RECOMMENDATIONS FOR LONG TERM MONITORING

TABLE OF CONTENTS

						<u>Page</u>
7.1	Introduc	ction		en de la companya de La companya de la co		7-4
7.2	Objecti	ves of a	Long	Term Monitoring Prog	gram	7-5
7.3	Consider	rations f	or th	e Design of a Long 1	Term Monitoring Progr	am 7-6
	7.3.1 7.3.2 7.3.3 7.3.4 7.3.5 7.3.6 7.3.7	Data Qua Data Man Data Ana	and lity ageme lysis	Analytical Methods		7-6 7-6 7-7 7-8 7-9 7-10
7.4	Design (Details o	f the	Long Term Monitorin	ng Program	7-10
	7.4.1 7.4.2	General Ambient 7.4.2.1	Ambi (a)	Monitoring ent Water and Susper Objectives	nded Sediments	7-10 7-12 7-13 7-13
		7 4 2 2	(b) (c) (d) (e)	Site Locations Sampling Methodolog Parameters Data Reporting	JY	7-14 7-14 7-14 7-16
		7.4.2.2 (a)		ogical Monitoring tail Shiners Objectives Site Locations Sampling Methodolog		7-16 7-17 7-17 7-18 7-18
		(b)	(4) (5) Atta (1)	Parameters Data Reporting ched Filamentous Alg Objectives	gae (Cladophora glome	7-20 7-20 rata) 7-21 7-21
			(5)			7-21 7-22 7-22 7-23
	7.4.3	Point Soint 3.1 7.4.3.2 7.4.3.3 7.4.3.4	Obje Para Disc	Monitoring (Industri ctives meters harge Effluent Monit rnal Waste Stream Mo) 7-23 7-23 7-24 7-24 7-26
		7.4.3.4	(a) (b)	Than waste Stream Mo Industrial Sources Municipal Sources	in to thy	7-26 7-27

	TABLE OF CONTENTS (continued)			
		<u>Page</u>		
	7.4.3.5 Biomonitoring	7-27		
	7.4.3.6 Limitations and Other Concerns	7-27		
	(a) Resource Limitations	7-27		
	(b) Monitoring Criteria	7-28		
7.4.4	Special Studies	7-29		
	7.4.4.1 Sediment Coring - Niagara River Bar	7-29		
	7.4.4.2 Sediment Coring - Power Reservoirs	7-29		
	7.4.4.3 Contributions from the Tonawanda Creek and			
	its Tributaries	7-30		
	7.4.4.4 Contributions from Welland River, Buffalo			
	River, and other Tributaries	7-30		
	7.4.4.5 Conventional Parameters and Point Source			
	Discharges	7-31		
7.5 Impleme	entation	7-32		
References		7-33		
<u>Tables</u>				
Table 7.1	Implications of Typical Ambient Water Concentrations	7- 9		
Table 7.2	of Various Parameters on the loadings to Lake Ontario Recommended Monitoring Program Framework			
	we commended them to the transfer to	7–25		
F igu res				
Figure 7.1	Water and Suspended Sediment Monitoring Stations	7-15		
Figure 7.2	Biological Monitoring Stations	7-19		

7.1. Introduction

The Niagara River Toxics Project represents a renewed spirit of cooperation between Canadian and United States agencies in attacking the problem of toxic substances pollution of the Niagara River. Previously, few attempts had been made to coordinate the monitoring activities of both countries. As a result, a total picture of the extent of toxic substance contamination in the Niagara River system has been lacking. This project has provided information to fill in some of the existing gaps regarding the sources, types, quantities, and fate of chemicals in the water, sediment, and biota of the Niagara River. The NRTC has used this information to determine the effectiveness of present pollution abatement programs, to recommend refinements in current programs, and to suggest need for additional ones. The effectiveness of these recommendations in controlling toxic substances in the river can be determined only through a continuing coordinated monitoring program. Indeed, this was recognized in the third objective of the Niagara River Toxics Committee:

"Recommend a long term monitoring program for the Niagara River that will allow evaluation of the effectiveness of control programs".

Development and implementation of a long term monitoring program for the Niagara River must consider the domestic jurisdictional requirements of federal, provincial, and state agencies, the binational requirements under the Boundary Waters Treaty (1909), and the 1978 Canada-United States Great Lakes Water Quality Agreement. Coordination of activities allows more effective use of fiscal resources and ensures that data collected are compatible for reporting and interpretive purposes.

The Committee notes the existence of several other important activities on the river which address more conventional water quality parameters. The Long Term Monitoring Program outlined in this Chapter is directed specifically at toxic substances in the river system.

7.2 Objectives of a Long Term Monitoring Program

As a basis for designing a long term monitoring program, three overall objectives have been formulated. These appear below in order of priority:

- Achievement of and Compliance with Criteria, Guidelines, Standards, and Objectives: To assess the degree to which jurisdictional control requirements are being met. To provide definitive information on the degree to which criteria, guidelines, etc., are being met or exceeded in receiving waters as a basis for determining the efficacy of implemented control programs or the need for more stringent control requirements.
- through the analysis of temporal and spatial trends in concentrations of chemicals of concern in water, sediment, and biota. Results of these evaluations will be used for:
 - * assessing the effectiveness of remedial and preventative measures;
 - * identifying the need for further technology development and research activities; and
 - * identifying emerging problems, eg. significant upward deviation from a downward trend in the concentration or loading of a specific substance, or the detection of previously unidentified compounds.
- iii) Identification of Sources: To identify the sources of toxic substances inputs (including the contribution from Lake Erie) to the Niagara River.

7.3 Considerations for the Design of a Long Term Monitoring Program

7.3.1 General

Designing a monitoring program to achieve the stated objectives requires selecting the parameters of concern and the specific media in which they are to be measured, and specifying the manner in which they should be Sampling and analytical methodology should meet specified accuracy in order to determine water quality conditions and changes in conditions. Crucial considerations in the program design are the specification of "acceptable" detection limits as well as the accuracy or precision with which changes in concentrations or detection frequencies must be determined, so that the measurements can be interpreted with confidence and used to achieve the monitoring program objectives. The program design needs to specify quality control/quality assurance protocols for data assessment and interpretation to ensure high quality, compatible data. Finally. the jurisdictions must agree on how the results are to be interpreted, eg., the exceedances of objectives and criteria which will be considered significant enough to require action, and the temporal increases which will be of concern.

