ meaning young-of-the-year) as a bioindicator of toxic chemicals in the St. Lawrence River. Although the species is ubiquitous in this river, it may not be found at all predetermined stations. Therefore, the use of \underline{Perca} flavescens 0+ (yellow perch; perchaude) was proposed as a replacement species, since it is also very common in the river.

Some of the specific questions addressed by this pilot study can be summarized as follows: do forage fish accurately reflect ambient contamination; can one species replace another; can forage fish be used for heavy metal monitoring; how site-specific are they in reflecting local variations on point sources?

Forage fish were taken at 29 stations between Cornwall and Quebec City by means of seining. Station locations were chosen as a function of the water quality network, since one of the objectives was that the forage fish component should complement the traditional water sample (Fig. 1). In Lake St. Louis, a higher density of stations (11) was used in order to study very local variations due to point sources (in this case the St. Louis River, receiving Hg-laden effluents from a chlor-alkali plant; Talbot and Sérodes 1979).

Contaminant analyses (Table 3) were carried out on five samples (several individuals combined) per species (spottail shiner and yellow perch). The national WQB laboratory analyzed the heavy metals (WQB methodology), and Novalab Ltée carried out the PCB/OC analyses (BEST 1980).

Study Results

Sampling took place between September 4 and October 16, 1983, and a total of 47 species of fish were caught, including spottail shiner and yellow perch. At this period of the year, N. hudsonius O+ is 3-4 months old, while P. flavescens O+ is 4-5 months old.

Table 3. Organochlorinated Compounds and Heavy Metals Analyzed in Forage Fish, with Detection Limits

Parameter	Detection limit (mg/kg)
Organochlorinated compounds	
нсв	0.001
Aldrin	0.001
Heptachlor	0.001
p,p'-DDE	0.001
Mirex	0.001
Arochlor 1242	0.01
Arochlor 1254	0.01
Arochlor 1260	0.01
α-BHC	0.001
β-BHC	0.001
Lindane	0.001
Cis-chlordane	0.001
Trans-chlordane	0.001
o,p'-DDD	0.005
o,p'-DDT	0.001
p,p'-DDD	0.001
p,p'-DDT	0.001
Methoxychlor	0.005
lpha-Endosulfan	0.002
β-Endosulfan	0.002
Dieldrin	0.001
Endrin	0.001
<u>Heavy metals</u>	
Heavy metals	
Нg	0.01
Pb	0.1
Cu	0.2
Zn	0.1
Cd	0.02
Cr	0.20
Ni	0.05
•••	

 $[\]underline{N}$. $\underline{hudsonius}$ O+ was caught in abundant numbers throughout the river between Cornwall and Portneuf. Even though previous reports placed the geographical limit of this species at Trois-Rivières (Scott and Crossman 1973), it was found well represented at Portneuf, about 75 km downstream. \underline{P} . $\underline{flavescens}$ O+ was found to be less abundant than \underline{N} . $\underline{hudsonius}$. However, at all locations where \underline{N} . $\underline{hudsonius}$ was not caught, it was present in sufficient numbers to be used as a replacement species.

Analytical results (all expressed as milligrams per kilogram wet weight) showed that heavy metals, Hg and PCBs were well over detection limits (Table 4; for simplicity, only stations where both species were caught have been presented). Of the organochlorinated pesticides, only DDE and HCB were detected at significant levels.

Table 4. Concentrations of Organochlorinated Compounds and Heavy Metals

•		<u>N</u> .	<u>hudsonius</u> 0+	<u>P</u> . <u>flav</u>	escens 0+
Contaminant	Station	Х	S.D.	Х	S.D.
PCBs	3	0.208	0.016	0.120	0.018
	6	0.096	0.023	0.060	0.020
	7	0.037	0.005	0.038	0.013
	11	0.420	0.056	0.440	0.115
	14	0.194	0.018	0.205	0.045
	26	0.123	0.023	0.182	0.082
	27	0.096	0.005	0.060	0.000
DDE	3	0.020	0.007	0.010	0.000
	6	0.023	0.005	0.009	0.001
	7	0.003	0.004	0.003	0.003
	11	0.028	0.004	0.032	0.012
	14	0.032	0.004	0.020	0.008
	26	0.020	0.000	0.024	0.005
	27	0.013	0.005	0.010	0.000
НСВ	3	0.001	0.000	0.001	0.001
	6	0.002	0.001	0.001	0.001
	7	0.002	0.002	0.001	0.002
	11	0.010	0.000	0.015	0.005
	14	0.003	0.001	0.006	0.002
	26	0.002	0.001	0.001	0.001
	27	0.001	0.001	0.001	0.000
Hg	7	0.054	0.005	0.048	0.008
	8	0.038	0.004	0.065	0.010
	11	0.158	0.013	0.155	0.012
	15	0.080	0.017	0.091	0.017
Pb	7	0.060	0.030	0.060	0.030
	8	0.100	0.080	0.070	0.050
	11	0.130	0.050	0.080	0.040
	15	0.050	0.000	0.050	0.000
Cu	. 8	0.780	0.120	1.220	0.080
	11	1.140	0.090	1.220	0.090
	15	0.760	0.210	0.820	0.100

Table 4. Continued

		N. <u>hudsonius</u> O+		P. flavescens 0+		
Contaminant	Station	Х	S.D.	Х	S.D.	
Zn	7	44.100	3.070	21.500	1.310	
	8	41.380	2.030	28.250	2.220	
	11	45.660	1.160	26.770	1.220	
	15	42.070	0.550	21.170	1.180	
Cd	7	0.012	0.004	0.010	0.000	
	8	0.048	0.008	0.017	0.005	
	11	0.046	0.013	0.020	0.014	
	15	0.010	0.000	0.010	0.000	
Cr	7	0.810	0.590	0.950	0.760	
	8	0.100	0.000	0.830	0.940	
	11	0.140	0.050	0.380	0.040	
	15	0.410	0.450	0.480	0.330	
Ni	7	0.190	0.150	0.130	0.060	
	8	0.090	0.020	0.610	0.700	
	11	0.080	0.020	0.210	0.030	
	15	0.300	0.340	0.340	0.025	

whether stations were significantly different establish regarding contaminant values, the variation within stations had to be determined first. This was done by analyzing separately results from different strata within a station. It was found that the coefficients of variation ranged from 10% to 20% for PCBs, Hg and some of the metals, irrespective of whether it was within stations or between stations, and whether sample size varied from 5 to 10 samples. little analytical variation within the lab for Based on these findings it was concluded that five samples homogenate. per station were sufficient, and that within a station the various catches could be combined and then split into five subsamples in order to provide enough material per sample for the chemical analyses.

Since the sampling period was spread out over a six-week period, a time period significant with regard to the 3-6 months age of the fish, two stations sampled at the beginning were sampled again at the end of the sampling period. It was found that there was a slight increase in Hg levels but not in PCB concentrations. DDE increased significantly in \underline{N} . $\underline{hudsonius}$, almost tenfold, while HCB doubled in concentration. There was a general increase in heavy metal concentrations, except for Zn. The limited number of samples and the fact that some concentration values were close to detection limits, however, preclude any definite

conclusion on short-term variation. It is recommended that any future sampling take place within a two- to three-week timeframe, and that a similar temporal verification be made but with more samples to increase statistical confidence.

To determine whether \underline{P} . $\underline{flavescens}$ could be used as a replacement species for \underline{N} . $\underline{hudsonius}$, results for these two species at stations where both were caught were compared (Table 4). In general, values for PCBs and Hg were similar at the same stations. This, then, allows the replacement of \underline{N} . $\underline{hudsonius}$ with \underline{P} . $\underline{flavescens}$ at stations where the former cannot be found, but the latter is present. In this way, we were able to obtain for the pilot study a more continuous spatial record of Hg and PCBs in the St. Lawrence River than would be possible with only one species (Figs. 2 and 3). In Figures 2 and 3, corrected data for lipid content are presented; a simple linear correlation, however, has not been established.

As can be seen from these figures, values are not the same throughout the river system. In Figure 2, the uncorrected data for PCBs show a definite pattern: high concentrations just downstream from Cornwall (stations 1, 2 and 3 in Lake St. Francis), and increasing near the end of the lake (station 5). Stations located in the Ottawa River water had much lower contaminant levels (stations 7 and 8), as did stations on the northern shore of Lake St. Francis (station 6) and at the entrance of Lake St. Louis north of the Beauharnois Canal (station 9).

From previous studies (e.g. Sloterdijk 1977), it is known that Lake St. Francis (Great Lakes water) is much more contaminated than Lac des Deux Montagnes (Ottawa River water). Results for the forage fish in this study corroborate these findings. Therefore, in this respect, young-of-the-year fish seem to be good indicators of environmental levels of PCBs.

It is interesting to note that the high uncorrected values found just downstream from Montreal (stations 22, 23, 24) or the Montreal West Island (station 31) may be partly explained by concomitant high lipid values. Consequently, one must be prudent when comparing levels of lipophilic substances at various localities and always consider lipid levels. Unfortunately, we have not been able to establish a statistically significant correlation between lipid levels and PCB concentrations, as can be found for Hg with respect to size or age of a fish. Corrections for lipid levels did not alter the differences between PCB levels found upstream from Montreal, i.e., levels in Lake St. Francis (Great Lakes water) versus Lac des Deux Montagnes.

A higher number of stations in Lake St. Louis were sampled than elsewhere in the river to evaluate whether the young-of-the year fish would reflect local variations (in this case due to a point source for Hg, the St. Louis River [Sloterdijk 1979; Talbot et Sérodes 1979]). Results for mercury are presented in Figure 3. As can be seen, stations at the entrance of Lake St. Louis (stations 4 and 8) show the lowest levels of mercury, while station 12 at the mouth of the St. Louis River presents very high levels of Hg. Again, significant

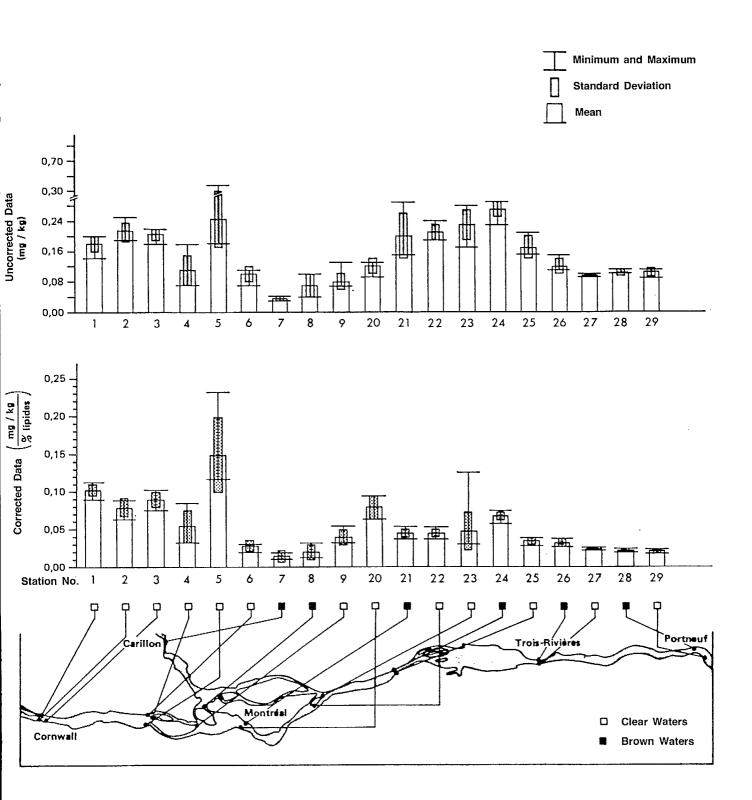
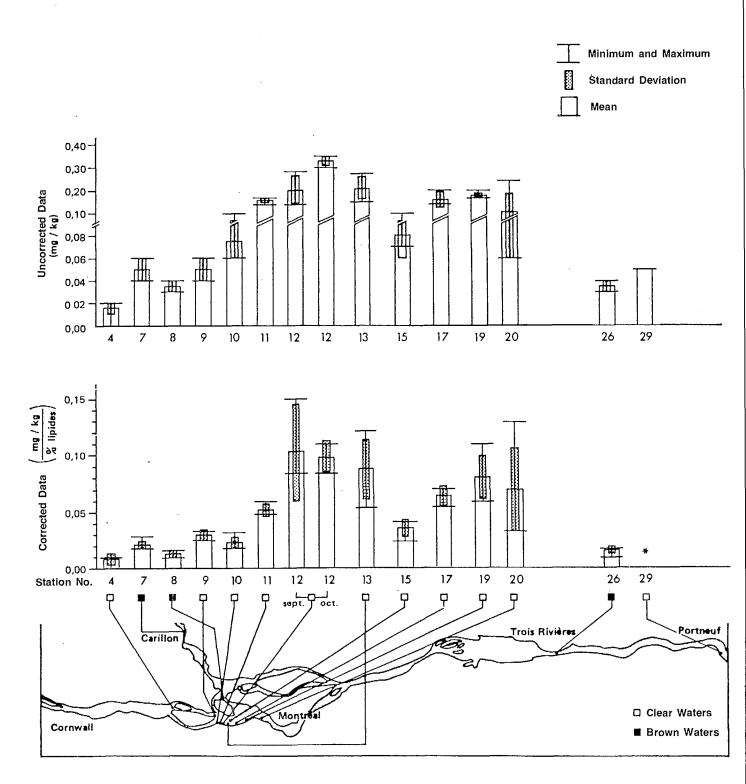


Figure 2. PCB concentrations in young-of-the-year fish from the St. Lawrence River.



* At station 29, lipid content not measured.

Figure 3. Mercury concentrations in young-of-the-year fish from the St. Lawrence River.

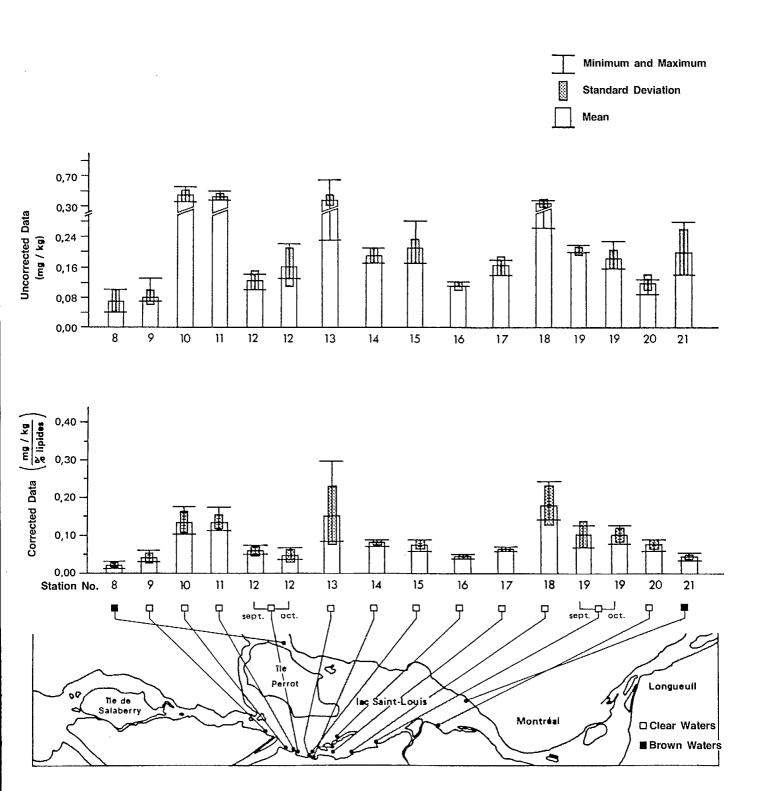


Figure 4. PCB concentrations in young-of-the-year fish from Lake St. Louis.

differences are noted between stations upstream and downstream from this tributary (stations 9 and 10 vs. stations 13, 17, 19 and 20; station 15 is located outside the zone of influence of the St. Louis River).

These observations confirm the value of forage fish in detecting very local differences. This is highlighted by results for PCBs, which are presented in Figure 4. Two stations (10 and 11) stand out because of very high levels (up to 0.7 mg/kg). The two stations are located just below the hydroelectric dam at Beauharnois in front of the Union Carbide industrial complex, but it is not yet known what the exact source of contamination is. These high levels persist at stations located downstream, stations 13 and 18. Stations 14, 15, 16 and 17 are located outside this zone of influence, either by a physical barrier (station 14) or because they are located more offshore (stations 15, 16 and 17).

CONCLUSIONS AND RECOMMENDATIONS

The major problem in the St. Lawrence is the dissemination of toxic chemicals. Two major sources have been identified: the Great Lakes and the international section of the river, and the industrial and urbanized Montreal-Sorel corridor. Three groups of substances were found to be specifically problematic: PCBs, Hg and heavy metals.

The traditional water quality network was found to be inadequate to provide useful information on the presence of these toxic chemicals in the St. Lawrence River. Values were either too close to or below detection limits. Any statistical interpretation was therefore impossible.

A pilot study was carried out to evaluate the use of young-of-the year forage fish (spottail shiner and yellow perch) as a bioindicator of the toxic chemicals identified as problematic in the St. Lawrence River. The results of the study established the following:

- Contaminant concentrations in the two species of the O+ age group were well above detection limits for PCBs, Hg, Cu, Cr, Ni and Zn; close to detection limits for DDE, HCB, Cd and Pb; while the other organochlorinated pesticides were mainly below detection limits
- Spottail shiner and yellow perch are ubiquitous throughout the river between Cornwall and Portneuf, but not necessarily at all stations
- Yellow perch was found at stations where spottail shiner was not present
- Comparison of contaminant levels for the two species at the same station suggested that yellow perch can be used as a replacement species of spottail shiner for organochlorinated compounds such as PCBs, DDE and HCB, as well as for Hg

- The results for the evaluation of short-term variation are not conclusive, but it seems that a significant accumulation of certain substances (Hg, DDE, HCB, Pb, Cd) took place over the six-week sampling period
- The analysis of variation within substations (strata) and between substations indicated that in general, substation catches can be combined and then split up into five samples per station (this assures sufficient sample quantity for the various chemical analyses, when some catches per substation are insufficient)
- Spatial comparison of the contaminant concentrations at various stations with known degrees of contamination confirmed the value of this bioindicator to reflect ambient contaminant levels; this was found to be true even at a very local level, e.g., stations upstream and downstream from a source
- the study confirmed that young-of-the-year forage fish are good quantitative indicators of the presence of the following substances: PCBs, DDE, HCB and Hg. Heavy metal data are still too limited to make a complete evaluation, but more results for these are forthcoming.

Spottail shiner 0+ and yellow perch 0+ can be successfully used to complement the regular water quality network. They can also be used to identify local "hotspots," or sources of toxic chemicals. However, their use seems to be limited to substances that are lipophilic and that are present at high enough levels in the environment to be accumulated by the fish over a four- to six-month period.

It must be understood that concentrations in these small fish reflect the dissolved and bioavailable fraction of toxic substances. It is not known whether the presence of adsorbed chemicals on suspended sediments play a role and, if so, to what extent. It is also not known whether there is significant contaminant transfer from the female parent fish to the yolk-sac fry and if so, to what extent it influences the site-specific nature of the bioindicator.

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QUEBEC WORKING GROUP SESSION

Attendees

H. Vaughan (Chairman) Western and Northern (WQB)

D. Bondy (Recorder) Headquarters (WQB)

H. Sloterdijk (Presenter) Québec (WQB)

A. Chau Analytical Ecology Division (NWRI)
H. Dobson Aquatic Ecology Division (NWRI)

A. Hamilton Ottawa (IJC)

L. Lau Hydraulics Division (NWRI)

J. Merriman Ontario (WQB)

C. Murthy Applied Physics and Systems Division (NWRI)

I. Orchard Ontario (EPS)

S. Rao Analytical Methods Division (NWRI)

E. Watt Headquarters (WQB)

M. Whittle Great Lakes Fisheries Research Branch (DFO)

NWRI - National Water Research Institute, Department of the Environment

WQB - Water Quality Branch, Department of the Environment

EPS - Environmental Protection Service, Department of the Environment

IJC - International Joint Commission

DFO - Department of Fisheries and Oceans

The session started with discussion on the objective of the working Establishment of a "better" monitoring program, one which included sediments and biota, was accepted by the group as the primary objective. Work began with the assumption that present resources would not be significantly increased. Therefore, the goal was to establish the most efficient and effective monitoring possible, and not to design the ideal program, then trim it down to fit resource constraints. monitoring program would consist of the standard fixed network and special studies as interactive components. Interaction with research community, through the special study component, was considered by all the group to be highly desirable. Similarly, the concept of ongoing reassessment of the monitoring program received a great deal of attention. Any monitoring program should be flexible, responsive and with the assessment of system health and concentrations. The objectives should be scientifically defensible, supply management with the information they require, and should be reviewed frequently throughout the program to ensure that the most cost efficient and scientifically sound monitoring program is being employed.

The group then decided to discuss the Quebec presentation and make comments on areas within the program that could be improved in the future, to provide a holistic monitoring program. The major concern with this monitoring program on the St. Lawrence River was that it did not assess environmental effects. Even the use of the biomonitoring tool (forage fish) dealt solely with concentrations. Although the group agreed effects monitoring or ecosystem health monitoring were extremely difficult with present state of the art knowledge, a greater effort toward these objectives was needed. Concentrations in water represent instantaneous values, and therefore are highly variable and

extremely difficult to interpret, while concentrations in forage fish (although seen as an integrated value over time) are not comparable among river basins, which differ greatly in hydrology, loading, etc. The group, however, was pleased to see that the forage fish component had been incorporated, and all felt that this component brought the program one step closer to the most desirable monitoring effects.

A second concern discussed by the group was the selectivity of the spottail shiner for contaminants uptake. It has been shown that the spottail shiner bioconcentrates PCBs and DDT, but the group felt that it could not be used as an early warning system of hitherto unknown Bottom or suspended sediment sampling may prove more contaminants. useful for this objective. Data obtained from other agencies (e.g., EPS for loadings and effluent discharges) would be very helpful. It was pointed out, however, that the spottail component of the study did identify the "hot spots" within the study area, providing a focus of further monitoring or research efforts, something the costly water component to the study had not. The traditional water-oriented monitoring programs and NAQUADAT, the national storage bank (almost exclusively for water analysis), were deemed to be of little use. monitoring, developed under multi-media the concept of sampling, should result in background information and problem/emerging At that point the advice and cooperation of issue identification. researchers should be actively sought in the design and implementation of special studies while at the same time a review of the generated data would result in fewer stations and/or parameter and/or sampling frequencies.

