Report to the

Great Lakes Water Quality Board

Guidance on Characterization of Toxic Substances Problems in Areas of Concern in the Great Lakes Basin

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A Report from the
Surveillance Work Group
Based on Recommendations
from the Monitoring in
Areas of Concern Workshop
Held at Canada Centre
for Inland Waters
October 3-4, 1985

Windsor, Ontario
March, 1987

PREFACE

Annex 11, Section 1 of the 1978 Canada-United States Great Lakes Water Quality Agreement stipulates:

> Surveillance and monitoring activities shall be undertaken to provide definitive information on the location, severity, areal or volume extent, frequency and duration of non-achievement of the Objectives, as a basis for determining the need for more stringent control requirements.

The International Joint Commission (IJC), in its Third Biennial Report of 1986, reported that it considers the designation of Areas of Concern and the development of remedial action plans to be an important initiative deserving widspread recognition and support. Further, the IJC reported that it is dependent on information collected by the jurisdictions in order to carry out its responsibilities under Article VII of the 1978 Agreement and that it views continuous and reliable surveillance and monitoring as critical to its functions under the Agreement and to the implementation of the Agreement itself. The IJC recommended the Parties and jurisdictions review the support structure available for monitoring and surveillance and determine the extent to which the existing support structure is adequate to meet the expressed Agreement needs.

This report is provided to assist the Water Quality Board, IJC, Parties and jurisdictions in fulfillment of their responsibilities.

The statements and views presented in this report do not necessarily reflect the views or policies of the IJC or its Great Lakes Water Quality Board.

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1.0 INTRODUCTION

The Water Quality Board of the International Joint Commission has identified 42 Areas of Concern in the Great Lakes basin where 1978 Great Lakes Water Quality Agreement objectives or jurisdictional standards, criteria or guidelines are exceeded and remedial measures are needed to restore the most sensitive uses. Of the 42 Areas of Concern, 39 have toxic substances problems. Since synthetic organic compounds and metals constitute the major problems identified for these regions, this document focuses on toxic substances. This does not imply that regional problems related to eutrophication and habitat destruction do not exist; rather, the toxic substance issue has become the primary concern.

Areas of Concern in the Great Lakes system include rivers, harbors, connecting channels and large embayments. Many of the Lake and Connecting Channel Task Forces, which are responsible for updating the Great Lakes International Surveillance Plan (GLISP), have already developed surveillance and monitoring plans for the connecting channels and large embayments that are Areas of Concern. In contrast, these Task Forces have had difficulty developing surveillance and monitoring plans for rivers and harbors that are Areas of Concern. In most cases, surveillance and monitoring plans were not developed due to a lack of sufficient toxic substances data or the available data were not current (>10 years old). In addition, toxic substances monitoring is more difficult in hydrodynamically and limnologically complex rivers and harbors. Therefore, it was recommended by the Surveillance Work Group of the Water Quality Board that a state-of-the-art guidance document be developed to assist investigating agencies in the characterization of toxic substances problems in Areas of Concern. It was apparent to the Surveillance Work Group and its Task Forces that the toxic substances problems must be well defined and the cause-and-effect relationships adequately understood before either a remedial action plan or a surveillance and monitoring program could be completed. A pragmatic, scientifically defensible, approach was needed to accomplish this.

The purpose of this document is to provide a practical "guide" for the assessment of toxic substances problems in Areas of Concern and to specify the cause-and-effect relationships between sources and environmental effects. The strategies outlined in this document are based on protocols recommended at the Monitoring in Areas of Concern Workshop held at Canada Centre for Inland Waters on October 3-4, 1985. A list of workshop participants is presented in Appendix 1.

The workshop structure consisted of four groups: biota, sources, water and sediments. Each group was asked, prior to the meeting, to address a series of specific questions concerning what data and information were necessary to delineate toxic substances problems and how to obtain such a data base in a river/harbor Area of Concern. The workshop provided an opportunity for the four groups to integrate their recommendations into one comprehensive approach. While state-of-the-art technology was addressed, a practical approach was emphasized which would not compromise the quality of the study.

In order to narrow the scope of the workshop and focus efforts on specific objectives, those items not expected from the workshop or the resulting document were identified:

1. Concerns not related to contaminants, i.e. eutrophication, habitat.

2. Individual Area of Concern surveillance and monitoring programs.

3. Remedial action plans.

4. Designated uses.

5. Compliance.

6. Limited use zones.

7. Costs.

In an effort to synthesize the recommendations from the workshop, a flowchart was developed which incorporates the recommendations into a sequence of steps for the characterization of toxic substances problems in Areas of Concern (Figure 1). Three separate phases have been defined in the overall study plan:

1. Compilation and review of all available data and information.

2. Confirmation of toxic substances problems.

3. Field study.

The first phase involves compilation of all available data and information prior to any new field studies. Table 1 outlines the three basic types of information considered necessary. The historical information outlined provides the documentation of the degradation of the region. These data can be helpful in locating historical sources, tracing the movement of contaminants from sources into the nearshore zone and providing information on conditions prior to degradation. Current information helps determine the adequacy of the data base. Questions need to be answered concerning source identification, nature of the contaminants being released into the system, loading, and qualitative and quantitative information on contaminants found in sediments, water and biota. Last, future information needs to be compiled and addressed so plans can be developed with long-term goals.

The second phase provides a protocol for confirming reported problems. If the information compiled during the first phase is considered inadequate, i.e. too outdated or limited to develop a remedial action plan and/or a surveillance and monitoring plan, then a field verification step may be necessary in order to update the current information base. This step is specifically designed to provide a field confirmation of the reported problem and is not intended to provide detailed information concerning possible

FIGURE 1. A generalized process for developing a remedial action plan for toxic substances problems in Areas of Concern. The numbers presented to the right of the decision boxes refer to the specific recommendations on Biota, Sources, Water, Sediments and Statistical Consideration.

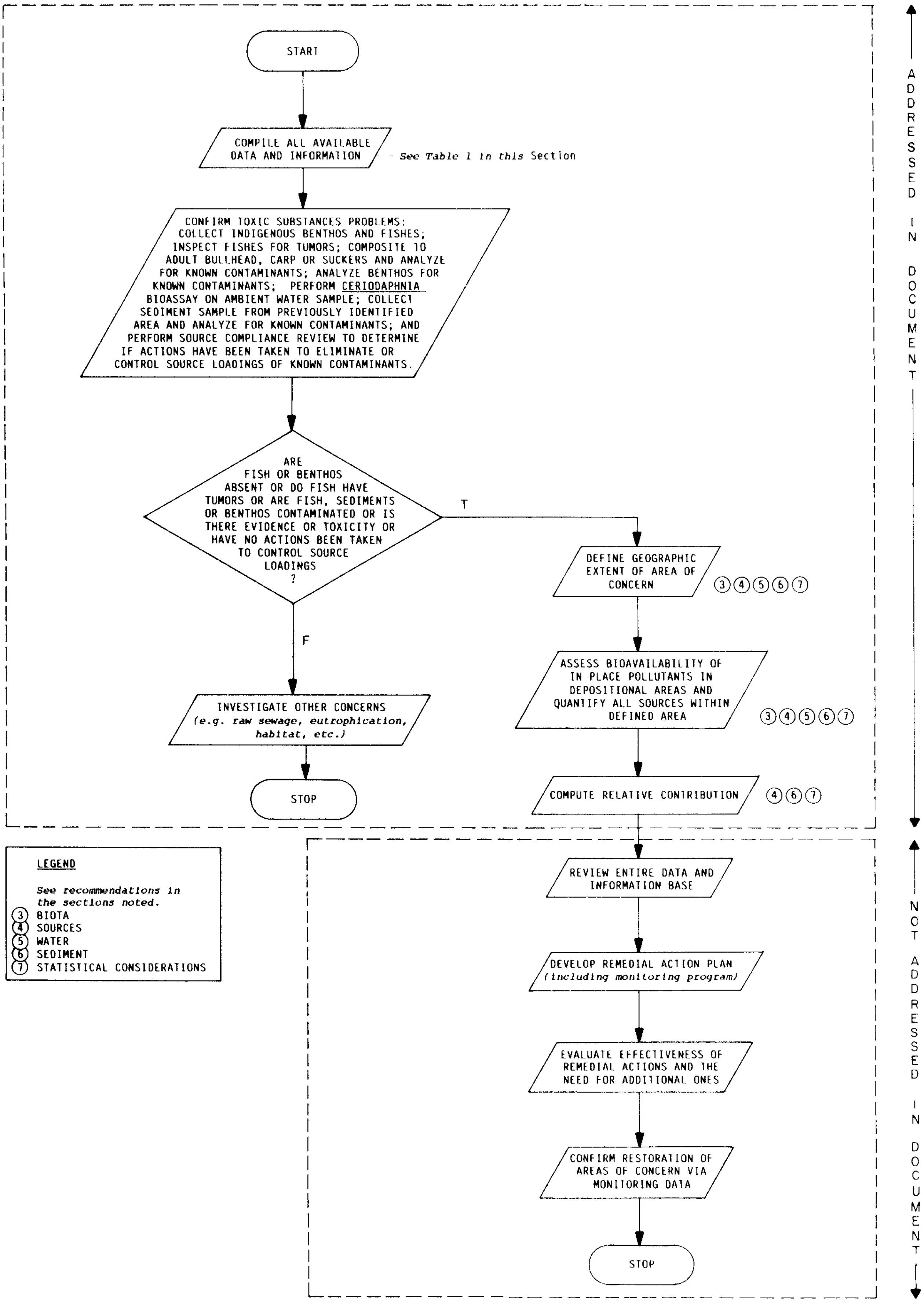

TABLE 1. Outline of data and information necessary to review for development of a remedial action plan or a surveillance and monitoring plan in Areas of Concern.

I HISTORICAL INFORMATION:

- a. History of land use patterns.
- b. History of water usage (industries, municipal wastewater treatment plants, power plants, municipal water intakes).
- c. History of river/harbor morphology (including alterations and structures).
- d. Historical changes in biota (including habitat, wetlands, spawning and nursery grounds).
- e. History of dredging (including disposal of dredge spoils).

II CURRENT INFORMATION (≤ 10 yrs.):

- a. Precise description of designated uses.
- b. Description of consumptive uses.
- c. Quantity and quality of inputs:
  1. Municipal wastewater treatment plants (identify those who accept industrial waste).
  2. Industries.
  3. Landfills.
  4. Urban runoff.
  5. Combined sewer overflows.
  6. Agricultural runoff.
  7. Groundwater.
  8. Atmosphere.
  9. In place pollutants.
  10. QA/QC documentation of inputs (sampling protocol, sampling regimes, frequency, period of record, etc.).
- d. Impacts (include geographic extent; implicit is an understanding of system hydrodynamics).
  1. Use impairments (including health advisories on biota, swimming prohibitions, restrictions on dredging for navigational purposes, drinking water restrictions, special requirements for disposal of dredge spoils - CDF, etc.).
  2. Sediment contamination.
  3. Biological community structure and composition.
  4. Bioaccumulation of contaminants.
  5. Bioassay results.
  6. QA/QC documentation of impacts.
- e. Description of unimpacted area.
  1. Upstream.
  2. Offshore.
  3. Nearshore (remote).

III FUTURE INFORMATION:

- a. Descriptions of planned redevelopment
  1. Land use.
  2. Water use.
- b. Description of planned dredging.
  1. Channel management.
  2. New CDFs.
- c. Biological management (goals).
  1. Target species (e.g. management for walleye).
  2. Artificial reefs.

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sources or fates of specific toxic substances. This step may be most frequently implemented if the data base for the region is more than 10 years old or the data are limited. Section 2.0 of this document provides detailed information on this portion of the flowchart.

The third phase of the process provides a sequence of steps that will develop detailed information on the toxic substances identified as problems in the Areas of Concern. The information derived from this phase will enable a mass balance to be developed for individual contaminants and help in understanding the links between sources of toxic substances and biological effects. Four steps are outlined:

1. Define the geographical extent of the Area of Concern.

2. Define the depositional areas within the river/harbor mouth and assess the bioavailability of in-place contaminants.

3. Quantify all sources within the geographic extent of the Area of Concern.

4. Compute the relative contribution of toxic substances from sources.

The specific information necessary to implement these four steps of the field study is detailed in sections 3 through 7.

SECTION	TOPIC
3	BIOTA
4	SOURCES
5	WATER
6	SEDIMENTS
7	STATISTICAL CONSIDERATIONS

These five sections contain information on what protocol is appropriate for the specific task and why a certain procedure is recommended over others. Actual procedural information will be presented in a subsequent document.

It is not envisaged that development and implementation of remedial action plans will be a quick process. Areas of Concern have evolved through toxic substances abuse over decades; the process of complete restoration may take at least as long. It is felt, however, that an orderly process as outlined in this document will allow effective progress in resolving toxic substances problems in Areas of Concern.

The Steering Committee recommends that three initiatives be undertaken as a follow-up to this document:

1. The tests identified to confirm toxic substances problems in Figure 1 should be field tested in both an Area of Concern and an "unimpacted" area for validity (See Section 2.0 for further information on these tests);

2. All literature containing the specific methods, i.e. detailed documentation of techniques recommended in this document should be compiled and housed in the IJC Great Lakes Regional Office Library; and

3. A comparative study should be undertaken to field test (in the same place at the same time) the methods recommended in the Biota Section of this document. Such a comparative study would greatly improve our ability to determine how these biological methods can best be used to aid assessment in Areas of Concern.

2.0 CONFIRMATION OF TOXIC SUBSTANCES PROBLEMS

In the flow chart presented in Figure 1 of Section 1.0, it is recommended that following compilation of all data and information, one should confirm the toxic substances problems, since the data are quite often old (>10 years) and/or limited. To provide a current assessment at relatively low cost, eight tests or initiatives are recommended to confirm toxic substances problems in Areas of Concern (See Figure 1 in Section 1.0). The purpose of this section is to describe in greater detail those tests or initiatives recommended to confirm toxic substances problems, provide the rationale and present specific methods (including references). If any of the eight tests or initiatives confirm toxic substances problems (see Figure 1 in Section 1.0), it is recommended that an intensive investigation be initiated to define the geographic extent of toxic substances problems, assess bioavailability of toxic substances in sediments, quantify all sources within the defined area, and compute relative contribution from sources (see sections 3.0 - 7.0 for specific recommendations).

Table 2 presents an overview of the recommended tests or initiatives to confirm toxic substances problems, the rationale for each and the criteria for acceptability. Presented below is a more detailed discussion of the concerns identified in Table 2:

- <u>Contaminated Sediment</u>. Sediment contamination represents a significant problem in Areas of Concern, particularly as a residual source of contamination. Even after all active sources of toxic substances have been eliminated, sediment redistribution and focussing by physical processes may concentrate contaminated sediment in depositional areas, thus constituting a region which may contaminate the benthos and associated food chain. In addition, if sediment delivered to the open lake from tributaries and harbors is contaminated, it may contribute to open-lake problems. Toxic substances accumulate in sediments at much higher concentrations than in water, thus sediments can serve as a "source" and/or "sink" of toxic substances. A sediment sample should be collected from a previously identified contaminated area, i.e. depositional area, using either a Ponar, Shipek, Mini-Shipek or Birge-Ekman sampler and the surficial sediment (top 3 cm) should be analyzed for known toxic substances using standard analytical laboratory procedures. Further discussion of standard analytical laboratory procedures is presented in Section 6.0 of this document.

- <u>Contaminated Fish</u>. Fish are important indicators of contamination in Areas of Concern. Toxic substances accumulate in fish at much higher concentrations than in water through biomagnification. Moreover, fish deserve special consideration because of their direct utilization by humans. Thirty-four of the 42 Areas of Concern have elevated levels of toxic substances in fish. As a result, it is recommended that ten adult, resident, demersal fishes be collected, composited and analyzed for the

TABLE 2. An overview of recommended tests to confirm toxic substances problems in Areas of Concern (including rationale and criteria for acceptability).

CONCERN	APPROACH	RATIONALE	CRITERIA FOR ACCEPTABILITY
CONTAMINATED SEDIMENT	Collect sediment sample from previously identified area and analyze for known contaminants.	Contaminants accumulate in sediments at much higher concentrations than in water.	Concentrations less than or equal to background levels presented in Table 3
CONTAMINATED FISH	Composite 10 adult bullhead, carp or suckers and analyze for known contaminants.	Contaminants accumulate in fish at much higher concentrations than in water and many Areas of Concern have health advisories on those species.	Fish present and contaminants concentrations less than Great Lakes Water Quality Objectives or less than detection limits* (See Annex 1 of the 1978 Great Lakes Water Quality Agreement).
CONTAMINANTS BIOACCUMULATING IN BENTHOS	Collect indigenous benthos from previously identified contaminated area and analyze for known contaminants.	Contaminants biomagnify through food chain.	Benthos present and contaminant concentrations less than detection limits* (See Annex 1 of the 1978 Great Lakes Water Quality Agreement).
TUMORS IN FISH	Collect indigenous fishes and inspect for tumors.	Certain contaminants are known to cause tumors in fish in Areas of Concern	No tumors found.
TOXICITY	Perform <u>Ceriodaphnia</u> bioassay on ambient water sample.	This bioassay tests for low-level, acute and chronic effects. <u>Ceriodaphnia</u> is easy to culture and results are reproducible.	No significant effects relative to controls ($P < 0.05$).
ELIMINATION OF SOURCE LOADINGS	Perform compliance inspection evaluation to determine if actions have to be taken to eliminate or control source loadings of known contaminants.	Actions may already have been taken.	Actions have eliminated loadings from known sources.

*as determined by best available technology.

TABLE 3. Basin specific background levels of pollutants in sediments of the Great Lakes (mg/kg). Additional work is necessary to quantify background levels of pollutants in the basins where no data currently exists.

	LAKE SUPERIOR					LAKE HURON		LAKE MICHIGAN					LAKE ERIE		LAKE ONTARIO			Recommended Dredging Guideline[4]
	DSB	TBB	IRSB	MaB	KB	NoB	SaB	FB	MwB	WaB	SoB	GHB	WeB	CeB	NiB	MiB	RoB	
Total P	800	700	N/A	1200	1000	1000	700	N/A	N/A	N/A	N/A	N/A	700	1100	1000	700	1600	1000
Total N	3070	3000	N/A	3070	2670	3600	4270	N/A	N/A	N/A	N/A	N/A	1500	1500	2700	2300	2300	2000
Ammonia	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	100
Hg	0.08	0.08	N/A	0.08	0.07	0.04	0.08	N/A	N/A	N/A	0.03	N/A	0.1	0.1	0.08	0.03	0.09	0.3
Pb	18	23.2	N/A	24.6	20.4	16.2	14.4	N/A	N/A	N/A	27.5	N/A	28	28	32	32	30	50
Zn	117	108	N/A	105	118	88	60	N/A	N/A	N/A	120	N/A	70	110	121	101	108	105
Fe	59400	53700	N/A	56000	58800	51600	32200	N/A	N/A	N/A	22278	N/A	N/A	N/A	52500	46200	46200	45500
Cr	50.7	51.8	N/A	49.8	57.1	28.5	30.0	N/A	N/A	N/A	37.1	N/A	N/A	N/A	N/A	N/A	N/A	120
Cu	69	57	N/A	61	69	51	31	N/A	N/A	N/A	21	N/A	30	40	56	46	46	45
Cd	0.9	0.5	N/A	0.8	0.5	1.0	0.4	N/A	N/A	N/A	0.6	N/A	2.0	2.0	1.5	0.9	1.0	1.5
Ni	63.5	59.7	N/A	57.7	64.4	61.1	29.9	N/A	N/A	N/A	32.8	N/A	N/A	N/A	N/A	N/A		90
Mn	0	1000	N/A	1200	900	1100	400	N/A	N/A	N/A	446	N/A	600	600	2300	2300	1700	1625
As	N/A	N/A	N/A	N/A	5	6	3	N/A	N/A	N/A	1.1	N/A	N/A	N/A	N/A	N/A	N/A	8
Cyanide	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.1
Volatile Solids { LOI 600°C	26300	22900	N/A	27300	24000	27800	35200	N/A	N/A	N/A	N/A	N/A	10000	20000	18400	19100	18400	60000
COD	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	50000
PCB	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.05
Oil & Grease	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	1500
Other Organic Contaminants	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	Below detection using best available technology. (GLWQA, 1978)

CEB - Central basin
DSB - Duluth sub basin
FB - Fox basin
GHB - Grand Haven basin
IRSB - Isle Royale sub basin
KeB - Keweenaw basin
MaB - Marathon basin
MwB - Milwaukee basin
MiB - Mississauga basin
NiB - Niagara basin
NoB - Nottawasaga basin
RoB - Rochester basin
SaB - Saginaw basin
SoB - Southern basin
TBB - Thunder Bay basin
WaB - Waukegan basin
WeB - Western basin

1 - Kemp and Thomas, 1976
2 - Kemp *et al*. 1978
3 - Robbins, J (pers. comm.)
4 - Thomas and Mudroch, 1979
N/A = not available

known contaminants to confirm the existence of fish contaminant problems in the identified Area of Concern. Fish are best collected using overnight bottom gill net sets (electrofishing or hoop or fyke netting are alternative methods). Select the ten largest carp, suckers or bullhead, because they are bottom feeders and they are usually readily available in Areas of Concern, generally resident, and often on health advisory lists. After collection, weigh, measure and wrap whole fish in hexane-rinsed aluminum foil and store at -25°C until homogenization.

In the laboratory, grind fish to a homogenous consistency with a commercial meat grinder, e.g. Hobart Chopper from which a 50g subsample (aliquot) is taken. Subsample homogenates are stored in acid-washed and acetone-hexane rinsed glass containers at -25°C until trace metal and organic residue analyses are completed using standard analytical laboratory techniques. Subsample homogenates should be analyzed for previously identified toxic substances.

- <u>Contaminants Bioaccumulating in Benthos</u>. Because bioaccumulation of contaminants and contaminated sediments are identified problems in most Areas of Concern, e.g. 39 of the 42 Areas of Concern have sediments contaminated with toxic substances, it is necessary to assess bioavailability of toxic substances from sediments. Indigenous benthos are recommended for assessing bioavailability of toxic substances from sediments because these animals are in direct contact with contaminated sediments and many species directly ingest large volumes of sediment. Therefore, any bioavailable contaminants will most likely be taken up by indigenous benthos. Furthermore, benthos can be a food resource for higher trophic levels, thus resulting in biomagnification of contaminants.

  If sufficient biomass, e.g. as little as 100 organisms or 0.5 g of midges or worms, can be collected from the depositional zone where there is known contamination, it is recommended that the organisms be sieved in the field, digestive tract contents purged in distilled water for 24 hours and the organisms analyzed for known contaminants as a measure of bioavailability.

  The precise methodology for this assessment of bioavailability is presented in Oliver (1984). By comparing the concentrations of toxic substances in sediments with those found in indigenous, benthic invertebrate fauna and resident fishes, both bioavailability and biomagnification can be assessed.

- <u>Tumors in Fish</u>. Correlations between the incidence of tumors in fishes and the presence of toxic substances have been established in Areas of Concern, e.g. Black River, and verified in laboratory studies (Baumann <u>et al</u>. 1982). Identifying tumors in fish is an important part of assessing potential effects of toxic substances. Following field collection of fishes via overnight bottom gill net sets, electrofishing, or hoop or fyke netting (see Contaminated Fish Section), all specimens should be analyzed for tumors. The manual, "Handbook for the Identification of Tumors in Great Lakes Fish" (to be published by the Great Lakes Fishery Commission in the near future) is recommended for identifying tumors in fish.

o Toxicity. Invertebrate bioassays help to evaluate the nature and degree of harmful effects of toxic substances on aquatic organisms. Cladocerans have been used extensively for aquatic toxicology testing because they are readily available, adaptable to laboratory conditions, require little space, and are sensitive to a wide variety of chemical pollutants. They also are an important link in aquatic food webs.

The *Ceriodaphnia* seven-day, three-brood test is recommended as a relatively rapid test to assess the chronic toxicity of ambient waters. Ambient water samples should be collected from the impacted area, i.e. harbor or mouth of river, for the bioassay. The choice of control waters and the storage of test waters, if necessary, are crucial to test success. The test is designed to be conducted during a regular work week and is suitable for small, mobile laboratories. Consequently, prolonged storage (>12 hr) of test waters should be avoided. Results are usually sensitive to identifying impacts. Survival and reproduction are key factors for evaluation.

The three-brood *Ceriodaphnia* life-cycle test using renewal techniques was developed at the U.S. EPA's Environmental Research Laboratory at Duluth by Mount and Norberg (1984) for on-site testing of complex effluents and receiving waters. The use of *Ceriodaphnia* *affinis*/*dubia* over *Daphnia magna* in chronic toxicity testing has been suggested for several reasons:

1. The organism is more easily cultured than *D. magna*.

2. *Ceriodaphnia affinis*/*dubia*, unlike *D. magna*, is found locally in the Great Lakes region.

3. It is more sensitive to a variety of toxicants than other cladocerans (Mount and Norberg 1984).

4. The short maturation time allows for three broods to be produced *per* adult female in seven days at 25°C, resulting in a shorter chronic test period compared to either *D. magna* or *D. pulex*.

The *Ceriodaphnia* test is conducted for seven days at 25°C with a 16-hour photoperiod. Ten replicate beakers, each with one animal, are used for each test solution and control. Place a single young (neonate) into a 25 ml pyrex beaker containing 15 ml of test water. The young should be two to four hours old, although it is often more practical to use neonates that are up to 12 hours old. The test is renewed on days three and five by transferring animals with an eyedropper to a new beaker and new test water. Individuals are fed daily by adding yeast suspension at the rate of 250 µg (0.05 ml of 5 mg/ml solution of dry yeast dissolved in distilled water) per animal per beaker. Throughout the bioassay, beakers are loosely covered with parafilm to decrease evaporative cooling during incubation. Survival of test animals is monitored daily.

On day five, if young have been produced, they are counted and discarded upon transfer of the adult to fresh test water. At the end of day seven, survival of the original females is recorded, total young per female counted and number of broods per female estimated. If males occur in the test replicates, they are included in the survival data, but excluded from the calculations for mean young and mean brood per female.

- <u>Elimination of Source Loadings</u>. A source compliance review should be performed to determine if actions have been taken to eliminate or control source loadings of known contaminants. If actions have been taken to control source loadings, a historical discharge problem may be present, e.g. in-place pollutants. If no actions have been taken, there is an obvious need to identify the sources of contaminants, quantify loadings and compute relative contributions before remedial actions can be identified.

  A review of known sources should be undertaken to determine if changes have occurred in loadings of a parameter. Changes which may lead to significant reductions in loadings include:

  1. Plant closing--a facility known to have a significant loading is no longer operating.
  2. Process change--a facility known to have a significant loading has changed its process so it no longer discharges the parameter.
  3. Compliance with a new permit or control order--a facility known to have a significant loading has been issued a new permit or control order and is in compliance with new limitations.

  If any of the above changes have occurred since the area was listed as an Area of Concern, these sources may no longer be contributing significant loadings and confirmation of toxic substances problems must be obtained by one of the other seven tests described above.

  The necessary information on plant closing, process change and compliance (see items 1-3 above) may be obtained by a simple three-step process:

  <u>Step 1</u>: Inventory the Area of Concern for past and current source data for the parameter of interest. This can be accomplished via a STORET inventory retrieval for U.S. areas and an inventory of the municipal and industrial point-source data bases in Ontario. Not only will this inventory reveal which sources discharge a given parameter, but the period of record also will be identified. If the data base is not current for the parameter of interest, this indicates that the facility has closed or changed its process. This should be confirmed with the jurisdiction.

  <u>Step 2</u>: Retrieve the effluent limitations for the source over the period of record. If the limits have changed for the parameter, then this is an indication that a new permit or control order has been issued.

  <u>Step 3</u>: Retrieve current source data for the parameter of interest. If the reported data are less than the limitations, this indicates that the source is meeting its new requirements and may no longer be a significant source of loading. This should be

confirmed, preferably by obtaining a compliance inspection report from the jurisdiction. A typical compliance inspection involves a jurisdictional sampling crew entering the facility, verifying that pollution-control equipment is operating and sampling the effluent for the same parameters that the facility reports in its monthly compliance report.

All of the above sources of information relate to point sources. Since mandatory controls do not exist for non-point sources, a review of historical information is not likely to uncover the changes discussed in this section.

Following completion of the tests and initiatives presented above to confirm toxic substances problems in Areas of Concern, one could ask the following questions:

- Are fish or benthos absent?
- Do fish have tumors?
- Are sediments, benthos or fish contaminated?
- Is there evidence of toxicity? and
- Has no action been taken to control source loadings of toxic substances?

If the answer to any of these questions is yes, based on the criteria presented in Table 2, the following systematic approach is recommended:

A. Define geographic extent of Area of Concern;

B. Assess bioavailability of in-place contaminants in depositional areas and quantify all sources within the defined geographic area; and

C. Compute the relative contribution of contaminants from confirmed sources.

The recommendations on specific methods and approaches to acquiring these requisite data are presented in the following sections on biota, sources, water and sediment. References are given as required.

2.1 REFERENCES

Baumann, P.C., W.D. Smith and M. Ribick, 1982. "Hepatic tumor rates and polynuclear aromatic hydrocarbon levels in two populations of brown bullhead (Ictalurus nebulosus)." In: M.W. Cook, A.J. Dennis and G.L. Fisher, eds. Polynuclear Aromatic Hydrocarbons: 6th Int. Symp. Physical and Biological Chem. Battelle Press, Columbus, OH, pp. 93-102.

Kemp, A.L.W. and R.L. Thomas, 1976. "Cultural impact on the geochemistry of the sediments of Lakes Ontario, Erie and Huron." Symp. Great Lakes Sed. Proc. Geoscience Canada 3:191-207.

Kemp, A.L.W. et al. 1978. "Impact of man's activities on the chemical composition of the sediments of Lakes Superior and Huron." Water, Air Soil Pollut. 10:381-402.

Mount, D.I. and T. Norberg. 1984. "A seven-day life-cycle cladoceran toxicity test." Environ. Toxicol. Chem. 3:425-434.

Oliver, B.G., 1984. "Uptake of chlorinated organics from anthropogenically contaminated sediments by oligochaete worms." Canadian J. Fish. Aquatic Sci. 41:878-883.

Thomas, R.L. and A. Mudroch. 1978. Small Craft Harbours Sediment Survey - Lakes Ontario, Erie and St. Clair. Dept. Fish. and Oceans, Burlington, ON.

3.0 ASSESSING IMPACTS OF POLLUTANTS ON BIOTA IN AREAS OF CONCERN

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3.1 INTRODUCTION

Most problems in any Area of Concern relate to chemical contaminants. Difficulties in addressing chemical contaminants result from: 1) the number of different chemicals and their fate and distribution; and 2) whether chemical contaminants are being discharged from active sources, e.g. industries, sewage treatment plants, and/or occur as in-place pollutants from historical discharges. The degree of pollution the public is willing to tolerate in Areas of Concern will rarely be determined by the concentration of specific chemicals; rather, as noted by Ravera (1975), the effects of these chemicals on biota will more likely elicit response for corrective measures by the public and resource management agencies. Consequently, determining the impacts of contaminants on biota is a critically important aspect of defining problems in Areas of Concern, developing and implementing the Remedial Action Plan (RAP), and subsequently assessing the effectiveness of remedial actions by tracking environmental quality trends via monitoring and surveillance programs.

Many methods are available to assess contaminant effects on a wide variety of biotic groups and more methods are likely to be available in the near future. The challenge is to choose among the array of available tests to obtain the most information on the impacts of perturbations on biota in a timely and cost effective manner and thereby influence the decision-making processes. Ideally, it would be desirable to choose among standardized methods that have been widely tested with agreed-upon protocols and quality assurance procedures. Unfortunately, few such methods exist.

The earliest tests of pollutant effects on biota were single species/single chemical laboratory bioassays. Although offering controlled conditions and relative ease of interpreting potential effects, such interpretations often are difficult to relate to conditions in nature. This concern has resulted in the elaboration and sophistication of laboratory tests often using multiple species at different levels of biological organization (Cairns 1984) and conducted at conditions more closely resembling field situations. The term "ecotoxicology" is being used more frequently to indicate this trend away from the laboratory to more field-oriented, ecologically interpretable biological methods (Levin et al. 1984). Field studies offer the integration of physicochemical and biological variables but it is often difficult to distinguish causal relationships between a particular pollutant or pollutant mixtures and an observed biotic effect. Consequently, experiments in the field or under conditions closely simulating the field are being conducted in enclosures of water and sediment called cosms or limnocorrals, e.g. Grice and Reeve 1982.

The ecology of river mouths and harbors in the Great Lakes is generally poorly understood. In fact, these areas were substantially polluted and physically transformed by the end of the 19th century, before research and monitoring of ecosystem components began. Researchers and managers in the Great Lakes basin are now attempting to look beyond chemical pollution toward a more holistic perspective on ecosystem integrity, protection, restoration and rehabilitation (Francis, et al. 1979). Although it is desirable to promote a better understanding of the ecology of rivers and harbors on the Areas of Concern list and to strive toward rehabilitation, this document focuses on specific biological studies (both structural studies and functional tests). The species or communities were chosen which yield the best and earliest indication of biological stress and impact due to toxic contaminants.

3.1.1 Call for Comparative Study of Methods

All of the recommended methods are to a greater or lesser extent in need of further evaluation and verification of their reliability and how their results should be interpreted. Therefore, recommended methods should be used in parallel for the investigation and delineation of problems in Areas of Concern. It is recommended that the IJC coordinate a study within three years, to compare as many of the different proposed methods as possible. Results from such a study would greatly improve our ability to determine how biological methods can best be used to aid in the assessment of problems in Areas of Concern. Hamilton Harbour represents an Area of Concern ideally suited for this type of study due to the proximity of the laboratory facilities at the Canada Centre for Inland Waters (CCIW).

3.2 GUIDE TO CHOICE OF METHODS

Numerous biological methods for assessing impact were reviewed and consensus was reached on recommended methods (Table 4). Field studies on community structure and functional toxicity tests each have a role in assessing impacts of pollution on biota. Different methods are applicable for assessing the effects of relatively dilute contaminants in the water column, as opposed to those concentrated in the sediments (Table 4). Moreover, planktonic organisms should obviously be used to assess the effects of waterborne chemicals, rather than those adsorbed on sediments (in which case tests using periphyton or benthos would be more appropriate).

3.2.1 Relationship of Methods to Pollutants

Toxic substances, especially persistent organics and heavy metals, are the major pollution problems in Areas of Concern. However, human health and eutrophication (nutrients) are also important issues. The following matrix has been developed to assist in the selection of the most useful methods for evaluating a particular type of pollution problem (Table 5). At the top of the table are lists of various recommended methods, while the left side lists common pollution problems found in the Great Lakes. An "X" is placed under each method that the Work Group recommends to evaluate the problem. In problem areas where the cause is unknown, all methods should be used. However, in such cases, it should be possible to obtain some indication of the type or types of problems which are involved through a preliminary biological characterization, thereby eliminating the need to use some of the methods. In some areas, where multiple problems are present, all the methods should be applied. Information on sources, water and sediment should further assist in methods selection.

3.2.2 Relationship of Methods to Specific Applications

The method or methods chosen must also consider the type of information required in the Area of Concern. In the process flowchart presented in Figure 1, Section 1.0, it is recommended to: 1) confirm toxic substances problems;

TABLE 4

RECOMMENDED METHODS FOR ASSESSING EFFECTS OF CONTAMINANTS ON BIOTA IN AREAS OF CONCERN

	WATER		SEDIMENT	
BIOTIC GROUP	Structural	Functional	Structural	Functional
Heterotrophs		Microtox		
Plants		algal (AFB or GPP) Bioassay	Paleolimnol. (algae)	
Zooplankton		*Ceriodaphnia* Bioassay		
Benthos	Community indicators and indices		Community indicators & indices	Paleolimnol/ deformities. Bioassay (*C. tentans*)
Fishes		Toxicity Deformities Body burden		Deformities Body burden
Humans	Bacterial contaminant indicators	Body burden Ames/V 79		Body burden

GPP = gross primary productivity
AFB = algal fractionation bioassay

TABLE 5

METHODS FOR ASSESSING THE EFFECTS OF VARIOUS TYPES OF POLLUTION ON BIOTA IN AREAS OF CONCERN

Method Problem	HETEROTROPHS	PLANTS				ZOOPLANKTON	BENTHOS			FISH			HUMANS	
	Microtox	Paleo	Peri-phyton	GPP	AFB Bioassay	M-N Bioassay	Indices	Paleo	Bioassay	Toxic Effects	Deformities	Body Burden	Body Burden	Ames V 79
Persistent Organics	X		X	X	X	X	X	X	X	X	X	X	X	X
Metals	X		X	X	X	X	X	X	X	X	X	X	X	X
Nutrients		X	X	X	X	X	X	X						
Health													X	X
Unknown	X	X	X	X	X	X	X	X	X	X	X	X	X	X

2) define the geographic extent of the Area of Concern; and 3) assess bioavailability of in-place pollutants. In addition, it may be desirable to differentiate as much as possible between the bioavailability of active sources and the bioavailability of in-place pollutants. Assessment of bioaccumulation and toxicological effects also will be required as part of the monitoring program. The methods for each of these applications are listed in Table 6 and the rationale for the choice of methods is discussed here. Further discussion can be found in the sources, water and sediment sections. The location of these discussions is noted in Table 6.

Confirm Toxic Substances Problems

Current Conditions

Confirmation of toxic substances problems is recommended because the available data may not be recent, i.e. they may be a decade or more old, or detailed enough to adequately define the problem. Therefore, it is recommended that confirmation of existing toxic substances problems be assessed using body burden analyses of adult, resident, demersal fishes and by conducting the Ceriodaphnia test (See Section 2).

Historical Perspectives

Although not specifically recommended, it is desirable to assess existing problems in an Area of Concern with respect to historical conditions. Biological surveys are recommended where historical data bases are available for comparison with current conditions. In the absence of historical records from past studies, historical changes can be traced by paleolimnological investigations of biotic remains in sediment cores.

Biological Surveys. Early biological surveys in the Great Lakes, such as the late 1920s and early 1930s studies of Lake Erie (Wright 1955, Fish 1960), have provided invaluable benchmarks of biological status from which future comparisons can be made. Comparisons of biological conditions in the 1960s and 1970s with the 1920s and 1930s studies provided much of the documentation of the ecological decline in Lake Erie that elicited pollution controls and which subsequently resulted in water quality improvements. Therefore, it would be desirable to have available up-to-date, comprehensive biological surveys of plants and animals in Areas of Concern, from the smallest microbes to fish and wildlife.

Realistically, it is not feasible to conduct comprehensive biological surveys on each Area of Concern. Competition for limited financial and personnel resources make such surveys on a broad scale prohibitive. Moreover, it is often difficult to establish one-to-one casual relationships between chemical contaminants and biological community structure. Functional tests and experiments on the effects of specific chemicals or chemical mixtures on representative biota are required. Nonetheless, biological surveys are recommended in Areas of Concern to help identify impacted areas and determine changes in the biological community based on comparisons of current data with historical published or unpublished data. Documentation of the current biological condition of an Area of Concern is necessary so that when any remedial measures are implemented, one can assess their effectiveness.

TABLE 6

RECOMMENDED METHODS FOR SPECIFIC APPLICATIONS AND LOCATION OF FURTHER DISCUSSION IN THIS DOCUMENT

Confirmation of Toxic Substances Problems	Page
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Mutagenicity Tests	35
Ames	36,147
Metabolic Cooperation	36
Bioconcentration/Bioaccumulation	36
Benthos	37
Spottail Shiner	37

* young-of-the-year

The choice of which biological components to sample should be based largely on the kinds of information available in the historical data base. Although the data base is likely to be largest for those biotic groups most often studied, e.g. larger phytoplankters, crustacean zooplankters, macrobenthos and fish, other lesser known biotic groups may yield valuable information. Gannon and Robertson (1980) noted how little information is available on many biotic groups in the Great Lakes, and Davis (1969) aptly stated that we "... need to broaden and deepen our Great Lakes investigations so that future generations of investigators will not curse us for leaving them so little information."

Paleolimnological Investigations. In the absence of real or direct historical data, indirect methods can offer useful alternatives for determining the extent and rate of past changes of biotic communities in Areas of Concern. Although various groups of biota can be examined from a paleolimnological perspective, algal communities, especially diatom frustules and mallomonad scales, preserve well in sediments, and species can be identified from their siliceous remains. Major changes in the environments in which these species grow will cause changes in species dominance which will be reflected in the sediment record. Sampling stations will have to be selected carefully because the hydrodynamically complex nature of river mouths and harbors and the disruption of development and dredging operations severely limit places where the historical record in sediment cores has remained undisturbed.

Defining Geographic Extent

Biota studies can assist in defining the extent of the Area of Concern. Obviously, it is not possible to strictly define the extent of the Area of Concern in the water column because water movements disperse and dilute waterborne contaminants over a wide area. Biological community structure of phytoplankton and zooplankton can be useful but data are often difficult to interpret with respect to the effects of eutrophication and/or toxic contaminants. Moreover, short-term temporal and spatial variability may mask attempts to map the specific geographic area of notable impact. The geographic extent of the Area of Concern, therefore, should focus on benthos and sediment contamination (see Sediments Section 6.0). Benthos are sedentary and act as integrators of environmental conditions at specific locations in the Area of Concern.