The Committee recognizes that many of the details of a Long Term Monitoring Program can be addressed only by discussion among the agencies responsible for program implementation. Some general guidelines are provided below.

7.3.2 <u>Chemical Parameters</u>

Chapter VI of this report outlines the process by which the Committee determined chemicals of concern in the Niagara River ecosystem. The Committee recommends that, based on this information, priority be placed on the analysis of Group I chemicals in the Niagara River Long Term Monitoring Program. Chemicals in Group II, for which additional data are required to make an adequate assessment of the significance of the compound, should also be considered. Additional compounds may be detected in the river

at some later date (i.e., newly identified contaminants), and should be added to those requiring investigation. Some chemicals may not presently be in any of the groups of Chapter VI because they occur at such low levels as to be presently non-detectable, which does not necessarilv preclude occurrence at a detectable level at some future date. Leaving the adequacy of appropriate detection limits aside at this point, two possible mechanisms of detecting the presence of substances presently undetected are, a) to conduct appropriate GC/MS scans on a number of environmental samples to flag newly suspected peaks in the chemical analyses, and b) to ensure that other available sources of information, such as chemical inventories and SPDES permits or Control Orders, are scrutinized carefully in concert with the results from environmental measurements. This would provide at least a first line defense against any new future "surprise" chemicals showing up in the river system.

7.3.3 <u>Sampling and Analytical Methods</u>

There must be agreement among the different agencies regarding sampling and analytical methodologies. This does not necessarily mean that methodologies should be standardized, but proposed methodologies should provide compatible results and attain the desired accuracy and precision.

One issue of particular concern is agreement on acceptable analytical detection limits. A wide variety of detection limits were used in the present Niagara River Toxics Project as a result of the many participating laboratories. As pointed out in Chapter IV of this report and the Data Quality Subcommittee Report (DQS, 1984), this led to difficulty comparing data, a situation that should be resolved before implementation of the proposed Long Term Monitoring Program.

The Committee does not feel it is in a position at this time to specify detection limits for each of the parameters to be measured in each medium (eg. water, sediments, biota, effluents, etc.). Many detection limits are parameter and media specific. Historically, agencies have selected

limits based on their own requirements. detection For example. agencies, for regulatory purposes usually set detection limits to meet permitted effluent requirement levels, while other agencies, for purpose of measuring ambient environment samples, set them to the most sensitive level possible bv state-of-the-art analytical methodology. The Committee recommends that, prior to implementing the proposed Long Term Monitoring Program, the responsible agencies ensure that the detection limits chosen for each of the Program components and activities are adequate to attain the overall objectives of the Program.

The critical nature of detection limits, particularly in the ambient environment, is best exemplified by the implications of extremely small concentrations of toxic substances in water in terms of the loadings from the Niagara River to Lake Ontario. This has been alluded to in the Ambient Chapter of this report and is further summarized in tabular form here in Table 7.1. Table 7.1 illustrates that even at extremely small concentrations (ng/L), given the volumes of flow in the Niagara River, the loadings to Lake Ontario can be very substantial. The case of mirex puts these figures into perspective. It is estimated that approximately 680 kg (1500 lb) of mirex entered Lake Ontario over a 10-year period (Holdrinet, et al, 1978). This is equivalent to a loading of 68 kg (150 lb) of mirex per year or an equivalent water concentrations of 0.1-1.0 ppt, which is admittedly extremely small. Yet the overall result was contamination of a broad band of sediment along the entire south shore of Lake Ontario and closure of the sports fishery because mirex levels exceeded the human health protection guidelines of 0.1 ug/g in the edible portion of fish.

7.3.4 <u>Data Quality</u>

The quality of data is critical to the Monitoring Program. If the Niagara River system is to be assessed as a whole as well as in localized areas, and if the work is to be divided up among agencies, then a coordinated data quality assurance program must be implemented prior to the initiation of the field sampling program. This is reflected in the recommendations of the

TABLE 7.1

IMPLICATIONS OF TYPICAL AMBIENT WATER CONCENTRATIONS OF VARIOUS PARAMETERS IN THE NIAGARA RIVER ON THE LOADINGS TO LAKE ONTARIO*

PARAMETER CONCENTRATION	LOADING TO LAKE ONTARIO (KG/YR)	EXAMPLES
10 ppm (mg/L) 10 ppb (ug/L) 10 ppt (ng/L) 1 ppt (ng/L)	2.0 x 10 ⁹ 2.0 x 10 ⁶ 2.0 x 10 ³ 200	Sodium Total phosphorus PCB, alpha-BHC HCB, gamma-BHC,
0.1 ppt (ng/L)	20	pentachlorobenzene p,p'-DDE, beta-endosulfan alpha-endosulfan, DDT (Total) beta-chlordane gamma-chlordane

^{*}Kuntz, personal communication.

Data Quality Subcommittee Report to the Niagara River Toxics Committee. The Committee notes that several Task Forces within the International Joint Commission Surveillance Work Group are currently working on developing a coordinated QA/QC program for joint agency surveillance and monitoring activities. The committee recommends that the IJC's results be carefully scrutinized by agencies responsible for implementing the proposed Long Term Monitoring Program, and that a well designed QA/QC program be in place before the Program is initiated. In the interim, the Data Quality Sub-committee recommends that the U.S. EPA document titled "Guidance for Preparation of Combined Work/Quality Assurance Project Plans for Water Monitoring" be used as a guide.

7.3.5 <u>Data Management</u>

Coordinated data management is a key element in the Program design. A high priority must be given to interagency access to data collected as part of the Long Term Monitoring Program to ensure complete analysis and timely reporting.

