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Report of the Aquatic Ecosystem Objectives Committee to the Great Lakes Science Advisory Board 1980

Aquatic Ecosystem Objectives Committee

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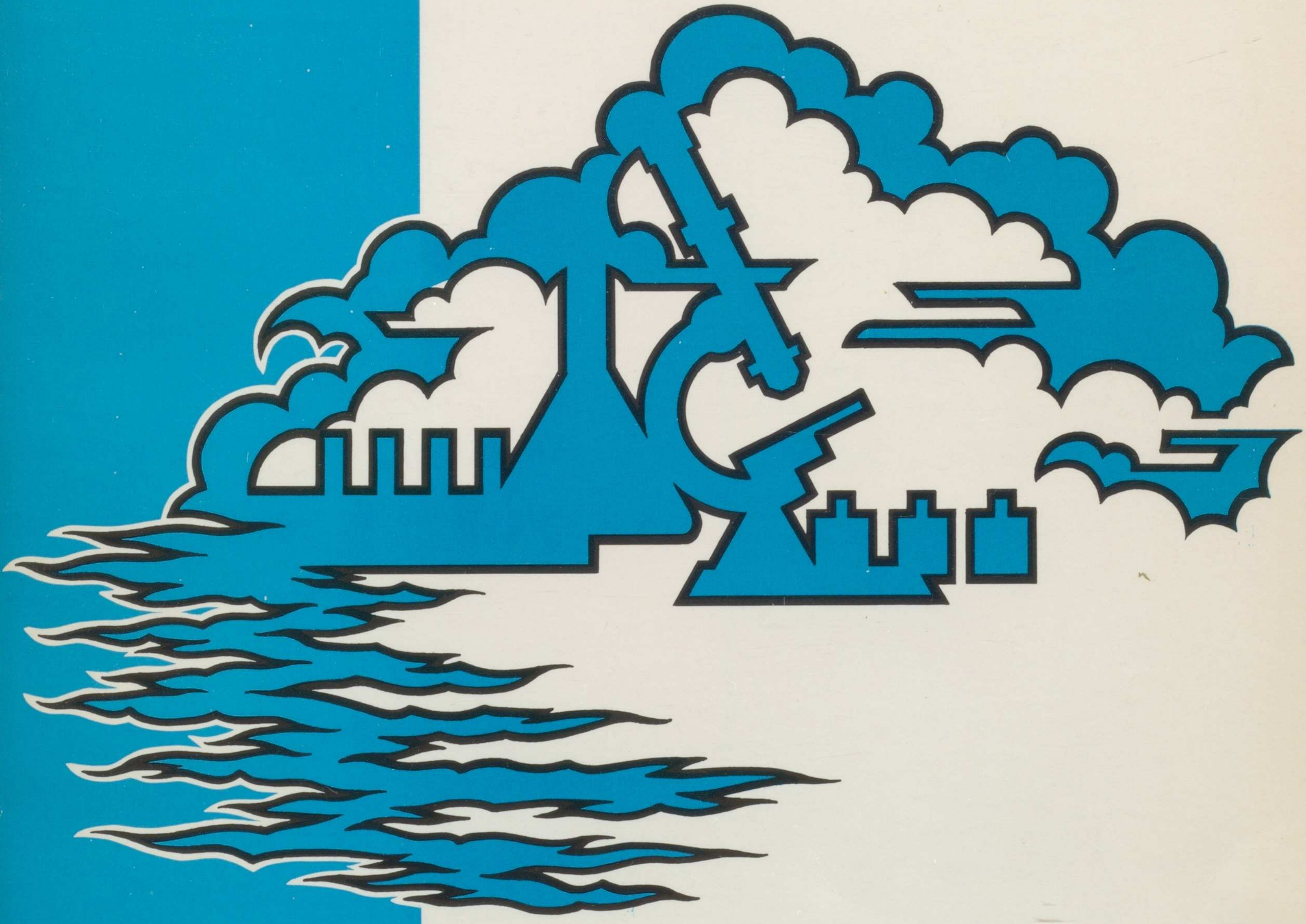
GREAT LAKES
SCIENCE ADVISORY BOARD



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REPORT OF THE AQUATIC ECOSYSTEM OBJECTIVES COMMITTEE

GREAT LAKES SCIENCE ADVISORY BOARD

REPORT OF THE AQUATIC ECOSYSTEM OBJECTIVES COMMITTEE

NOVEMBER 1980

This report is available from:

Great Lakes Regional Office
International Joint Commission
100 Ouellette Avenue
Windsor, Ontario N9A 6T3

PREFACE

This report to the Science Advisory Board was prepared by the Aquatic Ecosystem Objectives Committee. Though the Board has reviewed and approved this report for publication, some of the specific conclusions and recommendations may not be supported by the Board.

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SUMMARY AND RECOMMENDATIONS

SUMMARY

Chapter 1 describes the background for and the importance of objectives, the types of objectives contained in the 1978 Great Lakes Water Quality Agreement, and the application of these objectives to the waters of the Great Lakes. The chapter summarizes the framework utilized by the Aquatic Ecosystem Objectives Committee (AEOC) to develop objectives. Chapter 1 also relates the ecosystem concept to objectives and summarizes the uses of Great Lakes waters which are to be protected. The chapter further relates objectives to standards and, finally, discusses the social and economic assessment of objectives.

Chapter 2 describes the activities of AEOC to date, including development of new specific water quality objectives, review of the adequacy of the data base for present objectives and for deferred substances, development of a holistic approach for specific objectives, and development of an example of an aquatic ecosystem objective.

Chapter 3 presents recommended objectives and supporting rationale for pentachlorophenol, 2,3,7,8-tetrachlorodibenzo-para-dioxin, a microbiological indicator, nutrients, and lead.

Chapter 4 discusses the status of objectives previously proposed, but not incorporated into the 1978 Great Lakes Water Quality Agreement: dissolved oxygen, chlorine, silver, cyanide, temperature, and nutrients. Recommendations on action to be taken are presented.

Chapter 5 describes the future directions of AEOC and presents some candidates for possible future objectives.

RECOMMENDATIONS

AEOC recommends the adoption of the following objectives into the 1978 Great Lakes Water Quality Agreement, to be used, where applicable, together with the existing objectives:

PENTACHLOROPHENOL

Pentachlorophenol in water should not exceed a concentration of 0.4 μg/L for the protection of aquatic life.

POLYCHLORINATED DIBENZODIOXINS

For the protection of all life forms, 2,3,7,8-tetrachlorodibenzo-para-dioxin (TCDD) should be absent from all compartments of the ecosystem including air, land, water, sediment, and biota.

NOTE 1: Absent means not detectable as determined by the best available technology.

NOTE 2: The present (1980) detection limit for TCDD is 0.01 μg/kg in tissue and in sediment and is 0.00001 μg/L in water.

NOTE 3: Other tetrachlorodioxin isomers and higher chlorinated dioxin congeners are of concern in the Great Lakes Ecosystem. However, the data base is inadequate to support a scientifically defensible recommendation at this time.

MICROBIOLOGICAL INDICATOR

PRESENT MICROBIOLOGICAL OBJECTIVE

Waters used for body contact recreation activities should be substantially free from bacteria, fungi, or viruses that may produce enteric disorders or eye, ear, nose, throat and skin infections or other human diseases and infections.

RECOMMENDED ADDITION

For the protection of human health, the level of fecal coliform bacteria shall not exceed a logarithmic mean of 200 fecal coliforms per 100 mL of sample, based upon a minimum of five samples taken over a 30-day period, nor should more than 20% of the total number of samples taken during any 30-day period exceed 800 fecal coliforms per 100 mL of sample.

LEAD

PRESENT OBJECTIVE

The concentration of total lead in an unfiltered water sample should not exceed 10 micrograms per litre in Lake Superior, 20 micrograms per litre in Lake Huron and 25 micrograms per litre in all remaining Great Lakes to protect aquatic life.

RECOMMENDED NEW OBJECTIVE

Concentrations of total lead in an unfiltered water sample should not exceed 2 μg/L in Lake Superior, 3 μg/L in Lake Huron, 4 μg/L in Lake Erie and in Lake Michigan, and 5 μg/L in Lake Ontario to protect aquatic life.

NOTE: This recommendation will not necessarily protect aquatic biota from the effects of alkyl lead compounds.

AEOC also recommends that the following objectives, proposed previously, be adopted into the 1978 Great Lakes Water Quality Agreement:

CHLORINE

Total residual chlorine, as measured by the amperometric (or equivalent) method, should not exceed 0.002 mg/L in order to protect aquatic life.

SILVER

Concentrations of total silver in an unfiltered water sample should not exceed 0.1 μg/L to protect aquatic life.

CYANIDE

Concentrations of free cyanide in unfiltered water samples should not exceed 5 μg/L for the protection of aquatic life.

TEMPERATURE

1. *Thermal additions to receiving waters or a designated segment thereof should be such that thermal stratification and subsequent turnover dates are not altered from those existing prior to addition of heat from artificial origin.*

2. *Maximum Weekly Average Temperature*
   This is the mathematical mean of multiple, equally spaced daily temperatures.

   A. *For Growth*
   The maximum weekly average temperature (MWAT) in the zone inhabited by the species at that time should not exceed one-third of the range between the optimum temperature (To) and the ultimate upper incipient lethal temperature (Tu) of the species, in order to maintain growth of aquatic organisms at levels necessary for sustaining actively growing and reproducing populations. Thus,

$$MWAT = To + \frac{Tu - To}{3}$$

   The optimum temperature is assumed to be for growth but other physiological optima may be used in the absence of growth data. The MWAT must be applied with adequate understanding of the normal seasonal distribution of the important species.

   B. *For Reproduction*
   The MWAT for reproduction should not exceed those limits for normal spawning; in addition these objectives must protect gonad growth and gamete maturation, spawning migrations, spawning itself timing and synchrony with cyclic food sources, and normal patterns of gradual temperature changes throughout the year. The protection of reproductive activity must take into account normal months during which these processes occur in specific water bodies for which objectives are being developed.

   C. *For Winter Survival* *(applicable at any place inhabitable by fish)*
   The MWAT for fish survival during winter should not exceed the acclimation, or plume, temperature (minus a 2.0 C° safety

factor) that raises the lower lethal threshold temperature above the normal ambient water temperature for that season. This temperature limit will apply in any area to which the fish have access and would include areas such as unscreened discharge channels. This objective is necessary to eliminate fish kills caused by rapid changes in temperature due to plant shutdown or movement of fish from a heated plume to ambient temperature.

3. *Short-term Exposure to Extreme Temperature*

   A. *For the Season of Growth*

   The temperature objective for (1) short-term exposure during the growth season is the 24-hr. median tolerance limit, minus 2 C°, at an acclimation temperature approximating the MWAT for that month; and (2) short-term exposure during the spawning season is the upper temperature for successful incubation and hatching. These exposures should not be too lengthy or frequent or the species could be adversely affected. The length of time in minutes (t) that 50 percent of a population will survive temperatures above the incipient lethal temperature (T in °C) can be calculated from the following regression equation:

$$\log (t) = a + b(T)$$

   where a and b are intercept and slope, respectively, which are characteristics of each acclimation temperature for each species.

   B. *For the Season of Reproduction*

   The short-term maximum temperature for the season of reproduction should be based on the maximum incubation temperature for successful embryo survival. The maximum temperature for spawning is probably an acceptable alternative.

NUTRIENTS

PRESENT PHOSPHORUS OBJECTIVE

The concentration should be limited to the extent necessary to prevent nuisance growths of algae, weeds and slimes that are or may become injurious to any beneficial water use.

RECOMMENDED NUTRIENT OBJECTIVES

1. *The lake-wide mean total phosphorus concentration in the spring in Lake Superior should not exceed 5 μg/L to maintain the lake in its present oligotrophic state.*

2. *The lake-wide mean total phosphorus concentration in the spring in the main body of Lake Huron, Georgian Bay, and the North Channel should not exceed 5 μg/L to maintain the lake in its present oligotrophic state.*

3. *The area-wide mean total phosphorus concentration in Saginaw Bay in the spring should not exceed 15 µg/L to prevent nuisance growths of aquatic weeds and algae.*

4. *The lake-wide mean total phosphorus concentration in Lake Michigan in the spring should not exceed 7 µg/L to return the lake to its natural oligotrophic state.*

5. *The basin-wide mean total phosphorus concentration in the Western Basin of Lake Erie in the spring should not exceed 15 µg/L to reduce the present levels of algal growth and to prevent nuisance growths of aquatic weeds and algae in this basin.*

6. *The basin-wide mean total phosphorus concentration in the Central Basin of Lake Erie in the spring should not exceed 10 µg/L to restore year-round aerobic conditions in the bottom waters of this basin.*

7. *The basin-wide mean total phosphorus concentration in the Eastern Basin of Lake Erie in the spring should not exceed 10 µg/L to reduce the present levels of algal growth and to prevent nuisance growths of weeds and algae in this basin.*

8. *The lake-wide mean total phosphorus concentration in Lake Ontario in the spring should not exceed 10 µg/L to prevent nuisance growths of weeds and algae in this basin.*

1 INTRODUCTION

BACKGROUND

Objectives in the 1972 Great Lakes Water Quality Agreement were revised and expanded, and new objectives developed, by two committees: the Water Quality Objectives Committee (WQOS) of the Water Quality Board, and the Scientific Basis for Water Quality Criteria Committee (SBWQC) of the Research Advisory Board (now the Science Advisory Board). Many of the recommendations of these two groups appear in Annex 1 of the 1978 Great Lakes Water Quality Agreement. Because of concerns that these objectives did not take account of the interdependence of all parts of the ecosystem, nor of the interactions of toxicant effects on both aquatic organisms and wildlife, the 1978 Agreement broadened the scope of the objectives to include ecosystem quality rather than the narrower focus of water quality utilized in the 1972 Agreement. The task of developing these objectives was assigned to the Aquatic Ecosystem Objectives Committee (AEOC) of the Science Advisory Board. This report is the first response to that charge.

IMPORTANCE OF OBJECTIVES

The definition of an objective, as given in the 1978 Water Quality Board report, "Group 2 - Proposed New and Revised Water Quality Objectives," can be adapted to take account of ecosystem concerns. The modified definition of an objective is: the criteria for describing a desired state of an ecosystem, a concentration of a substance, or a description of a condition that is considered protective of the most sensitive use. Objectives have been chosen as minimum goals by the governments of Canada and the United States as a part of the 1978 Agreement.

As for the 1972 Agreement, objectives are the underpinnings of the 1978 Agreement. Objectives provide a basis for measuring progress under the Agreement and for determining the overall state of the Great Lakes. Objectives are therefore central to programs in the United States and Canada for ensuring desired ecosystem quality. Objectives provide a valuable ingredient in hazard assessment and in determining the degree of waste treatment required.

The 1978 Agreement states that "water quality standards and other regulatory requirements of the Parties shall be consistent with the achievement of the General and Specific Objectives. The Parties shall use their best efforts to ensure that water quality standards and other regulatory requirements of the State and Provincial Governments shall similarly be consistent with the achievement of these Objectives."

Water quality standards are objectives which have been included as a part of the enforceable environmental control laws of a unit of government. Standards usually relate to a specific use and contain a schedule for compliance.

The influence and utilization of Agreement objectives in the formulation and adoption of legally enforceable jurisdictional standards for the Great Lakes System is the subject of a report entitled, "A Review of the Impact of Water Quality Agreement Objectives on Water Quality Standards," prepared for the Water Quality Board by K.H. Walker and published in June 1980. The report concludes that the Agreement objectives have had a strong influence on the development of standards in the several jurisdictions.

TYPES OF OBJECTIVES

The 1978 Agreement contains both general and specific objectives. The general objectives are non-numerical, non-specific with respect to substances, and largely provide for aesthetic uses. The specific objectives given in Annex 1 describe "the minimum levels of water quality desired in the boundary waters of the Great Lakes System. . . ." They are intended to protect specific uses, such as habitat for aquatic life and recreation, from identified chemical substances.

Ecosystem objectives are a new class of objectives which describe desired states of the Great Lakes; as such, they are true goals (see discussion on pages 9 and 10).

APPLICATION OF OBJECTIVES

The 1978 Agreement states that "all reasonable and practicable measures shall be taken to maintain or improve the existing water quality in those areas of the boundary waters of the Great Lakes System where such water quality is better than that prescribed by the Specific Objectives, and in those areas having outstanding natural resource value." The difference between an objective value and existing conditions must not be considered as a sink for additional disposal. Indeed, objectives "are not intended to preclude the establishment of more stringent requirements."

The 1978 Agreement provides for designation of limited use zones, "within which some of the Specific Objectives may not apply." These limited use zones can be of two types: (1) those ". . . in the vicinity of present and future municipal, industrial and tributary point source discharges . . ." and (2) those ". . . inshore waters [where] natural phenomena exist which, despite the best efforts of the Parties, will prevent the achievement of some of the Specific Objectives." Further discussion of the relationship of objectives to limited use zones is given in Chapter 5.

FRAMEWORK FOR SPECIFIC OBJECTIVES

The scientifically defensible framework for the development of new water quality objectives and for the review of present objectives was developed by WQOS/SBWQC. AEOC endorses this framework with the understanding that it also include the aquatic ecosystem and also not necessarily be restricted to objectives for concentrations in water. This framework is clearly enunciated in the IJC report, "New and Revised Great Lakes Water Quality Objectives," Volume II, published in 1977. The framework is summarized below:

1. In developing specific water quality objectives the philosophy of protecting the most sensitive use was employed.

2. Adoption of objectives does not preclude the need for studying the aquatic environment and effects of conditions on related organisms and uses. Because infinite combinations of water quality characteristics may occur, the objectives could not take into account antagonistic, synergistic and additive effects.

3. Because new data may lead to modified recommendations, the objectives should be subject to continual review.

4. Because no adequate scientific data base exists for establishing scientifically justifiable numerical objectives for certain unspecified non-persistent toxic substances and complex wastes, criteria for developing an objective for local situations have been recommended.

5. Biological effect levels were recognized as well as the concentration of a substance or level of physical effect.

6. The objectives should serve as a minimum target wherever water quality objectives currently are not being met.

7. For jurisdictionally-designated areas which have outstanding natural resource value and existing water quality better than the objectives, the existing water quality should be maintained or enhanced.

8. Specific water quality objectives were designed to be met at the periphery of mixing zones. This assumes that water quality conditions better than the objectives will result beyond the mixing zones. The objectives should be implemented in concert with limitations on the extent of mixing zones or zones of influence and localized areas as designated by the regulatory agencies.

9. In recommending objectives to protect raw drinking water supplies, it has been assumed that a minimum level of treatment is provided before distribution to the public for consumption.

ECOSYSTEM CONCEPT AND OBJECTIVES

A philosophy of the Great Lakes Basin as an ecosystem is presented in the 1978 report of the Research Advisory Board entitled, "The Ecosystem Approach." That report defined the Great Lakes Basin as "an Ecosystem composed of interacting elements of the hydrosphere (natural waters), atmosphere, lithosphere (soils, rocks, sediments) and biota (encompassing man) in the drainage basin of the St. Lawrence River at or upstream from the point at which this river becomes the international boundary between Canada and the United States."

The ecosystem concept for objectives is reflected in the fact that the 1972 Agreement contained water quality objectives, whereas the 1978 Agreement has dropped the word "water", giving greater emphasis to the interdependence of the various parts of the system. This philosophy is also reflected in the terms of reference of AEOC, as well as in other portions of the 1978 Agreement, the terms of reference of the Water Quality Board and the Science Advisory Board, and the nature of many of the supporting programs.

USES OF THE GREAT LAKES

AEOC predicates specific objectives on provision for, and protection of the most sensitive use of the waters of the Great Lakes. The uses and values considered by AEOC include:

1. Public water supply
2. Maintenance of natural biological communities
3. Production of aquatic biota for human consumption
4. Recreation in and on the water
5. Navigation
6. Irrigation
7. Industry
8. Power generation
9. Aesthetics
10. Disposal of treated waste

In the development of objectives, AEOC considers a wide variety of scientific data related to effects by chemical substances or physical conditions on desired uses. AEOC also considers historical points in the development of the Great Lakes in determining the desired state of the lakes to be sought. Generally, the most sensitive uses to be protected are public health and aquatic biota and wildlife.

SOCIAL AND ECONOMIC IMPLICATIONS OF OBJECTIVES

Responsibility for assessing the social and economic implications of proposed objectives lies with the Water Quality Board. The IJC and the Water Quality Board have tried different procedures to obtain this type of information, including public hearings for those objectives proposed between 1975 and 1977 by WQOS/SBWQC. Although little social and economic material resulted from the hearings, most of these proposed objectives were ultimately incorporated into the 1978 Agreement.

Recognizing the paucity of social and economic information so received, the Water Quality Board formed, as a test case, a task force to assess the proposed chlorine objective and to determine whether a formal mechanism could be established within the Agreement structure to provide information to complement the scientific and technical information utilized to develop and substantiate a proposed objective. Details of the social, economic, and technological findings of the Chlorine Objective Task Force may be found in their 1980 report. Implications of their findings for the proposed chlorine objective are discussed in Chapter 4. Among other recommendations, the task force recommended to the Water Quality Board that, in the future, such assessments be carried out by the jurisdictions when objectives are being translated into standards. The IJC has now directed the Water Quality Board to deal with the policy implications of proposed objectives on an *ad hoc* basis; no formal mechanism currently exists for social and economic review.

2 ACTIVITIES

The activities of the Aquatic Ecosystem Objectives Committee (AEOC) are determined by its terms of reference (page 121). These activities fall into four general areas:

1. Development of new specific water quality objectives
2. Review of the adequacy of the data base for present objectives and for deferred substances
3. Development of a holistic approach for specific objectives
4. Development of aquatic ecosystem objectives.

NEW SPECIFIC OBJECTIVES

Although AEOC acknowledges the large number of chemical substances which exist, it is interested in developing objectives only for those substances which are an identified or a potential concern for the Great Lakes Ecosystem and for which a suitable data base exists. AEOC identifies substances of concern according to the following criteria:

1. Has a given substance or its degradation product(s) been found in the Great Lakes Ecosystem? For example, is it listed in the 1976 or the 1977 Appendix E's, which summarize organic substances and heavy metals found in the Great Lakes Basin; or has a substance been detected as the result of more recent studies?
2. What is the substance's potential adverse effects, e.g. acute toxicity, carcinogenicity, mutagenicity, teratogenicity, persistence, bioaccumulation, aesthetics, and chronic adverse effects. Information is gleaned from several sources including the scientific literature; the activities of other Agreement groups, such as the Health Effects Committee, which has been conducting an assessment of Appendix E substances from a human health point of view; from assessments conducted by various jurisdictions, such as the Michigan Critical Materials Register; and from priorities established by jurisdictions in the Great Lakes Basin.
3. What are the quantities of the substance produced and/or used, the volumes discharged, and in what locations in the basin?

Other factors in the selection of candidate substances are the professional knowledge and perception of the committee members themselves and of their colleagues.

Objectives may be developed by a task force, assignments to committee members, and assignments to professionals and scientists within the various agencies. The procedure followed ensures consideration of all available information, provides for thorough peer review at all stages of the development of an objective, and also incorporates the unique Great Lakes perspective.

If an adequate data base is not found for a substance, then research needs to develop the required information are submitted to the Science Advisory Board.

For this report, specific objectives are presented for pentachlorophenol, microbiological indicators, and 2,3,7,8-tetrachlorodibenzo-para-dioxin. These are presented in Chapter 3.

REVIEW OF ADEQUACY OF PRESENT OBJECTIVES AND DEFERRED SUBSTANCES

WQOS/SBWQC began developing water quality objectives in 1973. Each objective which was developed was based on data published or available at the time. WQOS/SBWQC also examined a number of substances for which no objectives were proposed, since the extant data base was inadequate (Table 1).

TABLE 1

SUBSTANCES RESEARCHED BY WQOS/SBWQC FOR WHICH
INSUFFICIENT SCIENTIFIC DATA TO RECOMMEND DEFENSIBLE OBJECTIVES

Antimony
Asbestos
Barium
Boron
Cobalt
Manganese
Molybdenum
Vanadium
Organotin compounds
Elemental phosphorus
Polynuclear aromatic hydrocarbons

AEOC periodically reviews the literature to determine if sufficient new information exists to justify revising an existing objective or to warrant developing an objective for a deferred substance (Chapter 5).

HOLISTIC APPROACH TO SPECIFIC OBJECTIVES

AEOC has adopted the philosophy that an objective should be broadly based. For this, it should consider the concept of contaminant cycling within the ecosystem; the importance of mechanisms to describe residence times, exposures, and pathways; and the concentration limitations in water, sediment, and fish flesh. These objectives should be designed to limit adverse effects to aquatic biota and to consumers of aquatic biota, as well as to any other uses as previously outlined.