Assessment of Bioavailability and Bioaccumulation of Sediment Contaminants

Because bioaccumulation of contaminants and contaminated sediments are identified problems in most Areas of Concern, e.g. 34 of the 42 Areas of Concern have elevated levels of toxic substances in fishes and 39 have sediments contaminated with toxic substances, it is necessary to assess bioavailability of toxic substances in sediments. For example, one needs to determine whether or not sediments are a source of toxic substances to biota.

Body burden analyses, especially of benthos, are recommended to assess bioavailability of in-place pollutants in sediments. The methods for assessing bioavailability of toxic substances in sediments are still in the research and development phase; however, there is an immediate need to assess bioavailability of sediment contaminants. As a result, the recommendations presented here represent a consensus on the best methods currently available.

Assessment of Toxicological Effects

As discussed previously, it is often difficult to differentiate between toxicological effects of contaminants from eutrophication and other effects on biological community structure in Areas of Concern. In most instances, field studies must involve an experimental design to truly elucidate toxicological effects. Various bioassays on phytoplankton, zooplankton and benthos are recommended, including acute and chronic tests (Tables 4 and 6). Moreover, detection of morphological deformities in benthos and fish can be useful in indicating physiological or possibly even genetic responses to contaminant exposure.

3.3 BIOLOGICAL COMMUNITY STRUCTURE

An important component of a biological assessment of environmental status in Areas of Concern is the examination of community structure integrity. Aquatic ecosystem structure may be defined as the composition of the biological community including species, numbers, biomass, life history and distribution in space and the concomitant quantity and distribution of the abiotic materials such as nutrients, water, etc. Examination of structural integrity would examine all components of the aquatic ecosystem; however, such detail is neither practical nor necessary for impact assessment. Aquatic ecosystems may be separated conveniently into different communities representing different trophic levels, each of which may be utilized in ecosystem assessment. The characteristics of the various communities and their appropriateness for monitoring in Areas of Concern are summarized in Table 7 and discussed below.

The criteria considered for assessing the suitability of a group are:

Distribution: Providing that the group is present in the types of habitat encountered.

Ease of Quantitative Sampling: Realistic assessment requires the application of statistical techniques to data collected from monitoring; however, collection and analysis of such samples should not be too costly.

Temporal heterogeneity: This refers to the rate at which the community changes in time. Rapid changes in community structure necessitate more frequent sampling; therefore, communities comprised of organisms with longer life histories are preferred.

Spatial heterogeneity: This refers to the variability of communities in space. The smaller the scale on which such variability occurs, the greater the number of samples required to establish spatial patterns.

Mobility: The mobility of organisms affects their suitability for monitoring. Highly mobile organisms make interpretation difficult because occurrence or non-occurrence cannot easily be associated with changes in habitat status. This affects the numbers of samples required to determine the relationship between the organism and the habitat.

TABLE 7: CHARACTERISTICS OF VARIOUS BIOLOGICAL GROUPS FOR USE IN MONITORING PROGRAMS

	BACTERIA	PHYTOPLANKTON	ZOOPLANKTON	PERIPHYTON	MACROPHYTES	BENTHOS	FISH
PRESENCE IN AREAS OF CONCERN HABITATS	+	+	+	+	-	+	+
EASE OF QUANTITATIVE SAMPLING	-	+	-	+	-	+	-
TEMPORAL HETEROGENEITY	-	-	-	+	+	+	+
SPATIAL HETEROGENEITY	-	+	-	+	-	+	-
MOBILITY (Site Representativeness)	o	o	o	+	+	+	-
SAMPLE PRESERVATION	o	+	+	+	+	+	+
TAXONOMY	-	-	+	-	+	+	+
KNOWN RESPONSES TO POLLUTANTS	-	+	+	+	-	+	+

+ = suitable
- = not suitable
o = marginal

Taxonomy: Ease of correctly identifying species is important, since many assessments are based upon changes in species composition. Some groups require specialized expertise for identification. In some cases, identification may not be possible. Simplicity of taxonomy or availability of guidance will have important effects on the cost and turnaround time of data.

Response to Pollutants: These will affect the interpretability of data and ultimately their value.

BACTERIA

While bacteria are ubiquitous in aquatic habitats, they have considerable limitations for assessing general water quality conditions. Quantitative sampling is difficult, the taxonomy is not well established and temporal variation is large. Bacteria are useful, however, to evaluate sewage contamination. Guidelines exist for measurement of fecal coliform bacteria levels in water used for both primary and secondary contact recreation. If sewage contamination is an issue, fecal coliform analyses are a useful monitoring device when performed on a frequent basis (at least weekly).

PHYTOPLANKTON

Phytoplankton are relatively easy to sample and estimate quantitatively, and the toxicity of many materials to phytoplankton species has been documented. However, to avoid errors associated with both spatial and temporal heterogeneity, considerable sample replication is required. Phytoplankton identification requires considerable expertise.

PERIPHYTON

The attached algae or periphyton have essentially the same advantages and disadvantages as the phytoplankton except that sampling methods are less standardized, and with the exception of diatoms, the background literature is sparse. The periphyton may be particularly useful when employing artificial substrates.

MACROPHYTES

Macrophytes are not generally suitable for monitoring programs. They should be used only when they, themselves are an issue. They may be useful for measuring bioaccumulation of toxic materials. In general, their distribution is too local, and quantitative sampling too difficult for effective use in a monitoring program.

ZOOPLANKTON

Many of the same problems apply to the use of the zooplankton as outlined for the phytoplankton, particularly the large spatial and temporal heterogeneity and consequent labor costs. Further quantitative sampling techniques are still the focus of considerable discussion.

BENTHIC INVERTEBRATES

Benthic invertebrates are present in most aquatic habitats. They are relatively easy to sample quantitatively. They have known community responses to water quality changes and their taxonomy is well established. Furthermore, populations are relatively stable in time, thereby requiring less frequent sampling. They are comparatively non-mobile and representative of the area being sampled, and sampling equipment is inexpensive. However, taxonomy (to the species level) can be difficult, and spatial heterogeneity might be high, requiring a great deal of sample replication. The sample processing time can also be considerable, precluding a rapid enumeration and assessment. These factors result in relatively high costs.

FISH

While in the political and social context fish may be the most obvious group to use in a monitoring program, they have several extreme disadvantages as a monitoring tool. Individuals are highly mobile and many species are migratory, making cause/effect relationships and spatial representativeness difficult to establish. Quantification is also difficult and costly.

RECOMMENDATION

Of the various biotic groups, benthic invertebrates are recommended for monitoring change in community structure. This is based upon their ease of quantitative sampling, their temporal and spatial representativeness and their documented response to pollutants.

This material is oriented toward the IJC Areas of Concern and particularly small harbours and embayments, and areas that have already been impacted and have impaired uses. Therefore, two questions are invoked:

Is the "where" and "when" of the impact known
if so, then
the impact must be inferred from spatial pattern alone
if not, then
the "when" and "where" of the impact must be established (Green 1979).

According to Green (1979), this latter situation is an extreme case and by definition an impact has already occurred, resulting in identification of an Area of Concern. This may not necessarily be true in the benthic community. In many cases, therefore, the "when" and particularly the "where" must be established.

3.4 FUNCTIONAL BIOLOGICAL MONITORING

3.4.1 Introduction

Biological monitoring is the use of biological responses to examine changes in the environment, that ultimately allow establishment of causal, quantifiable relationships. Biological monitoring is often used in the investigation of anthropogenically induced stresses on local populations, communities or their surrogates.

While a holistic approach is of paramount importance for both an understanding and ultimately the protection of ecosystems, our often insufficient understanding of interactions and interrelationships, combined with other factors, e.g. financial, limits us to a less than ideal approach to problem assessment. An examination of the changes in functioning of the individual biotic ecosystem components offers both a pragmatic solution to this dilemma and an acceptable starting point upon which subsequent refinements can be built, bringing us closer to our ideal.

Most of the early work in bioassessment had a taxonomic, structural emphasis. Community structure and indicator species analyses have provided us with detailed records of biological responses to a variety of anthropogenic and naturally induced changes. While this information is acquired comparatively inexpensively, and relatively easily generated, it usually lacks the degree of specificity required to affect a regulatory change.

Functional tests or bioassays offer an approach which can be specific and quantifiable. Individual tests or assays are usually insufficient either to define the problem completely or to affect a remedial action. Therefore, a series of tests which are combined as a sequence, battery or in a tiered approach are necessary to adequately document biological effects and establish causal relationships.

Functional biological monitoring has been broadly defined as the measurement of any rate process (response) of the ecosystem. These measures can be separated further into taxonomic and non-taxonomic parameters (Mathews _et_ _al_. 1982). Taxonomic functional tests, which are used less frequently than non-taxonomic examinations, include measures of species colonization or emigration rates and rates of re-establishment related to equilibrium densities following a disturbance (Cairns, _et_. _al_. 1979). Non-taxonomic tests, whether in the field (_in situ_) or in the laboratory, include short-term (acute) and longer term (chronic) measures of behaviour, biochemical changes, genetic alteration, reproductive failure, bioaccumulation and death.

Field bioassays offer the investigator a first approximation of the combined effects of the natural environment and allow some measure of experimental control to be maintained. Often it is impossible or impractical to conduct certain tests in the field because of the need to provide strict control over experimental conditions in order to save time (by testing a number of factors at once) or to ensure reproducible results. The investigator is therefore forced to sacrifice environmental "realism" and conduct the bioassays in the controlled but artificial environment of the laboratory.

This section describes functional bioassays for use in the field or the laboratory for the examination of effluents, ambient water and sediments. While these are not the only bioassays available for such purposes, they represent recommended tests based on several criteria: simplicity, practicality, interpretability and reproducibility. Single-species bioassays are gradually being replaced or at least augmented by "ecotoxicological" and "ecoepidemiological" approaches which are believed to provide a better understanding of natural ecosystem effects. The current state of our knowledge in these areas and the need to provide practical approaches to the problem precluded recommending these techniques. Instead, the techniques recommended are generally widely used throughout the Great Lakes basin and often have extensive literature describing protocols and results from numerous applications. Biological monitoring methods are highly dynamic and constantly evolving, and will therefore require re-examination and updating in succeeding years.

3.4.2 Acute Sublethal Tests

Acute toxicity tests examine biological effects or manifestations, which can be observed over a short period of time, usually less than one week, but not more than one generation. A further criterion is that the tests be conducted at ambient concentrations. This latter stipulation is to allow for real space - time and exposure equivalence. Acute tests include: observations of behavior, e.g. gill fluttering or respiratory distress and avoidance of effluents by fish in a control tank; physiological/biochemical changes, e.g. mixed function oxidase response by fish, changes in adenosine, mono, di- and tri-phosphate ratios, adenylate energy change (Ivanovici 1979), reduction in luminescence by bacteria (Microtox™), algal gross primary production, scope for growth, and Ceriodaphnia reproduction (Widdows 1985). A new technique which examines caged phytoplankton communities may provide valuable information (K. Nicholls, Ontario Ministry of the Environment, personal communication). Procedures for those tests which have been widely tested and appear to be readily reproducible are included. Acute lethality (death), usually to fingerling fish or planktonic invertebrates, is discussed in the next section (3.4.3).

Tests measuring a sublethal response should only be conducted once the investigator is assured that death of the test organism will not occur at the exposure concentration. If, for instance, one is interested in measuring the gross primary production of algae exposed to ambient water near an effuent, one should ensure that the water is non-toxic at the ambient concentration. This is most easily accomplished by first running a Ceriodaphnia acute lethality test. If it is toxic, then either another site should be chosen for the algal bioassay or the water should be suitably diluted to sublethal levels.

Bacterial Luminescence Bioassay

Microtox™ is a bacterial luminescence bioassay developed by Beckman Inc. as a rapid screening alternative to standard acute toxicity testing with fish and invertebrates. This test is based on the bioluminescence of the bacterium (Photobacterium phosphoreum) (NRRL B-11177). The rationale for the development of this assay is that evolutionary conservative biochemical pathways are common to many organisms. Therefore, bacteria can be used as surrogate test organisms for many toxicants.

The Microtox™ test is easy and requires only about 30 minutes to complete. This assay has been extensively studied and compared to acute bioassays with both fish and daphnids for a large number of compounds.

In addition to the use of Microtox™ as an analog bioassay, it is important as an independent assay. As an independent assay, Microtox™ can be used to assess the effects of mixtures of toxicants on a prokaryotic organism for the assessment of present and potential environmental effects on the microbiological flora of the decomposer population.

The test can be performed on ambient water, pore water and sediment elutriate. Microtox™ is recommended as a priority method.

Gross Primary Productivity (GPP)

Phytoplankton photosynthesis is important to monitor because: 1) phytoplankton biomagnify organic contaminants about 10^3 times ambient levels, and the functional responses of phytoplankton are immediate and readily measured using traditional ^{14}C techniques for the estimation of gross primary productivity (GPP); 2) the functional response of the natural community can be determined both in the Area of Concern and in control areas; and 3) the tests can be conducted in the field with natural phytoplankton assemblages, avoiding problems with the storage and aging of water samples.

McNaught (1980) described a net-nannoplankton bioassay for detection of the effects of PCBs. Control water was injected with PCBs of varying concentrations or with water from the Area of Concern in varying amounts, (10, 25, and 50% mixed effluent by volume) and then with ^{14}C-bicarbonate. After *in situ* incubation, scintillation counting enabled calculation of GPP (mg C $m^{-2}t^{-1}$). Experimental results were then expressed as percent of control, as evidence for inhibition or stimulation of baseline photosynthesis by waters from Areas of Concern.

This bioassay was developed from a similar concept first employed in marine waters by Charles Wurster's laboratory (as referenced in Powers *et al*. 1977), and further modified for freshwaters by Glooschenko *et al*. (1975). The modification by McNaught *et al*. (1980) allowed analysis of the impact of purified contaminants or mixed effluents on GPP. This test can also be used on sediment elutriates with either natural assemblages or monospecific cultures. Recently, it has been named the algal fractionation bioassay (AFB) by Munawar and associates and has been applied most extensively to the assessment of sediment contaminants (see below).

Algal Fractionation Bioassay (AFB)

The nannoplankton of the Great Lakes, particularly the ultraplankton and picoplankton, are sensitive to heavy metals (Munawar and Munawar 1982). These organisms are important since they constitute a main source of food for the zooplankton (Ross and Munawar 1981).

A procedure for differential fractionation for carbon-14 uptake studies (Munawar *et al*. 1978) has been applied in toxicological research to study the impact of heavy metals, individually and combined, on various size assemblages of phytoplankton (Munawar and Munawar, 1982). The procedure has been successful in demonstrating the differential response of various size fractions and in identifying the component under stress. The same procedure was then called "Algal Fractionation Bioassays" (AFBs) and adapted for assessment of sediment-elutriate toxicity to natural phytoplankton.

The AFB is a short-term screening test to evaluate the net result of contaminant and nutrient loading. The procedure is rapid, sensitive and relatively inexpensive for screening potentially toxic substances and constitutes an early warning test system. Also, algal bioassessment of Chelex-100™ treated standard elutriate provides data which can determine the toxicity of the dissolved metals. High elutriate concentrations added to the test population can cause increased turbidity, which can be a problem during incubation. Turbidity can be overcome by using lower elutriate concentrations or carefully monitoring the bioassay.

Ceriodaphnia Bioassay

Rationale for the use of this test appears earlier in Section 2.0 of this document. In addition, this test can examine either acute effects (lethality) or chronic effects (reproductive failure), using the full life cycle test. These tests can be performed on ambient water, effluents, pore water or sediment elutriate.

3.4.3 Acute Lethality

As indicated earlier, *Ceriodaphnia* or other planktonic invertebrates such as *Daphnia magna* can be used to test for acute lethality. The predominant organisms used in this test are fish, either fathead minnow (*Pimephales promelas*) or rainbow trout (*Salmo gairdneri*). Fathead minnows are used extensively in the United States because they can also be used for sublethal bioassays examining reproduction.

The tendency to use standard species seems to be reasonable in that results are fairly representative of the reactions for a broad spectrum of fish. Differences between species with respect to their susceptibility to a toxicant are generally less than might be expected. Indeed, the variability of results within a single species tested in different types of water can be greater than the variability between different species. Some contaminants are especially toxic to certain invertebrates or plants. Fish bioassays, therefore, should not be the sole means of assessing acute lethality.

An acute assay can be conducted *in situ* using caged fish (Flood *et al*. 1986) or under controlled laboratory conditions. Laboratory testing can either be static or flow-through. The flow-through test is often preferred because there is no need to disturb the fish by changing the water, and the concentration of the test material remains relatively constant unless it evaporates or is adsorbed onto the container. In the latter case, the concentration will be lower than desired; however, special precautions can be taken to overcome these problems.

Young fish, preferably less than eight centimetres or five grams should be used. This provides standardization and effectively reduces the size of the holding tanks required. In addition, the actual dose of the test material required to ascertain lethality will be less; transport, acclimation and holding will be simplified, and the cost of test organisms will be reduced compared with using adults.

The acute fish lethality test is strongly recommended for effluent and ambient water examinations. A complete description of the protocol can be found in Sprague (1973).

3.4.4 Chronic Sublethal Tests

Long-term or chronic exposure to toxic contaminants can result in problems which are tested in a variety of ways: genetic damage, including mutagenesis and carcinogenesis; teratogenesis or birth defects as well as developmental abnormalities, e.g. assymetry in fish; and reproductive failure which may be genetic in origin or simply due to prolonged high stress levels.

Information acquired through field observation for fish tumors and other deformities is a necessary part of a biological monitoring program, but presents inconclusive data on its own. The cause or causes of such deformities cannot be specifically ascertained. Investigations will be required to link the deformities to known chemicals present (by inference from known laboratory bioassays) and to conduct further laboratory tests on the complex mixtures present.

Numerous short-term bioassays currently available examine the potential mutagenicity, carcinogenicity and teratogenicity of chemicals. These bioassays were developed and validated using individual contaminants and are principally used to evaluate the hazards of several chemicals, generally one at a time. The tests, while of short duration, are designed to mimic long-term or chronic exposure. Organisms or cells are exposed to concentrations of chemicals or complex mixtures several times greater than those found in the natural environment. In this way, potential effects can be examined within one or a few generations.

The causes of reproductive failure, often inferred by the absence of one or more age classes of fish or entire species (comparing one survey to the next), cannot be linked to toxic effects with a high degree of certainty. A partial life cycle or a multi-generation bioassay conducted in the laboratory is used to establish cause and effect relationships. Therefore, these tests must be conducted on rapidly maturing/reproducing organisms.

While there may be strong resistance from agencies to undertake complicated and often expensive bioassay programs (particularly in assessing genotoxicity), these bioassays form critical links for examining the impacts from effluents, ambient water and sediments.

Morphological and Histological Indicators of Stress

Fish can function as contamination indicators in Areas of Concern. Moreover, they deserve special consideration because of their important position in the aquatic food chain, including direct use by humans. Many organic contaminants bioaccumulate in fish tissue. Consequently, analyses of contaminant body burdens in resident species is an important component of biotic assessment in Areas of Concern. The target species recommended are adult, demersal species such as carp, suckers and bullheads, as well as young-of-the-year (YOY) spottail shiner. Fishes also should be examined for deformities, tumors, lesions, etc. that may serve as indicators of stress due to contaminants.

Correlations between the incidence of deformities, tumors, lesions, etc., in fishes and the presence of environmental stressors have been established in the Great Lakes and shown in laboratory studies. Reviews of pollution-associated diseases of fish have been published by Sindermann (1984), Hendricks (1982), and Kraybill et al. (1977).

Identification of tumors and other deformities in fish from an impacted area is a first step in monitoring. A handbook for identifying tumors in Great Lakes fishes will be published soon by the Great Lakes Fishery Commission. It is recommended that investigators undergo some practical instruction in addition to using the handbook because some deformities can be confused with neoplasia; many factors affect occurrence of neoplasia in fishes such as season, age and sex. An internal examination is also essential since liver lesions are of particular interest. Knowledge of "normal" incidence of deformities is required in interpreting all occurrence data.

This direct examination yields information on the incidence of tumors and other deformities which result from the integrated effects of exposure to ambient water, sediments, effluents and contaminated food. To apply the condition to individual ecosystem components, bioassays such as the direct exposure of fish to sediment contaminant extracts (Black 1983) or more often the Ames/Salmonella microsome test are required to isolate effects.

Head capsules of midge larvae (Chironomidae) with morphological deformities, recovered from recent sediments and sediment cores, may be the result of toxic contamination (Warwick 1980; 1986). Examination of sediments (or sediment cores in paleolimnological studies) for head capsule deformities may be valuable in certain Areas of Concern. If core segments can be properly dated, this field assessment technique may identify when deformities began to emerge and possibly some comparative information on the severity of the problem through time.

Mutagenicity Tests

Short-term tests based on the principles of genetic toxicology provide a reliable indication of a substance's potential to cause mutations and/or cancer in mammals. These tests can predict within a few weeks, the outcome of long-term animal bioassays which may take three to five years to complete (Brusick 1980). There is growing evidence that carcinogenesis involves several distinguishable stages, including initiation and promotion. Initiation may result from an irreversible event within a cell after its exposure to physical, chemical or viral agents that damage or change the DNA molecule. Promotion, on the other hand, depends upon repeated treatment of the initiated cell by physical or chemical agents that are weak or non-carcinogenic initiators. Consequently, the following tests for mutagenicity include a component for both initiation (Ames/Salmonella test) and promotion (Metabolic Cooperation test).

Ames Salmonella/microsome assay (Initiation)

The Salmonella/microsome assay places a suspected mutagen or sample in a medium containing a low concentration of histidine. The medium is seeded with a strain of *Salmonella typhimurium*, which is unable to grow because of a mutation in an enzyme of the histidine biosynthetic pathway. The rate of reversion to histidine-independence estimates mutagenicity and is easily determined by counting the number of colonies growing in the histidine-deficient medium.

Many chemicals that produce cancer in mammals are not mutagenic until they have metabolized in the liver and other tissues. Since some mammalian metabolic pathways are not present in bacteria, the "activation" process does not occur and some mammalian mutagens register as negative in the Ames test. This problem has been alleviated somewhat by the inclusion of a rat liver microsome preparation ("S9") into the bacterial assay system.

The Ames *Salmonella*/microsome assay has the following advantages: it has been subjected to a diverse group of chemical mutagens; is generally reproducible, a detailed protocol has been published; and it can be used with an S9 activation system. Disadvantages of this test include: it does not work well with certain compounds, e.g. heavy metals, dioxin; and it does not detect clastogenic (chromosome-breaking) compounds, since bacteria lack chromosomes.

Methods and procedures for this test are described by Ames *et al*. (1975), Brusick (1980) and Maron and Ames (1984).

Metabolic Cooperation Test (Promotion)

Considerable evidence has accumulated which suggests that intercellular communication may play an important role in restricting cancer development by inhibiting the proliferation of 'initiated cells'. When cell-to-cell communication is blocked, clonal expansion of the initiated cell could occur and an autonomously growing tumor cell could be selected. The metabolic cooperation test is one way to estimate the ability of a substance to interfere with cell-to-cell communication.

Methods and procedures for this test are described by Gupta *et al*. (1985) and Trosko *et al*. (1981).

3.4.5 Bioconcentration/Bioaccumulation

Measurement of chemical residues does not describe actual adverse effects. However, such measurements do indicate exposure and often provide evidence of bioavailability from sediments and water, and the presence of a compound when concentrations are below the detection limit in the ambient water or effluent. Analysis of the body burden of chemical contaminants is recommended in benthos and resident adult, demersal fishes for the confirmation of toxic substances problems in Areas of Concern (see Section 2). For further examination of bioconcentration/bioaccumulation, the use of young-of-the-year spottail shiner and *Chironomus tentans* is recommended.

Chironomus tentans

Benthic macroinvertebrates (especially oligochaete worms and chironomid midges) collected from the Area of Concern are recommended for body burden analyses (Oliver 1984).

The dipteran midge, *Chironomus tentans*, is suggested as a representative benthic invertebrate for laboratory toxicity testing and bioaccumulation studies. This species is widely distributed throughout the United States and spends most of its life cycle in tunnels in the upper few centimeters of sediment. The chironomids can often account for a significant portion of the benthic biomass and are important in the cycling of residues in and from the sediments. *Chironomus tentans* completes its life cycle in approximately 30 days at 20°C and can be reared in the laboratory. The methodology for assessing body burdens of toxic contaminants using *Chironomus tentans* is described by Oliver (1984).

Spottail Shiner

Analysis of fish tissue for organic and heavy metal contaminants is a well established monitoring tool in the Great Lakes. The methodology for long-term monitoring of whole fish samples from open lake waters is described in the Great Lakes International Surveillance Plan (GLISP). Moreover, sampling protocols and data bases on contaminant burdens in edible portions of sport and commercial species exist. Sampling and analysis of these species should be continued in those Areas of Concern where specific health advisories have been established.

Especially applicable to Areas of Concern is the monitoring of contaminants in young-of-the-year (YOY) spottail shiner (*Notropis hudsonius*). This species has a limited range during its first year of life and, therefore, is suitable for both long-term trends and for monitoring point sources in Areas of Concern where breeding populations exist. The methods for body burden analysis using the spottail shiner are described in Suns *et al*. (1981, 1983). Where spottail shiners are not available, another YOY resident minnow-like species (Notropis spp.) should be selected.

Wildlife

Recent evidence indicates that the more overt effects of toxic substances are appearing in fish-eating birds, rather than other biotic groups in the Great Lakes, e.g. (Gilbertson 1983; Harris *et al*. 1985). However, due to their high degree of mobility, none are specifically confined to individual rivers and harbors. Other groups of organisms are more appropriate for examination and analysis in these Areas of Concern, although research investigations on wildlife, e.g. contaminants in over-wintering waterfowl, are encouraged. In connecting channels and large embayments designated as Areas of Concern, investigation of contaminant body burden in fish-eating birds should receive high priority. For example, a recent survey found that PCBs in Detroit River ducks ranged from 2.7 to 20.0 ppm (Smith *et al*. 1985). It was suggested that these ducks accumulate PCBs from their food, which consists largely of oligochaetes and aquatic plant tubers gathered from the bottom of the Detroit River.

Humans

Obviously, one-to-one casual relationships between specific contaminants in Areas of Concern and human morphological or physiological disorders are extremely difficult to establish. The mobility of individuals, the variety of contaminant exposure routes and variability in diet and lifestyle affecting exposure to contaminants, adversely influence the use of humans as bioindicators in Areas of Concern. However, in some instances where a high risk sub-population can be identified, short-term tests as indicators of mutagenic initiation (Ames/*Salmonella* test) and promotion (V79/metabolic cooperation test) are recommended. Moreover, follow-up body burden analyses for contaminants and epidemiological studies in such high risk sub-populations are warranted.

Measurements of body burden in humans living adjacent to Areas of Concern are vital to understanding the impacts of contaminants. Samples of adipose and liver tissues are desirable. The Human Health Effects Committee of the IJC can provide advice and further the development of such investigations as warranted.

3.4.6 Statistical Considerations

Most analyses of data collected in a monitoring and surveillance context involve assessing whether a particular variable is different from a given value, e.g. violation of a standard or different from some "control" parameter. The strength of such comparison results lie in statistical tests of differences and ultimately in the faith one has in the measurement. This is true for assessment of standards violations and for measuring the effects of "mixed-effluents" on biota or other empirical measures of an ecosystem's response to water and sediment in the Areas of Concern. A second, equally important, issue is control site selection. This issue is extremely important to the performance of all functional bioassays. See Section 7.0, Statistical Considerations for a discussion of tests of differences (page 165).

Controls

Comparing the status of an Area of Concern, usually by measuring concentrations of properties with prescribed standards, is straightforward, provided the important foundations of the requirements for test applications are observed. New approaches have been suggested recently that assess the effluent effects on "larger" ecosystem processes, e.g. primary productivity, zooplankton fecundity. In these approaches source water (effluent) is mixed with receiving water and process responses are monitored. Similar protocols could be developed for Areas of Concern where water from the Area of Concern would be the source water and perhaps the open lake would represent the receiving water. The test hypothesis becomes: Does Area of Concern water influence open lake water? If the answer to that question is no, then the Area of Concern water is not problematic within the confines of the test. Two important questions arise: 1) what is the receiving water, and 2) what is the control? These may seem similar, but are in fact quite separate questions; the first is more easily answered. Selecting the receiving water is based on decisions of what the Area of Concern should ultimately become if fully "restored". If the ultimate design is to make it resemble the open lake, then that is the most appropriate receiving water. If it is a small embayment and the ultimate design is to have an unpolluted embayment, then such a site should be used as the receiving water. Selection of control water is more difficult, because any perturbation of receiving water can be expected to elicit a response. When testing effluent discharged into a river flowing into an embayment, a proper control could be river water upstream of the discharge. In the case of Area of Concern water as the source water, control water could be from a site of similar morphometry or unpolluted nearshore water.

REFERENCES CITED

Section 3.1

Cairns, J. Jr. 1984. "Editorial: Multispecies toxicity testing." Environ. Toxicol. Chem. 3:1-3.

Francis, G.R. *et al*., eds. 1979. Rehabilitating Great Lakes Ecosystems. Great Lakes Fish. Comm. Tech. Report 37, Ann Arbor, MI.

Grice, G.D. and M.R. Reeve, eds. 1982. Marine Mesocosms: Biological and Chemical Research in Experimental Ecosystems. Springer-Verlag, N.Y.

Levin, S.A. and K.D. Kimball, eds. 1984. "New perspectives in ecotoxicology." Environ. Mngt. 8:375-442.

Ravera, O. 1975. "Critique of concepts and techniques regarding biological indicators." Bull. Zoo. 42:111-121.

Section 3.2

Davis, C.C. 1969. Plants in Lakes Erie and Ontario, and Changes of Their Numbers and Kinds. Bull. Buffalo Soc. Nat. Sci. 25:18-44.

Fish, C.J. 1960. Limnological Survey of Eastern and Central Lake Erie, 1928-1929. U.S. Fish. Wildl. Service Special Report Fish. 334.

Gannon, J.E. and A. Robertson. 1978. "Development of checklists for Great Lakes biota." J. Great Lakes Res. 4:104-105.

Wright, S. 1955. Limnological Survey of Western Lake Erie. U.S. Fish Wildl. Service Special Report Fish. 139.

Section 3.3

Green, R.H. 1979. Sampling Design and Statistical Methods for Environmental Biologists. Wiley & Sons, N.Y.

Section 3.4

Ames, B.N., J. McCann and E. Yamasacki. 1975. "Methods for detecting carcinogens and mutagens with *Salmonella*/mammalian mutagenicity test." Mutation Res. 31:347-364.

Black, J.J. 1983. "Field and laboratory studies of environmental carcinogenesis in Niagara River fish." J. Great Lakes Res. 2:326-334.

Brusick, D. 1980. Principles of Genetic Toxicology. Plenum Press, N.Y. and London.

Cairns, J. Jr., D.L. Kuhn and J.L. Plafkin. 1979. "Protozoan colonization of artificial substrates." In: R.L. Wetzel, ed. Methods and Measurements of Attached Microcommunities: A Review. American Soc. for Testing and Materials, Philadelphia, PA, pp. 39-51.

Flood, K. et al. 1986. Jackfish Bay: Acute Lethality and Chlorophenol Bioconcentration in Fish Exposed to a Bleached Craft Mill Effluent Plume. Ontario Ministry of the Environment, Toronto, ON.

Gilbertson, M. 1983. "Etiology of chick endema disease in herring gulls in the lower Great Lakes." Chemosphere 12:357-370.

Glooschenko, V. and W. Glooschenko. 1975. "Effect of polychlorinated biphenyl compounds on growth of Great Lakes phytoplankton." Canadian J. Bot. 53:653-659.

Gupta, R.S., B. Singh and D.K. Stetsko. 1985. "Inhibition of metabolic cooperation by phorbol esters in a cell culture system based on adenosine kinase deficient mutants of V79 cells." Carcinogenesis 619:1359-1366.

Harris, H.J., J.J. Hubiak and J. Trick. 1985. Microcontaminants and Reproductive Impairment of the Forster's Tern on Green Bay. Univ. Wisconsin Sea Grant Inst. Report ES-105, Madison, WI.

Hendricks, J.D. 1982. "Chemical carcinogenesis in fish." In L.J. Weber, ed. Aquatic Toxicology. Raven Press, N.Y., pp. 149-225.

Ivanovici, A.M. 1979. Adenylate Energy Charge: Potential Value as a Tool for Rapid Determination of Toxicity Effects. Fish. Marine Service Tech. Report 862, pp. 241-255.

Kraybill, H.F. et al, eds. 1977. "Aquatic pollutants and biologic effects with emphasis on neoplasia". Ann. N.Y. Academy Sci. 298:604pp.

Maron, D.M. and B.N. Ames. 1984. "Revised methods for the Salmonella mutagenicity test." In: Kilbery, B.J. et al., eds. Handbook of Mutagenicity Test Procedures, 2nd ed., Elsevier, N.Y., pp. 93-14.

Mathews, R.A., A.L. Buikema Jr., J. Cairns Jr., and J.H. Rodgers Jr. 1982. Biological Monitoring Part IIA - Receiving System Functional Methods, Relationships and Indices. Water Res. 16:129-139.

McNaught, D.C. et al. 1980. Inhibition of Productivity by PCBs and Natural Products in Saginaw Bay, Lake Huron. Report to Environ. Res. Lab., U.S. EPA.

Munawar, M. et al. 1978. "Relative importance of nannoplankton in Lake Superior phytoplankton biomass and community metabolism." J. Great Lakes Res. 4(3-4):462-480.

Munawar, M. 1982. Toxicity Studies on Natural Phytoplankton Assemblages by Means of Fractionation Bioassays. Canadian Tech. Report Fish. Aquat. Sci. 1152.

Munawar, M. et al. 1984. An Overview of Sediment-Associated Contaminants and Their Bioassessment. Canadian Tech. Report Fish. Aquat. Sci. 1253.

Oliver, B.G. 1984. "Uptake of chlorinated organics from anthropogenically contaminated sediments by oligochaete worms." Canadian J. Fish. Aquat. Sci. 41:878-883.

Powers, C. et al. 1977. "Response to polychlorinated biphenyls of marine phytoplankton isolates cultured under natural conditions." Applied Environ. Microbiol. 34:760-64.

Ross, P.E. and M. Munawar. 1981. "Preference for nannoplankton size fractions in Lake Ontario zooplankton grazing." J. Great Lakes Res. 7:65-67.

Sinderman, C.J. 1984. "Fish and environmental impacts." Arch. Fisch Wiss. 35:125-160.

Smith, V.E. et al. 1985. "Organochlorine contaminants of wintering ducks foraging on Detroit River sediments." J. Great Lakes Res. 11:231-246.

Sprague, J.B. 1973. "The ABCs of pollutant bioassay using fish." In: J. Cairns, Jr. and K.L. Dickson, eds. Biological Methods for the Assessment of Water Quality. American Society for Testing and Materials Special Tech. Pub. 258, Philadelphia, PA.

Suns, K. et al. 1981. Organochlorine Contaminant Declines and Their Present Geographic Distribution in Great Lakes Spottail Shiners (*Notropis hudsonius*). Ontario Ministry of the Environment, Toronto, ON.

Suns, K. et al. 1983. "Organochlorine contaminant residues in spottail shiners (*Notropis hudsonius*) from the Niagara River." J. Great Lakes Res. 9:335-340.

Trusko, J.E. et al. 1981. "*In vitro* assay for tumor promoters." In: H. Stich and R.H.C. San, eds. Short-term Tests for Chemical Carcinogens, Springer-Verlag, N.Y., pp. 420-427.

Warwick, W.F. 1980. Paleolimnology of the Bay of Quinte, Lake Ontario: 2800 Years of Cultural Influence. Canadian Bull. Fish. Aquat. Sci. 206.

Warwick, W.F. 1985. "Morphological abnormalities in Chironomidae (Dipfera) larvae as measures of toxic stress in freshwater ecosystems: indexing antennal deformities in *Chironomus Meigen*." Canadian J. Fish. Aquat. Sci. 42:1881-1914.

Widdows, J. 1985. "Physiological responses to pollution." Marine Pollut. Bull. 16:129-134.

4.0 GUIDANCE FOR QUANTITATIVE ASSESSMENT OF CONTAMINANT SOURCES TO AREAS OF CONCERN

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4.1 INTRODUCTION

Historically, source monitoring has been directed primarily towards the conventional pollutants, those that resulted in oxygen depletion, reductions in water clarity and nutrient enrichment. Although such problems persist in many Areas of Concern, most areas also are subject to significant contamination from metals and toxic organic chemicals.

Identifying sources of pollution is a complex task because the verified impact may be due to non-persistent pollutants, e.g. biochemical oxygen demand (BOD), chlorine (Cl_2), nitrate (NO_3), etc., or the source may be a transient or an intermittent discharge. The latter discharges can result from planned or unplanned variations in the discharging processes or from precipitation events which may cause: i) toxic waste dumps to discharge, ii) agricultural runoff to increase, iii) urban runoff from combined sewer overflows (CSOs) and/or storm sewers to discharge accumulated toxic material, or iv) malfunctions at sewage treatment plants.

This Section provides a strategy for comprehensive and continued source monitoring in Areas of Concern so that the relative contribution and significance of pollutant loadings from this sector can be assessed. Such an assessment is an essential element of a cost-effective remedial action plan and associated long-term surveillance program.

The three flow charts depicted in Figures 2, 3 and 4 outline the recommended generic approach for source examination. The general flow chart (Figure 2) includes all the steps necessary to determine the relative contaminant loadings in an Area of Concern, while considering the interaction with such media as the water, sediment and biota. Since process screening involves several decisions, two specific flow charts are provided; 1) preliminary or "desk top" screening (Figure 2: also see Section 4.3) and 2) detailed screening which involves collection and analysis of new data (Figure 4: see Section 4.4). In addition, Sections 4.5 and 4.6 provide a rationale and procedures for determining the relative contribution of all potential pollution sources.

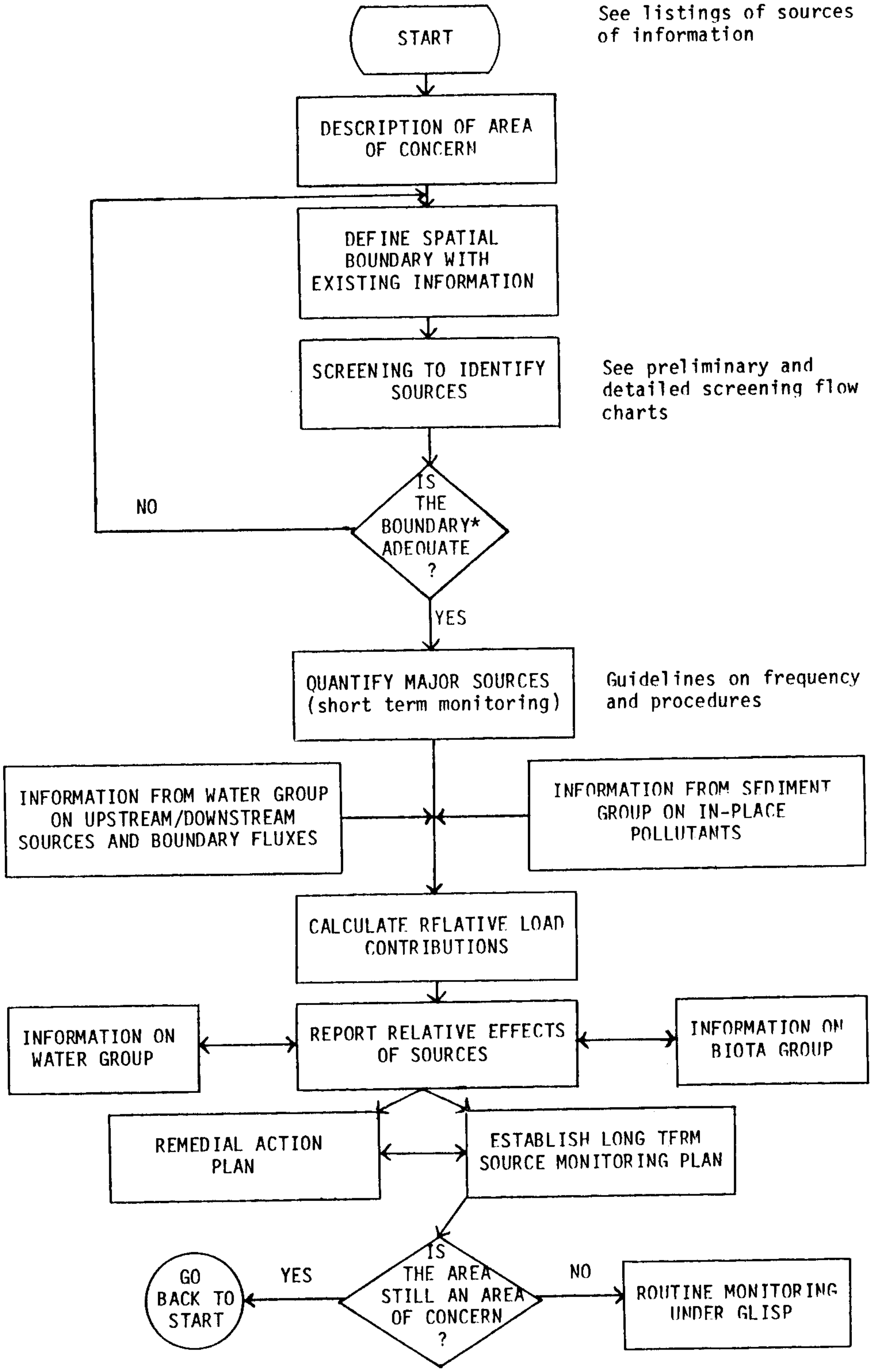
Boundaries defining the geographical extent of required remedial action are established according to the rationale for listing an Area of Concern. Upstream, or in some specific situations, downstream fluxes of materials are then treated as sources. Determining the impact of these fluxes may require using a conservative tracer, such as chloride or conductivity, to estimate the loading. The Water Section (5) of this document provides further guidance on determining flux loadings.