7.3.6 Data Analysis and Reporting

Data analysis and reporting have historically been a neglected aspect of Great Lakes monitoring programs due to the limited time available for interpretation. The Long Term Monitoring Program will be successful only to the extent that the data are analyzed and interpreted to provide meaningful feedback to managers of pollution abatement programs. Additional resources may be required to bring this task up to the standards needed for the annual assessment of water quality, even at the expense of curtailing some data collection activities.

An additional concern in data analysis and reporting is that data be interpreted similarly by each participating agency so that individual assessments can be combined to provide a unified evaluation of water quality in the Niagara River.

7.3.7 Agency Support and Implementation

Both Canadian and United States agency participation in all aspects of the Long Term Monitoring Program is critical to its success. High priority for this participation must be given by all agencies. In general, the Committee feels that it is not in the position to dictate which agencies should carry out the individual activities identified in the proposed Long Term Monitoring Program. This should be decided by the responsible agencies at the time of implementation.

7.4 Design Details of the Long Term Monitoring Program

7.4.1 General

The recommended Long Term Monitoring Program has two components. The first consists of monitoring that is designed to demonstrate the addition of toxic substances along the Niagara River. This is to be accomplished by examining the trends in differences between inputs to the Niagara River from Lake Erie and outputs from the Niagara River to Lake Ontario. Sampling and

analytical procedures must be designed to provide firm evidence for improvement or degradation. The success of the end of river monitoring approach depends on decisions regarding the significance to be attached to differences between input and output concentrations. Appropriate decisions will avoid the expenditure of resources on programs based on differences which are either temporary or insignificant.

Gross input-output differential monitoring provides no information on specific sources of increased (or decreased) contaminant contributions to the Niagara River system. Therefore, the second component of the Long Term Monitoring Program consists of collecting samples from point sources and localized areas. Point source information will provide confirmation that jurisdictional control requirements are being met and permit a more timely response to degradation confirmed by localized or end of river monitoring. Also, it will alert jurisdictions to the possibility of future degradation, particularly in cases where loadings from individual dischargers can be masked by the effects of dilution due to the high flow of the river and natural background variation.

Non-point sources are also potential contributors of contaminants to the river system and should be considered in the monitoring programs. Monitoring the contributions from non-point sources is very difficult, however, and in most cases requires site specific programs. While the Committee recognizes that the development of such programs is needed, they are beyond the present scope of this Program. The Committee recommends, therefore, that such programs be developed as required, and that the information obtained be used in interpreting the results of the Long Term Monitoring Program outlined in this chapter.

The design of the Long Term Monitoring Program outlines a <u>minimum</u> program which the Committee feels is necessary to address the overall program objectives as stated. A number of agencies will continue to conduct specific monitoring activities outside the present program design, which will provide meaningful additional data to augment this Program. Examples of such ongoing

programs include monitoring raw drinking water intakes, clams, benthic macro-invertebrates, sport fish, and conventional pollutants in effluents. To the extent possible, results of these activities should be incorporated into the assessments produced from this Program where they can provide more meaningful interpretation of results.

7.4.2 Ambient River Monitoring

Ambient river monitoring forms the core of the Long Term Monitoring Program for the Niagara River System. The specific objectives of this component are as follows:

- a) To measure the change of specific chemicals of concern over time in appropriate environmental media;
- b) To compare the concentrations of chemicals of concern to given criteria, guidelines, standards, and objectives in specific environmental media;
- c) To determine the spatial distributions of chemicals of concern by river segment within the Niagara River System;
- d) To report on the presence of previously undetected and unidentified chemicals in the Niagara River System; and
- e) To determine the presence of significant differences in contaminant loadings (or ratios of detection frequencies) between Lake Ontario (Niagara-on-the-Lake) and Lake Erie.

Three activities are needed to accomplish these objectives; ambient water monitoring, suspended sediments monitoring, and biological monitoring. All three activities address toxic substances in the various compartments of the ecosystem and are to be conducted on a long term basis.

7.4.2.1 Ambient Water and Suspended Sediments

Many of the chemicals of concern to be measured as part of the ambient river monitoring component—particularly the persistent organic substances—occur in extremely low concentrations in water. Furthermore, many of these substances partition themselves between the aqueous and the sediment phases in the river. Some occur almost exclusively in the water phase, some in the sediment phase. Therefore to obtain an accurate picture of the total water column, both phases must be measured. The experience of stripping sorbed organics from the sediment fractions of whole water samples has proved that it is more effective to measure both fractions separately and obtain a total concentration by adding the concentrations in the two fractions.

(a) <u>Objectives</u>

The objectives of measuring ambient water and suspended sediments are as follows:

- (i) To determine the trends in the concentrations of specific chemicals in the water and suspended sediments of the Niagara River;
- (ii) To compare the measured concentrations of chemicals of concern to given ambient criteria, standards, guidelines, and objectives, and report on significant exceedances that will require agency action; and
- (iii) To estimate the relative differences in the loadings of chemicals of concern between the river's source and mouth.

The data collected from this activity contribute to other overall objectives of the plan (trend assessment and identification of new emerging problems), but the primary output will be directed to the three objectives stated above.

(b) Site Locations

It is proposed that two sites (Figure 7.1) be sampled, one at Niagara-on-the-Lake (Niagara River outlet) and one at Fort Erie (Niagara River inlet). The site at Niagara-on-the-Lake was chosen because it has been determined that there is no lateral or cross-sectional variation in the water chemistry at the mouth of the Niagara River due to the thorough mixing at Niagara Falls and at the whirlpool (Chan, 1977). This location is ideal because of its accessibility and readily available source of power. Lake Erie should be sampled in open lake water, not along the eastern near shore area, where the flows carry the input from the various sources in that area.

(c) Sampling Methodology

While small volume (2L) samples may be adequate for metals analyses, large volume water samples (200L) are required for the analysis of organic substances. The Water Quality Branch, Ontario Region and the National Water Research Institute of Environment Canada have had considerable success in applying large volume field extraction techniques for water and centrifugation methods for suspended sediments. The methodologies have been documented elsewhere and are not discussed here (Kuntz, 1982). The Committee recommends that the agency or agencies responsible for carrying out this activity consider the continued use of this methodology.