It was recognized that research technology that is too complex and not easily transferable to an operation level was of limited use to a monitoring program. The research community must commit the effort to the technological transfer stage. Many logistic difficulties can result during the application of new technology and, all too often, the researcher has either lost interest in the project or is working on one. Similarly the monitoring group must specifically define their research needs so that development and application of new technology does not require years of routine (non-research) work. Active interaction and communication were seen by the group as critical for a technological transfer to occur. The group did recognize the difficulties (i.e., distance between the research group in Burlington and the monitoring groups in the various regions) but felt that better coordination at the management and working levels would prove beneficial. Personal contacts were considered preferable to bureaucratic structures.

The group felt that storage of fish and water samples as well as the chromatographs from analyzed samples for later analyses of any new priority pollutants was advisable. It also felt that excessive time was spent on the measurement and interpretation of single compounds. Toxic contaminants often have a cumulative (synergistic) effect. Therefore, there is a need to develop a monitoring tool to address this problem. A simple additive or multiplicative model, as presently used in many water quality indices, was suggested as a good start.

The group also discussed the public's (client) perception and understanding of monitoring. Often the language (jargon) used is too specialized for our clients to understand. Objectives monitoring program should be written simply and reflect just those of the scientific concerns, and not or managerial The example of monitoring for carcinogens or papilomas in fish, rather than simple concentrations in biota, or water and sediment, was given. Often the added cost factor to obtain information of direct interest to the public is small in comparison to the cost of the overall monitoring program. Although it was recognized by the group that IWD had no mandate to do fish population studies, the group felt fish health (population studies) would be something the public could easily relate to, versus ecosystem health (a somewhat abstract Interaction with DFO could perhaps prove extremely useful to IWD if this concept were employed. This type of effects monitoring would also be of more use to management in the establishment of policy or understanding trends, or for the establishment of scientifically defensible objectives.

The interaction of a regional with a national program was also discussed. The group agreed that regional issues should not be distorted to suit a national program. However, there is a need for a consistent national strategy and central coordination of the monitoring programs. This coordination should rely heavily on regional input. National assessments may need a separate initiative and a reporting structure other than at the basin or regional level.

National trends for a variety of pollutants also received a great deal of attention. Difficulties due to data inconsistencies, changes in laboratories or analytical techniques, detection limits, etc., were all identified as major drawbacks. The data record was seldom long enough to do national trends, although some regional programs have been successful (e.g., TP in the Great Lakes).

The development of national screening tools as stress indicators The group felt that the most potential appears to be was discussed. with the microbiological parameters. The main objective of the screening tool would be to identify, quickly and inexpensively, areas Within the river basin requiring further investigation. Difficulties associated with this technique were also identified (e.g., disturbances of microbiological populations be equated with jeopardization of socially accepted values: can the obtained be converted to the establishment of objectives to protect or conserve the quality of the environment). The group felt that a screening tool technology needed to be explored and that research could and should actively interact with the routine monitoring component to develop and implement cost-efficient screening tools.

ONTARIO REGION

Water Quality Investigations in Ontario's Arctic Watershed

by

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ABSTRACT

A water quality sampling network was established in the major rivers of Ontario's arctic watershed to provide baseline information. Based on data generated by the network sampling, several short-term studies were carried out to address concerns particular to these specifically, these studies were conducted More (1) identify and enumerate the benthic macroinvertebrate communities; (2) investigate the distribution of heavy metals and contaminants in water, sediment and fish; (3) examine the relative mobility of various elements through the analyses of sorbed and lattice-bound sediment fractions; (4) assess atmospheric depositions of organic pollutants in the region by sampling the wetlands; and (5) characterize the major colloid types in these northern waters and determine the relative binding capacity of the dissolved and colloidal These follow-up studies have provided information for assessing the source and fate of contaminants and for describing ambient environmental conditions. Selected results are presented.

INTRODUCTION

The Ontario arctic watershed, with a combined drainage area of extends over substantial portions αf physiographic regions, the Canadian Shield and the Hudson Bay Lowland. The Shield portion of the watershed is composed of ancient crystalline granites interspersed with metasedimentary and metavolcanic rocks. Outcrops of bedrock are common, since much of the overlying material was stripped away by glacial action (Hutton and Black 1975). Hudson Bay Lowland (HBL) is a vast and gently sloping coastal plain, located between the Canadian Shield and the south and west shores of Hudson and James Bay. This region is of particular national importance as a nesting and feeding area for many species of geese, ducks and shorebirds, and represents a unique wetland environment which is sparsely populated and supports few resource-based activities. characterized by a sedimentary limestone bedrock overlain with marine Virtually the entire Lowland area is poorly drained, and features extensive bog and fen complexes in combination with a myriad of pools, ponds and lakes. The Ontario portion (265 000 $\rm km^2$) of this immense peat complex is dissected by five major rivers: the Moose. Albany, Attawapiskat, Winisk and Severn. Except during spring freshet, these highly coloured waters are generally shallow and slow moving. River beds and banks are widened and deepened in many areas by the scouring action of ice and spring flood waters (Hutton and Black 1975). The resulting riverbanks commonly rise 5 to 15 m to forested levees.

As part of a multi-disciplinary baseline program, the Water Quality Branch, Ontario Region (WQB-OR), has undertaken a study to establish baseline water quality conditions in the five major rivers. largely being achieved by a water quality network. Several other studies, however, have been carried out to provide information on the source, fate and compartmentalization of contaminants in these northern watersheds. this In paper, the development of a multi-phase environmental sampling program (Fig. 1) and selected results are presented. Detailed descriptions of the sampling sites and methods can be obtained from previous reports.

PILOT STUDY

Prior to the establishment of the Northern Water Quality Network, a pilot study was conducted in the Moose River basin. This watershed is located in the northeast sector of the Province of Ontario, and drains an area of approximately 109 000 km². The three main tributaries, the Missinaibi, Mattagami and Abitibi, descend approximately 500 m over a distance of 500 km from their source on the Shield to the mouth of the Moose River on James Bay (Fig. 2). The lower reaches of the Moose River and estuary present a complex pattern of islands and channels. Langford (1963) suggests that salt water enters the Moose River and travels upstream to a point just north of Moosonee, while tidal movements can be observed upstream from the south end of Bushy Island (Fig. 3). The maximum range of tides at the mouth of the Moose River is approximately 3 m. Water levels in several of the headwater streams are also regulated to maximize hydroelectric generation. This

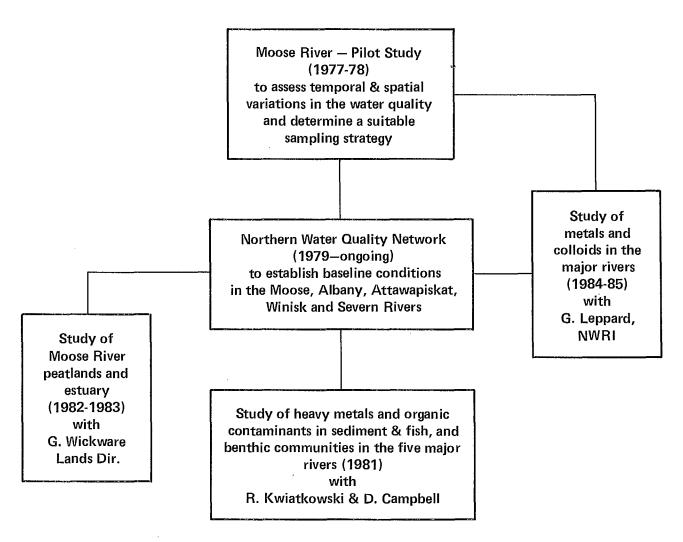


Figure 1. Development of a multi-phase sampling program in Ontario's arctic watershed.

regulation results in substantial changes in the discharge of both the Abitibi and Mattagami rivers.

The main objectives of the pilot study were to assess spatial and temporal variations, and to design a suitable sampling strategy for determining seasonal variations and long-term trends in the water quality of the lower Moose River. The approach adopted was to sample the Moose River upstream from Moosonee on a transect located at the south end of Bushy Island. Four sampling sites were selected (Fig. 3), and eight surveys were carried out between March 1977 and March 1978. Because of dangerous ice conditions the river could not be sampled during spring break-up and fall freeze-up.

Each survey was scheduled to consist of two consecutive days of sampling; unpredictable events such as adverse weather conditions and equipment failure, however, sometimes altered the schedule. During each day of sampling, six samples (three at low tide and three at high tide) were collected from all stations at a depth of 1 m. In the

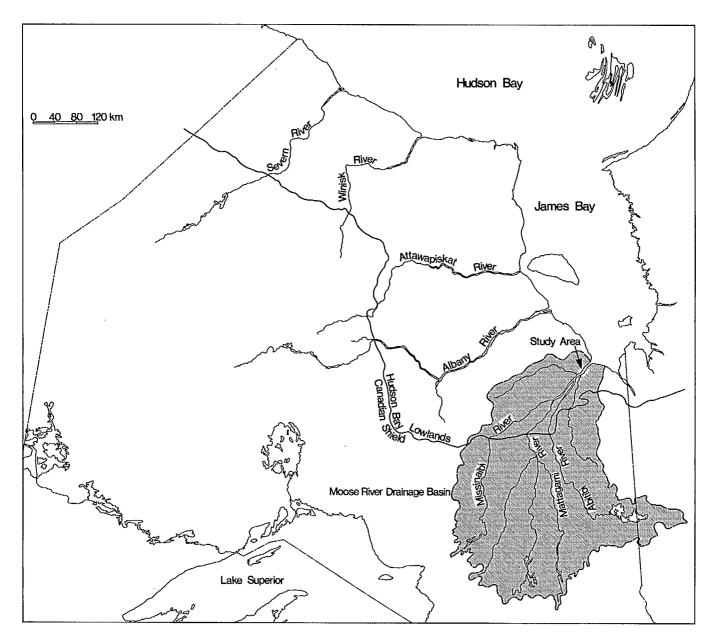


Figure 2. Moose River drainage basin.

winter months, a hole was drilled through the ice and after the stagnant water and ice chips had been removed, a sampling device was lowered into the free-flowing water (below the ice) to collect the water samples. All sample preparation such as filtering and preserving was completed within 8 h of collection. The samples were then returned to the Water Quality Branch laboratory in Burlington for the analysis of major ions, nutrients and trace metals (Environment Canada 1979).

A two-way analysis of variance was performed on data from the four most complete surveys to determine whether short-term variations (T), those differences observed at any station over the two-day sampling periods, and/or lateral variations (L) were significant (Table 1). The

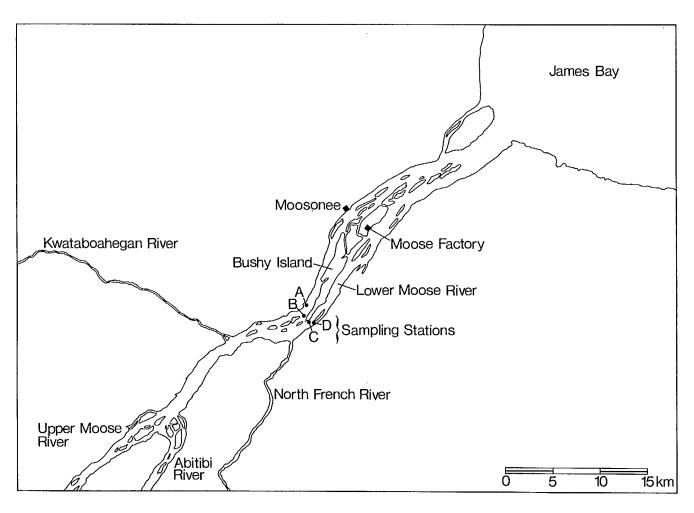


Figure 3. Moose River and tributaries.

UCLA Biomedical computer program BMD OV8 (Dixon 1971) was used to calculate the F-values. If the calculated F-value exceeded the critical F-value, then the observed changes were considered to be significant.

Short-Term Variation

Less than 20% of the cases tested for temporal variation (T) had F-values greater than the critical F-value (at the 95% confidence level). Those cases showing significant concentration difference with time (P > 0.05) usually varied by only 5%-10% from the mean value of samples collected at that station during the two-day surveys. Although statistically significant, this magnitude of short-term variation was relatively unimportant when compared with the large seasonal variation exhibited by most parameters.

Lateral Variation

As a result of reconnaissance survey carried out in 1976, it was postulated that distinct channels of differing water quality might

Table 1. Temporal and Lateral Variance in the Lower Moose River Water Quality

	Surv May 10	ey 2 11, 1977		Survey 4 July 9-10, 1977		y 5 ⊢31, 1977		Survey 6 October 18-19, 1977	
Parameter	Hay 10-	T T	L L	T	L	T	L	T	
Alkalinity, total	148.0	2.10	88.0	1.71	41.0	2.35	417.0	0.20	
Calcium	82.0	2.77	21.0	1.68	100.0	1.89	57.0	1.18	
Chloride	65.0	1.38	147.0	1.19	43.0	1.02	40.0	0.44	
Magnesium	218.0	1.50	436.0	11.3	77.0	1.95	107.0	0.45	
Potassium	10 ¹¹	10 ⁻⁹	47.0	1.50	45.0	1.00	11.4	1.00	
Sodium	308.0	1.00	167.0	2.25	92.0	2.62	17.6	0.55	
Sulphate	14.7	5.61	7.1	0.41	2.3	6.08	14.6	2.17	
Carbon, diss. organic	0.7	3.88	4.8	0.27	43.0	5.04	1.8	0.50	
Carbon, part. organic	21.1	0.58	1.4	4.70	-	-	23.1	2.56	
Nitrogen, part.	10.4	1.70	0.2	2.74	-	-	37.5	1.81	
Nitrogen, total Kjeldahl	39.0	0.58	11.8	1.32	6.0	0.10	15.4	0.97	
Phosphorus, total	50.0	5.96	1.9	2.14	29.0	9.60	16.7	0.54	
Turbidity	134.0	4.57	26.0	7.41	20.0	1.79	7.5	1.56	
Conductivity	68.0	2.66	61.0	4.69	1.5	1.08	1870.0	1.00	

L = Variance between sampling locations (calculated F-values).

T = Variance between sampling times (calculated F-values).

^{95%} Critical F-value: L = 3.86, T = 3.86

 $[\]frac{1}{2}$ 99% Critical F-value: L = 6.99, T = 6.99

occur in the lower Moose River owing to the convergence of the Kwataboahegan, upper Moose, Abitibi and North French rivers (Fig. 3). The four sampling sites A, B, C and D were selected to reflect the water quality of these rivers. Results of analysis of variance (Table 1) showed that 88% of the cases tested had significant lateral (L) variations (P > 0.05). Physical evidence such as sharp changes in colouration and distinct differences in turbidity across the river also indicated strong channelization of flow. Although lateral variations were significant throughout the year, they were at a minimum in the summer and maximum in the winter for many of the parameters investigated. Figure 4 illustrates relative concentrations across the Moose River for calcium.

Seasonal Variation

The largest variations in the water quality of the lower Moose River occurred on a seasonal basis, with some parameter concentrations showing flow-related changes. Discharge of the Moose River into James Bay, as derived from the summation of the tributary discharges, varied greatly during the study period (Fig. 5). Maximum values approaching 10 000 cm.s⁻¹ were found during spring freshet, April 23-25, 1977;

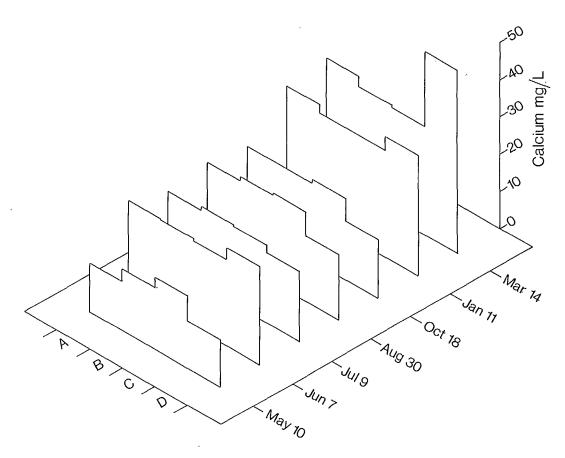


Figure 4. Lateral variation in the concentration of calcium across the lower Moose River, May 1977 to March 1978.

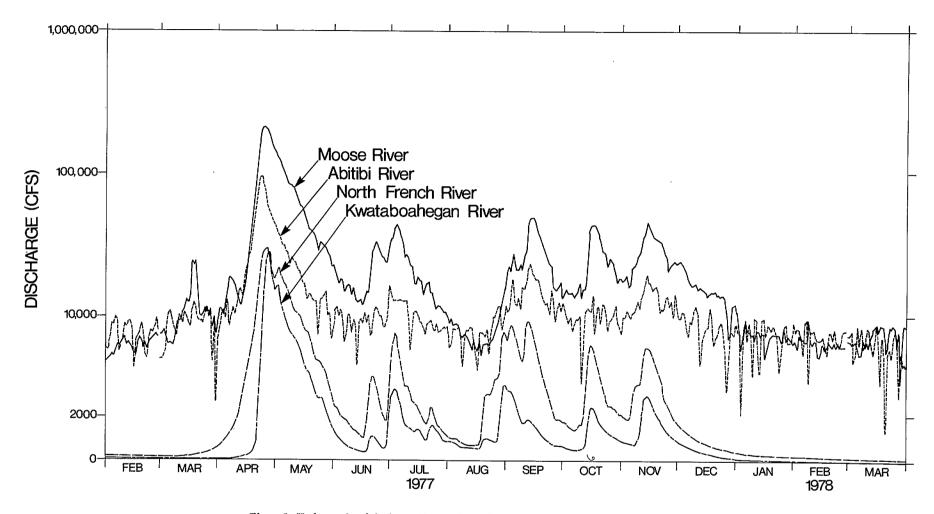


Figure 5. Hydrographs of the lower Moose River tributaries, February 1977 to March 1978.

minimum discharge levels averaging 420 cm.s⁻¹ were observed during the winter months, January to March 1978. The sharp fluctuations in the discharge of the Abitibi and upper Moose rivers were due to hydroelectric dams upstream holding back or impounding the water to maximize electrical generation. The North French and Kwataboahegan rivers were undammed and had natural flow regimes.

The maximum seasonal variation in the major ion chemistry was found in the side channels. Conductivity, a measure of the ionic constituents, varied by 200% at stations B and C, and up to 600% at stations A and D. Individual ions such as sodium, potassium and chloride were extremely variable; concentrations of the latter element were found to vary up to 2800% at station D. In general, the major ion concentrations varied inversely with flow. A six-year record of discharge and conductivity for the Moose River at Moose River Crossing typifies this relationship (Fig. 6).

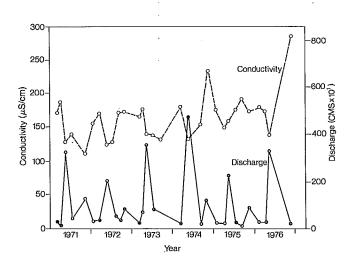


Figure 6. Seasonal discharge and conductivity of the upper Moose River.

Concentrations of nutrients and trace metals, which in many cases reflected both dissolved and particulate species, did not vary directly with flow but were strongly affected by flow. While spring runoff tended to dilute the concentration of dissolved species, severe erosion tended to increase bottom the banks and river Of the various metals investigated, iron and aluminum concentrations. were the most noteworthy, as concentrations approaching 1 ppm were not Elevated levels of total iron in May 1977 reflected the high suspended sediment load associated with freshet (Fig. 7).

carbon (DOC). a measure of aquatic Dissolved organic these northern waters. major component of substances. was a Concentrations were commonly found in the range of 15 to 25 mg. L^{-1} and exceeded levels of all riverborne constituents except calcium and Relatively low levels in May and June 1977 reflected the dilution effect of spring runoff, whereas the decrease found during the winter months was likely due to the freeze-up of creeks that drain the peatlands (Fig. 8). Concentrations of particulate organic carbon, which average 0.8 mg. L^{-1} , were a small fraction of the total organic carbon.

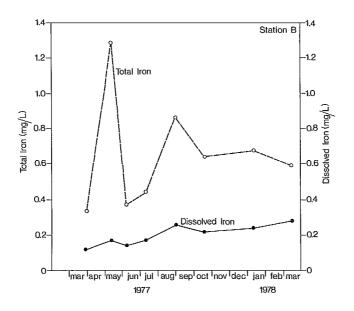


Figure 7. Total and dissolved iron in Moose River.

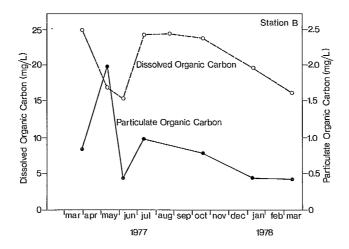


Figure 8. Dissolved and particulate organic carbon in the Moose River.

In summary, results from this study revealed the following information about the lower Moose River:

- Short-term (temporal) variations in the water quality were insignificant, and therefore, water quality sampling at the Bushy Island transect could be conducted independent of time of day.
- 2. Lateral variations in the water quality across the lower Moose River were very significant throughout the year for most parameters. These differences in water quality resulted from the channelized flow in the lower Moose River.
- 3. The greatest single factor affecting the major ion concentration of the Moose River was the annual flow cycle. Highest concentrations occurred during periods of lowest flow (fall and winter) and lowest chemical concentrations were found during spring runoff. Both flow and major ion concentrations were highly variable. In any single year, flow may vary up to 2000%, while chemical concentrations may vary up to 2800%.
- 4. The high suspended sediment load associated with spring runoff caused substantial increases in the concentration of total iron, extractable aluminum and particulate organic carbon, whereas the concentration of dissolved organic carbon decreased as a result of the dilution effect of spring runoff.

Since there was insignificant variation in the short-term and substantial concentration changes between surveys carried out on a five- to six-week time interval, it was felt that bi-weekly sampling would be suitable for establishing baseline water quality conditions. Sampling in two midstream channels (B and C), which accounts for 90% of the total discharge of the lower Moose River, would be most cost-effective.

Based on this study, a native resident of Moosonee was offered a contract to collect water samples from the two midstream stations.

NORTHERN WATER QUALITY NETWORK

Following a reconnaissance survey in 1979, a water quality sampling program was established to provide baseline information on all major rivers of Ontario's arctic watershed. Samples for nutrient, major ion and trace metal analyses were collected on a bi-weekly basis 10 to 20 km upstream from the mouths of the Moose, Albany, Attawapiskat, Winisk and Severn rivers (Fig. 2). Aliquots for organochlorine pesticides and PCBs were collected on a monthly basis. Results of the network data will be discussed along with fish and sediment data in the next section.