The contaminated sediments, present in the vast majority of the existing Areas of Concern, must be considered potential sources, and their relative contributions determined. Techniques for estimating the contribution of sediments to loading are described in the Sediment Section (6).

Procedures presented to deal with relative contribution involve identifying and quantifying sources of many different chemicals. On application of the methods outlined in this chapter, a table of loadings by source and parameter, along with their relative contribution, will be produced. This information is critical to the development of an RAP.

FIGURE 2

SOURCE GROUP PROCESS FLOW CHART



See listings of sources of information

See preliminary and detailed screening flow charts

Guidelines on frequency and procedures

*The boundary is adequate when detailed screening indicates that observed effects in the Area of Concern can be related directly to sources and are not due to upstream conditions.

FIGURE 3

SCREENING TO IDENTIFY POSSIBLE SOURCES

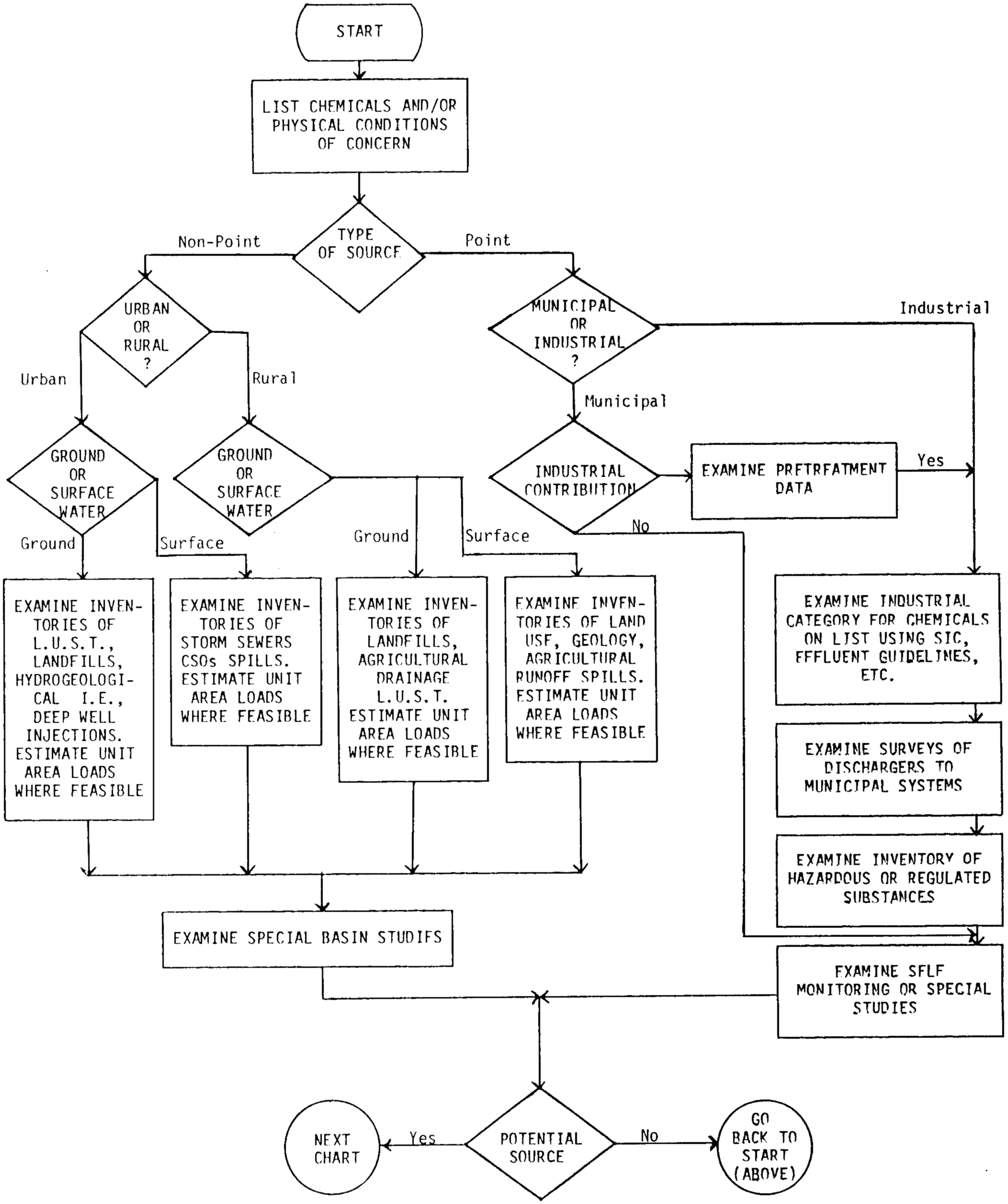
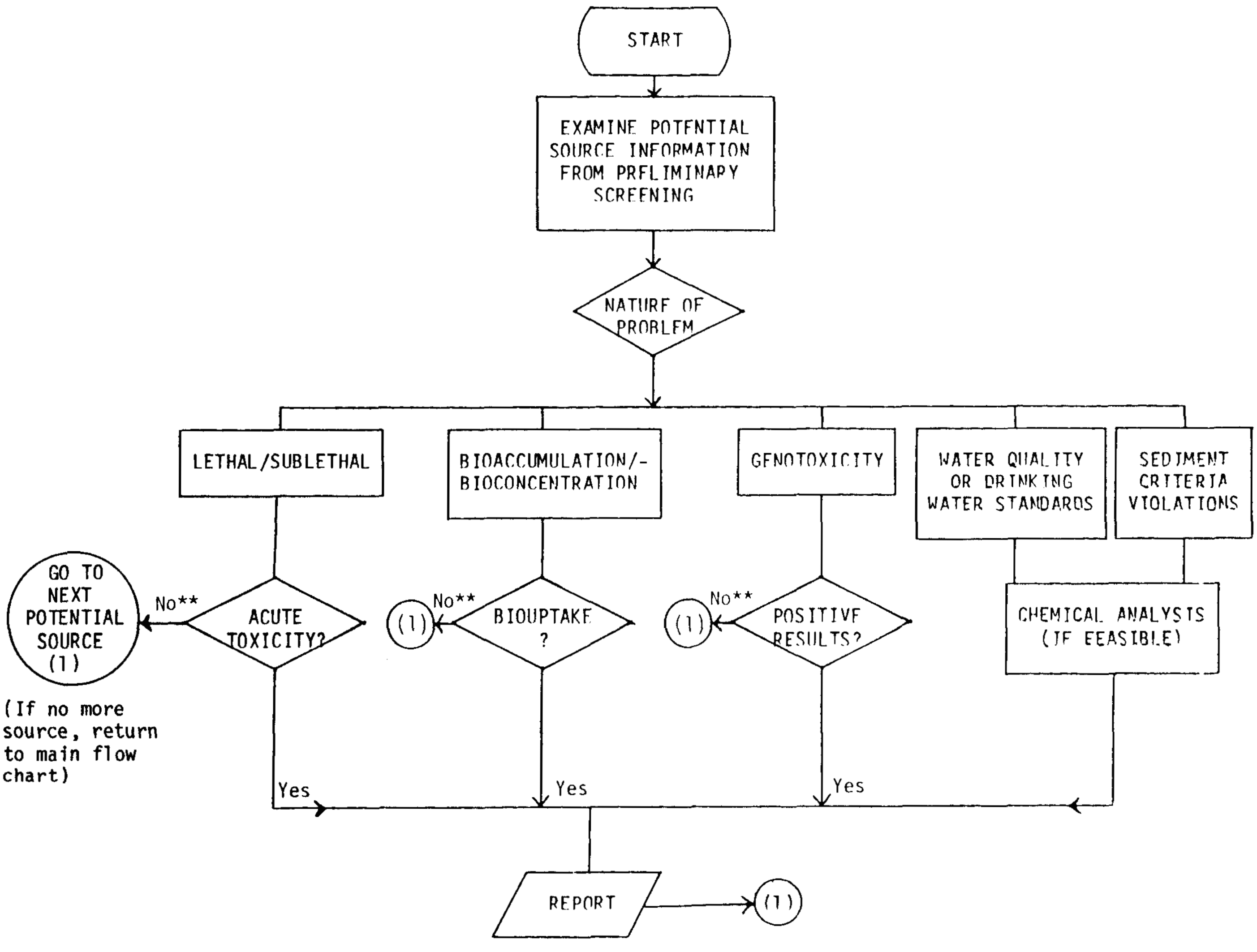


FIGURE 4

DETAILED SCREENING FOR SUSPECTED SOURCES



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*From the definition of the Area of Concern.

** If no in-vitro effects are found in effluents, move to new effluent. If no effluent is found to exert effect, expand boundary and consider synergism where constituents from more than one effluent combine in stream to exert effect.

The following recommendations will greatly improve and assist the execution of this process.

1) All inventories of information should be computerized in a standardized format and made available to those studying the area.

At present, some inventories are not computerized or are not accessible, making the development of a source monitoring plan and the efficient use of resources extremely difficult.

2) Bioassays to be performed on sources should be standardized.

There are a variety of bioassays that could be used for effluent testing. Procedures for conducting a given bioassay also differ from jurisdiction to jurisdiction (see recommendations, Biota Section (3)).

4.2 PRELIMINARY INFORMATION SOURCES AND BOUNDARY DEFINITION

4.2.1 Historical Information

Before implementing the more detailed investigation phase described in Section 4.3, it is imperative that a comprehensive compilation of all the available data and information within the watershed be made and the boundaries for each of the listed pollutants be established. When this phase is completed, a detailed information base and a preliminary list of sources by pollutant and location will have been assembled.

The information used to describe an Area of Concern to date is, for the most part, noted within various Water Quality Board reports. Quite often the references in these Board reports are internal reports with a limited distribution or were based on an anonymous interpretation of unpublished data generated by the jurisdictions. These references should be assembled and reviewed as a starting point.

The next step is to secure an historic perspective. Table 1 in the Introduction presents an outline of the information deemed essential for preparing a remedial action plan and surveillance program. This historic perspective is necessary because, while a source may no longer be physically present, its legacy of pollution may endure either on or off site. Love Canal, New York is probably the most notorious example of such a legacy. A specific, but not exhaustive, list of information for this type of compilation appears in Table 8.

4.2.2 Boundary Definition

The initial definition of an Area of Concern boundary comes from the Water Quality Board's description. These descriptions may require further interpretation to obtain a boundary definition that is likely to include potential pollution sources. For example, the Raisin River is listed as an Area of Concern, but only the last three miles of the river exhibit the problems described.

TABLE 8

HISTORICAL INFORMATION FOR SOURCES

Information Source	Comment
Fish Kill Records	Geographical location of potential sources.
Power Plant Demonstrations	Required under 316 a) and b) of Clean Water Act.
Local Sewer Maps	Available from municipality.
Emergency Remedial Response Inventory System (ERRIS) [U.S.]	Locates known dump sites.
National Priority List (NPL) [U.S.]	Type and concentration of pollutants known to exist within certain dump sites.
Drinking Water Supply Chemical Analysis [U.S.]	Inventories required under Clean Water Act.
Regional 208 Agencies [U.S.]	Water quality information and locations of storm sewers and urban runoff points.
Industrial Facilities Discharge (IFD) Data Base [U.S.]	Location and type of point sources.
Permit Compliance System (PCS) [U.S.]	NPDES compliance information.
Form II C [U.S.)	Priority pollutant analysis for new and renewed NPDES applications.
STORET Effluent File (EF)	Raw data on pollutant concentrations and limits.
CSO Inventories	Paul Horvatin, U.S. EPA, GLNPO 536 So. Clark St., Chicago, IL (313) 353-3612
Special Studies	Academic institutions, other government agencies, other state agencies.
Municipal and Industrial Strategy for Abatement (MISA)	Ontario point source system (currently being implemented).
U.S. Army Corps of Engineers	Dredging records.
Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)	
Resource Conservation and Reclamation Act (RCRA)	
Comprehensive Environmental Response, Compensation and Liability Act ("Superfund")	
Section 201, Clean Water Act. Underground Injection Program Facility Planning Documents	

The process of setting an Area of Concern boundary becomes a dynamic and iterative one, subject to the results of ongoing screening. At the end of each step outlined in Figure 2, the adequacy of the current boundary should be re-evaluated and a decision made on the need for redefinition. In addition, each parameter of concern may require a different boundary. For example, zinc may be a problem in a harbor where a plating company discharge is located, but pesticides applied to croplands 20 miles up river may also require consideration.

Preliminary screening (Section 4.3) should indicate sources within the Area of Concern which are contributing to the problem. If no likely sources are determined, the boundary of the Area of Concern must be redefined with the aid of the historical information previously described to incorporate additional potential sources. As a result, the boundary would normally be moved further upstream.

If no source can be confirmed after the detailed screening step outlined in Section 4.4, then the boundary should be defined once again. Another redefinition may be required following the quantification step, if sources of significant quantities remain unaccounted for.

4.3 PRELIMINARY SCREENING

4.3.1 Parameters of Interest

The Water Quality Board has identified 11 Critical Pollutants which are common to many Areas of Concern (Table 9). The screening process described in this chapter must be carried out for every parameter on the current Water Quality Board Critical List. For example, if an area is listed due to PCBs in fish and mercury in sediments, then screening must take place for both PCBs and mercury.

TABLE 9
CRITICAL 11 POLLUTANTS COMMON TO MANY AREAS OF CONCERN

Total polychlorinated biphenyl (PCB)
Mirex
Hexachlorobenzene
Dieldrin
DDT and metabolites
2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD)
2,3,7,8-tetrachlorodibenzofuran
Benzo-a-pyrene
Alkylated lead
Toxaphene
Mercury

4.3.2 Possible Sources

The screening begins with the development of a list of possible sources based on the historical information. Each source is then evaluated by the techniques described below to determine the likelihood of it contributing to the parameters of interest. This may be as simple as deciding that a steel mill should be considered as a source of iron or as difficult as determining that a landfill buried 20 years previously may contain PCBs. The scope of this step should be broad because it is performed without any sampling and thus it is best to include too many suspected sources at this stage than too few.

4.3.3 Identification of Suspected Sources

Point Sources

The term 'point source' refers to the direct discharge of wastewaters through a conduit or pipe at a fixed location into a receiving waterbody. This section contains background information on evaluating various point source programs and notes their utility as sources of information to describe relative contributions of a particular pollutant to an Area of Concern.

Municipal

A municipal point source is unlikely to be major contributor of contaminant loadings to Areas of Concern if its effluent is made up entirely of properly treated domestic wastewater. However, most municipal treatment plants receive industrial discharges and historically, this source of wastewater has not received the same regulatory scrutiny as industrial effluents discharging directly into a waterbody. Programs are underway to rectify this situation as noted below.

Jurisdictional Pretreatment Requirements

Controlling industrial discharges into municipal treatment plants will prevent interference with treatment plant operations, pass-through of pollutants to the environment, municipal sludge contamination and exposure of treatment plant workers to chemical hazards. Such protection can be achieved by regulating the nondomestic users through pretreatment programs.

Through pretreatment programs, many municipalities in the Great Lakes basin have developed, or are developing, the procedures to control inorganic priority pollutants. Currently, some jurisdictions are attempting to control organic pollutants. However, at present, only limited influent monitoring of toxic contaminants is carried out at selected municipal plants by the jurisdictions in the Great Lakes basin. Thus, the conclusions of the Water Quality Board's Municipal Abatement Programs Task Force, on the status of pretreatment programs in the basin remain valid and include:

1) There are insufficient data available upon which to assess the adequacy of industrial pretreatment programs for control of toxic organic and/or hazardous substances.

2) Not all of the necessary U.S. EPA categorical pretreatment standards are available to fully implement the program.

3) The programs are not stabilized and an assessment of their effectiveness has not been made.

4) The need for additional program resources is apparent.

In Ontario, permissible concentrations for industrial waste constituents have been outlined in a proposed model sewer-use bylaw. Permissible concentrations are based on known toxicities or potential adverse effects on municipal sewage treatment plant operation. Although the current model bylaw recommends limits for inorganic toxic substances, organic toxic compounds are not addressed in detail. The bylaw is adopted or adapted at the discretion of the municipality.

In the United States, a municipal pretreatment program is required for all treatment facilities with a design flow of more than five million gallons (19,000 m^3) per day and other plants that receive wastes from industrial sources subject to pretreatment requirements. Where a pretreatment program is developed, the municipality is responsible for enforcement of the national pretreatment standards, as well as any local or state standards. In the Great Lakes basin, 93% of the municipal pretreatment programs at these larger facilities have been approved by the U.S. Environmental Protection Agency.

In summary, effluents from municipal wastewater systems that receive industrial wastewaters are likely to contain toxic pollutants. Ideally, a wastewater treatment plant will be able to quantify the load of critical pollutants so relative contributions can be calculated; however, knowledge may be limited to influent loadings. In this event, the treatment plant effluent must be monitored to determine concentrations which, when multiplied by flow, will yield the desired loading information. Therefore, the first step in the preliminary screening process is to request from the treatment plant a master list of all industries contributing to the municipal treatment system. If such a list is not available, one should be developed using information sources such as: existing sewer authority files, water use and billing records, utility company records, sewer connection permits, business license records, Chamber of Commerce rosters, the local telephone directory, property tax records, and city, state and other industrial listings. For each industry identified, information gathered for analysis should include: name and address of facility, standard industrial classification (SIC) codes, wastewater flow, types, concentrations and mass of pollutants contained in the discharge, products manufactured, locations of discharge points and raw materials used or stored. Confirmation of data gathered could require a monitoring program for all or individual industries.

Regulation of Sewage Treatment Plants

Effluent

There is more uniformity in sewage treatment plant design than any other area of jurisdictional programs in the Great Lakes basin. The Great Lakes states and the province of Ontario are participants in the Ten States Committee which developed and continues to update the "Recommended Standards for Sewage Works: Policies for the Review and Approval of Plans and Specifications for Sewage Collection and Treatment" (Great Lakes Upper Mississippi River Board of State Sanitary Engineers, Health Education Service, Inc., Albany, New York, 1978).

The Ontario Ministry of the Environment Policy No. 08-01, adopted in April 1983 requires secondary or equivalent level of treatment at municipal sewage treatment works discharging to surface waters. Effluent requirements for Ontario, shown in Table 10, have been revised to accommodate the intent of this policy. A relaxation of these standards may be allowed on a case-by-case basis, providing studies indicate that this deviation will not impair stream water quality. In such instances, the minimum degree of treatment will be primary. Conversely, higher than normal levels of treatment may be implemented by the province in order to protect or improve existing receiving water quality. The wastewater treatment approval process also requires that an environmental assessment review be undertaken and that the conditions of operation, including effluent requirements, be specified in the "Certificate of Approval."

In addition to Ontario's effluent limitations on conventional parameters, certifications may also include ceilings on discharges of toxic contaminants. However, because the primary thrust of these certificates is control of conventional pollutants and not the removal of toxic pollutants, it is not adequate to examine a compliance report for a municipal wastewater treatment plant and assume it is not a source of contaminants even if it complies with BOD, suspended solids and total phosphorus limitations. Rather, industrial dischargers into the sewer system must be inventoried and some estimate of their contaminant contribution obtained. Ontario has no self-monitoring requirements for industrial contributions (see pretreatment discussion).

In the United States, sewage treatment plants with designed capacity in excess of 1 million US gallons per day are required to provide at least secondary treatment with phosphorus removal to 1 mg/L in the effluent. Forty Codified Federal Record (CFR) Part 133 provides information on the level of effluent quality attainable through application of secondary or equivalent treatment. As noted previously, U.S. EPA or the state requires self-monitoring of industrial inputs to the sewer system through NPDES/SPDES permits, and noncompliance is to be reported by the permittee.

Where effluent analyses are performed, organic priority pollutants in the effluent from municipal sewage treatment plants are commonly found in excess of "acceptable criteria" for the protection of aquatic life and human health in open waters.

Sludge

Sludge monitoring for specific metals is recommended by Canadian jurisdictions, while in the United States a demonstration of sludge quality is the responsibility of each state through individual permits. In the United States, if land application is practised, a more stringent analytical surveillance program is required. Sludge disposal, be it by landfilling, land application or incineration, should be considered as a potential source of contamination and should not be overlooked in the screening process.

TABLE 10

REVISED ONTARIO EFFLUENT GUIDELINES FOR WASTEWATER TREATMENT FACILITIES
(MOE POLICY 08-01)

LEVEL OF TREATMENT	REQUIRED EFFLUENT QUALITY		
	BOD	SUSPENDED SOLIDS	TOTAL PHOSPHORUS
Primary			Total phosphorus effluent concentration shall be $\leq$1.0 mg/L at all facilities requiring phosphorus removal. A value less than 1.0 mg/L may be required as site specific conditions warrant.
(without P removal)	30% removal	50% removal	
(with P removal)	50% removal	70% removal	
Secondary			
(without P removal)	25 mg/L	25 mg/L	
(with P removal)	25 mg/L	25 mg/L	
Continuous Discharge Lagoon			
(without P removal)	30 mg/L	40 mg/L	
(with P removal)	30 mg/L	40 mg/L	
Seasonal Discharge Lagoon			
(with P removal	30 mg/L	40 mg/L	
(batch dose P removal)	25 mg/L	25 mg/L	
(continuous dose P removal)	30 mg/L	40 mg/L	

Note: Where warranted, a higher degree of treatment shall be required to meet "Site-Specific" effluent requirements developed for each particular receiving water.

Combined Sewer Overflows and Treatment Plant Bypasses

Combined sewer overflows (CSOs) and "bypasses" are discharges of raw or inadequately treated wastewaters that generally occur when rainwater or other inflows to a conveyance/treatment system exceed:

1) the capacity of the conveyance system to either retain or transport flows;

2) the ability of the treatment system to either retain or adequately treat the flow; or,

3) the capacity of the conveyance/treatment system as a whole.

Most, if not all, of the urban centers in the Great Lakes basin have at least some portion of their sewer collection system designated as "combined", meaning that there is a linkage between the sanitary sewer system carrying residential, commercial and industrial wastewater and the storm sewer system. It is a design characteristic of such systems that significant precipitation events will result in the overflow of mingled untreated runoff and wastewater directly to the receiving waterbodies, bypassing the treatment system.

Although the terms "CSO" and "BYPASS" are sometimes used interchangeably, the term "CSO" usually describes the impact of storm runoff attributable to snow melt or direct precipitation on a sewer system where storm and sanitary sewerage are combined.

The term "BYPASS" can be defined as the intentional diversion of waste streams from any portion of a treatment facility, and applies to either a combined system or separate sanitary waste system. Whereas a CSO is supposed to occur only during wet weather conditions, bypasses can occur during wet or dry weather.

While separated stormwater systems technically should not have discharges from the sanitary system, experience in the Great Lakes basin indicates that some separated sanitary systems experience bypassing during wet weather similar to combined systems. As a result, while they are technically "separated," monitoring and controls are still needed to minimize bypassing during wet weather.

Where combined sewers are still in use, overflows of untreated wastewater routinely occur. Changes in municipal populations, land use, surface characteristics or poor maintenance practices often have resulted in increased overflow volumes and frequencies. In some cases, increased wastewater flows have caused overflows to occur even in dry weather. As an illustration of the magnitude of discharges from this source sector, it is estimated that combined sewer overflows in Ontario contribute about 3,700 tonnes of BOD, 17,000 tonnes of suspended solids, and 130 tonnes of phosphorus to the Great Lakes system annually. Based on a literature survey of available U.S. construction grant studies for 27 major municipal metropolitan areas in the Great Lakes states, it was estimated that overflows in these areas contribute an annual phosphorus load of 805 tonnes.

No new combined sewer systems have been installed in the Great Lakes basin since the early 1960s. In fact, many municipalities have completed, or are initiating, sewer separation programs. As a consequence, most municipalities currently categorized as serviced by combined sewers are in reality serviced by complex systems of separated and combined sewers. Cost plays a major role in determining the degree and extent to which new sewer separation and rehabilitation programs will be implemented.

CSOs often violate water quality criteria and standards, particularly bacterial standards. Data regarding frequency, volume and duration of flow from CSOs may be collected by the municipalities as part of their discharge permit monitoring requirements. However, insufficient data are available to adequately quantify loads of other contaminants, such as metals and organic compounds, from CSOs. Individual assessments are necessary to identify the extent of CSO impacts on water quality and to provide justification for site specific control programs.

The preceding information indicates that CSOs and bypasses should be considered significant sources of conventional and toxic pollutants to watersheds in many of the Areas of Concern, particularly during precipitation events. Models may be useful for determining an initial approximation of contaminant loadings from these sources (see Section 4.5.2). However, any comprehensive monitoring plan for Areas of Concern where CSOs and bypasses contribute a significant volume of untreated wastewater to the receiving water on an event or continuous basis must include programs for direct measurement to quantify pollutant loadings.

Although the overflow discharge points are well defined, being typically large sewer conduits, the origins of the discharged water cannot be so clearly distinguished. As a result, the status of CSOs as point sources (due to their discharge characteristics), or nonpoint sources (given their various inputs) has not been clearly established. Typically, where only a few CSOs exist in an urban area, they may be regarded as point sources; however, in a large urban area such as Detroit, with several hundred CSO discharge points, they are often treated as a diffuse, nonpoint source. Bypasses, however, should always be treated as point sources.

A complete CSO assessment is needed to identify the degree of control required to meet water quality criteria, standards or objectives. The assessment should include the following:

1) Map of the sewer system depicting:

    a) portions of the community served by combined sewers and separate sanitary sewers and

    b) location of each overflow and affected receiving waterbody.

2) List of industrial and other sewer users contributing to overflows.

3) Size of receiving waterbody watershed and population serviced by each overflow.

4) Land use, zoning classification and projected growth patterns in the vicinity of each overflow, using the following classifications: residential, commercial, industrial, recreational, agricultural.

5) Actual or potential use of the affected waterway for human contact activities.

6) History of complaints regarding the stream and surrounding environment at or downstream of overflow.

7) History of complaints concerning the sewer system.

8) Description of structural and physical condition of sewer system including age of system, incidence of sewer collapses and bottlenecks in the system.

9) Inspection of stream in and around vicinity of each overflow for sludge deposits, sewage-related odors, floating debris of sanitary sewage origin and any other visible sign of pollution impact; characterization of sludge deposits should also be considered.

10) Sediment and biological surveys downstream of the overflow points and

11) Water column chemistry:

    a) upstream/downstream and overflow sampling.

    b) wet weather/dry weather sampling.

    c) diurnal sampling for dissolved oxygen (D.O.) and

    d) parameters including BOD_5, suspended solids, volatile suspended solids, ammonia, phosphorus, metals and priority pollutants.

Since CSO discharges are dependent on wet weather events that occur simultaneously with high flow events in tributaries, sampling strategies analogous to those proposed by Richards and Holloway, "Monte Carlo Studies of Sampling Strategies for Estimating Tributary Loads" could be used to determine the type and quantity of pollutants from this source.

Determining Routine Discharge Significance From Municipal Sources

To begin the assessment of municipal sources, the discharge inventory maintained by the jurisdictions for the IJC should be examined. This inventory contains self-monitoring data reported by the municipalities and is available in computerized form in the EPA STORET effluent file (EF) for all Great Lakes jurisdictions, including Ontario. Any quantitative pollutant loading data secured from this source should be considered as preliminary and not conclusive as there are very limited data on non-conventional toxic substances.

Following the examination of the discharge inventory, state, provincial or regional federal staff should be queried regarding influent and effluent data from special studies, compliance surveys, the existence of pretreatment programs or records of industrial/commercial dischargers to the plant, including typing by Standard Industrial Classification (SIC) Code and identification/quantification of pollutants from specific industrial sources. In the absence of direct measurements, SIC Codes should be used to develop a list of probable pollutants discharged by the sewer user.

At this point, involvement of the district environmental agency and municipal personnel is crucial. If the information from district environmental agency personnel remains inconclusive, the municipal authorities, including the individual plant supervisor, must be involved. Information regarding loading quantity and quality, design and structure of the collection system, location of outfalls including CSO discharge points, frequency of bypasses, design and operating capacity of the plant, etc., should all be secured.

Industrial Point Sources

Permitting System

As noted in the municipal sources section, although an industrial facility is in compliance with its permit or control order, it still may be a source of contaminants. The following is provided as background to the regulations in both countries.

Canada

Under the federal Fisheries Act, fish processors, meat and poultry plants, potato processors, petroleum refineries, metal mining, and the pulp and paper industries are subject to regulations (for new and expanding plants) or guidelines (for existing plants). Regulations, which are legally enforcable, prescribe specific effluent limitations, whereas guidelines indicate minimum acceptable standards of practice and are not legally enforceable. Protection of the local receiving water from industrial impacts is not ensured by the application of these constraints.

Under Ontario legislation, all new or expanded facilities must receive a Certificate of Approval from the Ministry of the Environment before construction begins. Current practice includes permissible discharge levels, but approvals issued in the past may not include specific contaminant discharge limitations. Certificates of approval are available for public scrutiny.

United States

Every direct discharger is issued a National Pollutant Discharge Elimination System (NPDES) permit which limits discharges of specific pollutants, including the conventional pollutants such as BOD, suspended solids and total organic carbon, as well as selected other substances as deemed appropriate. Monitoring and reporting requirements are also set out in these permits. The permits are public documents which can be obtained through EPA regional offices.

First Screening

a) Effluent Guidelines

In developing effluent control programs, guidelines have been derived based on anticipated contaminants from individual processes and the adequacy of available treatment technology to remove such contaminants. These guidelines are one of the tools used in establishing technology-based limits on discharged substances. The guidelines are applied uniformly to every facility in an industrial category, regardless of the receiving water condition.

b) Matrix of Priority Pollutants Potentially Discharged from Industrial Categories

Table 11 lists 25 industries by category and the potential priority pollutants associated with each group. A listing in this table does not mean that every facility within a specific group discharges a particular pollutant; rather there is a high probability that it will be discharged, based on a national survey conducted by EPA. It also does not mean that other priority pollutants will not be found in significant quantities, but in general, the manufacturing process and raw materials involved do not lead to the discharge of these unlisted pollutants. This information is subject to change and some industry groups may not be regulated. For additional information contact Paul Horvatin, U.S. EPA, Great Lakes National Program Office, Chicago, IL (313-353-3612).

The EPA Industrial File Index System (IFIS) also contains chemical-specific information extracted from documents supporting the EPA industry-based regulations/guidelines issued for 83 industrial categories. The system cross references chemicals with the industry-regulation portions of statutes, such as effluent guidelines in the Clean Water Act and new source performance standards in the Clean Air Act. IFIS contains over 5,000 chemical entries covering approximately 1,000 chemicals. For each chemical and industry listed, the following information is provided:

- Chemical Abstracts Service (CAS) number
- Uses within the regulated industry, ie. feedstocks, intermediates, products, byproducts, contaminants, solvents, etc.
- Regulatory status (explicitly regulated, implicity regulated, not regulated, or unknown).
- Control technology (mostly defined by the Clean Water Act and the Clean Air Act such as Best Available Technology, Best Practical Technology, Best Control Technology, etc.).
- Precision of quantification, i.e. empirical or estimate.
- Affected media
- Descriptor field, which is a catch-all for additional information, e.g. NT means the chemical is not treatable by current methods; RL means below normal detection limits, etc.

TABLE 11 8/31/84

EFFLUENT GUIDELINES DIVISION
PROPOSED AND FINAL RULES - PRIMARY CATEGORIES
FEDERAL REGISTER CITATIONS
(1979 - Present)

Industry	40 CFR PART	TYPE RULE	SIGNATURE*	FEDERAL REGISTER CITATION	
o Aluminum Forming	467	PROPOSED	11/05/82	47 FR 52626	11/22/82
		PROMULGATION	09/30/83	48 FR 49126	10/24/83
		Correction	02/29/84	49 FR 11629	03/27/84
o Battery Manufacturing	461	PROPOSED	10/29/82	47 FR 51052	11/10/82
		PROMULGATION	2/27/84	49 FR 9108	03/09/84
		Correction	4/09/84	49 FR 13879	04/09/84
		Correction	7/09/84	49 FR 27946	07/09/84
o Coal Mining	434	PROPOSED	12/30/80	46 FR 3136	01/13/81
		PROMULGATION	09/30/82	47 FR 45382	10/13/82
		Correction	--	48 FR 58321	11/01/83
		Prop. Amend.	--	49 FR 19240	05/04/84
		Ext. of Comments	--	49 FR 24388	06/13/84
o Coil Coating					
Phase I	465	PROPOSED	12/30/80	46 FR 2934	01/12/81
		PROMULGATION	11/05/82	47 FR 54232	12/01/82
		Amendment	--	48 FR 31403	07/08/83
		Amendment	--	48 FR 41409	09/15/83
		Correction	--	49 FR 33648	08/24/84
Phase II (Canmaking)	465	PROPOSED	01/31/83	48 FR 6268	02/10/83
		PROMULGATION	11/08/83	48 FR 52380	11/17/83
		Correction	03/29/84	49 FR 14104	04/10/84
o Copper Forming	468	PROPOSED	10/29/82	47 FR 51278	11/12/82
		PROMULGATION	08/04/83	48 FR 36942	08/15/83
		Amendment	--	48 FR 41409	09/15/83
o Electrical/Electronic Components					
Phase I	469	PROPOSED	08/11/82	47 FR 37048	08/24/82
		PROMULGATION	03/31/83	48 FR 15382	04/08/83
		Interim Final/ Prop. Amend.	--	48 FR 45249	10/04/83
		Final Amendment	--	49 FR 5921	02/16/84
Phase II	469	PROPOSED	02/28/83	48 FR 10012	03/09/83
		PROMULGATION	11/30/83	48 FR 55690	12/14/83
		Correction	--	49 FR 1056	01/09/84
o Electroplating [Pretreatment - PSES]	413	PROPOSED	01/24/78	43 FR 6560	02/14/78
		PROMULGATION	08/09/79	44 FR 52590	09/07/79
		Prop. Amend.	--	45 FR 45322	07/03/80
		Prop. Amend.	--	46 FR 9462	01/28/81
		Prop. Amend.	--	46 FR 55200	09/02/81
		Prop. Amend.	--	46 FR 43972	09/02/81
		Prop. Amend.	--	47 FR 38462	08/31/82
		Prop. Amend.	--	48 FR 2776	01/21/83
		Final Amend.	--	48 FR 32462	07/15/83
		Correction	--	48 FR 43682	09/26/83
		Final Amend.	--	48 FR 41409	09/15/83
o Foundries (Metal Molding and Casting	464	PROPOSED	10/29/82	47 FR 51512	11/15/82
		Notice of Additional Data	--	49 FR 10280	03/20/84
		PROMULGATION	(12/84)	--	---
o Inorganic Chemicals					
Phase I	415	PROPOSED	07/10/80	45 FR 49450	07/24/80
		PROMULGATION	06/16/82	47 FR 28260	06/29/82
		Correction	--	47 FR 55226	12/08/82
Phase II	415	PROPOSED	09/30/83	48 FR 49408	10/25/83
		PROMULGATION	07/26/84	49 FR 33402	08/22/84

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* Administrator's signature; ( ) is the projected schedule approved by the court on August 25, 1982; October 26, 1982; August 2, 1983; January 6, 1984; and July 5, 1984.

NOTE: THIS LISTING DOES NOT INCLUDE RULEMAKING ACTIVITIES SUBSEQUENTLY PUBLISHED BETWEEN PROPOSAL AND PROMULGATION UNLESS THE SCHEDULED PROMULGATION HAS NOT YET BEEN COMPLETED. THESE, AND PUBLICATIONS ISSUED PRIOR TO 1979, ARE IDENTIFIED IN THE PREAMBLES TO EACH PROMULGATED REGULATION.

EFFLUENT GUIDELINES DIVISION
PROPOSED AND FINAL RULES - PRIMARY CATEGORIES
FEDERAL REGISTER CITATIONS
(1979 - Present)

- continued -

	Industry	40 CFR PART	TYPE RULE	SIGNATURE*	FEDERAL REGISTER CITATION	
o	Iron & Steel Manuf.	420	PROPOSED	12/24/80	46 FR 1858	01/07/81
			PROMULGATION	05/18/82	47 FR 23258	05/27/82
			Correction	-	47 FR 24554	06/07/82
			Correction	-	47 FR 41738	09/22/82
			Final Amend.			
			Correction	-	48 FR 51773	11/14/83
			Prop. Amend.	-	48 FR 46944	10/14/83
			Correction	-	48 FR 51647	11/10/83
			Final Amend.	-	49 FR 21024	05/17/84
			Correction	-	49 FR 24726	06/15/84
			Correction	-	49 FR 25634	06/22/84
o	Leather Tanning & Finishing	425	PROPOSED	06/13/79	44 FR 38746	07/02/79
			PROMULGATION	11/07/82	47 FR 52848	11/23/82
			Correction/ Notice of Availability/ Amendment	-	48 FR 30115	06/30/83
			Amendment	-	48 FR 31404	07/08/83
			Correction	-	48 FR 32346	07/15/83
			Correction	-	48 FR 35649	08/05/83
			Correction/ Amendment [PSES]	-	48 FR 41409	09/15/83
			Notice of Availability	-	49 FR 17090	04/23/84
o	Metal Finishing	433	PROPOSED	08/11/82	47 FR 38462	08/31/82
		& 413	PROMULGATION	07/05/83	48 FR 32462	07/15/83
			Final Amend.	-	48 FR 41409	09/15/83
			Correction	-	48 FR 43682	09/26/83
o	Nonferrous Metals					
	Phase I	421	PROPOSED	01/31/83	48 FR 7032	02/17/83
			PROMULGATION	02/23/84	49 FR 8742	03/08/84
			Correction	-	49 FR 26739	06/29/84
			Correction	-	49 FR 29792	07/24/84
	Phase II	421	PROPOSED	05/15/84	49 FR 26352	06/27/84
			Ext. of Comments	-	49 FR 33026	08/20/84
			PROMULGATION	(11/84)	---	---
o	Nonferrous Metals Forming	471	PROPOSED	02/03/84	49 FR 8112	03/05/84
			PROMULGATION	(10/84)	---	--
o	Ore Mining	440	PROPOSED	05/25/82	47 FR 25682	06/14/82
			PROMULGATION	11/05/82	47 FR 54598	12/03/82
o	Organic Chemicals and Plastics & Synthetic Fibers	414 & 416	PROPOSED	02/28/83	48 FR 11828	03/21/83
			Notice (Confidential Information)	-	49 FR 34295	08/29/84
			PROMULGATION	(02/85)	---	---
o	Pesticides	455	PROPOSED	11/05/82	47 FR 53994	11/30/82
			Proposed (Analytical Methods)	-	48 FR 6250	02/10/83
			Notice of Availability	-	49 FR 24492	06/13/84
			Ext. of Comments	-	49 FR 30752	08/01/84
			PROMULGATION	(11/84)	---	---
o	Petroleum Refining	419	PROPOSED	11/27/79	44 FR 75926	12/21/79
			PROMULGATION	09/30/82	47 FR 46434	10/18/82
			Prop. Amend.	-	49 FR 34152	08/28/84

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EFFLUENT GUIDELINES DIVISION
PROPOSED AND FINAL RULES - PRIMARY CATEGORIES
FEDERAL REGISTER CITATIONS
(1979 - Present)

- continued -

Industry	40 CFR PART	TYPE RULE	SIGNATURE*	FEDERAL REGISTER CITATION	
o Pharmaceuticals	439	PROPOSED	11/07/82	47 FR 53584	11/26/82
		PROMULGATION	09/30/83	48 FR 49808	10/27/83
		Correction	--	48 FR 50322	11/01/83
		PROPOSED - NSPS	--	48 FR 49832	10/27/83
		BCT Cost	--	49 FR 8967	03/09/84
		Extension	--	49 FR 17978	04/26/84
		Notice of Availability	--	49 FR 27145	07/02/84
o Plastics Molding & Forming	463	PROPOSED	02/03/84	49 FR 5862	02/15/84
		PROMULGATION	(09/84)	---	---
o Porcelain Enameling	466	PROPOSED	01/19/81	46 FR 8860	01/27/81
		PROMULGATION	11/05/82	47 FR 53172	11/24/82
		Final Amend.	--	48 FR 31403	07/08/83
		Final Amend.	--	48 FR 41409	09/15/83
		Prop. Amend.	--	49 FR 18226	04/27/84
o Pulp & Paper	430	PROPOSED	12/11/80	46 FR 1430	01/06/81
	& 431	PROMULGATION	10/29/82	47 FR 52006	11/18/82
		Notice of Availability	--	48 FR 11451	03/18/83
		Correction	--	48 FR 13176	03/30/83
		Final Amend.	--	48 FR 31414	07/08/83
		Notice (FDF)	--	48 FR 43682	09/16/83
		Correction	--	48 FR 45105	10/06/83
		Public Hearing (NPDES decision)	--	48 FR 45841	10/07/83
		PROPOSED (PCB)	--	47 FR 52066	11/18/82
		Extension	--	48 FR 2804	01/21/83
o Steam-Electric	423	PROPOSED	10/03/80	45 FR 68328	10/14/80
		PROMULGATION	11/07/82	47 FR 52290	11/19/82
		Final Amend.	--	48 FR 31404	07/08/83
o Textile Mills	410	PROPOSED	10/16/79	44 FR 62204	10/29/79
		PROMULGATION	08/27/82	47 FR 38810	09/02/83
		Notice of Availability	--	48 FR 1722	01/14/83
		Correction	--	48 FR 39624	09/01/83
o Timber	429	PROPOSED	10/16/79	44 FR 62810	10/31/79
		PROMULGATION	01/07/81	46 FR 8260	01/26/81
		Final Amend.	--	46 FR 57287	11/23/81

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Information on the IFIS system is available from Ms. Daryl Kaufman, U.S. EPA, Washington, D.C. (202-382-5506).

c) Inventories of Hazardous Materials

Several jurisdictions in the Great Lakes basin have developed lists of hazardous contaminants used in their area which:

1) Are used as a raw material or process material, or are a byproduct of industrial or manufacturing activities.