(d) Parameters

See Section 7.3.2 of this Chapter.

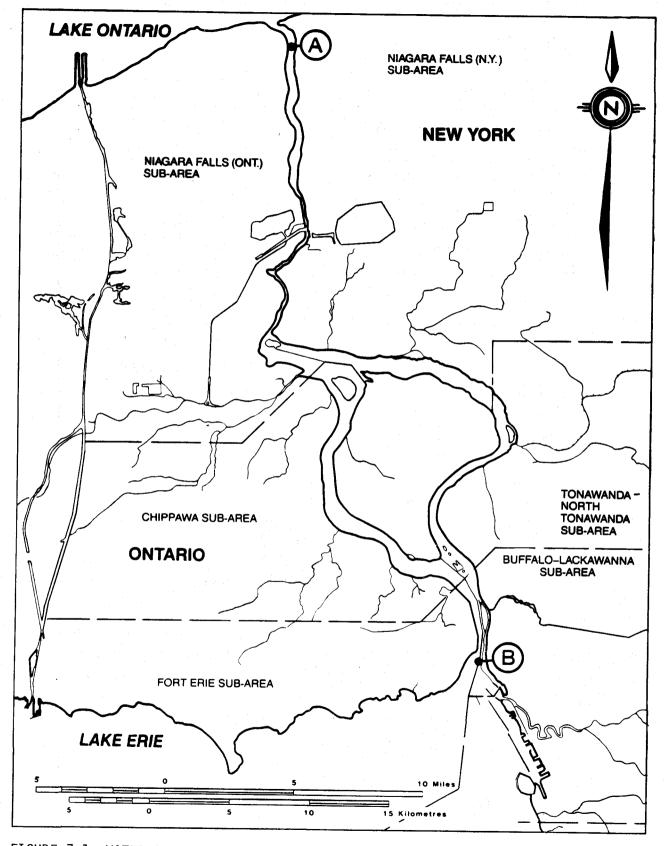


FIGURE 7.1 WATER AND SUSPENDED SEDIMENT SAMPLING STATIONS ON THE NIAGARA RIVER

(e) Data Reporting

The results of the large volume water and suspended sediment sampling can be assessed by both parametric and non-parametric statistics. Work on this project (see Chapter IV) suggests that for most substances, the detection limits may not be sufficient to allow the use of parametric statistics. Therefore, procedures will have to be worked out to analyze trends in terms of non-parametric statistics. It will be essential for the jurisdictions to agree on the statistical trends and on significant exceedances of objectives or criteria that will require agency action.

The water and suspended sediments data will be used to compare the water quality of the Niagara River with appropriate standards in Canada and the U.S. and with the Great Lakes Water Quality Objectives as outlined in the Canada-U.S. Agreement on Great Lakes Water Quality.

7.4.2.2 Biological Monitoring

The biological monitoring component serves as the basic means for evaluating the effect of contaminant discharges to the river on river water quality as well as on resident biota (i.e., some measure of the health of the ecosystem). It will provide an indication of localized areas of contamination as well as the relative degrees of contamination in various segments of the river.

Aquatic biota and fish in particular tend to be integrators of aquatic systems and, as such, provide one of the best indicators of the health of those systems. Past assessment of water quality in the Great Lakes has been based largely on measurements of physical and chemical characteristics which have certain spatial and temporal limitations. Some contaminants may be present in the water in concentrations below the detection limits of standard analytical procedures. As a result, routine analytical methodology is not adequate for predicting possible deleterious effects on the system. Some components of the biota that serve as

integrators and concentrators of these contaminants can be used as indicators of water quality and trends in water quality.

(a) Spottail Shiners

Due to a relatively small geographical migration range (0.5 - 1 km) in their early life stages, resident young-of-the-year spottail shiners are useful indicators of recent point source and non-point source area inputs of trace contaminants in nearshore areas. These fish offer a high degree of sample comparability because of similarities of fish age and lipid contents. In addition to point source evaluations, the specificity of this type of biological monitoring is particularly useful for the follow-up and evaluation of remedial action and comparison with Agreement guidelines or objectives.

In the Niagara River, PCBs, organochlorine pesticides, and mercury residue data are available for populations of spottail shiners from Niagara-on-the-Lake since 1975 and in the Chippawa Channel since 1980. An additional upstream control site in Thunder Bay, Lake Erie has been sampled since 1978 (Suns et al. 1978, 1983). Sites more specific to certain source areas or point sources in the river have also been sampled in recent years (see Chapter IV).

(1) Objectives

The objectives of this biological monitoring are as follows:

- (a) To determine the trends in the concentrations of specific chemicals in spottail shiners from localized areas of the Niagara River;
- (b) To compare the measured concentrations of chemicals in spottail shiners to given criteria, standards, guidelines and objectives;

- (c) To assist in the trackdown of the source of substances which end of the river monitoring indicate are not being effectively controlled; and
- (d) To identify any new or emerging problems.

(2) Site Locations

Based on the results of the Niagara River Project, it is proposed that eight sites which have been shown to be near potential source areas to the Niagara River (Figure 7.2) be sampled yearly for the determination of long-term trends of contaminant inputs. These are, Lake Erie (Thunder Bay), Black Rock Canal/Buffalo River (Peace Bridge, N.Y.), Lake Erie (Peace Bridge, Fort Erie, Ont.), entrance to Chippawa Channel, entrance to Tonawanda Channel, the Chippawa Channel (Chippawa, Ont., opposite Navy Island), the upper Tonawanda Channel (Gratwick-Riverside Park, N.Y.), the lower Tonawanda Channel (Search and Rescue Station, Niagara Falls, N.Y.), and from the lower Niagara River to Lake Ontario (Niagara-on-the-Lake, Ont.). An additional upstream control site in Thunder Bay, Lake Erie is also recommended. Other sites in the river which are more specific to certain source areas can be added in alternate years or as required to evaluate trends in inputs from previously identified problem areas (e.g., Love Canal/102nd Street, Cayuga Creek, Pettit Flume).