AN INVESTIGATION OF CONTAMINANTS AND BENTHIC COMMUNITIES

A study was undertaken in 1981 to investigate various inorganic and organic contaminants in water, fish and sediment, and provide information on the benthic macroinvertebrate communities for assessing

ambient environmental conditions. The approach adopted was to sample the five major rivers of Ontario's arctic watershed just upstream from their mouths near the northern water quality network sampling stations.

A field crew of five was flown to the sampling areas, and surveys were conducted from freighter canoes. Macroinvertebrate samples were collected in replicates of five at four to nine sites in each river using a 15 cm by 15 cm mini-Ponar. Visual estimates of the bottom substrate type were made as a percentage of pebble, sand, silt, clay and organic matter. Contents of each grab sample were hand-sieved using a standard No. 30 (0.59-mm mesh) sieve bucket. The sieved material was transferred to 2-L bottles and kept in river water until the live macroscopic organisms could be hand-picked. All samples were sorted and preserved within 24 h of collection.

Bottom sediment grab samples for trace contaminant analyses were also collected with a mini-Ponar. The top 1 cm of sediment was carefully removed and stored at -20°C in polyethylene bags and tin-plated containers for metal and organic analyses, respectively. Two species of freshwater fish common to the five rivers were captured using gill nets near the network sampling stations. The species chosen represent two trophic levels: northern pike, a top carnivore, and common white sucker, a bottom scavenger. Immediately after collection, each fish was wrapped in solvent-washed aluminum foil, placed in polyethylene bags and stored at -20°C. Ages of the northern pike and common white sucker were established by counting cleithral opercular annuli. The fish were homogenized and aliquots of the homogenate stored in acid-washed and acetone-hexane rinsed glass containers for trace metal and trace organic contaminant analyses, respectively.

Benthic Communities

The benthic communities were primarily dominated by chironomids and oligochaetes in each river except in the east channel of the Moose River where gastropods were also a common taxon (Fig. 9). Despite the harsh conditions associated with long winters and intense spring break-up periods, 126 species of macroinvertebrates were collected.

Diversity, as measured by the Shannon-Weiner diversity index for the individual stations, was found to range from 0 to 4.3. A one-way analysis of variance at the 5% level showed that there was no significant difference between station means among the five rivers. Species richness of the five rivers was also insignificantly different as determined by Q-statistics (Hendrickson 1978). Analysis of the individual station data showed that species richness was related to substrate composition, river velocity and water depth but not to any of the water chemistry variables measured.

Community structure analysis was performed using three indices: Coefficient of Community, Jaccard's coefficient and Percent Similarity of Community (Jaccard 1908; Whittaker and Fairbanks 1958; Sanders 1960). These indices showed that rivers geographically closest together resembled each other the most (Fig. 10).

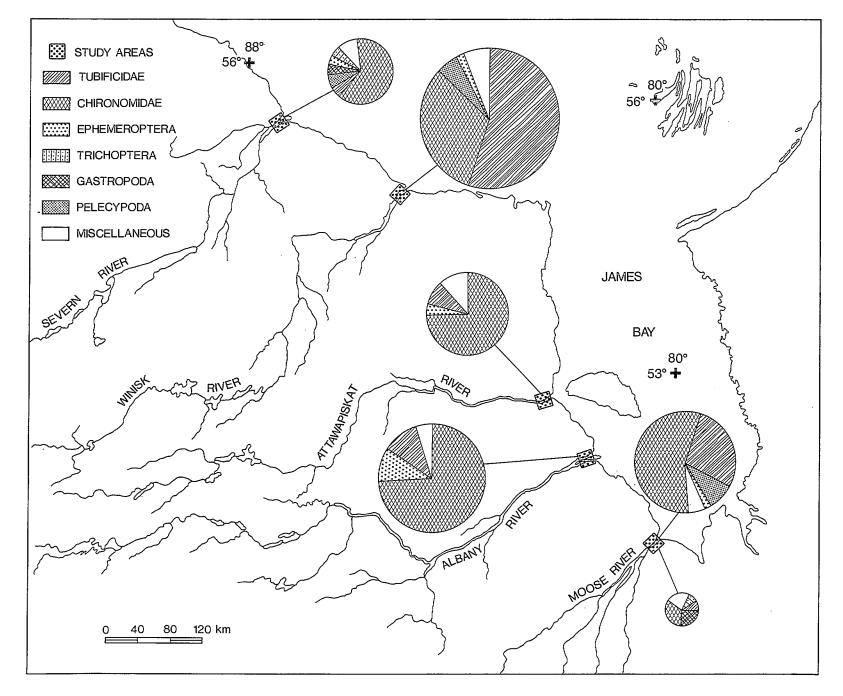


Figure 9. Macroinvertebrate species and their relative abundances found in the Hudson Bay Lowland. Circle size indicates relative numbers of individuals collected at each location.

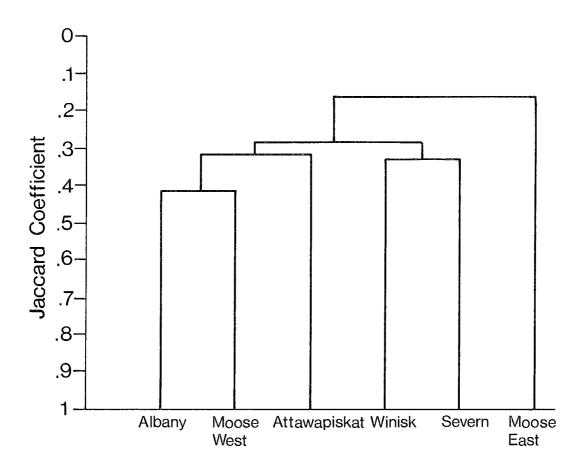


Figure 10. Results of cluster analysis on the benthic communities of the Hudson Bay Lowland rivers using the Jaccard coefficient and simple weighted pair groups.

Cluster analysis tended to confirm results of the three community structure indices. The east channel of the Moose River did not cluster strongly with the other rivers, whereas the Moose West, Albany and Attawapiskat clustered as did Winisk and Severn. Although there are obvious similarities and differences in the benthic communities, these northern rivers appeared to have the same level of diversity. Most of the values fell within the category (D = 1 to 3) for moderately stressed environments (Wilhm and Dorris 1968). Factors such as pH, dissolved oxygen and suspended sediment load, which normally limit species diversity and numbers of individuals, did not appear to limit the occurrence of macroinvertebrates. The low diversity indices were likely due to the natural processes of these harsh environments.

Water

Major ion analyses of the network samples showed that these waters are of the alkaline-earth-bicarbonate type, with conductivities ranging from 100 to 350 μ S on a seasonal basis in each river. These northern waters were often highly coloured and had elevated levels of dissolved organic carbon, which ranged from 10.1 to 14.5 mg.L⁻¹ (Table 2). Heavy metal analyses indicated the presence of high levels of total iron in each river; mean concentrations ranged from 260 to

860 $\mu g.L^{-1}$. Individual iron values often exceeded the Ontario Ministry of Environment (MOE) objective of 300 $\mu g.L^{-1}$ for the protection of aquatic life (MOE 1978). The percentage of exceedances in the five rivers ranged from 45% to 100%, with a greater proportion occurring in the Moose and Severn rivers. Overall, exceedant concentrations were found in 79% of the samples collected from the five watersheds.

Table 2. Mean Concentration of Selected Elements ($\mu g.L^{-1}$) and Organochlorine Contaminants ($ng.L^{-1}$) Present in Raw Water Samples Collected from Rivers of the Hudson Bay Lowland, June 1980 to December 1981

Parameter	Moose	Albany	Attawapiskat	Winisk	Severn
Aluminum ^l	450	470	100	60	330
Arsenic	0.7	0.3	0.6	0.2	0.4
Copper	5	4	5	2	3
Iron	860	260	380	350	840
Lead	2	1 .	1	1	7
Nickel	2	1	1	_	1
Zinc		3	4	4	5
α-BHC	5.0	5.5	8.4	6.0	7.2
Y-BHC	0.6	0.9	0.9	0.4	1.5
Cis-chlordane	0.5	0.4	0.1	0.1	0.1
Trans-chlordane	0.2	0.1	0.2	0.1	0.1
p,p'-DDE	0.1	0.1	0.1	0.1	0.1
Dieldrin	0.4	0.1	0.1	0.3	0.1
НСВ	0.2	0.2	0.1	0.6	0.2
PCBs	8	9	11	6	16
DOC2	14.5	12.7	11.6	10.1	11.2

All heavy metal analyses are total, with the exception of aluminum which is extractable.

The major inorganic species of iron in natural waters is ferric hydroxide. However, it has a very low solubility in the pH range of 5 to 8 (Wetzel 1975). Sholkovitz and Copeland (1980) have demonstrated that the solubilities of Fe, Ca, Ni, Cd, Co and Mn are opposite to those predicted by inorganic solubility considerations, and that complexation with humic substances is an important process. Weathering of mineral soils and sediments is often enhanced by naturally occurring organic acids and may increase the concentration of these soil

² Refers to dissolved organic carbon; concentrations are expressed in milligrams per litre.

constituents in aqueous solutions to levels far in excess of their normal solubilities (Schnitzer 1981). Owing to the elevated levels of DOC, which is a measure of aquatic humic substances, it is likely that a significant proportion of total iron in each river was complexed to humic fraction.

Previous water quality investigations of the Moose River have shown that on average 200 $\mu g.\,L^{-1}$ of iron was present in the dissolved phase, which accounted for 25% of total concentrations. The high non-filterable iron concentrations were largely due to suspended sediments, as the Moose River is shallow and resuspension of bottom sediments is common.

Of the various organochlorine pesticides and metabolites detected in water, $\alpha\text{-BHC}$ was by far the most concentrated with levels ranging from 5.0 to 8.4 ng.L $^{-1}$. Trace amounts of $\gamma\text{-BHC}$, cis-chlordane, trans-chlordane, dieldrin, p,p'-DDE and HCB were also detected in each river (Table 2). Polychlorinated biphenyls (PCBs), which are a group of industrial chemicals, were found at higher concentrations than any of the organochlorine pesticides. Mean concentrations ranged from 6 to 16 ng.L $^{-1}$. The hydrophobic contaminants were likely maintained in these northern waters due to binding capacity of humic substances.

In view of the remoteness of the study areas, concentrations of organochlorine contaminants found in these northern waters were indeed elevated. In fact, these concentrations were similar to levels found in the Niagara River, which is impacted by major municipal and industrial discharges as well as leachates from chemical waste dumps. Since these northern rivers are essentially free from direct contaminant inputs and the same contaminants were present in all rivers and comparable levels, the probable source of these compounds was atmospheric.

Sediment

Bottom sediment grab samples for elemental analyses were subjected to a two-part analytical scheme for $1 \, \underline{N}$ HCl extractable and residual determinations. The $1 \, \underline{N}$ HCl extractable fraction is an estimation of the sorbed or non-lattice bound component and is indicative of past and potential mobilization in the environment. Extractable analyses of the river sediments showed that sorbed concentrations were in the following order: Ba>Pb>Co=Zn>Cu=Ni>V>Cr>Cd>Be (Table 3). Several elements, such as Cr, V, Be, were relatively inert, as by far the greater proportion was found in the lattice bound fraction. Other elements, which include Pb, Co, Ba and Cu, exhibited a less conservative behaviour, as the percentage present in the sorbed fraction ranged from 20% to 40%. The most striking feature of the data was the high percentage of Cd (88%-100%) in the non-lattice bound fraction, which indicated that this element has a relatively high mobility in these northern watersheds.

Total concentrations of various elements investigated were similar in all five rivers. In many cases, these concentrations ranged between the high calcium granitic and deep-sea carbonate data reported by Turekian and Wedepohl (1961).

Table 3. Mean 1 \underline{N} HCl Extractable (ex) and Total (t) Concentrations ($\mu g.g^{-1}$, dry weight) for 12 Elements in Bottom Sediments from the Five Major Rivers of Ontario's Arctic Watershed, 1981

Location	Ва	Be	Cd	Cr	Со	Cu	Pb	Мо	Ni	Р	٧	Zn
Moose (ex)	32	0.04	0.25	1.6	3.0	1.3	3.5	-	1.8	-	1.2	4.7
Albany (ex)	80	0.05	0.21	1.0	3.1	3.6	6.5	_	1.8	_	1.8	5.7
Attawapiskat (ex)	55	0.05	0.31	0.2	3.1	1.4	4.5		1.2	_	0.7	2.2
Winisk (ex)	60	0.05	0.42	0.2	3.3	1.6	4.0	_	1.3	-	0.5	3.2
Severn (ex)	45	0.05	0.25	0.2	3.2	1.0	4.3	-	1.3		1.3	2.0
Moose (t)	220	0.9	0.25	29	9.3	8.0	11	1.8	11	230	35	34
Albany (t)	230	1.2	0.24	27	9.4	9.0	12	1.2	12	340	42	29
Attawapiskat (t)	130	1.1	0.35	23	9.5	8.3	12	1.5	14	320	40	35
Winisk (t)	340	1.2	0.48	24	9.3	6.5	10	1.7	12	310	34	25
Severn (t)	170	1.0	0.25	29	9.0	8.1	13	1.5	13	260	39	25
Granitic*	420	2	0.13	22	7	30	15	1	15	920	88	60
Carbonate*	190	2	0.13	11	7	30	9	3	30	350	20	35

^{*}Mean elemental concentrations in granitic and deep sea carbonate rocks; Turekian and Wedepohl (1962).

Note: Total concentrations are the sum of the 1 $\underline{\text{N}}$ HCl extractable and residual determinations.

Composite bottom sediment samples were prepared for each river, and analyzed for a wide range of organochlorine pesticides, chlorobenzenes, phthalates and polyaromatic hydrocarbons. Results indicated that the river sediments were free from these classes of compounds, and only trace amounts of PCBs were detected in samples collected from the Moose and Severn rivers. The virtual absence of organochlorine contaminants indicated that the accumulation of hydrophobic contaminants in bottom sediments was a relatively unimportant fate in these northern rivers. Hassett and Anderson (1982) have demonstrated that dissolved organic in natural waters can reduce the sorption of hydrophobic compounds by riverborne particulates. Previous water quality sampling of the Moose River has also shown that the concentration of dissolved organic carbon was approximately 20 times greater than particulate organic carbon (McCrea and Merriman 1981). In view of the binding capacity of humic substances, and the relative abundance of dissolved and particulate carbon, sorption of organic contaminants to sediments may not readily occur.

Fish

Mercury was found in all of the 46 fish analyzed with mean concentrations ranging from 0.14 to 0.28 $\rm ng.g^{-1}$ in northern pike and 0.16 to 0.32 $\rm ng.g^{-1}$ in common white sucker (Tables 4 and 5). Concentrations in the largest pike (68 cm) and white sucker (46 cm) collected from the Moose River were found to approach the 0.50 $\rm ng.g^{-1}$ limit for consumption with concentrations of 0.40 and 0.45 $\rm ng.g^{-1}$, respectively. Sources of mercury to these fish are not known; elevated levels of this element in fish from the many tributaries of the Moose River, however, indicated that mercury contamination is widespread in the watershed (Johnson 1984). Even though the Moose River basin has major pulp and paper, and mining operations, which may have contributed to mercury levels in the past, natural sources of this element should not be disregarded. Concentrations of mercury in fish collected from the other four rivers were considerably lower and corroborate the provincial consumption guide (MOE 1978).

Organic analyses showed that only trace amounts of a few contaminants were detected in the whole fish tissue of either species. The most prominent contaminant was PCBs with mean concentrations ranging from 0.01 to 0.06 $\rm ng.g^{-1}$ in pike and 0.01 to 0.09 $\rm ng.g^{-1}$ in white sucker. Trace amounts of $\alpha\textsc{-BHC}$, p,p'-DDE and HCB were occasionally detected; mean concentrations were less than 0.0005 $\rm ng.g^{-1}$.

Little or no information is available regarding the bioaccumulation of organochlorine contaminants in humic waters. However, a significant reduction in the biological uptake of petroleum hydrocarbons from seawater containing 3.0 mg.L $^{-1}$ of dissolved organic carbon was reported by Boehm and Quinn (1976). In this study, bioaccumulation factors showed that there was a low level of uptake in both species (Table 6).

Table 4. Mean Concentrations (µg.g⁻¹) of Selected Contaminants in Northern Pike Collected from Five Ontario Rivers of the Hudson Bay Lowland, 1981

Parameter	Moose	Albany	Attawapiskat	Winisk	Severn
Age	13 +	10 +	8 +	13 +	13 +
Length (cm)	63	58	50	68	68
Weight (kg)	1.74	1.29	0.83	2.16	2.22
Mercury	0.28	0.21	0.14	0.18	0.20
α-BHC	-	0.003	_	-	-
p,p'-DDE		0.003		0.004	•
HCB			-	0.001	-
PCBs	0.04	0.06	0.01	0.01	0.01

Table 5. Mean Concentrations (µg.g⁻¹) of Selected Contaminants in Common White Sucker Collected from Five Ontario Rivers of the Hudson Bay Lowland, 1981

Moose	Albany	Attawapiskat	Winisk	Severn
10 +	6 +	10 +	10 +	11 +
44	38		· =	45
				0.109
0.32	0.16			0.18
			_	0.002
0.002	_	0.001	_	0.001
_		_	-	0.001
0.09	0.06	0.01	0.01	
	10 + 44 1.10 0.32 0.002 0.002	10 + 6 + 44 38 1.10 0.67 0.32 0.16 0.002 0.003 0.002 -	10 + 6 + 10 + 44 38 42 1.10 0.67 0.86 0.32 0.16 0.19 0.002 0.003 - 0.002 - 0.001	10 + 6 + 10 + 10 + 44 38 42 41 1.10 0.67 0.86 0.82 0.32 0.16 0.19 0.24 0.002 0.003 0.002 - 0.001 -

Table 6. Bioaccumulation Factors (fish/water) for Various Organochlorine Contaminants in Fish from the Major Ontario Rivers of the Hudson Bay Lowland

Organochlorine contaminant	Northern pike	Common white sucker
α-BHC	2 x 10 ²	3 x 10 ²
p,p'-DDE	2 x 10 ⁴	1 x 10 ⁴
PCBs	2 x 10 ³	3 x 10 ³

In summary, the presence of humic substances appeared to play an important role in the water chemistry of these northern aquatic systems. Elevated levels of iron and aluminum indicated that high molecular weight organic acids can enhance the mobilization and solubilization of various heavy metals to levels far above their normal solubilities in inorganic waters. In addition, the data suggested that dissolved organic matter can alter the solubility, partitioning and bioaccumulation of organochlorine contaminants.

AN INVESTIGATION OF SEVERAL PEATLANDS AND ESTUARY SITES OF THE MOOSE RIVER BASIN

As a follow-up to the discovery of organochlorine contaminants in the major rivers of Ontario's arctic watershed, a survey was conducted in the Moose River basin to provide additional information regarding the source and fate of these toxic substances.

The Moose River basin drains an area of 109 000 km² and extends over substantial portions of three physiographic regions (Fig. 11). The upper portions of the basin are characterized by rolling to rugged uplands typical of the Canadian Shield. Wetlands cover approximately 20% of this area, primarily as small open bogs and spruce swamps. The central portion of the basin, referred to as the Great Clay Belt, represents the largest physiographic region, 50% of which is covered by extensive deposits of peat. In all, 58 000 km², or 53%, of the entire Moose River basin is covered by peatland terrain. Of the various wetland types, peat bogs are of particular interest, as they receive all of their water input from atmospheric sources and are thus excellent indicators and accumulators of airborne pollutants.

Moose River water has typically a yellow-brown colour, which is largely derived from the seepage of humic matter originating in the surrounding wetlands. Dissolved organic carbon, a measure of aquatic humic substances, has been found to be a major constituent of these northern waters having a mean concentration of $14.5~\rm ng.L^{-1}$. With the exception of spring runoff, discharge of these coloured waters into James Bay occurs primarily at ebb tide (Langford 1963) and provides an important source of nutrients to the adjacent coastal marshes. These salt marshes are periodically covered and uncovered by tidal waters, which have a maximum range of 3.1 m (Fisheries and Oceans Canada 1985). Contours of surficial waters at the southern extent of James Bay indicate that salinity is between 22% and 25% (Prisenberg 1982). Several studies have suggested that a portion of the riverborne humic matter may precipitate on contact with seawater (Sholkovitz 1976; Sieburth and Jensen 1968).

Since atmospheric deposition was considered a potential source of organochlorine contaminants to the northern watersheds, water from several peatland types common to the Moose River basin was sampled in August 1982. The water samples were collected from five peatland sites near Cochrane, Ontario (Fig. 11) by submerging solvent-washed glass bottles into existing bog-pools or small pits dug into the organic mat. In addition, sediment and vascular plants were collected from six

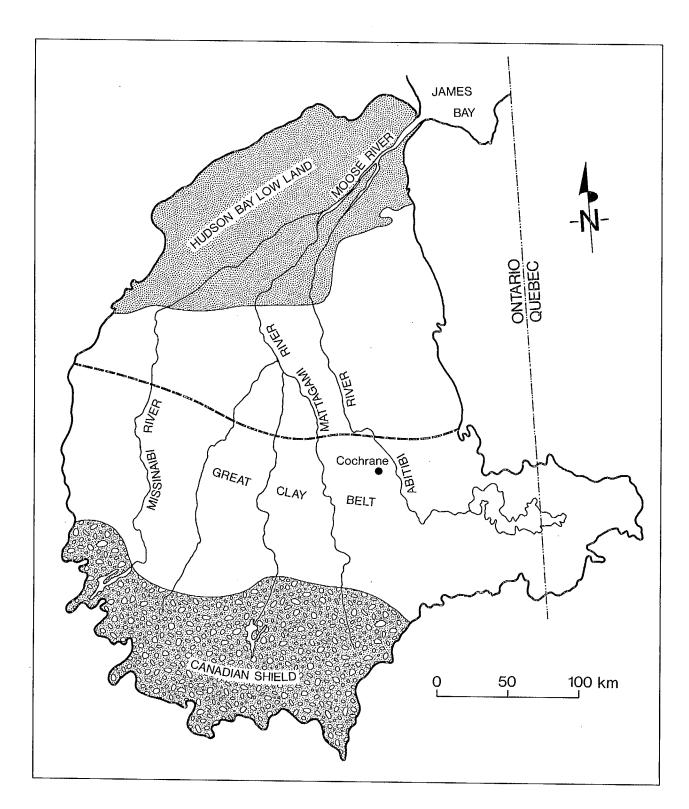


Figure 11. Major physiographic regions of the Moose River basin.

coastal marsh and tidal flat sites of the Moose River estuary to assess accumulation of deposition and riverborne organochlorine contaminants which may result from estuarine mixing. At each estuary site, exposed sediment from the top 1-cm layer was carefully removed during ebb tide with a steel trowel and transferred into solvent-washed Estimates of sediment texture and organic matter content were noted using a hand texture classification (Ontario Institute of Pedology 1982). Seed heads of <u>Triglochin maritima</u> L., an important food source for migrating geese (Thomas and Prevett 1980; Prevett et al. 1979), were collected at four marsh sites. Roots of latifolia L. were obtained along a small tidal creek.