The lead objective has been strengthened to reflect this broader, more holistic concern for more than the water column alone. Data were required on rates of transport, complexation, particulate adsorption, sedimentation, and methylation; and on availability and toxicity of lead at each stage in the transport chain. This new rationale clearly indicates that the data either do not exist or are fragmentary in nature, and are not easily related to one another. The result is that objectives were formulated only for inorganic lead concentrations in water. It is likely that this situation also exists for most toxic substances. Therefore, until data on transport, transformation, and toxicity of contaminants are collected in a comprehensive and consistent way, it will not be possible to adequately formulate holistic objectives for compartments other than water.

AQUATIC ECOSYSTEM OBJECTIVES

An aquatic ecosystem objective is envisaged as a desired state of the system and integrating all aspects of the ecosystem. An aquatic ecosystem objective is intended to recognize the integrated nature of the ecosystem and can contain several indicators of the system's state of well being. An aquatic ecosystem objective can provide a perspective to a number of present physical, chemical, and other properties of the ecosystem; many of these are described, for example, by the present Agreement objectives. For the overall aquatic ecosystem objective to be met, these specific objectives would also have to be met, in addition to the yet-to-be-developed ecosystem indicators.

These indicators might be chlorophyll levels and nutrient concentrations, or such emergent properties as species composition, yields, and community diversity. Deviations from specified values would be indicative of a perturbation. If a deviation is observed, then the nature of the stress can be investigated through scientific studies and corrective programs or measures. A stress may be due to the introduction of a chemical contaminant, but may also arise from other human factors, natural occurrences or, more commonly, a combination of simultaneous factors.

AEOC has begun to develop indicators of ecosystem health, a goal which complements activities of other agencies, such as the Great Lakes Fishery Commission. Recognizing the great number of desirable uses of the Great Lakes Ecosystem upon which an ecosystem objective could be based, AEOC selected the following: maintenance of a cold-water community of native organisms, within which lake trout are the top predators and therefore the controlling compartment of the steady-state community.

This aquatic ecosystem objective is currently under detailed development and will be the subject of a future report by AEOC to the Science Advisory Board. Pending the outcome of this exercise and an assessment of the approach taken, other aquatic ecosystem objectives may be developed to measure ecosystem stability and stress.

and fish flesh. These objectives should be designed to limit adverse effects to aquatic biota and to consumers of aquatic biota, as well as to any other uses as previously mentioned.

The lead objective has some shortcomings in reaching this broader, more holistic objective for more than the water column alone. Data were required on rates of transport, complexation, particulate adsorption, sedimentation, and methylation; and an understanding and analysis of loss at each stage in the transport chain. This and the more clearly indicates that the data either do not exist or are fragmentary or scattered, and are not easily related to one another. The result is that objectives were formulated only for inorganic lead concentrations in water. It is likely that this situation also exists for most toxic substances. Furthermore, until data on transport, transfer, mass, and toxicity of contaminants are collected in a comprehensive and consistent way, it will not be possible to adequately formulate holistic objectives for compartments other than water.

AQUATIC ECOSYSTEM OBJECTIVES

An aquatic ecosystem objective is envisioned as a desired state of the system and protecting all aspects of the ecosystem. An aquatic ecosystem objective is intended to recognize the integrated nature of the ecosystem and can contain several indicators of the system's state of well being. An aquatic ecosystem objective can provide a perspective to a number of present physical, chemical, and other properties of the ecosystem many of these are described, for example, by the present specific objectives. For the overall aquatic ecosystem objective to be met, these specific objectives would also have to be met, in addition to the yet-to-be developed ecosystem indicators.

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AESC has begun to develop indicators of ecosystem health, a goal which complements activities of other agencies, such as the Great Lakes Fishery Commission. Recognizing the great number of desirable uses of the Great Lakes Commission, which an aquatic ecosystem objective would be based, AESC selected the following: maintenance of a coldwater community of native organisms, of which lake trout are the top predators and therefore the controlling compartment of the steady-state community.

This aquatic ecosystem objective is currently under detailed development and will be the subject of a future report by AESC to the Science Advisory Board. Pending the outcome of this exercise and an assessment of the approach taken, other aquatic ecosystem objectives can be developed to measure ecosystem stability and stress.

3 RECOMMENDED OBJECTIVES

Proposed objectives and supporting rationale are presented in this chapter for:

AEOC recommends that these be incorporated into the 1978 Great Lakes Water Quality Agreement.

PENTACHLOROPHENOL

RECOMMENDATION

Pentachlorophenol in water should not exceed a concentration of 0.4 µg/L for the protection of aquatic life.

RATIONALE

Pentachlorophenol (PCP) is a white solid with a water solubility of 14 mg/L at 20°C. It behaves as a weak acid, pK ~5.0, and hence will be largely in its dissociated form in the Great Lakes. Much of the published environmental data on PCP is also relevant to sodium pentachlorophenate (NaPCP) and *vice versa.* The acid is relatively non-volatile (0.12 mm Hg at 100°C), but it has been noted in the air around a wood-treatment plant in Idaho (53) and hence the atmosphere is indicated as a possible transport route.

Pentachlorophenol and NaPCP are non-selective biocides widely used on a large scale as preservatives, sterilants, herbicides, and fungicides. By far the largest single use of PCP is the preservation of cut wood and outdoor wooden structures from microbial and insect attack. It may enter the environment either through accidental discharge at wood treatment plants, or by leaching from exposed wooden structures. In addition, PCP may be formed inadvertently during the chlorination of waste waters, especially those from the pulp and paper industry and municipal sewage. Its use as a biocide in water cooling systems may also lead to its loss to the aquatic environment. The high-volume production of this substance (approximately 25 x 10^6 kg/a in Canada and the U.S., of which approximately 40% is in the Great Lakes Basin) (15) and multiple uses indicate PCP is a contaminant of considerable concern.

PCP has been widely observed in the Great Lakes Ecosystem - in streams and embayments, in municipal and industrial effluents, as well as in snow samples. Fox (17) and Robinson and Smillie (39) noted levels of 0.003 - 23 µg/L in many Canadian tributaries and bays of each of the Great Lakes, with highest levels being associated with point sources in Thunder Bay (Lake Superior), the mouth of the Detroit River, and the Bay of Quinte (Lake Ontario); even remote areas frequently had levels of 0.01 µg/L. Municipal effluents containing PCP at levels as high as 1.3 µg/L have also been observed, and levels in fishes from the Bay of Quinte and Lake Superior were up to 0.23 µg/g (17). A report by the Ontario Provincial Pesticide Testing Laboratory on wood shavings used as livestock litter (cited in 15) indicated most samples contained detectable amounts of PCP, with levels as high as 135 µg/g being reported. PCP in such material does enter the human food chain (13,16).

The 1978 Great Lakes Water Quality Agreement defines a persistent toxic substance as "any toxic substance with a half-life in water of greater than eight weeks". By that criterion, PCP is not a persistent contaminant.

Photochemical degradation occurs readily (22,52), and reviews of its microbial degradation indicate it does not persist in soil media or in sewage effluents (6,44). However, the occasional observations of PCP in food (15,16), sediments (17,45), sewage effluents (17), soils (21), and fish (17) indicate either that the above conclusions may not be universal or that input rates exceed those of degradation.

Uptake of PCP by fish and other aquatic organisms is rapid although, relative to polychlorinated biphenyls, the bioconcentration of PCP is not great. Bioaccumulation factors of up to 1000 were observed for whole fish exposed to sublethal concentrations of waterborne PCP (30,33), and these appear to be related to fat content (40). PCP in the gall bladder of fish reached a bioaccumulation factor of 5400, perhaps due to active elimination by conjugation and decomposition (30). Elimination of body burdens of PCP in fish occurs fairly rapidly once exposure ceases, with clearance half-lives of as little as 10 hours for goldfish *Carassius auratus* (30). Excretion of PCP was largely in the form of the conjugate, pentachlorophenyl sulphate. In a model ecosystem study, tetrachlorohydroquinone and pentachlorophenyl acetate were found as degradation products in addition to the conjugates (34); neither of the former two compounds is appreciably toxic (36).

PCP residues may not arise directly from exposure to the phenol itself. Metabolism of hexa- and pentachlorobenzene (32) and of lindane (27,31) are all reported to result in PCP formation.

PCP persistence has been investigated in a variety of mammalian species, including man, and was found to have a half-life measured in hours (4,8). It is excreted mainly through the urinary tract (7).

PCP is acutely toxic to most aquatic and terrestrial flora and fauna at low concentrations. The principal mode of toxicity in both mammals and fish is the inhibition of oxidative phosphorylation (51). Toxicity was also observed in snails at PCP concentrations in water as low as 130 μg/L (50). Acute lethality of PCP to fish varies from 30 μg/L (48-hour LC_{50}) for bluegill, *Lepomis macrochirus* (25) and 37 μg/L (96-hour LC_{50}) for coho salmon, *Oncorhynchus kisutch* (14), to 210 μg/L (96-hour LC_{50}) for fathead minnows, *Pimephales promelas* (2). Mortality of fishes is rapid at lethal concentrations, so that concentrations producing mortality within 24 hours are only slightly higher than those producing mortality during longer periods of exposure. Goodnight (19) noted that water temperatures and water hardness had little effect on the toxicity of PCP; decreasing pH below 6.6, however, caused PCP toxicity to increase.

Very little published data on sub-acute effects of PCP on fish exist. Webb and Brett (49) reported threshold median effective concentrations for inhibition of growth rate and food conversion efficiency of under-yearling sockeye salmon, *Oncorhynchus nerka*, at 1.74 and 1.80 μg/L NaPCP, respectively. The lowest reported effect observed for rainbow trout, *Salmo gairdneri*, was 27% growth inhibition which occurred at 8 μg/L (35). PCP has been tested for lethality with other fishes which were found to be less sensitive than the salmonids (1,10). It is not known, however, whether this decreased sensitivity also extends to sub-acute effects.

Chapman and Shumway (11) observed 100% mortality of steelhead trout alevins that were exposed to NaPCP concentrations of 10 µg/L in combination with dissolved oxygen levels of 3 mg/L. This set of conditions might well be expected in the Great Lakes. A safe level cannot be derived from such data, but it does indicate a need for a level below 0.5 µg/L (using a 0.05 safety factor applied to lethal effects). Little mortality occurred at these oxygen levels in the absence of NaPCP. Shumway and Palensky (43) observed flavour impairment of fish flesh at PCP concentrations of 20 µg/L.

A study of temperature effects on chronic PCP toxicity to young rainbow trout demonstrated adverse effects on mortality and growth rates at concentrations greater than 10 µg/L. These effects were aggravated by temperatures greater than 12°C (23).

Many other freshwater aquatic organisms, including plants, are tolerant of much higher concentrations of PCP. One alga, *Chlorella pyrenoidosa*, however, responded at 7.5 µg/L (72-hour EC_{100}) (24) and an invertebrate, *Daphnia magna*, had a 48-hour LC_{50} of 600 - 1500 µg/L (3). Snails suffer significant reductions in egg production and viability in the presence of as little as 50 µg/L PCP (37).

The toxicity of PCP or NaPCP to terrestrial organisms has been studied more extensively. Acute levels (LD_{50}) vary between 50 - 500 mg/kg for such mammals as rats, rabbits, dogs, sheep, and cattle (20,28,29,36). Seed germination was found to be inhibited at 5 - 7 mg/kg in the soil (46). Bacteria are reported to be inhibited by levels of 4 - 250 mg/L of NaPCP (12).

PCP was not carcinogenic when administered to rats in their diet on a chronic basis (42). In addition, PCP has not shown mutagenic activity in the Ames Test (5), the host-mediated assay (9), or the sex-mediated lethal test on *Drosophila* (47).

Chronic toxicity studies with rats exposed to 20 - 500 mg/kg in food over 8 months indicated enzymatic changes (aryl hydrocarbon hydroxylase and glucuronyl transferase) at 20 mg/kg (18,26), but these effects could be interpreted as due to contaminants in technical grade PCP. In other studies with rats, 25 mg/kg in their diet had no growth or blood effects over 12 weeks (29), but PCP fed at dose rates of 35 - 50 mg/kg•d was believed likely to be toxic to calves and hoggets (20); a dose rate of 7.6 mg/kg•d caused no observable effect over five weeks. Embryotoxicity has been described for pregnant rats when the oral dose of PCP was more than 5 mg/kg•d (41). No teratogenic effects were found.

The most important of a number of ubiquitous contaminants of commercial PCP are the polychlorodibenzo-para-dioxins. The hexa-, hepta-, and octa-analogs are normally found in the low mg/kg range, and the toxicity of these compounds may contribute to the observed toxicity of PCP. Polychlorinated dibenzodioxins are the subject of another objective recommended in this report.

The U.S. Federal Register (38) indicated the following PCP guidelines: for the protection of aquatic life, 6.2 µg/L based on invertebrate acute toxicity; and for drinking water 680 µg/L (140 µg/L is published, but the calculations presented indicate 680 µg/L). The lower of these two levels is based on acute toxicity testing with invertebrates and is very close to deleterious effect levels observed for fishes. The most sensitive response noted in experiments relevant to the Great Lakes Ecosystem was the growth inhibition of sockeye salmon under-yearlings at 1.74 µg/L. Applying the safety factor of 0.2 used on non-lethal but observable-effect concentrations for aquatic organisms (48), the level of 0.35 µg/L is derived. The objective for PCP is recommended at 0.4 µg/L.

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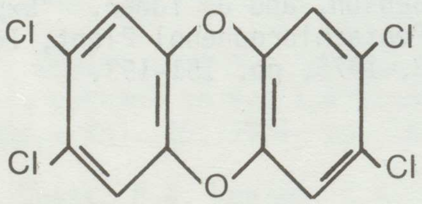
POLYCHLORINATED DIBENZODIOXINS

RECOMMENDATION

For the protection of all life forms, 2,3,7,8-tetrachlorodibenzo-para-dioxin (TCDD) should be absent from all compartments of the ecosystem including air, land, water, sediment, and biota.

NOTE 1: Absent means not detectable as determined by the best available technology.
NOTE 2: The present (1980) detection limit for TCDD is 0.01 µg/kg in tissue and in sediment and is 0.00001 µg/L in water.
NOTE 3: Other tetrachlorodioxin isomers and higher chlorinated dioxin congeners are of concern in the Great Lakes Ecosystem. However, the data base is inadequate to support a scientifically defensible recommendation at this time.

INTRODUCTION



2,3,7,8 - tetrachlorodibenzo - para - dioxin

Polychlorinated dibenzo-para-dioxins (PCDD's) are a class of organochlorine contaminants consisting of 75 different congeners with a common dibenzo-para-dioxin nucleus. There are eight groups of isomers substituted with from one to eight chlorine atoms, respectively. Tetrachlorodibenzo-para-dioxins (TCDD's) are one group consisting of 22 isomers substituted with four chlorine atoms. One isomer of the TCDD group, 2,3,7,8-TCDD, is the most toxic man-made substance known.

Point sources of PCDD's entering the Great Lakes have been indicated at Saginaw Bay (Tittabawasee River), Lake Huron (20) and at Bloody Run Creek, Niagara River (55). Potential sources include pentachlorophenol (PCP) production (15), 2,4,5-T herbicide production and application (33), and potential atmospheric deposition of TCDD from low-temperature industrial and municipal incineration of organochlorine-containing material (12).

Concern has arisen over the possible bioaccumulation of TCDD's in the Great Lakes food web after the recent report of parts per trillion levels (ng/kg) of TCDD in beef fat and human milk in the United States, and in sediment and fish from the Tittabawasee River in Michigan (33). Press releases were made in April 1979 by the State of New York reporting the detection of 4.6 and 5.4 ng/kg of TCDD in two Lake Ontario fish.

This rationale addresses the total "dioxin problem" by attempting an objective assessment of the known facts on source and production of PCDD's, data on environmental persistence and fate, bioaccumulation, and toxicology. This rationale considers which, if any, PCDD's of the 75 possible congeners might be expected to be present and have detrimental effects in the Great Lakes Ecosystem.

SOURCES - PRODUCTION OF CHLORINATED PHENOLS

PENTACHLOROPHENOL (PCP)

Pentachlorophenol has been utilized widely in North America and Europe as a wood dressing or preservative. Chlorination of phenols requires temperatures greater than 95°C. This process may produce PCDD's and polychlorinated dibenzofurans (PCDF's) which are similar in structure and toxicity. PCP produced by seven different manufacturers using older methods contained hexa-, hepta-, and octa-PCDD's at roughly equivalent concentrations ranging from approximately 1 to 38 µg/kg for each congener (15). Later, improved methods of PCP production gave some reduction in levels of PCDD's to 1, 6.5, and 15 µg/kg for total hexa-, hepta-, and octa-CDD's (13).

A recent Swedish study on combustion of PCP-treated wood showed the production of low levels of PCDD's. When there was an insufficient oxygen supply, higher concentrations of tetra-, penta-, hexa-, hepta-, and octa-CDD's were formed. Combustion of wood treated with tri- and tetrachlorophenol also produced high concentrations of PCDD's (24). These results were used as the basis for banning chlorophenol formulations in Sweden.

TRICHLOROPHENOL PRODUCTION AND USAGE (2,4,5-T HERBICIDES)

Formulations of 2,4-dichlorophenol herbicides were shown to contain no detectable PCDD's. However, 2,4,5-trichlorophenol herbicide formulations contained from 1.4 to 6.2 µg/kg of 2,3,7,8-TCDD, with lower amounts of other TCDD's (15). Formulations containing 2,4,5-T in high concentrations included "Agent Orange", utilized in Vietnam as a defoliant, and the herbicide Silvex.

COMBUSTION OF ORGANOCHLORINES

Incineration of municipal refuse has been shown to produce a broad spectrum of PCDD's which have been detected in fly ash and flue gases produced in the Netherlands (37), in Switzerland (4), and in Japan and in Ontario, Canada (12). Tetra-, penta-, hexa-, hepta-, and octa-CDD's were detected in all cases. TCDD concentrations ranged from 2 to 10 µg/kg in fly ash. The concentrations of total hexa-, hepta-, and octa-CDD's always predominated, being approximately 10 to 100 times higher than TCDD concentrations.

TOXICITY - BIOLOGICAL AND BIOCHEMICAL EFFECTS

The 2,3,7,8 isomer of TCDD has been studied most extensively, particularly for acute and sub-acute lethal effects. The lethal dose (LD_{50}) for mammals is between 0.6 μg/kg for male guinea pigs and 116 μg/kg for male or female rabbits (46). Rhesus monkeys exhibit intermediate sensitivity: LD_{50} = 70 μg/kg (28).

Chronic toxicity studies are more relevant to environmental exposure. Level of exposure is more critical than duration of exposure for 2,3,7,8-TCDD, and threshold levels of chronic exposure are reached for which there are permanent effects. TCDD has a relatively short half-life of 12 to 15 days in rats (56), which may explain the threshold effect with no effects or accumulation of TCDD at lower levels of exposure.

The most recent and most definitive result on no-effect levels comes from a three-generation reproductive study of rats receiving 0.001, 0.01 and 0.1 μg of 2,3,7,8-TCDD per kg of body weight per day. At 0.1 μg/kg.d, the first generation of rats showed significant decreases in fertility and neonatal survival. At 0.01 μg/kg.d, fertility was significantly decreased in the second and third generations but not in the first; litter size was decreased, more pups were stillborn, and growth was altered. At 0.001 μg/kg.d, there was no effect on the reproductive parameters measured of any generation (32). Therefore, 0.001 μg/kg.d is the present known no-effect level for 2,3,7,8-TCDD without any safety factor being applied.

As stated previously, 2,3,7,8-TCDD is only one of 22 possible tetrachloro isomers that may be produced in minor amounts in all known sources of PCDD's. There are many indications that other TCDD isomers, as well as higher chlorinated PCDD congeners, are also extremely toxic. Poland and Glover (40) were the first to show that any PCDD congener with a chlorine substituted in at least three out of the four positions (2, 3, 7, or 8 on the dibenzo-para-dioxin molecule) and containing at least one unhalogenated carbon atom was a potent inducer of aryl hydrocarbon hydroxylase and ALA-synthetase enzymes, which are indicative of more general toxic effects. The most toxic appear to be 2,3,7,8-tetra-, 1,2,3,7,8-penta-, 1,2,3,6,7,8-hexa-, and 1,2,3,7,8,9,-hexa-CDD's. Generalities about specific groups of isomers cannot be made, since toxicity can vary by a factor of approximately 10^3 within one group of isomers (27).

Congeners which have relatively low acute mammalian toxicity include 1,2,3,4-tetra- and hepta-, octa- and di-CDD's at levels of approximately 10 mg/kg (46). The latter compounds should be considered relatively safe for controlled laboratory experiments.

The threshold level for acute toxicity to young salmon was determined to be approximately 0.023 μg/L of 2,3,7,8-TCDD in water for exposures of 24 to 96 hours. Exposure levels of 0.00006 μg/L TCDD in water resulted in delayed mortality and 0.056 μg/L resulted in 55% mortality within 24 hours (30).

Fish-eating birds such as herring gulls may be subject to chick edema disease, and PCDD's are one class of compounds known to cause symptoms of this disease such as hydropericardium. Tri-, tetra-, hexa-, hepta-, and octa-CDD's all cause chick edema disease (5,16).

Porphyria has been caused in rats by 2,3,7,8-TCDD and by technical PCP formulations which contain mixtures of tetra- to octa-CDD's (17).

RELEVANCE TO THE GREAT LAKES ECOSYSTEM

SOURCES AND PERSISTENCE OF PCDD'S

Evidence would indicate that there are ample potential sources of not only TCDD, but all PCDD's. Specific sources include the Hyde Park-Love Canal and Bloody Run, a stream running into the Niagara River, where TCDD has been identified at levels of 7.5 μg/L (48), and the Tittabawassee-Saginaw River System (20). All possible industrial and agricultural sources documented in the introduction (production and usage of PCP, 2,4,5-T, industrial and municipal incinerators) are also present and potentially influence PCDD levels in the Great Lakes watershed.

The probable physical persistence of PCDD in emissions from these sources is also important. One striking feature of the PCDD molecule is its ability to absorb ultraviolet light energy from wavelengths available in sunlight. This energy can be utilized for bond scissions or nucleophilic displacement reactions. Since the relative toxicity of PCDD's is very specific to the structure, any alteration of the molecular structure by light will, most probably, change the toxicity. Crosby *et al.* (8) showed that the photolysis of octa-CDD in methanol was much slower than 2,3,7,8-TCDD under controlled conditions. The rate of photolysis of 2,3,7,8-TCDD was extremely fast. The half-life was 6 hours in methanol under simulated sunlight (8). TCDD in herbicide formulations of 2,4,5-T was virtually lost in one day when exposed to natural sunlight on leaves, soil, or glass plates (9). A recent paper showed evidence that the mechanism of photolytic breakdown is via reductive dechlorination. Chlorine atoms bonded to carbon atoms adjacent to the oxygen substituent (positions 1, 4, 6, and 9) are most stable, whereas chlorine atoms substituted to carbon atoms in the 2 position (2, 3, 7, and 8) are most rapidly removed by sunlight irradiation (11). Since the presence of chlorine atoms in the 2, 3, 7, and 8 positions is critical for toxicity (40), it is the toxic compounds which are the least stable in sunlight. The photolytic half-life of the toxic 1,2,3,7,8,9-hexa-CDD isomer was 5.4 hours when exposed to sunlight in hexane solution, whereas the less toxic 1,2,4,6,7,9-hexa-CDD isomer had a half-life of 47 hours (11).

The photo-degradation of 2,3,7,8-TCDD in aqueous solution was negligible by comparison to photolysis in methanol under similar conditions (7). However, photolytic products of residues of other organochlorine compounds, which are much less photo-labile than 2,3,7,8-TCDD in organic solvents, are prevalent in the Great Lakes aquatic ecosystem. Photomirex is present in Lake Ontario biota at approximately one-third the concentration of the parent compound mirex (19,34). Photomirex is formed very slowly, 5% conversion occurring after exposure to sunlight for three months on silica gel plates (57). Model aquatic ecosystem studies using TCDD did not consider photo-conversion of 2,3,7,8-TCDD to less toxic tri- and di-CDD's, which may account for some apparently high accumulations of TCDD-^{14}C in organisms without any symptoms of toxic effects being evident (23,26).