(3) Sampling Methodology

Young-of-the-year spottail shiners (3-4 months old, about 5 cm in length) should be collected annually in September with a 20 m bag seine (0.6 cm mesh). It is important to time these annual collections to coincide with the previous years' collections, thus minimizing the effects of seasonality on contaminant levels. Individual fish should be measured (length), wrapped in hexane-washed aluminum foil (organics analysis) or placed in plastic bags (inorganic analysis) and frozen in the field using dry ice. Samples should be stored at -20°C before analysis. Composites of 20 fish per replicate

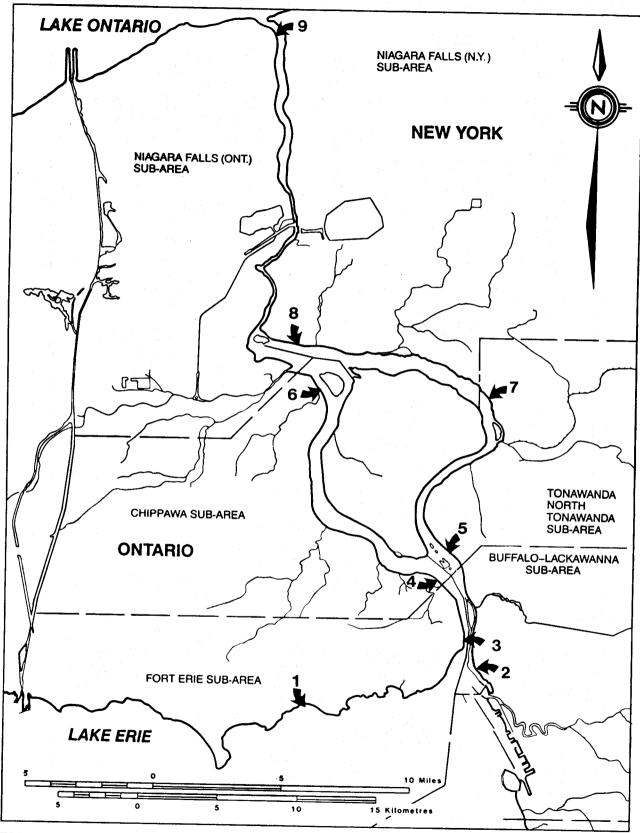


FIGURE 7.2 NIAGARA RIVER BIOMONITORING LOCATIONS

should be used for dioxin residue analysis, whereas composites of 10 fish each are sufficient for other contaminant analyses. This methodology has been proven effective in the past and was adopted by agencies responsible for sampling spottail shiners as part of the Niagara River Toxics Project.

(4) <u>Parameters</u>

See Section 7.3.2 of this Chapter.

Results of past analyses have indicated that spottail shiners are effective bioaccumulators of the following parameters (underlined parameters appear in Group I and Group II, Chapter VI:

Organics: (i) PCBs (total)

- (ii) Organochlorine pesticides <u>aldrin</u>, <u>dieldrin</u>, <u>BHC</u>
 (alpha, beta, gamma), <u>chlordane</u> (alpha, gamma), <u>DDT</u>
 (p,p'), <u>DDD</u>, <u>DDE</u>, <u>endrin</u>, <u>endosulphan</u> (alpha, beta), <u>heptachlor</u>, <u>heptachlor</u> <u>epoxide</u>, <u>hexachlorobenzene</u>, <u>mirex</u>.
- (iii) Chlorinated aromatics 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, 1,2,3,4-trichlorobenzene, hexachlorobenzene, pentachlorobenzene, octachlorostyrene.
- (iv) Chlorinated phenols 2,4,5-trichlorophenol, 2,4,6-trichlorophenol, pentachlorophenol.
- (v) Dioxin 2,3,7,8-TCDD.

Inorganics: Arsenic, cadmium, lead, mercury.

Future fish collections should be analyzed for the above parameters. This analytical list should be reviewed annually and, based on these results as well as analysis of selected fish for "new" contaminants, be revised accordingly.

(5) <u>Data Reporting</u>

The collection of data from this component will be used to determine temporal trends of trace contaminant levels in naturally occurring resident

fish populations in the river. Comparison of contaminants in fish from the various sites can be used as an indication of water quality differences in the river and the presence of inputs of contaminants adjacent to or upstream of the collection site. Data for PCBs, DDT, mirex, and mercury in spottail shiners can also be compared to specific objectives for the protection of fish-consuming birds and animals as outlined in the Annex 1 of the Canada-U.S. Agreement on Great Lakes Water Quality (1978). Agreement will need to be reached among the agencies on how objective exceedances will be interpreted so that agency response will be based on statistically significant findings.

(b) Attached Filamentous Algae (Cladophora glomerata)

As a result of its growth habits (attached to rock substrates) and ready availability in the Niagara River, this green alga can serve as a useful biomonitor of point source and source area inputs. The non-mobile nature of this alga makes it useful for evaluating the impact of point source discharges, particularly in a riverine situation where there is usually unidirectional flow. Because <u>Cladophora</u> grows attached to shallow rocky substrates by means of a holdfast cell and does not possess a true root system, any increases in concentration of contaminants can be directly related to recent uptake from the water column. Past studies on the Niagara River have indicated that <u>Cladophora</u> is particularly useful for studying metals in water. This activity, therefore, is intended to complement the Spottail Shiner work, which is related primarily to organic substances.

(1) Objectives

See objectives for Spottail Shiner monitoring, p. 7-18.

(2) <u>Site Locations</u>

The same nine sites previously proposed for spottail shiner monitoring (Figure 7.2) should be used for <u>Cladophora</u>, particularly for the evaluation of metals input to the river. Other sites in the river which are more specific to certain source areas can be added in alternate years or as

required to evaluate trends in inputs from previously identified problem areas.