Analyses of the unfiltered peatland water samples showed that PCBs were present at each site with concentrations ranging from 28 to 65 ng.L⁻¹. These levels were indeed elevated, as concentrations were several times greater than had been reported for the Moose River. the various pesticides studied, the hexachlorohexane isomer $\alpha-BHC$ was the most concentrated, with values ranging from 0.5 to 12.1 ng.L $^{-1}$. An investigation of organic compounds in Canadian surface waters has also revealed that of the 27 sites sampled, the highest concentrations of PCBs were present in a fen located 80 km west of Moose River These data further substantiate the atmospheric (Lawrence 1978). deposition of organochlorine contaminants in the region and demonstrate the importance of peatlands as accumulators of toxic substances. view of the extensive peatland area in he Moose River basin, and the concentration of contaminants found, it is likely that water draining from the peatlands was an important source of PCBs and $\alpha\text{-BHC}$ to the Moose River.

Sediment texture at the six estuary sites ranged from silty clay with humus in the upper marsh to fine and medium sand in the tidal flats. Analyses of nine sediment samples showed that organochlorine pesticides and PCBs were not present in either the tidal flats or coastal marsh sites. Samples of <u>Triglochin maritima</u> and <u>Typha latifolia</u> were also free from PCBs. Although significant amounts of several contaminants have been transported into the Moose River estuary, no evidence of deposition or accumulation has been found.

AN INVESTIGATION OF HEAVY METALS AND COLLOIDS

Elevated levels of several metals have been found in raw water samples collected from all five major rivers of Ontario's arctic watershed. In particular, the northern network data have shown that concentrations of iron and aluminum are commonly above the MOE objectives of 300 and $100~\mu g.L^{-1}$ for the protection of aquatic life. Overall, the mean percentage of exceedances of total iron and extractable aluminum in these watersheds was 79% and 60%, respectively.

Previous investigations of the Moose River have also shown that the major portion of these heavy metals was due to the suspended sediment load. Nevertheless, concentrations of iron and aluminum in the dissolved phase ($\stackrel{>}{\sim}0.45~\mu m$) were indeed elevated and far above their normal solubilities with mean concentrations of 200 and 70 $\mu g.L^{-1}$, respectively. In view of the levels of aquatic humic substances and

their binding capacity, it was felt that complexation and/or adsorption of heavy metals to the humic fraction was an important process in these northern rivers. With this in mind, a study was undertaken with Dr. G. Leppard, NWRI, to investigate the compartmentalization of heavy metals in the dissolved and colloidal phase, characterize the major colloid types, and determine the relative binding capacity of each fraction.

Two-litre samples reflecting the water quality in the various seasons were collected from the northern rivers and subjected to a two-part fractionation technique yielding several fractions (Fig. 12). Raw, aqueous, dissolved and colloidal water fractions were analyzed for total iron, extractable aluminum, dissolved and/or particulate organic carbon. Aliquots of each of the four fractions were precipitated with ruthenium red and later examined with an electron microscope (Burnison and Leppard 1983). At the time of preparation of this document, sampling and analyses was on-going.

Preliminary results have shown that the fractionation process, outlined in Figure 12, has been effective in isolating colloids, and that the colloidal fraction is an important component. Analyses of Severn River water, collected as part of the first sample set, showed that by far the greater proportion of the non-particulate iron and aluminum was associated with the colloidal fraction (Table 7).

Table 7. Distribution of Iron and Aluminum in Severn River Water Collected in March 1984

Fraction	POC (mg.L ⁻¹)	DOC (mg.L-1	Iron (mg.L ⁻¹)	Aluminum (mg.L ^{-l})
Raw	0.65	_	0.43	0.082
Aqueous		10.5	0.13	0.017
Dissolved		10.1	0.021	0.001
Colloidal		0.5	0.096	0.011

CONCLUSION

The network data have provided an effective means for establishing baseline water quality in Ontario's arctic watershed. More important, it has provided a basis for recognizing environmental issues particular to these basins and for developing short-term goal-specific studies to address these concerns. The follow-up studies, which account for only a small fraction of the entire sampling effort, combined with the network data have yielded information for assessing environmental conditions as well as the source, distribution and fate of heavy metals and organic contaminants in these watersheds.

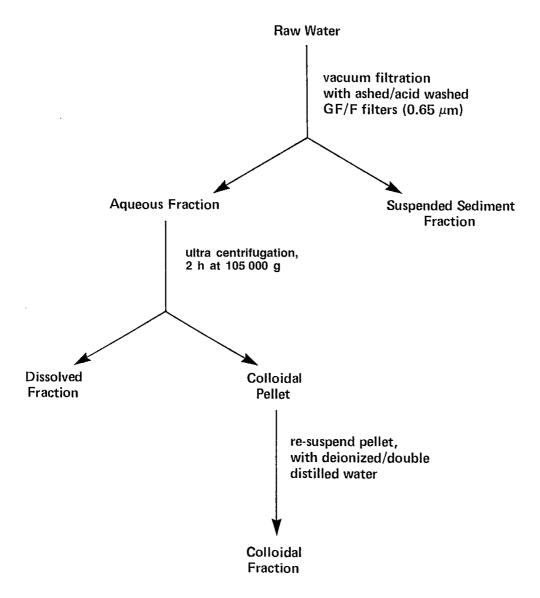


Figure 12. Flow diagram of the procedures used to separate the particulate dissolved and colloidal fractions.

ACKNOWLEDGMENTS

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ONTARIO WORKING GROUP SESSION

Attendees

T. Pollock (Chairman) Atlantic (WQB)
L. Désilets (Recorder) Headquarters (WQB)

R. McCrea (Presenter) Ontario (WQB)

U. Borgmann Great Lakes Fisheries Research Branch (DFO)

W. Glooschenko Aquatic Ecology Division (NWRI)
G. Leppard Aquatic Ecology Division (NWRI)

W. Strachan Environmental Contaminants Division (NWRI)

NWRI - National Water Research Institute, Department of the Environment

WQB - Water Quality Branch, Department of the Environment

DFO - Department of Fisheries and Oceans

The meeting began with discussion on the need for monitoring, surveys and special studies, and where interaction between WQB and NWRI could occur. It was agreed that WQB had the responsibility to carry out monitoring, but that NWRI should become more involved in surveys and special studies. Communication was identified as the key to this involvement. Only with a thorough knowledge of what is required or expected can the research community respond in an effective manner to the needs of the monitoring group. Historically, this communication has not occurred, and when it has, the requests were too broad in scope and not well defined. Personal contacts were considered preferable to a coordinating committee.

The working group then decided to describe a generic river basin monitoring program, outlining the various levels of planning and providing a checklist of activities that should be addressed by the project leader. Comments on when and where NWRI assistance would be best incorporated were also added.

Stage 1 Discovery

The group discussed the need to obtain as much information as possible on the river basin to be monitored, prior to any design considerations. Information should be acquired on the following areas:

geology
hydrology
meteorology
land use (forestry, agricultural, industrial, urban)
water chemistry
sedimentology
aquatic biology (benthos, algae, fish)
the dominant aquatic food web
terrestrial predators of aquatic life (birds, muskrats, mink,
etc.)
present and predicted water uses
chemical use (from sources such as Commercial Chemicals
Branch of EPS and/or Pest Control products Act)
available water quality objectives or guidelines.

It was recognized that information on all of these areas would not always be available; an effort to obtain as much information as possible, however, should be made. Sources for the information include previous studies, other government agencies (federal and provincial), universities, colleges, newspapers, local citizens and consulting firms.

All too often baseline studies are carried out on river basins when a substantial amount of information already exists. This results in a duplication of effort and the potential loss of acquiring valuable insight into the major issues within the river basin. information gathered during the discovery stage provides the project leader with initial answers to these questions: are there any problems/issues or potential problems/issues within the river basin; where are they located; when in the hydrological cycle is problem/issue most acute; is there a need for a pilot study, survey, special study, or can a routine monitoring program be designed? Without this baseline ecology information there is no rational way to establish station location, sample parameter lists, or sampling Gaps in knowledge should be identified and assistance from frequency. NWRI requested. If no information gaps exist, and problems/issues are identified, routine monitoring for the identification and determination of levels, concentrations, trends and natural variations of chemical compounds in water, sediments, and biota can be carried out.

Stage 2 Program Development

the problems/issues within Once the basin identified, the project leader should actively seek the participation of scientists for the establishment of a scientifically defensible hypothesis, and a statistically sound sampling program. Again, the group stressed the importance of having a holistic program. therefore expert advice should also be sought from provincial or other federal departments. A written proposal, or preferably an oral presentation, should be made to the research community, outlining as thoroughly as possible the of objectives the study baseline/background information available. For their part, it mandatory that NWRI management or management of other agencies encourage participation staff in both program development implementation.

Concern was expressed by the group that these efforts, which may consume a considerable amount of time, may go unrecognized, or be considered inappropriate for research scientists. The working group, however, felt that unless the scientist is involved at these early levels of monitoring development, participation at a later date is difficult and often useless. The entire group stressed the importance of effective communication and timeliness. NWRI work plans are done in the fall for the following year, and thus requests for assistance must be made prior to this. The concept of developing an expertise directory, within both WQB and NWRI, was discussed. It was felt that at the early stage of development, direct contact with the research scientists to determine the work load would be a superior route to follow, rather than the historically traditional project leader to management WQB, to management NWRI to scientist. This formal route

could be established once the project leader and scientist had made some preliminary estimates of the need for, and resource requirements of, the research component of the monitoring program.

Stage 3 Monitoring for Problem Identification

Discussions revolved around the need to have ecological (holistic, ecosystem) information. Multimedia sampling was identified as mandatory for all studies. Some discussion was held on community structure analyses versus biomass measurements, studying energy flow through the food web, etc. It was concluded that each river basin had to be studied individually and the information requirements established on a case by case basis. Table I was produced as a general guide for project leaders to follow. Due to the high costs often associated in travelling to a sampling site, it was also recommended that as wide a range of measurements as possible be taken at each site.

Table 1. Parameter Matrix to Consider for Monitoring Programs

Parameter set	Water	Medium sediment	Biota
Major ions	+	-	
Nutrients	+	+	· -
Total metals	ł·	+	+
Organic carbon	+	+	
Physical parameters	+	+	-
OCs and PCBs	+	+	+
Local pesticides	+	+	?
Radionuclides	۲	+	+
GC/MS scan	ŀ	+	+

The use of biotic indicators as a monitoring tool for problem identification was discussed by the group. Both functional (within an individual) and structural (within the community) biomonitoring were considered as valuable monitoring tools. Forage and large fish, benthic invertebrates, periphyton, microbes, and plankton (lakes) were all considered. Again, depending on the issues to be addressed, some of the above lists are more appropriate for monitoring than others. The group also identified the need to set objectives for biological organisms or biotic communities.

Also the importance of establishing a statistically valid sampling program received a great deal of discussion. Sites representative of the river basin. and based on the identified problems/issues, should be established. Review of historical data to ensure adequacy with respect to the number of stations, their location, parameters to be measured and sampling frequency, to provide statistical sound results, must be done.

Stage 4 Evaluation

The value of any monitoring program can only be assessed after the data have been collected and interpreted. No monitoring program should have data collection as a sole objective. Timely interpretation with review of the network, with respect to station location, measured parameters and sampling frequencies is a step that must be taken annually to ensure that routine monitoring does not degrade to a data gathering exercise. NWRI staff can play a large role in the interpretation and review process. Information gaps can be identified at this stage and interaction of NWRI researchers with WQB coordinated so that the monitoring program naturally evolves to meet its objectives.

WESTERN AND NORTHERN REGION

Water Quality Monitoring in the South Saskatchewan River Basin

by

D.J. Munro

Water Quality Branch Inland Waters Directorate Environment Canada Regina, Saskatchewan

ABSTRACT

The Water Quality Branch monitoring in the Western and Northern Region is to a large degree made up of two activities: routine long-term monitoring at fixed intervals, at fixed stations for a wide spectrum of variables and intensive short-term studies designed to address specific concerns and complement the routine monitoring. This presentation on water quality monitoring in the South Saskatchewan River basin was prepared to provide a basis of discussion on water quality monitoring in the Western and Northern Region for this workshop on water quality monitoring. The presentation provides a brief description of the river basin, the water quality issues in the basin and the Water Quality Branch monitoring activities. Routine monitoring is conducted at 13 stations throughout the basin as part of four different programs and/or agreements, each program having slight differences in parametric coverage or frequency. In addition to the routine monitoring, an intensive study to examine nutrient and contaminant input to Lake Diefenbaker is being conducted.

INTRODUCTION

The request for input to this monitoring workshop asked for a presentation on water quality monitoring within each region; this was to be accomplished by describing a basin study. In the Western and Northern Region, it was felt that it would be more appropriate to make presentation on our routine monitoring program and how it is complemented by intensive studies. The South Saskatchewan River basin is a major interprovincial river system in the Western and Northern encompassing most of southern Alberta and southwestern It was felt that the water quality monitoring in this Saskatchewan. river system was representative of the Water Quality Branch monitoring activities in the Western and Northern Region and thus would make a good basis for discussion at this workshop. The following presentation describes the South Saskatchewan River basin, the water quality issues, the routine monitoring program and an intensive study undertaken in the No attempt will be made to present any detailed interpretation of the data, as the intensive study is not completed and the routine monitoring data have in the past simply been reported with no interpretation and such an interpretation is beyond the scope of this presentation.

DESCRIPTION OF THE SOUTH SASKATCHEWAN RIVER BASIN

The South Saskatchewan River (Fig. 1) rises in the Rocky Mountains of Alberta as three main rivers, the Oldman, the Bow and the Red Deer. The Oldman River and its tributaries drain the most southern part of southwestern Alberta and northwestern Montana, including such places as Glacier National Park in Montana and Waterton National Park The Oldman flows east through southwestern Alberta, through Lethbridge, and joins the Bow River west of Medicine Hat to form the South Saskatchewan River. The Bow River originates in the mountains west of Calgary, and the river and its tributaries drain much of Banff National Park and the Kananaskis Country. The Bow River flows east out of the mountains through Calgary joining the Oldman River west of Medicine Hat. The South Saskatchewan River then flows through Medicine Hat to cross the Saskatchewan border due east of Calgary. The Red Deer River, which drains south-central Alberta, originates in the northern portion of Banff National Park and flows east through Red Deer and through the Drumheller Badlands, meeting the South Saskatchewan River just east of the Saskatchewan/Alberta border. The South Saskatchewan River flows through southwestern Saskatchewan, Lake Diefenbaker (which was formed in the mid-1960s) and Saskatoon to converge with the North east of Prince Albert where it becomes the The drainage area of the South Saskatchewan River Saskatchewan River Saskatchewan River. Basin is about 148 000 km^2 and it is about 1500 km from its origin to the confluence with the North Saskatchewan River.

Flow conditions for the South Saskatchewan River basin vary widely throughout the year and between years. The typical annual hydrologic pattern (Fig. 2) in the basin is low flow during the winter months followed by two spring peak flow periods: one representing snowmelt in the prairie regions, which usually occurs in April, and the second the result of mountain snowmelt, which occurs in late June and July. The

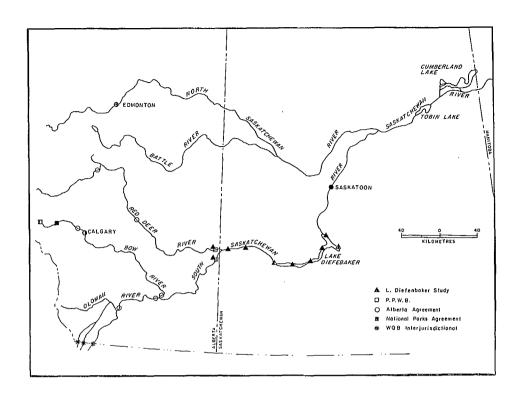


Figure 1. Saskatchewan River basin showing sampling sites in the South Saskatchewan River basin.

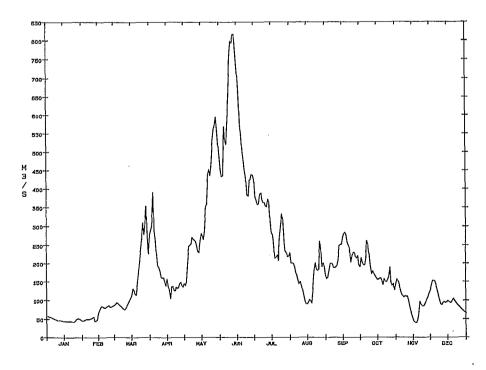


Figure 2. Daily flow in the South Saskatchewan River at Highway 41 in 1978.

magnitude of the two peak flow periods depends on the snow conditions in the two areas, but mountain snowmelt generally produces higher flows. The summer peak is followed by a gradual decline to winter low flow conditions. Flow conditions, however, are often altered by the operation of the numerous control structures throughout the drainage basin.

WATER QUALITY ISSUES IN THE BASIN

There are numerous water use concerns (drinking water, fisheries, recreation) in the South Saskatchewan River basin. These concerns result from deteriorated water quality caused by eutrophication; input of agricultural pesticides; irrigation return flows as they impact on eutrophication, input of agricultural pesticides and water salinity; and industrial and urban discharge of contaminants.

Vast areas within the drainage basin are agricultural lands used for cereal cropping. Large amounts of fertilizer and pesticides are applied within these agricultural areas. Much of the soil within the agricultural areas of the basin has high phosphorus concentrations and the use of nitrogen fertilizer plus the addition of nutrients from the major urban centres often leads to very high nutrient levels in the water. For example, total phosphorus in excess of 0.25 mg/L and total nitrogen concentrations greater than 1.0 mg/L are common. These high nutrient levels raise considerable concern for the trophic condition within the basin, particularly in the numerous reservoirs.

The concern about the agricultural pesticides in the basin can be seen by examining the annual application of herbicides within the basin. A 1984 Use Survey suggested that an amount in the order of 4.2 million kilograms (active ingredient) of the six most widely used herbicides (2,4-D, triallate, trifluralin, MCPA, diclofopmethyl and bromoxynil) were applied in the basin in 1983. The sheer magnitude of the use of pesticides creates the potential for contamination (by both parent and breakdown compounds) of the water within the basin.

Irrigation return flows are of concern due to the potential impact on the ion balance and increased salinity in the river and the potential for increased input of agricultural pesticides and nutrients. At present, there are about 400 000 ha of irrigable land within the basin (Fig. 3). The impact of irrigation return flows from this land has not been determined, and numerous proposals exist to increase substantially the irrigable land in the basin.

The concerns about discharge of contaminants from industrial and urban centres on the water quality of the river are much the same as anywhere, most notably the discharge of toxic chemicals and nutrients. Industry has grown considerably over the past few years, such as that related to petrochemicals, and there has been significant population growth, most notably in Alberta. The major urban centres within the basin include the Alberta cities of Calgary, Red Deer, Lethbridge and Medicine Hat, and Saskatoon in Saskatchewan.

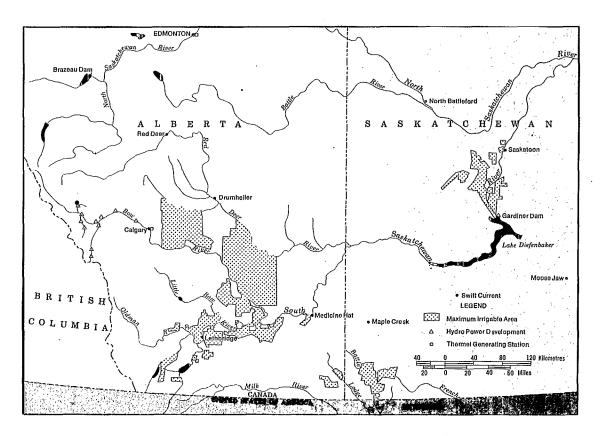


Figure 3. Map of irrigable land in the South Saskatchewan River basin.

WATER QUALITY MONITORING CONDUCTED BY THE WATER QUALITY BRANCH

The Business of the Water Quality Branch (WQB 1985a) states the Water Quality Branch has two basic roles: (1) to provide scientific and technical information and advice to government, private agencies and the public, and to promote the wise management of the quality of water in inland waters of federal interest, and (2) to detect emerging water quality problems and to evaluate water quality issues on Canada's inland waters. In response to these roles the Water Quality Branch conducts routine monitoring to identify pollution problems, maintain an inventory of baseline water quality information, identify trends in aquatic quality, determine compliance of waters with objectives, and by participating with provinces in joint cooperative, and cost-shared programs defined by federal provincial agreements.

Water quality monitoring has been conducted by the federal government in the South Saskatchewan River basin in some form since the early 1950s. Routine monitoring by the Water Quality Branch in a form similar to that being conducted now began about 1970. At present, the Branch conducts routine monitoring at 13 locations within the basin (Fig. 1). A brief description of each sampling location and the NAQUADAT station numbers are given in Table 1. This routine monitoring is conducted under four different programs or agreements, including

Table 1. Routine Monitoring and Study Stations in the South Saskatchewan River Basin

Stations	NAQUADAT No.
WQB Interjurisdictional Stations St. Mary's River near the International Boundary Belly River at Highway 6 Waterton River at Highway 6	00AL05AE0001 00AL05AD0060 00AL05AD0005
National Parks Agreement Stations Bow River at Highway 1 above Lake Louise Bow River 4.5 km above Canmore	00AL05BA0011 00AL05BE0013
Alberta Agreement Oldman River near Lethbridge Oldman River at Highway 36 Bridge Bow River at Cochrane Bow River near the mouth Red Deer River above Red Deer Red Deer River at Drumheller	00AL05AD0002 00AL05AG0001 00AL05BH0017 00AL05BN0001 00AL05CC0004 00AL05CE0001
Prairie Provinces Water Board Red Deer River near Bindloss South Saskatchewan River at Highway 41	00AL05CK0001 00AL05AK0001
WQB Sask. DOE S. Sask./Lake Diefenbaker Study Red Deer River near Bindloss South Saskatchewan River at Highway 41 South Saskatchewan River near Leader South Saskatchewan River near Lemsford Lake Diefenbaker at Saskatchewan Landing Lake Diefenbaker near Goodwin Lake Diefenbaker near Main Center Lake Diefenbaker at Riverhurst Ferry Lake Diefenbaker at Douglas Point Lake Diefenbaker near Danielson	00AL05CK0001 00AL05AK0001 00SA05NB0002 00SA05NB0001

Water Quality Branch interjurisdictional monitoring, ad hoc agreements with the National Parks and Alberta Department of Environment, and an agreement with the Prairie Provinces Water Board.