The major input of mirex to the Lake Ontario aquatic ecosystem was via the Niagara River proximate to the Love Canal and Bloody Run. Considerable opportunity for photolysis of PCDD's from the Bloody Run source should therefore have been available, by analogy to the degradation of mirex, before entry into the food web. PCDD's emitted to the atmosphere (i.e. from fly ash and flue gas) would also appear to be potentially subject to some degree of photolysis before becoming available to an aquatic food web.

These arguments form the major support to the theory that TCDD's may simply not be present in high enough concentrations, or for long enough periods in the Great Lakes water column for bioconcentration or bioaccumulation of residues to take place. This would not pertain to a major industrial spill or an effluent containing TCDD-contaminated material (e.g. 2,4,5-T herbicide) which would affect the ecosystem as long as the source remained unchecked. It appears that hexa-, hepta-, and octa-CDD's, which predominate in all sources, are as or more likely to persist in the Great Lakes environment than TCDD's. Further work is necessary to determine if indeed hexa-, hepta-, and octa-CDD's are present in Great Lakes biota.

TCDD's are extremely insoluble in water (0.20 µg/L), even relative to other organochlorines such as DDT (1.2 µg/L) (26). Because of this insolubility, 2,3,7,8-TCDD was shown to bind very tightly to sea sand and sandy loam and to be completely resistant to leaching by water. Half-lives of TCDD is soils were extremely long: up to 1 year (25). The half-life was 88 days in alkaline soils under desert conditions (53). Although TCDD was persistent in these materials, it did not appear to be biologically available for microbial breakdown or for translocation into plants. It appears that the only way in which soil-adsorbed TCDD's can reach an aquatic site is via erosion (22). This information supports the preceding theory and infers that TCDD's bound up in organic detritus and sediment will remain there, unavailable for direct biological uptake in aquatic ecosystems. From knowledge of sedimentation rates, which are high in the eutrophic lower Great Lakes (41), PCDD's not bound up at the source would only be biologically available for uptake in a small area immediately about the source. However, in this "dioxin zone" considerable environmental damage could take place. It seems most likely that hexa-, hepta-, and octa-CDD's would predominate if such a zone were to occur, since they are more resistant to photochemical breakdown and are present in higher concentrations at the source.

BIOACCUMULATION POTENTIAL OF PCDD'S IN INVERTEBRATES AND FISH

Only two studies have been carried out on TCDD's in model aquatic ecosystems: Matsumura and Bezenet (26) and Isensee and Jones (23). Both studies dealt with the bioconcentration of 2,3,7,8-TCDD, either directly from water to fish, or from a potential food chain of invertebrates to fish in model (aquarium-type) ecosystems. Both studies were short term (three to seven days).

Bioconcentration factors, or the ratio of the concentration of a compound in the organism to that in the water, are used as one measure of the bioaccumulation potential of a contaminant in aquatic ecosystems. However, bioaccumulation of a contaminant in real ecosystems is dependent on factors other than the ability of a compound to bioconcentrate, as predicted from the solubility in water, or partition coefficients between organic solvents and water (21,45,49). Such factors include growth rate of the organism, food conversion efficiency, and rate of metabolism of the compound, particularly into polar or water-soluble derivatives which are more easily excreted (35). Steric properties of the molecule may prevent rapid absorption from the gills or gut (21).

The two studies on bioconcentration of 2,3,7,8-TCDD show TCDD uptake from water into mosquito larvae (9,222X)(26), daphnia (7,800 to 31,000X)(23), and mosquito fish (1,000 to 63,000X)(23). There is considerable variability in the results within each study and between the two studies. This is at least partially due to small sample sizes (two fish were used by Isensee and Jones (23)). In many experiments, the concentration of TCDD in water was either at or well above the known solubility of 0.20 µg/L. Few environmental situations where bioaccumulation is a problem occur at saturation or at supersaturation concentrations. Bioconcentration factors determined by Isensee and Jones (23) are calculated on a dry weight basis and are therefore approximately ten times greater than bioconcentration factors which are calculated on a fresh weight basis.

In both studies, it was shown that TCDD is extremely immobile when absorbed to soil particles - leaching from soil or sediment was virtually nil. No metabolic or chemical breakdown into polar compounds was found. The technique used did not determine whether TCDD was photochemically degraded to non-polar tri- and di-CDD's.

The conclusions reached by both papers are noteworthy. Matsumura and Bezenet (26) considered that "TCDD is not likely to accumulate in as many biological systems as DDT". This is likely due to the low solubility of TCDD's in water and lipids, as well as its low partition coefficient in lipids. Since microbial degradation is not expected to be a major factor, it was also concluded that the predominant mode of elimination of this compound in the environment is photodecomposition by sunlight.

Isensee and Jones (23) concluded "that under certain circumstances, e.g. discharge of storm runoff from recently (2,4,5-T) treated rangeland into a small pond, water eroded surface soil or debris may contain enough TCDD for measurable (part per trillion quantities) residues to accumulate in fish or other aquatic organisms. However, TCDD (originating from 2,4,5-T applications) discharged into large lakes, streams or estuaries would probably be sufficiently diluted so that no measurable accumulation would occur". This conclusion is supported by a study on erosion of heavily contaminated soil

(0.01 to 0.71 μg/kg) from a test area, into an adjacent stream, which resulted in concentrations of 0.01 to 0.35 μg/kg of TCDD in silt, but only at the soil-water interface. No TCDD was detectable beyond this location (54). The conclusions of Isensee and Jones are valid only in a limited context, since persistence of the compound in the organisms used and within the ecosystem as a whole was not considered in their experiments.

That TCDD has not only a low solubility in water, but also in lipids and organic solvents, must be emphasized. Solvent/water solubility ratios for TCDD are 10^4 times lower than for DDT (26). The solubility of TCDD in benzene, which is normally a good solvent for aromatic compounds, was also low (47 mg/g). In most cases, compounds which bioaccumulate exhibit high partition coefficients in non-polar solvents such as n-octanol, hexane, or benzene (21). The model ecosystem evidence for bioconcentration of TCDD's is, at best, incomplete. No long-term studies have been performed and there is no information on clearance half-lives of TCDD's in fish. Without this information, nothing definitive can be said about the potential for biomagnification of PCDD's in aquatic food webs.

BIOACCUMULATION POTENTIAL OF PCDD'S IN MAMMALS

Information is somewhat more complete for mammals. Low solubility in lipids may account in part for the short half-life of TCDD in organisms such as rats (12 to 15 days (56); and 21 days (38)). In contrast, the half-lives in rats of hexa-, hepta-, and octa-CDD's are 75.7, 87.8, and 274 days, respectively (14).

Structurally and toxicologically similar tetrachlorodibenzofurans (TCDF's) have been shown to be eliminated intact in rat urine (10). Radioactivity from TCDD-^{14}C was similarly detected in the urine of rats between one and ten days after dosage, the highest concentration at day one equalling 3% of the dosage (38). Bile and urine are the major routes of excretion of polar metabolites but not of intact, parent organochlorines. Urinary excretion appears to be a property peculiar to TCDD's and TCDF's and probably reflects their low solubility in any medium.

Tissue distribution studies indicate that once TCDD is absorbed into the body it is distributed rapidly and becomes localized or concentrated in the liver and fat. Levels of TCDD in tissues had reached equilibrium after only seven days of exposure (38). Toxic effects in nursing rat pups when females are fed TCDD would indicate that TCDD is excreted in milk (31). PCDD's are found in the milk and blood of cows fed pentachlorophenol (14). The PCDD's found, however, were hexa-, hepta-, and octachloro congeners at concentrations approximately one half those found in the fat of the cows.

BIOACCUMULATION POTENTIAL OF PCDD'S IN BIRDS

No studies have been performed on the half-life of TCDD's in birds, but the chemically similar TCDF's were either excreted relatively quickly compared to polychlorinated biphenyls (PCB's), or they were not absorbed initially from the gut by mallard ducks (35). These results are consistent with the short

TCDD half-lives found in rat studies. This rationale does not apply to hexa-, hepta-, and octa-CDD's, which have longer half-lives in mammals.

In 1973 and 1974, common tern and herring gull chicks residing on Lake Ontario were reported to have symptoms similar to chick edema disease (59). Chick edema disease can be caused by relatively high concentrations of TCDD with a threshold level of 1 µg/kg daily oral dosage and does not occur from TCDD accumulation of sub-threshold dosages (46). Any detrimental biological response that has manifested itself in herring gull chicks which appears similar to chick edema disease seems highly unlikely, therefore, to have been due to TCDD. In 1973, chick edema disease, as well as almost total reproductive failure, was evident in Lake Ontario herring gull colonies. Only reproductive failure was evident in 1976. Extracts of organochlorines which would have contained chick edema factors of PCDD's, if present, were taken from eggs collected in 1976 from Lake Ontario. No effects were found when the 1976 Lake Ontario egg extracts were injected into herring gull eggs on a relatively uncontaminated colony in New Brunswick which was exhibiting normal reproductive success (58).

NEED FOR CONFIRMATION OF TCDD'S IN GREAT LAKES SAMPLES

A discussion of possible artifacts of false positive results for TCDD in environmental samples from the Great Lakes Ecosystem is necessary. During 1979, there was considerable controversy over the validity of TCDD analysis in sediment and fish samples from the Tittabawassee River, downstream from the Dow 2,4,5-T herbicide factory at Midland, Michigan. In April 1979, New York State reported the presence of TCDD at extremely low levels (approximately 0.005 µg/kg in two fish from Lake Ontario. Since this time, there has been considerable concern that PCDD's may be accumulating in the Great Lakes food web. This controversy was further fueled by reports of TCDD in Bloody Run draining into the Niagara River.

The U.S. Food and Drug Administration has recently reported that TCDD is *not* found in fish from the Saginaw Bay area at or above 0.05 µg/kg (47), and that TCDD has *not* been found at or above 0.01 µg/kg in a fish composite sample taken from the Niagara River below Bloody Run (55). Sediment from Bloody Run Creek was found to contain 7 µg/kg TCDD, and water samples from the Love Canal area contained levels at 0.0016 to 0.0046 µg/L TCDD (55).

It is well known that fish from Saginaw Bay and Lake Ontario contain high levels of other organochlorine residues including PCB's, DDT, DDE, DDD, DET, heptachlor epoxide, oxychlordane, dieldrin and, in some cases, toxaphene (51,52). PCB's and DDE have been shown to interfere with high-resolution direct-probe mass spectrometric (MS) analysis at a resolution of 10,000 (1). In the case of high-resolution MS analysis, various column chromatographic procedures have been utilized to remove PCB and DDE interference (1,36). However, no column or liquid chromatographic procedure has been proven to remove dieldrin, heptachlor epoxide, oxychlordane, DDD or DDT, or toxaphene from eluant fractions, nor has the MS resolution required to eliminate potential interference from these compounds been considered.

High-resolution glass-capillary gas chromatography, coupled with single or multiple ion monitoring, similar to the techniques used by Buser and Brossart (3) and by Jansson and Sundstrom (24), is the preferred technique to cope with this type of interference. Low-resolution MS was used in the preceding studies, in part due to sensitivity considerations.

Diagnostic ions have been used to differentiate between TCDD's and tetrachlorobiphenyl methyl ethers (18). Isomers of both compound types have identical molecular ions, similar column chromatographic properties, and similar retention times on gas chromatography. Methoxylated PCB's exhibit an M-43 loss (M-$COCH_3$) and not the M-63 loss (M-COCl) diagnostic of PCDD's. A series of tetra-, penta-, hexa-, and heptachloro-PCB methyl ether isomers were identified in adult herring gull lipid tissue. These were only present when the tissue was extracted by saponification in methanolic KOH. A series of review papers on the various TCDD analytical techniques are presented in References (6) and (42).

Because of the potential interference from high levels of organochlorine contaminants, all reports of TCDD in Great Lakes samples should be accompanied by a complete listing of the major residues and their levels, along with the detailed clean-up and separation steps used for TCDD analysis. Only in this way can validity of the data be judged.

HUMAN HEALTH IMPLICATIONS

The carcinogenic potential of any substance is difficult to ascertain in a relatively long-lived species such as primates. The Seveso accident (2,39,43,44) and other alleged accidents or exposures of sizeable populations in Vietnam, Florida, and Missouri have been to variable doses released into the air from venting or spraying, or releases into water of large amounts of herbicide contaminated with TCDD. The short-term effects have been widespread; the long-term effects, i.e. function of offspring or those directly contaminated, or development of neoplasms, remain unrecorded at present. The absence of background data in Vietnam, the difficulty in interpreting the effect of "Agent Orange" on the personnel exposed in light of subsequent occupational exposures or the natural history of certain neoplasms in the populations from which these soldiers came, has made appropriate support of their case difficult. Although a number of morphological studies on the aborted embryos in the Seveso area are listed, the authors admit that there are no background data about either the abortion rate, or the malformation rate and type in the Seveso area. Thus, a small, if significant increase in the malformation rate or that of types of abnormalities cannot be detected and associated with that accident. The long-term effects, save for those shattering anxieties shared by the residents of the Love Canal area, are not significant, so far as is known.

To date, there is no clear evidence that carcinogenicity, mutagenicity, or teratogenicity are significant problems in populations at risk of significant exposure to TCDD despite the laboratory data to the contrary. The synergistic and "enabling" effects of chlorinated dioxins are of grave concern in vertebrate biology, to wit, the completion of carcinogenicity and enhancement of the effect of weak carcinogens by combined application of the carcinogen and TCDD. The profound acute toxicity of 2,3,7,8-TCDD to primates is well recorded by McNulty (29) in a preliminary experiment, where Rhesus monkeys were killed by doses of "toxic fat" containing several μg/kg of TCDD in the total dose. In fact, these young monkeys were especially sensitive to tiny daily doses of less than 1 μg/kg.d which were lethal.

SUMMARY

2,3,7,8-tetrachlorodibenzo-para-dioxin (TCDD) has been considered for development of an aquatic ecosystem objective in the Great Lakes because it is extremely toxic with a high acute toxicity (LD_{50} in mammals as low as 0.6 μg/kg, 70 μg/kg in monkeys) and extremely high chronic toxicity with effects on fertility occuring at dietary concentrations as low as 0.010 μg/kg.d. Although the compound has characteristics which make it less environmentally persistent than other common organochlorines such as PCB's, there is still potential for localized exposure of biota to chronic and acute levels of TCDD due to the high toxicity of the compound. A recommendation was developed on the basis of these toxicity data.

Although data are sparse on other chlorinated dioxin isomers and congeners, they should also be regarded as particularly hazardous to the Great Lakes Ecosystem. A numerical objective could not be developed for them in a scientifically defensible manner at this time. The procedural objective for persistent toxic contaminants, outlined in Appendix A to the 1974 report of the Water Quality Board (60), should therefore be employed. This calls for concentrations of such compounds to be limited to the detection limits of the best available technology.

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MICROBIOLOGICAL INDICATOR

RECOMMENDATION

For the protection of human health, the level of fecal coliform bacteria shall not exceed a logarithmic mean of 200 fecal coliforms per 100 mL of sample, based upon a minimum of five samples taken over a 30-day period, nor should more than 20% of the total number of samples taken during any 30-day period exceed 800 fecal coliforms per 100 mL of sample.

INTRODUCTION

Pathogenic organisms are difficult to monitor due to problems with collection and analytical techniques. As a result, surrogates have been historically used as indications of the microbiological quality of the water. Coliforms have been the traditional indicator for over 50 years, but they are not pathogenic organisms. The fecal component of the total coliforms represents those bacteria that are present in the feces of warm-blooded animals. Fecal streptococci represents that fraction that is uniquely due to the activities of man but it is relatively difficult to monitor and analyze. The presence of coliforms does not establish the presence of disease-producing bacteria. Both total coliforms and fecal coliforms are found in water courses due to the presence of normal agricultural activities, high concentrations of wildlife, or the activities of man. Statistical analysis can show that if the fecal coliform count reaches a certain level, there is a high probability of the presence of some types of human pathogens.

Historically, water has had a significant role in the transmission of disease, particularly via the fecal-oral route. The science of sanitary bacteriology was born when Von Fritsch in 1880 recognized *Klebsiella pneumoniae* in human feces, and Escherich established *Bacillus coli* (now *Escherichia coli*) as a common fecal bacterium which could be used as an indicator of fecal contamination of water. Since that time microbiological indicators have been used to determine or indicate the safety of water for drinking, swimming, and shellfish harvesting. The relationship between indicator organism concentration and the risk of infection is further complicated by variations in the pathogen-to-indicator ratio, uncertainties about the infectious dose, and variability in the defense mechanism of different human hosts. Nevertheless, there is general agreement that the presence of substantial numbers of fecal indicator organisms in water suggests a potential for the transmission of waterborne disease and is therefore of public health concern.

The most common indicators in use today are the coliform bacteria. This group includes all aerobic and facultatively anaerobic, gram-negative, non-sporeforming, rod-shaped bacteria that ferment lactose with gas formation within 48 hours at 35°C or which produce a dark colony with a metallic sheen within 24 hours on an Endo-type medium containing lactose. This grouping includes the genera *Escherichia, Citrobacter, Enterobacter, Klebsiella*, and *Aeromonas*. While all these organisms are found in the human intestine, *Enterobacter, Klebsiella*, and *Aeromonas* also thrive freely in other nutrient-enriched environments. The adoption of the entire group rather than, say, *Escherichia coli*, was one of expediency because the detection of members of this group is possible with simple one-step laboratory procedures. For this reason and because the coliform bacteria are conservative estimators of the bacteriological safety of water, they continue to be used in monitoring the quality of drinking water.

While it has been pointed out that the coliform test does not adequately prove the absence of viral pathogenic agents in water, it appears that application of state-of-the-art treatment technology in combination with bacterial standards for raw and finished water does not produce a demonstrable hazard of viral disease in the populations served.

The fecal coliform group is that portion of the total coliform group capable of forming gas within 24 hours at 44.5°C. This test is more specific for intestinal bacteria of the *Escherichia, Enterobacter*, and *Klebsiella* types, and numerical results obtained with this test more closely reflect the level of bacteria presumably derived from the intestines of warm-blooded animals including humans. Because of this relative specificity, the fecal coliform test is preferred over the total coliform test for the purpose of monitoring the bacterial quality of surface waters for indications of pathogenic organisms. Current techniques have made possible the detection of many pathogenic bacteria and viruses in sewage, sewage effluents, and surface waters, but these procedures are not currently accepted sufficiently for large-scale, routine application. For this reason, and because the pathogens are usually greatly outnumbered by the indicator bacteria, standards based on indicator bacteria and particularly fecal coliforms are considered meaningful and practical for the monitoring of water quality in the Great Lakes.

MICRO-ORGANISMS IN RECREATIONAL WATERS

Recreational use of water in the form of body-contact recreation is normally perceived as swimming, wading, or the inadvertent contact with water by boaters, hunters, or fishermen. There are virtually no studies with respect to the last group, and relatively few epidemiological studies on bathing. Cabelli (2) defined swimming as "significant exposure of the upper-body orifices to the water".

Early work on this subject is by Smith (10) on the Ohio River and by Smith and Woolsey (11) on the Ohio River and Long Island beaches. Streeter (13) compared the bacteriological standards of various jurisdictions for the Ohio River Valley Water Sanitation Commission (ORSANCO) and recommended that the monthly arithmetic average (MPN) for total coliforms not exceed 1000 per 100 mL nor should total coliforms in 20% of the samples for any given month exceed 2400 per 100 mL.

Stevenson (12) attempted to correlate illness from swimming with water quality at Lake Michigan beaches, the Ohio River, and Long Island. He found a significant increase in illness incidence among swimmers when the total coliform count equalled or exceeded 2300 per 100 mL.

The ORSANCO Water Users Committee (9) estimated a relationship of approximately 1:5 of fecal to total coliforms in the Ohio River and determined that fecal coliforms were the more accurate bacteriological indicator of fecal contamination from warm-blooded animals and humans.

Most recently, Cabelli and coworkers (3,4) conducted a major epidemiological study of bathers at the Coney Island and Rockaways Beaches of New York City. These authors suggest that a significant difference exists between the Coney Island Beach which is barely acceptable at a total coliform count of 2400 per 100 mL and the relatively unpolluted Rockaways Beach. Illness was defined as highly creditable symptoms reported by the bathers during a follow-up interview, and the differences were between swimmers and non-swimmers at the respective beaches. The results are clouded by very substantial differences in the incidence of illness between the two non-swimming control populations. More recently, the authors have extended their data base and derived additional support for their conclusions from studies at the highly polluted ocean beach of Alexandria, Egypt. Cabelli also suggests that *Enterobacter* or *Streptococcus faecalis* may be superior indicators of bathing beach quality. The type of illness observed at the beaches was to a large extent "gastroenteritis of unknown etiology" which more recently has been ascribed to infection with rotavirus. Cabelli's studies deal with marine waters and, as Stevenson (12) already pointed out, results on marine beaches cannot be immediately applied to freshwater beaches.

McCabe (8) combined the effect level of 2400 total coliforms per 100 mL of Stevenson with the fecal-to-total coliform ratio from the ORSANCO report and, by applying a safety factor of approximately two, arrived at a maximum recommended level of 200 fecal coliforms per 100 mL for recreational water.

RAW WATER FOR DRINKING PURPOSES

The utilization of indicators for the protection of public water supplies has been followed for many years. The protection of raw water supplies depends on the multi-barrier principle and on the effectiveness of the water treatment plant. The principle would include the continuous disinfection of all waste discharges and complete treatment at the water treatment plant including flocculation, coagulation, sedimentation, filtration, and disinfection. The most commonly used disinfectant is chlorine and, by maintaining a free chlorine residual in the water distribution system of 0.05 - 0.10 mg/L, the public could be assured of a bacteriologically safe drinking water. The goal of "no coliforms" for drinking water cannot be analytically determined but, by maintaining this chlorine residual, a healthful water is assured. Hence, effective water treatment is the controlling factor, within limits, in assuring a safe supply of drinking water at the tap. It is recognized, however, that the over-utilization of chlorine has environmental as well as adverse health effects. The use of other disinfectants is under study, but their total environmental or health impacts are not fully understood.

In Streeter's study on the Ohio River, the raw water quality averaged 40,000 coliforms per 100 mL, but indications were that a limiting average coliform density of 10,000 per 100 mL could be tolerated by effective water treatment plants. With normal filtration processes and lower residual or "marginal chlorination", water treatment plants can develop both safe and potable effluents from raw waters containing monthly averages not exceeding 5,000 per 100 mL. The current manual of practice by the American Water Works Association indicates that the efficiencies of filters in bacterial removal, with proper pretreatment, should exceed 99% (1). Post-chlorination following filtration could reduce bacteria levels to insure that they yield a water of satisfactory and safe bacteriological quality. The normal criterion would be to provide minimum free and combined chlorine residuals of 0.05 - 0.10 mg/L and 1.0 - 2.0 mg/L, respectively, at distant points within a water distribution system.

JURISDICTIONAL POSITIONS

The various states and Ontario have taken different but compatible positions with respect to indicator organisms. The controlling use for almost all the standards is for recreational waters. Since this use is more restrictive than for raw water supplies, it is applied by most jurisdictions to protect the latter use.

The first raw water standard was adopted by the International Joint Commission prior to 1920 with a yearly *Bacillus coli* index not exceeding 500 per 100 mL in the raw water. It was based on the assumption that waters carrying such a bacterial load actually could be purified by methods in use at the time to meet the drinking water standard, i.e. an index of 2 per 100 mL (5). The 1972 Great Lakes Water Quality Agreement specified a numerical limit of 1,000 total coliforms per 100 mL and 200 fecal coliforms per 100 mL as a geometric mean of not less than five samples taken over a 30-day period. However, the 1978 Agreement does not contain any numerical limit. Rather, it uses the non-numerical statement included in the 1972 Agreement which is specific for body-contact recreation only. Since many of the jurisdictional positions are in a state of flux, it is not felt appropriate to utilize these in the development of a microbiological objective for the Great Lakes.

EXISTING WATER QUALITY

A review of STORET data for 1979 indicates that the offshore waters of the Great Lakes contain more bacteria than might be anticipated. Table 1 presents information on total coliform, fecal coliform, and fecal streptococci. This information, from STORET, indicates a number of problems because the U.S. Environmental Protection Agency includes data from a variety of sources, some of which may be subject to question. Additionally, different types of tests are used, and the tests are not always compatible so that comparisons for the same organism are difficult.