2) Are lost or released into the wastewater stream.

3) Indicate the type of discharge, either direct or indirect, into the receiving stream.

4) Indicate amounts of a substance used, lost or released as reported or estimated by the activity operator.

In 1983, Ontario developed a list of 254 hazardous substances and an associated geographic usage pattern for the province. However, this listing does not identify particular industrial locations, and thus will be of limited use in determining discharge characteristics for individual industries. It is available from the Hazardous Contaminants Coordination Branch, Ontario Ministry of the Environment, Toronto, ON (416) 965-2401.

As its contribution to the development of a hazardous materials inventory, the State of Michigan has developed a Critical Materials Register. All industries are required to report use, storage or discharge of potentially hazardous materials. This information is used in the development of a Cumulative Hazard Assessment Score.

Self-Monitoring Data

For every U.S. industrial discharger into surface waters in the Great Lakes basin, monthly effluent self-monitoring data is available in computerized form in the EPA STORET effluent file (EF) (see page 60). These data include flow and every parameter for which monitoring is specified in the discharger's NPDES permit.

Also, for the over 100 direct industrial dischargers in Ontario, monthly effluent self-monitoring data on conventional and a selected and limited number of metals and organic contaminants are collected and summarized annually for the IJC. These Ontario records are maintained by the Commission in printed form and a program is now underway to integrate Ontario industrial data into the EPA STORET electronic data base. The 1984 Ontario effluent data is available in STORET and 1985 data and beyond will be included as soon as practical.

While these data should be reviewed for direct dischargers located in a defined Area of Concern, they are not adequate in breadth or precision to conclusively assess the environmental impact of the effluent stream.

Literature Search

Literature reviews and EPA, Environment Canada, state and provincial information on discharge characteristics (including the SIC Codes) of particular industrial sectors, plus any other appropriate research, could be useful in narrowing the search for possible dischargers. In some cases, recent effluent characterization studies or compliance surveys may be available either from the jurisdictions or the federal agencies. While effluent data contained in these studies generally would be superior to those in the annual IJC discharge summaries, they would in most cases be indicative rather than statistically representative in quantifying most of the discharge parameters studied.

In Ontario, the regional and district Ministry of the Environment offices may have additional data on effluent quality and quantity, and although these data could be requested, they are frequently maintained on a confidential basis. These offices should also be able to describe individual processes within an industrial complex and the contaminants possibly discharged into the effluent.

Information from the individual industry should also be sought in specifying and enhancing the information base. A compilation of all information should allow development of an individual corporate profile.

Nonpoint Sources

Nonpoint sources generally cover a broad, diffuse area that does not terminate at the end of a pipe or outlet structure. The notable exception is the combined sewer overflow (CSO), which may be considered as either a point source or a nonpoint source, depending on physical conditions. For the purposes of this document, nonpoint sources of pollution have been divided into urban and rural categories.

Urban Nonpoint

Landfills

Impacts from landfills may include degradation of surface water and groundwater due to elevated groundwater tables and/or leaks from fill sites. Groundwater pollution from operating or abandoned landfills may ultimately have an impact on surface water resources. Any comprehensive treatment of the landfills source category must include sites currently and/or previously used for disposal of domestic wastes, solid wastes and hazardous wastes. Locations of licensed and regulated active sites should be verified. Abandoned sites may or may not be readily identified. In addition, abandoned fills or waste disposal sites may at present be developed for housing, transportation, businesses, etc., or may be associated with an active manufacturing operation.

Inventories of active or abandoned fills may be available at the municipal, state or provincial jurisdictional level. Data on active sites may include volume or fill mass per time period, type of material being disposed of and operational management procedures. Historical data outlining location, types and quantities of materials disposed of, operational data, and associated environmental degradation allegations may be available for inactive or abandoned sites. In the United States, these data are contained in the comprehensive Environmental Response Compensation and Liability Information System.

In Ontario, the Waste Management Branch of the Ontario Ministry of the Environment maintains a registry of closed and active landfill sites. This inventory can provide information on the location, approximate size and type of dumped waste. Since 1972, all active sites operate under a certificate from the Ministry. The majority of those that ceased operation prior to 1972 also should be listed in these records. The Canadian federal government maintains a record of landfill sites on federal property in Ontario; however, investigators should review land titles, historical records, etc., to ensure that a long abandoned site is not overlooked.

An example of a groundwater contamination inventory is "Assessment of Groundwater Contamination: Inventory of Sites," Groundwater Management Strategy for Michigan, Task 3, July 1982, Michigan Department of Natural Resources, Groundwater Quality Division, P.O. Box 30028, Lansing, MI 48909. This inventory lists location, contamination source and type, extent of contamination, documentation status and remedial action.

If, after examination of landfill inventories and incidents of known groundwater contamination, it is determined that there are landfills containing significant quantities of hazardous materials or the groundwater is contaminated within the boundaries of the Area of Concern, containment structures must be evaluated for: (a) the likelihood that wastes will be released to the environment; and (b) the rate at which such releases occur or will occur.

Release movement potential is a function of the structural integrity of the containment and the physical state of the waste materials. Recognizing that perfect containment is rarely achieved and that detailed information regarding containment is not normally available or may not exist, site containment should be classified as "adequate," "inadequate" or "unknown."

To be considered an adequate containment, the file or site visit information must indicate that the structure's design, construction and operation effectively prevent chemical emissions from entering the environment. Containment must therefore be <u>unquestionably</u> adequate in order to be scored as such. Any condition less than unquestionably adequate should be scored as inadequate or unknown and then be considered as a possible source of pollution.

If containment is considered inadequate, a hydrogeological study must be initiated to verify if waste material is leaking from the fill site, at what rate and in what direction. Rate and direction data, along with data on chemical composition, will provide an estimate of potential or actual loadings into the receiving stream.

An example on how to conduct hydrogeological studies is contained in "Hydrogeologic Study Handbook," Task 7 of Groundwater Management Strategy for Michigan, March 1982, Michigan Department of Natural Resources, Groundwater Quality Division, P.O. Box 30028, Lansing, MI 48909.

Leaking Underground Storage Tanks

Leaking underground storage tanks (L.U.S.T.) contain any number and quantity of chemicals (generally gasoline) and may pose a threat to the subsurface water table. Tanks may develop leaks through puncture, a condition which creates low volume losses. These low volume losses may be barely detectable over a short time; consequently, contamination associated with leaking tanks may be overlooked.

Data regarding leaking tanks are infrequent, scant and disparate. Generally, most incidents of tank leakage are found in response to an emergency situation. Some data pertaining to the age of the tank, type and volume of material being stored, and any known leak events may be available from local levels of government.

The Ontario Ministry of Consumer and Commercial Relations is proposing an inventory of all underground fuel storage tanks in urban and rural settings. The Ministry has jurisdiction over the use and maintenance of these fuel storage tanks. While the underground fuel storage tanks located at the 8400 retail facilities in the province are well catalogued and are now subject to a program which will upgrade or replace all tanks by 1991, private farm storage tank locations are not well documented. The Ontario Cabinet has approved a program to register all tanks within the next few years and the Ministry is now locating the resources to do so.

Combined Sewer Overflows and Stormwater

Rainfall results in runoff over roads, parking lots, roofs, etc., with ultimate discharge to water courses or waterbodies. This runoff contains pollutants such as street litter, automotive lubricants, de-icing compounds and contaminants washed from the atmosphere. However, neither the quantity nor quality of stormwater runoff are determined on a routine basis in communities in the Great Lakes basin.

As noted on page 58, most urban centres in the Great Lakes basin have combined storm and sanitary sewers with newer areas having separated sewers. If the combined sewers cannot be treated as point sources (see page 59), they will have to be considered nonpoint sources, along with separated storm sewers. In this case, their impact will have to be assessed by developing unit area loads (page 70) or using modeling (page 86).

Spills

Accidental spills from manufacturing operations, site-maintained tanks, or from transportation or transfer may enter waterways directly or indirectly via contaminated soils.

Records are maintained by various governmental agencies and may include date, estimated volume, type of substance, receiving stream affected and any environmental impacts on species. Fish and wildlife agencies also may have data related to spills and associated impacts on terrestrial and aquatic life.

Unit Area Load (UAL) Estimation

Nonpoint sources represent the cumulative effect of a large number of diffuse sources that are difficult to identify, let alone quantify. For some parameters, such as total phosphorus, suspended solids and metals, an approach is available to estimate loadings from these sources (Heidtke, et al. 1985). Information required to develop these preliminary estimates include land use and soil texture. Table 12 is an example of a UAL matrix for total phosphorus in the Lower Fox River watershed. A more comprehensive discussion of nonpoint source loading estimation is available in the modeling section (page 86).

TABLE 12
TOTAL PHOSPHORUS UAL MATRIX (kg P/ha year)

LAND USE	COARSE	SOIL TEXTURE MEDIUM	FINE
Residential	0.06	0.13	0.18
High Tillage Cropland	0.55	0.74	0.92
Low Tillage Cropland	0.22	0.29	0.37
Pasture	0.06	0.07	0.09
Woodland/Residual	-	0.02	0.04

For each sub basin requiring a preliminary loading estimate, the proper values are selected from the matrix and multiplied by the sub basin area to calculate the estimated annual loading. All subbasins in the Area of Concern are summed and the resultant loading compared to other sources. If nonpoint loading appears to be an important fraction of the total, it becomes a suspected source for detailed assessments as outlined in Section 4.5.

Rural

Landfills

Rural landfills tend to be dominated by sanitary rather than industrial and hazardous wastes, simply due to location. However, if they have been operational for some time, it should not be assumed that significant quantities of industrial wastes or pesticides are absent. Refer to page 67 for additional information on potential impacts and data sources.

Leaking Underground Storage Tanks

Storage tanks for gasoline and home heating fuel are frequently found at farmsteads. Deterioration of these tanks may cause leakages of stored material. Refer to the previous discussion on page 69.

Agricultural Drainage and Runoff

Few, if any, direct measurements exist for drainage and runoff contaminant contents from individual acreages in the watershed of the current Areas of Concern; however, information exists which allows some estimation of the extent to which drainage and runoff are contaminated by conventional pollutants and pesticides.

Estimation of Pesticide and Fertilizer Application Rates

In Ontario, pesticide use is estimated every five years using a questionnaire to survey a representative sample of farmers in each county. Estimates of use for 1973, 1978 and 1983 are now available. Approximately 8,000 tonnes of agricultural pesticides are used annually in Ontario. Sam Singer of the Ontario Ministry of Agriculture and Food (416-965-9921) can provide details on this program.

The U.S. Department of Commerce (U.S. DOC), Bureau of Census has collected similar data by type or category of pesticide on the number of acres where pesticides or other chemicals have been used. They also estimate the dollars spent on agricultural chemicals other than commercial fertilizer. Data are available for 1978 and 1982. The same department also maintains data on the acres of cropland, pasture land and range land fertilized in 1982 as well as expenditures for commercial fertilizer.

The EPA has used the U.S. DOC data to derive county level use estimates for 52 pesticides. The Economic Analysis Branch, Benefits and Uses Division, Office of Pesticides Programs is responsible for developing this estimation technique. Part of this survey is available in a D Base III format on floppy disk. Ron Lauster of the U.S. Department of Agriculture, Soil Conservation Service (202-382-8524), can provide information on this program.

Resources for the Future, a Washington-based foundation, also has developed a data base for quantification of nonpoint source water pollution problems. The contaminants estimated are, with few exceptions, conventional and heavy metal pollutants. Sedimentation rates are also estimated. Other aspects of the RFF data deal with point and urban dischargers. Further information can be obtained from Resources for the Future, Washington, D.C., or through the Nonpoint Source Subcommittee, Water Quality Board, International Joint Commission.

Land Use and Geology

Various land uses, particularly agricultural uses, may increase sediment, nutrient and pesticide loads. Drainage through, or over, strata which contain naturally occurring metals may serve as a background source of contamination. While land use inventories and geological maps are available from jurisdictional agencies, data bases delineating their impact on the aquatic environment are not comprehensive.

Spills

Refer to urban nonpoint spills section, page 69.

Unit Area Load Estimation

Refer to urban nonpoint unit area load section, page 70.

4.4 DETAILED SCREENING OF SUSPECTED SOURCES

Introduction

The screening procedures outlined in the preceding sections were designed to identify candidate pollutant sources. These candidate sources must be verified as contributors and their significance determined. The following section will recommend some bioassay procedures that will establish the potential biological significance of identified sources. The recommended procedures are intended to meet the first three of the five categories of use impairment considered in the Areas of Concern development. The last two categories are covered in sections 4.4.2. These five categories are:

a) Evident, repeated and documented fish kills and/or depressed or unusual aquatic community structure as compared with potential or anticipated capacity of the environment.

b) Accumulation of pollutants in tissues of resident aquatic biota to a level where a consumptive warning has been issued. Such accumulations are symptomatic of a sublethal or chronic condition that may also result in a depressed biotic potential as identified in (a) above, and are elevated with respect to lakewide or Great Lakes basin-wide data.

c) Presence of tumors/cancers or deformities in resident aquatic biota at frequencies greater than background levels. Such a finding is indicative of the presence of pollutants that may or may not bioaccumulate and may or may not result in depressed biotic potential.

d) Unsuitable water quality, identified by violation of drinking water standards, aquatic life protection guidelines or other water quality standards or objectives, e.g. aesthetics.

e) Pollutants present in sediments in excess of specific sediment criteria for the disposal of dredged material or other applicable sediment guidelines.

4.4.1 Bioassays

The first step is to determine if a potential source is acutely lethal. The two recommended standard tests for acute lethality are the rainbow trout and fathead minnow static bioassays (96 hours LC_{50}). It should be noted that the choice between the two tests is predicated not only on laboratory capabilities or agency preference but also on ambient conditions. If the receiving body of water is classified as warm water, the fathead minnow bioassay would be appropriate; conversely, if classified as cool/cold water, the rainbow trout bioassay should be considered.

Acute bioassays should be performed in conjunction with an effluent chemical analysis which will be used in calculating the relative contribution of the source to the problem (see section 4.5). Positive results verify the contribution of the candidate source to the problem.

The acute static lethality test will permit the calculation (interpolation) of a LC_{50} value[1]. This information will be used further to determine the dilution or percent reduction in effluent concentration necessary to render the effluent nonlethal, thus allowing chronic and bioconcentration assays to be conducted.

If the test results are negative, two possibilities must be considered before eliminating the candidate source as a contributor to an acute problem. First, the source may be a problem in combination with the ambient conditions. This situation is commonly referred to as a synergistic environmental effect. In this case the in situ test results recommended in the water and sediment sections must be evaluated. If results from the bioassay and the water and sediments test are all negative, then an intermittently toxic source is a second possibility, and a chronic lethality flow-through test or in-plant monitoring is required. A positive result from this latter test verifies the candidate source as a contributor and its relative contribution needs to be determined.

Since conducting a flow-through/in-plant test is expensive, a detailed process characterization (see page 80) should first be attempted. It may also be possible to conduct a series of less expensive static acute lethality bioassays when various batch processes are operating within the plant. If this is not possible, the flow-through/in-plant test must be employed.

The next step is to determine if a potential source is contributing to the other listed problems, i.e. bioaccumulation and/or sublethal/chronic toxicity. Several bioaccumulation tests are available for verification of a candidate source as a contributor to the designated problem. These tests include, but are not limited to, subjecting caged organisms to the candidate source effluent for various lengths of time, e.g. between 14 to 28 days. Tissue from the test organisms is analyzed for contaminant concentration and compared to controls to assess the degree of biouptake. The organisms used in this type of test could include: larval fish, e.g. fathead minnows, spottail shiners; rainbow or brown trout, and clams. Protocols for these tests are referenced in the Biota Section (3). These tests are not as yet standardized for source evaluation, therefore, the protocols and determinations are not yet universally accepted.

In addition to the acute lethality and bioconcentration assays, a test should be performed to determine the potential effects of an effluent on reproductive success. The recommended tests are described in the Biota Section (3) of this document. Positive results from these tests verify the candidate source as a contributor to the designated problem.

The more sinister aspect of genotoxicity presents the investigator with a complex set of problems. Incidences of neoplasms and deformities in fish and invertebrate species in many areas throughout the Great Lakes basin are being reported with increasing regularity. It is difficult to determine the rate at which these problems developed as they may have been present for some time but have only been recently documented .

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[1] LC_{50} is the concentration at which 50% of the test organisms die over a prescribed time period.

Numerous short-term bioassays are currently available to detect the potential mutagenicity, carcinogenicity and teratogenicity of chemicals. These bioassays were developed and validated using individual contaminants; their principal utility is to evaluate the hazard of numerous chemicals on a single exposure basis. However, the potential genotoxic hazard is usually present in the ecosystem in the form of complex chemical mixtures which may continually undergo further chemical and biological transformations in the environment. Biological exposure is, therefore, more commonly a multifactor phenomenon. In areas where endemic species are affected, there is a clear need to investigate the sediments and the sources for genotoxic potential.

Chemical analysis can be used to detect known hazardous compounds, provided the extraction procedures and detection limits are appropriate and the chemical and biological transformation products are known. This is an extremely time consuming and expensive task which ignores the fact that a biological effect cannot be reliably predicted solely from a knowledge of its constituents. Therefore, the whole effluent should be subjected to bioassay testing prior to evaluating its constituents for genotoxicity (see Bergmar _et al_. 1986).

The fact that bioassays alone cannot establish which individual constituent(s) of an effluent or sediment are responsible for the biological activity observed suggests the need for a stepwise and iterative application of chemical and biological methods to evaluate the genotoxic hazard associated with complex environmental mixtures. Chemical fractionation coupled with bioassays may enable the investigator to isolate the individual chemical agent responsible for the observed biological effect.

Complex mixtures may be separated and bioassayed in defined chemical fractions. The results of these short-term screening tests can then be used to guide further fractionation, leading to a more comprehensive biological testing program. For a detailed discussion of chemical and biological procedures refer to Walters _et al_. 1980 and Parkhurst _et al_. 1979.

Many types of data may be needed to guide decisions on dealing with complex effluents with genotoxic properties that enter the aquatic ecosystem. It may be necessary to define possible risk following exposure which, combined with estimates of the number of individuals exposed, the level and duration of exposure, and the cost of eliminating the material from the environment, may dictate the priority and the feasibility of remedial measures. Therefore, it is difficult to generalize about the choice of testing methods. It may be necessary only in some jurisdictions to demonstrate the clear potential for genotoxicity to affect some regulatory/remedial action. In the case of such pre-emptive action, the need to develop a detailed and expensive risk assessment may not be necessary.

The two main approaches to genotoxic testing have been hierarchical (tier) and matrix or battery test procedures. Tier approaches are usually applied when the number of substances to be tested is large because all of the substances should be subjected to first level testing. These tests should be rapid, reliable and inexpensive. Many mixtures or fractions may be eliminated on the basis of their test results, leaving fewer samples for further evaluation. As an effective tool, these tests will allow for rapid assessments at relatively low cost but must possess uniform protocols, be easy to perform and evaluate, and produce few positive or negative results which cannot be supported by tests in animal systems .

The battery or matrix approach to testing provides several levels of evaluation, conducted simultaneously. This approach provides a screening mechanism that identifies chemicals or mixtures likely to produce mutations or carcinomas. A group of tests should overlap in response to most, but not all, genotoxic agents; therefore, complete agreement among the results of all tests in the battery should not be expected. Due to technical limitations in currently available tests, some genotoxic agents may be missed; however, careful selection of the tests should keep such results to a minimum. The tier approach represents a cost effective program but it may take more time than the battery approach to obtain a definitive answer. A complete and in-depth discussion of these two approaches, with decision trees, recommended tests, and test protocols can be found in "Principles of Genetic Toxicology," by D. Brusick (1980).

It is strongly recommended that the investigator at least employ the Ames test on the unconcentrated final effluent to test for gross genotoxicity.

While there may be a tendency on the part of the investigating agency to shy away from complicated, expensive and sometimes ambiguous testing procedures associated with genotoxic assessments, they are critical to the ranking of sources for abatement actions designed to alleviate observed problems in the Areas of Concern. However, due to the need for some exceedingly specialized equipment, laboratory facilities, and trained personnel, it is evident that source investigations personnel may need to engage external assistance.

4.4.2 Criteria Violations

Water Quality and Drinking Water Criteria

Given the number of regulatory agencies in the Great Lakes basin, it is not surprising that there are a plethora of objectives, guidelines, criteria and standards governing the contaminant content of various media (water, sediments, biota, etc.). Rather than attach a partial listing of such criteria to this document, an excellent starting reference would be "Great Lakes Water Quality Objectives, Guidelines, Criteria and Standards," Great Lakes Regional Office, International Joint Commission, July 1985.

Another useful compendium was assembled by the state of New York as part of the Environmental Conservation Act, Part 700-705, "Classifications and Standards of Quality and Priority." Further information on this document can be obtained from the Criteria and Standard Section, Bureau of Water Quality Management, Division of Water, New York State Department of Environmental Conservation, 50 Wolf Road, Albany, N.Y. 12233-3508, (518-457-3656).

If a parameter is under consideration because of a drinking water standard violation, a candidate source can often be confirmed by direct chemical measurement. The analytical procedures required must be rigorous enough to verify the source and permit the relative contribution calculation. As it would be unlikely that a effluent would have a concentration less than that found in the ambient environment, considering the effect of dilution, a significant amount should be present for analysis at source. Therefore, it is probably sufficient for the analytical procedures to have a detection limit equal to the drinking (or water quality) standard in question. The section on water analysis should be consulted for further guidance.

Sediment Criteria

If a parameter is under consideration due to exceeding sediment criteria, a source may also be confirmed by direct chemical measurement. However, the analytical detection limits should be considerably lower than the sediments concentration because sediments tend to accumulate persistent chemicals. Careful confirmation work may be necessary.

4.5 QUANTIFICATION OF LOADINGS FROM SOURCES

4.5.1 Point Sources

Chemical Analysis

When direct quantification of loadings by chemical analysis and flow measurements is attempted, four basic factors should be considered:

a) Sample Collection
b) Sample Preservation
c) Sample Analysis
d) Data Reporting

Some of these factors may have been considered previously in the screening exercise, but now a thorough review of each is essential to develop the required loading information.

For conventional parameters and most metals, quantification of loadings from point sources will involve accurate chemical and flow measurements over the time period of interest. Some organic chemicals will be difficult to measure in an effluent even though they may accumulate in the sediment, or bioconcentrate in the biota. This may be due to analytical interferences in the effluent or to an inability to quantify the substance analytically. In this case, process characterization provides an alternative way of estimating loadings.

Sample Collection

This section addresses the questions of when, where and how to sample. The mechanics of where and how to sample are well described in the "EPA Handbook for Sampling and Sample Preservation of Water and Wastewater" (EPA 600/4-82-029 and NTIS Report #PB83-124503). This handbook includes detailed methodology for sampling municipal, industrial and agricultural point sources. A similar document for municipal point sources is available from the Ontario Ministry of the Environment (MOE Policy #08-06).

The question of when to sample is directly related to the variability of the source. Quoting from Heidtke and Armstrong (1979):

> "To characterize the probability distribution f(x) for individual dischargers, an empirical data base must be established and updated regularly. Ideally, effluents would be sampled at a frequency that would yield a representative description of the normal temporal variation in pollutant loading from each point source. However, constraints on available sampling resources and a lack of uniformity among effluent monitoring policies often may preclude compilation of a desirable data base for statistically describing the loading distribution for individual dischargers. This is certainly one of the major obstacles to effective application of the present approach."

The desired statistical confidence required to initiate source reduction activities has not yet been specified by the WQB, nor is it likely that such generic criteria can be generated without considering source and site specific conditions. For discussion purposes, assume that it is necessary to model the relationship between load and aquatic ecosystem time-dependent concentrations to within a factor of 50% at the 95th percentile confidence level. Since other sources of error will be compounded in such a model, assume further that it is desirable to know the point source load contribution to within ±20% of the actual load at the 95th percentile confidence level. The number and distribution of sampling events required to achieve the desired accuracy and precision of load quantification are functions of the variability of the discharge.

For facilities with continuous processes running 24 hours per day, seven days per week, only minor variability in process wastewater composition would be anticipated, unless holding tanks are filled and emptied on a cycle, process areas are washed down on a cycle or recirculated treated cooling water is discharged on a cycle. In facilities with batch processes, the wastewater composition can be highly variable, depending on the product, the manufacturing time and the timing of process initiation. Facilities in this latter category require quantification of the discharge composition and loading rate, thus the sampling program requires a detailed understanding of the process cycles, including an understanding of the points of origin, comingling of process waste streams, and the sequence and duration of process hardware utilization.

The greatest sampling difficulties are presented by facilities of intermediate size with five to 15 batch processes having differing cycles initiated on independent schedules with highly variable products, involving unique mixes of raw materials, intermediates and byproducts, i.e. the custom chemical plant. Such a facility will warrant a process evaluation to develop a process-based sampling program. This evaluation should involve personnel from the facility under study.

Determining the appropriate sampling frequency for Publicly Owned Treatment Works (POTWs) or municipal waste water treatment plants follows much of the same logic as that used for industrial facilities. The effluent concentration cycles of very small POTWs with one or two small industrial contributors, and very large POTWs with one or two very large industrial contributors, will exhibit a cycle strongly influenced by the process cycles of the contributing industries. Process evaluation for the contributing industries should reveal the appropriate sampling cycles for pollutant chemicals under consideration. If the contributing industries employ continuous processes, one grab sample taken at any particular time should be similar in composition to a sample taken at any other time, given the detention in the clarifiers and aeration lagoons.

Where a number of small industrial facilities or a few large facilities having a variety of processes and operating schedules are discharging into a small or intermediate size POTW, a statistically-based sampling scheme should be developed to reveal daily, weekly and seasonal cycles. If it is assumed that the processes contributing to POTW loading are occurring randomly, relative to one another, then the probability distribution function (pdf) which describes the daily, weekly and seasonal cycles should follow a normal distribution. Heidtke and Armstrong (1979) found, for example, that the daily chloride loads from two industries discharging to the Great Miami River in Ohio were normally distributed. The greater the number of independent contributing processes, the greater the likelihood that the pdf can be adequately modeled as a normal distribution.

Where the concentrations of toxic pollutants in the POTW's effluent are strongly correlated with the concentrations of one or more conventional pollutants or indicator parameters, the results of daily monitoring for these latter parameters can be used to construct a pdf for the pollutants of interest and develop a statistically-based sampling scheme. To demonstrate such a correlation, sufficient samples collected according to a statistically-based schedule must have been analyzed for the toxic and conventional pollutants simultaneously. McCarty and Aieta (1984) studied the relationships among the concentrations of various pollutants being discharged from a POTW and determined that total organic halogen (TOX), total organic nitrogen (TON) and total trihalomethane formation potential (TTHMFP) served adequately as surrogates for the "presence of certain important classes of organic compounds." Where such correlations do not exist, the use of conventional pollutants or indicator parameters as surrogates for toxic pollutants is precluded. Unfortunately, the number of data points required to demonstrate such a correlation may limit the utility of such an approach for broad applications within the Great Lakes basin community.

In analyzing for non-volatile material, samples can be composited with daily averages obtained via 24-hour composite sampling, weekly averages by compositing daily samples, monthly average by compositing the weekly samples, and seasonal average by compositing the monthly samples. Analyses could then be run on only the four seasonal composites, although a minimum of monthly analysis is strongly recommended. Where holding time becomes problematic, the samples can be extracted and the extracts composited according to the above scheme.

For volatile samples, where compositing is largely precluded, a minimum of four grabs per day for four weeks would probably be required to define the weekly cycle, four grabs per week for four months to define the monthly cycle and four grabs per month for 12 months to define the seasonal cycle.

While these sampling schemes appear to impose an unreasonable sampling and analytical burden on the POTW, these are necessary because only limited information is available to characterize the processes and process effluent compositions contributing to POTW loading. The greater the information on process hardware, chemistry, cycles, schedules, effluent composition and flow, the fewer the number of samples that need to be analyzed for calculating average loadings with acceptable accuracy and statistical confidence. Ultimately, the sampling and analysis burden should be shifted to the contributing facilities. Methods such as those suggested by Heidtke and Armstrong (1979) could then be used to establish a statistically sound sampling schedule to accurately define the POTW loading rates. Additional statistical bases for compliance sampling have been discussed by Oliver (1985) for air sources, Schweitzer and Black (1985) for groundwater and soil studies and by Ball and Vath (1983) for wastewater sources.

Where adverse biological effects have been detected in a point source effluent using appropriate indicator organisms, effluent sampling should be timed so that the frequency and amplitude of toxic pollutant concentrations contributing to the time-integrated toxicity are revealed with the desired accuracy and precision. Dominic DiToro of Manhattan College, Department of Environmental Engineering, Bronx, NY is developing a model of time-integrated acute and chronic toxicity to fish upon which to base a statistical sampling program design of potentially toxic point sources.

Sample Preservation

The accuracy of measurements can depend on the time elapsed between sample collection and sample analysis. Some parameters, especially if preserved properly, may be held indefinitely before analysis, while others must be analyzed immediately to obtain acceptable results. Details of sample preservation for point sources can be found in the "EPA Handbook" (EPA 600/4-82-029), MOE Policy #08-06 or 40 CFR 136.

Sample Analysis

The analytical chemistry requirements for sample preparation, cleanup, digestion, extraction, identification and quantification must also be considered. EPA has established analytical guidelines for pollutants (40 CFR 136) which incorporate many of these considerations. If it is not possible to quantify loadings with the recommended procedures due to high detection limits or interferences, alternatives must be found. Analytical methods for trace level contaminant measurements are constantly under development and newer methods should be considered, if available. Another alternative is process characterization, which is described later in this chapter.

Data Reporting

Understanding the variability involved in point source data is critically important to the overall assessment of an Area of Concern. Consequently, data reporting must involve more than mean pollutant concentrations over a time period. Data reporting requirements for load quantification include:

1) Sample type (composite or grab).

2) Collection time.

3) Flow rate (see next section).

4) Concentrations of each parameter and associated measurements such as temperature, pH, conductivity, alkalinity, hardness, suspended solids, total organic carbon, and any available measurements that will aid in characterizing the discharge information should all be presented:

5) Analytical methodology.

6) Detection limits.

7) Percent recovery of spiked samples and

8) Blank values.

The above information will help answer questions regarding source variability and measurement accuracy.

Flow Measurement

While methods for flow measurement are relatively well established compared to analytical chemistry methods, selecting the proper flow measurement technique is as important as the choice of chemical methodology. In fact, since the goal is to obtain the most accurate loading possible, the best possible flow measurement technique should be used.

Where toxic pollutant concentrations and effluent flows are strongly correlated, flow-proportional sampling will be required to accurately quantify POTW loading rates. In this case, inaccurate flow measurements will lead to further inaccuracies in composite concentrations.

Flow measurement methods can be broadly grouped into four categories:

1) Closed conduit flow measurement.
2) Flow measurement for pipes discharging into the atmosphere.
3) Open channel flow measurements and
4) Miscellaneous methods of flow measurement.

Each category is described in detail in the "EPA Handbook" cited previously (EPA 600/4-82-029).

Process Characterization

The concept of industrial process characterization which is a comprehensive review of industrial operations, has been used in a limited fashion since its introduction in 1979. The need for its expanded use has become more apparent as regulatory agencies pursue ever lower concentration levels for a growing list of chemicals.

Process characterization has two important uses: 1) to identify potential sources of toxic substances found in the ambient environment for which no historical or on-going manufacturer in the area has been identified, and 2) to identify substances likely to be present in process wastewaters from specific facility unit processes, following comingling of waste streams or after treatment. The characterization procedure is especially useful for "newly manufactured" chemicals.

Process characterization, as currently conceived, involves: 1) listing raw materials, known trace contaminants of raw materials, intermediates, products and byproducts; 2) characterizing reaction conditions and chemistries of production and waste treatment; 3) evaluating possible formation chemistries of trace contaminants in raw materials, intermediates and products based on chemical principles and logic; 4) characterizing facility hardware configurations to locate entry routes into the environment and optimum sampling points; 5) evaluating manufacturing and waste treatment cycles to determine optimum sampling frequency and duration; 6) listing candidate substances for which traditional/routine sampling and analytical methods are inadequate; and 7) developing or adapting appropriate sampling and analytical methods.

This protocol is described in detail in "Methodology For Estimating Environmental Loadings From Manufacture of Synthetic Organic Chemicals" (EPA-600/3-83-064).

4.5.2 NONPOINT SOURCES

Background

For the purposes of this chapter, the nonpoint source issues to be addressed include the movement of contaminants associated with urban and rural runoff, and groundwater transport of contaminants. For areas that contain a myriad of minor combined sewer overflows (CSOs), that cannot be effectively treated as point sources, some of the modeling techniques discussed earlier may be suitable to estimate their impact. Direct atmospheric deposition into bodies of water within the boundaries of the particular Area of Concern is assumed insignificant, deposition on land is transported via runoff, and the resuspension of contaminants deposited in sediments is addressed in the Sediments Section (6). The discussion of nonpoint sources presented here is designed to give those at the managerial level an adequate overview of the significant nonpoint issues and some awareness of their implications.

Additional technical information is listed in the references; however, this document assumes that competent, trained and experienced field personnel will carry out the required work with minimal dependence on this document for precise guidance.

Assessment of Nonpoint Source Pollution Issues

The flow chart presented in Figure 5 outlines a strategy to identify significant nonpoint sources and estimate their impact and to derive and assess the effectiveness of a remedial program. The flow chart and Table 13, which amplifies the issues noted in the figure, overlap information presented in other flow charts. This cross reference will place the nonpoint issues in context with other issues.

FIGURE 5

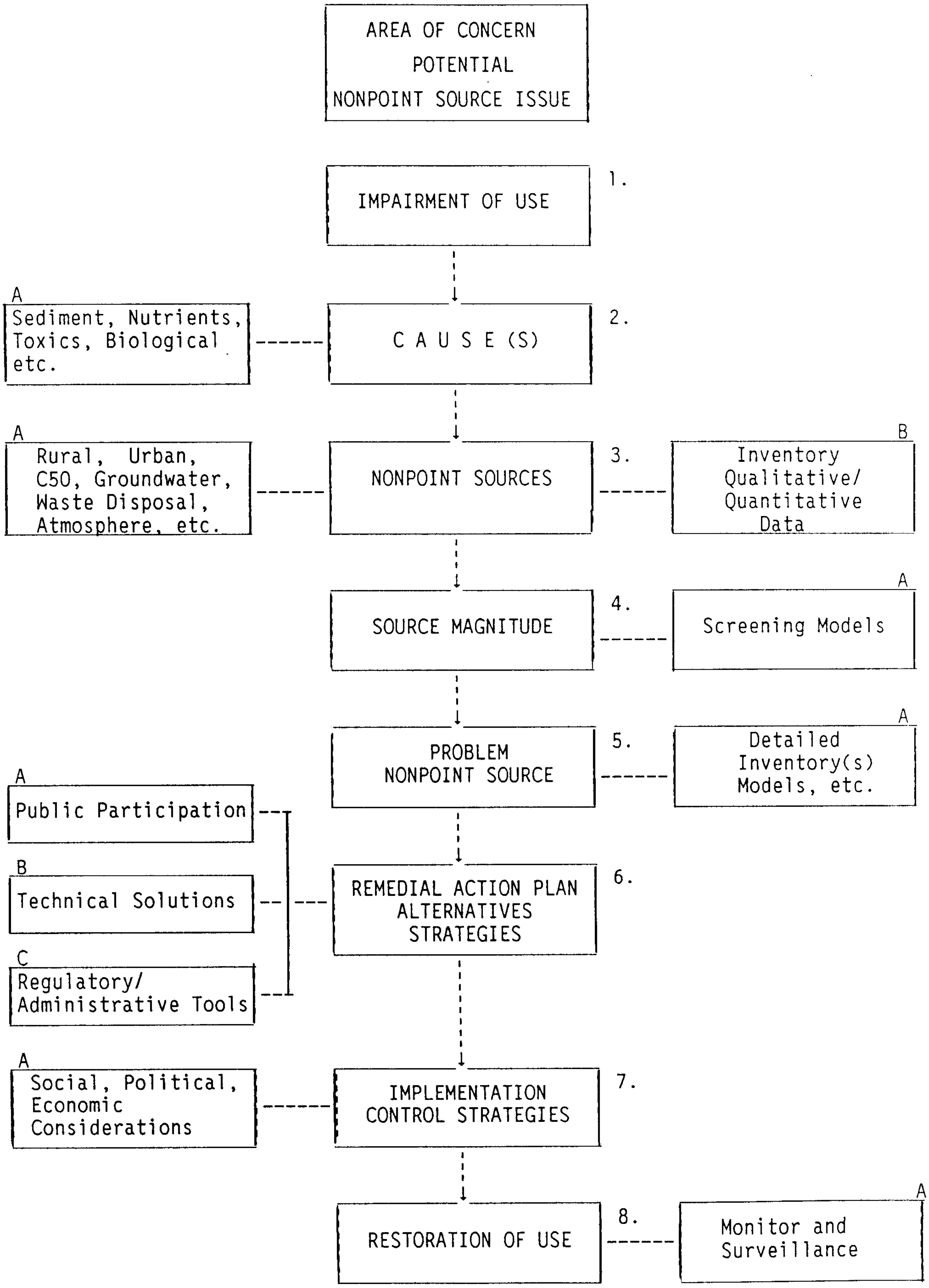
AREA OF CONCERN
POTENTIAL
NONPOINT SOURCE ISSUE
1.
IMPAIRMENT OF USE
A
Sediment, Nutrients, Toxics, Biological etc.
2.
C A U S E (S)
A
Rural, Urban, C50, Groundwater, Waste Disposal, Atmosphere, etc.
3.
NONPOINT SOURCES
B
Inventory Qualitative/ Quantitative Data
4.
SOURCE MAGNITUDE
A
Screening Models
5.
PROBLEM NONPOINT SOURCE
A
Detailed Inventory(s) Models, etc.
A
Public Participation
B
Technical Solutions
C
Regulatory/ Administrative Tools
6.
REMEDIAL ACTION PLAN ALTERNATIVES STRATEGIES
A
Social, Political, Economic Considerations
7.
IMPLEMENTATION CONTROL STRATEGIES
8.
RESTORATION OF USE
A
Monitor and Surveillance

TABLE 13, PAGE 1 OF 3

AREAS OF CONCERN: DESCRIPTION OF FLOW CHART

ASSESSMENT OF NONPOINT SOURCE POLLUTION PROBLEM

1. Impairments - Identify impairments that are restricting the use of the Area of Concern. Predominant impairments identified in the Areas of Concern include:

   Fish Consumption - Advisory
   Fish Population Degraded or Tainted
   Fish Tumors or Other Deformities
   Bird Deformities or Reproductive Problems
   Groundwater → Source Contamination
   Navigation/Dredging Restricted
   Degraded Benthos
   Eutrophication/Undesirable Algae
   Drinking Water Taste and Odor
   Beach Closings
   Aesthetics Degraded
   In-Place Contaminants (sediments)

2. Potential Causes (of Impairments)
   (a) General Causes
      - Sediment Issues
      - Nutrient Issues
      - Toxic Issues
      - Biological Issues
      - Other Issues

      Specific Identification of Cause(s)
      - Arsenic
      - Alkyl Lead
      - Heavy Metals
         Mercury
         Lead
         Cadmium
         Other
      - Phenols

TABLE 13, PAGE 2 OF 3

AREAS OF CONCERN: DESCRIPTION OF FLOW CHART

- Toxic Organics
  - PCBs
  - Furans
  - Dioxins
  - DDT
  - Mirex
  - Pthalates
  - PAHs
  - Chloroform
  - Trichloroethylene
  - Perchloroethylene
  - Carbon Tetrachloride
- BOD/DO
- Bacteria
- Phosphorus
- Other Conventional Pollutants
- Habitat Destruction

3. Potential Sources of Nonpoint Source Pollution
   (a) General Sources to be Evaluated
   Rural
   Urban
   Combined Sewer Overflow (CSO)
   Groundwater
   Waste Disposal Sites (Active & Abandoned)
   Atmospheric Deposition

   (b) Methods to Evaluate Potential Source
   - Inventories (existing or new)
   - Qualitative or Quantitative data (existing or new)
   - Unit Area Loadings (using existing, extrapolated or new data)

4. Relative Magnitude of Nonpoint Sources of Pollution

   (a) Establish which nonpoint sources of pollution are significant relative to the total pollution load (point and nonpoint)

   (b) Some screening models may be available to assist in establishing the relative significance of some of the nonpoint sources, e.g., rural nonpoint

TABLE 13, PAGE 3 OF 3

AREAS OF CONCERN: DESCRIPTION OF FLOW CHART

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5. Establish Significant Nonpoint Source Pollution Problem

   Conduct detailed investigations to provide sufficient information so that solutions to the problem can be proposed

   (a) Detailed inventories of site specific problem areas may be required. Detailed models may be available that may be used to obtain clearer definition of the problem or to test alternative cost-effective remedial programs.