(3) Sampling Methodology

Submerged <u>Cladophora</u> (0-50 cm water depth) should be collected by hand at the time of peak biomass in the river (late June). Material at a given location should be composited over the required area and rinsed in ambient water to remove particulate and other extraneous matter and squeezed of excess water by hand. Approximately 500 g (wet weight) of biomass per station should be wrapped and transported on ice to the laboratory. <u>Cladophora</u> should then be dried to constant weight at 50°C, powdered, and stored in the dark until analyzed. About 5 g (dry weight) of sample is adequate for one replicate analysis (inorganics or PCBs).

This methodology has been proven effective in the past and was used during the Niagara River Toxics Project.

(4) Parameters

See Section 7.3.2 of this Chapter.

Analysis on a dry weight basis has been shown to give a five-fold increase in detectability and improved within-sample homogeneity. Unfortunately, the drying procedure invalidates analysis for the more volatile organochlorine pesticides which are a part of the routine PCB/organochlorine pesticides scan. Nevertheless, <u>Cladophora</u> has proven to be an effective bioaccumulator of the following (underlined parameters appear in Group I and Group II, Chapter VI):

Organics: PCBs (total)

Inorganics: <u>arsenic</u>, <u>aluminum</u>, barium, beryllium, boron, cadmium, chromium, cobalt, <u>copper</u>, <u>lead</u>,.

manganese, mercury, nickel, selenium, strontium

titanium, vanadium, zinc, nickel, potassium

(loss on ignition-desirable analysis)

(5) <u>Data Reporting</u>

Data from <u>Cladophora</u> analyses will be used to determine both temporal trends and spatial differences in contaminant concentrations, particularly metals in the river. Where possible, these will be related to contaminant inputs and the effectiveness of remedial programs.

7.4.3 <u>Point Source Monitoring (Industrial, Municipal, Urban)</u>

7.4.3.1 Objectives

- (a) To determine long term trends of specific substances for the identification of emerging problems;
- (b) To assist in determining the source of problems identified in the ambient measurements program;
- (c) To monitor compliance of industrial and municipal discharges with regulatory requirements: and
- (d) To identify previously undetected substances in point source discharges.

The Point Source Monitoring component includes three activities: discharge/effluent monitoring, internal wastewater monitoring, and biomonitoring. The program structure is presented in Table 7.2. All activities address the measurement of toxic substances in point source discharges and, excluding biomonitoring, would be carried out on a long-term basis.

If this program component is to accomplish its objectives it must be tied in with the ambient component. Agencies must agree on the parameters to be measured and the frequencies with which samples are to be taken at each facility. It is recommended, however, that trace organics monitoring, based on the complete set or selected sub-set of the EPA Priority Pollutant List and the NRTC Group I chemicals, occur at least annually for all major sources

and more frequently where deemed appropriate by the responsible regulatory agency.

7.4.3.2 Parameters

The parameter list, including metals and organics, will be specific to each industry, municipal treatment plant, and combined storm sewer on the point source inventory. Regulatory agencies will specify this list based on their knowledge of the industrial operations, municipal treatment plants, and sewer systems under their jurisdiction. Specific factors to be considered in the development of a parameter list include:

- . parameters measured in the ambient component of the program
- industrial raw materials, products, by-products
- . industrial processing operations
- . industrial and municipal treatment processes
- . historical monitoring data
- specific upstream inputs to municipal treatment plants and combined/storm sewers

7.4.3.3 <u>Discharge Effluent Monitoring</u>

Monitoring the levels of selected Group I chemicals and EPA priority pollutants known to be present in industrial discharges, municipal wastewater treatment plant effluents, and contaminated combined storm sewer overflows is necessary to measure trends and variability in loadings, and to assess specific limitations and requirements. compliance with Point monitoring also identifies jurisdictional sources of specific chemicals of concern and compliments the Ambient River Monitoring program's objective of determining spatial distribution by river segment. Periodic organic and heavy metal scans of the discharges would highlight previously undetected or unidentified contaminants for which surveillance in the river can be carried Discharge monitoring also identifies sources requiring additional out. treatment or modifications in discharge requirements.

RECOMMENDED MONITORING PROGRAM FRAMEWORK: LONG TERM POINT SOURCE MONITORING FOR THE NIAGARA RIVER

		SIGNIFICANT INDUSTRIAL SOURCES*		MUNICIPAL WWTPs/WPCPs AND CONTINUOUS CSOs ²		SELECTED INTERMITTENT CSOs ²	
COMPONENT ACTIVITY	PARAMETERS AND FREQUENCY	PP Metals & Cyanide	PP & Group 1 Organics ⁵	PP Metals & Cyanide	PP & Group 1 Organics5	PP Metals & Cyanide	PP & Group 1
Intake Monitoring	Parameters	Same as for	Same as for	3	3	N/A	Organics ⁵
(Industrial)		discharge if river source or	discharge if river source or				N/A
or Influent Monitoring (Municipal)	Suggested Minimum	contaminated groundwater	co ntaminated groundwater ¹				
Ni sahansa Marit	Frequency*	Monthly	Monthly	3	3	N/A	N/A
Discharge Monitoring (Industrial) or	Parameters	Site Specific in excess of cut-off ⁴ and	Site Specific in excess of cut-off ⁴	Site Specific in excess of cut-off ⁴	Site Specific in excess of cut-off		
Effluent and Continuous CSOs2 (Municipal)		others as required	others as required	others as required	others as required	Site Specific	Site Specific
or Intermittent CSOs2 Monitoring (Municipal/Industrial	Suggested Minimum Frequency*	Monthly for over cut-off ⁴ Less frequently for others	Monthly for over cut-off ⁴ Annually for others	Monthly for over cut-off ⁴ Less frequently for others	Monthly for over cut-off ⁴ Annually for others	During selected storm events	During selected storm events
Internal Wastestream Monitoring (Industrial) or	Parameters	Site Specific for undiluted process streams	Site Specific for undiluted	Quantitative	Semi-	6	. 6
Sludge (Municipal)	Suggested Minimum	•	process streams	scan	quantitative scan all peaks		
Jpstream Sources (CSOs)2	Frequency*	As per discharge	As per discharge	Annually or 3	Annually	6	6
3iomonitoring	Acute/ Chronic	erriaent and defet	ng-term bioassays de mine bio-uptake and	esigned to assess the	e acute and chronic	*10 0 0 - 16	
special studies)	Toxicity and	effluent and determine bio-uptake and accumulation of organics and heavy metalse.g., a 16- week, continuous flow bioassay with rainbow trout or fathead minnows exposed to various dilutions (determined by effluent toxicity and modelling of the limited use zone) of the effluent. A					
	Bio-Uptake	annacr of the feat	ilon would be sacri	TICED AT DESIGNATED	times for editie n	antian and thele fi	sh
Significant industrial son		and nermit develor	mont Carduated	. Such studies would for effluent evaluate site in mobile trail	tion, the identific	ation of new compou	and inds,