The sample collection and analyses vary somewhat between the programs but basically consist of monthly collection of water samples for a wide range of variables including major ions, nutrients, metals and organic contaminants. The major differences in the analyses conducted under the four monitoring programs are that metals and organic contaminant analyses are conducted quarterly at the Alberta Agreement sites; organic analyses are conducted at only one of the

Table 2. Summary of 1980 and 1981 Nutrients in Water Data

1 phosphorus	<0.003	
alvad phacphagus		0.016
olved phosphorus	<0.003	0.003
l nitrogen	0.11	0.27
olved nitrogen	0.09	0.16
1 phosphorus	0.15	0.40
olved phosphorus	0.11	0.20
l nitrogen	1.05	2.40
olved nitrogen	1.20	2.30
1 phosphorus	0.071	0.29
olved phosphorus	0.031	0.16
l nitrogen	1.00	2.03
olved nitrogen	0.79	
	olved phosphorus I nitrogen olved nitrogen I phosphorus olved phosphorus I nitrogen	1 nitrogen 1.05 colved nitrogen 1.20 al phosphorus 0.071 colved phosphorus 0.031

National Parks sites; and metals and organic contaminants analysis are not conducted at one of the Water Quality Branch Interjurisdictional sites. A complete description of these programs and the parametric coverage is available in the Western and Northern Region Program Outline 1985/86 (WQB 1985b).

RESULTS OF ROUTINE MONITORING PROGRAM

The results of the routine monitoring are provided to the various agencies for whom they are collected. They are also published as detailed data reports prepared by the Water Quality Branch. Historically, only minimal interpretation of the data has been carried out. Tables 2 to 4 give examples of nutrient and toxic chemicals data found in the basin. In each of these tables the downstream deterioration of the water quality is apparent. The water at the

Table 3. Summary of 1980 and 1981 Pesticides in Water Data

Parameter	Detection* (%)	Maximum (µg/L)
Alpha-BHC	50	0.007
Alpha-BHC	100	0.010
Lindane	35	0.001
2,4-D	75	0.020
Alpha-BHC	100	0.010
Lindane	50	0.005
2,4-D	90	0.30
	Alpha-BHC Alpha-BHC Lindane 2,4-D Alpha-BHC Lindane	Parameter (%) Alpha-BHC 50 Alpha-BHC 100 Lindane 35 2,4-D 75 Alpha-BHC 100 Lindane 50

^{*}Percentage of samples with positive detection.

Note: No other pesticides were detected at these sites during 1980-1981.

upstream sites in the mountains has low nutrient concentrations and few positive detections of metals and pesticides. Downstream, the nutrient concentrations increase significantly, and the concentrations and number of positive detections of metals and pesticides increase.

LAKE DIEFENBAKER SOUTH SASKATCHEWAN RIVER STUDY

Due to the nature of the routine monitoring program there are limitations with respect to what can be determined by analysis of the data. As a result, the Water Quality Branch undertakes intensive short-term studies to address specific concerns or issues within a river basin and will augment the existing routine monitoring data.

In the case of the South Saskatchewan River basin, a joint one-year intensive study of Lake Diefenbaker is being conducted by the Water Quality Branch and Saskatchewan Department of Environment. The objectives of the study are to provide information on the input of nutrients, metals and organic compounds to Lake Diefenbaker, to provide additional information on the water quality of Lake Diefenbaker and to evaluate the water quality in relation to the present and future uses of the reservoir. The study objectives roughly divide the field

Table 4. Summary of 1980 and 1981 Metals in Water Data

Station	Parameter	Median (mg/L)	Maximum (mg/L)	Detection [*] (%)
Bow River 4.5 km	Mercury (μg/L)	<0.02	0.02	4
above Canmore	Nickel	<0.002	0.013	50
	Copper	0.001	0.006	100
	Cadmium	<0.001	0.001	12
	Lead	<0.004	0.006	12
	Zinc	0.002	0.011	100
Bow River near the	Mercury(μg/L)	<0.02	0.05	17
mouth	Nickel	<0.002	0.012	50
	Copper	0.002	0.003	100
	Cadmium	<0.001	0.002	28
	Lead	<0.004	0.002	25
	Zinc	0.004	0.011	100
South Saskatchewan	Mercury (μg/L)	<0.02	0.05	8
River at Highway 41	Nickel	0.002	0.012	100
	Copper	0.002	0.008	100
	Cadmium	<0.001	0.002	8
	Lead	<0.004	0.006	5
	Zinc	0.004	0.037	7 00

^{*}Percentage of samples with positive detection.

sampling into two parts: (1) river work to assess input and (2) lake work to determine the present quality of the reservoir. To reduce logistical problems and to make the best use of personnel in the two groups, the Water Quality Branch undertook the river sampling and Saskatchewan Department of Environment undertook the lake work. The field sampling portion of the study began in the spring of 1984 and continued until July of 1985. Data analysis is presently in progress.

Sampling at the six lake sites (Figure 1) was conducted on a biweekly basis during July and August and every three weeks during the rest of the study period, conditions permitting. Samples from each site were analyzed for nutrients, residue, chlorophyll and bacteria. In addition, samples were taken for phytoplankton identification and enumeration. Samples for major ion analyses were collected at two sites on each sampling trip, Saskatchewan Landing and Riverhurst Ferry. Samples for metals and organic analysis were collected at each site on a quarterly basis. In addition to the routine suite of organic analysis, samples were taken for triallate, trifluralin and diclofopmethyl analysis.

Also included in the lake portion of the study was a one-time nearshore sampling, which was conducted at eight sites. This nearshore study was to identify constituents that may have exceeded water quality objectives for nearshore uses. This work consisted of intensive sampling for nutrients, residue, chlorophyll, bacteria, phytoplankton, dissolved oxygen and temperature and was done in mid-August when it was expected biological activity and recreation use would be greatest.

Sampling in the river was conducted at four locations on nine occasions during the course of the study to provide data under a wide range of flow conditions. Two of these locations were also sampled monthly as part of the Prairie Provinces Water Board program. Three depth-integrated water samples were collected equidistant across the river at each site. Each sample was analyzed for nutrients, major ions, chlorophyll, trace elements and metals. In addition, two large-volume (4 L) water samples composited from the three points across the river were taken for organic analysis. Organic analysis included phenoxy acid herbicides, organochlorines and PCBs.

In addition to the water samples, continuous flow centrifugation was used at three of the sites on each visit, except during the winter, to provide sufficient quantities (50 to 100 g) of suspended sediment for analysis. Depending on the suspended sediment load, the length of time of centrifugation varied from 1 to 4 hours at a flow rate of The centrifuge was operated from a boat anchored in midstream intake pump suspended at approximately mid-depth. suspended sediment was split into a number of sub-samples prior to Analysis of the suspended sediment included biologically analysis. phosphorus, metals and organochlorines. In addition a portion of the sediment was chemically fractionated and the fractions were screened for toxicity using a nematode bioassay (Samoiloff et al. 1980). Additional chemical analyses have been conducted on toxic fractions to attempt to determine the cause of the toxicity. remaining sediment splits have been stored for subsequent analyses if necessary.

The Water Quality Branch also collected bottom sediment samples in August from 13 sites on Lake Diefenbaker. These samples have been analyzed in the same manner as the suspended sediment samples collected from the river.

Forage fish were collected to determine the presence of selected toxic substances in their tissues. Analysis for metals, organochlorines and PCBs were conducted on samples of whole fish collected in late August at the four river sites and two sites on Lake Diefenbaker. This work was done to complement the water and sediment work by determining whether any of these substances were accumulating in the fish and, if so, to provide possible early warning of emerging problems.

Many of the results of this joint study are not yet available, and with the field collections just completed, no attempt has yet been made to interpret the data that are available. Therefore no results from this study have been presented.

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WESTERN AND NORTHERN WORKING GROUP SESSION

Attendees

D. Munro Western and Northern (WQB)

(Chairman and Presenter)

D. Haffner (Recorder) Headquarters (WQB)

J. Barica Aquatic Ecology Division (NWRI)
F. Boyce Applied Physics and Systems Division (NWRI)

H. Eisenhauer Toxic Chemical Management Program (ECS)

S. Esterby Aquatic Ecology Division (NWRI)

D. Johannsson Great Lakes Fisheries Research Branch (DFO)

C. Langlois Quebec (WQB)
K. Lautenschlager Regina (SE)

J. Metcalfe Environmental Contaminants Division (NWRI)

S. Painter Aquatic Ecology Division (NWRI)

T. Reynoldson Windsor (IJC)

P. Whitfield Pacific and Yukon (WQB)

NWRI - National Water Research Institute, Department of the Environment

WQB - Water Quality Branch

ECS - Environmental Conservation Service, Department of the Environment

IJC - International Joint Commission

DFO - Department of Fisheries and Oceans

SE - Saskatchewan Environment

The meeting began with a discussion on the issues faced by the WQB within the Western and Northern Region. Water was identified as the region's most valuable resource. Three broad issues of concern to the prairies were discussed.

First, eutrophication continues to be an important issue. During spring runoff when flows are high, as much as 80% of the phosphorus can be particulate and essentially unavailable for biological uptake. During the winter, however, the dissolved forms predominate. In the case of the Bow River, 80% of the phosphorus input into the basin is from the city of Calgary. Some recreational losses have already been identified in the western provinces (e.g., loss of a trout fisheries below Calgary due to excessive macrophyte growth, a result of nutrient enrichment; massive fish kills in various reservoirs due to dissolved oxygen sags).

Secondly, toxic monitoring has centred mainly on the high-use pesticides such the organochlorine insecticides and as Both direct agriculturally important phenoxy acid herbicides. application, atmospheric transportation and deposition are considered important routes to the surface waters. Potential coal mining in the foothills, which could adversely affect spawning streams, presents another western concern.

Thirdly, irrigation (consuming as much as 50% of the base flow) is potentially the greatest single source, resulting in changes in the

ionic strength and ionic proportions in the surface waters of the prairies. Compounding this problem is the fact that 30% of the base flow can be lost through evaporation during the summer months. Existing dissolved salt concentrations are not viewed as being a concern to aquatic life but do limit drinking water use.

The group also identified two other issues (potable drinking water supply, and establishment of water quality objectives at border areas) as being of concern to water quality managers in the Western and Northern Region.

As most of the large river basins within the prairies concern varying degrees of all these issues, any monitoring program developed would have to address all of the above issues. The group then proceeded to describe the necessary characteristics of a monitoring program. The group agreed that the water quality assessment must be dynamic and must integrate the physical, chemical and biological components of the aquatic system.

Four main objectives were identified and discussed by the group.

- 1. Long-Term Trends the group decided that a fixed station network with a fixed frequency based on the hydrograph was needed to meet this objective. Although it was recognized that no normal year for flow could be identified, the following six hydrograph periods could be considered as critical time periods for the establishment of environmental conditions for prairie rivers:
 - low flow under ice conditions
 - local spring runoff events
 - low flow period between local and mountain runoff events
 - mountain runoff events
 - summer low flow when biological activity is high
 - fall low flow when biological activity is low.
- 2. Establishment and Use of Water Quality Objectives the group all agreed that this was a research concern now facing water quality management. The need to develop river-specific water quality objectives as a management tool was discussed within the group. Establishment of objectives not only for chemical levels in water but also in other media (sediment and biota) as well as establishment of objectives for biological structure or function (aquatic health) were highly recommended. Objectives were seen as an efficient means to protect the most sensitive use of a water body. Limited use zones for non-compliance were not seen as a good environmental management concept.
- 3. Assessing Environment Impact identification of the source (cause) of the impact as well as its effect was identified as a necessary objective of a monitoring program. Reservoirs within the river basin could be used as integrators of the environmental effects of the various upstream inputs. Specific issue identification, such as effects of potential industrial development, potable drinking water supplies, would be addressed under this component of the monitoring program.

- 4. Mass Transport mathematical relationships between chemical concentration and flow need to be established for each river basin to assist in the interpretation of data (see points (1), (2) and (3)). Although this information was deemed critical, especially to the water management of reservoirs, present levels of resources are often insufficient for the establishment of these relationships.
- 5. General Surveillance, which included the establishment of an early warning component for hitherto unknowns, and the federal presence in areas of political concern, was also recognized as important.

The group noted that presently too many monitoring programs are "menu" (priority list) driven, rather than system, knowledge or state of the art driven. A network of some 10 to 12 fixed index stations was seen as needed to meet the above objectives for the river system under study. Multimedia sampling was seen as a must, with sediments and biota being sampled annually or biannually. The group felt that metals and toxic organics should not be monitored in the water at the index stations, because interpretation of the data, with respect to ecosystem health, was virtually impossible.

Special surveys were seen as the mechanism for the study of many of the more specific issues that needed to be addressed (e.g., input and effects of nutrients from Calgary, effects of irrigation return flows, productivity in reservoirs, concentration of contaminants in water, bioaccumulation factors, etc.).

Present day monitoring efforts were seen by the group as weak in interpretation; virtually non-existent with respect to establishment of basin-specific water quality objectives; needing improvement in capabilities in ambient assessment; and needing greater technological transfer with respect to the development of reliable monitoring methodologies. Table 1 was developed showing where improvements are presently needed.

Table 1. Needed Improvements

	Monitoring prese	ently effe	ective	Monitoring need	s develo	pment
<u>Objectives</u>	Eutrophication	Toxics	Ions	Eutrophication	Toxics	Ions
Long-term trends	x		x	x	x	x
Development of water quality objectives				x	X	x
Environmental impact				x	X	x
Mass transport General	x		X	X		Х
surveillance	X	x	X	X	X	X

Additional topics discussed by the group and deemed important for any monitoring program included:

- the need for inter-agency cooperation e.g., tying together information obtained from effluent monitoring (EPS, provinces) with ambient monitoring
- the need for the proper resources to be set aside for timely data interpretation. A balance between data collection and interpretation with respect to O&M and PYs needs to be established
- the need for communication between management and the project leaders to ensure that the desired information is indeed obtained by the monitoring program.

The meeting ended with discussion on Water Quality Branch "clients." The group agreed that water managers (federal and provincial) were the Branch's primary "clients"; the Branch, however, should always be cognizant of the Department's responsibility to the general public, the true "clients."

PACIFIC AND YUKON REGION

Water Quality Surveys on the Stikine River

bу

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ABSTRACT

The Water Quality Branch carried out a study on the Stikine River between 1981 and 1983 to describe current conditions with regard to the potential effect of proposed hydroelectric developments on the quality of water flowing across the international border with Alaska. objectives were to conduct quality control studies, to examine spatial and temporal variability, and to look for relationships chemical, physical, and biological varjables. The information generated by this study would provide input to the design of a water quality monitoring program, and to the development of water quality objectives, should they be required for the Stikine River.

Results of quality control studies showed that the non-filterable residue technique used by the Water Quality Branch provided a lower estimate of total suspended sediment concentration than the evaporation technique used by the Sediment Survey Section, Water Resources Branch. This discrepancy resulted from the procedure of pouring off an aliquot for the analysis of non-filterable residue. The non-filterable residue method in the Pacific and Yukon Region has now been changed so that the contents of the whole bottle are used for analysis.

Survey results showed that the three routine monitoring sites on the Stikine River were distinct from one another under a variety of hydrological conditions, and that a single grab sample provided a good estimate of water quality for most variables studied. Considerable short-term variability at each site suggests that water quality measurements should be made as frequently as possible, at a variety of discharges and suspended sediment concentrations until a valid baseline is established.

Factor analysis identified two principal factors that accounted for 78% of the variance at each site. First, "high ground water - low discharge" included those variables such as sodium, sulphate, calcium, and others associated with high levels of dissolved constituents in ground water and low dilution by surface runoff. Secondly, "high sediment - high discharge" contained those variables associated with elevated levels of suspended sediment during the freshet period. These included non-filterable residue, turbidity, particulate organic carbon, total phosphorus, river discharge, and bacterial counts. After several years of data collection through the routine monitoring program another application of factor analysis might result in using certain variables as predictors of others, thus eliminating measurements and reducing analytical costs.

INTRODUCTION

1.1 Relationship of Surveys to Monitoring

Water quality monitoring in the Pacific and Yukon Region was conducted by the Western and Northern Region until 1972. During this period there was a grid of sampling sites throughout the province which was sampled approximately four times per year, primarily for chemical In 1972, the Pacific and Yukon Region was formed and the transition was made to a surveys approach. This approach stressed the river basin or subbasin as the sampling unit and emphasized intensive studies of one- to five-year duration or longer, with a gradual evolution to include the sampling of sediments and biota in addition to An obvious result of this approach was that the geographical coverage around the province was considerably reduced, and that the quality and quantity of information from the sub-basins chosen for intensive study were improved. In 1979, there was the gradual addition of a systematic monitoring approach, which established an increased number of sampling stations and stressed a frequency of sampling sufficient for long-term trend analysis.

The Water Quality Branch, Pacific and Yukon Region, currently has both a surveys program and a monitoring program. These programs are integrated within the proposed Federal-Provincial Water Monitoring Agreement with British Columbia, which includes provision for "station evaluations," intensive studies ultimately to be carried out at all sites. These studies will address spatial and temporal variability, frequency of sampling, choice of variables, the necessity of sampling biota and sediments and, if necessary, in what form. Α very important aspect of station evaluation is the quality assurance component to ensure that sampling, preservation, and storage procedures are adequate.

The principal purpose of the Stikine River survey initiated in 1979 was to describe current conditions with regard to the potential effect of proposed hydroelectrical developments on the water quality at the international border with Alaska. In this report we shall describe the environmental setting of the river basin, the issues and uses within the river basin, and the objectives of the Water Quality Branch survey. We shall outline the principal aspects of sampling design including station locations, variables, frequency of sampling, and sampling methods. A selection of biological, chemical, and physical data will be presented to illustrate typical results in the areas of quality control, spatial and temporal variability, and the examination of interrelationships between variables. Finally, we will describe the principal conclusions from this study, including a critical evaluation of the approach and recommendations for future monitoring.

1.2 Environmental Overview of the River Basin

The Stikine River originates in the Cassiar and Skeena mountains of northwestern British Columbia, drains an area of 51 000 km² and crosses the international border into the Alaskan panhandle before discharging into the Pacific Ocean (Fig. 1). The upper portion of the

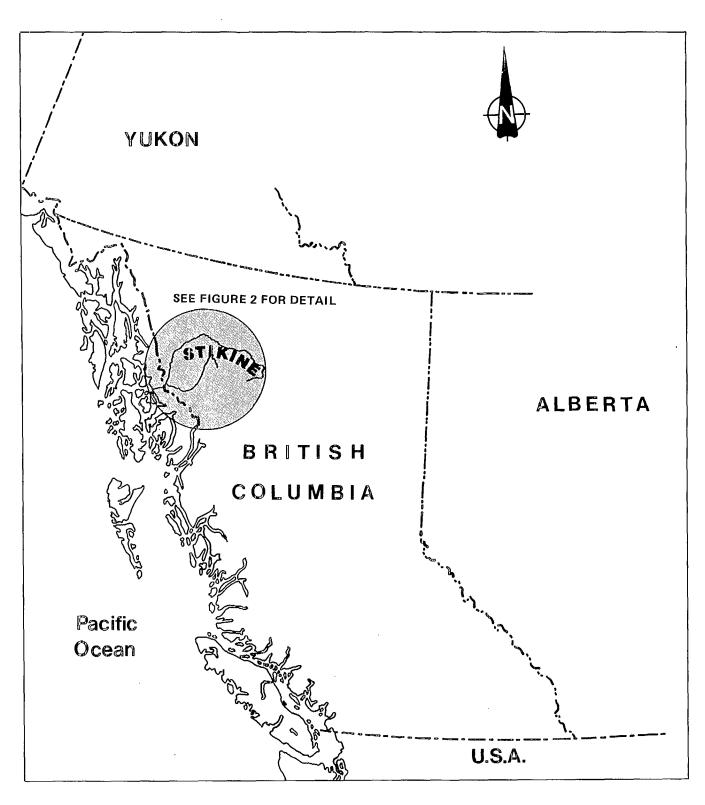


Figure 1. Location of Stikine River basin in northwestern British Columbia.

Stikine River drains the Stikine plateau, a semi-arid region with rainfall averaging 25 cm/yr; the lower portion drains a heavily area with rainfall varying over 190-380 cm/vr. kilometres upstream from the international border the Stikine River is joined by the Iskut River which drains Kinaskan Lake, flows through a heavily glaciated region of the coast mountains, and provides approximately 25% of the flow at the gauging station near Wrangell, The combination of geography and climate in the Alaska (Fig. 2). Stikine River basin results in a complex hydrological regime, with major discharge peaks (Figs. 3 to 5) in spring (snowmelt), summer (glacial melt) and fall (heavy rainfall). All three discharge peaks are preceded or accompanied by high suspended sediment concentrations These suspended sediments are transported across (Fig. 5). international border where they contribute to delta accretion and provide nutrients for estuarine and marine organisms.

1.3 <u>Uses</u>

Various uses of the Stikine River affect or may be affected by ambient water quality. The major potential development in the Canadian portion of the river basin is hydroelectric power generation at several proposed dam sites on the Stikine and Iskut rivers (Fig. 2). The total generating capacity of these proposed dams is 2700 MW, exceeding that of the W.A.C. Bennett dam on the Peace River. Moreover, the interior region is rich in mineral deposits including copper, molybdenum, and coal, and is the site of current mining exploration. Construction of access roads associated with these developments may lead to increased recreational use including hunting, fishing, and river exploration. Logging for spruce and cottonwood has begun along the margins of the Stikine River, in the area upstream from the international border. Stikine is also a salmon-rearing river, and a Canadian commercial fishery has been initiated near the confluence of the Iskut and Stikine In addition to supporting an extensive wildlife population, the Stikine is a scenic wilderness area used for a variety of recreational activities. The Stikine River basin supports a permanent population of approximately 500 (located primarily in the towns of Telegraph Creek and Glenora, on the Stikine River, and Iskut, near Eddontenaion Lake).

After crossing the international border, the river divides and flows through an estuary and delta formed by sediments carried by the Iskut and Stikine rivers. This region sustains various aquatic organisms, components of food chains that support bottom fish and five species of commercial salmon. The river also carries suspended sediments and into Sumner. Stikine and Zimnovia straits, potentially nutrients contributing to the productivity of the local fishery. portion of the Stikine River has been assigned a "Wild and Scenic River" designation by Congress and is used for recreation during the summer. Population in the Stikine estuary is concentrated in Wrangell, a town of approximately 2000 inhabitants who are mainly supported by the fishing, lumber, and tourist industries.