STATISTICAL ANALYSIS

The recommended objectives for microbiological indicator organisms are unique because they include a statistical determination. The precentile

TABLE 1

COMPARISON OF MEAN MICROBIAL INDICATORS IN OFFSHORE WATERS[a]

INDICATOR[b]	TEST METHOD[c]	LAKE ONTARIO		LAKE ERIE		LAKE HURON		LAKE SUPERIOR	
		No. of Samples	Mean/ 100 mL	No. of Samples	Mean/ 100 mL	No. of Samples	Mean/ 100 mL	No. of Samples	Mean/ 100 mL
TC	MF DLENDO	3714	52.	1615	87.	976	15.	879	28.
TC	MF IMENDO	18	230	5600	460	500	120	-	-
TC	MF IMLES	-	-	18	820	1864	4000	101	310
TC	MPN Conf	-	-	633	4900	-	-	31	110
FC	MF M-FCBR	423	29.	2190	15.	2537	58.	275	22.
FC	MPN ECMED	-	-	27	880	-	-	-	-
FS	MF KFAGAR	-	-	1284	14	57	29.	231	5.8
FS	MF MENT	-	-	289	3.3	375	9.6	58	10.

a. Average minimum distance to shore: 3 - 4 km. STORET data for 1979. Mean values to two significant figures.

b. Key:
TC = Total coliform
FC = Fecal coliform
FS = Fecal streptococcus

c. Key:
MF = Membrane filter
MPN = Most probable number
DL = Delayed incubation
IM = Immediate incubation
ENDO = M-Endo media
LES = Les-Endo Agar
Conf = Confirmed
M-FCBR = M-FC Broth
ECMED = EC Media
KFAGAR = KF Agar
MENT = M-Enterococcus Agar

clauses in "Quality Criteria For Water" ("Red Book" (6)) and other documents are intended to reflect the error in bacteriological determinations and laboratory error. Additionally, it is meant to reflect limitations for temporary excursions due to storm conditions and temporary malfunctions of sewage treatment plants. The development of the geometric mean of 200 fecal coliforms per 100 mL has been discussed previously.

If the geometric mean of 200 fecal coliforms per 100 mL is accepted as the no-effect level, then the translation of this criterion into statistically acceptable terms is relative. The "Red Book" states, "Based on a minimum of five samples taken over a 30-day period, the fecal coliform bacterial level should not exceed a log mean of 200 per 100 mL, nor should more than 10 percent of the total samples taken during any 30-day period exceed 400 per 100 mL". However, the "Red Book" does not justify the 10% but uses this value to allow for "variations in environmental conditions". Many jurisdictions have adopted this approach.

Fuhs (7) examined the statistical approach in some depth. Based upon a detailed statistical analysis of 58 bathing beaches in New York State, he observed that the 20% clause, by definition, requires that the minimum number of samples per month be five. Additionally, he found that the logarithmic standard deviation (base 10) of the log normal distribution of fecal coliform organisms is typically around 0.7. At a log mean of 200, the minimum observed standard deviation of 0.3 corresponds to 20% of the samples exceeding 360, and 10% of the samples exceeding 500 fecal coliforms per 100 mL. At a standard deviation of 0.7, 20% of the samples will exceed 800, and 10% will exceed 1600 fecal coliforms per 100 mL. If the percentile clause should represent "typical" conditions, so that increasing pollution in well mixed waters will cause the log mean to be exceeded, while in the case of increasing pollution in poorly mixed waters, or at a beach which is affected intermittently by wastewater plumes, the percentile clause can be invoked. Hence, the requirement that 10% of the samples not exceed 400 fecal coliforms per 100 mL would always be more stringent than the requirement of a log mean of 200 per 100 mL. The key, therefore, is the derivation of the standard deviation. The value of 0.3 corresponds to extremely well mixed waters. The 0.7 represents an average value, representing moderately well mixed waters. If any plumes of polluted water hit a beach intermittently (poorly mixed conditions), standard deviations of 1.0 to 2.0 logarithmic units can occur. Therefore, it is recommended that the standard deviation of 0.7 be utilized unless new information dictates otherwise.

SUMMARY

The problem of establishing a microbial objective is complex indeed and must address the relationships of pathogens, indicators, and statistics. The goal of having no pathogens in amounts that will produce enteric disorders or eye, ear, nose, throat, and skin infections or other human diseases can be best achieved through the establishment of an appropriate indicator organism level.

Recreation is the most sensitive use to be protected because of the high probability of ingestion of raw water. Due to dilution and natural die off, there will be a significant difference in levels found in nearshore waters and open waters of the Great Lakes. Normally, bathing beaches are restricted to one-half to one kilometre from the shoreline, while boating activities such as water skiing generally occur in the one-to-two kilometre range. Based upon experimental data, it would appear that a log mean of 200 fecal coliforms per 100 mL of sample should be a no-effect level to insure the achievement of the goal. However, a statistical deviation must be considered for laboratory and collection errors as well as for temporary excursions due to storm incidents. Fuhs' analysis is based in part upon bathing beaches in Lake Ontario and, hence, has direct application here. The "20 percent from not less than 5 samples during any 30-day period should not exceed 800 fecal coliform per 100 mL" is based upon both a logarithmic standard deviation of 0.7 and a geometric mean of 200 fecal coliforms per 100 mL. Unless existing data would establish a more restrictive standard, it would appear to be sufficiently protective to insure achievement of the goal. To use the 400 fecal coliform value in combination with a mean value of 200 per 100 mL would deny existing statistics and make the 400 figure the controlling value.

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NUTRIENTS

(Note: This recommendation and the supporting rationale were originally presented in the July 1978 report of the Great Lakes Research Advisory Board to the International Joint Commission. The rationale presented below now includes relevant material given in the 1978 Great Lakes Water Quality Agreement. These additions are denoted in brackets.)

RECOMMENDATION

1. *The lake-wide mean total phosphorus concentration in the spring in Lake Superior should not exceed 5 µg/L to maintain the lake in its present oligotrophic state.*

2. *The lake-wide mean total phosphorus concentration in the spring in the main body of Lake Huron, Georgian Bay, and the North Channel should not exceed 5 µg/L to maintain the lake in its present oligotrophic state.*

3. *The area-wide mean total phosphorus concentration in Saginaw Bay in the spring should not exceed 15 µg/L to prevent nuisance growths of aquatic weeds and algae.*

4. *The lake-wide mean total phosphorus concentration in Lake Michigan in the spring should not exceed 7 µg/L to return the lake to its natural oligotrophic state.*

5. *The basin-wide mean total phosphorus concentration in the Western Basin of Lake Erie in the spring should not exceed 15 µg/L to reduce the present levels of algal growth and to prevent nuisance growths of aquatic weeds and algae in this basin.*

6. *The basin-wide mean total phosphorus concentration in the Central Basin of Lake Erie in the spring should not exceed 10 µg/L to restore year-round aerobic conditions in the bottom waters of this basin.*

7. *The basin-wide mean total phosphorus concentration in the Eastern Basin of Lake Erie in the spring should not exceed 10 µg/L to reduce the present levels of algal growth and to prevent nuisance growths of weeds and algae in this basin.*

8. *The lake-wide mean total phosphorus concentration in Lake Ontario in the spring should not exceed 10 µg/L to prevent nuisance growths of weeds and algae in this basin.*

RATIONALE

Organisms need a large number of chemical elements for growth and reproduction. Many of these elements are required only in trace quantities.

however, certain elements, especially carbon, nitrogen, oxygen, hydrogen, sulfur, and phosphorus, are needed in larger amounts as they are the basic building blocks of organic matter. If any of the required elements is in short supply in a biological community, growth and reproduction will be limited as will be the biomass or yield of the community.

It is now well established that it is phosphorus that most commonly limits yield in freshwater phytoplankton communities, although nitrogen or more rarely some other vital element may play this role in certain environments (10,21,30). Substantial additions of phosphorus to a lake or stream, whether intentional or inadvertent, usually cause increases in photosynthesis and algal biomass. Such fertilization also causes many other changes in the water body. The species of phytoplankton shift to types that are better adapted to nutrient-rich environments. The increased algal productivity and biomass result in increased decompositon of organic matter which often causes depletion of oxygen. Such oxygen depletion occurs especially during the summer in the lower layer of hypolimnion of those lakes that become thermally stratified, because the stratification cuts this layer off from exchange with atmospheric oxygen. The animals also undergo profound shifts in abundance and relative numbers of the different types. With different types of algae present and with the chemical conditions altered, animal communities that are entirely different than those present before fertilization are favored.

These chemical and biological changes that accompany phosphorus additions are usually, although not always, detrimental to man's interests. Water contact sports are often affected by the increased concentrations of algae, which may even float as green mats on the surface and pile up and decay on the beaches. The thick growths of algae may also clog the intakes of water treatment plants and add unpleasant tastes and odors to the water. In addition, the types of fish change, usually toward increased numbers of fish not favored by sport and commercial fishermen and fewer of the types in demand.

Such changes often occur naturally in a lake usually over a long period of time. However, in the Great Lakes such changes, often referred to collectively as eutrophication, have been occurring at an accelerating rate recently (1,2,20). This speed up of eutrophication is believed to be largely due to the addition of phosphorus derived from human activities. Large amounts of phosphorus are added to the lakes from such sources as: agricultural and urban runoff, discharges from industrial plants, and effluents from municipal sources carrying human sewage, detergents, and garbage.

The Great Lakes Water Quality Agreement of 1972 recognized the seriousness of the problem of accelerating cultural eutrophication and established a general water quality objective that the boundary waters of the Great Lakes ". . . should be free from nutrients entering the waters as a result of human activity in concentrations that create nuisance growths of aquatic weeds and algae" (27). Further, in Annex 2 the [1972] Agreement lays out a program for the control of phosphorus, including objectives for environmental restoration and enhancement. *No objectives for nutrient concentrations in the Great Lakes are stated, however.*

[The 1978 Agreement similarly recognizes the seriousness of the problem when it states that "these waters should be free from nutrients directly or indirectly entering the waters as a result of human activity in amounts that create growths of aquatic life that interfere with beneficial uses." Annex 3 of the 1978 Agreement presents the goals of phosphorus control, the supporting programs which are to be developed, and future phosphorus loads. However, like the 1972 Agreement, the 1978 Agreement also contains no specific objectives for nutrient concentrations.]

Thus, while the basic objectives for desired environmental conditions are specified, they are not put in terms of specific values for nutrient concentrations in lake waters. It is the purpose of the following report to suggest objectives and a rationale for the upper limits to nutrient concentrations which will allow the objectives of the Agreement to be met. The adoption of such concentration objectives will provide a more convenient and measurable goal against which to measure progress toward achievement of the rather vague environmental objectives that are presently in the Agreement.

NUTRIENTS TO BE CONSIDERED

Three elements, phosphorus, nitrogen, and silicon, have been implicated, at least to some extent, in the limitation of biological production of the Great Lakes. As pointed out earlier, phosphorus is by far the most important limiting factor. However, under certain conditions especially when man's activities add large amounts of phosphorus, nitrogen may become the major limiting factor (9,23). Silicon, although not required by most types of phytoplankton, is essential for the growth of one very important group in freshwater, the diatoms. In the Great Lakes the amounts of this element which are available can become so low that the growth and yield of the diatoms are limited (20). Thus, these three nutrients have been considered for the development of objectives; although, for reasons explained later, objectives are actually developed only for phosphorus. It has been suggested that other elements, especially carbon, may at times limit plant production in the Great Lakes, but there seems little or no evidence to support such claims.

TIME AND SPACE SCALES

The concentrations of the three nutrients vary greatly within and between each of the five Great Lakes and also seasonally at any one place. Thus, it is impractical to develop a single objective for all areas at all times.

The variations imposed by seasonal fluctuations may be largely ignored if objectives are developed that apply to one time period, the early spring. At this time, before the algae start their yearly period of active growth, total nutrient concentrations are usually at their maxima (9). In late spring and summer when algal growth and cell concentrations are higher, sinking cells tend to carry nutrients to the bottom and to reduce the total nutrient concentrations in the lake surface waters. Subsequently, the cells decompose and nutrients are again released to the water. Thus, it is the concentrations of nutrients available at the start of the growing season that largely determine the potential limits of growth and yield throughout the year.

With regard to spatial scale, objectives have only been developed for lake-wide averages or, in the cases of Lakes Huron and Erie for two or three major sub-basins. In Lake Huron, Saginaw Bay is so different and separate from the main lake that it was deemed necessary to develop a separate objective for it. Also the three basins of Lake Erie differ so greatly from each other that separate objectives have been developed for each of them. Nearshore areas, where the localized effects of rivers and direct discharges are present, are specifically excluded from this consideration of lake-wide or large area averages. Developing objectives for such large areas ignores localized problems and conditions; and so the objectives will not, even when met, cure all environmental deterioration due to nutrient enrichment. Local or regional problem areas that remain after the general objectives are achieved should be considered on a case by case basis by the local jurisdictions involved.

PRESENT CONDITIONS

Spring concentrations of total phosphorus, inorganic nitrogen, and total reactive silica in the upper layers of the Great Lakes are presented in Table 1 along with summer epilimnetic concentrations of two important indicators of surface water quality, total chlorophyll a and Secchi disc depth. Since Secchi depth decreases as plankton biomass increases, inverse Secchi depth (16) is also included.

Several investigators (6,8,28) have suggested that a concentration of 20 µg/L total phosphorus may be used as an approximate lower limit to the condition where eutrophication is well advanced (eutrophy). They also have suggested that below 10 µg/L few if any of the effects of eutrophication are evident and such waters are in a nutrient-poor condition (oligotrophy). Between 10 and 20 µg/L is the intermediate or transitional state (mesotrophy).

Using these limits as guidelines, the present trophic status of the Great Lakes can be summarized as shown in Figure 1. Only Lakes Superior and Huron are safely in the oligotrophic state. Lake Michigan is approaching the mesotrophic state; while the Lower Lakes and Saginaw Bay must all be classified as eutrophic, although Lake Ontario and the Central and Eastern Basins of Lake Erie are not strongly so, as of yet.

PHOSPHORUS

In the following, specific objectives for phosphorus concentrations are suggested which will meet the general environmental objectives of the Great Lakes Water Quality Agreement.

LAKE SUPERIOR AND THE MAIN BODY OF LAKE HURON

Annex 2 of the [1972] Water Quality Agreement states that one objective of the phosphorus control program is the ". . . stabilization of Lake Superior and Lake Huron in their present oligotrophic state." Thus, the Agreement calls for maintenance of the present water quality; and as both of

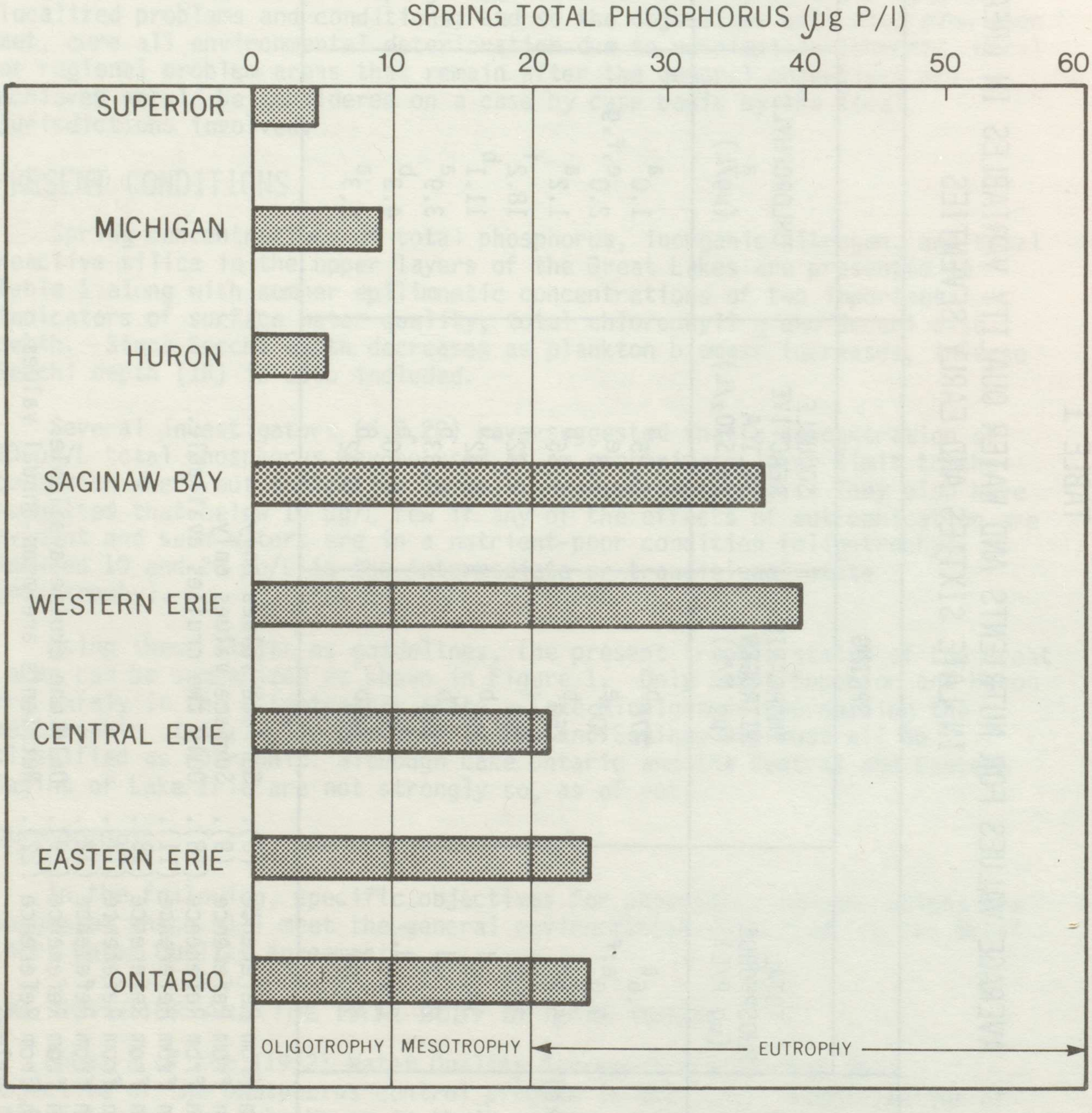
TABLE 1

AVERAGE VALUES FOR NUTRIENTS AND WATER QUALITY VARIABLES IN GREAT LAKES IN LATE SIXTIES AND EARLY SEVENTIES

LAKE	SPRING				SUMMER	
	TOTAL PHOSPHORUS (µg P/L)	INORGANIC NITROGEN (µg N/L)	SOLUBLE REACTIVE SILICA (mg SiO_2/L)	CHLOROPHYLL a (µg/L)	SECCHI DEPTH (m)	INVERSE SECCHI DEPTH (1/m)
Superior	4.6^{a}	275^{b}	2.25^{b}	1.0^{a}	8.8^{a}	0.114
Michigan	$9.0^{e,f}$	200^{e}	1.5^{e}	$2.0^{e,f,g}$	$\sim 6.0^{c,h}$	0.127
Huron (Main Lake)	5.2^{a}	259^{b}	1.36^{b}	1.2^{a}	8.3^{a}	0.120
Saginaw Bay	30.2^{i}	304^{i}	0.82^{i}	18.2^{i}	1.3^{i}	0.79^{i}
Western Erie	39.5^{d}	631^{b}	1.32^{b}	11.1^{b}	1.5^{b}	0.667
Central Erie	21.2^{d}	133^{b}	0.33^{b}	3.9^{a}	4.4^{a}	0.227
Eastern Erie	$23.8^{d,j}$	180	0.30^{b}	4.3^{b}	4.5^{b}	0.222
Ontario	24.0^{d}	279^{b}	0.42^{b}	5.3^{a}	2.5^{a}	0.400

a. Information from Reference (8). Surface values only.
b. Information from Reference (9). Surface values only.
c. Information from Reference (18). Only two cruises available.
d. Information from Reference (11).
e. Information from Reference (13).
f. Information from Reference (17).
g. Information from Reference (12).
h. Information from Reference (19). Only one cruise available.
i. Information from Reference (22). Nutrients are mean annual values.
j. Mean annual value.

Figure 1. CURRENT TROPHIC STATUS OF THE GREAT LAKES



these lakes seem to be phosphorus limited (9), phosphorus concentrations should be maintained at no greater than their present levels. Therefore, based on the present conditions as specified in Table 1, it is recommended that the lake-wide mean of total phosphorus in the spring in Lake Superior and the main body of Lake Huron should not exceed 5 µg/L.

LAKE MICHIGAN

As this lake lies completely within the United States, it is not specifically mentioned in the Agreement. However, it is broadly connected to Lake Huron through the Straits of Mackinac, and its outflow waters empty into that lake. Thus, it is not possible to limit nutrient additions to Huron without also controlling additions to Michigan. For this reason a phosphorus objective is proposed for Michigan. The rationale for the level of the proposed objective is based on the close connection of the two lakes and on the fact that the environmental conditions of the two are naturally quite similar. Therefore, the two lakes should have similar objectives. However, Chapra (3) simulated historical phosphorus concentrations in the Great Lakes using a mathematical model and he calculated that the phosphorus concentrations in Michigan before large-scale human intervention were several micrograms per liter higher than those of Huron, and so the recommended objective is also somewhat higher. It is recommended that the lake-wide average of total phosphorus in the spring in Lake Michigan should not exceed 7 µg/L.

SAGINAW BAY

The [1972] Agreement does not deal with Saginaw Bay as separate from Lake Huron. Yet this bay is so large that its overflow has a substantial effect on the water quality conditions in the boundary waters of the main lake (26). Further, the main lake objective cannot be applied to this bay because the present phosphorus concentrations, as well as those that prevailed before large-scale human settlement in the area, are much higher than in the main lake (5). Thus, it seems essential to develop a separate objective for this area.

Article II, section (e) of the [1972] Agreement states that the waters of the Great Lakes System should be ". . . free from nutrients entering the waters as a result of human activity in concentrations that create nuisance growths of aquatic weeds and algae." Applying this general objective to an area such as Saginaw Bay requires that we know what part of the phosphorus comes from human activities. Chapra and Robertson (5) suggest that Saginaw Bay naturally had total phosphorus concentrations somewhat above 10 µg/L based on a mathematical model of the phosphorus inputs and concentrations in the Great Lakes. Further, recent observations by Thomas (25) suggest that the growths of *Cladophora* reach nuisance levels in the Great Lakes at about 15 µg/L. Thus, it is recommended that the area-wide mean total phosphorus concentrations in the spring in Saginaw Bay should not exceed 15 µg/L.

WESTERN LAKE ERIE

The conditions in this part of Lake Erie in a number of ways bear a strong similarity to those in Saginaw Bay. Both areas presently have very high total phosphorus concentrations and severe eutrophication problems and both were also naturally areas of high phosphorus concentrations relative to most of the other parts of the Great Lakes (5). The natural concentrations in western Erie were, however, probably somewhat lower than in Saginaw Bay, around 7 or 8 µg/L (3).

As pointed out for Saginaw Bay the [1972] Agreement calls for the prevention of nuisance growths of algae in the Great Lakes. More specifically it sets up as one of the objectives of the phosphorus control program the ". . . reduction in present levels of algal growth in Lake Erie."

Thus, to reduce these levels and for basically the same reasons as for Saginaw Bay, it is recommended that the basin-wide average total phosphorus concentration in the spring in western Lake Erie should not exceed 15 µg/L.

CENTRAL LAKE ERIE

Annex 2 of the [1972] Agreement states that an objective of the phosphorus control program is the ". . . restoration of year-round aerobic conditions in the bottom waters of the central basin of Lake Erie."

The anaerobic conditions that now often exist during the summer result from the decomposition of large amounts of organic matter. This material is produced by the algae in the upper lighted waters and then falls to the bottom and decomposes as the algae become senescent and die. Such decomposition requires oxygen and this gas is removed from the water as this process proceeds. If the waters where decomposition is occurring are in contact with the air, the dissolved oxygen that is removed is quickly replaced from the atmosphere and anaerobic conditions do not develop. However, during the summer the Central Basin of Lake Erie is thermally stratified so the hypolimnetic waters are not in contact with the air. Further the Central Basin is fairly shallow so the hypolimnion is only a few meters thick. Thus, any decomposition that occurs along the bottom withdraws oxygen from this limited hypolimnetic reservoir and substantial decomposition quickly leads to oxygen depletion.

To restore year-round aerobic conditions, phosphorus concentrations must be controlled to the point where the amounts of organic matter produced and then settling to the bottom and decomposing are not so large as to use up the oxygen supply of the bottom waters. Chapra (4) has developed a mathematical model that allows calculation of this concentration. According to his calculations a spring-time, average phosphorus concentration that does not exceed 10 µg/L will assure that no appreciable area of the Central Basin will become anaerobic during summer stratification. Thus, it is recommended that the spring, basin-wide average concentration of total phosphorus should not exceed 10 µg/L.