6. Develop Remedial Action Plan Strategy(s)

   Use all existing data to develop remedial action plan(s)

   (a) Technical solution(s) to be developed

   (b) Employ regulatory/administrative tools to assist in plan(s) development

   (c) Public participation may be used to evaluate public concern over alternative approaches to solving nonpoint source pollution problems

7. Develop Implementation Control Strategies

   Illustrate a step-by-step implementation plan to control the nonpoint source pollution problem

   (a) Consider social, economic and political issues that may affect implementation

8. Restoration of Use

   (a) Develop time tables to illustrate the proposed restoration of use(s) that will result from the implementation of nonpoint source controls

   (b) Establish (if necessary) a monitoring and surveillance program that will track the progress of the nonpoint source pollution control implementation program and proposed restoration of use

In using the flow chart and associated table, the restrictions mentioned above should be recalled, i.e. atmospheric deposition in the particular geographic area is not considered significant, although a few exceptions to this generalization may become evident, and CSOs are a nonpoint issue only when it is impossible to address them as a point source. Some suggestions on locating available landfill site data have been offered in the point source section; once such sites are considered significant, appropriate sampling strategies are discussed in this section.

Methods to Evaluate Potential Sources and Determine their Magnitude

Landfill siting and content data may be available from municipal and other jurisdictional agencies, along with pesticide application or usage estimates for rural and urban settings. Runoff estimates from large parking lots, city streets and storm sewer loadings should also be available from various site-specific studies and will be useful in initial loading estimation.

While it is not practical to offer a comprehensive list of the quantitative or qualitative data that should be considered, a review of this document will indicate what additional data should be available or secured when assessing an Area of Concern. Water quality data from rural tributaries and groundwater, particularly individual wellwater, could be of great assistance in determining the potential significance of past or ongoing pesticide and fertilizer applications.

i) Modeling

Model application should be considered for the determination of potential nonpoint sources and for the estimation of their magnitude and significance. This segment provides an overview of models and their utility in predicting and determining the impact of nonpoint source pollution. Due to the variety of models available at this time and the significant resources required in using them, a brief outline of the principal characteristics of selected models and limitations is provided.

A more complete guide to nonpoint source models can be found in "Review and Analysis of Available NPS and Integrated Watershed Models" by A.S. Donigan Jr. et al., Anderson-Nichols & Co., Palo Alto, CA. Tables 14, 15 and 16 are reprinted from this report, which was prepared under contract to Woodward-Clyde Consultants.

Before considering the available information on specific models, the following points should be considered.

1) Modeling alone is not a panacea for determining impacts of nonpoint source pollution. To obtain data of any quality beyond that of a first approximation requires laborious calibration and verification. Field sampling programs and, ideally, an historical record of some length and detail are necessary for proper model calibration and verification.

TABLE 14

PRELIMINARY LIST OF NPS AND INTEGRATED WATERSHED MODELS SELECTED FOR REVIEW

MODELS	NAME	SOURCE	REFERENCE
Loading/Screening Procedure			
Hydroscience	Hydroscience Simplified Model	Hydroqual/EPA	EPA 1976
EPA Screening Procedures	EPA Water Quality Screening Procedures	EPA	McElroy et al. 1976; Mills et al. 1982
WLFNPS	Watershed Loading Functions for Non-Point Sources	Cornell Univeristy	Haith and Tubbs 1981
WRENS	Water Resources Evaluation of Non-Point Silvicultural Sources	U.S. Forest Service 1980	U.S. Forest Service
SWMM - Level I	SWMM - Level I	EPA	Heaney et al. 1976
NPS Runoff Models			
HSPF/PERLND & IMPLND	Hydrological Simulation Program - FORTRAN (land simulation modules)	EPA	Johanson et al. 1984
ARM	Agricultural Runoff Management Model	EPA	Donigian et al. 1977
NPS	Nonpoint Source Model	EPA	Donigian and Crawford 1977
CREAMS/CREAMS 2	Chemicals, Runoff, and Erosion From Agricultural Management Systems	USDA	USDA 1980
ANSWERS	Areal, Nonpoint Source Watershed Environment Response, Simulation Model	Purdue University	Beasley et al. 1980 Beasley and Huggins 1981
ACTMO	An Agricultural Chemical Transport Model	USDA/ARS	Frere et al. 1975
SWMM	Stormwater Management Model (land simulation modules)	EPA	Huber et al. 1975
STORM	Storage, Treatment, Overflow Runoff Model	COE	HEC 1977
MUNP	Management of Urban Nonpoint Pollution Model	Univ. of Maryland	Sutherland and McCuen 1978
ILLUDAS/DRAINQUAL	Illinois Urban Drainage Area Simulator	Illinois State Water Survey	Teratriep and Stall 1974
DRJM	Distributed Routing Rainfall-Runoff Model	USGS	Alley and Smith 1982a, 1982b
PRMS	Precipitation-Runoff Modeling System	USGS	Leavesley et al. 1983
Simplified SWMM	Simplified SWMM	EPA/M&E	Lager et al. 1976
Integrated Watershed Models			
HSPF	Hydrological Simulation Program - FORTRAN	EPA	Johanson et al. 1984
SWMM	Stormwater Management Model	EPA	Huber et al. 1975
PRS	Pesticide Runoff Simulator	EPA/CSC	CSC 1980
UTM-TOX	Unified Transport Model for Toxics	Oak Ridge/EPA	Patterson et al. 1983
SWAM	Small Watershed Model	USDA/ARS	DeCoursey 1982

Table 15 Characteristics and Capabilities of Selected NPS Runoff Procedures and Models

	LAND USE/LOAD SOURCES						HYDROLOGY			WATER QUALITY			TIME SCALE			DATA NEEDS			SPACE SCALE		
	Urban	Agriculture	Forest /Natural	Mining	Precipitation	Chemical: Application	Surface Runoff	Subsurface Flow	Snowmelt	Sediments	Nutrients	Pesticides/Toxics	Annual Loads	Event Loads	Continuous Simulation	Detailed	Moderate	Minimal	Segmented/ Multiple Catchments	Lumped/ Single Catchment	Use, Documentation, Support
LOADING/SCREENING PROCEDURES																					
Hydroscience	●						●		●		●		●					●		●	A/M
EPA Screening Procedures	●	●	●		●					●	●	●	●	●				●		●	A
WRENS			●				●		●	●	●	●	●					●	●		A
WLFNPS		●	●				●		●	●	●			●			●		●		M/A
SWMM - Level I	●						●	○		●	●		●				●			●	A
RUNOFF MODELS																					
Simplified SWMM	●						●				●			●	●		●		●		M
ARM		●				●	●	●	●	●	●	●		●	●	●				●	E/A
NPS	●	●	●				●	●	●	●	●			●	●	●			●		E/A
HSPF/PERLND & IMPLND	●	●	●	●	○	●	●	●	●	●	●	●		●	●	●			●		E
CREAMS/CREAMS 2		●	●			●	●			●	●	●		●	●	●				●	E
ANSWERS		●	●	●			●	●		●	●			●		●			●		A
ACTMO		●				●	●	●	●	●	●	●		●	●	●			●		M
SWMM	●						●	○	●	●	●			●	●	●			●		E
STORM	●						●	○	●	●	●				●		●			●	E
MUNP	●						●			●	●			●			●			●	M
ILLUDAS/DRAINQUAL	●						●	●			●			●		●	●		●		A
DR3M	●				●		●	○		●					●	●			●		A
PRMS			●				●	●	●	●				●	●	●			●		A

Notes: ● - Capability included in model

○ - Capability not explicitly included but can be user-defined

Use/Documentation/Support

E - Extensive

A - Adequate

M - Minimal

Table 16 Characteristics and Capabilities of Integrated Watershed Models

	WATERBODY & FLOW CONDITIONS						WATER QUALITY									TIME SCALE		DATA NEEDS		SPACE SCALE			
INTEGRATED WATERSHED MODELS	Rivers/Streams	Lakes/ Impoundments	Estuaries	Confined Flow	Drainage/ Control Structures	Point Source Discharges	Temperature	D.O./BOD/NBOD	Suspended Sediment Transport	Sediment Scour/ Deposition	Sediment Contaminant Interaction	Nutrient Kinetics	Pesticides/ Toxics	Biologic Simulation	Dynamic	Steady-State	Detailed	Moderate	Multi Land Use Multiple Catchments	Single Land Use Single Catchment	Data/File Management	Use, Documentation, Support
HSPF	●	●		○	●	●	●	●	●	●	●	●	●	●	●		●		●		●	E
SWMM (RECEIV)	●	●	●	●	●	○		●				●	○	●	●		●		●			E
PRS	●	●											●		●		●		●			A
UTM-TOX	●		●		●	●	○		●	●			●		●		●		●			M
SWAM	●	●					●		●	●		●	●		●		●		●			M/A

Notes: ● - Capability included in model

○ - Capability not explicitly included but can be user-defined

Use/Documentation/Support

E - Extensive
A - Adequate
M - Minimal

2) The original models were designed to estimate the loadings of conventional pollutants, e.g. as BOD, COD, nitrate, phosphorus, sediment and suspended solids. Since 1980, some have been adapted for heavy metal and toxic organic determinations, but this use is still under development.

3) While continuing improvements to microcomputer capabilities indicate that an increasing amount of modeling work can be done on these machines, the application of a sophisticated model that includes transport phenomena, to a watershed or basin of significant size continues to demand a high level of computer expertise and resources.

4) While more rigorous theoretical approaches are available, the entire area of nonpoint source pollution continues to contain a significant amount of the empirical estimation and application of gross assumptions (8).

Prior to the consideration of specific models, a review of the material outlined in Hartigan (1978) is appropriate. The variability evident in the meteorological and hydrogeological data, e.g. air quality, sampling techniques, study area homogeneity, public works practices, monitoring techniques and representative field studies, are factors to be emphasized in the application of a model.

a) Urban Models

An urban runoff model, the Macroscopic Planning model (MAC), was applied in the San Francisco Bay area in the late 1970s (W.G. Smith 1980). As a first approximation model, it is a composite of eight local Surface Runoff Plans and is of some utility for the broad prediction of possible impacts. The modelers suggest that the lack of local water quality and quantity data can be overcome with the use of historical records and national runoff data. Its utility in a specific Great Lakes Area of Concern would be limited.

HAZPRED (G. Zukors 1986), a model developed by Environment Canada and a Canadian consulting company, Canviro, could have some applicability to the urban Areas of Concern. The model is designed to predict concentrations and loadings of hazardous contaminants in dry weather sewage flow, urban storm runoff and combined sewer overflows. It will operate on an IBM PC-AT, and requires input data on concentrations of residential, commercial and industrial wastewaters, as well as the magnitude of dry weather infiltration. Estimates are determined by the application of various probability distributions.

HAZPRED is still under development and only the dry weather outputs have been verified. Additional verification against catchment data for precipitation events has yet to be carried out for specific basins, and any prospective users would be required to perform this verification. The Conservation and Protection Office of Environment Canada in Toronto (416-973-5840) can provide further details regarding this model.

characteristics; tillage methods, conservation practices, cropping patterns, pesticide use, irrigation flows and population densities.

An agricultural model which has been in use for some time is ARM (Agricultural Runoff Management). A.S. Donigan provides a manual describing the steps involved in applying this model to a watershed. ARM will simulate runoff, including that from snow accumulation and melting, and can incorporate sediment, pesticides and nutrients in its determinations. Pesticide degradation can also be estimated by the model, while specific soil zones and depths are also considered. However, it assumes uniform land use, and no channel routing procedures are included. Thus, it is restricted to watershed sizes of less than five square kilometers, depending on the complexity of the given terrain.

CREAMS (Chemicals, Runoff and Erosion from Agricultural Management Systems) is a more recent amplification of the ARM work. It is applied to field size plots and can incorporate toxic contaminants into its matrix.

One of the more recently developed models is ANSWERS (Areal Nonpoint Source Watershed Environment Response Simulation). A user's manual (Beasley and Huggins) outlines the purpose, theory and application of this model to watersheds with agriculture as their primary land use. The model is designed for application during and immediately following a rainfall event; it is a distributed parameter approach rather than a lumped parameter, and thus more demanding of computer facilities. However, its output should be a more accurate simulation of catchment behavior, since it avoids the assumed linear relationships often employed in lumped parameter models.

ANSWERS depends on the characterization of events within a number of small discrete "elements" of a subbasin or watershed. Element sizes vary from one to four ha within watersheds of less that 10,000 ha. Because a given study area may consist of numerous elements, costs for preparing an elemental data file can be significant.

ii) Groundwater Sampling

As intense effort and high cost are characteristic of groundwater sampling, the preliminary assessment procedures outlined in the previous sections should be implemented fully before initiation of any sampling is contemplated. If such an assessment indicates that further investigation is warranted, background information on geology, hydrology and soils should be assembled, where available. Information on engineering activities in the vicinity, including filled areas, buried trenches, storm drains, infiltration galleries and canals should be sought before any sampling is initiated.

Local private and public wells in the vicinity should be located and their pumpage determined or estimated. Water level data should be available from these wells which may indicate a need to monitor more than one aquifer system. Comprehensive analysis of selected water samples from such wells could also be considered as part of preliminary data collection.

Seismic techniques and ground penetrating radar are methods of mapping the subsurface geology. Resistivity surveys are useful in locating items with high metal content such as pipes and drums and can also determine the water table at relatively shallow depths. Although application of these techniques may not be feasible in all areas, their use should at least be considered in any intensive program to characterize groundwater because they are relatively inexpensive in comparison to drilling and sampling programs.

If groundwater sampling is required, it is strongly recommended that the following publication be among those reviewed in detail, "Practical Guide for Ground-water Sampling", by M.J. Barcelona, J.P. Gibb *et al.*, Department of Energy and Natural Resources, IL (EPA/600/2-85/104).

Additional useful information is also contained in "Site Assessment System for the Michigan Priority Ranking System under the Michigan Environmental Response Act (Act 307, P.A. 1982)," Michigan Department of Natural Resources, Site Assessment Unit, Groundwater Quality Division, P.O. Box 30028, Lansing, MI, 48909.

These publications explain the steps involved in the development of a viable long-term groundwater monitoring effort which are:

1. Evaluation of hydrogeologic setting and program information needs.
2. Proper well placement and construction.
3. Evaluation of well performance and purging strategies and
4. Execution of effective sampling protocols, which include the appropriate sampling mechanisms selection and materials as well as sample collection and monitoring procedures.

a) Essential Elements

Quality Assurance

Any valid groundwater survey must be subjected to a rigorous quality assurance program from the outset. Such a program extends beyond a concern for the quality of sample analyses to include such topics as the representativeness of the sample site(s), the selection of appropriate methods to develop and protect the well site(s) from contamination, selection of sampling procedures that minimize possible contamination, appropriate calibration of equipment, and maintenance of adequate descriptor records. All choices and decisions made during the program should be documented, along with the rationale associated with them and references to state of the art procedures, where appropriate. The entire exercise assumes a high level of training and expertise among the sampling crew.

Representative Groundwater Sampling

Groundwater sampling poses more difficulties in obtaining a representative sample than most other sampling programs. Significant temporal and spatial variation among samples taken at various sites can be anticipated in any groundwater sampling program, with high costs often precluding the execution of a program that will yield statistically representative data.

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Groundwater sampling poses more difficulties in obtaining a representative sample than most other sampling programs. Significant temporal and spatial variation among samples taken at various sites can be anticipated in any groundwater sampling program, with high costs often precluding the execution of a program that will yield statistically representative data.

The detail and precautions to be considered when planning a sampling program can only be addressed when a large amount of quality information is available from historical records, previous programs, remote sensing or a preliminary survey. The types and distribution of geologic materials, the occurrence and movement of groundwater through the materials, determination of the regional groundwater flow system, the relative permeability of the materials, and the subsequent interactions among these factors must all be considered.

It has been demonstrated repeatedly that the extent of an aquifer system can vary from the extremely localized to the regional. Guidelines are available in the literature for evaluating aquifer representation, either through a review of the historical record or a preliminary survey.

In addition, the sampling team must be aware of the influence of well placement, sampling frequency, the mobility and persistence of possible contaminants and the effect of their physical and chemical properties. It should be apparent that a thorough and complete determination of the representativeness of the data set may only be possible after extensive preliminary sampling.

As with any preliminary sampling activity, an assessment of the error associated with the selected sampling procedure and apparatus should be performed in the laboratory. While such an assessment must also be duplicated in the field, the laboratory determination will give some indication as to the lower limit of error which could be associated with the methodology, thus providing further guidance in the selection of specific methods. If an extensive laboratory verification is not possible, at least procedures and equipment which can be linked to proven procedures in the literature should be used.

Hydrogeologic Setting

The geological materials encountered in groundwater monitoring programs can be categorized as follows; 1) porous media, 2) fractured media and 3) fractured porous media. Porous media include sand and gravels, silt, loess, clay, till and sandstone. In fractured media, groundwater and associated contaminants move through cracks or solution crevices in material such as dolomites, shales, granites and crystalline rock. The third category embraces a situation where transport is occurring via both the porous and the fractured routes. Fractured tills, fractured sandstone and some fractured shales exhibit this behavior.

Once a determination of the geologic setting is made, the hydrology of the specific site must be assessed. Horizontal and vertical groundwater flow paths must be determined, as well as the approximate rates of such movement. Bulk flow rates are best estimated by hydraulic conductivity as a measure of the stratum permeability and gradient data from the testing of wells in the field. Laboratory testing to determine hydraulic conductivity often yields data which vary by orders of magnitude from the actual field values.

To estimate the actual or linear flow velocities, the effective (or dynamic) porosity of the material must be determined. Given that methods for measuring effective porosity are still under development, drainage porosity is often used as an approximation. Once these factors have been estimated, an approximate rate of travel can be determined which should indicate the number of monitoring wells required and their appropriate locations, as well as the sampling frequency.

Sampling Frequency

The frequency of sampling is dependent on the characteristics of the source being evaluated, that is whether it is a spill, slug, intermittent or continuous source. This assessment of source, coupled with the information discussed above, should be adequate to determine a preliminary sampling frequency.

b) Implementation of Sampling Program

Consideration of Parameters

Any successful sampling program must incorporate a robust, coherent sampling protocol and proven analytical schemes. Each step of the program development and sampling execution needs to be carefully documented. Rather than focussing immediately on the suspected contaminants of interest, the preliminary sampling program should collect more chemical and hydrogeological information than may appear to be immediately necessary. In a situation where no chemical data are available, complete mineral analysis should be performed in addition to the routine field determinations (pH, Eh, temperature, conductance and alkalinity). These results should allow definition of the major ion solution chemistry. The chemical data are valuable for obtaining a better sense of the subsurface system, and indicate what significant matrix effects can be anticipated to influence the sampling and analysis. Only when a complete mineral analysis and a careful assessment of information needs are in hand should any additional chemical parameters be considered.

Total dissolved solids content, e.g., Na, Cl, SO_4 is traditionally determined in any groundwater sampling program. In choosing sample collection and handling methods, degassing (loss of CO_2) and oxygenation, causing loss of iron and other trace metals, are typical of the concerns which must be addressed.

A common assessment approach is to enhance the collection of the traditional parameters with the analysis for TOC (Total Organic Carbon) and TOX (Total Organic Halogens). These two additional parameters may give a preliminary indication of the impact of waste releases on groundwater systems. Particular care must be taken in quantifying the volatile fraction of both TOC and TOX. Chemical parameters to be quantified in a typical detection monitoring program include pH, Eh, Ω^{-1} (solution conductivity) TOC, TOX, alkalinity, total dissolved solids, Cl, NO_3, SO_4, PO_4, SiO_2, Na, K, Ca, Mg, NH_4, Fe and Mn.

In further refining a list of parameters, the sampling team must be aware that the organic mixtures often present in samples include not only the pollutants of interest but their byproducts or substituted congeners as well.

Well Placement and Construction

While it is not the intention of this document to examine the placement and construction of wells in any detail, a few salient points deserve some emphasis. Before determining the placement of any wells, the contaminant flow path must be clearly defined in three dimensions. Once well drilling and construction begin, special emphasis must be given to the collection of accurate water level data. The selection of drilling equipment is, of course, dependent on the type of geology present, required sampling depth and equipment availability; however, the nature of the contaminants being sought and the required data quality must also be considered. The selected method should be one which minimizes the disturbance of the geological materials penetrated as well as the introduction of contamination by air, fluids and muds. Cost must not be the primary selection criterion for this phase of work since the effort and expense of other segments of a sophisticated sampling program will overshadow this particular element. Inappropriate techniques and equipment could severely compromise the utility of the data.

Once an appropriate drilling method has been selected, consideration should be given to well design. The well diameter should be held to the smallest practical size to minimize dilution and the chemical changes that can occur in standing well water. Diameters of five cm are preferable, except where sampling depths require use of larger diameters. Depth is also a factor in the selection of well casing materials. While Teflon™ is the preferred material to minimize sample contamination by the casing, its strength is not adequate for use at depths in excess of 100 M. Other materials, such as stainless steel, can be substituted in the upper casing segment while Teflon™ is used at the sampling level.

Screen size is another important consideration in the well design. The screen length should be held to a minimum (generally 60 cm or less) to ensure that the sample is from the stratum of interest. Screen slot size should be adequate to retain 90% of any gravel pack materials used around the screen. The pack material should also be as inert as possible; silica sand or glass beads are recommended. Should packing not be used, a slot size adequate to retain 60 to 70% of the materials opposite the screen should be used.

Wells should be sealed adequately to prevent the entry of water from the surface, or from formations above the sample depth. Sealing materials should also be isolated from the sampling level by a 30 cm layer of relatively inert material such as Ottawa or silica sand. All well construction details should be thoroughly and carefully documented by drilling logs and a well construction diagram. The use of multiple completion wells is not encouraged because the effectiveness of well seals between sampling points is often inadequate to prevent contamination.

Well Development

Proper well development to minimize the impact of intruding fines is an essential part of the sampling program. Water samples should be free of suspended solids; failure to achieve this goal could bias the chemical data and cause frequent clogging of field filtering systems. A number of techniques are outlined in the literature. Again, adequate cleaning of the well with minimal disruption of the subsurface sampling site is crucial in the selection of any particular technique.

In assessing the well performance, field determinations of the hydraulic conductivity should be made, instead of a laboratory determination. Conductivity tests should be performed on every well in the monitoring system to ensure that the hydraulics of the site are well understood and to provide information for determining sampling procedures and frequencies. Slug and bailing techniques, as described in the literature, can be used to determine hydraulic conductivity, or pump tests can be attempted. Hydraulic conductivity determined by any of these methods should not be considered any more precise than ±20%. Should execution of such tests to an adequate level of accuracy prove difficult or impossible, historical water level data can be analyzed by procedures also available in the literature.

Well maintenance procedures must be outlined and followed to ensure that samples from each location remain representative. Water levels should be monitored carefully; any exposure of the screened segment of the well to the atmosphere during a low water period can compromise the validity of the sample data. Turbidity or decreases in hydraulic conductivity may be indications of the need to redevelop particular wells. Chemical encrustation or bacterial growth on the well screen may also result in decreased well performance and an alteration in the chemical properties of the collected samples.

Sampling of Wells

The number of methods for measuring water levels range from the use of steel tape to pressure transducers. Again, a method should be selected which is consistent with the necessary data quality. Prior to the sample collection, wells must be purged of standing water since such water is not representative of aquifer water quality. Given the small surface area of the exposed aquifer being sampled and the preference for low purge and sampling rates, care should be taken to ensure that samples do not contain any portion of standing water. Mathematical techniques for determining the sources of water at various times in the sampling are available in the literature.

Sampling techniques and materials must be selected to ensure minimal well disturbance and sample contamination. The effect of any alteration in sampling protocol between the preliminary and the final program on data quality should be assessed by direct comparison sampling, e.g. a shift from bailing to the use of a bladder pump. Sampling for dissolved gases or volatile organics is particularly prone to significant error, and although further refinement of techniques is anticipated in the near future, positive displacement bladder pumps appear to offer more assurance of quality sampling than bailers, suction-lift or air-lift devices.

Selection of appropriate materials for each application in the well sampling program should be made on the basis of durability, ease of cleansing and the minimization of secondary effects such as sorption or leaching. Tubing is among the most critical selections to be made in the design of a sampling system. All commonly used tubing materials sorb organic compounds to some extent. The effect is most pronounced for polyvinyl chloride and silicon rubber. Teflon™ components appear superior to all other materials for groundwater sampling, and its use, alone or in combination with other structurally stronger materials, is encouraged.

In performing the preliminary sampling, a geologist should log the well. Head measurements should be obtained at various depths using temporary screens and water samples should be taken continuously as the well is drilled. Analysis of these samples could provide a preliminary water quality profile estimate through the well depth.

All preliminary sampling wells should be fully screened to discourage sample contamination. Geophysical properties can be noted while the hole is uncased. An indication of required screen size can also be obtained from the drilling data.

While many sampling programs incorporate sample filtration in the field, use of such a procedure while collecting TOX and TOC data should be discouraged. Settling and decanting is the preferred technique in this case; any necessary filtration should be performed in the laboratory. Filters constructed of materials appropriate to the sampling and analytical protocol should be used. Vacuum filtration of groundwater samples is not recommended.

Often it is best to perform analysis of inorganic constituents such as pH, alkalinity, ferrous iron, sulfide, nitrite and ammonium in the field, rather than preserve samples for shipment back to the laboratory. Every attempt should be made to minimize the time between sample collection and analysis.

c) Quality Assurance

Any sampling program must incorporate the use of field blanks and standards. Spiked samples and blind controls provide a realistic estimate of analytical recoveries and subsequent accuracy. All such measures should be performed for at least the most sensitive chemical constituents on each sampling date. Field spiked samples and blind controls should be prepared in the field by spiking stock samples into the appropriate background solution. Particular attention should be paid to the storage and transport of samples from the field.

Analysis of Samples

As emphasized previously, the analytical segment must contain the same level of quality assurance and documentation as all other aspects of the sampling program. Close and continued coordination among the field sampling team, the analytical staff and the supervisor of the project must be maintained to ensure that the objectives of the program are met through whatever necessary modifications. The analytical program should also be driven by the most sensitive parameter, but determinations of the quality of the other parameters analyzed must not be ignored. If possible, all samples should be analyzed by a single laboratory, with a second laboratory providing quality assurance through analysis of spikes and split samples.

d) Conclusion

The preceding discussion was extracted from a more comprehensive document to indicate the substantive issues which any groundwater sampling program must address. It should not be considered a complete guide; rather, it should encourage those who must undertake such programs to seek out the most current information in the literature and to retain competent staff with the level of experience such an effort requires.

4.6 CALCULATION OF RELATIVE LOADING

4.6.1 Information From the Water Section

After a boundary has been defined by the screening process, material fluxes from upstream and downstream boundaries become sources. Quantification of these fluxes is required to put the major sources in perspective. Ideally, these fluxes will represent background levels and should be near zero. In cases where the boundary flux is a major percentage of the total load, the boundaries have been inadequately defined.

For every parameter listed in an Area of Concern, synoptic loading estimates are required under a variety of meteorological conditions. At a minimum these would include spring runoff and low flow. Upstream loading estimates should be straightforward, especially if the stream gauge is nearby, but the downstream flux, if needed, may be difficult to quantify due to complicated hydraulics. The techniques for these procedures are described in the Water Section (5).

4.6.2 Information From the Sediment Section

Since the vast majority of Areas of Concern have significant quantities of in-place pollutants, the sediments in these areas must be considered as potential sources. The variables that influence the contribution of in-place pollutants include: current stress due to wind, high flow or ship traffic, and hydraulic action due to groundwater flow. Therefore, quantifying the relative contribution from sediments will include calculations for resuspension and diffusion. In some cases, the loading from in-place pollutants will be a major percentage of the total load and this will indicate a remedial action. However, in all cases, it is necessary to put the importance of sediment loadings in perspective. This is accomplished by a worst-case analysis that indicates the quantity of material available for reintroduction into the water column and its concentration. The techniques for this estimate are available and are described in the Sediment Section (6).

4.6.3 Relative Load Calculation

Once loading estimates are available from all major sources, the relative contributions can be estimated. However, it is necessary to use consistent time periods over which the determination is to be made. For example, if source estimates are available for the month of August, it would not be appropriate to use the following formula with boundary loads and in-place pollutant resuspension estimates from the spring runoff period. Once a consistent time frame is selected, the following equation should be used to calculate the relative contributions from each source:

$$\% L_i = \frac{L_i \times 100}{\sum_{i=1}^{n} L_i}$$

where L_i is the load in kg/day of source i over the appropriate time period
and $\sum_{i=1}^{n} L_i$ is the sum of all sources or the total load (including boundary fluxes and in-place pollutant loading estimates.)

The % L_is should be ranked from highest to lowest and presented in a table. The table should include the name of the source, the rank, the percentage of the total load (% L_i) and the cumulative percentage.

REFERENCES

Auer, Martin T. et al. Trophic State Response to Nonpoint Pollution Control: Application of Coupled Microcomputer Models to the Great Lakes. Michigan Tech. Univ., Dept Civil Eng., Houghton, MI.

Ball, R.O. and C.A. Vath. 1984. Selection of Statistically Appropriate Compliance Sampling Intervals, ERM-North Central, Inc., 200 South Prospect Avenue, Park Ridge, IL, personal communication.

Beasley, D.B. and L.F. Huggins. ANSWERS User's Manual. Purdue Univ., Agricultural Eng. Dept., West Lafayette, IN.

Brusick, D. 1980. Principles of Genetic Toxicology. Plenum Press, N.Y. and London.

Donigan, A.S. et al. 1976. Modeling Nonpoint Pollution from the Land Surface. Hydrocomp Inc., Palo Alto, CA, July, 1976.

Donigan, A.S. et al. 1978. User's Manual for Agricultural Runoff Management (ARM) Model. Hydrocomp Inc., Palo Alto, CA, 1978. (EPA-600/3-78-080)

Hartigan, J.P. et al. 1978. "Calibration of urban nonpoint pollution loading models". ASCE Specialty Conf. Verification of Mathematical and Physical Models, Proc. College Park, MD, August 9-11, 1978.

Heaney, J.P. et al. 1979. Urban Stormwater Management Modeling and Decision Making. Univ. Florida, 1975. (EPA 670/2-75-022)

Heidtke, T.M. and J.M. Armstrong. 1979. "Probabilistic sampling model for water quality management." J. Water Pollut. Control Fed. 51(2):2916-2927.

International Joint Commission, Pollution From Land Use Activities Reference Group. 1980. Pollution in the Great Lakes Basin from Land Use Activities. An IJC Report to the Governments of the United States and Canada. International Joint Commission, Windsor, ON.

McElroy, A.D. et al. 1976. Loading Functions for the Assessment of Water Pollution from Nonpoint Sources. Midwest Research Institute, Kansas City, MS, 1976. (EPA-600/2-76-151)

McCarty, P.L. and E.M. Aieta. 1984. "Chemical indicators and surrogate parameters in water treatment." J. Am. Water Works Assn., October: 98-105.

Oliver, R.M. 1985. "Predicting future pollution exceedances under emissions controls." Environ. Sci. Tech. 19(3):225-231.

Schweitzer, G.E. and S.C. Black. 1985. "Monitoring statistics." Environ. Sci. Tech. 19(11):1026-1030.

Smith, Metcalf and Eddy Inc. 1980. "Use of a simplified surface runoff model," Kuo Chin, ed., National Symp. Urban Stormwater Mngt., Proc., Palo Alto, CA, June 19-20, 1980.

Southerland, E. et al. 1981. "A continuous simulation modeling approach to nonpoint pollution management". WPCF Annual Conf., Detroit MI, Oct. 4-9, 1981.

Waters, M.D. et al. 1980. "Short-term bioassays in the analysis of complex environmental mixtures II." 2nd Symp. Application of Short-Term Bioassays in the Fractionation and Analysis of Complex Environmental Mixtures, Proc., Williamsburg, VA, March 4-7, 1980.

Wullschleger, R.E. et al. 1976. Methodology for the Study of Urban Storm Generated Pollution and Control. Envirex Inc., Milwaukee, WI. (EPA-600/2-76-145)

Zukors, G. et al. 1986. Development of the HAZPRED Model. Canviro Consultants Ltd., Toronto, ON. Submitted to the Stormwater and Water Quality Model Users Group.

5.0 GUIDANCE FOR WATER MONITORING IN AREAS OF CONCERN

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5.1 INTRODUCTION

All but three of the 42 Areas of Concern currently designated in the Great Lakes basin have identified problems associated with one or more toxic substances (metals and/or synthetic organic chemicals) i.e. concentrations exceed guidelines or objectives for the protection of aquatic life, human health, or for the open water disposal of dredged materials. These problems relate almost exclusively to contaminant concentrations in fish tissue and sediments. For organics, specifically, there is a paucity of data on the concentrations of these substances in ambient water. This is not surprising given that reliable quantification of these substances at the extremely low concentrations generally encountered in water usually requires applying state-of-the-art sampling and analytical methodologies, which are not generally used by most agencies charged with routine surveillance and monitoring responsibilities. Even when these more sophisticated methodologies are used, concentrations for the majority of these organic compounds in the water column are either non-detectable or extremely low, i.e. in the pg/L, e.g. dioxins, furans, to ng/L, e.g. PCB, HCB range.

A plethora of "standard methods" have been published for a number of these compounds in various environmental media. Unfortunately, the detection limits are not sensitive enough to provide quantitative results for concentrations normally encountered in ambient water samples. Consequently, we are usually faced, in both this situation and in situations where no published "standard methods" exist, with having to accept or reject data generated by individual investigators who have either developed their own methodology or modified existing ones. This brings into question the whole issue of method validation, QA/QC, etc. Even using acceptable state-of-the-art techniques and quality control procedures, the precision and accuracy of analyses performed at these low levels may be subject to considerable variation. This inherent high degree of variability in results, caused by methodological and natural factors, increases the difficulty in interpreting the data and obtaining a good definition of the significance of the problem and thus the most effective remedial actions.

Methodological considerations aside, where reliable data do exist, they indicate that the concentrations of metals and organics exhibit a large degree of spatial and temporal variability in the water column. Furthermore, there are considerable differences in how various metals and organic compounds or classes of compounds partition themselves between the "dissolved" and "particulate" phases in water.

The formation of particles by chemical reactions and biological processes and their role in the cycling and removal of chemicals in natural waters have been of interest for at least a century. The distribution of chemical substances between "solution" and the suspended particulates has been widely recognized as a major factor in their geochemical behavior, transport and biological effects. Different results have been noted when comparing batch extraction techniques on whole water samples versus summing the analytical results from samples which have been phase separated, i.e. "dissolved" + particulate fractions. This is probably due to different extraction efficiencies using the two approaches. The differences appear to be greater with increasing particulate concentrations (B. Oliver, CCIW, NWRI, pers.

comm.) This could be significant in some of the harbor and river mouth Areas of Concern.

Given these considerations, it is strongly recommended that ambient water samples be phase separated into "dissolved" and suspended particulate fractions prior to analysis and that the concentration of suspended particulate material in the water also be quantified. It should be noted that all future references to analysis of "water" in this section should be interpreted as analysis of both the "dissolved" and suspended particulate phases.

While ambient water is a good medium for monitoring concentrations of metals, major ions, nutrients and hydrophilic organics, e.g. NH_3, phenols, it is not the best medium for measuring hydrophobic organics. These are, in most cases, the classes of substances identified as causing problems in the 42 Areas of Concern. A more cost-effective strategy for remedial actions could be developed by monitoring specific sources. In this regard, Figure 1 of this document, which outlines the generalized process for developing a remedial action plan, emphasizes the importance of water measurements in defining problem sources.

Despite the difficulties, there are many reasons why knowledge of trace contaminant concentrations in the water column is desirable. Water is the primary transport mechanism for substances into the system and their ultimate removal either to recipient water bodies (i.e. lakes) or to sinks (i.e. sediments and atmosphere). By introducing and dispersing these substances in the system, water is the initial exposure route to organisms and sediments in the system, and the subsequent absorption/adsorption and bioaccumulation mechanisms that further distribute these substances throughout the various environmental compartments. With few exceptions, e.g. determination of compliance with established water quality criteria; determination of trends in concentrations, measurements of trace contaminant concentrations in water alone do not provide a strong basis for determining impact and consequently the need for remedial actions or the effectiveness of such actions. Even those exceptions cited have not been without their difficulties in interpreting and applying the results (this is further discussed below). The importance of measurements in water relates directly to the extent to which these measurements augment data collected on sources and measurements on biota and sediments. Water measurements provide a better understanding of the nature and extent of the problem, a better definition of impact, a focussing of efforts to remediate sources, and aid in tracking the effectiveness of these actions. These are the stages, in effect, to characterize and deal with an Area of Concern.

5.2 APPROACH

Characterizing problems in an Area of Concern requires careful consideration of the sampling program design and analytical protocols including sample location, number of samples, number of replicates, sampling frequency, sampling devices, sample handling techniques, analytical methods, sample storage, parameters to be measured, etc. The variation in the types and sources of problems and the different hydrodynamic regimes of the 42 Areas of Concern precludes the development of any generic water sampling plan with the level of detail that would provide adequate data for every area. There are, however, some fundamental considerations in setting up any water sampling and analytical program. The general statistical considerations for sampling design are addressed in Section Seven of this document. Consequently, the approach taken in the remainder of this section is to consider, in general terms, why the measurement of trace contaminants in ambient water is a concern; considerations for sample collection and preparation; and some general guidelines on analytical protocols which would provide state-of-the-art data.

5.3 WHY MEASURE AMBIENT WATER?

As stated in the Introduction, water is probably not the best medium for characterizing problems in these 42 Areas of Concern, considering the problems and chemical compounds present. Indeed, when determining the nature and extent of a problem, measurements in water are important only insofar as they augment measurements in other media and/or delinate sources of the problem, including inputs and upstream/downstream extent of influence. The Water Group was consequently faced with answering the question of the utility of sampling ambient water.

In answering this question, the Group identified seven categories for which measurements of trace contaminants in water would be important. These seven categories and their implications in terms of management of the problem in an Area of Concern include:

CATEGORY		MANAGEMENT IMPLICATION
1. Source identification 2. Loading contributions 3. Compliance	} 1.	Problem identification/verification - nature/extent/sources
4. Pathways 5. Biological impact	} 2.	Problem understanding - impact
6. Trends	} 3.	Success of remedial actions
7 Emerging problems	} 4.	New potential problems

Two points regarding the categories presented above need to be emphasized. First, while the categories are listed in a linear fashion, they form an iterative process along with their associated management implications. Specifically, results from categories six and seven could indicate the need for new or additional work in categories one through five. Second, and most significant, the major requirements for water measurements are directly related to categories one through three, i.e. characterizing/ verifying the toxic substances problems in Areas of Concern, nature, extent and sources. Assessment of impact relies almost exclusively on measurements in other media, specifically sediments and biota. Each of the seven categories are discussed below with some brief comments where applicable on possible limitations.

Source Identification: The ultimate objective in Areas of Concern is to restore beneficial uses by ameliorating the problems that cause degradation. Implicit in this goal is identification and remediation of problem sources.

Many studies have been useful for tracking specific or previously unrecognized sources by analyzing ambient water for concentration gradients of particular contaminants. Unless some previous information is available on chemical inventories, e.g. source monitoring, this can be hit or miss and consequently an expensive approach to the problem. Considerable debate has taken place over whether problems or potential problems should be identified and perhaps averted by the implementation of a good point source monitoring program or whether point source monitoring requirements should be dictated by the identification of problems in the "ambient" environment. There are obviously cases in which each approach would be more advantageous. Where sources are known, it is more desirable to analyze samples collected from point sources rather than ambient water samples. Concentrations in the effluent will be higher and, despite problems that may be encountered as a result of effluent matrix problems and/or variations in concentrations due to process changes, the difficulties are not as great as those associated with measuring the extremely low concentrations likely to be encountered in ambient water samples. Furthermore, it is possible that by the time many of the organics of concern reach detectable concentrations in ambient water, other problems will have already manifested themselves at higher levels in the food chain.

Loading Contributions: Two aspects of loading contributions are important for characterizing Areas of Concern. First, define the boundaries of the river or harbor area to be assessed. This will require collecting samples at or near the upstream and downstream boundaries. Loading calculations at these boundaries (inputs and outputs) will require accurate flow measurements and a knowledge of basin hydrodynamics. Second, determine the relative magnitude of all source inputs to the Area of Concern; a knowledge of incoming substances from upstream and; to some extent, what is leaving the area at the lower boundary is necessary.

Samples of "dissolved" and suspended particulates should be analyzed for contaminants of interest and the concentrations of suspended solids should be quantified. The dissolved phase should be extracted in the field as soon as possible after collection to minimize chemical loss due to volatization.