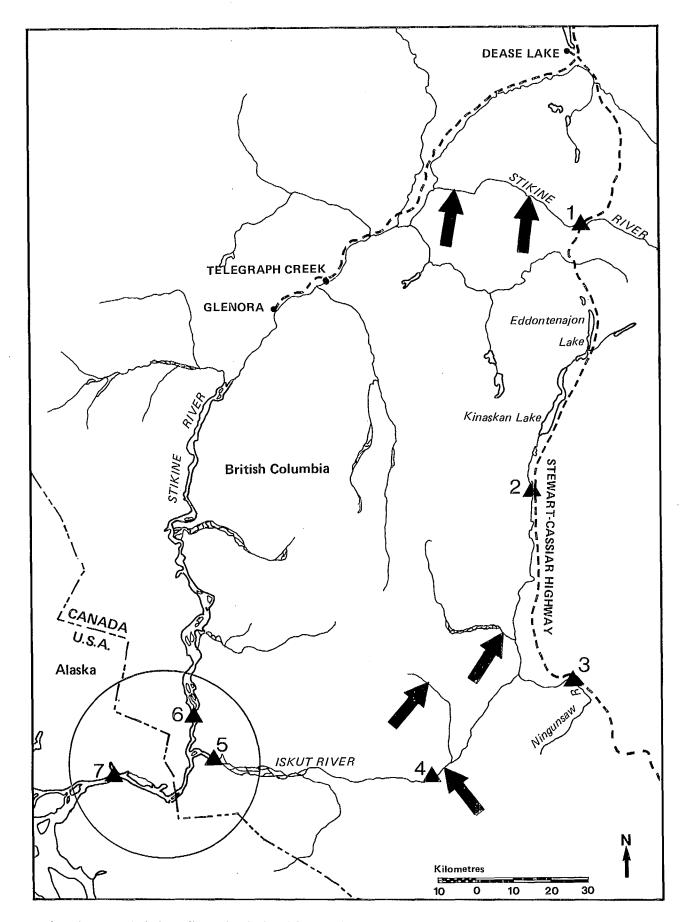


Figure 2. Seven principal sampling stations in the Stikine River basin. Arrows indicate the proposed location of dams or diversions.

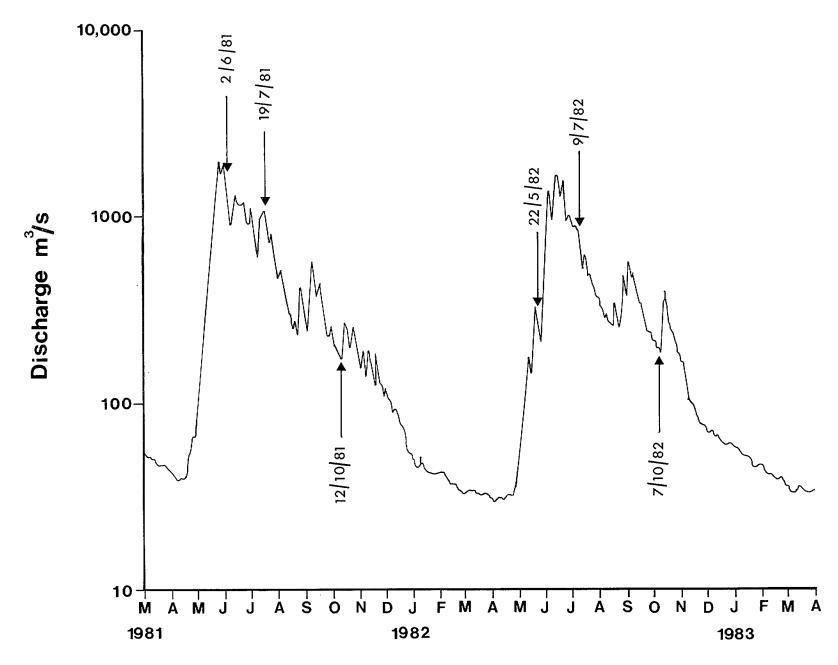


Figure 3. River discharge from March 1981 to March 1983 at Station 1 in upper Stikine River. Arrows indicate sampling times.

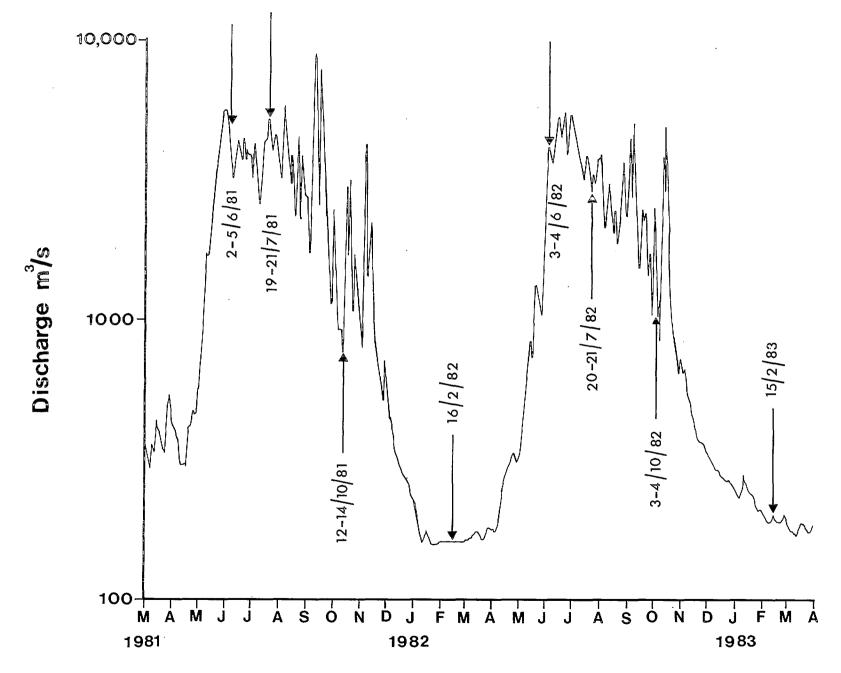


Figure 4. River discharge from March 1981 to March 1983 at Station 7 near mouth of Stikine River. Arrows indicate sampling times.

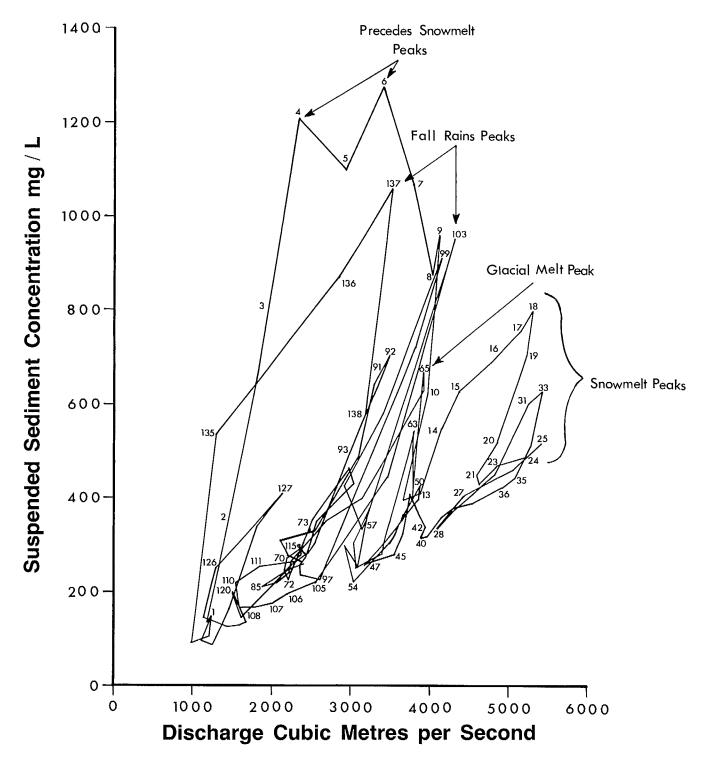


Figure 5. Relationship between discharge and suspended sediment concentration at Station 7 during the period of daily sampling from May 28 to October 13, 1982. Numbers indicate consecutive days of sampling starting from May 28, 1982. Not all daily sampling numbers have been included.

1.4 Objectives

1.4.1 Overall Objective

The overall objective of this study was to describe current water quality conditions with regard to the potential effect of proposed hydroelectrical developments on the quality of water flowing across the international border with Alaska. Impoundments will potentially lower the concentration of suspended sediments and associated nutrients, and change river morphology, reducing the area of sloughs, backwaters, and floodplains that provide rearing and feeding areas for aquatic organisms. To address these concerns and to increase our understanding of biological and geochemical features of northern rivers, a study of ambient water quality conditions in the Stikine River was conducted from 1979 to 1983. The information generated by this study should provide input to the design of a water quality monitoring program and to the development of water quality objectives, should they be required for the Stikine River.

1.4.2 Specific Objectives

The specific objectives of the study were as follows:

- (a) To determine the degree of spatial and temporal variability in selected water quality variables at three locations in the border reach of the Stikine River.
- (b) To look at differences in water quality between seasons and between locations at seven sites within the Stikine River basin. These sites were chosen to represent conditions in the border reach and near potential dam sites; the latter information was required to interpret data from the border area.
- (c) To find relationships between chemical, physical and biological variables using data collected in (a) and (b).
- (d) To compare the quality of water and bed sediments in the main channel with the quality of water and bed sediments in a representative backwater area in the border reach of the Stikine River.

1.5 Variables

The variables measured in the Stikine River project were chosen to represent baseline conditions in two principal areas:

- (a) nutrients, bacterioplankton, phytoplankton and dissolved ions and
- (b) sediment mineralogy.

These two groups reflected an interest in allocthonous inputs that might affect estuarine productivity, and in partitioning the river basin to predict physico-chemical changes resulting from sediment

impoundment and flow alteration. Specifically, variables were as follows:

<u>Water</u>: Field measurements, non-filterable residue, total metals, mercury, major ions, nutrients (total phosphorus and various forms of carbon, nitrogen), bacterioplankton (counts, activity, and carbon) phytoplankton (identification, counts, and carbon).

Suspended Sediments: Analysis of selected elements with an Inductively Coupled Plasma Spectrometer (ICP), X-ray diffraction analysis of clays.

Bed Sediments: Elements by ICP, organic carbon, nitrogen, particle size, bacterial enumeration (counts, activity, and carbon), algal enumeration (identification, counts, and carbon), limited identification, and counts of benthic invertebrates.

2. METHODS

2.1 Field Methods

2.1.1 Sampling Stations

There were three groups of sampling stations in the Stikine River basin:

- (1) Seven principal sampling stations, located on the Iskut and Stikine rivers (Fig. 2).
- (2) Three sampling stations on the Ketili River, chosen to represent a backwater area which might be eliminated as a result of upstream impoundments (Fig. 6).
- (3) Eleven tributary stations, selected to characterize glacial and nonglacial inputs to the lower portion of the river basin (Fig. 6).

2.1.2 Sampling Frequency

2.1.2.1 Seven Principal Sampling Stations

The timing of sampling trips was selected based on historical streamflow data to correspond approximately to the periods of snowmelt freshet, glacial melt freshet, fall floods, and ice cover (Figs. 3 and 4). All seven stations were sampled for nutrients, major ions, metals, elements, clay types, phytoplankton, and bacterioplankton in June, July, October 1981 and June, July, October 1982. Each station was sampled at three different locations in a cross section except for stations 2 and 3, at which three successive samples were obtained at the same location. Water samples were also obtained at three locations at stations 5, 6 and 7 in February 1982 and February 1983.

In June, July and October of 1981 and 1982, stations 5, 6 and 7 were each sampled intensively on two days for a limited set of variables to determine the degree of spatial variability through a cross section of the river.

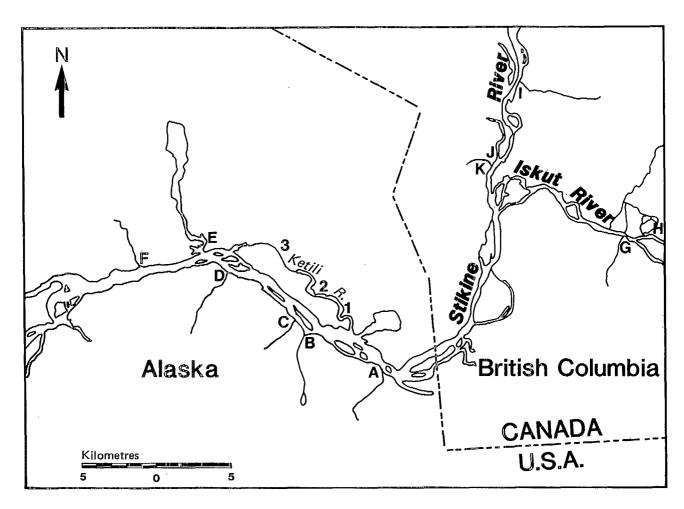


Figure 6. Sampling sites on the Ketili River and on tributaries to the Iskut and Stikine rivers.

2.1.2.2 Sampling Stations on the Ketili River

The three stations on the Ketili River were sampled, when accessible, in June, July, October 1981 and June, July, October 1982. Samples of both water and bed sediment were collected; for purposes of comparison, bed sediment samples were also obtained from the Stikine River near Wrangell, Alaska.

2.1.2.3 Tributary Stations

Tributary stations were sampled in October 1981 and June, July and October 1982.

2.1.3 Sampling Methods

Details on sampling may be found in Churchland and Schreier (1984). Depending on the accessibility of the sampling site a peristaltic pump, bottle within a metal frame, or hand-held sample bottle were used to collect water samples. Stations 1 to 4 were sampled with a bottle

within a frame, 5 to 7 with a peristaltic pump, and slough and tributary sites using a hand-held sample bottle. Sediment samples were taken with a Ponar dredge.

2.2 Analytical Methods

Analytical methods for most chemical variables in water are as described in Inland Waters Directorate (1979). Variations from these techniques, plus analytical methods used for sediment mineralogy and enumeration of bacteria and algae, are described in Churchland and Schreier (1984).

3. RESULTS AND DISCUSSION

3.1 Quality Control

An essential precursor to a monitoring program at any particular site is the appropriate quality control studies to determine the precision of the data. The four examples selected from the Stikine River project present data on sampling techniques for suspended sediments (Table 1), storage times for nutrients (Table 2) and bacterial activity (Fig. 7), and a comparison between non-filterable residue and total suspended sediment concentrations (Table 3).

With modification of the sample bottle, standard methods for suspended sediment collection such as point-integrated or depthintegrated samplers can be used for the collection of water quality samples. Collection of such samples, however, is time-consuming and replicates cannot easily be obtained. Pumped samples offer advantages in speed and ease of collection, and bottles may be filled in rapid succession allowing a close approximation of replicate sampling. For each river system where a pump is used, however, it is necessary to show that a representative sample of suspended sediments is obtained. Table 1 shows that there was good agreement between values obtained with a depth-integrated sampler and a peristaltic pump for total suspended sediment concentration, percent sand, percent silt and percent clay, at a site on the lower Iskut River. Similarly good agreement between the peristaltic pump and a point suspended sediment sampler was found at several locations and several suspended sediment concentrations on the lower Fraser River (Churchland 1981).

In a remote study area such as the Stikine River basin, it is particularly important to assess the effect of time between sample collection and analysis on sample degradation. Table 2 shows that extreme caution should be used in the interpretation of nitrogen species when a storage period is involved. Ammonium ion is the form most affected by storage, with a substantial decline between the first and third days after sampling. It is also possible that a large amount of ammonium was lost between the time of collection and the first day of analysis. Both total dissolved nitrogen and nitrate/nitrite declined slowly in concentration in the first week of storage, and rapidly after three weeks. The three replicates for total dissolved nitrogen all behaved similarly over time, while one of the three sample bottles for NO_2/NO_3 was responsible for most of the drop in

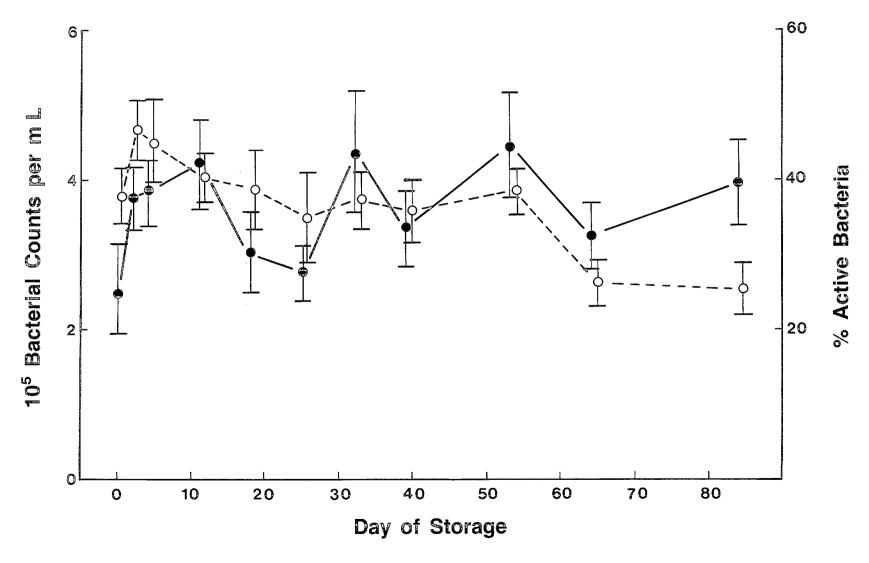


Figure 7. Effect of storage time on bacterial counts (solid circles) and activity (open circles). Numbers are arithmetic means of 20 microscope fields and 95% confidence limits.

Table 1. Comparison in Suspended Sediment Concentrations Collected with Depth-Integrated Sampler and Peristaltic Pump, Iskut River below Johnson River 12/7/80

Sampling method	Suspended sediment conc.(mg/L)	Percent sand	Percent silt	Percent clay
Depth-integrated sampler*	378	30	41	29
	<u>+</u> 30	<u>+</u> 6	<u>+</u> 4	<u>+</u> 7
Peristaltic pump†	391	31	47	22
	<u>+</u> 78	<u>+</u> 9	<u>+</u> 7	<u>+</u> 3

^{*} Numbers are arithmetic means and 95% confidence intervals from nine points in a river cross section.

Table 2. Effect of Storage Time on Concentration of Nutrients

Days of storage	Total* dissolved nitrogen	NO ₂ /NO ₃ *	№‡*	Total [†] inorganic carbon	Total† organic carbon
1	0.223	0.123	0.060	11	8.2
3	0.203	0.096	0.037	12	6.7
5	0.206	0.098	0.033	12	8.9
7	0.212	0.095	0.028	11	8.2
14	0.199	0.078	0.018	וו	6.2
21	0.160	0.072	0.015	12	4.7
28	0.162	0.064	0.013		_
35	0.143	0.057	0.015	12	9.0

^{*} Arithmetic mean of three replicates.

† Single values.

[†] Numbers are arithmetic means and 95% confidence intervals from five depth-integrated verticals across the river.

Table 3. Comparison of Non-filterable Residue Concentration with Total Suspended Sediment Concentration (mg/L)

_		Location	
Date	Stikine above	Iskut below	Stikine near
	Choquette	Johnson	Wrangell
03/06/82	722 <u>+</u> 67*	303 <u>+</u> 17	498 <u>+</u> 52
	1100 [†]	5 8 1	1070
04/06/82	680 <u>+</u> 52	276 <u>+</u> 19	550 <u>+</u> 35
	1080	423	875
20/07/82	120 <u>+</u> 18	127 <u>+</u> 14	125 <u>+</u> 20
	341	278	220
21/07/82	143 <u>+</u> 11	151 <u>+</u> 12	179 <u>+</u> 58
	280	285	300
04/10/82	46 <u>+</u> 9	49 <u>+</u> 5	46 <u>+</u> 6
	114	67	85

Numbers are arithmetic means and 95% confidence intervals for non-filterable residue values from nine points in a river cross section.

concentration as shown in Table 2. Concentrations of total inorganic carbon remained consistent, whereas concentrations of total organic carbon were variable and replication would be required to determine whether there was any systematic change in concentration over time.

Because of the lack of facilities in the remote Stikine River area, samples of bacterioplankton were preserved with 1% formalin and analyzed in the Vancouver laboratory. In an experiment to determine the effects of storage time on counts and bacterial activity measurements (Fig. 7), activity declined significantly (p > 0.99) after 50 days of storage. This would support the findings of Zimmermann et al. (1978) that storage of up to 30 days was possible. Although bacterial counts were variable throughout the period, there was no overall decline in counts after 80 days of storage.

A comparison between non-filterable residue concentrations determined by the Water Quality Branch and total suspended sediment concentrations measured by the Water Resources Branch (Inland Waters Directorate 1984) and the U.S. Geological Survey (1983) showed an obvious discrepancy

[†] Number is total suspended sediment concentration from a single depth-integrated vertical sample through the water column.

Non-filterable residue values ranged from 35% to 73% of (Table 3). suspended sediment concentrations, a difference not explained by the differences in sampling procedures (cf. Table 1). Subsequent comparisons on a variety of rivers in British Columbia and Yukon have shown that the procedure of pouring off an aliquot for analysis of consistently non-filterable residue was responsible for The Water Quality Branch, Pacific and Yukon Region, now difference. the contents of the whole sample bottle for analysis of non-filterable residue.

3.2 <u>Spatial and Temporal Variability</u>

In addition to quality control it is also necessary to understand temporal and spatial variability at each site before a monitoring program is designed. This understanding is required so that recommendations can be made concerning frequency and location of sampling. Tables 4 to 6 and Figures 8 and 9 present some typical results of studies in temporal (between days and between sampling trips) and spatial (between points in a river cross section and between sampling stations in the river basin) variability.

Table 4 shows that there can be a considerable difference between two days of sampling for certain water quality variables. Those variables such as non-filterable residue, total phosphorus and total organic carbon associated with suspended sediments show approximately a 100% variability between sampling days. This difference is not accompanied by a proportional difference in river discharge rates. Conductivity does not change and total inorganic carbon shows a small increase in concentration with a decrease in river discharge.

Table 4. Differences between Sampling Days in Selected Water Quality Variables, Iskut River below Johnson River

Variable	19/7/81	21/7/81
Conductivity (µS/cm)	111 <u>+</u> 5	110 <u>+</u> 1
Non-filterable residue (mg/L)	969 <u>+</u> 56	453 <u>+</u> 27
Total phosphorus (mg/L)	1.27 <u>+</u> 0.3	0.637 <u>+</u> 0.080
Total inorganic carbon (mg/L)	10.6 <u>+</u> 0.2	11.3 <u>+</u> 0.2
Total organic carbon (mg/L)	6.4 ± 0.5	2.0 <u>+</u> 0.3
River discharge (m³/s)	1680	1340

Note: Numbers are arithmetic means and 95% confidence intervals of values from nine points in a river cross section.