EASTERN LAKE ERIE

The Agreement objectives of reduction of algal growths and prevention of nuisance conditions that apply to western Lake Erie also apply to the Eastern Basin. The environmental conditions here are quite different than those in the shallow western end, however. This basin is much deeper and is farther removed from most large sources of nutrient inputs. Thus, its present phosphorus concentrations (as well as those that occurred before man's intervention) are much lower than the concentrations in the Western Basin, and this area is one of potentially oligotrophic conditions. As discussed earlier 10 µg/L total phosphorus can be taken as the approximate upper limit of oligotrophy. Restoration to such a state should reduce the algal levels and restore high water quality. Thus, it is recommended that the spring, basin-wide average concentration of total phosphorus should not exceed 10 µg/L.

LAKE ONTARIO

This lake has experienced substantial degradation of water quality and major alterations in biota due to man's activities. The recently completed International Field Year for the Great Lakes (IFYGL) program has revealed the severe deterioration that has occurred in its ecosystem. Detailed studies by Stoermer, Bowman, Kingston, and Schaedel (24) on the phytoplankton and McNaught and Buzzard (14) and McNaught, Buzzard, and Levine (15) on the zooplankton have shown that the lake is presently inhabited quite largely by enrichment tolerant (eutrophic) forms. These authors and others believe that the lake's original condition and biota were those characteristic of a much less eutrophic situation. In fact, Chapra's (3) model estimates the phosphorus concentrations in this lake originally fell within the oligotrophic range. Enrichment has led to large increases in phytoplankton production and hence to nuisance growths of algae. The Agreement objectives of reduction of algal growths and prevention of nuisance growths apply here. The lake should be returned to a state closer to its original oligotrophic condition. To meet this goal, it is recommended that the lake-wide average total phosphorus conditions in the spring should not exceed 10 µg/L.

THE IMPACT OF THE PROPOSED PHOSPHORUS OBJECTIVES ON WATER QUALITY

While phosphorus is the major cause of accelerated eutrophication in the Great Lakes, it is difficult to interpret concentrations of this element directly as a measure of lake trophic status. A more effective interpretation can be obtained by relating the objectives proposed in this report to parameters that more directly measure algal biomass and water transparency. One way to do this is by the use of the empirical correlations such as those developed by Dillon and Rigler (7).

PHOSPHORUS: CHLOROPHYLL A

Chlorophyll a can be plotted against total phosphorus and a linear regression with a zero intercept can be used to estimate the relationship between these two variables. The zero intercept is based on the fact that, in the absence of the dependent variable, the independent variable would not be expected to be present. For example, if the lake were devoid of all phosphorus, it would not be expected to contain chlorophyll a. The result of the regression (4) is:

$$\mathrm{Chla} = 0.24\ \mathrm{TP} \qquad (1)$$

where Chla = summer chlorophyll a and TP = vernal total P.

CHLOROPHYLL A: SECCHI DEPTH

Chapra (4) has used Great Lakes data to develop a preliminary estimate of the relationship of chlorophyll a to Secchi depth:

$$S = 17.28 \frac{1}{1 + 0.963 \text{ Chl } \underline{a}} \qquad (2)$$

where S = summer Secchi depth.

Equations (1) and (2) can be used to estimate the effect of the proposed objectives. Table 2 shows that Lake Michigan would be improved from a marginally mesotrophic state to an oligotrophic state with summer chlorophyll a of approximately 1.7 µg/L and a summer Secchi depth of about 6.6 m. Western Lake Erie would be moved from highly eutrophic to a mid-mesotrophic state with summer chlorophyll a of approximately 3.6 µg/L and a summer Secchi depth of about 3.9 m. This latter amounts to an improvement in water clarity of approximately 2 meters. Eastern Erie and Ontario would be lowered to marginally oligotrophic with summer chlorophyll a levels of about 2.4 µg/L and summer Secchi depths of over 5 meters.

NITROGEN

Nitrogen in combined inorganic forms such as nitrate, nitrite, or ammonium ion is required for algal growth, but most algae cannot make use of nitrogen gas that is dissolved in natural waters in relatively large quantities. However, certain types, notably the blue-green algae, can fix gaseous nitrogen, i.e. convert it to ammonia and so make it available for their growth.

The evidence presently available suggests that, before man began adding his wastes to the Great Lakes in large quantities, phosphorus was the limiting factor almost everywhere in these lakes. That is the ratio of phosphorus to nitrogen was such that the plants used up the available phosphorus before they exhausted the available nitrogen. However, the effluents from sewage plants and the runoff from agricultural and urban lands often contain much more phosphorus than nitrogen, relative to plant needs. Thus, in certain parts of the Great Lakes, especially Lake Erie and to a lesser extent Lake Ontario, nitrogen appears to be, at times, the factor limiting the growth of most algal types (9). This condition favors the nitrogen-fixing blue-greens, and these algae are especially likely to cause water quality problems, such as tastes and odors in drinking water and the curtailment of recreational activities due to masses of algal material floating on the lake surface and piling up on the beaches.

Because of this ability of blue-greens to fix gaseous nitrogen, it is very difficult, if not impossible, to control eutrophication problems through limitations on nitrogen inputs to a water body. There is an inexhaustible supply of gaseous nitrogen in the atmosphere and so, as the gaseous nitrogen in the water is used up by the nitrogen-fixing algae, it is readily replaced from the atmosphere. Further, the nitrogen-fixing forms favored when nitrogen is limiting are especially prone to cause water quality deterioration. For

TABLE 2

PROPOSED OBJECTIVES FOR TOTAL PHOSPHORUS WITH ESTIMATED LEVELS OF CHLOROPHYLL A, SECCHI DEPTH, AND TROPHIC STATE THAT WOULD RESULT

	TOTAL PHOSPHORUS (μg P/L)	TOTAL CHLOROPHYLL *a* (μg/L)	SECCHI DEPTH (m)	TROPHIC STATE
Superior	5	1.2	8.0	Oligotrophic
Michigan	7	1.7	6.6	Oligotrophic
Huron	5	1.2	8.0	Oligotrophic
Saginaw Bay	15	3.6	3.9	Mesotrophic
Western Erie	15	3.6	3.9	Mesotrophic
Central Erie	10	2.4	3.9	Mesotrophic
Eastern Erie	10	2.4	5.2	Oligomesotrophic
Ontario	10	2.4	5.2	Oligomesotrophic

these reasons then, it is impractical and, in fact, counterproductive to attempt to control eutrophication by restricting inputs of nitrogen even in areas where it is currently limiting to growth of most algal forms. To rehabilitate such areas, phosphorus inputs must be lowered to the point where phosphorus replaces nitrogen as the limiting factor and then lowered further so that the growth and yield of all algal forms is reduced.

SILICON

Algae belonging to the diatom group usually predominate throughout the year in the phytoplankton of nutrient-poor (oligotrophic) lakes. Diatoms are generally considered desirable from man's point of view because they serve as good food for zooplankton and usually do not increase to nuisance levels although this can occur with certain species.

Diatoms have a special requirement for silicon that most other algal groups do not share. This element, in a form available to the algae, is required so that they can form their siliceous cell walls. If available silica levels fall too low, the diatoms can no longer obtain this requirement, and they are replaced by other forms, usually green and blue-green algae that do not need silica.

Schelske and Stoermer (20) have shown that phosphorus additions to Lake Michigan have stimulated diatom growth so much that available silica levels (measured as soluble, reactive silica) in the summer are approaching the point where they limit continued diatom growth. Yet, there is still adequate phosphorus for other types of algae to grow and so take over the community. This process has probably already occurred in Lakes Erie and Ontario as shown by the fact that the soluble, reactive silica levels are low there (Table 1), and the diatoms are of much less relative importance during the summer in these lakes than in the Upper Lakes (29).

Thus, silica deficiency seems to be an existing and increasing problem in the Great Lakes. However, the problem is the reverse of that with phosphorus. For that element the concentrations are increasing allowing increased algal growth and causing shifts to less desirable types. For silica the concentrations are decreasing causing shifts away from desirable types. Therefore, as the problem is too little rather than too much silica, there is no necessity to set an objective limiting input. Further, the limitations proposed in this paper for phosphorus should reduce algal growth and so eliminate silica deficiencies in most areas.

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LEAD

OBJECTIVE

Concentrations of total lead in an unfiltered water sample should not exceed 2 µg/L in Lake Superior, 3 µg/L in Lake Huron, 4 µg/L in Lake Erie and in Lake Michigan, and 5 µg/L in Lake Ontario to protect aquatic life.

Note: *This recommendation will not necessarily protect aquatic biota from the effects of alkyl lead compounds.*

RATIONALE-DERIVATION OF THE OBJECTIVE

The recommended objectives are a refinement of those recommended by the Water Quality Objectives Subcommittee in Appendix A to the 1975 Fourth Annual Report on Great Lakes Water Quality (44,96) and subsequently included in Annex 1 of the 1978 Great Lakes Water Quality Agreement. The above concentrations are one-fifth of those in the 1978 Agreement, based on experimental evidence developed using Lake Ontario water. This included a high sensitivity to lead (10 µg/L) of algae tested in lake water compared to a laboratory medium (Table 11), chronic mortality and behavioral abnormalities of invertebrates between 3 and 30 µg/L lead, and chronic hematological and neurological damage to fish between 13 and 22 µg/L lead (Figure 4). From these data, an objective for lead in Lake Ontario water of 5 µg/L to protect aquatic life is recommended. Objectives of 2,3,4, and 4 µg/L in Lakes Superior, Huron, Michigan, and Erie are derived by applying to the Lake Ontario objective the slope of an observed relationship between chronic lead toxicity to fish and water alkalinity (or hardness; see Figures 4 and 5).

Objectives for lead loading rates to the lakes and lead concentrations in biota and sediments are desirable for a more holistic perspective, but there were inadequate data to justify such objectives. The same was also true for concentration-based objectives for organic lead compounds, in particular alkyl leads.

SUMMARY (REFER TO FIGURE 1 AND TABLE 1)

Anthropogenic lead enters the Great Lakes via air and water, primarily as a result of its use in gasoline. Inorganic lead concentrations in excess of 1,000 - 10,000 µg/L quickly react with complexing materials in lake water and precipitate to the sediments. Particulate lead is not available to predatory fish through uptake across the gills, but there are data to suggest it is available to filter-feeding zooplankton, herbivorous fish, and fish that sift bottom mud for food organisms. Non-complexed lead at concentrations <1,000 µg/L is readily taken up by aquatic biota; however, since it is also available for adsorption to particulates, it should quickly disappear. Consequently, aquatic biota should be exposed to significant concentrations of non-complexed lead only near mixing zones of municipal and industrial effluents and river mouths. Bottom-feeding and herbivorous fish and

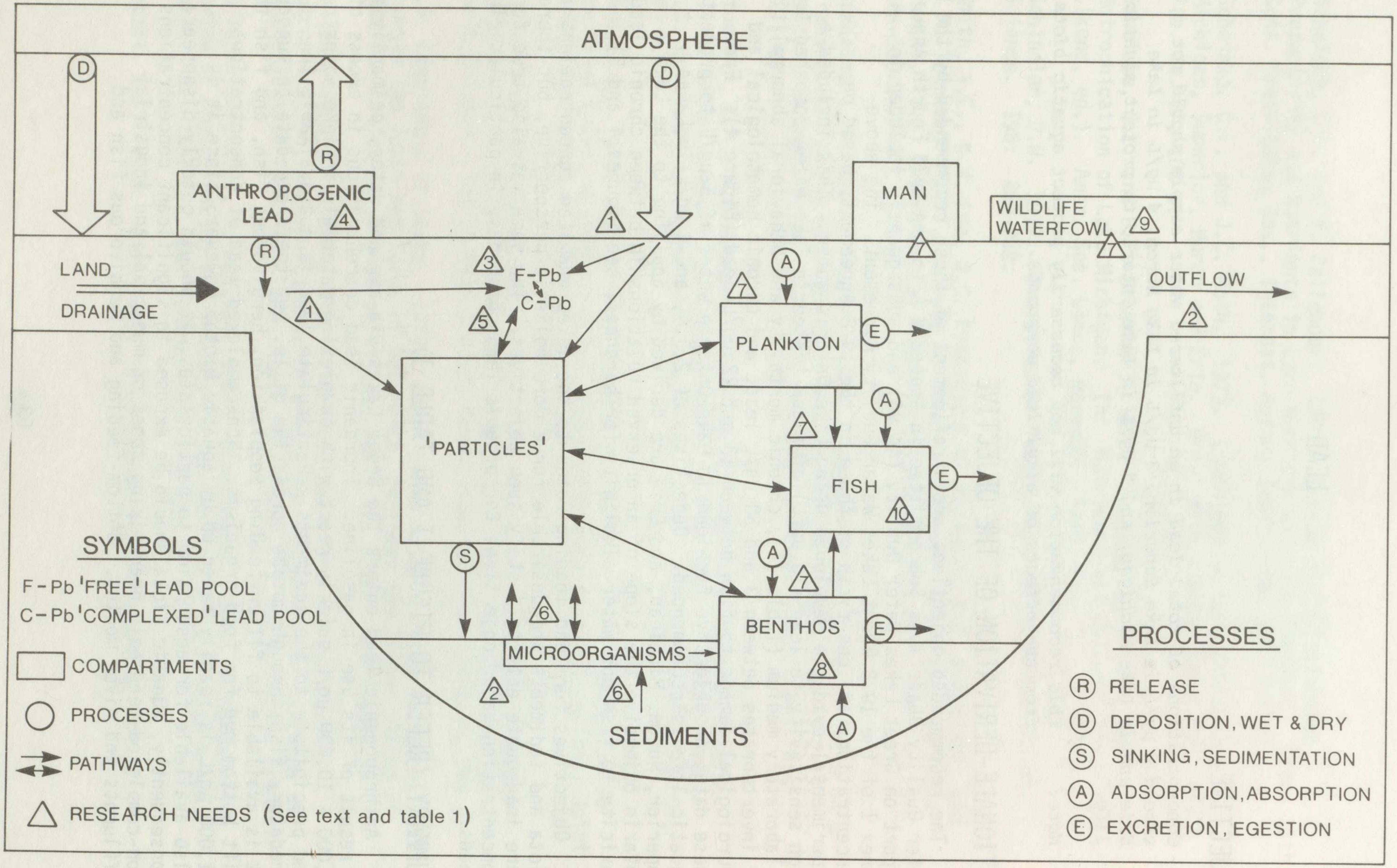


FIGURE 1. SYMBOLIC OVERVIEW OF LEAD FLUX IN LAKE ECOSYSTEMS

TABLE 1
RESEARCH NEEDS IN THE GREAT LAKES

(NOTE: THE NUMBERS BELOW REFER TO FIGURE 1 AND NOT TO RESEARCH PRIORITIES)

QUANTIFICATION

1 Estimate, by source, loading of lead to each lake and identify contamination "hot spots" in relation to known point sources.

2 Estimate the rate of lead accumulation in the sediments of each lake and amount of sediment leaving each lake via resuspension.

3 Determine background lead concentrations in lake and river waters using "ultra-clean" methods.

4 Cost strategies that will reduce the primary anthropogenic lead sources, gasoline additives, and production in the Great Lakes Basin.

* Compute maximum permissible anthropogenic loadings based on the overall fate and effect of lead in each lake and the objectives presented.

TRANSFORMATION

5 Determine the exchange kinetics between different forms of lead (e.g. between "free" and particulate lead) in lake waters as a function of trophic status, season, hardness, organic content, etc.

6 Estimate the rates of lead alkylation in, and lead releases from, lake sediments and the contribution of lead from this source to biota and other ecosystem compartments.

7 Evaluate the availability of different forms of lead to the various classes of biota, and explore the use of "fingerprinting" techniques (e.g. isotope ratio variations) to show the contribution of different sources of lead to levels found in biota, particularly fish.

EFFECT

8 Determine the response of benthos to "free" lead in lake water, sediment-bound lead, and lead in interstitial waters, and the role of microbes in lead toxicity to benthos.

9 Examine the impact of alkyllead on aquatic biota and wildlife.

10 Measure the sensitivity of fish to lead as a component of liquid effluents released into the lake, and as a function of their food habits (e.g. planktivores vs. benthic detritivores).

filter-feeding zooplankton would also receive significant exposures anywhere that lead-contaminated particulates or sediments drift. The continual movement of fine-grained sediments in the Great Lakes will therefore cause widespread low-level contamination of these organisms. Further lead contamination may be caused by biological and chemical methylation processes in sediments; alkyl lead compounds have been observed in Great Lakes fishes. Other sources of organic lead in fish could be industrial wastes and spillage and evaporation of leaded gasoline. The lipophilic organo-lead compounds will behave differently from inorganic lead and will tend to accumulate easily and quickly in biological tissues.

Impacts of lead will be associated with point sources where aquatic biota respond to free lead in water, and in areas where contaminated sediments settle. The overall impact on aquatic biota is difficult to assess, but it will probably be greatest in long-lived organisms that are non-migratory and live near high-level point sources, since they will acquire a high lifetime exposure. Sensitive zooplankton and phytoplankton may be severely affected by drift through mixing zones, but presumably large population sizes would allow recolonization of affected water as it mixes with clean water. Adverse impacts are best documented for wildfowl populations that exhibit high mortality rates due to ingestion of spent lead shot. Lead contamination of drinking water is probably not a problem, based on existing surveillance data. However, since these data are generally collected offshore, there may be unknown instances of contamination of inshore intakes.

Inorganic lead contamination of fish as human food does not seem to be a problem, since total lead levels in wild fish or in fish exposed to high inorganic lead concentrations in the lab do not exceed previously published food guidelines. However, these guidelines have been recently withdrawn and are under review.

INTRODUCTION

Lead is a bluish-white metal with a high density, softness, flexibility, malleability, and weldability and with a low melting point and elastic limit. It has an atomic number of 82 and atomic weight of 207.19. Lead may exist as a divalent (plumbous) salt, which is the inorganic form usually found in water, and as a tetravalent (plumbic) compound which is the form in most organic alkyllead compounds. Most tetravalent salts are relatively unstable and decompose in water. Lead may also be amphoteric, forming stable plumbates and plumbites with other cations (66). The properties of lead allow a variety of uses (Table 2). These, plus mining, milling, and smelting of lead and other metal-containing ores, and burning of fossil fuels, cause a loss of lead to aquatic ecosystems at a rate above normal weathering. As an example, Nriagu (66) has estimated that, of 1,360 thousand tonnes (1 tonne = 1,000 kg) of lead used in the U.S. in 1970, about 760 thousand tonnes (approximately 56%) entered the environment in one form or the other.

The following review briefly outlines the sources of lead inputs to the Great Lakes Ecosystem; the forms of lead in air, water, and sediments; the lead concentrations in various ecosystem compartments, especially edible portions of commercial fish species; and lead toxicity to aquatic biota.

TABLE 2

REPRESENTATIVE INDUSTRIAL USES OF LEAD[a]

CLASS	
Coatings and dyes	Paints, pigments, dyes, metallurgical coatings, ceramic glazes, stained glass, mirrors, wood preservatives, corrosion inhibitors.
Electrical components and Electronics	Batteries, electrolytes, electrical insulation, semiconductors, photosensitive electronic components.
Plastics, chemicals	Plastisols, phonograph records, photography processes, plastic stabilizers, catalysts, curing agent for resinous siloxanes, polymer synthesis.
Structural	Printers' type, solder, pipes, containers, fusible alloys, ammunition.
Medical	Veterinary medicines, ointments.
Combustion	Matches, pyrotechnics, explosives, fuel additives.
Miscellaneous	Lubricant, radiation shields.

a. Information from Reference (76).

INPUTS TO THE GREAT LAKES

The sources of lead in lake water include tributary inflows, industrial and domestic waste discharges, stormwater and coastal runoff, atmospheric deposition (dry particulate and rainfall), shoreline erosion, and dredged spoil disposal. Approximate mass balances for lead are available for Lakes Ontario, Erie, Huron, and Superior (Table 3) which indicate the relative contributions of lead from different sources. Tributary contributions to Lakes Huron and Superior are probably overestimated due to the difficulties of measuring low concentrations of lead (see section on lead in water). Thus, a major fraction (at least 40%) of the lead entering three of the lakes is derived from atmospheric precipitation. Lead in sewage discharges, which often includes storm sewer flows, is partly derived from transportation emissions.

Sediments are the dominant sinks for lead in these lakes. Of the annual load of lead to Lake Erie, 75% is retained in the sediments (Table 3) and, for Lake Ontario, 50% is retained. An estimate of the retention in the sediment of the other Great Lakes has yet to be done.

The 1972 budget for the industrial use of lead in Canada, and associated environmental releases (Figure 2) shows the importance of atmospheric emissions in the environmental lead cycle (50). In particular, gasoline lead accounts for 13,300 out of 18,700 tons total lead emissions to the air. In the Canadian portion of the Great Lakes and St. Lawrence drainage basin, gasoline accounts for 7,930 tons out of a total of 8,152 tons. These figures do not reflect transboundary transport of atmospheric lead or the growing reliance on coal-burning electric power plants with associated lead and other metal emissions.

The lead in atmospheric precipitation originates primarily from gasoline additives. On a global basis, about 70% of anthropogenic emissions to the air come from these additives and, in Canada, an additional 23% are from iron, steel, copper, and nickel production. Lead loading from precipitation ranges from 9 to 20 $mg/m^2.a$, in the Great Lakes Basin, but in highly contaminated areas, it is much greater (e.g. 116, 600, 600, and >6,000 $mg/m^2.a$ near a Sudbury smelter, a Toronto expressway, a Toronto incinerator, and a lead smelter, respectively).

FORMS OF LEAD

AIR

The forms of lead in the atmosphere are extremely complex and depend very much on the source of the pollutant (Table 4). Atmospheric lead is generally in amorphous particulate form. The particulates show a broad range of particle size and chemical composition. The variations reflect both the source characteristics and the aging history of the lead aerosols.

WATER

In the vast majority of freshwater systems in contact with the atmosphere, lead carbonate complexes ($PbCO_3$) dominate the inorganic chemistry of

TABLE 3

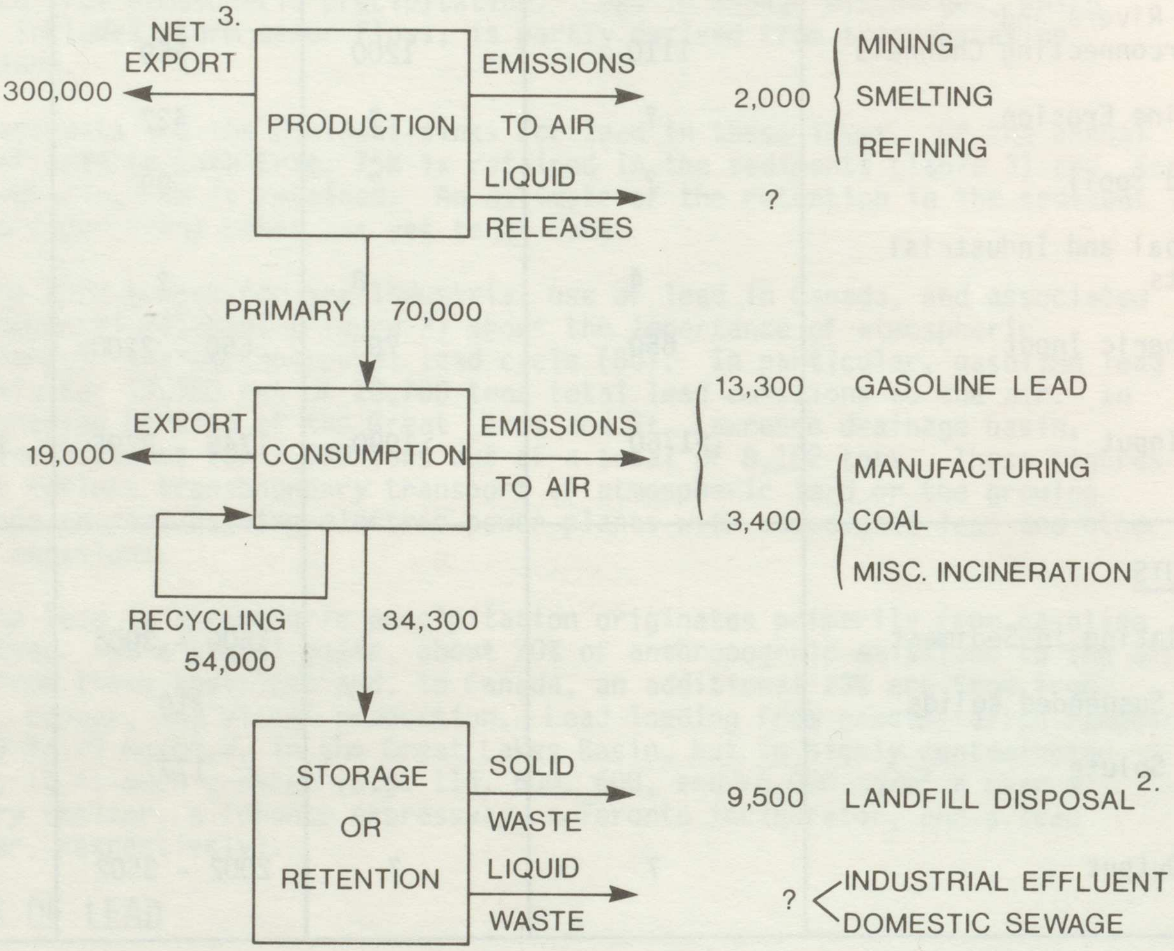
GREAT LAKES LEAD MASS BALANCES

	TONNES PER YEAR			
	SUPERIOR[a]	HURON[a]	ERIE[b]	ONTARIO[b]
INPUTS				
Suspended Solids and Solutes from Rivers and Interconnecting Channels	1110	1200	559	905
Shoreline Erosion	?	?	437	50
Dredged Spoil	?	?	99	65
Municipal and Industrial Inputs	4	8	?	?
Atmospheric Input	650	780	650 - 2200	280 - 440
Total Input	>1760	>1990	1745 - 3295	1300 - 1460
OUTPUTS				
Accumulating in Sediment			1500 - 3006	725
Output Suspended solids			319	547
Output Solute			177	207
Total Output	?	?	2002 - 3502	1479

a. Information from Reference (70).
b. Information from Reference (73).