To reduce costs, samples could be composited prior to analysis provided the objectives of the study are not compromised. Due to the inherent heterogeneity of aquatic systems, sampling frequency in time and space must be designed to meet the specific objectives, thus providing data with acceptable levels of confidence. Implicitly, this requires a knowledge of the variation to be expected in the system at the boundary locations. Often this information is not well defined beforehand.

Once again, the Water Group is of the opinion that where sources are known, it may be more cost-effective to monitor these.

Compliance: Jurisdictions have established water quality standards and Canada and the United States have established specific numerical objectives under the 1978 Great Lakes Water Quality Agreement. Measurements should be made to determine if contaminant concentrations in water exceed these standards and objectives. By definition, exceeding these objectives should be recognition, *de facto*, that there is a problem. Unfortunately, few standards and objectives for trace contaminants are based on their concentrations in water.

Furthermore, there appears to be no consistent definition among or even within jurisdictions as to what constitutes "compliance" with these objectives and standards. The decision in many cases seems to revert to subjective judgement. This issue needs to be resolved so that the ground rules are consistent in their application to all Areas of Concern.

Pathways: Analysis of ambient water samples is necessary for understanding pathways of trace contaminants in the ecosystem. The overall approach needs to be closely integrated with the sampling of sediments, biota and other media to ensure a meaningful interpretation of results.

Biological Impacts: Determining the relationship between concentrations of trace contaminants in ambient water and their effects throughout biological communities in Areas of Concern is limited by our inability to sort out complex interactions. Modelling is one tool used to address this complexity, but even models are based on more fundamental knowledge of the empirical relationships among chemicals and organisms.

Monitoring ambient water can identify chemicals of concern (see Emerging Problems below) but adverse biological effects will require much longer-term studies on a site specific basis (see also discussion on Bioassays, Section 3.4).

Trends: Ambient water is a good medium for monitoring trends in the concentrations of nutrients, metal ions and hydrophylic organics. It is not the best medium for monitoring hydrophobic organics which are, in most cases, the chemicals of concern in these areas.

Emerging Problems: Annex One of the 1978 Canada-United States Great Lakes Water Quality Agreement states that for those persistent toxic substances for which there are no specific numerical Agreement objectives ("Unspecified Organic Compounds"), they should be "substantially absent in water or aquatic organisms, i.e. less than detection levels as determined by the best scientific methodology available."

Ambient water samples should be analyzed annually in the spring during the high run-off period for rivers and under well mixed conditions in harbors for previously undetected organic and inorganic contaminants. In the case of organics this could be accomplished by a GC/MS scan in the full mode with appropriate follow-up work. In general, water is less temporally integrated than sediments and fish, and thus is a useful medium for identifying new compounds entering the system.

5.4 SAMPLE COLLECTION AND PREPARATION

Representative Sampling: Based on the analysis of existing data for the area and the hydrological data, including the influences of lateral and vertical heterogeneity, the sampling locations and times should be designed to be as representative of the environmental condition as possible. Composite sampling over extended time periods is preferred to grab sampling except when studying concentration variability. At least a river mouth station and a station upstream of potential sources should be established to define the boundaries for Areas of Concern; additional sampling stations should be established using a grid system for harbors and bays.

Collection: Dip sampling with appropriate bottles or containers is acceptable for small samples. Noncontaminating submersible pumps are available for pumping larger volume samples from the appropriate depth. Transfer tubing should be teflon or well-leached plastic to minimize possible interactions between the chemicals in the water and the walls of the tubing.

Phase Separation: All samples should be phase-separated into "dissolved" and "suspended particulate" fractions prior to analysis. Although this produces twice the number of analyses compared with using only "whole water" samples, the information gain for assessing impacts and pathways is well worth the extra effort. Either pressure filtration (preferred to vacuum filtration to minimize volatilization losses) or centrifugation are the selected methods. Both methods isolate a particulate and an operationally-defined "dissolved" fraction. Glass fibre filters (nominal pore size 0.3-0.4 μM) are normally used for the filtration process. Prior to use, filters for organics are muffle furnaced at 500°C to destroy potentially interfering compounds, and filters are acid treated prior to use for metal analysis (Fox 1985). Continuous flow centrifuges are also available. They recover most particulates (>0.2 uM) from water samples, including the Westfalia Separator, 9-10,000 RPM) (Thomas and McMillan 1978). Whatever method is used, the concentration of suspended solids in the sample must be quantified.

Note: A need has been identified to assess and compare the filtration and centrifugal methods for phase separation. Development of a method to separate the biotic component from the inorganic component of suspended particulates would also be of considerable use for assessing contaminant bioavailability.

5.5 LABORATORY TECHNIQUES

Organic Analysis:

"Dissolved" Component: The preferred method for isolating organic chemicals from water is by liquid-liquid extraction (LLE). The water sample is shaken or stirred with the appropriate immiscible high-purity solvent (dichloromethane and hexane are most often used) for a sufficient length of time to efficiently extract the organic (B.G. Oliver and K.D. Nicol 1984). Some pH adjustment to the water prior to LLE will be required for acidic or basic compounds. Samples for volatile organics should be collected in headspace-free vials to minimize compound loss and returned to the laboratory for purge and trap analysis (Longbottom and Lichtenberg 1982). If processing of the samples is not carried out in the field, the samples should be refrigerated at 4°C until extraction. The volume of water sampled is a critical factor in determining the detection limits of the organics under study. An easily achievable and practical volume for final cleaned-up extract is about 1 ml. Therefore, if a 20-liter sample is collected, a 20,000 fold concentration factor can be easily achieved prior to laboratory quantification. For samples up to 20 L, one gallon solvent bottles or 20 L stainless steel containers, e.g. soft drink containers, can be used for sample collection, storage and extraction. The largest volume batch extractor that has been tested and used is the Canada Centre for Inland Waters' 200 L APLE extractor which employs a 200 L stainless steel barrel for sample collection and extraction (McCrea and Fischer 1984; Oliver and Nicol 1985).

Particulate Component: Wet suspended particulates on filters or recovered from centrifuge bowls are usually soxhlet extracted for 24 hours to extract the organics. The solvent mixture 41% hexane/59% acetone is one common solvent combination that has been used for this type of analysis (Oliver and Nicol 1982).

Extract Cleanup: Extracts of the "dissolved" and particulate components must be cleaned up to remove interfering substances such as lipids prior to gas chromatographic quantification. Some combinations of gel permeation (size exclusion) chromatography, adsorption chromatography on Florisil™, silica, or alumina, or direct treatment with H_2SO_4 or H_2SO_4 on silica gel are common methods for sample cleanup. The method will vary with different chemicals. Some sulphur removal procedures (vortexing with mercury or copper filings) may be required for the particulate extracts.

Quantification: Due to its high resolution capabilities, capillary gas chromatography is the recommended approach for analyzing organics in water. A mass spectrometer or mass selective detector, with single ion monitoring (SIM) required in most cases to achieve the necessary sensitivity, is preferred for this analysis. Other selective detectors such as the electron capture (EC), photoionization (PI), etc., can be used after preliminary GC/MS data identify the significant presence of the chemical in the study area (Eadie et al. 1982; Oliver and Nicol 1984). The EC and PI detectors are best employed with a dual capillary column system in which two different polarity columns are used. Agreement between the two columns provides more confidence in the data and in the peak identification. Packed gas chromatographic columns probably do not provide enough efficient separation to be useful in water analysis.

Detection Limits: Presented below are examples of detection limits based on the dissolved component in a 20 L water sample and for particulates, that can be reasonably achieved with current state-of-the-art methodology:

Detector	Compound	Approximate Detection Limit (ng/L)
MS/SIM	Chlorobenzenes	0.5
EC	Dichlorobenzenes	0.5
EC	Hexachlorobenzene	0.005
PI	PAHs	0.5

Particulates Detector	Compound	Approximate Detection Limit (μg/g)
MS/SIM	Chlorobenzenes	10
EC	Dichlorobenzenes	10
EC	Hexachlorobenzene	0.1
PI	PAHs	10

It is always best to work at concentrations of at least 5-10 times detection limits when analyzing environmental samples (Keith et al. 1983). For the identification of emerging problems using GC/MS in the full scan mode, the detection limits are increased by approximately 100 times. Thus, large volume (1,000 liter) samples should be extracted for this purpose.

Metal Analysis:

Dissolved Species: The recommended procedure is a variation of the method developed by Riley and Taylor (1968, 1972) which has been studied and validated in many field investigations (Hart and Davies 1977; Lee et al. 1977; Lum and Leslie 1983). Essentially metal species (Al, Fe, Mn, Cu, Ni, Cr, Cd, Pb, Zn, Be, Co, Ag, V) are preconcentrated on a chelating ion-exchange resin (Chelex-100™, ammonium form) in the field. The resin can be brought back to the laboratory or if time and facilities permit, the resin can be eluted with dilute acid in the field. The usual concentration factor obtained is 40 (1 L to 25 ml).

The Chelex™ eluates can be analyzed by a variety of instrumental techniques depending on the elements desired. Cd, Pb, Cu, Co, Al, Fe and Ag should be analyzed using graphite furnace Atomic Absorption Spectrophotometry, (AAS) except for samples from grossly contaminated sites. The remaining elements can be analyzed using either a plasma emission spectrometer or flame AAS system.

Additionally, a check on the accuracy of the cadmium and zinc determination can be done through direct injection graphite furnace AAS. This may be the only alternative for samples from areas where the concentration levels are near background levels.

This procedure has the advantage of providing information on dissolved metal ion concentrations at ambient pH. Filtered or centrifuged water samples still contain particles which can release their adsorbed metal ions into the dilute acid commonly used to preserve the samples. While it may in principle be possible to chelate and solvent extract water samples at their ambient pH to estimate the dissolved bioavailable metal forms, the procedure requires an organic solvent to be taken into the field. Thus, one extra step is required compared with the chelating ion-exchange procedure viz., back extraction into acid to stabilize the concentrates and to provide a suitable matrix for graphite furnace AAS analysis.

Particulate Metals:

Particulates on Filters: The recommended procedure for particulates on acid-cleaned filters is: a) leaching with 1N HCl for two hours at room temperature and b) digesting the residue with aqua regia and HF or suitable substitute. The former reagent elucidates potentially available metal forms. Metal forms extracted by 1N HCl are well-correlated with bioavailability associated with polychaete worms and bivalves (Luoma and Bryan 1978; 1982). Elevated metal concentrations in water and sediment occur in many of the Areas of Concern. Identification of bioavailable metal concentrations is vital given their potential biological impacts (Kauss et al. 1981; Kauss 1983). The sum of the two extracts yields the total elemental concentration. The extracts are analyzed by graphite furnace and flame AAS, and plasma emission spectrometry.

Bulk Particulates: For a single, large volume (1,000 litres) sample collected for identification of emerging problems, it is recommended that 0.5 gram (dry weight) be subjected to a sequential chemical extraction procedure, which provides an operationally defined speciation (Tessier et al. 1979; Lum and Edgar 1983). At each step, a certain percentage of the total elemental content is extracted, giving an estimate of the strength of association/bonding to the particulate phase. Because the weakly bound forms are more likely to be bioavailable, this procedure will assess the potential risk associated with particulate-bound elements. The extracts may be analyzed by flame AAS or plasma emission spectrometry.

Detection Limits:

Dissolved Species: Element Detection Limit (µg/L) Cd 0.010, Pb 0.010, Cu 0.050, Zn 0.050, Ni 0.10, Cr 0.050, Co 0.050, Ag 0.010, Mn 0.10, Fe 0.10, V 0.050.

Particulate Species: Element Detection Limit (µg/g) Cd 0.05, Pb 1.0, Cu 0.10, Zn 1.0, Ni 0.50, Cr 0.50, Co 0.50, Fe 1.0, Mn 1.0, V 0.50.

5.6 MEASURING BIOLOGICAL EFFECTS

Water quality monitoring in Areas of Concern can be used to determine the possible biological impacts of environmental contaminants. Chemical analyses combined with structure activity relationships and toxicological data can be used to estimate persistence, solubility, bioaccumulation rates, and in some cases, the acute and chronic effects of chemicals on aquatic organisms. There remains the difficulty, however, in sorting out the numerous complex interactions between chemicals and organisms.

Sensitive bioassays are the most accurate way to assess the biological impact of water quality in Areas of Concern. A number of bioassay protocols have been developed for fish and invertebrates. These procedures are reviewed by Maciorowski et al. (1980). Cairns, Dickson, and Maki (1982) describe the applicability of these tests for assessing the hazard of toxic chemicals to aquatic ecosystems. This approach was developed primarily to assess the potential hazard of single chemicals, but the technique has been successfully used to estimate the hazards of complex industrial effluents and receiving waters (Sprague 1973). Sequential tier testing begins with acute lethal toxicity to fish and invertebrates (usually Daphnia) and progresses towards more sensitive sublethal indicators of adverse effects. These include embryo/larval toxicity tests and adverse effects on reproduction. A typical sequential hazard assessment scheme might be:

- Static 96-hour acute lethal fish bioassay
- Seven-day, 3-brood Ceriodaphnia bioassay
- Flow-through fish bioassays

- Algal toxicity tests

For additional information on bioassay procedures see Section 3.4.

Algal Bioassays: Fish bioassays are time consuming, logistically difficult and almost always limited to one or two species under laboratory conditions. On the other hand, algal bioassays are of short duration, require very little test material and, perhaps most importantly, are suitable for multi species testing _in situ_. Wong and Couture (1985) reviewed a variety of techniques available for algal toxicity testing. These included cell growth, fluorescence, C-14 assimilation, enzymes, adenylate energy charge and nucleic acids. These tests are particularly interesting because of their sensitivity and applicability as field bioassays.

Sensitivity of phytoplankton to toxic chemicals is well known; Wong _et al_. (1978) demonstrated that metal mixtures (at concentrations equal to water quality objectives) were toxic to phytoplankton. Similarly, Munawar and Munawar (1982) reported that metal mixtures inhibited photosynthesis in natural phytoplankton. More recent studies by Munawar _et al_. (1983), using sediment elutriate, showed that natural assemblages of phytoplankton were adversely affected (reduced C-14 uptake) by contaminants released from the sediment. The same technique may be useful in determining the relative toxic contributions of contaminants dissolved in the water phase and those adsorbed onto suspended sediments.

Prediction of Toxicity: Water quality monitoring is inappropriate for predicting adverse effects of hydrophobic contaminants such as PCBs, dioxin and mirex. Their solubility is below the concentration which causes acute or chronic biological effects; however, high contaminant levels in fish tissue can cause adverse effects. Lipophilic contaminants in water and suspended sediment strongly suggest that sediment and biota are bioaccumulating these substances. Estimates of bioconcentration and chemical fate can be made from partition coefficients (Branson 1978) but concentrations in water are unsuitable by themselves to predict biological impacts. This does not diminish the value of hazard assessment from chemical structure. Stern and Walker (1978) emphasized that predictions of chemical fate were essential components of the hazard assessment process by identifying the extent of chemical distribution, the chemical forms and concentrations, and the most likely biological targets.

5.7 GENERAL RECOMMENDATIONS

1. A clear and complete specification of objectives, including questions to be answered, hypotheses to be tested and parameters to be estimated, should be established at the beginning of this effort.

2. All available data and information should be compiled and subjected to statistical analysis in view of the objectives and other information (if necessary) to identify sources of variability present in the data.

3. Decisions should be made on the adequacy of the available information for planning a program to meet the objectives. If it is inadequate, a preliminary study should be planned to obtain the necessary data.

4. A plan should be developed which includes all details related to location, depth, time and frequency of sampling; measurements to be made (including phases and substances); number of replicates; and an outline of the method of statistical analysis.

5.8 SPECIFIC RECOMMENDATIONS FOR WATER

1. Ambient water is a useful medium for estimating loadings: identifying sources; understanding pathways and biological impacts; and evaluating compliance, trends and emerging problems.

2. However, ambient water is not always the best medium for the monitoring of contaminants. A much more cost effective strategy could be developed around the monitoring of specific sources. More emphasis should be devoted to point source monitoring.

3. Samples of ambient water should be analyzed annually in the spring (well-mixed period) to identify previously undetected organic and inorganic contaminants.

4. A need has been identified to assess and compare the filtration and centrifugal methods for phase separation. Development of a method to separate the biotic component from the inorganic component of suspended particulates would also be of considerable use for assessing the bioavailability of contaminants.

5. Research on methods to measure organic contaminants in pore water and water near the sediment-water interface is required in order to assess the importance of desorption from in-place sediments.

5.9 REFERENCES

Branson, D.R. 1978. "Predicting the fate of chemicals in the aquatic environment from laboratory data." In: Estimating the Hazard of Chemical Substances to Aquatic Life, J. Cairns, Jr., K.L. Dickson and A.W. Maki, eds., American Society for Testing and Materials Special Tech. Pub. 657, Philadelphia, PA, pp. 55-70.

Cairns, J. Jr., K.L. Dickson and A.W. Maki, eds. 1978. Estimating the Hazard of Chemical Substances to Aquatic Life. American Society for Testing and Materials Special Tech. Pub. 657, Philadelphia, PA.

Eadie, B.J., P.F. Landrum and W. Faust. 1982. "Polycyclic Aromatic Hydrocarbons in Sediments, Pore Water and the Amphipod Pontoporeia hoyi from Lake Michigan." Chemosphere 11:847-858.

Fox, M.E. 1985. A Practical Sampling and Extraction System for the Quantitative Analysis of Sub ng/L of Organochlorine Contaminants in Filtered Water and Suspended Solids. NWRI, Burlington, ON.

Hart, B.T. and S.H.R. Davies. 1977. "A batch method for the determination of ion-exchangeable trace metals in natural waters." Aust. J. Marine Freshwater Res. 28:397-402.

Kauss, P.B., M. Griffiths and A. Melkie. 1981. "Use of freshwater clams in monitoring trace contaminants in source areas." In: Tech. Transfer Conf. No. 1, Proc., November 24, 1981, Toronto, ON, pp. 371-78.

Kauss, P.B. 1983. "Studies of trace contaminants, nutrients and bacteria levels in the Niagara River." J. Great Lakes Res. 9(2):249-273.

Keith, L.H. et al. 1983. "Principles of environmental analysis." Analyt. Chem. 55:2210-2218.

Lee, C. et al. 1977. "The use of a chelating resin column for preconcentration of trace elements from seawater in their determination by neutron activation analysis." Talanta 24:241-245.

Longbottom, J.E. and J.J. Lichtenberg, eds. 1982. Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater. U.S. Environmental Protection Agency, Washington, D.C. (EPA-600/4-82-057)

Lum, K.R. and D.G. Edgar. 1983. "Determination of the chemical forms of cadmium and silver in sediments by Zeeman effect flame atomic absorption spectrometry." Analyst 108:918-924.

Lum, K.R. and J.K. Leslie. 1983. "Dissolved and particulate metal chemistry of the central and eastern basins of Lake Erie." Sci. Total Environ. 30: 99-109.

Luoma, S. and G.W. Bryan. 1978. "Factors controlling the availability of sediment-bound lead to the estuarine bivalve Scrobicularia plana." J. Marine Biology Assn. (U.K.) 58:793-802.

Luoma, S. and G.W. Bryan. 1982. "A statistical study of environmental factors controlling concentrations of heavy metals in the burrowing bivalve Scrobicularia plana and the polychaete Nereis diversicolor." Estuarine, Coastal and Shelf Sci. 15:95-108.

Maciorowski, A.F. et al. 1983. "Bioassays - procedures and results." J. Water Pollut. Control Fed. 55:801.

McCrea, R.C. and J.D. Fischer. 1984. Design and Testing of an Aqueous Phase Liquid-Liquid Extractor (APLE). Inland Waters Directorate, Ontario Region, Water Quality Branch, Burlington, ON.

Munawar, M. and I.F. Munawar. 1982. "Phycological studies in Lakes Ontario, Erie, Huron and Superior." Canadian J. Bot. 6:1837-1858.

Munawar, M. et al. 1983. "The impact of sediment-associated contaminants from the Niagara River mouth on various size assemblages of phytoplankton." J. Great Lakes Res. 9(2):303-313.

Oliver, B.G. and K.D. Nicol. 1982. "Gas chromatographic determination of chlorobenzenes and other chlorinated hydrocarbons in environmental samples using fused silica capillary columns." Chromatographia 16, 336-340.

Oliver, B.G. and K.D. Nicol. 1984. "Chlorinated contaminants in the Niagara River, 1981-1983". Sci. Total Environ. 39:57-70.

Oliver, B.G. and K.D. Nicol. 1985. "Field testing of a large volume liquid-liquid extraction device for trace organics in natural waters." Int. J. Environ. Analyt. Chem.?????

Riley, J.P. and D. Taylor. 1968. "Chelating resins for the concentration of trace elements from seawater and their analytical use in conjunction with atomic absorption spectrophotometry." Analyt. Chim. Acta 40:479-485.

Riley, J.P. and D. Taylor. 1972. Deep Sea Res. 19: 727.

Sprague, J.B. 1973. "The ABC's of pollutant bioassay using fish." In: Biological Methods for the Assessment of Water Quality. J. Cairns and K.L. Dickson, eds. American Society for Testing and Material Special Tech. Pub. 528, Philadelphia, PA, pp. 6-30.

Stern, A.M. and C.R. Walker. 1978. "Hazard assessment of toxic substances: environmental fate testing of organic chemicals and ecological effects testing." In: Estimating the Hazard of Chemical Substances to Aquatic Life. J. Cairns, Jr., K.L. Dickson and A.W. Maki, eds., American Society for Testing and Materials Special Publication 657, Philadelphia, PA, pp. 81-131.

Tessier, A., P.G.C. Campbell and M. Bisson. 1979. "Sequential extraction procedure for the speciation of particulate trace metals". Anal. Chem. 51:844-851.

Thomas, R.L. and R.K. McMillan. 1978 "Large volume water sampling for recovery of suspended solids in Great Lakes tributaries". Abstr. Int. Sed. Congr., p. 670. (Centrifuge method).

Wong, P.T.S., Y.K. Chau and P.L. Luxon. 1978. "Toxicity of a mixture of metals on freshwater algae." J. Fish. Res. Board Canada 35:479-481.

Wong, P.T.S. and P. Couture. 1986. "Toxicity screening using phytoplankton." In: Toxicity Testing Using Microorganisms, V. 2, B. J. Dutka and G. Bitton, eds. CRC Press, Boca Raton, FL, pp. 79-99.

6.0 RECOMMENDED METHODS FOR QUANTITATIVE ASSESSMENT OF SEDIMENTS IN AREAS OF CONCERN

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6.1 INTRODUCTION AND RATIONALE

Sediment contamination represents a significant problem, particularly as a residual source of contamination in Areas of Concern. The adsorptive capacity of sediment for hydrophobic compounds and elements of low solubility is well known. Adsorption can occur when direct interaction takes place between particulate material, water and biota during transport to depositional zones. Even after active source elimination, redistribution by physical processes concentrates contaminated sediment in areas of accumulation. This produces a region which may contaminate the benthic biota and associated food chain. Under the proper conditions, contaminants are slowly released to the overlying waters and to the biological system of the area. Finally, under most conditions, harbors and embayments deliver sediment to the open lake system and will continue to be a source of contaminants, aggravating conditions within the recipient water body. The continuing loss of sediment-bound mirex from the Oswego River to Lake Ontario is such an example.

No remedial action can be undertaken without full problem definition. This chapter therefore proposes techniques to identify the role of sediment in an Area of Concern as a component of an overall assessment protocol. The recommended study methods form a strategic approach for obtaining as complete an understanding of the sediment system as is reasonably possible. However, each component may be used individually for specific purposes.

The sediment component is a dynamic system in the short term yet static in the long term. Consequently, a historic record of environmental perturbation is represented in the sediment profile where changes can be measured. As a general rule, our concerns about sediments relate to sediment toxicity and contaminants bioavailability. The approach emphasizes biological screening to determine both toxicity and bioavailability before time and money is invested in more detailed assessments. The recommended strategy for assessing the need and extent of sediment studies is outlined in Section 6.2. Section 6.3 outlines the recommended techniques and the rationale for their selection. Detailed methodologies are referenced or will be provided in a subsequent document.

In summary, the contents of this section are intended to provide guidance to those responsible for developing monitoring plans for Areas of Concern by:

- Establishing the existence of sediment contamination.
- Mapping and determining the extent of accumulation, erosion and non-deposition areas.
- Assessing the relative significance of resuspension, mixing and transportation from source to deposition.
- Determining the rate of sediment accumulation and reconstruction of contaminant history.
- Determining the concentration of contaminants and nutrients.
- Assessing and quantifying input loads.

- Preparing a sediment mass balance (input, deposition, output) and translating this into a geochemical budget for contaminants and nutrients.

- Determining the potential bioavailability of sediment-bound contaminants and

- Assessing the toxicity of sediment-bound contaminants to organisms at all trophic levels.

For each component of this section, background material is provided and where possible, a brief review of the topic is presented. A rationale is developed for each particular methodology, why it was chosen over other techniques and possible alternatives; and what information the technique will provide, its advantages and disadvantages.

6.2 APPROACH

The recommended approach to assessment of sediments in Areas of Concern is based upon the steps listed below:

Step 1. Identification of "impact".
Step 2. Quantification of the extent and nature of the impact.
Step 3. If remedial action is taken, quantification of effectiveness.

This is a three-step process whereby movement to the next stage is dependent on action or results from the previous one. The remainder of this document describes each of the methods recommended by the Work Group to most cost-effectively provide the necessary information for decision-making.

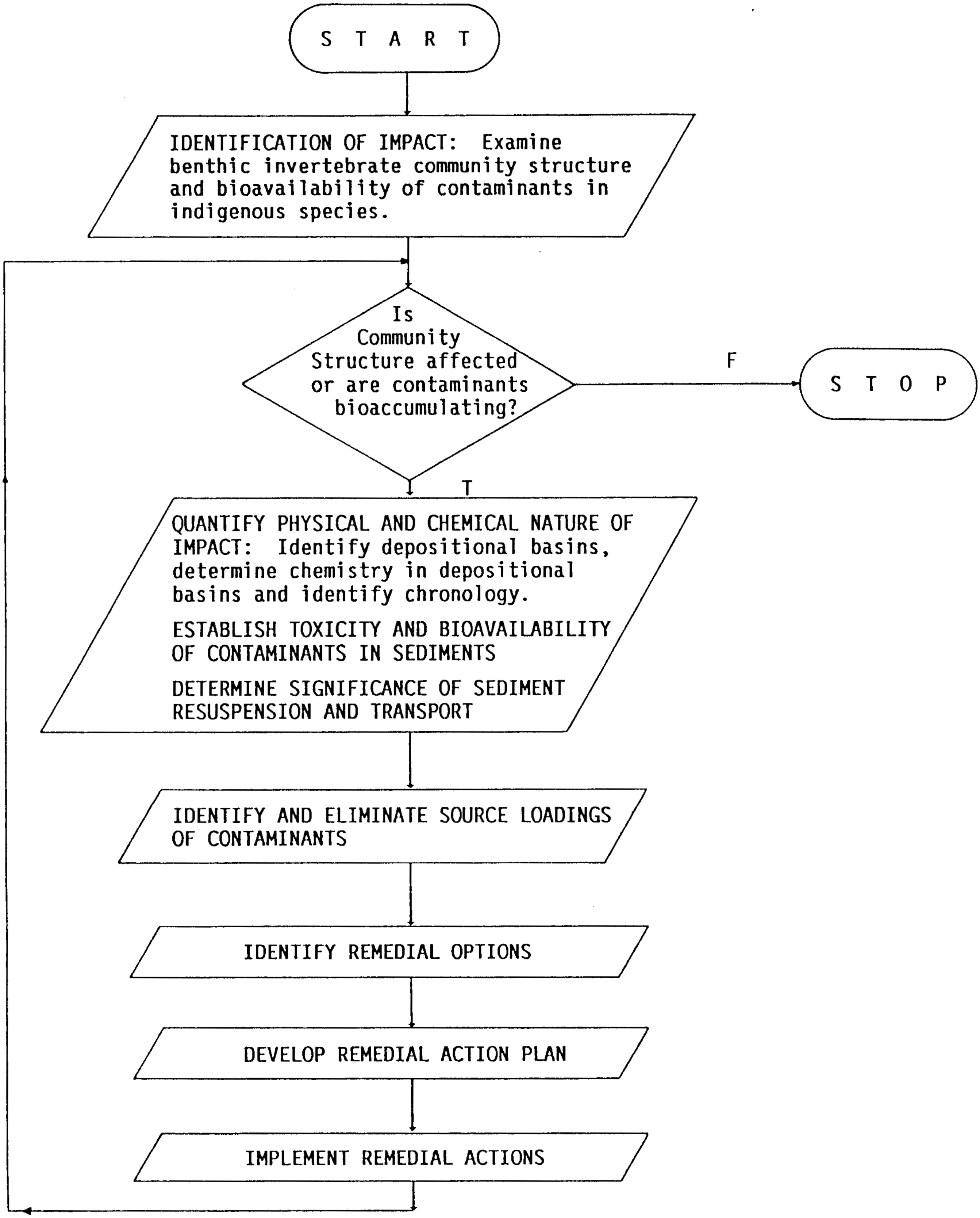
The flow chart (Figure 6) summarizes the steps that should be taken to determine the extent of sediment investigations in an Area of Concern. This includes:

Step 1. Identification of Impact

Biological assessment using benthic invertebrates is proposed as the first action. A preliminary biological assessment has been recommended because the biological expression or effect of the contaminant is the ultimate concern. Biota are sensitive and exhibit effects of exposure to a broad range of contaminants commonly present. Benthic invertebrates are the recommended tool since they are often numerically abundant, relatively long lived, immobile and live in immediate contact with the sediments. They will, therefore, best reflect contaminant impact. In addition, investigation costs are relatively low.

a) Assessment of benthic invertebrate community structure is recommended due to the relative ease of quantitative sampling, the temporal and spatial representativeness of the data, and the known responses of this group to pollutants.

FIGURE 6: A generalized process for assessing the significance of contaminated sediments in Areas of Concern.



b) Benthic invertebrate body burden measurements are recommended as estimators of contaminant bioavailability and as the entry point, from sediments, to the food chain. The presence of contaminants will thus be an indication of bioavailability.

If either assessment indicates an impact, quantification of the extent of that impact is required. If no effect is shown, no further work is required.

Step 2. Quantification of Impact.

If a documented impact has occurred, the "when" and "where" must be established. In part, this may be provided by community structure analyses; however, documentation is also required for the causative factors. The following steps are therefore proposed.

a) Determination of depositional basins - it is recommended that the greatest effort on sediment characterization should take place in the depositional basins, where most contaminants will reside and where remedial actions, in most cases, will be applied. In some instances transport processes may be significant, especially if time scales are long, but this will be the exception rather than the rule. An indication of these transport processes will be provided from Step 1 and from the examination of resuspension and transport (6.3.4).

b) Surficial chemistry - once the depositional zone is established, a sampling program should be initiated that will determine the surficial sediments chemistry in that zone, emphasizing selected nutrients, metals and organic chemicals.

c) Chronology and loadings - in addition to determining the spatial pattern of contaminants in the surficial sediments, the temporal pattern is required. This will determine the need for identifying the changes in the vertical and horizontal distribution of sediments. Cores should be taken to determine whether active sources still remain; if so, resuspension and transport will require examination. In conjunction, sediments will need to be assessed for the potential to be a secondary source of contaminants (6.3.2).

d) Toxicity and Bioavailability.

At the same time that surficial and subsurface sediment chemistry are determined, the toxicity and bioavailablity of sediment contaminants should be examined. Toxicity will be determined using a two-tiered system. First, acute toxicity should be determined using three tests on a range of organisms. Depending on the outcome of these tests, chronic toxicity may need to be examined. The potential for bioaccumulation will also be determined by a standard test using a benthic invertebrate.

Step 3. Quantification of Effectiveness of Remedial Action.

If remedial action is taken, one should assess the effectiveness of that action using the above techniques.

Summary:

Briefly the sequence of steps is to:

- Identify impacts using biological indicators which integrate responses, primarily community structure and body burdens.
- Conduct extensive physical and chemical analyses _if_ biological data indicate an impact has occurred.
- Map sediments.
- Resample sediments in the depositional zones.
- Assess the history of accumulation and loadings to the sediments.
- If active sources are established, identify partitioning between suspended particulates and bottom sediments in lentic and lotic habitats.
- If a contaminated sediment is identified, quantify the extent and degree of that impact, both by chemical means and by using a series of sediment bioassays, both chronic and acute and
- If remedial action is taken, assess the effectiveness of that action using the above techniques.

6.3 METHODS

The rationale for the recommended methodologies are described below for physical, biological and chemical techniques. Details such as sample replication, site selection and techniques are not included but further documentation is available from the Great Lakes Regional Office of the IJC and subsequent details on methodology are being developed. Methods for identification of impact identified in Step 1 of the approach, i.e. benthic invertebrate community structure and body burden assessment are outlined in the Biota section (Section 3.0).

This section outlines the remaining recommended methods:

- o Baseline mapping
- o Sampling
- o Loading assessment
- o Analysis
- o Bioassay

6.3.1 Baseline Mapping and Sediment Inventory

Bottom sediment distribution mapping is an essential yet normally overlooked ingredient of a study designed to understand the role of sediment in an environmental system. It accurately defines the geographic extent of accumulation areas versus nondeposition and erosion regions. This information allows loading calculations once the accumulation rate is known. It further determines the geographical extent required for remedial measures, leads to a subjective understanding of the physical conditions including implementing controls for sedimentation processes within the Area of Concern, and creates a knowledge base for the interpretation of geochemical and textural information. With the addition of textural data, these maps provide the basis for modelling resuspension and transport within the area and may provide additional information on the mechanisms of sediment movement into the receiving water body.

Mapping is the first step in obtaining a data base on sediments. Inexpensive qualitative methods are recommended for the mapping sediment deposition zones. Three techniques may be used: echosounding, seismic reflection and refraction. The first may be easily adopted with a minimum of training. The latter two must be conducted by a trained geophysicist or a qualified consulting company. In addition, side scan sonar may be used to provide direct acoustic mapping to determine the extent of specific features or obstructions and surface sedimentary structures. This technique provides valuable information on the directions and velocities of the overlying waters. Operation and interpretation requires the use of experts.

Echosounding is based on the fact that the water content of sediment allows variable penetration of high frequency acoustic sound with internal reflection of sound from internal changes in the sediment.

Seismic reflection is based on the same principle as echsounding but uses a lower frequency sound source such as a mud penetrator at 3.5 KHz or, more importantly, a high resolution seismic boomer source. Seismic refraction is based on the lateral movement of sound between an explosive source and a sound receiver. Time of arrival of specific responses is related to the thicknesses of the various units through which the sound travels. This allows deeper penetration even into coarse sediment. No further description is provided as this and the two subsequent techniques must be conducted by trained geophysicists.

Side scan sonar uses the return of bounced high frequency sound, swept laterally outwards from the vertical. Frequency can be varied depending on instrumentation but is normally 100 KHz. The intensity of the returning signal relates to the form and composition of the reflecting material and complete mosaics or acoustic maps can thus be prepared for the area.

6.3.2 Sampling Design and Techniques

This section recommends sediment collection procedures for subsequent chemical or biological analyses. Detailed consideration is not given to site selection, numbers of replicates and sampling devices. Two components of sediments are discussed separately as they relate to harbors and embayments: first, sediments and sediment-bed loads from incoming streams; second, sampling the depositional zone in the Area of Concern.

Streams & Suspended Sediments

Quality and quantity measurements of nutrients, metals and organic chemicals discharged from tributaries are critical to any program intended to assess the environmental status of an Area of Concern. Particular importance must be focussed on the role of sediment as a pollutant by itself, as a vehicle for transport of other pollutants and as a tool for evaluating pollutant sources. Any tributary sampling program must be capable of providing:

1. Estimates of seasonal and annual sediment and pollutant discharge.
2. The quality of suspended and fixed bed sediments during high and low flow periods.

To answer these questions several field measurements and/or sampling activities must be carried out. The key measurements are stream flow and sediment discharge in a program which includes a sufficient number of stream flow measurements to provide an accurate estimate of stream flow discharge.

Stream Flow

Stream flow discharge estimates are made either from daily record sites, where a continuous record of stream stage is developed using stage recording devices or partial record sites where periodic observations are made as detailed by Buchanan and Somers (1974). At a daily record site, a rating curve or relationship between stream stage and flow is developed by taking a series of stream flow measurements over time and plotting them against the corresponding stage measurements. The stream flow measurements are developed according to methods described by Carter and Davidian (1977) and Buchanan and Somers (1976). Development of the stage-discharge or rating curve will require a series of stream flow measurements taken over one or more hydrologic cycles or water years. Additionally, measurements must be made during periods of low (base) and high (storm event or winter/spring runoff) flow. Contemporaneous measurements must be made for sediment concentration. River stage is recorded continuously as described by Buchanan and Somers (1974), and in combination with the stage discharge relation, the discharge rating curve is calculated (Buchanan and Somers 1974). Partial record sites are sampled for flow in the same fashion except that a continuous record of stage is not maintained. Peak stage may be estimated using a crest stage gauge (Buchanan and Somers 1974). The partial record site will only provide data for the times when the specific measurement is made.

Stream flow measurements are carried out by taking a series of velocity measurements along a cross section, multiplying the velocity by the partial area of the cross section and summing the resulting discharges from each cross section. The location selected for the stream discharge measurement is critical to provide accurate flow and stage measurement. The general location should be in close proximity to an established gauging station, the physical characteristics of which have been described. A specific location should have a uniform cross section and a smooth and stable bottom of relatively well consolidated materials. This latter requirement is of particular concern when measurements are to be made by wading in a stream. Detailed information on establishing the operating gauging stations, making flow measurements and calculating stream flows can be found in USGS (1977). These activities are best performed by groups or jusisdictions with specific responsibility for this type of work.

Sediment Discharge

Sediment discharge from a stream or river to an open water system is important because of the role sediments play in the dynamics of the interactive physical, chemical and biological system. Sediments act as the transporter and processor of chemicals in the system. On discharge to the lake, harbor or embayment, sediments may further act as a source/sink, a process reactor for chemicals or as a substrate for environmental exposure. Because of sediment's multiplicity of roles in the aquatic system, it represents the element requiring the greatest sampling effort. Within the sediment system, the three principal components are suspended, traction or bed load, and fixed bed sediments.

Suspended material is the principal transport vehicle for chemicals within the fluvial system and is therefore the component that must receive the major sampling emphasis. Within the suspended sediment fraction the silt and clay size (<0.062mm) materials are chemically and biologically the most active (Ongley and Blachford 1982 and Golterman *et al*. 1983). Because of this activity and the relatively greater mobility of suspended material (Culbertson 1977), sampling for evaluation of chemical input via sediment transport should focus on the silt and clay size fraction. Bed sediments, particularly during low flow periods, may represent a reasonable media for evaluation of "base line" sediment quality. In many flowing systems there may be little, if any, unconsolidated bed sediments. In such cases evaluation of the fluvial system may justify sampling bedload (Miles 1977).

Suspended sediment sampling must follow two tracks: estimation of suspended material discharge and determination of its physical and chemical characteristics. The first step in evaluating the suspended sediment of a fluvial system is establishing the sediment discharge characteristics. This must be carried out in conjunction with the stream flow measurement. Details of sampling procedures and sampling equipment required to establish good estimates of fluvial sediment discharge are provided by the U.S. Geological Survey (USGS) (Guy 1973 and Guy and Norman 1973).

In establishing a sediment measurement program, location of the sampling site and timing of sampling are critical. For the purpose of investigating Areas of Concern there must be positive downstream movement of water. To achieve positive flow it may be necessary to move upstream, but the sample station must be located as close to the river mouth as possible. Establishment of a reliable sediment-discharge relationship, and therefore, an accurate estimate of sediment discharge is crucial. Thus, sampling is required during as many runoff events as possible in addition to base flow conditions over the entire hydrologic year. Less frequent suspended sediment quantity sampling will be carried out in addition to the sampling for sediment quality. Laboratory evaluation of the sediment calculation for discharge concentration should be performed according to Guy (1969). After the sediment-discharge rating has been established, the discharge of fluvial sediments may be calculated. These calculations should be carried out according to the USGS procedures detailed by Porterfield (1972).

Sampling suspended sediment for chemical quality analysis is not as well documented as determining sediment discharge. The primary problem with sediment sampling for quality analysis is obtaining a sufficient quantity of material. A method was described by McMillan and Thomas (1977) for pumping and continuous flow centrifugation of large volume samples. A comparable method using a different centrifuge was described by Ongley and Blachford (1982); proprietary equipment is available (Anon. 1981) under the trade name "Sedisamp System". The continuous centrifuge sampling system, while it collects a sufficient sample for full evaluation, has certain operational limitations which must be factored into its use. Collection of a depth integrated sample, as provided by standard sediment sampling equipment, is difficult. Similarly, collection from a large number of locations across a cross section is not feasible. Because of these limitations, preliminary evaluations are necessary to determine optimum sample collection points. Ongley and Blachford (1982) suggest sampling at the one-third points along cross section at a fixed depth. As reported by Culbertson (1977) there may be substantial vertical and horizontal variation. Identification of exact sample location should include evaluation of horizontal suspended sediment distribution from the sediment discharge measurements and site physical characteristics. Sampling frequency can be estimated from suspended sediment measurements. In general, 10 high volume sediment samples should be taken over a year including three to five runoff event samples. The samples should be collected at times and under conditions that will provide a good representation of the system's flow regime.