See 4 below for cut-off values. Minor sources fall into three categories: 1. those exceeding the cut-off values for the total loading of at least one pollutant category (e.g., purgeables); 2. those with no total category cut-off exceedences; 3. those deemed insignificant and not sampled. Minor sources in category 1 may require a monitoring frequency equal to significant sources. Categories 2 and 3 require less frequent monitoring.

6

⁼ EPA Priority Pollutant; NA = Not Applicable.

⁼ If industrial water supply is municipal drinking water or uncontaminated groundwater, intake monitoring optional.

⁼ CSOs (Combined Sewer Overflows) refer to municipal sewer discharges containing sanitary or industrial process wastewater that discharges continuously or intermittently.

³ = As required in support of industrial pretreatment studies. 4

⁼ All parameters discharged in excess of stated cut-off values monitored: Cyanide, Volatiles, Extractables, 4AAP Phenolics 0.227 kg/d, Mercury, Pesticides and PCBs - 0.0454: Heavy metals - 0.454 kg/d. 5

⁼ EPA volatiles, acid and base/neutral extractables, pesticides/PCBs, 4AAP Phenols, and additional compounds on Chapter VI Group I list. Analysis of Group 11 chemicals and identification of major additional peaks to be done annually (Group II compounds to be highlighted). = Site specific studies to identify or qualify sources to combined sewer overflows - parameters and frequency specific to the study plan.

Significant industrial and municipal sources should be monitored as indicated in Table 7.2. Compounds present above the cutoff values should be monitored on a more frequent basis than those below the cutoff.

In the case of contaminated combined storm sewer discharges, monitoring data could be used to identify the sources of upstream contamination and to direct control efforts deemed necessary by the responsible agency. Regular monitoring would be required only as long as untreated industrial/sanitary inputs continue.

Discharge/effluent specifics relating to frequency of sampling, parameters to be monitored, and the need for periodic scans for Group I chemicals and priority pollutants should be at the discretion of the responsible agency.

7.4.3.4 Internal Waste Stream Monitoring

Monitoring of internal waste streams can be used to detect substances that may be below the analytical detection limit in the discharge, but because of their toxic or bioaccumulative effects, may be of concern at very low levels. It can also be of use in detecting new chemicals entering the discharge. The need for internal waste stream monitoring should be established by the responsible agency on a site-specific basis.

(a) Industrial Sources

The monitoring of internal wastewater streams is required in some SPDES permits, and has the advantage of analyzing contaminants before they are diluted by the final combined effluent. The activities outlined above for discharge/effluent monitoring can be applied to internal waste streams on a site specific basis where, 1) the final effluent is composed mainly of cooling water, or 2) it is necessary to monitor the internal effluent from a given process or treatment unit.

(b) Municipal Sources

For municipal wastewater treatment plants, internal waste stream monitoring would normally apply to sludge. Some contaminants are concentrated in the sludge, and analysis can provide an indication of toxic compounds that may be present at levels below detection in the influent/effluent.

7.4.3.5 Biomonitoring

Biomonitoring of point source discharges would address acute and chronic aquatic toxicity of effluents on a routine basis as well as bio-uptake. Continuous flow short and long-term bioassays using fish (e.g. fathead minnow, rainbow trout) or crustaceans (e.g. daphnia) could be carried out periodically to monitor acute and chronic toxicity. A subset of the exposed species would be analyzed for organics to determine bio-uptake. The data generated would be used primarily for identifying previously undetected compounds, and to establish trends and variability in effluent quality, compliance with requirements, and effectiveness of abatement measures.

As for internal wastewater monitoring, the need for biomonitoring would be established by the responsible agency on a site specific basis, and would address major sources and selected minor sources.

7.4.3.6 <u>Limitations and Other Concerns</u>

a) Resource Limitations

Regulatory agencies do not have the field personnel or the laboratory capacity to implement a program of this magnitude alone. Shared responsibility between the regulatory body and the industries and municipalities, ultimately evolving to total self-monitoring over a period of time, must be considered. Factors involved in present resource limits include the following:

- (i) private contract laboratories or internal industrial/municipal laboratories must provide viable alternatives to regulatory agency laboratories. This requires standardization and accreditation and a rigorous program of quality control/quality assurance including analytical protocol standardization and development, split samples (inter-laboratory QA/QC), and duplicate samples and sample blanks (intra-laboratory QA/QC), and
- (ii) manpower requirements for field sampling must be supplied by each individual point source on routine basis, supplemented by periodic regulatory input (during agency surveys). This also requires standardization and QA/QC considerations including transportation blanks and sampling protocol standardization.

It should be noted that the U.S. has already developed requirements for self-monitoring for selected toxic pollutants (in SPDES permits) and has legislation in place addressing enhanced monitoring programs, shared responsibilities, and monitoring fees.