FIGURE 2

CANADIAN INDUSTRIAL LEAD BUDGET IN 1972 (Tons)[1.]



1. Derived from Reference 50
2. Calculated from recycling figure which is estimated to be 87% efficient
3. Net export = Export of lead ingots – Import of lead ingots

TABLE 4

FORMS OF ATMOSPHERIC LEAD ACCORDING TO SOURCE[a]

Automobile Emissions	$PbCl_2$; $PbBrCl$; $Pb(OH)Br$; $PbCl_2 \cdot PbBr_2Cl$; $PbO \cdot PbBr_2$; $PbO \cdot PbCl_2$; PbO_x; $PbSO_4$
Mining Activities	PbS; $PbCO_3$; $PbSO_4$; $Pb_5(PO_4)_3Cl$; $PbS \cdot Bi_2S_3$
Base Metal Smelting and Refinishing	Pb; $PbCO_3$; $PbSO_4$; PbO_x; $Pb \cdot PbSO_4$; $(PbO)_2PbCO_3$; Pb-silicates
Coal-fired Power Plants	PbO_x; $PbSO_4$; $Pb(NO_3)_2$; $PbO \cdot PbSO_4$
Cement Manufacture	$PbCO_3$; $Pb_5(PO_4)_3Cl$
Fertilizer Production	$Pb_5(PO_4)_3Cl$; PbO_x; $PbCO_3$
Rural Site (Percent Distribution)[a]	$PbCO_3$ (30%); $(PbO)_2PbCO_3$ (28%); PbO (21%); $PbCl_2$ (5.4%); $PbO \cdot PbSO_4$ (5%); $Pb(OH)Cl$ (4%); $PbSO_4$ (3.2%); $PbBrCl$ (1.6%); $(PbO)_2 \cdot PbCl_2$ (1.5%); $(PbO)_2PbBrCl$ (1%); $PbBr_2$ (0.1%).

a. Information from Reference (88).

dissolved lead. Between pH 6 - 8, lead will apparently be entirely complexed as the carbonate species, especially $Pb(CO_3)_2^{=}$; $PbCO_3^0$ also occurs at more acidic pH values (4,32). In oxygenated systems where sulphur-containing organic compounds are not present in measurable quantities, ordinary amino acids will not effectively complex lead because of their low stability constants with lead complexes ($\log K = 5.5$ - average for the amino acids complexed with Pb^{2+}). The glycine concentration must approximate the total carbonate concentration for the lead-glycine complex to dominate. On the other hand, strong, non-specific chelating agents, such as sodium nitrilotriacetic acid, at concentrations as low as 20µg/L, can have a noticeable effect on dissolved lead chemistry.

The forms of lead in Great Lakes waters have not been measured. Information from other natural water systems, although not directly applicable, can be taken as a reference for the Great Lakes.

Lead uptake by aquatic biota is a function of the concentration of biologically available lead and of the ability of biota to actively or passively regulate membrance transport of lead (see sections on lead content and toxicity to aquatic biota). In controlled experimental conditions, lead uptake by fish and sublethal toxicity can be correlated directly to "free" or "ionic" lead and to "total" lead (21,27,36,37,39,42,58,59); "free" or "ionic" lead measurements have been recommended as the basis for objectives (21). However, the impacts of lead on aquatic biota may not be typical only of "free" lead, since there is evidence suggesting that particulate lead may be available to herbivorous or detrital feeding fish and to invertebrates (see sections on lead content of aquatic biota). Although the rate of methylation of sediment lead is unknown, alkyl lead compounds have been measured in fish (see section on lead in fish), so that sediment lead conceivably may be available to fish in the alkyl form. Therefore, until the ultimate fate and effect of the various forms of lead are defined, a logical and protective basis for an objective is "total" lead.

SEDIMENT

Little information exists on species of lead compounds in sediment because of the limited knowledge of the characteristics of organic compounds in sediment. In anaerobic sediments, most of the dissolved lead will be immobilized as the sulphide (PbS). This situation has been exemplified by the Saguenay fiord sediments where 70 - 80% of the total lead is associated with the sulfide mineral phase (52).

Fulvic and humic acids constitute from 40 to 70% of the organic matter in soils and sediments and can form strong complexes with lead ions (64,82). Lead-fulvic acid complexes will dominate over $Pb(CO_3)_2^{=}$ at pH 6 and high carbon dioxide partial pressure (0.1 mm) if the fulvic acid concentration is greater than 10^{-4}M (66).

It has also recently been suggested (65) that soluble lead compounds react with phosphates in the soils to form trilead phosphate, $Pb_3(PO_4)_2$, plumbogummite and pyromorphites.

BIOTA

Lead may enter the biomass pool as soluble ions, organo lead molecules, or particulate materials. Within biota, lead is likely to be associated with organics in complexed forms. There is no literature available on the identification of chemical forms of lead in biota, although tetraalkyllead compounds have been reported in fish (14,85) (see section on lead in fish).

TRANSFORMATION

Incubations of sediment with organic and inorganic lead compounds produced tetramethyllead (103), and this process has been attributed to biological and chemical methylation (45,81). Several pure bacterial cultures (*Pseudomonas, Alcaligenes, Acinetobacter, Flavobacterium,* and *Aeromonas*) were able to transform trimethyllead acetate to tetramethyllead at various pH's (103).

The methylation of Pb(II) does not follow the methyl cobalamin mechanism implicated for mercury methylation, and it has been suggested that the carbonium ion, CH_3^+, is responsible for the methylation of Pb(II) (106).

LEAD DISTRIBUTION IN THE GREAT LAKES ECOSYSTEM

AIR

Lead in air is of special concern to human health due to fast respiratory uptake. The following is a verbatim quote from a Canada Department of National Health and Welfare report (25):

> As a result of automobile emissions, elevated lead levels are found in the atmosphere over large cities. Measurements made in the U.S. during 1954 - 1956 indicated that almost 95 percent of the air samples taken over 22 cities had lead concentrations less than or equal to 0.0039 mg/m³; variations in the samples correlated with the volume of automobile traffic. In a 1970 study, the major portion of urban air samples contained less than 0.0049 mg/m³, but levels of some samples were as high as 0.0099 mg/m³; in contrast, all air samples taken in non-urban localities were in the range 0.000019 to 0.00099 mg/m³. In Canada, samples of air taken at peak traffic periods in Vancouver, Toronto, and Montreal contained 0.0082, 0.0084, and 0.004 mg/m³, respectively. These levels were considered higher than general urban lead levels. Air samples collected from 72 sites across Canada during 1973, had lead concentrations between 0.00013 and 0.00322 mg/m³. Rainfall cleanses the atmosphere by "scrubbing out" the particles.
>
> Precipitation analysed in the U.S. had an average lead concentration of 0.034 mg/L. A study in Toronto showed lead to be present in the precipitation at an average of 0.05 mg/L.

WATER

Compliance with a lead objective clearly indicates the need for accurate determination of the baseline lead concentration in each lake. Despite numerous surveys, it is unlikely that accurate baseline lead concentrations in any of the Great Lakes have been measured, since reported concentrations in open lake waters range from <0.1 to 100 µg/L, and such data, obtained by conventional methods, remain suspect until confirmed by measurements in an ultra-clean laboratory under exhaustive contamination control. In general, lead levels measured elsewhere in ultra-clean facilities tend to be 10- to 100-fold lower than those obtained by conventional methods (71). Consequently, the recent report by Waller and Lee (94) that 52% of the reporting stations in Lake Ontario had lead concentrations in excess of 25 µg/L is probably erroneous.

Some recent data on lead concentrations in the Great Lakes suggest that the real lead levels in open lake waters are <1.0 µg/L (Table 5); considering possible sample contamination, the true concentrations are probably closer to 0.1 µg/L, if not lower.

SEDIMENTS

Lead in Great Lakes sediments was reviewed in the 1977 Annual Progress Report of the International Reference Group on Great Lakes Pollution from Land Use Activities (73). Since the arrival of early settlers, lead has been accumulating in sediments at a rate above that due to normal weathering and erosion, and this deposition rate is increasing (68).

Apparent anthropogenic enrichment increases through the lakes in the order Lake Erie < Lake Superior < Lake Huron, Georgian Bay < Lake Ontario. The low enrichment of Lake Erie, which receives the highest total loading, reflects both the higher sedimentation rates that dilute anthropogenic inputs, and slightly higher natural lead inputs.

Sediment concentrations tend to be highest in depositional zones (deep, relatively slow water movement) and least in nearshore or shallow zones, where water movements reduce sediment accumulation (Figure 3). Exceptions are "plumes" in Lake St. Clair and Lake Erie due to very high input rates from Sarnia, Detroit, and Toledo and local harbour contamination. There are also elevated sediment lead concentrations near the western shore of Lake St. Clair, perhaps due to lead shot from hunting. The mean (with standard deviation) depositional zone lead concentrations for Lake Superior, Georgian Bay, Lake Huron, Lake St. Clair/Lake Erie, and Lake Ontario were 60 ± 23, 67 ± 27, 66 ± 35, 112 ± 44, and 154 ± 43 mg/kg dry weight, respectively (73).

Harbour sediments from Oswego and Rochester had lead concentrations ranging from 17 to 148 and 9 to 39 mg/kg dry weight, respectively. Elutriate tests, however, showed that lead was not released from these sediments to water at concentrations over 58 µg/L, the detection limit (98). More contaminated harbours such as Hamilton Bay may contain up to 930 mg/kg lead (95). Mean sediment lead concentrations in Canadian harbours on Lake Huron ranged from 4.7 to 162.3 mg/kg, with the highest concentration in Collingwood and the next highest in Tobermory and Owen Sound.

TABLE 5

RECENT DATA ON LEAD IN GREAT LAKES WATERS

(Concentration in µg/L)[a]

LAKE SUPERIOR	LAKE HURON	LAKE ERIE	LAKE ONTARIO	REFERENCE
			0.83	12
0.4 (nearshore)	0.6 (nearshore)			74
<1.0	<1.0	1.5 (0.2-3.5)	0.7 (0.5-1.5)	111
1.0	1.0	2.0	0.5	70
			<0.3	67
		0.46 (0.15-1.40)		54
<1.0	≤0.5			97
<0.1-10.0	≤5-12			89

a. Values preceded by "less than" represent detection limits.

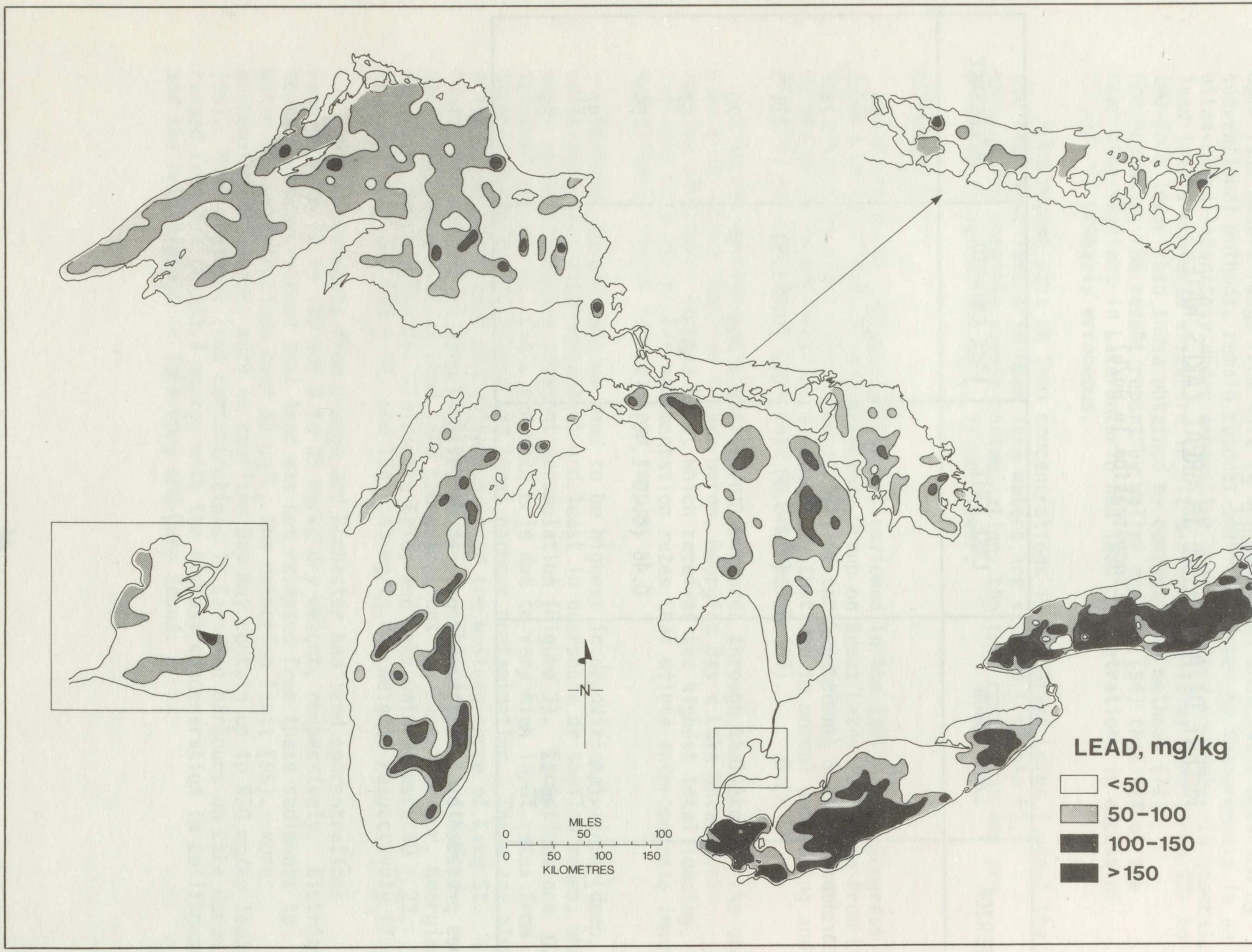


FIGURE 3 DISTRIBUTION OF LEAD IN LAKE SEDIMENTS: 0–3cm SEDIMENT THICKNESS.
Information from Reference 73.

While sediments have traditionally been regarded as sinks for lead, the possibility of microbial and chemical lead methylation exists (see section on transformation). Consequently, lead-enriched sediments may produce conditions hazardous to aquatic biota (see sections on toxicity to algae and toxicity to fish). In addition, there are very little data on toxicity of sediment lead to benthos and some indications of transfer to bottom-feeding fish (see section on lead content of fish). Therefore, high lead levels in sediments are important both as indicators of contamination and as potential hazards to the aquatic ecosystem.

PLANKTON

Very little data have been published on the lead content of Great Lakes plankton, despite their sensitivity to lead (see section on toxicity). Inventories of the distribution of contaminants in each of the Great Lakes Basins contain no lead data for plankton or benthos (43,98). A recent unpublished survey by Whittle (101) of lead content of mixed plankton samples and *Mysis relicta* collected from five offshore sites in Lake Ontario, showed that lead content of mixed surface plankton was consistently higher when compared to zooplankton samples collected at the same sites (Table 6; see Annex I for methodology). The considerable intra-site variability of lead concentrations in plankton may reflect the patchiness of the populations within an area. The zooplankton *Mysis relicta* spends a considerable amount of time near the bottom but also migrates vertically and, hence, lead levels for this species may reflect particulate or sediment lead levels. The total lead concentrations in these samples increase in relation to their proximity to industrialized areas of the Lake Ontario Basin. Filamentous algae from the littoral zone also reflect this trend. Keeney *et al.* (48) reported 9.5 to 12.2 µg/g total lead in freeze-dried filamentous algae from the eastern basin of Lake Ontario (Values on a wet weight basis would probably be 1/10 or lower). Samples from the Cobourg area contained 1.22 µg/g wet weight (107). Published concentration factors range from 20 for algal samples from the Great Lakes (48) to >100,000 for phytoplankton samples from the English Lake District (23).

FISH

Much of the information on lead in Great Lakes fish is the result of edible portion analyses and reflects a concern for human health. In areas of local contamination, such as Toronto Harbour, tissue lead concentrations were 1.78 µg/g (10). Elsewhere, muscle lead concentrations were uniformly <0.5 µg/g (53,89,90). Whole body concentrations in large migratory piscivores (e.g. lake trout) in 1975/76 were <0.08 µg/g in Lakes Huron and Superior (Table 7) (89), and similar concentrations were seen in the Lower Lakes (Table 8) However, smaller planktivores and omnivores collected at the same sites in the Lower Lakes by Whittle (101) had consistently higher concentrations (Tables 9 and 10; see Annex II for methodology). This observation is consistent with data presented by Leland and McNurney (51) for total lead concentrations in biota from urban and rural Illinois streams. Lead concentrations were highest in small planktonic or sestonic organisms with a high surface-to-body weight ratio, suggesting adsorption as a major mechanism of contamination. Herbivorous fish had higher lead concentrations than carnivorous fish, perhaps due to a smaller size, diet composition, or feeding by sifting contaminated

TABLE 6

TOTAL LEAD CONTENT OF LAKE ONTARIO PLANKTON SAMPLES IN 1979

LOCATION	NUMBER OF SAMPLES	MEAN SAMPLE DRY WEIGHT (g)	MEAN CONCENTRATION (µg/g DRY WEIGHT ± STANDARD DEVIATION)	RANGE
			NET PLANKTON (> 153 µm)	
Eastern Basin	5	1.38 ± 0.06	4.72 ± 2.02	2.8 - 7.9
Point Traverse	5	1.13 ± 0.02	7.54 ± 3.35	3.5 - 12.0
Cobourg	5	1.22 ± 0.20	6.84 ± 1.08	6.0 - 8.7
Port Credit	5	1.13 ± 0.04	5.30 ± 0.52	4.8 - 6.0
Niagara	5	1.24 ± 0.05	28.6 ± 9.40	17.0 - 43.0
			ZOOPLANKTON (*Mysis relicta*)	
Eastern Basin	10	1.12 ± 0.12	1.96 ± 0.45	1.3 - 2.6
Point Traverse	5	1.06 ± 0.5	1.64 ± 0.45	1.2 - 2.4
Cobourg	5	1.18 ± 0.08	1.20 ± 0.30	0.9 - 1.6
Port Credit	5	1.08 ± 0.04	5.1 ± 0.53	4.4 - 5.8
Niagara	4	1.09 ± 0.12	4.5 ± 0.75	3.9 - 5.6

TABLE 7

TOTAL LEAD CONCENTRATION OF WHOLE FISH SAMPLED OFFSHORE IN LAKES HURON AND SUPERIOR IN 1976

SPECIES	NUMBER[a]	UNWEIGHTED LAKE AVERAGE (μg/g Wet Weight)	
		LAKE HURON	LAKE SUPERIOR
Bloater Chubs *Coregonus hoyi*	20	0.08	0.06
Burbot *Lota lota L.*	20	0.05	0.04
Lake Trout *Salvelinus namaycush*	20	-	0.04

a. Each sample represents a composite containing at least four individual fish.

TABLE 8

TOTAL WHOLE BODY LEAD CONTENT OF PREDATORY FISH SAMPLED IN LAKES ONTARIO AND ERIE IN 1978

LOCATION	SPECIES	NUMBER (N)	MEAN WEIGHT (g)	MEAN CONCENTRATION[a] (µg/g WET WEIGHT ± STANDARD DEVIATION)	RANGE (µg/g)	% N < DETECTION LIMIT
LAKE ONTARIO						
Eastern Basin	Lake Trout (*Salvelinus fontinalis*)	50	836	<0.1	-	100
Point Traverse	Lake Trout	34	1320	<0.1	-	100
Cobourg	Lake Trout	7	1153	<0.1	-	100
Port Hope	Rainbow Trout (*Salmo gairdneri*)	39	1752	<0.1	-	100
Port Credit	Lake Trout	50	803	<0.1	-	100
Credit River	Coho Salmon (*Oncorhynchus kisutch*)	50	3464	0.12 ± 0.01	<0.10-0.13	92.0
Niagara	Coho Salmon	49	1101	0.13 ± 0.01	<0.10-0.20	47.9
LAKE ERIE						
Long Point Bay	Northern Pike (*Esox lucius*)	14	2058	0.10 ± 0.00	<0.10-0.10	92.9
Erieau	Walleye (*Stizostedion vitreum*)	11	148	0.18 ± 0.01	<0.10-0.18	81.8
Western Basin	Walleye	44	948	0.13 ± 0.03	<0.10-0.16	95.5

a. Mean of samples with a lead concentration greater than or equal to the detection limit (0.10 µg/g).

sediments. The net effect was an inverse food chain accumulation. Blood lead concentrations in fish from Hamilton Bay were highest in carp and bullhead and least in sunfish, again suggesting that predators pick up lead more slowly than bottom grazers (41).

Tissue residues of lead are generally highest in bone, gill, and kidney with lesser amounts in muscle, liver, and remaining tissues (26,27,37,42). Bone lead represents detoxification since it is relatively inactive metabolically, but tissue lead may be active since it is associated with high molecular weight proteins (>55,000)(75). Kidney lead, however, is associated with nephrotoxicity and anemia. Low lead concentrations in brain and neural tissue are surprising in light of lead neurotoxicity (see section on toxicity to fish). This may reflect either high neural sensitivity to lead or difficulties in analyzing small samples. Low concentrations in muscle suggest that "edible portion" or "whole body" analyses (mostly muscle) may provide misleadingly low estimates of lead contamination.

The amount of lead taken up and the resultant concentration factors are dependent upon the fish species, water quality, and waterborne lead concentrations. Log-log plots of tissue lead versus waterborne lead show that concentration factors decrease as waterborne lead concentrations increase, suggesting either accelerated depuration or a saturation of uptake mechanisms. In experiments with brook and rainbow trout in water from Lake Superior and Lake Ontario respectively, lead in all tissues increased about 6 - 7 times for each 10-fold increase in waterborne lead (37,42); however, lead accumulation rates by various rainbow trout tissues studied by Goettl and Davies (27) were much higher (16 - 154 times) than these values. Whole body concentration factors on a wet-weight basis are generally <1,000 (37).

Blood lead equilibrates with waterborne lead very quickly (<1 week), but other tissues require at least 2 - 4 weeks, and some tissues may require up to 20 weeks (27,39,42). However, on a whole body basis, the bulk of lead (>90%) is taken up in the first 4 weeks. In contrast, depuration is very slow. Blood lead of rainbow trout has a half-life of at least 4 weeks (39), but this may increase with lead exposure time (47). Half-lives in other tissues are not accurately determined, but lead lost from some tissues may be transferred to others instead of being excreted (91).