Fixed bed sediment samples (see following section) should be collected concurrently with centrifuged suspended sediment samples when flow and bottom sediment conditions permit.

Bottom Sediments

Surface sediment is collected at selected sampling stations to obtain information on horizontal distribution of contaminants. Sediment cores should be collected at selected sampling stations to determine the vertical distribution and historical inputs of contaminants. In addition, sediment samples may be stored for future reference and comparison.

From the mapping procedure, the depositional zone in the Area of Concern will have been identified. To determine the horizontal variation in the surficial sediments, a grid should be established covering the depositional zone and a minimum of 10 samples taken for subsequent analysis. The sampling locations within the grid should be randomly determined. In addition to examining surficial sediments, a number of core samples also should be taken to establish the chronology of contamination. Therefore, randomly selected core samples need to be taken at three to five locations. The recommended equipment for taking samples is easy to operate and readily available to consulting companies and government agencies (Table 17).

6.3.3 Dating and Accumulation

A major value of sediments is the historical perspective they offer. This is of particular significance in assessing the extent of impact on the Great Lakes from human perturbation. The following methodologies are recommended

TABLE 17

RECOMMENDED SAMPLERS IN DEPOSITIONAL ZONES

	SUITABLE FOR		COMMENTS
	Fine Sands, Silts & Clays (<0.1 mm)	Fine Gravel (0.5-4 mm)	
Ponar Grab	+	+	Requires winch - surficial sediments only
Shipek	+		Requires winch - surficial sediments only
Mini-shipek	+		Hand operable - surficial sediments only
Birge-Ekman	+	+	Hand operable - surficial sediments only
Benthos Gravity Corer	+		Requires winch - vertical profiles
K.B. Corer	+		Hand operated - vertical profiles

+ indicates suitability

for dating sediments, measuring contaminant accumulation and estimating loadings.

Dating

Many techniques have been developed for producing relative and absolute dates for lake sediments. These range from long term, up to 40,000 years (Lake Biwa), to within the historical record of the lake basin. The method selected in any one case depends on the lake basin and sediment characteristics as well as the availability of technical equipment and expertise. In virtually all cases, however, more than one method should be applied in order to produce internal verification and confirmation.

The dating methods used fall under three main categories: event related, stratigraphic and radiochemical (Table 18). Absolute dating is generally provided by radio-chemical methods. Once stratigraphy and events have been placed in a dated sequence, they in turn provide rapid absolute dates and correlation.

TABLE 18
TECHNIQUES FOR SEDIMENT DATING

EVENTS	STRATIGRAPHY	RADIOCHEMISTRY
Slumps	Magnetostratigraphy	C^{14}
Turbidities	Fossil Assemblages	Pb^{210}
Hydraulic Regime	Chemical	(Cs^{137})
Cs^{137}	Textural	
Flora & Fauna Change		
Anthropogenic Materials		

Events

Events constitute a horizon marker within the sediment column which can be related to a specific event occurring either in the lake, its basin or an external event of sufficient magnitude to provide a record of its influence in the sediment. These may be readily related to a known event for which the date is documented or may merely serve as a means of correlation between cores. The event horizons listed in Table 18 are as follows:

Slumps - slumps imply the mass downslope movement of sediment from one location to another due to some strong external stimulus such as an earthquake or storm. The material moved is generally similar to that occurring at the point of final deposition and may not be readily visible. An excellent example is given by Edgington and Robbins (1976), who showed the profile for excess Pb^{210} in a core from Lake Michigan where block deposits of constant Pb^{210} concentration occurred indicating instantaneous deposition. Three intense storms that occurred in 1915, 1940 and 1958 could have been the events responsible for the slumping.

Turbidities - High water turbidity results in density differences and may create water mass flow. Turbidity events can be triggered by storms, heavy fluvial loading of suspended materials or other events which induce resuspension. These high density water masses will flow down slopes as an integral mass of material. When flow ceases, the suspended material is redeposited with coarse material being deposited first and overlain by progressively finer material. The occurrences of turbidities have been recorded in many lakes. A good example from Lake Geneva has been provided by Vernet et al. (1984), who showed a change in deposition occurring at a depth of 12 cm, which resulted in a decrease in organic C, Cd, Hg, Zn and Cs^{137}. Turbidities are distinguishable from slumps by the fining upward sequence characteristic of the transport sedimentation process, whereas slumps are homogenized by the mass flow of sediment downslope.

Hydraulic Regime - major changes in the flow characteristics of the input to lakes may have a profound visual impact on the sediment. Changes are normally due to human influence, such as damming or channel modification. An excellent example has been given by Dominik et al. (1981) for Lake Constance. In 1900 the Upper Rhine River was channelized such that its outlet to the lake was shifted some eight kilometers northeast of its previous outlet. A core taken showed a significant change in composition at a depth of 11 cm, changing from a coarse grained homogenous material to a finer grained laminated sediment. Pb^{210} dating of this core indicated that in 1900 a break in sedimentation occurred, confirming the date of the change in sedimentation.

Cs^{137} - despite the fact that Cs^{137} is a radionuclide, it is included as an event marker rather than a radio-isotope dating technique. This is because Cs^{137} concentration in sediment cores and atmospheric fallout parallels the atmospheric testing of nuclear devices with maximum Cs^{137} activity in sediment profiles corresponding to the year 1964. From the corresponding peak in sediment Cs^{137} activity it is assumed that incorporation into the sediment is rapid and that post-depositional migration is not significant. This migration may occur (Lerman and Lietzke 1975; Robbins et al. 1979; Alberts et al. 1979; and Dominik et al. 1981), but it is generally agreed that, where a well defined profile and clear peak occur, the method can be used with considerable reliability. Studied distributions which are characteristic of the profiles from most lakes show that the data must be interpreted with caution but that, in general, the method under moderate to rapid continuous sedimentation provides excellent results.

Flora & Fauna Change - this type of event is one in which a rapid change in flora and fauna occurs as a result of a specific phenomenon. It does not relate to the slower evolutionary changes occurring in response to climate or changing lake conditions. One of the best examples that has been used extensively is the Ambrosia pollen rise in forested areas of eastern North America. The increase in this pollen can be observed easily and is a most effective marker. Ambrosia, or the common ragweed, increased as a result of deforestation and the increase in its open meadow habitat. Local records of land transfer provide precise dates at which deforestation occurred, for example in 1850 in Lake Ontario (Kemp and Harper 1976; McAndrews 1976).

Anthropogenic Materials - this technique has not been applied to a great extent but could be useful in certain areas. For example, the occurrence of fly ash and coal particles is common in the sediments of the Great Lakes. This material came from coal-fired steam vessels, and it is certain that if the spatial concentrations were to be mapped, the shipping tracks of the Great Lakes would clearly be seen. Such a study could be used to mark the onset of steam shipping, and the profiles would probably reflect the slower subsequent change to diesel motor vessels. This work has not been carried out but has wide applicability to other regions impacted by industrialization.

Stratigraphy

Stratigraphy emphasizes those single or composite changes which occur relative to natural, e.g. climatic changes or broad human-induced changes such as eutrophication, industrialization and most recently acidification. Some of these are described below.

Magnetostratigraphy - the basis for magnetostratigraphy has been well described by Thompson (1984). It is based on the fact that magnetic declination and inclination are continuously changing and the residual magnetism of particles in sediment cores retain a measurable record of these changes. Master curves have been prepared and dated for the entire Holocene record against which comparison may be based. Age estimations and correlations can thus be made, though it should be noted that this field requires specialized training and equipment.

Fossil Assemblages - the literature abounds with excellent studies on palaeolimnology which are based on stratigraphic evidence from plant remains. A compendium is provided by Haworth and Lund (1984) that provides a series of good examples. Most studies involve algal and/or pollen stratigraphy - the former to obtain an insight on changing lake conditions relative to external forces, while the latter represents sedimentary preservation of the changes in the basin as affected by both natural and human causes.

Chemical - these may be divided into a number of categories relative to the process or cause of chemical change in the sediment column. These include: eutrophication which can be verified by biologic stratigraphy; changes in weathering or soil erosion; and industrialization and the onset of pollutants which may be individually dated and collectively used to define the history of industrialization.

> Eutrophication: cultural eutrophication is the onset of increased and detrimental algal productivity resulting from increased human population and associated land use, thus increasing the supply of plant nutrients, P and N, to lake systems. A good example is given for Lake Constance by Müller *et al*. (1979).
>
> Weathering and erosion: Makareth (1966) and Engstrom and Wright (1984) have drawn attention to the fact that during periods of active erosion, the mass transport of raw unleached soils should increase levels of Na, K and Mg in lake sediments. During episodes of relatively stable soils, on the other hand, deep weathering should diminish the mineral material available for erosive removal, transport and sedimentation. Thus, elements that represent the mineral or detrital fractions should directly reflect erosion intensity in the basin.

Industrialization: the onset of the industrial revolution is strongly reflected in the lake sediment column. In the North American Great Lakes trace metal concentrations start to rise immediately following the arrival of Caucasians and the deforestation of the basin. The general increase accelerated at the turn of the century and was amplified by World War II. Certain responses by specific elements occur over and above the general trends. For example, increases in Pb concentrations is a response to the addition of Pb to gasoline, and Hg from the building of chlor-alkali mercury cell plants (Kemp et al. 1974). The post World War II era is characterized by the onset of the production of organic compounds which came under continuously increasing use after 1950. This increase in organochlorines has been documented in the Great Lakes by Frank et al. (1977, 1979a and 1979b) and by Thomas et al. (1984) for one core in Lake Geneva.

In general, the concentration of an element or compound in a dated sediment core closely follows the production or sales of the same material (Vernet et al. 1984; and Durham and Oliver 1983). Such data clearly and not surprisingly, suggest that environmental levels of contaminants are directly proportional to production, which may be translatable into sales and distribution.

Radiochemistry

Two major radiochemical techniques, C^{14} and Pb^{210}, are currently used for absolute dating of sediment cores. The former is generally used to establish the chronology of stratigraphic data. It is difficult to use and interpret, and is dependent on the core intercepting suitable biological material for analysis. With a half life of 5,736 years, it is useful in corroborating major events over the post-glacial period. Pb^{210} is becoming a standard dating tool in lake sediment studies and is rapidly replacing the more time-consuming stratigraphic and faunal change techniques. It is of particular value in determining the historical record from the latter part of the 19th century to present. It is not further described here since many excellent papers have been presented on the method, e.g. Krishnaswamy et al 1971; and Oldfield and Appleby 1984.

Accumulation

The techniques for establishing a core choronology have been described in the previous section. Using these techniques, a profile will have been created from which accumulation can be estimated along the length of the core and thus an estimation or measurement of variable sedimentation throughout the length of core sampled. In contrast, events will have identified only a single time zone within the core. Thus, variable sedimentation may only be estimated if more than one time zone has been identified. Constant sedimentation between zones or between a single time marker and the surface will otherwise be assumed.

Total sediment accumulation in a basin may be determined most simply by multiplying the average annual rate (determined at each core location) by the area of the basin as determined by mapping. This annual rate of sedimentation measured in dry sediment per year may then be used to calculate elemental accumulation using the average value for each element or compound measured.

The method above could be refined by increasing sampling and coring intervals and by determining areas of equal accumulation rates and elemental concentrations. However, the increased costs of such an exercise would be prohibitive, and it is doubtful that the improvement in resolution would be sufficient to warrant the increased work load. It is recommended, however, that three to five cores be taken to determine average sedimentation rate with a minimum of 10 surface samples to obtain mean elemental concentrations.

6.3.4 Sediment Resuspension and Transport

The problem of entrainment, resuspension and transport of sediment is a relatively new area of research. As such, the procedures for identifying the problem and characterizing its extent are at best *ad hoc*.

Field measurements of resuspension and transport are extremely difficult and expensive, particularly as the phenomenon is usually associated with storms or short duration, high intensity events. Instrumentation for making the required measurements is only now under development and therefore their use is not routine. Consequently, it is recommended that a resuspension and transport study and its correlation with events should be performed only after all other causes of suspected impairment have been explored.

Indicators and Criteria for Undertaking a Resuspension and Transport Experiment

Indicators to establish the need for a resuspension transport study have either a biological/chemical or physical/geological base. The judgement as to when a resuspension transport study needs to be performed should be determined by the need for further problem definition, i.e. area and magnitude or when the possible role of resuspension in bioavailability is considered potentially significant. Obviously, if considerable mortality or species impairment are noticed after storm events or following the passage of a large vessel, the role of resuspension of contaminated sediments needs to be assessed.

Supporting evidence that resuspension and transport might be sufficiently intense to warrant attention can be obtained by a simple physical/geological overview of the problem site. The following may be used as indicators:

a) The active storm patterns whose occurrence period is less than the time it would take the Area of Concern to flush out and the resuspended sediment settle or be transported from the system.

b) The storm patterns whose runoff volume is on the order of the water volume in the Area of Concern. These first two considerations are particularly pertinent during fall, winter and early spring.

c) The presence of a high percentage of clays, muds and silts in the grain size distribution. These substances which stay in the water column for long periods of time may be remobilized and are the particles most responsible for toxic substance transport.

d) In combining the first three considerations, it can be noted that intense, frequent storms with large runoff volumes will cause frequent resuspension and transport of clays and muds. If an Area of Concern has a large residence time and a high clay size fraction, it is reasonable to assume that after a storm event it will take a long time for the sediment to settle, therefore introducing not only acute but chronic effects:

e) Active ship channel traffic, especially in harbors with marginal or shallow draft.

f) Upstream dredging or shoreline construction.

g) Wide shallow basins with flood plains. Basins such as these have an intense response to small stormwater runoff volumes with increased velocities (shear and water elevation), therefore resuspension transport is high during storms. After storm passage, the flood waters in flood plains slowly release water, sediment and therefore toxicants, back into the system.

h) Evidence of resuspension and transport from sediment core profiles.

There is nothing hard and fast about these indicators. By themselves, they are not justified for a resuspension transport study; however, if biological or chemical indicators are present, in addition to the physical indicators, a strong indication of acute resuspension transport effects is present.

Generally, Areas of Concern are either tributary regions, i.e. a channel, draining into a Great Lake or the nearshore coastal zone offshore of a tributary region. The shear stress causing resuspension in each zone is affected by different overlying currents. In tributary channel areas, currents are unidirectional (except during brief storm surge flow reversals) and progress towards the open lake. Wind-induced waves in tributaries are not an important agent in resuspension. In the nearshore zone, currents result from overall wind-driven circulation of the lake and therefore may come from many different sectors. Wind waves can become large and also particularly important in causing resuspension.

Estimation of Water Column Loading

Modelling methods are available for resuspension zones which permit an estimate of a near bottom shear stress, given several easily obtained pieces of input data. This is particularly the case for the tributary region. Therefore, the estimation procedure concept is as follows: a) flow events which are considered to be of sufficient intensity to cause a loading are identified; b) the shear stress distribution over the bottom may be estimated using the appropriate numerical model for either a tributary zone (Bedford *et al*. 1983; Fread 1978) or a nearshore zone (Grant and Madsen 1979); c) the amount of material possibly resuspended into the Area of Concern then can be estimated using the modified Shields entrainment versus critical shear diagrams (Madsen and Grant 1977; and Lick and Kang 1986); and, d) the map of bottom sediment type and deposition layer thickness. No vertical distribution of sediments within the volume is predicted nor is any estimate of deposition obtained. It is assumed that during events all the material resuspendable by the critical shear stress is put into suspension and held there by the local turbulence generated during the event. Hence total sediment mass resuspended into the Area of Concern is estimated. As the pollutant/chemical characteristics of the bottom sediments are known, the total pollutant mass resuspended into the volume is also estimated.

6.3.5 Sediment Chemistry

A large number of analytical techniques are available for chemical quantification of sediments. To ensure comparability in time and space, the following methods are recommended for: metals, nutrients and organics, as well as determination of water content.

Metals

In most circumstances, ten metals require routine analysis for total metal concentration in Areas of Concern. If necessary and as information dictates, other analyses may be required.

Total Metals (Pb, Ni, Cu, Zn, Cd, Cr, Fe, Mn)

Many extraction procedures have been reported for analyzing heavy metals in aquatic sediments. These procedures are typically aimed either at determining the metal content of a particular metal fraction or sediment phase, or involve digestion with hydrofluoric, fuming nitric or perchloric acids for total metal determination. While many authors agree that severe sulphuric/hydrofluoric/nitric acid or perchloric acid digestion provide for total metal solubilization, factors such as the quantity of organic matter or the presence of various anions may affect the degree of metal recovery. In addition, perchloric, hydrofluoric and fuming nitric acids generally require either special equipment or great care to ensure operator safety. Several authors have shown that sufficiently long digestion by a 1:1 mixture of concentrated hydrochloric and nitric acids at a high temperature is comparable to digesiton methods using hydrofluoric and perchloric acids. Consequently, an extraction procedure using a mixture of hydrochloric and nitric acids (1:1) is recommended. This method requires no special safety or handling precautions and provides a technique for processing a large number of samples.

Exchangeable and Easily Reducible Metals

Several extraction schemes exist for determining metals associated with different sediment phases such as pore water, exchangeable, organic, easily reducible, moderately reducible, carbonate and residual. These techniques enable assessment of metal associations with different sediment components and provide limited information on what portion of a particular metal becomes available (bioavailable, water soluble, etc.) under different natural sedimentary conditions (changes in redox potential, release of carbon dioxide from decomposition of organic matter, etc.). In addition, the information can be used for predicting the potential release of metals when sediments are disturbed (dredging, wave and current mixing, bioturbation).

The most useful information is provided by the exchangeable and reducible metal fractions in the sediment. A few researchers recommend carrying out the extraction procedure in a nitrogen atmosphere to avoid the oxidation of iron and manganese hydroxides. However, the selective extraction procedure recommended in this document is carried out under laboratory atmosphere because the interpretation of metal availability associated with individual sediment constituents is still under investigation. The recommended method is that of Tessier et al. (1979).

Total Mercury

Mercury pollution has received considerable attention since the occurrence of methyl mercury poisoning in Minamata Bay, Japan and lake sediments have been found to be an important sink for mercury. The concentration of mercury is usually higher in the fine grained sediments of the depositional areas than in the coarser sediments at the nearshore zone. The reduction-aeration-cold vapor atomic absorption spectrometric technique is one of the best methods for the determination of mercury in sediments. The digestion procedure must be capable of extracting quantitatively all forms of mercury in sediments. The high correlation between mercury and organic matter in lake sediments indicates that the treatment must be capable of oxidizing all organic matter. A simple extraction method is recommended as the standard procedure for mercury determination. The method was compared with a number of extraction procedures and no significant differences were found in the recovery of mercury in sediment samples from the Great Lakes (A. Mudroch, pers. comm.).

Total Arsenic

Recently, a semi-automated system for determining arsenic and selenium by hydride generation has been developed (Golden, et al. 1981). The method identifies arsenic in sediment and fish tissue samples. Arsenic is one of the parameters in the Ontario Ministry of the Environment guidelines for open water disposal of dredged material.

Nutrients

Eutrophication is still a major problem in many Areas of Concern and a reason for classifying some localities as Areas of Concern. It is recommended that phosphorus be analyzed in sediment samples in two forms.

Total Phosphorus

Lake sediments may influence the phosphorus-induced eutrophication of lakes by virtue of their capacity to take up and release phosphorus under changing limnological conditions. The concentration of phosphorus is higher in fine grained sediments in the depositional basins than in the coarser nearshore sediment. However, high concentrations may occur in sediments from harbors or embayments which receive inputs from sewage treatment plants. It was shown that phosphorus in the sediment is closely associated with iron. Depletion of oxygen at the sediment-water interface results in solubilization of iron and associated phosphorus, increasing the concentration of phosphorus in the water column. Total phosphorus can be extracted from the sediment by sodium carbonate fusion or by perchloric acid digestion. Phosphorus in the extracts is then determined colorimetrically. Both extraction procedures give comparable results. Slightly less recovery is sometimes obtained by the perchloric acid digestion. Because of their comparability, both methods are suitable.

Bioavailable Phosphorus

A number of chemical fractionation techniques may be used to estimate potential biologically available phosphorus. An evaluation of these techniques by Williams et al. (1980) indicated that NaOH extractable phosphorus is closely indicative of the phosphorus available for uptake by phytoplankton under laboratory controlled bioassays.

Organics

Organic contaminants form the second major category of toxic materials in the Great Lakes, particularly in the Areas of Concern. The protocols developed by the U.S. EPA are recommended for sediment analysis (Federal Register, 1984).

It is recommended that total organic content be analyzed as a general indicator. Organic matter in the sediment is derived from residues of microorganisms, plankton, benthic organisms, macrophytes and the input of organic material from the drainage basin. Fine grained sediment in lake depositional basins contains a higher concentration of organic matter than the coarser material in the nearshore area. However, high concentrations of organic matter may occur in harbor sediments as a result of point sources around the harbor or diffuse sources such as a stream. Organic carbon is the major constituent (about 60%) of sediment organic matter. Other major constituents are organic nitrogen, hydrogen, oxygen, phosphorus and sulphur. Organic matter in sediments can be determined as organic carbon by various combustion or oxidation techniques, by measuring the CO_2 evolved or by ignition at a moderate temperature. The distinction between organic carbon and organic matter is based on the fact that only carbon is measured by the former method while total organic matter weight is represented by the latter method. The determination of carbon requires either special equipment or is a time consuming procedure. The ignition procedure is simple and sufficient for the information on organic matter content in the sediment. However, serious errors may enter into the different weight-loss methods for measuring the organic matter weight because other constituents such as salts, including carbonates, crystallinic water and hydroxide also influence the weight change. Consequently, the determination has to be carried out at a controlled moderate temperature.

Determination of Water Content in Sediment

Fine grained surface sediment contains up to 90% water. The water content decreases with the sediment depth. Coarse grained sediments contain less water. Quantitative determination of some sediment constituents is carried out on wet sediment. However, the concentration of these constituents is expressed per gram of sediment dry weight. Consequently, it is necessary to determine the water content. The water content can be obtained during the preparation of the sample for various analyses. The sediment water content and a visual description of the sediment or particle size analysis are useful information on the sedimentation/erosion processes at the sampling area. Freeze drying or oven drying is used to determine the water content in sediment and to prepare samples for further analysis. Freeze drying requires special equipment, while oven drying is an easy procedure, and similar results are obtained using both procedures (Adams et al. 1980).

6.3.6 Sediment Toxicity and Bioavailability

Approach

Contaminated sediments concerns ultimately relate to sediment toxicity and bioavailability. Available techniques were selected which provide the initial information necessary to assess sediments in Areas of Concern. The tests recommended and described below primarily address the toxicity of sediments. Bioavailability should be determined from body-burden analysis (bioaccumulation of toxics) in field populations rather than from organisms exposed to toxic substances in laboratory experiments. The Biota Section describes methods of assessing bioavailability of toxics from sediments. The following sequence is proposed for assessing biological impacts from potentially contaminated sediments in Areas of Concern.

Assessment of Community Structure and Bioavailability

The Biota Section (Section 3.0) describes techniques for assessing community structure required for Step 1 in Figure 6 to estimate the impacts of sediment contaminants on the biota. If the community is normal or not impacted, then no further laboratory tests are necessary. However, impacted community structure is cause for proceeding to laboratory toxicity tests if physical or seasonal factors have been eliminated as being responsible for the state of the community. Body burdens of indigenous species also should be examined.

Acute/Short-term Tests

If an impacted community is suggested from Step 1 observations (Figure 6), an initial suite of sediment toxicity tests is recommended, which examines three levels of biological complexity, viz prokaryote, eukaryotes and an invertebrate, as well as estimating mutagenicity/carcinogenicity. Specifically, these recommended tests are:

- Microtox™
- Algal Fractionation Bioassay (AFB)
- *Ceriodaphnia* Bioassay and
- Ames/V.79.

All acute tests should be conducted on pore water because the toxicity of pore waters is proportional to that of whole sediments.

If positive results are observed, then remedial actions must be developed to eliminate the observed toxicity. Such remedial plans will require supporting analytical chemical data and the development of objective levels for minimum impact. Use of a chronic test to establish such objective levels is also recommended. A lack of response in the acute tests may indicate that the observed impact on the indigenous community is due to chronic toxicity. In the presence of elevated values in the supporting chemical data, the recommended chronic test should be undertaken, even though acute responses may be lacking.

Chronic Tests

The recommended chronic test uses Chironomus tentans to describe life history impacts, e.g. growth, reproductive performance, emergence and egg viability, to integrate chronic sublethal effects that may impact benthic populations. To provide a standard assessment of bioavailability, tissue analysis should be performed at the conclusion of the test. The recommended chronic test is conducted on whole sediment.

The following sections provide supporting detailed information on recommended methodologies.

Sediment Pore Water Extraction

Assessment of sediment toxicity by bioassays on pore water extracts is recommended for the acute tests because pore waters are in equilibrium with trace contaminants adsorbed on to sediments and are the primary exposure vector for benthic organisms. Since the water solubility of many organo-xenobiotics is relatively low, the total concentration of these compounds in sediments may not be well correlated with either acute or chronic toxicity to benthic organisms. The pore water extract procedure is less complex than the whole-sediment bioassay and thus easier to conduct and less variable. Also, the pore water bioassay allows dilutions to be made so that the relative toxicity (LC_{50}) can be reported as a percentage. Dilution of sediment with reference sediment is difficult and may not adequately represent the actual toxicity. The pore water bioassay is superior to analysis of the constituent toxicants in predicting toxicity because it accounts for the interactions of all potential toxicants. If necessary for sediment-specific reasons, one can also conduct bioassays with whole sediments using the appropriate C. tentans bioassay.

Acute Techniques

Bacterial Luminescence Bioassay

Microtox™ is a bacterial luminescence bioassay developed by Beckman Inc. as a rapid screening alternative to standard acute toxicity testing with fish and invertebrates. This test is based on the bioluminescence of the bacterium (Photobacterium phosphoreum) (NRRL B-11177). This assay was developed because there are evolutionary conservative biochemical pathways which are common to many organisms. Therefore, bacteria can be used as surrogate test organisms. However, it must be recognized that the specific mode of action of toxicants results in different toxicities when different organisms are used. For this reason we now advocate the use of several types of organisms.

The Microtox™ test is not a complicated procedure and requires approximately 30 minutes to complete. The Microtox™ test is based on the inhibition of bioluminescence of P. phosphoreum. In this organism the property of bioluminescence is a result of the total metabolic processes of the cells and thus a measure of the viability of the population. This bioassay has been extensively studied and compared to acute bioassays with fish and daphnids for a large number of compounds (Bulich et al. 1981, Dezwort and Sloof 1983, Lebsack et al. 1981, Qureshi et al. 1982, Strosher 1984). The test has also been used for complex effluents and has been found to be comparable to standard acute fish and Daphnia bioassays. The greatest discrepancy between Microtox™ and standard fish and daphnid bioassays occurs for compounds which are very toxic or extremely non-toxic. The agreement is good for moderately toxic compounds. In a combined data set of 56 different compounds, the greatest deviation between Microtox™ and fish bioassays was approximately a factor of 10, which is acceptable considering literature values for acute toxicity tests for the same species and compound can vary by a factor of 10 and routinely vary by a factor of two to five. In fact, the reproducibility of bioassays using Microtox™ is generally better than that for fish bioassays, and similar to or better than that of daphnid bioassays.

In addition, Microtox™ is important as an independent assay for the effects of toxic mixtures on a prokaryotic organism and can be used to assess present and potential environmental effects on the microbiological decomposer population.

A number of other bacterial assays are available. These include plate tests, which measure microbial toxicity and substrate uptake tests, which measure lethality and inhibition (Algistatic effects). In general, these tests are less developed and there is a smaller data base on toxicity available; however, they do provide useful information. Microtox™ has been approved as a bioassay for the real-time assessment of toxicity by the U.S. EPA. It was chosen as the preferred microbial assay because of its simplicity and because of the need to encourage standard techniques among laboratories. Because the entire procedure is a "Turnkey" operation, standardization is facilitated.

The proposed methodology does not assess the effects of in-place pollutants on the microbial community which is present at a contaminated site. Rather, the Microtox™ methodology gives a measure of the relative toxic activity of sediments. To assess the condition of the microbial community, other techniques should be employed.

Algal Fractionation Bioassay (AFB)

Toxicological research on the lower trophic levels such as phytoplankton (particularly nannoplankton/ultraplankton) has been limited (Wong et al. 1978; Munawar 1982). This is rather surprising since nannoplankton/ultraplankton are abundant in the Great Lakes system and have been established as responsible for a significant portion of carbon fixation (Munawar et al. 1974; Munawar and Munawar 1981). It has also been demonstrated that the nannoplankton of the Great Lakes, particularly the ultraplankton and picoplankton, are sensitive to contaminants such as heavy metals (Munawar and Munawar 1982). These organisms are important since they constitute a main source of food for the zooplankton (Ross and Munawar 1981). Rhee (1982) recently presented a general overview of phytoplankton related contaminant problems and Munawar (in press) provided a detailed account of state-of-the-art techniques for the bioassessment of contaminated sediments with phytoplankton.

A differential phytoplankton size fractionation procedure for carbon-14 uptake studies (Munawar et al. 1978) has been applied in toxicological research to study the impact of heavy metals individually and in combination (Munawar and Munawar 1982). The procedure has been successful in demonstrating the differential response of various size fractions and in pinpointing the component under stress. The same procedure was called "Algal Fractionation Bioassays (AFBs)" and has been adapted for assessment of sediment-elutriate toxicity to natural phytoplankton (Munawar *et al*. 1983; 1984; Munawar and Thomas 1984).

The traditional sediment bulk chemical characterization and the sediment elutriate chemical composition provide basic quantitative and qualitative chemical data. Such data do not provide the needed toxicity information concerning the bioavailability of the contaminants to organisms, and how physiology and food chain dynamics are affected. Sediment-bound toxicity data, based on bioavailability instead of on chemical characterization, is necessary for the management of water and sediment quality in the Great Lakes. Therefore, the type and nature of bioassays and test organisms used must be carefully chosen from the variety of assays and biota potentially available. AFBs were chosen since they use an indigenous community representing natural field conditions. The alternative test determines the differential response of the various size components as a function of their inherent physiology as part of the test community. An alternative test population is a laboratory-grown culture which may not reflect conditions in the natural ecosystem. The AFB is a short-term screening test to evaluate the net result of contaminant and nutrient loading. The procedure is rapid, sensitive and relatively inexpensive for screening potentially toxic substances and constitutes an early warning test system. Also, algal bioassessment of Chelex-100™ treated standard elutriate provides data which can determine the toxicity of the dissolved metals. High elutriate concentrations added to the test population can cause increased turbidity which can be a problem during incubation. This problem can be overcome by using lower concentrations or careful monitoring the bioassay.

Ceriodaphnia Bioassays

Invertebrate bioassays help to evaluate the nature and degree of harmful effects produced in aquatic organisms by toxicants, and provide information required to protect aquatic systems and/or assess the presence and severity of toxins. Cladocerans have been used extensively for aquatic toxicology testing because they are readily available, adaptable to laboratory conditions, require little space, and are sensitive to a wide variety of chemical pollutants. Also, they are an important link in aquatic food webs. One disadvantage of these organisms for bioassays is that many variations exist in study design, leaving many procedural questions unanswered.

Although *Daphnia* has been used for a longer time than *Ceriodaphnia*, the latter has been chosen because it is easier to culture and has better population stability than *Daphnia magna* (Mount and Norberg 1984). Additionally, unlike *D. magna*, it is a common and widely distributed native species in North America. See Section 2.0 for detailed *Ceriodaphnia* methodology.

Mutagenicity Tests

Short-term tests, based on the principles of genetic toxicology, provide a reliable indication of the potential for a substance to cause mutations and/or cancer in mammals. This is based on the ability of these tests to predict, within a few weeks, the outcome of long-term animal bioassays which may take three to five years to complete (Brusick 1980). There is growing evidence that carcinogenesis involves several distinguishable stages, including initiation and promotion. Initiation seems to be the result of an irreversible event which happens to a cell after its exposure to physical, chemical or viral agents that are known to damage or change the DNA molecule. Promotion, on the other hand, depends on repeated treatment of the initiated cell by physical or chemical agents that are weak or non-carcinogenic initiators. Consequently, the following tests for mutagenicity include a component for initiation (Ames/_Salmonella_ test) and for promotion (Metabolic Cooperation test).

Chronic Tests

The macrobenthos of the Great Lakes is dominated by two taxonomic groups, the Amphipoda and Oligochaeta (Robertson and Scavia 1984). Members of these taxa are not considered as bioassay organisms because the rearing of these organisms is difficult and not well established (Smith 1972). Also, oligochaetes in the Great Lakes, while sensitive to trace metals (Chapman _et al_. 1980), have generally been thought to be less sensitive to contaminant-induced mortality. Accordingly, it was decided to use the more established _Chironomus tentans_ bioassay.

The dipteran midge, _Chironomus tentans_, is suggested as a representative benthic invertebrate for use in laboratory toxicity testing and bioaccumulation studies. This species is widely distributed throughout the Great Lakes basin and spends almost all of its life cycle in a tunnel in the upper few centimeters of sediment (Adams _et al_. 1985). The chironomids are important in aquatic systems accounting for a significant portion of the benthic biomass (Gerould _et al_. 1983) and are important in the cycling of residues in and from the sediments (Gerould _et al_. 1983). This species can be satisfactorily reared in the laboratory and has been used as a bioassay organism (Batac-Catalan and White 1982; Wentsel _et al_. 1977; Dorward and Barisas 1984). _C. tentans_ completes its life cycle in approximately 30 days at 20°C and reproduces sexually in captivity. Midges can be reared in the laboratory following the procedures developed by Mosher 1982; Mosher and Adams 1982; and Mosher _et al_. 1982.

Bioavailability of Sediment Contaminants

Bioaccumulation of contaminants from contaminated sediments has been identified as a problem in most Areas of Concern, e.g. 34 of the 42 Areas of Concern have elevated levels of toxic substances in fishes and 39 of the 42 Areas of Concern have sediments contaminated with toxic substances. It is necessary, therefore, to assess bioavailability of toxic substances in sediments to determine whether or not sediments are a source of toxic substances to biota.

The science of assessing the bioavailability of toxic substances in sediments is evolving; however, there is an immediate need to assess the bioavailability of sediment contaminants. As a result, the recommendations presented below represent a consensus on the best methods currently available.

As part of the initial screening process (Figure 1, Section 1.0), tissue analysis will have been conducted on the indigenous fauna. Methods are outlined in the Biota Section (3.0). If insufficient indigenous, invertebrate fauna biomass is available from the depositional zone of the Area of Concern, it is recommended that the *C. tentans* chronic bioassay be performed in the laboratory with contaminated sediments from the Area of Concern. On completion of the test, tissue analysis should be conducted to determine uptake from the sediment.

6.4 REFERENCES

Adams, D.D., D.A. Darby and R.J. Young. 1980. "Selected analytical techniques for characterizing the metal chemistry and geology of fine-grained sediments and interstitial water". In: Contaminants and Sediments, V.2., R.A. Baker, ed., Ann Arbor Sci. Pub., Inc., Ann Arbor, MI.

Adams, W.J., R.A. Kimerle and R.G. Mosher. 1985. "Aquatic safety assessment of chemicals sorbed to sediments." In: Aquat. Toxicol. and Hazard Assessment, 7th Symp. R.D. Caldwell, R. Purdy and R.C. Bahner, eds., American Society for Testing and Materials Special Tech. Pub. 854, Philadelphia, PA, pp. 429-453.

Alberts, J.J., L. J. Tilly and T.J. Vigersted. 1979. "Seasonal cycling of cesium-137 in a reservoir". Science 203(4381): 649-651.

Anon., 1981. Sedisamp System: Operator's Manual. Envirodata Ltd., Winnipeg, MB.

Batac-Catalan, Z. and D.S. White. 1982. "Creating and maintaining cultures of Chironomus tentans (Diptera: chironomidae)". Entomological News 93:54-58.

Bedford, K., R. Sykes and C. Libicki. 1983. "Dynamic advective water quality model for rivers." ASCE J. Environ. Eng. 109:535-554.

Brusick, D. 1980. Principles of Genetic Toxicology. Plenum Press, N.Y.

Buchanan, T.J. and W.P. Somers. 1974. "Stage measurement at gauging stations." Book 3, Chapter A7. Applications of Hydraulics, Techniques of Water-Resources Investigations of the United States Geological Survey. U.S. Dept. Interior, Washington, D.C.

Buchanan, T.J. and W.P. Somers. 1976. "Discharge measurements at gauging stations." Book 3, Chapter A8. Applications of Hydraulics, Techniques of Water-Resources Investigations of the United States Geological Survey. U.S. Dept Interior, Washington, D.C.

Bulich, A.A., M.W. Greene and D. Isenberg. 1981. "Reliability of the bacterial luminescence assay for determination of the toxicity of pure compounds and complex effluents". Aquat. Toxicity and Hazard Assessment, 4th Conf. D.R. Branson and K.L. Dickson, eds., American Society for Testing and Materials Special Tech. Pub. 737, Philadelphia, PA, pp. 338-347.

Carter, R.W. and J. Davidian. 1977. "General procedure for gauging streams." Book 3, Chapter A6. Application of Hydraulics, Techniques of Water-Resources Investigations of the United States Geological Survey. U.S. Dept. Interior, Washington, D.C.

Chapman, P.M. et al. 1980. "Heavy metal studies with oligochaetes". In: Aquatic Oligochaete Biology R.O. Brinkhurst and D.G. Cook, eds. Plenum Pub. Co., N.Y., pp 477-502.

Culbertson, J. 1977. "Influence of flow characteristics on sediment transport with emphasis on grain size and mineralogy". In: Workshop on the Fluvial Transport of Sed.-Associated Nutrients and Contaminants, Proc. H. Shear and A.E.P. Watson, eds. International Joint Commission, Windsor, ON.

DeZwort, D. and W. Sloof. 1983. "The Microtox™ as an alternative assay in the acute toxicity assessment of water pollutants". Aquat. Toxicol. 4:129-138.

Dominik, J.A., A. Mangini and G. Müller. 1981. "Determination of recent deposition rates in Lake Constance with radioisotopic methods." Sedimentology 28:653-677.

Durham, R.W. and B.G. Oliver. 1983. "History of Lake Ontario contamination from the Niagara River by sediment radiodating and chlorinated hydrocarbon analysis". J. Great Lakes Res. 9(2):160-168.

Edgington, D.N. and J.A. Robbins. 1976. "Records of lead deposition in Lake Michigan sediments since 1800". Environ. Sci. Tech. 10:266-274.

Engstrom, D.R. and H.E. Wright. 1984. "Chemical stratigraphy of lake sediments as a record of environmental change in sediments and environmental history". In: Lake Sed. and Environ. History. Haworth and Lund, eds., Leicester Univ. Press, Leicester, England, pp. 11-68.

Federal Register. 1984. "Guidelines establishing test procedures for the analysis of pollutants under the Clean Water Act; final rule and interim final rule and proposed rule." Federal Register 49, 209:1-210, EPA, Part VIII, Pub. No. 40 CFR, Part 136.

Frank, R. et al. 1977. "Organochlorine insecticides and pollutants in the sediments of Lake St. Clair and Lake Erie". Sci. Total Environ. 8:205-227.

Frank, R. et al. 1979a. "Organochlorine insecticides and PCB in sediments of Lake Ontario". J. Great Lakes Res. 5:18-27.

Frank, R. et al. 1979b. "Organochlorine insecticides and PCB in the sediments of Lake Huron (1969) and Georgian Bay and North Channel (1973)." Sci. Total Environ. 13:101-107.

Fread, D.L. 1978. DAMBRK: The NWS Dam-Bread Flood Forecasting Model. National Weather Service, Office of Hydrology, Silver Springs, MD.

Gerould, S., P. Landrum and J.P. Giesy. 1983. "Anthracene bioconcentration and biotransformation in chironomids: effects of temperature and concentration." Environ. Pollut. (Ser. A) 30:175-188.

Golden, P.D., D.H.J. Anthony and K.D. Austen. 1981. "Determination of arsenic and selenium in water, fish and sediments by inductively coupled argon plasma emission spectrometry". Analyt. Chem. 53:2027-2029.

Golterman, H.L., P.G. Sly and R.L. Thomas, eds. 1983. Study of the Relationship between Water Quality and Sediment Transport. UNESCO, Paris.

Grant, W.D. and O. Madsen. 1979. "Combined wave and current interaction with a rough bottom". J. Geophysical Res. 84 (C4):1797-1808.

Guy, H.P. 1969. "Laboratory theory and methods for sediment analysis". Book 5, Chapter C1. Laboratory Analysis, Techniques for Water-Resource Investigations of the United States Geological Survey. U.S. Dept. Interior, Washington, D.C.

Guy, H.P. 1973. "Fluvial sediment concepts". Book 3, Chapter C1. Applications of Hydraulics, Techniques of Water-Resources Investigations of the United States Geological Survey. U.S. Dept. Interior, Washington, D.C.

Guy, H.P. and V.W. Norman. 1973. "Field methods for measurement of fluvial sediment". Book 3, Chapter C2. Applications of Hydraulics, Techniques of Water-Resources Investigations of the United States Geological Survey. U.S. Dept. Interior, Washington, D.C.

Haworth, E.V. and J.W.G. Lund. 1984. Lake Sediments and Environmental History. Haworth and Lund, eds., Leicester Univ. Press, Leicester, England.