(b) Monitoring Criteria

The criteria by which the monitoring frequency, parameter lists, and other monitoring program specifics are determined for each point source are very important. Significant sources should be monitored more frequently than minor sources, and compounds detected at elevated concentrations should receive more attention than those below cutoff values (e.g. analytical detection limit or water quality/technology based discharge limit). For the purposes of the program presented in Table 7.2, the cutoff values used to specify parameters were those used to define significant sources:

Parameter_	kg/d	<u>lbs/d</u>
Volatile and extractable organics, total phenolics and cyanide:	0.227	0.5
Heavy metals:	0.454	1.0
Mercury, pesticides, and PCBs	0.0454	0.1

The monitoring frequency indicated in Table 7.2 is somewhat arbitrary. As the data base on each source is developed, statistical interpretation should be used to assess the frequency required for each individual compound on the parameter list.

7.4.4 Special Studies

The Committee can foresee the possible future need for additional special studies which would be required on a short-term basis and directed at addressing specific problems arising out of the Long Term Monitoring results. For example, information on localized areas of high contaminant input or the discovery of new compounds or aquatic effects could lead to studies or additional research efforts. These will have to be designed and implemented on a case by case basis in a coordinated fashion by the responsible agencies. A few such special studies are identified below.

7.4.4.1 <u>Sediment Coring - Niagara River Bar</u>

Past studies by Mudroch (1983), Thomas (1983), and Durham and Oliver (1983) have shown that sediment cores of the Niagara Bar can provide an excellent chronological record of contaminant inputs to Lake Ontario from the Niagara River and changes in these over time. Vertical spatial resolution within the core suggests that every 5-10 years would be a logical cycle to repeat this activity depending on the contaminants of interest. This should be considered as a special study.

7.4.4.2 <u>Sediment Coring - Power Reservoirs</u>

The power diversions on both sides of the Niagara River provide potential conduits for much of the contaminant load discharged to the river. On both sides of the river this diverted water spends some time in storage reservoirs where settling of solids can occur. These solids may carry with them adsorbed contaminants that could build up in the bottom sediments of

both reservoirs and constitute a potential source of contaminants to the river if disturbed at a future date. A series of sediment cores should be taken in the bottom sediments of both power reservoirs, dated with radioisotope techniques, and analyzed for toxic substances to determine if the reservoir bottom sediments may constitute a potential source of contaminants to the lower river, and if so, what remedial action is appropriate.

7.4.4.3 Contributions from the Tonawanda Creek and its Tributaries

During the navigation season, the State Barge Canal requires a flow of 1100 cfs (30 cms) to operate. The Canal acquires this water by reversing the direction of flow of Tonawanda Creek which includes the flow from The Canal flows are further augmented by water Ellicott and Bull Creeks. taken directly from the Niagara River at the mouth of Tonawanda Creek, just south of Tonawanda Island. Essentially, during the navigation season, the flows of the Tonawanda Creek drainge basin as well as a portion of the Niagara River's east shore flows are diverted into the Barge Canal and eventually enter Lake Ontario via a number of the lake's south shore As a result, contaminants originating in tributaries to the Niagara River and in the Niagara River itself enter Lake Ontario undetected via the Barge Canal during the navigation season. During the non-navigation season, the Barge Canal is closed, no water is drawn from the Niagara River, and flows of Tonawanda, Bull and Ellicott Creeks resume their natural flow direction to the Niagara River. A program should be established to monitor and determine the contaminants entering the Barge Canal from the Niagara River System during the navigation season. A program should also be established to monitor and determine contaminants entering the Niagara River from Tonawanda Creek and its tributaries during the non-navigation season.

7.4.4.4 Contribution from Welland River, Buffalo River and other Tributaries

(i) Field investigations in the Welland River Watershed conducted outside the scope of this study (Kaiser and Comba, 1983) have

indicated the presence of a number of organic compounds in the ambient environment. Some (e.g., DDT) appear to be the result of new or existing inputs to the system. Follow-up monitoring by the appropriate Canadian agencies should be designed to determine the source of these inputs and the extent to which the Welland Canal River may be contributor, of such contaminants to the Niagara River system and to Lake Ontario;

- ii) The study of the Buffalo River commenced (but not completed because of inadequate flow during the project season) under this Project should be completed and follow-up work pursued as appropriate; and
- iii) The final laboratory work on the Cayuga Creek dioxin investigation has not been completed. Work on this project should be completed.

7.4.4.5 <u>Conventional Parameters and Point Source Discharges</u>

Conventional parameters can be monitored at much lower expense than trace organic contaminants. Intense monitoring (daily, weekly and monthly, depending on the nature of the industrial processes or municipal effluent in question) of conventional parameters and metals can be combined with less frequent monitoring of trace organics. This has the added advantage of establishing a baseline of conventional data to use as a measure of the representativeness of the discharge/effluent at the time of organics sampling.

Conventional parameters are generally measured as a routine part of jurisdictional control requirements. The relation between toxic and conventional parameter loads has not been examined for the Niagara River, however, the Committee recommends that such relations should be investigated in hopes that reasonable conventional surrogates for toxic substances inputs might be developed.

7.5 <u>Implementation</u>

The continued operation of the Long Term Monitoring Program requires the establishment of a bi-national committee that will determine the direction of the plan and report on its implementation. This includes selecting parameters, determining sampling sites, frequencies, methods, and quality control procedures, interpreting results, and promptly informing the relevant jurisdictions of its findings.

Among the tasks of the bi-national committee is to recommend a precise definition of what constitutes an increasing contaminant burden contributed by Niagara River sources. Components of a precise definition include:

- * Determining a critical level of increase above which the bi-national committee will recommend that the jurisdictions take action to identify and reduce input from the sources. It is expected that components of the Long Term Monitoring Program will hasten the identification of the sources, and
- * Decide on a maximum time span over which an upward trend will be followed before action is suggested. Considerations involved with this point are:
 - a) that a sufficient number of samples be obtained to satisfy a level of statistical confidence;
 - b) that transient variations will not result in the initiation of expensive remediation; and
 - c) that long term harm from prolonged toxic substance release be prevented.

Agreement will be required on the application of appropriate statistical methods based on the quality of the data. It is expected that different methods will be used for different data sets.

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