Organolead compounds have been identified in both freshwater and marine fish (14,85). Chau *et al.* (15) demonstrated significant tetramethyllead residues in rainbow trout exposed to a constant concentration of the chemical in the water, and tissue concentrations were ten times higher than in trout exposed to inorganic lead (35). Fish sampled from various rivers and bays around Lake Ontario and from Lake St. Clair all contained measurable quantities of various tetraalkyllead compounds as well as "volatile" and "hexane extractable" lead (14). Concentrations were generally in the low µg/kg range. Maddock and Taylor (55) also found uptake by marine fish and invertebrates of alkyllead compounds during laboratory exposures, but concentration factors were 650X or less, which is typical of inorganic lead. Depuration was also observed, with muscle and liver half-lives in the range of 40 - 60 days.

TABLE 9

TOTAL WHOLE BODY LEAD CONCENTRATIONS OF YELLOW PERCH (*PERCA FLAVESCENS*) SAMPLED FROM LAKES ONTARIO AND ERIE IN 1978

LOCATION	NUMBER (N)	MEAN WEIGHT (g)	MEAN CONCENTRATION[a] (µg/g WET WEIGHT ± STANDARD DEVIATION)	RANGE	% N < DETECTION LIMIT
LAKE ONTARIO					
Eastern Basin	50	116	0.19 ± 0.01	<0.10 - 0.61	16
Toronto	28	35	0.40 ± 0.06	0.10 - 1.0	0
LAKE ERIE					
Long Point Bay	41	157	0.16 ± 0.01	<0.10 - 0.38	61
Erieau	36	200	0.20 ± 0.02	<0.10 - 0.40	33
Wheatley	44	114	0.16 ± 0.01	<0.10 - 0.28	23
Western Basin	29	86	0.15 ± 0.01	<0.10 - 0.28	28

a. Mean of samples with a lead concentration greater than or equal to the detection limit (0.10 µg/g).

TABLE 10

TOTAL WHOLE BODY LEAD CONCENTRATIONS OF RAINBOW SMELT (*OSMERUS MORDAX*) SAMPLED FROM LAKES ONTARIO AND ERIE IN 1978

LOCATION	NUMBER[a] (N)	MEAN WEIGHT (g)	MEAN CONCENTRATION[b] (µg/g WET WEIGHT ± STANDARD DEVIATION)	RANGE	% N < DETECTION LIMIT
LAKE ONTARIO					
Eastern Basin	10	14.9	0.12 ± 0.01	<0.10 - 0.12	80
Point Traverse	10	40.0	0.12 ± 0.01	<0.10 - 0.17	50
Cobourg	10	29.9	0.22 ± 0.02	<0.10 - 0.39	30
Port Credit	9	30.2	0.16 ± 0.02	0.11 - 0.28	0
Niagara	10	30.6	0.09 ± 0.01	<0.10 - 0.17	40
LAKE ERIE					
Long Point Bay	11	20.9	0.11 ± 0.01	<0.10 - 0.12	73
Erieau	10	30.7	0.12 ± 0.01	<0.10 - 0.16	60
Wheatley	13	33.6	0.13 ± 0.01	<0.10 - 0.19	39
Western Basin	10	35.7	0.13 ± 0.01	<0.10 - 0.21	60

a. Each sample consisted of a composite of five fish.

b. Mean of samples with a lead concentration greater than or equal to the detection limit (0.10 µg/g).

TOXICITY

ALGAE

Concentrations of lead toxic to algae are extremely variable, ranging from 10 µg/L (49) to more than 1,000 mg/L (77). This wide range is caused by temperature, growth medium composition, forms of lead tested, complexing capacity of the water, interaction between lead and other metals, and algal species sensitivity (Table 11). In general, lead toxicity increases with temperature due, perhaps, to increases in metal solubility, cell metabolism, or membrane permeability to the metal.

Composition of the test medium is also very important. Growth of *Ankistrodesmus falcatus*, a green alga common to the Great Lakes, was reduced 50% by 2 mg/L lead in a chemically defined medium (CHU-10), but only 10 µg/L was required for the same effect when the medium was Lake Ontario water (105). Cell growth rate of *Chlorella pyrenoidosa* was unaffected by 10 mg/L lead, but when the nutrients were diluted a thousand fold, 0.1 mg/L lead caused a 63% inhibition (31). Lead toxicity to *Chlamydomonas reinhardtii* was also reduced by phosphate additions to the medium (83). As these data suggest, the higher the lead complexing capacity of the medium, the lower the lead toxicity since lead is made less available. When lead (500 µg/L) was added to water from a variety of inland lakes with different measured complexing capacities, more algal growth was observed in lake waters with higher complexing capacity (13).

The interactions of several metals affect toxicity. For example, in one experiment, 25 µg/L lead, the 1978 Agreement objective (96), was not toxic to several species of freshwater algae when tested by itself, but the presence of other metals, also at nontoxic levels, caused growth inhibition in several species of freshwater algae (104) (see also section on invertebrates).

Alkylated leads are more toxic than non-alkylated ones. Triethyl, tributyl, and trimethyllead were more toxic to a green alga, *Scenedesmus quadricauda*, than were lead acetate, bromide, nitrate, and chloride. Volatile methylated lead (tetramethyllead) was twice as toxic as nonvolatile methylated lead and twenty times as lead nitrate (84,103).

Finally, the sensitivity of different algal species to lead effects should also be considered, since within one experiment, the most resistant species required 37 times more lead for growth inhibition than the most sensitive (Table 11). The most sensitive species of Great Lakes algae have not yet been identified in a systematic fashion.

INVERTEBRATES

Biesinger and Christensen (3) demonstrated a 50% reduction in reproduction of *Daphnia magna* after 3 weeks exposure to 100 µg/L lead and a 16% reduction at 30 µg/L (water hardness = 45 mg/L, alkalinity = 42 mg/L, T = 18°C). Reproductive impairment as used by Biesinger and Christensen means percentage decrease in young produced relative to controls and probably includes mortality, reduction in growth rate, and true inhibition of reproduction. Borgmann *et al.* (6) demonstrated a significant increase in chronic mortality

TABLE 11

EXAMPLES OF FACTORS AFFECTING LEAD TOXICITY TO ALGAE

FACTOR	ORGANISMS		LEAD CONCENTRATION CAUSING 50% INHIBITION	REFERENCE
Temperature	*Ankistrodesmus falcatus*		20°C 1-2 mg/L 9°C >10 mg/L 4°C <10 mg/L	107
Medium	*Ankistrodesmus falcatus*		CHU-10 medium 2 mg/L	105
			Lake Ontario water 10 μg/L	49
Forms of Lead	*Scenedesmus quadricauda*		$Pb(NO_3)_2$ 5 mg/L $(CH_3)_3PbAc$ 1.5 mg/L $(CH_3)_4Pb$ <0.5 mg/L	103
Complexation	*Scenedesmus quadricauda*		Lake water with <0.75 μmole/L complexing capacity 0.5 mg/L	13
Algal species variation	*Anabaena sp.*		15-18 mg/L	56
	Cosmarium botrytis		5 mg/L	
	Navicula pelliculosa		15-18 mg/L	
	Chlamydomonas reinhardii		15-18 mg/L	
	Microspora sp.	TIC[a]	1- 2 mg/L	102
	Mougeotia sp.	TIC	3-21 mg/L	
	Ulothrix sp.	TIC	4- 9 mg/L	
	Gongrosira sp.	TIC	14 mg/L	
	Stigeoclonium tenue	TIC	18 mg/L	
	Sporotetras pyriformis	TIC	35 mg/L	
	Cladophora glomerata	TIC	37 mg/L	

[a] TIC = Tolerance index concentration: the average of concentrations causing several adverse effects.

at 19 µg Pb/L, but not at 12 µg/L, of the snail *Lymnaea palustris* (hardness = 139 mg/L, alkalinity = 88 mg/L, T = 21°C). Growth was not affected by lead. At 48 µg Pb/L snail mortality equalled growth rates resulting in no net increase in population biomass. Spehar *et al.* (86) observed 60% mortality of amphipods *Gammarus pseudolimnaeus* at 32 µg Pb/L after 28 days exposure, with a calculated LC_{50} of 28.4 µg/L (hardness = 44 - 48 mg/L, alkalinity = 40 - 44 mg/L, T = 15°C). Mortality was continuous over time with no incipient LC_{50} observable after 28 days. Spehar *et al.*, however, found no significant mortality of stoneflies, caddisflies, or snails (*Physa integra*) after 28 days exposure to up to 565 µg Pb/L (possibly due to the high turbidity of the incoming water during these tests). Wilson (108) observed that the behavioural phototactic response of copepods (*Cyclops bicuspidatus thomasi*) was reduced by 11.5% from the control response at 3.2 µg Pb/L, 36% at 10 µg/L, and 48% at 32 µg/L in Lake Ontario water at 15°C. No response difference was observed at 1 µg Pb/L. With the exception of Biesinger and Christensen's experiments, all the above data were collected using flow-through bioassay systems.

Borgmann *et al.* (7), using a static system, observed a 20% reduction in the rate of biomass production of copepods in water from the Burlington Canal at anywhere from 240 µg Pb/L to over 10,000 µg/L depending on the time of year. In these natural waters, lead toxicity may have been reduced and variable due to high concentrations of particulate matter in the water (7) (note also suggestion by Spehar *et al.* (86) that low lead toxicity to some species may have been related to high turbidity during tests). Brown (9), also using static tests, showed that 100 µg/L lead inhibited the growth of *Asellus meridianus* (isopod) and that animals from lead-polluted areas were more tolerant to lead than those from clean areas.

It is important to note that Borgmann *et al.* (6), Spehar *et al.* (86), and Wilson (108) all observed no incipient level. Lead toxicity increased continuously with exposure time. Furthermore, Borgmann (8) has observed that metal toxicities are additive or slightly synergistic in their effect on copepod production rates so that the presence of other metals at concentrations near the water quality objective concentrations may influence the response to lead. The problem of metal mixtures is more thoroughly reviewed in a trial objective for metals mixtures in Chapter 5 of this report.

FISH

Acute lethality of lead to fish might be expected at concentrations above 1,000 µg/L in Great Lakes waters (105). Lethality may be expressed in terms of the median lethal concentration in water, or LC_{50} and this is time dependent. The 48-hour LC_{50} for rainbow trout (*Salmo gairdneri*) in water similar to that of Lake Superior was 1,000 µg/L (11) while the 96-hour LC_{50} for rainbow trout in Lake Ontario was 6,500 µg/L (49). At concentrations above 1,000 µg/L in Lake Ontario water, a visible precipitate of lead carbonate is observed. Toxicity of the remaining unprecipitated lead is believed to be a function of the amount of "free lead" (theoretically, lead ions as measured by pulse polarography) rather than of the amount of lead complexed by anions, such as carbonate, hydroxyl, and phosphate (21). Since "free" lead may include a variety of weak lead complexes, pulse polarography may not measure "free" lead consistently across different laboratories. It is estimated that lead concentrations above 1,000 µg/L in Lake Ontario water diminish to less than 1,000 µg/L within 24 hours due to the carbonate complexation and lead precipitation noted above (49). High concentrations of lead titrate the inorganic complexing capacity. When the capacity is completely utilized, residual uncomplexed lead is available for toxicity. However, mixing of this water with fresh water provides more complexing capacity so that lead continues to precipitate (49). Consequently, if efficient mixing occurs, it is unlikely that acutely lethal concentrations will be maintained long enough to kill fish in Lake Ontario. In Lakes Superior, Michigan, and Huron, the carbonate concentrations are much lower, and lead toxicity is greater in these soft waters. Therefore, lead would be maintained at concentrations greater than 1,000 µg/L for significant periods of time and lethality may be expected in these lakes. Lake Erie is close to Lake Ontario in carbonate concentrations, and it is doubtful that acute lethality would occur. Lingering or chronic mortality of larval fish due to sustained exposure occurs at concentrations as low as 84 µg/L (80). It is possible that these lower concentrations could be maintained for significant periods of time in Great Lakes water since precipitates are not observed. Experimentally, lead availability to trout is directly proportional to waterborne lead concentrations up to 1,000 µg/L in filtered Lake Ontario water (38).

Significant sublethal effects of lead on fish include haemotological, neurological, teratogenic, growth, and histological responses that occur at concentrations as low as 13, 8, 119, 22 - 65, and >1,000 µg/L waterborne lead, respectively (Table 12). Other enzymatic and physiological changes have been observed at similar lead concentrations. All of the above symptoms increase with increasing exposure time and concentration (e.g. Figure 4).

Lead toxicity to fish may be affected by a variety of physical, chemical, and biological factors that change the availability of lead to fish, the ability of the fish to take up lead, and the response of fish to lead taken up (35).

SOURCE AND FORM OF LEAD

Inorganic lead is very poorly taken up by fish from their diet and does not appear to contribute significantly to lead toxicity or lead levels in fish (37). This agrees with the observations of Leland and McNurney (51), noted in the section on lead levels in fish, and to the observation that in humans only 10% of dietary lead is absorbed. As a result of high accumulation rates, tetramethyllead could be ten times more toxic than lead nitrate to freshwater fish (35). A study of alkyllead toxicity to marine fish indicated that toxicity increased as the number of alkyl side chains increased (55). The 96-hour LC_{50}'s for tetramethyl and tetraethyllead were 50 and 230 µg/L, or about 3,600 and 700 times more toxic, respectively, than inorganic lead compounds. Since the exposures were in salt water, which tends to precipitate inorganic lead, the ratios of toxicity may be considerably less. The 48-hour LC_{50}'s for larvae of the marine fish *Morone labrax* were 100 and 65 µg/L for tetraethyl and tetramethyllead, respectively (57).

WATER QUALITY

Increased water hardness (or alkalinity) reduced chronic lead toxicity to fish (Figure 4) through carbonate complexation (described earlier) and through

TABLE 12

SUBLETHAL EFFECTS OF LEAD ON FISH

CLASS	SPECIFIC RESPONSES	MINIMUM EFFECTIVE LEAD CONCENTRATION (μg/L)	REFERENCES
Hematological	Inhibition of hemoglobin synthesis, red blood cell stippling, premature mortality of red blood cells (Haemolytic anemia), compensatory erythropoiesis.	13	17,20,22,34,37, 39,47,72,87
Neurological	Blackening of the caudal area, lordosis and scoliosis, neural degeneration in spinal cord, learning impairment.	8	21,36,37,40,42, 100,109
Teratogenesis	Lordosis and scoliosis.	119	42,69
Growth Impairment		22 - 65	16,40,80
Histopathology	Heart, intestine, pyloric caeca, liver, kidney, gonads, chemoreceptors.	>1000	18,19,29,30,79, 93
Miscellaneous	Enzyme inhibition in liver, intestinal tract, kidneys, ovaries, and spleen; increased skin mucus fluidity; increased plasma sodium and chloride.	various	17,47,60,61,78, 79,92

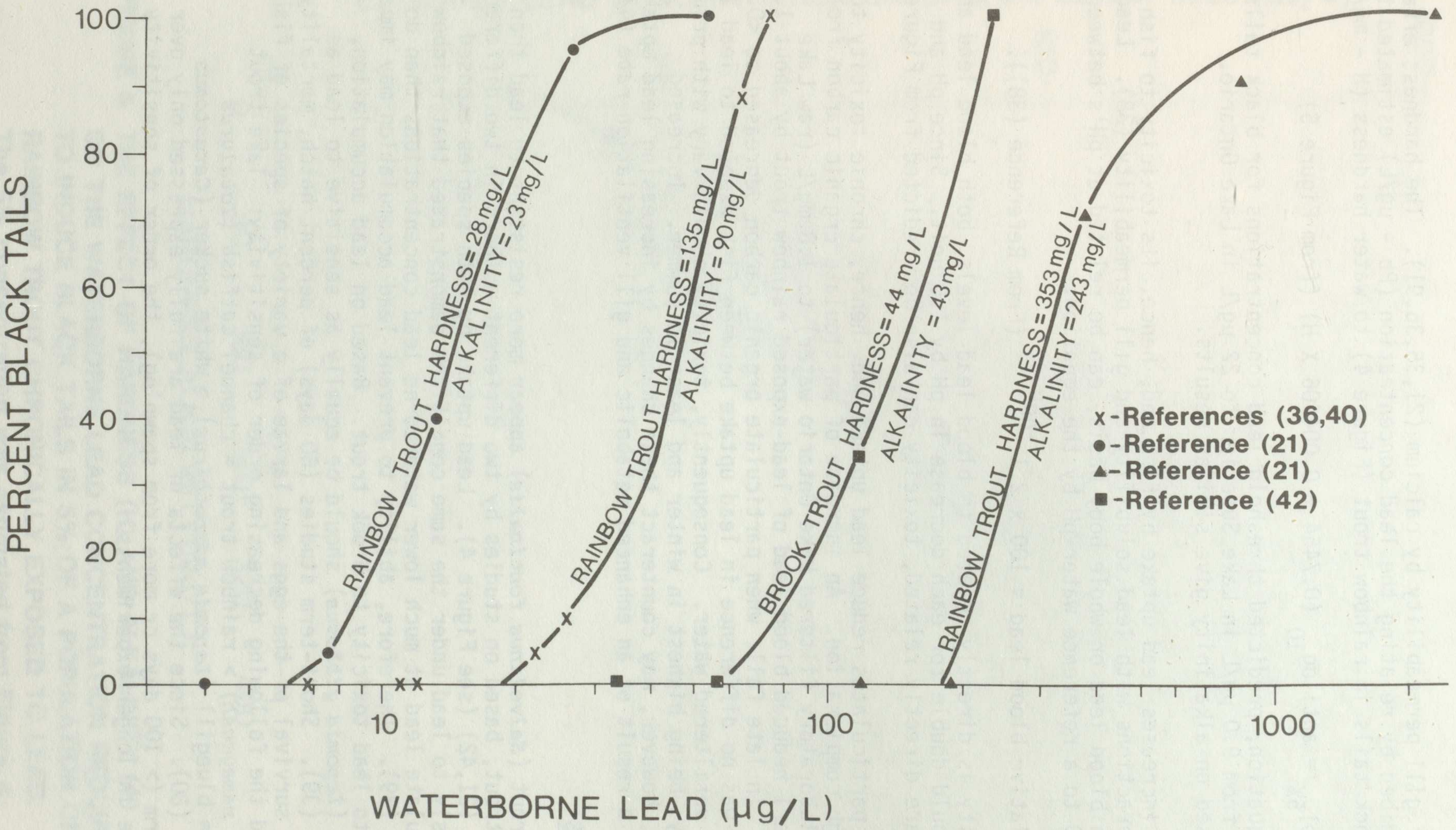


FIGURE 4 THE EFFECT OF CHRONIC EXPOSURE TO WATERBORNE LEAD ON THE INCIDENCE OF BLACK TAILS, A SYMPTOM OF LEAD NEUROTOXICITY, IN RAINBOW TROUT AND BROOK TROUT EXPOSED TO LEAD IN WATERS OF DIFFERENT HARDNESS AND ALKALINITY.

reduction of gill permeability by calcium (21,35,36,91). The hardness effect may be described by relating the lead concentration (Pb - µg/L) estimated to cause 5% black tails in rainbow trout (Figure 4) to water hardness (H - mg/L):

$$[Pb]_{5\%} = \text{antilog}_{10}\ (0.7454 + 0.004406 \times H) \quad \text{(from Figure 5)}$$

From this equation, predicted threshold lead concentrations for black tails in trout range from 9.0 µg/L in Lake Superior to 22 µg/L in Lake Ontario. Analyses based on alkalinity give similar results.

Acidity increases lead uptake by fish and, hence, its toxicity to fish, through interactions with lead solubility and gill permeability (38). Lead uptake, on a blood lead or whole body basis, can be related at pH's between 6.0 and 10.0 to a reference water pH by the equation:

$$\text{Relative blood lead} = 100 \times 2.1^{-\Delta pH} \quad \text{(From Reference (38))}.$$

Since toxicity is directly related to blood lead levels, both blood lead and toxicity should double for each decrease in pH by 1.0 unit. Since pH and alkalinity are directly related, toxicity can also be predicted from Figure 5.

Organic particulates reduce lead uptake and, hence, chronic toxicity to fish, through complexation. An increase of particulate organic carbon from <0.2 mg/L (laboratory filtered Lake Ontario water) to 1.8 mg/L (raw Lake Ontario water) reduced blood lead of lead-exposed rainbow trout by about 1.8 times (35). In late fall, when particulate organic carbon decreased to <0.2 mg/L, there was no difference in lead uptake between fish exposed to lead in filtered or unfiltered water. Consequently, toxicity should vary with primary productivity, being highest in winter and least in summer. Increased temperature, however, may counteract these changes by increasing lead uptake, probably as a result of an enhanced metabolic and gill ventilation rate (41).

FISH SPECIES

Brook trout (*Salvelinus fontinalis*) appear more resistant to lead than do rainbow trout, based on studies by two different authors in two different water types (21,42) (see Figure 4). Lead uptake by both species exposed simultaneously to lead under the same conditions demonstrated that rainbow trout accumulate lead at much lower waterborne lead concentrations than do brook trout (39). Therefore, ability to prevent lead accumulation may impart resistance to lead toxicity to brook trout. Based on lead accumulation, pumpkinseed (*Lepomis gibbosus*) should be equally as sensitive to lead as brook trout (39). Short-term studies (60 days) of percent hatch, mortality, growth, and survival of the eggs and larvae of a variety of species of fish demonstrated the following decreasing order of sensitivity: lake trout (*Salvelinus namaycush*) > rainbow trout = channel catfish (*Ictalurus punctatus*) = bluegill (*Lepomis macrochirus*) > white sucker (*Catastomus commersoni*) (80). Since the effects of lead are fully expressed only over the long term (> 100 days or more from spawning), the order of sensitivity might change in longer experiments.

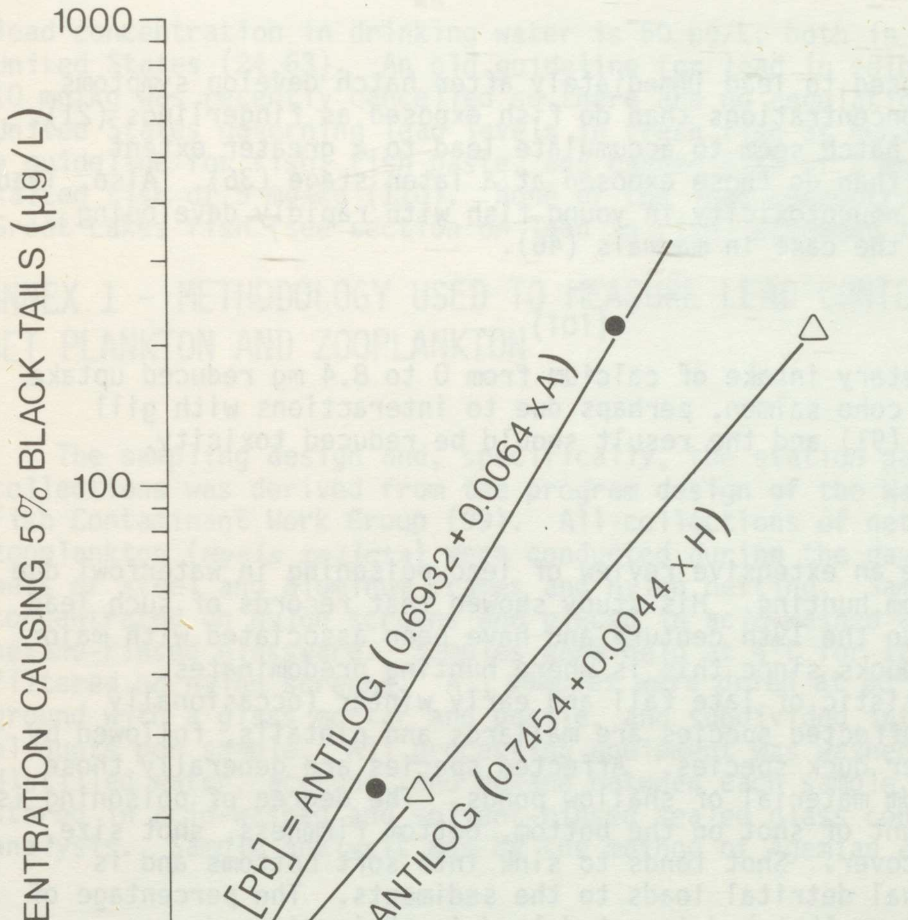


FIGURE 5 THE EFFECT OF HARDNESS (H) AND ALKALINITY (A) ON THE WATERBORNE LEAD CONCENTRATION REQUIRED TO INDUCE BLACK TAILS IN 5% OF A POPULATION OF RAINBOW TROUT CHRONICALLY EXPOSED TO LEAD. The 5% concentration was estimated from Figure 4.