Table 5. Comparison of Total Phosphorus Values between Three Replicate Samples and Nine Cross-Sectional Samples

Location	Date	Conc-REP (mg/L)	Conc-XSECT (mg/L)	
Stikine River, Choquette	05/06/81 12/10/81 18/02/82	0.467 ± 0.050 0.114 ± 0.057 0.008 ± 0	0.416 ± 0.069 0.139 ± 0.025 0.009 + 0.002	
	16/02/83*	0.011 ± 0.012	0.019 ± 0.052	
Iskut River,	05/06/81	0.283 ± 0.050	0.253 ± 0.027	
Johnson	21/07/81 12/10/81	$\begin{array}{c} 0.660 \pm 0.024 \\ 0.039 \pm 0.042 \end{array}$	$\begin{array}{c} 0.636 \pm 0.075 \\ 0.062 \pm 0.031 \end{array}$	
	17/02/82 17/02/83*	0.006 ± 0.005	0.005 ± 0	
	17/02/83*	0.037 ± 0.003	0.016 <u>+</u> 0.022	
Stikine River,	05/06/81	0.452 ± 0.020	0.365 ± 0.050	
Wrangell	12/10/81 16/02/82 15/02/83	$\begin{array}{c} 0.090 \pm 0.002 \\ 0.009 \pm 0.002 \\ 0.011 \pm 0.015 \end{array}$	0.085 ± 0.019 0.008 ± 0 0.016 ± 0.040	

^{*} Replicate (REP) and cross-sectional (XSECT) samples collected under different ice conditions.

Note: Numbers are arithmetic means and 95% confidence intervals.

Table 6. Comparison of Total Dissolved Nitrogen Values between Three Replicate Samples and Three Cross-Sectional Samples

Location	Date	Conc-REP (mg/L)	Conc-XSECT (mg/L)
Stikine above Choquette	12/10/81 18/02/82 16/02/83*	0.280 ± 0.700 0.253 ± 0.165 0.337 ± 0.105	0.140 ± 0.130 0.232 ± 0.040 0.184 ± 0.060
Iskut below Johnson	12/10/81 17/02/82 17/02/83*	$\begin{array}{c} 0.091 \pm 0.018 \\ 0.207 \pm 0.065 \\ 1.57 \pm 4.72 \end{array}$	$\begin{array}{c} 0.133 \pm 0.050 \\ 0.204 \pm 0.042 \\ 0.244 \pm 0.318 \end{array}$
Stikine near Wrangell	12/10/81 16/02/82 15/02/83	$\begin{array}{c} 0.183 \pm 0.140 \\ 0.193 \pm 0.050 \\ 0.189 \pm 0.073 \end{array}$	$\begin{array}{c} 0.128 \pm 0.050 \\ 0.210 \pm 0.044 \\ 0.211 \pm 0.012 \end{array}$

^{*} Replicate (REP) and cross section (XSECT) samples collected under different ice conditions.

Note: Numbers are arithmetic means and 95% confidence intervals.

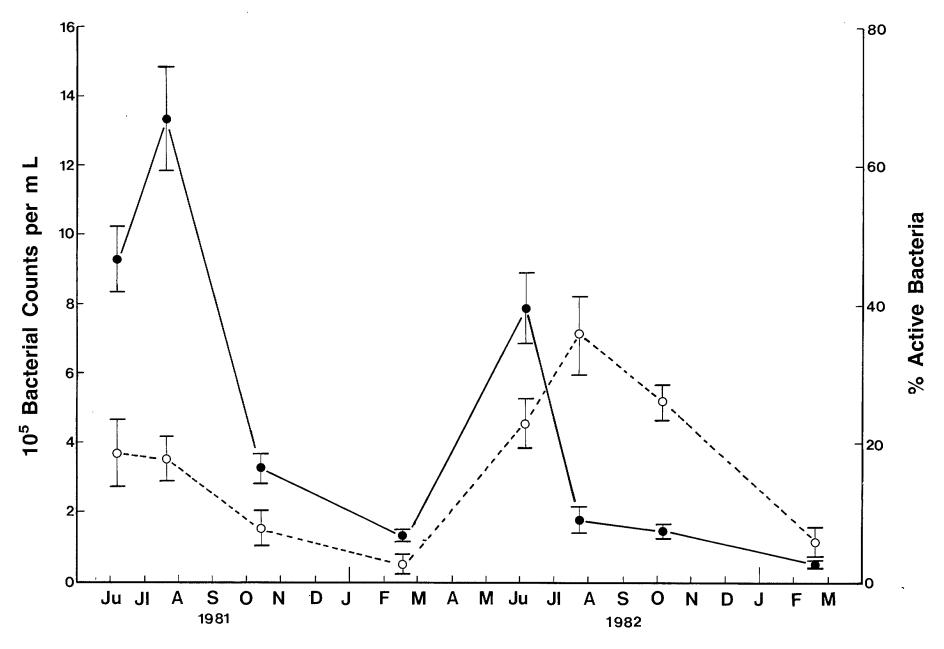


Figure 8. Temporal changes in bacterial counts (solid circles) and activity (open circles) in the Stikine River near Wrangell, Alaska. Numbers are arithmetic means of 30 microscope fields and 95% confidence limits.

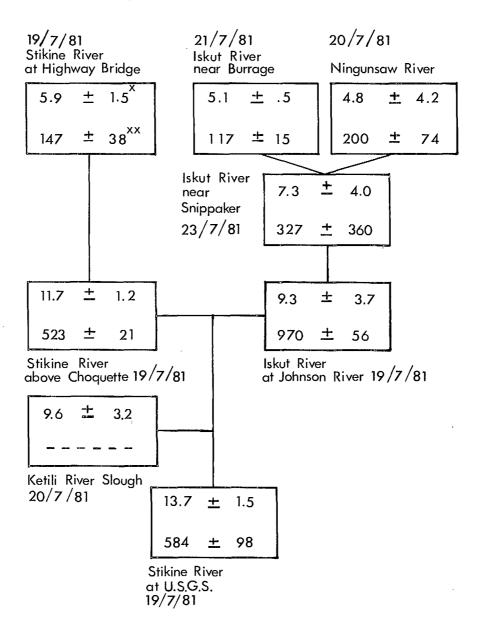


Figure 9. Variability of bacterial Counts^X and nonfilterable residue concentration^{XX} at eight sites within the Stikine River basin. Numbers are arithmetic means and 95% confidence intervals.

Figure 8 shows longer term temporal variability for bacterial counts and activities at Station 7 near the mouth of the Stikine River. It is not appropriate to make seasonal comparisons with these data, because sampling times may or may not correspond to seasonal peaks and there is considerable short-term variability in bacterial numbers. In addition, the large range of mean values was accompanied by a proportionally which range of sample variances, precluded a parametric statistical analysis and a detailed comparison between sampling times. All sampling stations showed the same pattern, however, with the lowest bacterial counts and activity measurements occurring during the winter period under ice. These data suggest that the highest counts may occur

during the June-July freshet. It should be noted that in neither hydrological year did the fall sampling trip correspond to the fall discharge peak (Fig. 4). A more detailed investigation is needed in order to determine the influence of the fall peak flow conditions on the stream regime. This event is highly important and episodic, of short duration, and carries a proportionally large amount of organic material from the Stikine River and its tributaries to the estuary.

Tables 5 and 6 examine spatial variablity through a river cross section at the three sites that currently form part of the routine monitoring program. Comparisons are made between replicate samples obtained with a single cast of a multiple sampler, and samples obtained with a peristaltic pump at several points through a river cross section. For total phosphorus (Table 5), which is related to suspended sediment concentration, agreement is excellent between the replicate samples and the cross-sectional samples. Although not shown in this report. agreement is also excellent between replicate and cross-sectional samples for conservative variables conductivity, major ions, and total inorganic carbon.

For total dissolved nitrogen, sample size is lower and there is considerable variability about the mean for both replicate and cross sectional samples. This variability, possibly combined with storage effects as described in Section 3.1, makes it very difficult to assess the adequacy of a single grab sample as a representation of mean water quality in a river cross section.

Figure 9 shows an example of spatial variability throughout the river basin for bacterial counts and non-filterable residue during a sampling trip in July 1981. These data, collected during a two-day period at seven of the eight sites, suggest an increasing concentration of both variables between the upper and lower stations in the river basin.

Stations 5, 6 and 7 were always sampled on the same day, and there were significant differences between the three sampling sites for most sampling trips, dependent on discharge and suspended sediment concentration.

3.3 Factor Analysis

The large degree of spatial and temporal variability led to a search for "unifying themes" within the water quality data. Factor analysis with varimax rotation was used to resolve the data into a simpler structure. Factor analysis, which essentially consists of factoring a correlation matrix to identify groups of variables which behave similarly, is subject to the same limitations as correlation analysis. For example, a cause-effect relationship cannot be established, and the "driving" variable may not have been measured at all. Moreover, interpretation of results from factor analysis is very difficult without a thorough knowledge of the system under investigation. Bearing in mind these limitations, factor analysis was conducted on the Stikine River data with the following consistent results.

Factor analysis using 24 variables and 24 observations at each of the three lower sites (Tables 7 to 9) identified two principal factors that accounted for a large proportion (76% to 80%) of the variance at each The first factor, identified "high as groundwater-low discharge," included those variables such as sodium, sulphate, calcium others that are associated with high levels of dissolved constituents in ground water and low dilution by surface runoff. Bacterial activity as well as pH and temperature had a negative loading on this factor. The second factor, "high sediment-high discharge," contained those variables associated with elevated levels of suspended sediment during the freshet period. These included non-filterable residue, turbidity, particulate organic carbon, total phosphorus, river discharge, and bacterial counts. When the data for the entire river basin were combined, with a total of 144 observations and 24 variables. the same two factors accounted for 60% of the variance.

In summary, the water quality of the Stikine River basin appears to be dominated by two hydrological conditions: low flow with low water temperatures and high concentrations of dissolved constituents from ground water, and high river discharge with high suspended sediment concentrations and seasonally elevated water temperatures.

Table 7. Results of Factor Analysis, Iskut River at Johnson River

Factor 1		Factor 2
High groundwater - low discharge	Percent of variance	High sediment - high discharge
Sodium Sulphate Magnesium Chloride Potassium Total inorganic carbon pH (-) Bacterial activity (-) Calcium Conductivity Silica Temperature (-)	62.6% 17.5%	Non-filterable residue Turbidity Particulate organic carbon Phosphorus Particulate organic nitrogen Total organic carbon Total algal counts Total bacterial counts River discharge

Note: Variables are listed in decreasing order of Eigen values.

(-) = negative loading on the factor.

Micheller Land Sec.

Table 8. Results of Factor Analysis, Stikine River near Wrangell, Alaska

Factor 1 High groundwater	Done	cent	Factor 2
- low discharge		riance	High sediment - high discharge
Total inorganic carbon Chloride Calcium Sodium Silica Sulphate Magnesium Conductivity Temperature (-) Bacterial activity (-) Nitrate/nitrite	— 58.3%	18.2%-	Total bacterial counts Potassium Phosphorus Turbidity Non-filterable residue Particulate organic carbon Total algal counts River discharge Particulate organic nitrogen

Note: Variables are listed in decreasing order of Eigen values.

(-) = negative loading on the factor.

Table 9. Results of Factor Analysis, Stikine River above Choquette River

Factor 1			<u>Factor 2</u>
High groundwater - low discharge	Perce of vari		High sediment - high discharge
Magnesium Total inorganic carbon pH (-) Silica Conductivity Calcium Bacterial activity (-) Nitrate/nitrite Sulphate Temperature (-) Sodium	60.6%	17.6%—	Total bacterial counts Turbidity River discharge Non-filterable residue Phosphorus Particulate organic carbor

NOTE: Variables are listed in decreasing order of Eigen values.

(-) = negative loading on the factor.

3.4 <u>Comparison between the Ketili River and the Main Stem of the Stikine River</u>

One of the major suggested effects of impoundments on the Stikine River was the potential elimination of sidechannels such as the Ketili Because such sidechannels may provide critical habitat for salmon and other aquatic organisms, a comparison was made between water quality conditions (concentrations of nutrients, algae and bacteria in water and bed sediments) in the Ketili River and the main channel of Stikine River at Station 7 (Table 10). Although there were differences between sampling trips for those variables such as total phosphorus which were associated with suspended sediments, there was no systematic difference in water quality conditions between the main channel and sidechannel during June or July. Differences between the two sampling sites were greatest in October, when the Ketili River became partially landlocked with limited water circulation and boat access. It is probable that had comparisons been made between the main channel and a smaller, less free-flowing sidechannel, differences would have been observed during all sampling trips.

A limited collection of benthic invertebrates from both main channel and sidechannel sites on the Stikine River showed very low numbers of predominantly Chironomidae, when compared with results from other coastal rivers.

4. CONCLUSIONS AND RECOMMENDATIONS

4.1 General Conclusions

- (a) The general observation can be made that the Stikine River is a biologically unproductive system, with low invertebrate numbers and low phytoplankton biomass because of high turbidity during the ice-free period. Although biomass of bacterioplankton exceeded that of phytoplankton, numbers were low compared with those reported for rivers in more temperate zones (Bell and Albright 1981; Loy and Rheinheimer 1980).
- (b) Intensive studies of spatial and temporal variability at three lower river sites showed that each of these sites was well mixed, with results from a single grab sample usually comparable to a mean value derived from nine points in the river section. There were significant differences between the three sampling sites for most sampling times, dependent on discharge and suspended sediment concentration. There was considerable short-term (samplings one to three days apart) and long-term (samplings several weeks apart) temporal variability at each of the three sampling sites. As in the case of the three lower river sites, the four upper river sites showed greater temporal than spatial variability.
- (c) A study of interrelationships between water quality variables showed a clear association between nutrients such as particulate organic carbon and suspended sediments. Should the Stikine River dams be constructed, a significant amount of the normal particulate load at the international border will be removed along

with associated minerals, nutrients, and bacteria. Dependent on velocity and carrying capacity, the reduced flow from the dams may then transport sediments that are normally deposited at the mouths of downstream tributaries. Whether the volume of particulate material provided for detrital food webs in the estuary will be significantly affected will depend on the quantity and quality of sediments introduced downstream from the impoundments.

(d) A comparison of conditions in a sidechannel with the margin of the main channel showed no clear differences in nutrient chemistry or

Table 10. Comparison of Biological Variables and Nutrients (C,N,P) in Water from the Ketili River and the Main channel of the Stikine River

			1981			1982	
Variable		June	July	October	June	July	October
Bacterial	(a)	10.2	9.6	7.0*	9.3	2.8	3.4†
counts X 10 ⁵ /mL	(b)	10.2	13.7	3.3	7.9	1.9	1.5
% Active	(a)	22	20	8*	29	31	19†
bacteria	(b)	17	18	8	23	36	26
Bacterial	(a)	6.4	5.8	4.3*	7.5	1.9	2.1†
biomass (mg/m ³)	(b)	5.0	7.9	1.9	5.6		0.9
Phytoplankton	(a)	0.3	0.3	0.1*	4.7	0.3	0.8†
biomass (mg/m ³)	(b)	0.4	2.7	0.1	4.1	0.3	0.5
Total	(a)	0.340		_	0.755	0.192	0.059†
phosphorus (mg/L)	(b)	0.372		0.085	0.938	0.260	0.129
Dissolved NO ₂ /NO ₃ (mg/L)	(a) (b)	-	0.052	0.100* 0.066	0.091 0.116	0.025 0.030	0.051† 0.040
Particulate organic carbon (mg/L)	(a) (b)	2.00 2.65	2.58 4.22	<0.167* 0.223	4.94 4.13	0.917 1.15	0.252† 0.600
Total organic	(a)	3.1	3.3	1.2*	7.4	3.4	3.6†
carbon (mg/L)	(b)	1.9	4.2	1.1	5.4	3.6	3.0

^{*} Samples from 1 station only

Note: Numbers are arithmetic means of samples from (a) 3 locations in the Ketili River and (b) 3 locations in the river cross section at Station 7.

[†] Samples from 2 stations only

biology of water or sediments, except when the sidechannel was landlocked at low flow.

4.2 Problems of the Stikine River Survey

- (a) In such a large and inaccessible river basin, all seven principal sites could not be sampled simultaneously, or at the same stage of river discharge. Moreover, the same sampling technique could not be used at all sites. Therefore, comparisons of water quality conditions throughout the river basin should be made with considerable caution.
- (b) Perhaps the most serious problem, the low frequency and duration of sampling, was limited by available funding. As a result the fall flood, perhaps the most important hydrological event in terms of detritus transport, was missed for two successive years. Moreover, the partitioning of the river basin based on sediment mineralogy might have been more successful had the river been sampled in August, when there was a greater proportion of glacial runoff. Finally, the appropriate application of factor analysis depends on a larger number of independent observations than variables, which would have required 24 sampling trips over the two-year period.
- (c) It would have been informative to sample intensively with time through a flood, establishing the relationship between sediment, water quality variables, and the peak of the discharge curve.

4.3 Conclusions and Recommendations re: the Routine Monitoring Program

Intensive surveys cannot be continued in this remote area because of the high cost of field work. The results of these surveys, however, can be used to make recommendations to improve the design of the routine monitoring program.

Currently, of the three lower two river sites are approximately six times a year, for a standard suite of variables. Without a large increase in funds, the frequency of sampling cannot be significantly increased, or complexities of sampling such as filtration introduced. Certain simple changes in the variables, however, can be made as a result of quality control and other survey results. First, the various forms of nitrogen should be excluded because of storage effects, or great care excercised in the interpretation of the data. Difficulties may arise when values for nitrogen are entered into a public data bank and interpreted without knowledge of the storage times their effects on concentration. Secondly, the non-filterable residue method should be changed so that the contents of the whole bottle are used rather than a sub-sample poured off for analysis. This change has already been made for all non-filterable residue analyses in the Pacific and Yukon Region. Thirdly, because of the interest in riverine inputs of carbon to detrital food chains in the Stikine estuary, total organic carbon should be added to the standard list of variables.

The intensive survey on the Stikine River has indicated that the three routine monitoring sites are distinct from one another under a variety of hydrological conditions and that a single grab sample provides a good estimate of water quality for most variables studied. Considerable short-term variability at each site suggests that water quality measurements be made as frequently as possible, at a variety of discharges and suspended sediment concentrations, until a valid baseline is established. After several years of data collection a further study of interrelationships could potentially result in using certain water quality variables as predictors of others, thus eliminating some measurements and reducing the costs of the monitoring program.

Should the Stikine River basin again become a high priority for water quality studies because of changing energy forecasts, the monitoring approach should include a combination of surveys and a more intensive routine monitoring effort to answer some of the remaining questions in this system.

ACKNOWLEDGMENTS

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PACIFIC AND YUKON WORKING GROUP SESSION

Attendees

G. Howell

R.P. Bukata (Chairman) Aquatic Physics and Systems Division (NWRI)

K. Thibault (Recorder) Headquarters (WQB)

L. Churchland (Presenter) Pacific and Yukon (WQB)

P. Brooksbank Headquarters (WQB)

B.K. Burnison Aquatic Physics and Systems Division (NWRI)

D. Donald Western and Northern (WOB)

A.H. El-Shaarawi Aquatic Physics and Systems Division (NWRI) P.F. Hamblin

Aquatic Physics and Systems Division (NWRI)

Atlantic (WOB)

K. Minns Great Lakes Fisheries Research Branch (DFO)

P. Wells Priority Issues Directorate (EPS)

NWRI - National Water Research Institute, Department of the Environment

WQB - Water Quality Branch, Department of the Environment

DFO - Department of Fisheries and Oceans

EPS - Environmental Protection Service, Department of the Environment

The meeting began with discussion of the importance of standardization (with respect to parameters, sampling methods and analysis) as a means to address national issues. It was noted that while national water quality issues could be addressed by long-term monitoring (trend assessment) at key stations (selection based on the issue), regional issues require both surveys and long-term monitoring. The latter plays an important role where international interprovincial water quality is an issue. A systematic approach to that is, a complete description an issue, of problem/issue and the development of a monitoring and sampling plan with definite objectives was favoured.

As the definitions for the terms "water quality criteria," "guideline," "objective" and "standard" were reviewed, the subject of effects was discussed (i.e. additive and synergistic effects on the environment). The problem of the time-frame (i.e. "must not exceed") within Which a guideline or objective will apply was discussed as was the significance of peaks in monitoring results for various parameters, especially in terms of their effects on the biota. The importance of gathering site-specific criteria (i.e. equally spaced sampling versus episodic versus continuous) and the role of these criteria in the development and negotiation of water quality objectives was also discussed. The group concluded that the approach of a monitoring plan will vary depending on the goal of the water quality assessment (whether for the development of water quality objectives or for other purposes).

The group then discussed the types of monitoring programs commonly used. It was agreed that at present monitoring plans are expected to respond to both specific (regional issues) and general (requests from Ottawa or national issues) questions, yet each of these questions requires a different design approach. Three categories of monitoring were determined:

- (1) trend assessment (overview approach)
- (2) compliance (violation of objectives or regulations)
- (3) problem identification.

It was suggested that a monitoring program must be designed to test a hypothesis (i.e. 5% change in a parameter or 10% change, etc.). The purpose of trend assessment was questioned and discussed in terms of an early warning system (e.g. detection of a trend in a parameter over time regionally or on a national basis).

Standardization (for measurement of suites of parameters and data format of interest to national issues) was discussed, as was the difficulty in defining regional and national issues. It was suggested that concentrating on a procedure and emphasizing the need for a thorough understanding of the question asked (or issue raised) as opposed to the present "shotgun" approach (i.e. if it can be analyzed, then look for it) should be incorporated into monitoring programs. For example, if the question is trend assessment, then the parameters selected for analysis should be supported by a rationale (i.e. testing a hypothesis).

Each of the above-mentioned monitoring categories is designed to address a particular question, and while not necessarily mutually exclusive, one monitoring design should not be expected to cover all questions from all three categories. Also, as each category has an associated question (hypothesis), it is mandatory that the statistical aspects of the program be determined, prior to sampling and not after, as is currently done.

The group agreed that common points to all three categories of monitoring activities (discussed earlier) emerge:

- (1) Problem definition
- (2) Hypothesis formulation
- (3) Sampling design (station selection, sampling frequency)
- (4) Data collection
- (5) Data interpretation.