Kemp, A.L.W. et al. 1974. "Sedimentation rates and recent sediment history of Lakes Ontario, Erie and Huron". J. Sed. Petrol. 44:207-218.

Kemp, A.L.W. and N.S. Harper. 1976. "Sedimentation rates and a sediment budget for Lake Ontario". J. Great Lakes Res. 2:324-340.

Krishnaswamy, S. et al. 1971. "Geochronology of lake sediments". Earth Planet Sci. Lett. 11:407-414.

Lebsack, M.E. et al. 1981. "Comparison of bacterial luminescence and fish bioassay results for fossil-fuel waters and phenolic constituents". In: Aquatic Toxicology and Hazard Assessment, 4th Conf., D.R. Branson and K.L. Dickson, eds. American Society for Testing and Materials Special Tech. Pub. 737, Philadelphia, PA, pp. 348-356.

Lerman, A. and T-A. Lietzke. 1975. "Uptake and migration of tracers in lake sediments". Limnol. Oceanogr. 20:497-510.

Lick, W. and W. Kang. 1987. "Entrainment of sediments and dredged materials in shallow lake waters". J. Great Lakes Res. 13: in press.

McAndrews, J.H. 1976. "Fossil history of man's impact on the Canadian flora: an example from southern Ontario". Canadian Bot. Assn. Bull., Suppl. 9:1-6.

McMillan, R.K. and R.L. Thomas. 1977. "Large volume water sampling for recovering of suspended solids in Great Lakes tributaries". 20th Conf. Great Lakes Res., Abstract. Univ. Michigan, Ann Arbor, MI.

Madsen, O.S. and W.D. Grant. 1977. "Quantitative description of sediment transport by waves". 15th Coastal Eng. Conf. II, Proc., pp. 1093-1112.

Makareth, F.J.H. 1966. "Some chemical observations on post-glacial lake sediments". Phil. Trans. R. Soc., B, 250:165-213.

Miles, R. 1977. "Anthropogenic influences of sediment quality at a source: pesticides and PCB's". In: Workshop on the Fluvial Transport of Sediment-Associated Nutrients and Contaminants, Proc. H. Shear and A.E.P. Watson, eds. International Joint Commission, Windsor, ON.

Mount, D.I. and T.J. Norberg. 1984. "A seven-day life-cycle cladoceran toxicity test". Environ. Toxicol. Chem. 3:425-434.

Müller, G., J. Dominik and A. Mangini. 1979. "Eutrophication changes sedimentation in part of Lake Geneva". Naturwissenschaften 66:261-262.

Munawar, M. 1987. "The bioassessment of contaminated sediments with phytoplankton". In: Ecological Effects of in-situ Sediment Contaminants. Hydrobiologia, in press.

Munawar, M. 1982. Toxicity Studies on Natural Phytoplankton Assemblages by Means of Fractionation Bioassays. Can. Tech. Rep. Fish. Aquat. Sci. 1152, Canada Centre for Inland Waters, Burlington, ON.

Munawar, M. and I.F. Munawar. 1981. "A general comparison of the taxonomic composition and size analyses of the phytoplankton of the North American Great Lakes". Verh. Internat. Verein. Limnol. 21:1695-1716.

Munawar, M. and I.F. Munawar. 1982. "Phycological studies in Lakes Ontario, Erie, Huron and Superior". Can. J. Bot. 60:1837-1850.

Munawar, M. and R.L. Thomas. 1984. "Bioassessment of Toronto-Toledo sediments". In: Evaluation of Sediment Bioassessment Techniques, p. 9-50. Report of the Dredging Subcommittee of the Great Lakes Water Quality Board, International Joint Commission, Windsor, ON.

Munawar, M., P. Stadelmann and I.F. Munawar. 1974. "Phytoplankton biomass, species composition and primary production at a nearshore and a midlake station of Lake Ontario during IFGYL". 17th Conf. Great Lakes Res., Proc., Pt.2:629-652.

Munawar, M. et al. 1978. Relative importance of nannoplankton in Lake Superior phytoplankton biomass and community metabolism". J. Great Lakes Res. 4(3-4):462-480.

Munawar, M. et al. 1983. The impact of sediment-associated contaminants from the Niagara River mouth on various size assemblages of phytoplankton". J. Great Lakes Res. 9:303-313.

Oldfield, F. and P.G. Appleby. 1984. "Empirical testing of Pb^{210} dating models for lake sediments". In: Sediments and Environmental History. Haworth and Lund, eds., Leicester University Press, Leicester, England, pp. 93-124.

Ongley, E.D. and D.P. Blachford. 1982. "Application of continuous flow centrifugation to contaminant analysis of suspended sediment in fluvial systems." Environ. Technol. Lett. 219-228.

Porterfield, G. 1972. "Computation of fluvial-sediment discharge." Book 3, Chapter C3. Applications of Hydraulics, Techniques of Water-Resources Investigations of the United States Geological Survey. U.S. Dept. Interior, Washington, D.C.

Qureshi, A.D. et al. 1982. "Comparison of a luminescent bacterial test with other bioassays for determining toxicity of pure compounds and complex effluents." In: Aquatic Toxicology and Hazard Assessment, 5th Conf., J.G. Pearson et al., eds. American Society for Testing and Materials Special Tech. Pub. 766. Philadelphia, PA, pp. 179-195.

Rhee, G-Yull. 1982. "Overview of phytoplankton contaminant problems". J. Great Lakes Res. 8:326-327.

Robbins, J.A., J.R. Krezoski and S.C. Morley. 1979. "Radioactivity in sediments of the Great Lakes: post depositional redistribution by deposit-feeding organisms". Earth Plant. Sci. Lett. 36:325-333.

Robertson, A. and D. Scavia. 1984. "The North American Great Lakes". In: Ecosystems of the World Lakes and Reservoir Systems, F. Taub, ed. Elsevier, N.Y., pp. 135-176.

Ross, P.E. and M. Munawar. 1981. "Preference for nannoplankton size fractions in Lake Ontario zooplankton grazing". J. Great Lakes Res. 7(1):65-67.

Smith, W.E. 1972. "Culture, reproduction, and temperature tolerance of Pontoporeia affinis in the laboratory". Trans. American Fish. Soc. 101(2):253-256.

Strosher, M.T. 1984. A Comparison of Biological Testing Methods in Association with Chemical Analysis to Evaluate Toxicity of Waste Drilling Fluids in Alberta. V. 1. Canadian Petroleum Association, Calgary, AB.

Tessier, A., P.G.C. Campbell and M. Bisson. 1979. "Sequential extraction procedure for the speciation of particulate trace metals." Anal. Chem. 51:844-851.

Thomas, R.L., J-P. Vernet and R. Frank. 1984. " ∑DDT, PCBs and HC in the sediments of Lake Geneva and the Upper Rhöne River." Environ. Geology 5:103-113.

Thompson, R. 1984. "A global review of palaemagnetic results from wet lake sediments." In: Lake Sediments and Environmental History. Haworth and Lund, eds., Leicester University Press, Leicester, England, pp. 145-164.

United States Geological Survey. 1977. National Handbook of Recommended Methods for Water-Data Acquisition, V. 1. U.S. Dept. Interior, Reston, VA.

Vernet, J-P., J. Dominik and P.Y. Favarger. 1984. "Texture and sedimentation rates in Lake Geneva." Environ. Geology 5:143-149.

Wentsel, R. *et al*. 1977. Sublethal effects of heavy metal contaminated sediment on midge larvae (*Chironomus tentans*). Hydrobiologia 56(2):153-156.

Wong, P.T.S., Y.K. Chau and L. Luxon. 1978. "Toxicity of a mixture of metals on freshwater algae." J. Fish. Res. Board Canada 35:479-481.

6.5 OTHER SUGGESTED REFERENCES

Abbott, M., J. Larsen and J. Tao. 1985. "Modelling circulations in depth integrated flows, Pt. I: The accumulation of evidence." J. Hydraul. Res. 23 (4):309-326.

Allen, J.R.L. 1977. Physical Processes of Sedimentation. Allen & Unwin Inc., Winchester, MA.

American Public Health Association. 1985. "Toxicity test methods for aquatic organisms." In: Standard Methods for the Examination of Water and Wastewater. American Public Health Assn., Washington, D.C., pp. 689-823.

American Public Health Association. 1976. Standard Methods for the Examination of Water and Wastewater. American Public Health Association, Washington, D.C.

American Society for Testing and Materials. 1980. Standard Practices for Conducting Acute Toxicity Tests with Fishes, Macroinvertebrates, and Amphibians. American Society for Testing and Materials, Philadelphia, PA.

Ames, B.N., J. McCann and E. Yamasacki. 1975. "Methods for detecting carcinogens and mutagens with Salmonella/mammalian microsome mutagenicity test." Mutation Res. 31:347-364.

Andrews, D.F. 1972. "Plots of high-dimensional data." Biometrics 28:125-136.

Armitage, P. 1971. Statistical Methods in Medical Research. John Wiley & Sons, N.Y.

Barr, A.J., J.H. Goodnight and J.P. Sall. 1979. SAS Users Guide. SAS Institute Inc., Raleigh, NC.

Batac-Catalan, S. and D.W. White, 1981. Creating and Maintaining Cultures of Chironomus tentans (Diptera: Chironomidae). Univ. Michigan, Dept. Zoology, Ann Arbor, MI.

Bedford, K. and D. Mark, 1985. The Effect of Storms on Lake Erie Loading Estimates From Sandusky Bay, NOAA Sea Grant. Ohio State Univ., Dept. Civil Eng., Columbus, OH.

Bedford, K. and M. Abdelrhman. 1987. "Analytical and experimental studies of the benthic boundary layer and their applicability to near-bottom transport in Lake Erie." J. Great Lakes Res. 13: in press.

Bird, R., W. Stewart and E. Lightfoot. 1960. Transport Phenomena. J. Wiley & Sons, N.Y.

Buikema, A.L., Jr. and J. Cairns, Jr. 1980. Aquatic Invertebrate Bioassays. American Society for Testing and Materials Special Tech. Pub. 175, Philadelphia, PA.

Buikema, A.L., Jr., J.G. Geiger and D.R. Lee. 1980. "Daphnia toxicity tests." In: Aquatic Invertebrate Bioassays. A.L. Buikema, Jr. and J. Cairns, Jr., eds. American Society for Testing and Materials Special Tech. Pub. 714, Philadelphia, PA, pp. 48-69.

Chavin, Walter, ed. 1973. Responses of Fish to Environmental Changes. Charles C. Thomas, Springfield, IL.

Daniel, C., F.S. Wood and J.W. Gorman, 1971. Fitting Equations to Data. John Wiley & Sons, N.Y.

Dixon, W.J. ed. 1970. "BMD. Biomedical computer programs." In: Automatic Computation. Ser. 2, 2nd ed. Univ. California Press, Los Angeles, CA.

Dorward, E.J. and B.G. Barisas. 1984. "Acute toxicity screening of water pollutants using a bacterial electrode." Environ. Sci. Tech. 18:967-972.

Draper, N.R. and H. Smith. 1966. Applied Regression Analysis. John Wiley & Sons, N.Y.

El-Shaarawi, A. 1977. "Marginal likelihood solution to some problems connected with regression analysis." J. R. Statistical Soc. B, 39:343-348.

El-Shaarawi, A. and R.E. Kwiatkowski. 1977. "A model to describe the inherent spatial and temporal variability of parameters in Lake Ontario." J. Great Lakes Res. 3:177-183.

Finney, D.J., 1971. Probit Analysis. 34th ed. Cambridge Univ. Press, Cambridge, MA.

Fischer, H. et al. 1979. Mixing in Inland and Coastal Waters. Academic Press, N.Y.

Fisher, R. A. 1941. "The negative binomial distribution." Ann. Eugenics. XI, (II):182-187.

Fisher, R.A., H.G. Thornton and W.A. Mackenzie. 1922. "The accuracy of the plating method of estimating the density of bacterial populations with particular reference to the use of Thornton's agar medium with soil samples." Ann. Appl. Biol. 9:325.

Glass, Gary E. 1975. Bioassay Techniques and Environmental Chemistry. Ann Arbor Sci. Pub., Inc., Ann Arbor, MI.

Gnanadesikan, R. 1977. Methods for Statistical Data Analysis of Multivariate Observations. John Wiley & Sons, N.Y.

Gupta, R.S., B. Singh and D.K. Stetsko. 1985. "Inhibition of metabolic cooperation by phorbol esters in a cell culture system based on adenosine kinase deficient mutants of V79 cells." Carcinogenesis 619:1359-1366.

Hammons, A.S., ed. 1981. Methods for Ecological Toxicology: A Critical Review of Laboratory Multispecies Tests. U.S. EPA, Office of Toxic Substances, Washington, D.C.

Harris, E.K. 1954. "Confidence limits for the LD_{50} using the moving average-angle method." Biometrics 15:424-432.

Jackson, M.L. 1958. Soil Chemical Analysis. Prentice-Hall, Englewood Cliffs, N.J., pp. 175-177.

Kalbfleisch, J.D. and D.A. Sprott. 1970. "Applications of likelihood methods to models involving large numbers of parameters (with discussion)." J. R. Statistical Soc. B 29:357-372.

Linsley, R., M. Kohler and J. Paulhus. 1982. Hydrology for Engineers. McGraw Hill Co., N.Y.

Litchfield, J.T. and F. Wilcoxon. 1949. "A simple method of evaluating dose-effect experiments." Pharmacol. Exp. Theor. 96:99-113.

Maron, D.M. and B.N. Ames. 1984. "Revised methods for the Salmonella mutagenicity test." In: Kilbery, B.J. et al, eds. Handbook of Mutagenicity Test Procedures. Elsevier, N. Y., pp. 93-141.

McIntyre, A.D. and C.F. Mills, eds. 1975. Ecological Toxicology Research: Effects of Heavy Metal and Organohalogen Compounds. Plenum Press, N.Y.

MIC Environmental Sciences. 1980. Standard Operating Procedures, Cleaning Culture Tanks and Test Aquaria. (Document EAS-80-SOP-003)

Mosher, R.G. 1982. Standard Operating Procedures for Culturing the Midge. Chironomus tentans. Monsanto Environ. Sci., St. Louis, MO. (EAS-82-SOP-44)

Mosher, R.G. and W.J. Adams. 1982. Method for Conducting Acute Toxicity Tests with the Midge Chironomus tentans. Monsanto Environ. Sci., St. Louis, MO. (ES-82-M-7)

Mosher, R.G., R.A. Kimerle and W.S. Adams. 1982. Environmental Assessment Method for Conducting 14-day Water Partial Life Cycle Toxicity Tests with the Midge Chironomus tentans. Monsanto Environ. Sci., St. Louis, MO. (ES-82-M11)

Munawar, M. et al. 1984. An Overview of Sediment-associated Contaminants and Their Bioassessment. Canadian Tech. Report Fish. Aquat. Sci. 1253, Canada Centre for Inland Waters, Burlington, ON.

Murphy, J. and J.P. Riley. 1962. "A modified single solution method for the determination of phosphate in natural waters." Analyt. Chim. Acta 27:31-36.

National Academy of Science. 1981. Testing for Effects of Chemicals on Ecosystems. Committee to Review Methods for Ecotoxicology, National Academy Press, Washington, D.C.

Ongley, E.D., M.C. Bynoe and J.B. Percival. 1981. "Physical and geochemical characteristics of suspended solids, Wilton Creek, Ontario." Canadian J. Earth Sci. 18:1365-1379.

Pipes, W. V., P. Ward and S. H. Ahn. 1977. "Frequency distributions for coliform bacteria in water". J. American Water Works Assn. 69:664.

Richards, R.P. 1985. "Estimating the extent of reduction needed to statistically demonstrate reduced nonpoint phosphorus loading to Lake Erie." J. Great Lakes Res. 11 (2):131-142.

Rodi, W., N. Pavlovic and S. Srivatsa. 1981. "Prediction of flow and pollutant spreading in rivers." In: H. Fischer, ed., Transport Models for Inland and Coastal Waters. Academic Press, N.Y.

Schwab, D., J. Bennett and A. Jessup. 1981. A Two-Dimensional Lake Circulation Modeling System. NOAA Tech. Memo ERL-GLERL-38, Ann Arbor, MI.

Schwab, D., J. Bennett and E. Lynn. 1984. A Two-Dimensional Lake Wave Prediction System. NOAA Tech. Memo ERL-GLERL-51, Ann Arbor, MI.

Shuba, P.J., H.E. Tatem and J.H. Gentile. 1977. "Guidance for performing liquid phase and suspended particulate phase phytoplankton bioassays. Appendix E." In: Criteria Dredged and Fill Material into Ocean Waters. Implementation Manual for Section 103 of Public Law 92-532, July 1977. Environ. Effects Lab., U.S. Army Eng. Waterways Experimental Station, Vickburg, MS.

Stora, G. 1975. "Computation of lethal concentrations." Marine Pollut. Bull. 5:69-71.

Strickland, J.D.H. and T.R. Parsons. 1965. A Manual of Sea Water Analysis. Fish. Res. Board Canada Bull. 125.

Syers, J.K., J.D.H. Williams and T.W. Walker. 1968. "The determination of total phosphorus in soils and parent materials." New Zealand J. Agric. Res. 11:757-762.

Thomas, R.L., A.L.W. Kemp and C.F.M. Lewis. 1972. "Distribution, composition and characteristics of the surficial sediments of Lake Ontario." J. Sed. Petrol. 42(1):66-84.

Trosko, J.E. et al. 1981. "In vitro assay for tumor promoters." In: Short-Term Tests for Chemical Carcinogens. H. Stich and R.H.C. San, eds. Springer-Verlag, N.Y., pp. 420-427.

U.S. EPA. 1985. Methods for Acute Toxicolgy Tests with Fish, Macroinvertebrates and Amphibians. Corvallis Environ. Res. Lab., Corvallis, OR.

U.S. EPA. 1978. Methods for Measuring the Acute Toxicity of Effluents to Aquatic Organisms. EPA Monitoring and Support Lab. Cincinnati, OH.

Vanoni, V. 1975. Sedimentation Engineering. American Soc. Civil Eng. Pub. Co., N.Y.

Warren, Charles E. 1971. Biology and Water Pollution Control. W.B. Saunders Philadelphia, PA.

Wetzel, G. R. and G. E. Likens. 1979. Limnological Analyses. W. B. Saunders Co., Philadelphia, PA.

Wilk, M. B. and R. Gnanedesikan. 1968. "Probability plotting methods for the analysis of data." Biometrika 55:1-17.

Wischmeier, W. and D. Smith. 1960. "A universal soil-loss equation to guide conservation farm planning." 7th Int. Conf. Soil Sci., Madison, WI.

Yaksich, S. et al. 1985. "Lake Erie nutrient loads, 1970-1980." J. Great Lakes Res. 11(2):117-131.

7.0 STATISTICAL CONSIDERATIONS

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7.1 INTRODUCTION

Statistics provide methods for making scientific inferences from observations and for developing efficient methods for designing experiments and data collection programs. The general aim is to make inferences about an Area of Concern or to compare the existing conditions of an Area of Concern with a standard or to develop a model for describing the existing variability and to predict future changes. Whatever the aim of the study, the statistician should be part of the study team in all phases of the project, rather than included for advice in analyzing the data only after the study has been completed.

In this section, some useful statistical concepts are briefly presented. These concepts are: summary statistics, sources of variation, some common probability distributions, goodness of fit, difference tests and significance, regression, and sample size.

7.2 SUMMARY STATISTICS

Suppose that the data $x_1, x_2, \ldots, x_n$ have been collected which represent measurements on sampling stations or experimental units and the information is to be summarized using one or two statistics. There are several classes of summary statistics, each of which could be used to represent a specific aspect of the data. The three most common classes are: 1) summary statistics which represent the location or the center of the data; 2) summary statistics for representing the dispersion of the data; and 3) summary statistics for representing the lack of symmetry in the data.

Summary Statistics for the Location:

The most popular statistics for this are:

1. The data mean $\bar{x}$, calculated by the following equation:

$$\bar{x} = \frac{\Sigma x}{n}$$

Although this is the most widely used measure of location, it is seriously influenced by wild observations and hence when outliers are present, $\bar{x}$ can be a bad measure of location.

2. The median M is found by ordering the data and selecting the middle observation. This estimate is least affected by the presence of outliers and hence can be called the most robust measure of location.

3. Trimmed mean $T_n(r)$. This is calculated as the mean of the n-2r central observations, i.e. the mean of the data after eliminating the smallest and the largest r observations from the data. Trimmed means may be preferable to the data mean or the median, depending on how the statistic is to be used and the distribution of the data.

Summary Statistics for the Dispersion of the Data:

The most common measure of dispersion is standard deviation. This is calculated by the formula:

$$s = \frac{\Sigma (x - \overline{x})^2}{n-1}$$

Like the data mean, it can be overly influenced by extreme values. The robust measure of dispersion is the interquantile range which is found by ordering the data and taking the difference between the observation that is exceeded by 25% of the data and the observation that is exceeded by 75% of the data. Another shortcut method is the data range (the largest observation - the smallest observation).

Summary Statistics for the Skewness of the Data:

The third central moment of the data

$$\mu_3 = \Sigma(x - \overline{x})^3/n$$

is commonly used to measure the skewness of the distribution. For a symmetric data set, it is expected that $\mu^{(3)}$ is close to zero. It is common to use $\gamma_3 = \mu^3/s^3$ as the coefficient of skewness. This is preferred since γ_3 is free from the unit of measurement and is zero for symmetric distribution.

For other measures of skewness, see Kendall and Stuart (1958).

Graphical methods such as the Box-plot, the histogram and probability plots are used frequently to summarize data. In fact, many investigators choose to plot their data first to look for outliers before calculating summary statistics. Accounts of the graphical methods can be found in Wilk and Gnanedesikan (1977).

7.3 SOURCES OF VARIATION

The sources of variation encountered in scientific investigations can be classified into two categories: 1) the explained variation; and 2) the unexplained or random variation. The explained variation can be attributed to known causes; for example, the changes in the rate of phytoplanktonic photosynthesis may be related to changes in light and temperature. The unexplained or random variation shows no reproducible pattern and cannot be assigned to a known cause. An example of this variation is the difference between oxygen concentration in duplicate oxygen bottles (Table 19), which probably reflects the variability of the experimental material. It is also convenient to classify the factors causing the variations into those which can and those which cannot be controlled during the course of the study. One wishes, as far as possible, to prevent the uncontrolled factors from altering, in a systematic way, the apparent effects of the controlled factors. Randomization is the statistical technique which can eliminate the effects of systematic bias on the controlled factors. Hence, in any experiment, the levels of the controlled factors should be assigned to experimental units by

TABLE 19

OXYGEN CONCENTRATION IN TWO REPLICATED LIGHT BOTTLES AT DIFFERENT DEPTHS AND THE INDICATOR VARIABLE I_i

DEPTH	OXYGEN BOTTLES x_i	 y_i	INDICATOR VARIABLE I_i
0	8.41	8.31	1
0.5	8.36	8.50	0
1.0	8.43	8.48	0
2.0	9.12	9.06	1
3.0	9.26	9.16	1
4.0	8.51	8.49	1
5.0	8.31	8.39	0
6.0	8.00	8.09	0
7.0	7.12	7.19	0
10.0	5.82	5.71	1
12.0	2.36	2.47	0

randomization. The randomization may be achieved by coin tossing, card drawing or a table of random numbers. A discussion of studies with and without randomization is given by Esterby (1985).

The characterization of the sources of variability allows us, in the planning stage, to use statistical techniques, e.g. blocking or stratification and the collection of other variables for covariance analysis, which increase precision and remove sources of bias (see below). Since each area will have its own characteristics, it is necessary to approach the planning for each area with these general principles in mind.

Random error can be estimated only from replicated measurements; this estimate is usually called the standard error of the experiment. The smaller the value of the standard error, the more precise the experiment will be. The precision of the estimate depends on: 1) the care taken in performing the experiment; 2) the variability of the experimental material; 3) the number of replicates used; and 4) the actual design of the experiment.

It is also important to differentiate between precision and accuracy. Accuracy involves, in some way, the difference between what is measured or observed and what is true; whereas, precision involves the concept of reproducibility of what is measured or observed. It is important to know that a high precision or agreement of results among themselves is no indication that the quantity under measurement has actually been determined. The difference between what is observed and what is true is known as bias.

The statistical evaluation of the sources of variability requires the specification of a probability model. This model contains parameters which characterize the variability and are usually unknown. Statistical methods provide a means of estimating these parameters and of testing the assumptions of the model. In the next section, a number of common probability distributions, which have been used extensively by biologists, are presented.

7.4 SOME COMMON PROBABILITY DISTRIBUTIONS

Known mathematical frequency distributions can be used as models for samples from a population. Three discrete probability distributions are often suitable models for the relationship between variance and arithmetic mean of a population:

Positive binomial
Poisson distribution
Negative binomial

These probability distributions and the normal distribution, which is continuous, are briefly described.

Positive binomial. This is the basis of binomial distributions and is an approximate model when the variance is significantly less than the mean.

The positive binomial distribution is used as a model usually when each individual in a sample can be recognized as: 1) having or not having an attribute; 2) being present or absent; 3) being successful or failing (a test). A full description of the application of the positive binomial is given in most statistical textbooks (Snedecor and Cochran 1967). If the positive binomial is used as an approximate model for samples, the following definitions are appropriate (Elliott 1977):

k is the maximum possible value for a sampling unit
p is the probability of any one of the possible units in the sampling unit being occupied by a value
q is the probability of non-occupancy of a value (q=1-p)

The expected probabilities are given by the expansion of $(q+p)^k$ and can be obtained from tables (Table 37 in Pearson and Hartley 1976). In general, this is an inappropriate model for environmental data because the variance is rarely less than the mean.

Poisson distribution. This is a suitable model when the variance is approximately equal to the mean. The Poisson series is associated with events which occur randomly in a continuum of space or time. Therefore, tests for agreement with a Poisson series are used as tests for randomness of distribution. The use of the Poisson as a mathematical model for the distribution of data involves the following conditions:

1) The probability of any given point in the sampling range occupied by a particular value is constant and small; consequently, there is a high probability of any point in the range not being occupied.

2) The value per sampling unit must be well below the maximum possible number that could occur in the sampling unit.

3) The occurrence of a value at a given point must not increase or decrease the probability of another value occurring.

4) The samples must be small relative to the population.

The probability distribution is given by

$$p(k) = \frac{e^{-\lambda} \lambda^k}{k!}$$

for k = 0,1,2,...

λ can be any positive number. An advantage of the Poisson distribution is that the mean and variance are both equal to λ.

Negative binomial. If the first and third conditions for using the Poisson series are not met, then the variance of the population is usually greater than the arithmetic mean and the population is clumped. In this case the negative binomial distribution is often a suitable model. This distribution is the mathematical counterpart of the positive binomial and the probability series is given by $(q-p)^{-k}$. Unlike the positive binomial, where k is the maximum possible value or number of individuals, a sampling unit could contain in the negative binomial the reciprocal of the exponent k (1/k), which is a measure of the excess variance or clumping of the individuals in a population. As 1/k approaches 0 (and k approaches infinity), the distribution converges to the Poisson series. Conversely, as 1/k approaches infinity the distribution converges to the logarithmic series.

Normal distribution. If an event has an equal chance of occurring or not occurring ($p=q=0.5$) and k approaches infinity, the probability series given by $(q+p)^k$ approaches a bell shaped curve.

This is the normal distribution associated with continuous variables (the normal distribution is rarely suitable for non-continuous variables, i.e. counts without correction). This is important because many statistical methods are associated with a normal distribution, e.g. t-tests, ANOVA, correlation coefficient, and the use of these methods requires that:

1) the data must follow a normal distribution,
2) the variance must be independent of the mean, and
3) the components of variance should be additive.

The positive binomial is approximately normal if n is large (>30). Both the Poisson series and the negative binomial can be approximately normal (when x and k increase in size). However, in all three distributions, mean and variance can increase together (Taylor's Power Law) and, therefore, the second condition of independence of variance and mean is rarely met. This difficulty is overcome by transforming data.

Using an appropriate transformation often results in approximate normality, and thus, standard formulae are available for finding the number of samples required to estimate a quantity with a specified precision or to detect a difference of a specified size. Calculations for more complicated situations such as regression are also possible (Cochran 1983).

Some situations will not be amenable to such treatment, e.g. there are levels below detection limits for some samples, and non-parametric methods may be used. The choice of the method will then allow calculation of the minimum number of samples required to obtain significance at a certain level, e.g. such a calculation was done for the sign test in El-Shaarawi and Esterby (1985). For further discussion, see section 7.7 on sample size.

7.5 GOODNESS OF FIT

In the previous section, several probability models were presented. Clearly, the conclusions obtained from a data set by performing the statistical analysis on the basis of a particular model are dependent on the chosen model. When an incorrect model is chosen, it is more likely that the results obtained are not correct; hence, it is appropriate to examine the suitability of the chosen model to represent the data. In this section, two methods for testing the goodness of fit of a particular model are given. One method is analytical, the other is graphical.

Chi-square goodness of fit test

Suppose that we have n observations from a continuous random variable x, and that it is required to test if the observations can be represented by the probability distribution g(x). The first step is to divide the range of x into k disjoint-intervals,

$$(\delta_0,\delta_1)(\delta_1,\delta_2),\ \ldots\ldots\ (\delta_{k-1},\delta_k)$$

The jth interval (δ_{j-1}, δ_j) includes all the values of x in the interval $\delta_{j-1} \le x < \delta_j$. The number of observations, f_j, falling in interval j $(j = 1,2,..,k)$ is then determined, and

$$f_1 + f_2 + .. + f_k = n.$$

According to the assumed model g(x), the probability that x falls within the jth interval (δ_{j-1}, δ_j) is

$$\begin{aligned} P_j &= \text{Probability } (\delta_{j-1} \le x < \delta_j) \\ &= \text{Probability } (x < \delta_j) - \text{Probability } (x \le \delta_{j-1}) \\ &= G(\delta_j) - G(\delta_{j-1}),\ j = 1,\ 2,\ ..,\ k. \end{aligned}$$

$G(\delta_j)$ is known as the cumulative distribution function of x and can be calculated by summation if x is discrete, by integration if x is continuous, and sometimes from statistical tables as in the case of the normal distribution. The expected frequency, if the model is correct, is

$$e_j = n\ p_j$$

and the chi-square goodness of fit is

$$\begin{aligned} D &= \sum_{j=1}^{k} \frac{(f_j - e_j)^2}{e_j} \\ &= \sum_{j=1}^{k} \frac{\text{observed frequency - expected frequency}}{\text{expected frequency}} \end{aligned}$$

The value of D has approximately a chi-square distribution with (k-1) degrees of freedom; hence, the value of D can be compared with the values of chi-square to test goodness of fit. If g(x) contains unknown parameters, then the values of those parameters are estimated from the data, and the value of D is calculated as above. The number of degrees of freedom in this case is k-1 - (the number of parameters estimated). If some of the expected frequencies e_j are less than five, it is usually advisable to pool the smaller groups so that every group contains at least five expected observations before the test is applied.

Graphical Methods

Graphical techniques provide useful and informal procedures for examining the suitability of a probability model to describe a data set and for suggesting appropriate methods for the analysis of data. The most common plotting techniques for examining models are known as probability plotting methods. A full description of these methods and of their use can be found in Wilk and Gnanadesikan (1968). The authors of this paper review a variety of statistical plotting techniques based on the cumulative distribution function and its ramifications. In particular, they discuss in detail the quantile probability (Q-Q plots), percentage probability plots (P-P plots) and extensions of these. Plotting techniques associated with regression analysis can be found in Draper and Smith (1966; Chapter 3), and Daniel et al. (1971). Multivariate data can be plotted using the methods given by Andrews (1972) and Gnanadesikan (1977).

7.6 DIFFERENCE TESTS AND SIGNIFICANCE

The simplest form of parametric difference test is the t-test, based on the Student's t-distribution. If it is desired to test whether a sample mean is different from a given standard, then the t-statistic is calculated in the following manner:

$$t = \frac{(\bar{x}-\mu)\sqrt{n}}{s}$$

where: $\bar{x}$ is the sample mean
μ is the standard
n is the sample size
and s is the sample standard deviation.

The t-value, thus obtained, is compared to the appropriate t-value from a table of the Student's t-distribution (available in any basic statistics text) for the desired significance level and degrees of freedom (sample size -1). If the calculated t-value exceeds the tabulated one, the difference is considered significant at the stated level.

There are many variations on the simple t-test for difference comparisons. There is also a test for multiple differences, called the analysis of variance (ANOVA). These methods may be found in any basic statistics text.

The two most serious factors affecting the outcome of a difference test, e.g. Student's t, is how well the variable is measured, i.e. its variance and how confident the investigator wants to be that the decision is correct, i.e. significance level. It is likely that a variable would test to be not unlike a given standard if the variable was measured poorly (but unbiased) with, for example, a coefficient of variation (=standard deviation divided by the mean) of 200%. Also likely is that a test would give different results if one required 95% confidence in the decision compared to 50%.

Significance Levels

The decision of what significance level should be required cannot and should not be predetermined for all properties. Selection of 95% or 90%

levels of significance for reasons of tradition are arbitrary and often inappropriate. Without getting deeply into a description of technical aspects, it is important to bring in the notion of risk assessment or attention to the risk associated with making an incorrect decision. This idea should dictate the appropriate level of significance for testing differences. When the chance of being wrong is highly dangerous, e.g. PCB levels in fish, one should require a high level of confidence in the test, e.g. 99%; when the danger is low, e.g. total P, lower confidence may be more appropriate, e.g. 85-90%. While subjective arguments like this one are fairly easy to make, quantification of relative risks is another matter. However, certain strides have been made recently in this area and one begins to think that bounds are available within which some risks can be compared.

The usual procedure for tests of differences is to calculate a test statistic and compare it to tabulated values for a given level of significance. Even after selecting an appropriate level of significance for the problem at hand, this procedure can lead to seemingly arbitrary decisions, especially for environmental data. It is better to state the attained level of significance for a test rather than the "pass/fail" approach usually used. For example, if one wishes to test whether a measured variable is less than some standard, there is more information in the report that it is less than the standard at a 94.5% level of confidence than that the difference is not significant at the 95% level. Does it make sense to enforce or suggest an important management decision if the level of confidence is 95% but not if the level is 94.5%?

7.7 REGRESSION

In the previous sections, methods were described which are suitable for the analysis of observations on a single variable, or when repeated measurements were made under essentially the same conditions. In the situations where the data represent observations or measurements on several variables, the objective is to examine the associations between these variables. It is highly recommended, as a first step in the examination of the association between two variables x and y, to prepare a scatter diagram by plotting the values of y against the corresponding values of x. This diagram will suggest the form of the distribution of each variable and will show the pattern of association between the two variables. Further statistical analyses is concerned with estimating the relationship between the two variables and predicting the value of one variable when the value of the other variable is known. The methods of regression analysis are the statistical tools that are usually applied when estimating the relationship between variables.

It is important to distinguish between association and causation. A variable is associated with another variable if changes in one variable can be predicted from the changes in the other variable; on the other hand, causation indicates that the variation in one variable has to be preceded by variation in the other. Also, it is important to distinguish between situations in which both variables are random, such as measuring the length and weight of a random sample of fish from a fish tank, and situations in which the value of one variable is deliberately selected by the investigator.

Simple Linear Regression

Assume that the values (x_1, y_1), .., (x_n, y_n) of the two random variables x and y are available for each of n independent individuals. The assumption that x and y are random variables permits us to define two types of regression equations: a) the regression equation of y on x and b) the regression equation of x on y. In the case where x is selected deliberately by the investigator, it is possible only to define the regression of y on x.

Suppose that the regression equation y on x can be described by the form

$$f(x_i) = \alpha + \beta x_i$$

Here the linear function f(x) represents the mean of the random variable y when the variable $x = x_i$. It is then described:

$$\begin{aligned} y_i &= f(x_i) + e_i \\ &= \alpha + \beta x_i + e_i, \; i = 1, 2, .., n \end{aligned}$$

where e_i is a random variable with zero mean and the coefficients α and β are unknown constants. From this, it is clear that the role of e_i is to link the regression equation with the observations. If the variance σ^2 of e_i is constant and independent of x_i, the regression model is called homoscedastic, while the case where σ^2 is not constant is called heteroscedastic. Further, it is assumed that the distribution of e_i is normal.

Under the above assumptions, the constants α and β can be estimated by the method of least squares with full efficiency. It is well known (Armitage, 1971; p. 151) that the least squares estimates of α and β are given by

$$\beta = \sum_{i=1}^{n} (x_i - \bar{x})(y_i - \bar{y}) \Big/ \sum_{i=1} (x_i - \bar{x})^2$$

and

$$d = \bar{y} - \beta\bar{x}$$

The value of the random variable y is then estimated as

$$y = 2 + \beta x$$

and the residual associated with the observation at $x = x_i$ (which is the difference between the observation y_i and its estimated value y_i) is

$$r_i = y_i - 2 - \beta x_i$$

Also, it can be shown that the variance σ^2 is estimated by

$$s^2 = \sum_{i=1}^{n} (y_i - y_i)^2/n-2$$

Several questions need to be answered when regression analysis is performed. First, check whether the true value of the slope β is zero. Testing this assumption is equivalent to testing if the two variables x and y are not linearly correlated. This can be done by calculating the standard error of β

$$s(\beta) = s/ \sum_{i=1}^{n} (x_i - \bar{x})^2$$

and the corresponding t is estimated by

$$t = \beta/S(\beta)$$

The value of t can be compared with the tail value of the t-distribution with (n-2) degrees of freedom and at the significance level α, t_{n-2}, α. In the same manner, the 95 percent confidence interval for β is given by

$$\beta \pm t_{n-2,\ 0.05}\ S(\beta)$$

Model Checking

The above analysis is based on many assumptions, and hence, the results obtained are correct if the assumptions are adequate. These assumptions can be tested by examining the residuals r_i, ..., r_n, which can be done graphically and analytically. Methods for the examination of residuals can be found in the following references: Draper and Smith (1966), and Daniel et al. (1971).

7.8 SAMPLE SIZE

As mentioned above, it makes little sense to compare a poorly measured property against standards. The typical arguments on accuracy and precision are applicable here as well. More important, how many samples need to be taken or experiments need to be performed? What is the appropriate coefficient of variation to require (expect?) for such data? Obviously, the larger the variance in the sample, the larger the differences must be for detection. Thus, the same argument applies here as for the level of significance above. Important or potentially dangerous decisions must rely on firm data (<10% coefficient of variation is suggested). The notion that more data will reduce the variance is often true but sometimes misleading. If a reasonable estimate of the distribution and variance of a population is known, it is possible to determine from formulae found in most statistical texts, how many samples would be required to achieve a given level of confidence. However, the requirement of sampling from a static population is seldom possible. For example, increasing the sample size by adding data from a seasonally varying property could increase the variance if the data were not properly stratified. Data collection must also closely match the stated objectives of the standards. For example, a standard requiring that concentration of a certain chemical never exceed 10 mg/L for an annual average cannot be tested adequately with even a million samples all taken within one month.

Sample size calculations provide a guide in planning, but if the calculations are performed without identifying the sources of variation, the estimated sizes will be unrealistic and often too large, since variances will have been calculated from inhomogeneous sets of data.

When sampling water, there are three dimensions to the spatial variability; the temporal components are seasonal, diurnal and systematic or sporadic due to point sources. Given a set of objectives, the importance of each component can be assessed. Knowledge of the flow will be needed to determine how to sample if composite samples are used to estimate loading of toxic substances since the individual sample sizes making up the composite can be made proportional to flow.

7.9 REFERENCES

Andrews, D.F. 1972. "Plots of high-dimensional data." Biometrics 28: 125-136.

Armitage, P. 1971. Statistical Methods in Medical Research. Wiley & Sons, N.Y.

Cochran, W.G. 1983. Planning and Analysis of Observation Studies. Wiley & Sons, N.Y.

Daniel, C., F.S. Wood and J.W. Gorman. 1971. Fitting Equations to Data. Wiley & Sons, N.Y.

Draper, N.R. and H. Smith. 1966. Applied Regression Analysis. Wiley & Sons, N.Y.

Elliott, J.M. 1977. "Some methods for the statistical study of seven grubs used for sampling benthic invertebrates in rivers." Freshwater Biol. 11: 245-261.

El-Sharawi, A.H. and S.R. Esterby. 1984. Statistical Analyses of Niagara River Data for the Niagara River Toxics Committee Report. NWRI Contribution 84-37, Burlington, ON.

Esterby, S.R. 1985. Statistical Methods for Studying Biotic Responses to Persistent Toxic Substances. NWRI Contribution No. 85, Burlington, ON.

Gnanadesikan, R. 1977. Methods for Statistical Data Analysis of Multivariate Observations. Wiley & Sons, N.Y.

Kendall, M.G. and A. Stuart. 1958. The Advanced Theory of Statics, 3 vols. Charles Griffin & Co., London and High Wycombe.

Pearson, E.S. and H.O. Hartley. 1976. Biometrika Tables for Statisticians. Charles Griffin & Co., London.

Snedecor, G.W. and W.G. Cochran. 1967. Statistical Methods, 6th ed. Iowa State Univ. Press., Ames, IA.

Wilk, M.B. and R. Gnanedesikan. 1968. "Probability plotting methods for the analysis of data." Biometrika: 55, 1-17.

APPENDIX 1

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