The group expressed frustration at the lack of time to explore fully points (1), (2) and (5) within present monitoring programs. The importance of water quality objectives as a means to relate water chemistry data to effects on uses was discussed, as was the interrelationship between monitoring for data to develop water quality objectives and subsequent monitoring for compliance.

The problem of identifying a basic list of parameters for a national overview was discussed. It was agreed that no parameter should be included unless it is to test an hypothesis (i.e. is there a change over time). This was countered by the fact that other parameters are needed to understand the system more fully.

In designing a monitoring plan, one should remain cognizant of the main issue areas, particularly in terms of

(1) Where are the problems?

(2) Is there a threat to human or aquatic life?

(3) What are the levels of input?

(4) Which compartments are/will be affected?

Many observed that questions motivating monitoring activities not always well formulated, thus leading to difficulty developing a plan to yield the maximum production per unit resource. The identification of a problem is related to the users/uses Comments on the overlap of many of the water in the river basin. disciplines in problem identification (biology, physics, toxicology, chemistry, etc.) and the need for increased knowledge about these disciplines and their collective interrelationships were put forth. The importance of the end-use of a study for interpretation purposes and the need for research (good science) were also tabled. agreed by all that more dialogue among the scientists within various disciplines is necessary, particularly in the choice of parameters and media selection. This brought up the question of monitoring cause(s) There was agreement on the importance of monitoring biological effects and some items for consideration in the use of biota included

- (1) Species diversity
- (2) Population studies
- (3) Biological effects (oncogenicity, teratogenicity, etc.)
- (4) Bioassays, etc.

The underlying question in monitoring is whether or not there is a threat to aquatic life and human health. Trend assessments can be justified within the context of an overview of use impairment and in this way can be justified on a national basis (Canadian uses).

The working group agreed to work through the specific case of a study of dioxins in starry flounder. This study involved the discovery of elevated levels of chlorophenols in the starry flounder (ppm concentrations) and in water samples taken from the lower Fraser River. There is, therefore, a potential for elevated dioxin levels in fish species. Levels of dioxin, in higher than trace concentrations, were detected in the fish. Human consumption of these fish is an identified use. This problem was detected as a result of a study funded by Toxfund.

Comments were made on the historical emphasis placed on the chemistry of water quality. The group commented on the importance of biological monitors and research in identification of problems. It was suggested that two questions motivate this study: (1) What is the source of the contaminant and (2) what are the hazards. The group recognized the need to identify the requirements of interpretation prior to designing a monitoring strategy, and to resist the considerable pressure to monitor immediately.

Research opportunities in this study were discussed, particularly in terms of pathways data, which in turn could be used for the selection of station sites. In general, the difficulty in establishing a relationship between studies carried out by the region for a regional/national problem was recognized.

The group favoured using some sort of biological component to complement an overall assessment. Although no one representative species was discussed at length, it was generally felt that all biological data are valuable and valid for an overall assessment. Since the biota act as integrators, bioassays allow a measurement of concentration and effects. It was noted that the sensitivity in different species is less than the variation in sensitivity due to differences in the aquatic environment. Modelling was also discussed as an important component of problem definition and interpretation stage. The discussion concluded with consensus on the need for multi-media sampling.

The working group session ended at this point, with the working group making the following six recommendations.

- 1. The establishment of the monitoring programs should be primarily a regional responsibility, the driving force behind them being regional issues and concerns. Each region (or regions, where a common basin is shared) should be responsible for the selection of parameters (chemical. physical. toxicological. biological, statistical) which should be monitored. parameters common to two or more regions should form the basis for the federal monitoring program.
- 2. The criterion for the selection of a parameter is that it be subjected to hypothesis testing. Where baseline data exist for a particular parameter, data variability should be considered. Where no baseline data exist, or where the suitability of a particular parameter is debatable, data should be probationally included until such time as suitability may be confidently ascertained.
- 3. For those parameters that constitute the national program, standardization of analytical and sampling techniques and data formatting must be implemented.
- 4. Considerable improvement must be directed towards problem definition, and should be considered in concert with the data interpretation anticipated from the monitoring activities. Problem definition should include scientific and technical inputs from all pertinent disciplines.
- 5. More attention should be given to addressing the environmental problem to be solved than to addressing the restrictions of interdepartmental government mandates.
- Appropriate modelling (fate, physical, chemical, biological and statistical) should be an integral component of both the problem definition and interpretation phases.

Monitorology The Study of Monitoring

by

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INTRODUCTION

There is a growing realization that a sound economy is based on a sound environment, the two sides must develop in concert if progress is to be maintained.

The World Conservation Strategy United Nations Environment Program

Water quality monitoring/research is necessary to identify natural as well as man-made pollution sources to determine the remedial action necessary to enhance or maintain water quality. This paper the multijurisdictional interactions that occur monitoring of environmental issues. It is not the intent of the authors to describe the perfect monitoring program, because each environmental issue requires its own perfect monitoring design. Instead, the authors attempt to present an outline of the activity It is hoped that awareness of the intricate interplay monitoring. between the various monitoring components will promote understanding. communication and thereby better monitoring efforts.

WORKING GROUP COMMENTS

"A tremendous amount of data is being generated in ongoing monitoring programs, but little information is being obtained from this effort."

"Monitoring programs fail to meet the full range of demands for high quality data and analysis."

"Monitoring programs fail to use well-established scientific principles in design, operation, analysis and interpretation."

"There is poor coordination among existing monitoring efforts, resulting in duplication and wasted time and resources."

"There is too much 'feather bedding' in monitoring programs. Designs are set to keep existing staff and resources busy, not to address the question."

"Objectives for monitoring are poorly stated and therefore unobtainable."

These statements on monitoring, recorded during the working group sessions of the Water Quality Branch monitoring workshop, indicate the need to reassess how water quality assessments are conducted in Canada. Why is there so much interest and concern about monitoring? Basically, effective management decisions on the exploitation, conservation or protection of the environment can only be made through an understanding of the complex physical, chemical, geological and biological interactions that occur within it, and not solely in terms of natural processes but also in terms of man's impact.

The public at large has been awakened to the necessity of protecting Canada's natural resources and its environment, both for the sake of long-term economic prosperity, and for the overall quality of Much of the public's concern presently is focused on water. Indeed. any degradation of its quality requires immediate action by governmental agencies (Pearse et al. 1985). In the present climate of expenditure restraint, it is increasingly important to demonstrate the utility of monitoring programs. This should not be viewed as a criticism but rather as a necessary part of any program, to ensure that objectives are met in the most efficient, cost-effective manner. through the process of constant review can monitoring programs adequately reflect new management concerns, as well as make use of the latest technological state of the art advancements in data collection. The process must be evolutionary, rather than revolutionary. scale changes to monitoring programs often result in reduced efficiency during the transition period.

presentations and The workshop working group findings presented in these Proceedings, reflect, on the most part, those of the Water Quality Branch (WQB), Inland Waters Directorate (IWD), Department of the Environment (DOE). However, it is important to note that monitoring of the aquatic environment within the federal government is conducted as part of a management program. The data collected are used by various governmental agencies (federal and provincial), institutes, private industry, academic environmental | groups. private individuals.

Before discussing IWD's component to a monitoring program, it is important to understand the overall program - the coordination and participation of the various agencies and institutions, and the integration of their activities into the various components of a program.

What is monitoring? Unfortunately, a monitoring program is often defined in its simplest form — the data collection and interpretation component. The Water Quality Branch has stated that

Monitoring involves the systematic collection of water samples, usually at fixed locations for a fixed suite of variables and substrates over an extended period of time.

Water Quality Branch (1985)

This definition simply describes the actions or mechanics of monitoring, without giving the reader an appreciation of the complex interplay of conceptual and practical components, the flow of

Within the federal government, monitoring of the aquatic environment is primarily carried out by four departments: Department of the Environment, Department of Fisheries and Oceans, Department of Agriculture, and the Department of National Health and Welfare.

information through the information web, vertically (within the Department) or horizontally (between Departments) at either managerial or scientific levels. This is somewhat analogous to describing a man as having two legs, a head and a body. Although anatomically correct, the definition fails to adequately describe the entity - man.

To provide the reader with a greater appreciation of the entity - a monitoring program, a case example, a toxics monitoring program, will be described, with IWD's monitoring component identified and discussed.

TOXIC CHEMICALS MONITORING PROGRAM

Background

"Ecotoxicity" is the term presently being used to describe a phenomenon affecting today's environment. When working with the idea of ecotoxicity, it is important to define what is meant by "toxic substances" and why they have caused so much concern in the scientific It is also necessary to state what the prefix "eco" represents and why it is fundamental to the study of toxic substances. An "ecosystem" is a naturally definable unit, consisting of biotic and abiotic factors and their interactions. Its nature is dynamic, one which changes constantly over time and represents the framework for all environmental concerns. Toxic substances are biocides; they kill living organisms either by direct exposure or by causing long-lasting effects that erode the viability of a population. Ecotoxicity is therefore the study of substances having harmful effects on the biotic (living) components of an ecosystem. Since a "toxic substance" is only defined as such when it has a deleterious effect on a living organism, the topic of "toxics" should be studied in terms of (1) exposure to the chemical substance and (2) the effect it produces.

"Exposure" is the measurement and characterization of the environmental transfer media. A transfer medium is the pathway (air, water or land) which causes a living organism to come in contact with a toxic substance. When this contact is made, an "effect" may occur within the organism. These organisms (plants and animals, including man) are the renewable resources of Canada, while the transfer media represent the compartments that can be controlled. Both the federal and provincial governments have the responsibility to ensure that the media and the resource are maintained for present and future generations.

The Interdepartmental Program

Before implementation of a monitoring program, a conceptual framework is needed to resolve the objectives of the plan, to delegate responsibilities and to identify how information about toxics is to be collected and utilized. Toxic substances do not behave according to government divisions. This does not mean, however, that the existing agency structure cannot be effectively used to study toxics in the environment.

The first important concept to accept is that in any plan there is a practical level of measurement and a conceptual level of direction which operate together to form a program. In addition, scientific study requires lateral thinking and operation, whereas management requires a vertical structure to respond to scientific needs and recommendations. A vertical structure, typical of government plans, will allow a meshing of the practical and conceptual levels of The lateral structure will be used to delegate the framework. responsibility while demonstrating that all components (water, land, air and biota) are equally important to the study of toxics in the environment. The framework must also be operational for all types of studies, i.e., a single chemical approach as well as a systems Figure 1 is a five∸level conceptual framework which identifies DOE's role in toxic studies and the interaction of other departments in this activity.

Starting from what was described as the conceptual level. the first element in the framework identifies the direction or purpose of In the diagram, this has been called "environmental management" and represents the overall purpose of studying toxic Within the overall direction (Level 1), the issue (Level 2) is then identified. This is obviously "toxics." The implications of this term are broad-based, and this box may contain a single chemical name to be studied in the environment; it may contain an hypothesis about toxic substance behaviour; or it may represent a gamut of chemicals in various contexts. It is important to note the role of research and monitoring to Level 2. It is research/monitoring activities which originally identify the issue and formulate the Management must assess the magnitude of the issue and adjust scarce resources within a department to address the issue. flexibility given to this box allows the framework to be used by a service within a single department, the department as a whole or the federal government. It is the pivotal point for a common approach At this level the term "toxics" summarizes a between departments. of federal responsibilities backed by both mandate variety legislation.

The third step in the framework's conceptual level is the key to creating a structure that functions within a multi-agency government. The federal government's most long-term and easily grasped responsibility relates to Canada's renewable resources. By using the idea of renewable resources as the third level in an operational framework, many of the esoteric conservation statements are put into a perspective that must be, and in fact already are, accepted by upper government and the Canadian public. In other words, the concept is easy to handle and to justify. The lateral structure of this level is success of critical to the cooperative effort. а Fisheries, Agriculture, Wildlife, Forestry and Man represent not only renewable resources but also the government agencies who manage them. framework therefore functions on two levels, by focussing on areas of concern (for example, Fisheries) with respect to toxics and by showing how agencies can interact.

The fourth level in the framework (inputs/exposure media) represents a turning point from the conceptual level to the practical

LEVEL 1 Identification of Direction Environmental Management

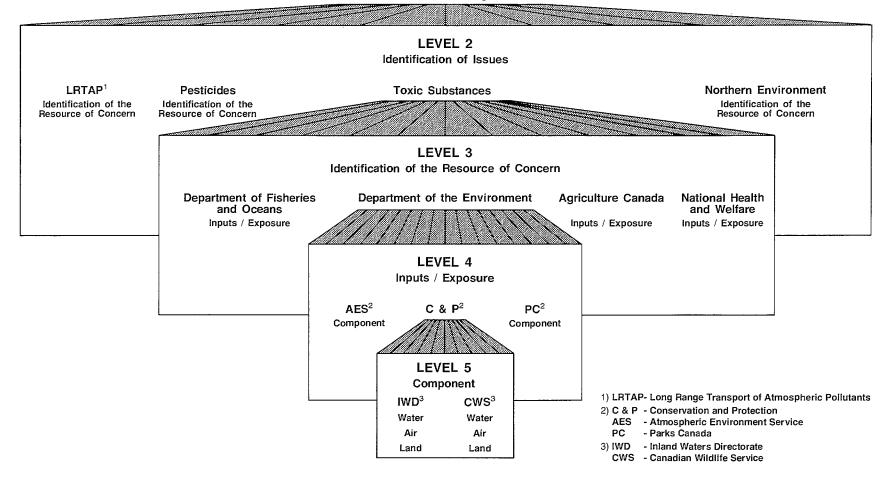


Figure 1. Conceptual framework identifying the DOE role in toxic studies and the interaction of other departments in this activity.

level. The federal government has officially accepted the ecosystem approach to environmental | study and yet still responsibilities. Because of this, the potential for overlaps in responsibility will obviously exist, as the ecosystem does not function within discrete units. Irrespective of the renewable resource chosen, there are three basic exposure media common to every resource, issue These are the transfer media (air, water and terrestrial considerations) common to a11 ecosystem interactions. environmental implication of toxic substances must be broken down in terms of the media because every living thing exists in reference to any combination of these three elements. The federal Department of the Environment and its provincial counterparts are directly responsible for the health and well-being of the transfer media and hence is the key agency in the study of toxic substances from an environmental management point of view. It is perhaps more apparent now why water is the renewable resource level. placed at Water has significance than is implied in the resource level, since it is the means by which to study contaminants in all living things and to ensure their viability as a renewable resource. DOE's internal structure reflects its rather pervasive position in the proposed framework. has a Waters Directorate, a Lands Directorate and an Atmospheric Service as well as a responsibility at the renewable resource level with respect to wildlife and forestry.

Within the study of water (Level 4) as a means of ensuring the health of Fisheries (Level 3), with particular reference to toxic substances (Level 2), IWD has a responsibility to supply scientific advice and information based on monitoring effects, even though it is not an agency within the Department of Fisheries and Oceans. tuning of responsibility is agreed upon at an interdepartmental committee level where overlaps in responsibilities are acknowledged and clearly stated. Since no one department has the resources or mandate to study all aspects of toxics, it is obvious that a cooperative effort For example, the analysis of edible portions of fish are needed. whole fish concentrations for the setting of ecosystem guidelines and the effects of toxic substances on the population stress of a fishery clearly require three different monitoring approaches, each of which pertains to separate departments (National Health and Welfare, Department of the Environment, and Department of Fisheries and Oceans).

The fifth level in the framework identifies the practical units used in both the measurement and the characteristic components of environmental studies. Each exposure medium is broken down into the environmental compartments which exhibit the effects of exposure to substances. Each compartment can also represent responsibility of a particular service within an agency, but what is most important to note is the lateral structure of this level and the repeatability of the compartments on the framework. It is important to common approach needed in environmental emphasize the irrespective of the department in question.

With respect to the issue of toxic substances, the coordination of steps (1) and (2) occurs within the Toxic Chemicals

Management Program (TCMP). Step (3) is coordinated by the Interdepartmental Committee on Toxic Chemicals (ICTC), and steps (4) and (5) are accomplished by the department's agencies, services, etc., under the guidance of the ICTC.

IWD's Component - Monitoring/Research

Although IWD plays a role in levels 1 to 4, through issue identification and hypothesis formulation, level 5 represents its major (resource) level of input. IWD has the responsibility to design a systematic, comprehensive monitoring program which will supply the scientific input needed for the understanding of the aquatic resource. Development of obtainable objectives (Table 1) and coordination of resources within IWD are key activities within the program.

Objectives 1 to 4 (Table 1) have traditionally been addressed by routine monitoring programs carried out by the Water Quality Branch. Objectives (5) to (7), which can be regarded as research in support of monitoring activities, have traditionally been handled by WQB's sister agencies, the National Water Research Institute and the National Hydrology Research Institute. Although there are defined divisions of labour within the monitoring program, some overlap does occur to ensure scientific and technological transfer.

Monitoring efforts in these Proceedings constantly allude to the need for interaction of the research and monitoring components. importance of multimedia sampling, quality assurance/quality and the establishment of basin specific water objectives was stated by all five regions. The business of the WQB is to provide scientific and technical information and advice to the governments, private agencies and the public (WQB Unfortunately, in all natural aquatic systems, a complex interaction of physical and biochemical cycles exists. The annual and the long-term hydrographs of a river basin are a result of the basin's hydrological Superimposed on these are the biochemical cycles such as the diurnal cycle which is measured in terms of hours, and the seasonal cycle which is measured in terms of months. Water temperature affects saturation values for dissolved gases, alters metabolic rates aquatic organisms and affects the specific gravity of water, producing substantially altered mixing characteristics. Light supplies the driving force for primary production and therefore influences the uptake and depuration rates of toxics. Sediments act as a transport mechanism for absorbed substances, alter light regimes and directly affect aquatic organisms. As a result, all aquatic systems are Unfortunately, change. many monitoring programs are continuously describing only this variation, without attempting to understand it. Due to the stochastic nature of natural processes and the short duration of many monitoring programs, or the tendency to carry out synoptic (snapshot) sampling at fixed points in space and time, the interactions of these natural cycles with the physical. chemical and biological components of the system are often missed or misinterpreted.

Table 1. IWD Monitoring Objectives

	Objective	Purpose
1.	Identification	To determine the presence of known or hitherto undetected problems within river basins in Canada
2.	Quantification	To establish the location, severity, areal or volume extent, frequency and duration of unacceptable levels of pollutants
3.	Compliance	To assess the degree to which guidelines, objectives or standards are being met
4.	Trends	To predict when guidelines, objectives or standards will be exceeded
		To assess the effectiveness of decisions or actions undertaken by management for the protection of the environment
5.	Characteristics	Research which generates information on the chemical, physical and biological properties of the toxic chemicals, including their toxicity, pathways and fate in the environment
6.	Impact	Establish environmental levels, trends, partitioning tendencies, transport and accumulation patterns in order to define properly fate and impact of the in-use toxic substance either singly or cumulatively on the aquatic environment
7.	Models	Development of mathematical equations, structure activity relationships and the implementation of ecosystem models to toxic chemicals

Optimum sampling design with respect to station patterns, sample frequency and parameter lists, to identify the spatial and variance of various parameters as we11 interrelationships, requires a constant effort and frequent review. Due to time lags, spatial and temporal heterogeneity, and synergistic and antagonistic relationships, cause-effect relationships can only be established through the integration of research and results. This scientific information generated by the coordinated research-monitoring efforts is then fed into the information web to augment the efforts of other Departments.

WORKSHOP PROCEEDINGS

The theme of the workshop carried out in Burlington was water quality monitoring. The presentations and findings of the working group sessions were not restricted to the issue of toxic chemicals. The intricate interplay of activities within and between departments, however, is similar, irrespective of which issues are discussed. As a result, monitoring is often subjected to a great deal of verbal abuse by individuals, at a given conceptual or practical level, seeking information from the activity monitoring. Rarely are these individuals concerned enough to look at the program in its entirety, rather, they reluctantly concede to its massive bureaucratic existence and only focus attention on the fact that their personal needs are not totally met.

The Water Quality Branch is a coparticipant in many monitoring programs (LRTAP, Toxics, Great Lakes, etc.). It is therefore of paramount importance that the Water Quality Branch develop a systematic, pragmatic procedure for its monitoring efforts to ensure that the Branch is able to meet its mandate responsibilities (e.g., supply scientific advice and information). Only through scientifically sound water quality information can managers resolve present and future environmental problems.

RECOMMENDATIONS

During the three-day workshop a number of recommendations were made by the five established working groups to improve data collection, interpretation and information flow:

- 1. Objectives for the monitoring program should be written simply and should reflect public concerns, not just those of the scientific or managerial community. The underlying question in monitoring is whether or not there is a threat to aquatic life or human health. No monitoring program should have data collection as a sole objective.
- 2. The importance of a holistic program cannot be overstressed. Multi-media sampling (sediment and biota) was identified as mandatory for all studies. Both functional (within an individual) and structural (within the community) biomonitoring were considered as valuable monitoring tools. Excessive emphasis has been placed

on the measurement and interpretation of single compounds in water. The influence of ground water must be considered, as well as the importance of biological monitors or screening tools as stress indicators. Which media or species of biota to use in any given study depends on the study area and the issues.

- 3. Any monitoring program should be responsive and concerned with the assessment of system health and not just concentrations. Regional issues should not be distorted to suit a national program. However, there is a need for a consistent national strategy and central coordination of the monitoring programs.
- 4. Historically, insufficient time has been allotted for problem identification, hypothesis formulation and data interpretation. Efforts in these regards, which may consume a considerable amount of time, often go unrecognized.
- Monitoring programs are too often more menu (priority list) driven, rather than system or knowledge driven.
- 6. There is a need to develop river-specific water quality objectives as a management tool, not only for chemical levels in water but also in other media (sediment and biota).
- 7. The research component must commit effort to technology transfer. Research technology that is too complex and not easily transferable to an operational level is of limited use to a monitoring program.
- 8. The first step to monitoring is for an historical review of all pertinent data to be carried out. Due to the various agencies involved in monitoring, a great deal of information often exists but may not necessarily be on any central data bank. All too often baseline studies are carried out on river basins when a substantial amount of information already exists. This results in a duplication of effort and the potential loss of acquiring valuable new insights into the major issues within the river basin.
- 9. Initial monitoring should result in background information and problem/emerging issue identification. At that point, the advice and cooperation of researchers should be actively sought in the development of study objectives and hypothesis testing. Unless scientists are involved at the early stages of monitoring development, participation at a later date is difficult and often useless.
- 10. Monitoring programs must be designed to test a scientifically defensible hypothesis (e.g., 5% change in a parameter over a given time period). It is mandatory that the statistical aspects of the program be determined prior to sampling and not after.
- 11. Station density, parameter list and sample frequency should all reflect the diffuse and point source inputs in the basin, bearing in mind the land use activities.

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