FISH AGE

Rainbow trout exposed to lead immediately after hatch develop symptoms faster and at lower concentrations than do fish exposed as fingerlings (21). The fish exposed from hatch seem to accumulate lead to a greater extent throughout their life than do those exposed at a later stage (36). Also, lead may have its greatest neurotoxicity in young fish with rapidly developing nervous systems as is the case in mammals (46).

DIET

An increase in dietary intake of calcium from 0 to 8.4 mg reduced uptake of waterborne lead by coho salmon, perhaps due to interactions with gill membrane permeability (91) and the result should be reduced toxicity.

WATERFOWL

Bellrose (2) wrote an extensive review of lead poisoning in waterfowl due to spent lead shot from hunting. His study showed that records of such lead poisoning dated back to the 19th century and have been associated with major flyways of migrating ducks since this is where hunting predominates. Poisoning is characteristic of late fall and early winter (occasionally spring) and the most affected species are mallards and pintails, followed by geese, swans, and other duck species. Affected species are generally those that consume the bottom material of shallow ponds. The degree of poisoning is a function of the amount of shot on the bottom, bottom firmness, shot size, water depth, and ice cover. Shot tends to sink into soft bottoms and is covered over with annual detrital loads to the sediments. The percentage of wildfowl taken by hunters that had ingested lead in their gizzards was: Canada geese (< 1); blue and snow geese (< 3); buffleheads, green-winged teals, mergansers, wood ducks, shovelers, and gadwalls (<2); blue-winged teals, baldpates, and common goldeneyes (2 - 5); ruddy ducks, mallards, black ducks and pintails (5 - 10); and canvas backs, lesser scaups, redheads, and ring-necked ducks (> 10). Of the gizzards containing shot, 64.7% contained one pellet, 14.9% two pellets, and 7.4% more than six pellets. Ingested lead produced weakness and fatigue in wild mallards that reduced their ability to migrate and increased their susceptibility to hunting. Mortality of mallards increased by 9%, 23%, 36%, and 50% due to ingestion of 1, 2, 4, and 6 pellets per bird, respectively. It is estimated that one quarter of the wild mallards of North America in any year ingest lead shot and that 4% of those in the Mississippi Flyway die due to lead poisoning. Another 1% are poisoned, but are shot by hunters before dying. For all waterfowl species in North America, 2 - 3% annual mortality is estimated as a result of lead poisoning.

In the Great Lakes, lead shot poisoning of wildfowl will be characteristic of any marshy area open to hunting, but will be especially important in the major waterfowl habitats such as the marshes of Lake St. Clair and Long Point Bay (Lake Erie) (see section on lead in sediments).

HUMANS

Numerous extensive reviews exist on this subject (5,28,33,46,62,66) and the information need not be repeated here. The current maximum permissible lead concentration in drinking water is 50 µg/L, both in Canada and the United States (24,63). An old guideline for lead in edible marine products of 10 mg/kg was recently cancelled so there are no regulations in Canada or the United States governing lead levels in fresh fish as human food. England has a guideline for fish, fish paste, and canned fish of 2 mg/kg and for fried and salted fish of 5 mg/kg (110). None of the lead concentrations measured in Great Lakes fish (see section on lead in fish) exceeded these guidelines.

ANNEX 1 - METHODOLOGY USED TO MEASURE LEAD CONTENT OF LAKE ONTARIO NET PLANKTON AND ZOOPLANKTON[101]

The sampling design and, specifically, the station pattern, for plankton collections was derived from the program design of the Water Quality Board's Fish Contaminant Work Group (99). All collections of net plankton (>153 µm) and zooplankton (*Mysis relicta*) were conducted during the day with collection nets of steel and aluminum frames and nylon netting. Samples were concentrated on nylon screens and placed in acid-washed and acetone-hexane-rinsed glassware. Samples were held at 4°C for 12 hours and then filtered on nylon screens. All samples were dried at 60°C for 24 hours, ground with a glass mortar and pestle, and subdivided into a minimum of five aliquots per sample. All processing equipment was washed and rinsed in distilled water, acetone, and hexane between each sample. All samples were stored in acid-washed and solvent-rinsed sealed glass containers until analysis. Sample analysis was by the method of Agemian *et al.* (1).

ANNEX II - METHODOLOGY USED TO MEASURE LEAD CONTENT OF WHOLE LAKE ONTARIO FISH[101]

The sampling design for the fish collections was that of the Water Quality Board's Fish Contaminant Work Group (99). After collection, individual whole fish were wrapped in acetone-rinsed aluminum foil and stored at -25°C until homogenization. Individual fish were weighed, measured, and sexed and homogenized a minimum of five times with a commercial meat grinder. The whole fish tissue was further homogenized for five minutes with a large stainless steel food blender. All equipment and processing instruments were washed between samples and rinsed in distilled water, acetone, and hexane. A 50 g aliquot of the homogenate was stored in an acid-washed and acetone- and hexane-rinsed glass container at -25°C until analysis by the method of Agemian *et al.* (1).

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4 PENDING OBJECTIVES

Six specific objectives are pending at various points in the review and implementation process: dissolved oxygen, chlorine, silver, cyanide, temperature, and nutrients. The status of each is presented below.

DISSOLVED OXYGEN

The dissolved oxygen objective in the 1972 Agreement was:

> *In the Connecting Channels and in the upper waters of the Lakes, the dissolved oxygen level should be not less than 6.0 milligrams per litre at any time; in hypolimnetic waters, it should not be less than necessary for the support of fishlife, particularly cold water species.*

The 1976 objectives report had proposed an objective which would account for, among other factors, the temperature of the water:

> *Dissolved oxygen should not be less than the values specified below for the protection of aquatic life:*

	Oxygen Concentration	
Water Temperature °C	*Percent Saturation*	*mg/litre*
0	*69*	*10.0*
5	*70*	*9.0*
10	*70*	*7.9*
15	*71*	*7.2*
20	*79*	*7.2*
25	*87*	*7.2*

The Water Quality Board did not consider this proposal to be the best objective for the Great Lakes and, consequently, in 1978 asked the Research Advisory Board (now the Science Advisory Board) to further investigate the dissolved oxygen requirements for the Great Lakes system. A review committee was struck which, in January 1979 proposed to the Science Advisory Board the following revised objective:

> *In connecting channels and in all the waters of the Great Lakes, the dissolved oxygen level should not be less than an average of 6.5 mg/litre nor less than 5.5 mg/litre at any time over 24 hours and across a temperature scale of 0°C - 25°C.*

In June 1979, AEOC commented on this proposed revised objective and recommended:

> *6.0 mg/L applicable at any time and at any place within the waters of the Great Lakes.*

This was the same as the 1972 Agreement objective, except that the hypolimnetic waters were now included.

In the meantime, on November 22, 1978, the second Agreement was signed. The dissolved oxygen objective was unchanged from that contained in the 1972 Agreement.

The Water Quality Board, on July 15, 1980, agreed to recommend to the IJC that, since the proposed revised objective is similar to the 1978 Agreement objective, no change is warranted. AEOC notes, however, that this would not include a specific numerical value for hypolimnetic waters. AEOC still supports its recommendation of June 1979 but plans no further action on this proposed objective.

CHLORINE

The 1974 objectives report recommended the following chlorine objective:

> *Total residual chlorine, as measured by the amperometric (or equivalent) method, should not exceed:*
>
> 1. *0.002 mg/L in order to protect trout, salmon, and sensitive fish food organisms.*
> 2. *0.01 mg/L in order to protect warmwater fish and most fish food organisms.*

The Water Quality Board established a Chlorine Objective Task Force to report on the technical capabilities of monitoring such low concentrations and to investigate methods for achieving the proposed objective. That Task Force reported in 1976 that:

1. Disinfection of sewage treatment plant discharges was required to protect public health.
2. It would be technically impossible to achieve the proposed objective at all times and in all locations.
3. The costs of implementing the proposed objective could be very high.
4. Several technical issues needed further study.

A revised objective was submitted in the 1976 objectives report:

> *Total residual chlorine, as measured by the amperometric (or equivalent) method, should not exceed 0.002 mg/L in order to protect aquatic life.*

As with other objectives, this objective is based solely on scientifically defensible considerations.

The Water Quality Board, recognizing the need to consider the social and economic implications of achieving proposed ambient objectives, established a second Chlorine Objective Task Force. This group was also charged with considering alternative technologies and strategies to the use of chlorine for disinfection of sewage treatment plant effluents and to investigate the extent to which chlorine disinfection contributes to chlorinated organic chemicals in the Great Lakes. Further discussion about the objectives and the social and economic findings of this Task Force is given in Chapter 1 of this report and in the April 1980 Task Force report to the Water Quality Board. Discussion here is limited to the implications of their findings for the scientific basis of the proposed chlorine objective.

The Chlorine Objective Task Force discussed protection of public health from bacterial contamination in raw water supplies and in recreational waters. AEOC notes that the microbiology values quoted (page 48) in the 1980 Chlorine Objective Task Force report are from a rough draft of a proposed revised microbiology objective and were not included in the final draft recommended to the Science Advisory Board.

The Chlorine Objective Task Force also addressed protection of aquatic life, especially from chlorine toxicity. Their report noted that there is little, if any, evidence of residual chlorine problems in the Great Lakes; therefore, aquatic life is not threatened under present or proposed chlorination practices. The cost of achieving the proposed objective is related to the size of the limited use zone which would be associated with a discharge, but the inference is that the size of such zones, if any, would not affect aquatic life in the lake.

AEOC is concerned about the Task Force's inference that, if an objective is agreed to, then the stepwise use of intermediate sub-objectives is a viable approach to achieving the objective (pages 17-18). AEOC feels that this approach would be costly for municipalities and industries to achieve, since it implies additional installations periodically. Such an approach would be self-defeating.

From scientific considerations, AEOC could perceive no basis in the report of the Chlorine Objective Task Force which would indicate any need to change the proposed chlorine objective. Further, the Task Force made no conclusions or recommendations about altering the proposed objective. AEOC therefore recommends the adoption of the chlorine objective as presented in the 1976 report.

The proposed chlorine objective was also the subject of a review, as a result of the July 1978 public hearing of the IJC on water quality objectives. This is discussed in the next section.

ORPHAN OBJECTIVES

The 1975 objectives report had proposed specific objectives for cyanide and temperature, and the 1976 objectives report had a proposed objective for silver. These proposed objectives are:

CYANIDE

Concentrations of free cyanide in unfiltered water samples should not exceed 5 μg/L for the protection of aquatic life.

SILVER

Concentrations of total silver in an unfiltered water sample should not exceed 0.1 μg/L to protect aquatic life.

TEMPERATURE

1. *Thermal additions to receiving waters or a designated segment thereof should be such that thermal stratification and subsequent turnover dates are not altered from those existing prior to addition of heat from artificial origin.*

2. *Maximum Weekly Average Temperature*

   This is the mathematical mean of multiple, equally spaced daily temperatures.

   A. *For Growth*

   The maximum weekly average temperature (MWAT) in the zone inhabited by the species at that time should not exceed one-third of the range between the optimum temperature (To) and the ultimate upper incipient lethal temperature (Tu) of the species, in order to maintain growth of aquatic organisms at levels necessary for sustaining actively growing and reproducing populations. Thus,

$$MWAT = To + \frac{Tu - To}{3}$$

   The optimum temperature is assumed to be for growth but other physiological optima may be used in the absence of growth data. The MWAT must be applied with adequate understanding of the normal seasonal distribution of the important species.

   B. *For Reproduction*

   The MWAT for reproduction should not exceed those limits for normal spawning; in addition these objectives must protect gonad growth and gamete maturation, spawning migrations, spawning itself timing and synchrony with cyclic food sources, and normal patterns of gradual temperature changes throughout the year. The protection of reproductive activity must take into account normal months during which these processes occur in specific water bodies for which objectives are being developed.

   C. *For Winter Survival (applicable at any place inhabitable by fish)*

The MWAT for fish survival during winter should not exceed the acclimation, or plume, temperature (minus a 2.0 C° safety factor) that raises the lower lethal threshold temperature above the normal ambient water temperature for that season. This temperature limit will apply in any area to which the fish have access and would include areas such as unscreened discharge channels. This objective is necessary to eliminate fish kills caused by rapid changes in temperature due to plant shutdown or movement of fish from a heated plume to ambient temperature.

3. <u>Short-term Exposure to Extreme Temperature</u>

A. <u>For the Season of Growth</u>

The temperature objective for (1) short-term exposure during the growth season is the 24-hr. median tolerance limit, minus 2 C°, at an acclimation temperature approximating the MWAT for that month; and (2) short-term exposure during the spawning season is the upper temperature for successful incubation and hatching. These exposures should not be too lengthy or frequent or the species could be adversely affected. The length of time in minutes (t) that 50 percent of a population will survive temperatures above the incipient lethal temperature (T in °C) can be calculated from the following regression equation:

$$\log(t) = a + b(T)$$

where a and b are intercept and slope, respectively, which are characteristics of each acclimation temperature for each species.

B. <u>For the Season of Reproduction</u>

The short-term maximum temperature for the season of reproduction should be based on the maximum incubation temperature for successful embryo survival. The maximum temperature for spawning is probably an acceptable alternative.

These proposed objectives, along with chlorine, were among those presented at a public hearing held in July 1978. At the hearing, a number of questions were raised. For this and other reasons, the Parties directed the IJC to further consider the four abovenamed proposed objectives.

The Science Advisory Board was asked to review the hearing transcript to determine if the testimony contained any scientific or technical information which might alter the proposed values. The Board passed the request on to AEOC. In a letter dated April 11, 1980, AEOC addressed each of the points raised about the scientific basis for silver, cyanide, and temperature. AEOC concluded that there is no real basis for altering the three proposed values.

Chlorine was the subject of a special study into the social and economic implications of meeting the proposed objective; details were presented earlier. In addition, AEOC found no material presented at the public hearing which would challenge the scientific basis for the proposed chlorine objective.

AEOC concludes that no scientific evidence has been presented since the objectives for silver, cyanide, temperature, and chlorine were first proposed, to warrant any further delay in their incorporation into the 1978 Agreement. AEOC therefore recommends that these objectives be adopted.

NUTRIENTS

In the July 1978 report of the Research Advisory Board, a nutrient objective was proposed for the Great Lakes. The objective and the supporting rationale are presented in the preceding chapter. Action by the Research Advisory Board was, however, deferred because a number of related activities were under way. These other activities included the renegotiation of the 1972 Agreement, and the specific work regarding phosphorus being conducted under the auspices of Task Group III. The latter's report provided the basis for Annex 3 in the 1978 Agreement, which proposes phosphorus loadings into each of the Great Lakes.

In effect, the proposed nutrient objective and its substantiating rationale were accepted by Task Group III and utilized in its deliberations. Similarly, the Phosphorus Management Strategies Task Force, which was constituted by the Research Advisory Board in the spring of 1978 to investigate alternative strategies for managing phosphorus inputs to the Great Lakes, also accepted the proposed nutrient objective. The report of the Phosphorus Management Strategies Task Force was published in July 1980.

AEOC concludes that the proposed nutrient objective and its rationale are sound, and that the scientific basis for the objective is unchanged since it was first proposed in 1978. Therefore, the proposed objective should be adopted as written.

5

FUTURE DIRECTIONS

DIRECTIONS AND ACTIVITIES

AEOC is considering future directions for the development of objectives, recognizing that objectives need not be developed for every substance. Such consideration is in addition to present ongoing development of both specific and ecosystem objectives (lake trout as an emergent property of the ecosystem, mercury, and pathogenic organisms). The guidelines for selection of substances as candidates for development of new specific objectives were presented in Chapter 2.

Another approach to be considered is the development of "collective objectives." The 1978 Agreement lists the following collective objectives:

1. Unspecified persistent toxic substances
2. Other non-persistent pesticides
3. Unspecified non-persistent toxic substances and complex effluents.

Such objectives can be too general, and development of specific numerical objectives may be possible as more scientific information becomes available. AEOC is also considering effluent objectives, objectives by compound class, and procedural objectives for complex mixtures (e.g. bioassays).

A difficult problem is the designation of limited use zones. A mixing zone, or limited use zone, as it is called in the 1978 Agreement, is an area where one or more of the Agreement objectives are not met, i.e. certain uses are not protected. The 1978 Agreement requires that their "size shall be minimized to the greatest possible degree." However, the usefulness of an objective, either as a direct or an indirect management tool, is limited by the lack of any real definition of, or means of applying a mixing zone or limited use zone in the 1978 Agreement.

CANDIDATES FOR OBJECTIVES

PRESENT OBJECTIVES AND DEFERRED SUBSTANCES

Preliminary review of the scientific literature for the present specific objectives and deferred substances (see Chapter 2) indicates a need to re-examine the following thirteen substances:

AMMONIA

The objective for un-ionized NH_3 is currently based on the most sensitive use only and does not take into consideration the modifying effects of water quality.

ASBESTOS

Recently published data indicate that asbestos fibres ingested with drinking water penetrate the human digestive tract lining and enter the bloodstream. These data justify a fresh look at the potential hazards of known sources of asbestos pollution on components of the Great Lakes Ecosystem.

CHROMIUM

The existing objective of 50 μg/L is based on protection of raw water for public water supplies. Literature published since 1975 tends to support this objective, except for one publication on chromium toxicity to *Daphnia magna*, suggesting an objective of 10 μg/L or less. The literature on chromium should be thoroughly reviewed to determine whether a revision of the objective is warranted.

COPPER

The existing objective of 5 μg/L is based on the protection of aquatic biota. Publications since 1975 on copper toxicity to aquatic biota support this objective and may provide a basis for a unique objective for each of the Great Lakes, based on the modifying effects of water quality.

DIAZINON

Concentrations below the objective are noted as having significant effects on aquatic invertebrates.

LINDANE

The objective will be re-evaluated to consider current information on carcinogenicity.

MERCURY

An attempt is being made to develop objectives for mercury which specifically address more aspects of the ecosystem than the aquatic effects considered in the present objective. This activity is similar to that recently completed for lead (Chapter 3).

MIREX/PHOTOMIREX

The present objective will be re-evaluated on the basis of lower state-of-the-art detection limits, and current long-term chronic toxicity studies on photomirex.

POLYCHLORINATED BIPHENYLS

The present objective will be re-evaluated on the basis of current information on the specific toxicity and the mutagenicity of the higher isomers, relative to previous information on commercial PCB mixtures.

POLYNUCLEAR AROMATIC HYDROCARBONS

PAH's are present in fuel oils and crude oils, and result from the combustion of fossil fuels. Studies on acute and chronic toxicity and on mutagenicity will be evaluated.

SELENIUM

The present objective for selenium, 10 µg/L, is based on protection of raw water for public water supplies. Studies published since 1975 demonstrate chronic toxicity of waterborne selenium at concentrations greater than or equal to 50 µg/L, and of dietary selenium at concentrations between 3 and 13 µg/g wet weight. In addition, field studies show accumulation in sediments of waterborne selenium near power plant effluents, and subsequent kills of fish feeding on or around these sediments. The uptake and depuration kinetics of selenium in fish suggest that simultaneous exposures to dietary and waterborne concentrations, considered non-toxic by themselves, may elicit a toxic response. The evaluation of this possibility is planned. The present objective will be reviewed and, if necessary, revised.

VANADIUM

Several current reports on vanadium toxicity to aquatic biota will be reviewed to determine whether an objective can be formulated.

ZINC

The present objective for zinc, 30 µg/L, is based on protection of aquatic biota. Publications since 1975 indicate a greater breadth of knowledge and perhaps sufficient data to justify calculating a separate zinc objective for each of the Great Lakes. In addition, recent unpublished results demonstrate that 30 µg/L zinc is quite toxic to algae. When published, these results could provide the basis for a lower objective.

NEW CANDIDATES

The following substances are candidates for future new objectives because they have been noted in the Great Lakes Ecosystem and it is believed that they may be toxic:

1. Chlorinated alkanes
2. Chlorinated styrenes
3. Chlorinated dibenzofurans

Current data and studies on atmospheric emissions in the Great Lakes Ecosystem, environmental persistence, occurrence in Great Lakes biota, toxicity, and mutagenicity will be evaluated.

TENTATIVE MIXTURES OBJECTIVE

The following objective and rationale were developed as a first attempt at limiting the adverse effects of mixtures of contaminants. The mixtures considered were limited to the metals, due to the availability of data on sublethal effects of mixtures and to avoid excessive complexity. As the mechanism for dealing with mixtures is developed, more contaminants will be included.

There are two basic approaches to limiting mixture effects:

1. Procedural objectives based on experimental measurement of effects of real or defined mixtures
2. Calculated objectives that utilize existing toxicological data on contaminants tested singly.

The latter approach was chosen for this tentative objective because it is simpler and uses the large volume of existing toxicological data.

Reviewers of this objective are requested to send their comments and criticisms to AEOC to foster the development and refinement of a mixtures objective.

RECOMMENDATION

It is proposed that the following new objective be adopted for mixtures of metals in Great Lakes waters:

> *The sum of the ratios between each metal concentration (Mi) and its respective objective concentration (Oi) should not exceed 1.0, i.e.*

$$\Sigma \left[\frac{Mi}{Oi} \right] \leq 1.0$$

RATIONALE

Environmental pollution usually results in the presence of several metals simultaneously (10,14,20). Water Quality Agreement objectives, however, are based on studies with individual metals and do not protect aquatic organisms from the combined effects of mixtures.

Most of the available literature on metal mixtures suggests that *the toxicity of a mixture to aquatic biota is greater than that of any of the metals tested singly* (cumulative toxicity) (Table 1). Cumulative toxicity to algae has been observed with both binary mixtures (4,14) and mixtures of ten metals (22), to ciliates with both binary and tri-metal mixtures (11,15), and to invertebrates in both lethal (2,16) and sublethal experiments (3,7). Cumulative toxicity to fish of mixtures was demonstrated in studies of acute

TABLE 1

EFFECT OF VARIOUS METAL MIXTURES ON AQUATIC ORGANISMS

SPECIES	METALS TESTED	RESPONSE	REFERENCE
Algae			
Chlorella vulgaris & Haematococcus capensis	Cu & Ni	Cumulative toxicity to cell growth	14
Chlorella vulgaris	Cd & Se	Se reduces Cd toxicity	14
Amphidinium carteri, Thalassiosira pseudonona, & Skeletonema costatum	Cu & Zn	Cumulative toxicity to cell growth	4
Phaeodactylum tricornutum	Cu & Zn	Zn reduces Cu toxicity	4
Scenedesmus quadricauda	10 metals	All metals present simultaneously at water quality objectives level reduce primary productivity by 68 - 78%. At one tenth W.Q.O. levels, they reduce primary productivity by 21 - 40%.	22
Ciliates			
Cristigera spp	Hg, Pb & Zn	Cumulative toxicity to cell growth	11
Uronema marinum	-	Cumulative toxicity to cell growth	15
Crustaceans			
Nitocera spinipes (Copecod)	Cu & Hg	Cumulative toxicity 24-hr. lethal test	2
Marinogammarus marinus (Amphipod)	Cu & Hg	Cumulative toxicity - lethal tests	16
Artemia salina (Brine Shrimp)	Cu & Hg	Toxic unit concept overestimates time to 50% mortality by up to 35%	6
Acartia clausi (Copepod)	Cu & Hg	Toxic unit concept overestimates time to 50% mortality by up to 16%	6
Paratya tasmaniensis (Shrimp)	Cd & Zn	Toxic unit concept overestimates 96-hr. mortality by 10%	21
Tigriopus japonicus (Copepod)	Cu & Cd	Cumulative toxicity to growth and reproduction	7
Cyclops vernalis & C. bicuspidatus thomasi (Copepods)	Cu, Cd, Hg Zn, Pb & As	Cumulative toxicity to growth - toxic unit concept predicts toxicity of 5 metal mixtures reasonably well (error - 6%)	3
Fish			
Fundulus heteroclitus (Mummichog)	Cd, Cu & Zn	Cumulative toxicity - lethality after 96-hr. exposure	9
Salmo gairdneri (Rainbow Trout)	Cu, Zn & Ni	Toxic unit concept works well in predicting toxicity - 48-hr. lethal tests	5
Salmo salar (Atlantic Salmon)	Cu & Zn	Toxic unit concept works well for incipient lethal levels	20
Literature review on early lethal studies	-	Toxic unit concept works well for lethal thresholds	18
Carassius auratus (Goldfish)	Se & Hg	Se reduces toxicity of Hg	12
Cyprinus carpio (Carp)	Se & Hg	Cumulative toxicity to egg hatchability	13
Salmo gairdneri (Steelhead trout)	Cu & Zn	Cumulative toxicity during 60-day chronic exposures of alevins and fry	10
Pimephales promelas (Fathead minnow)	Cu, Cd & Zn	Toxic unit concept works at high (lethal) levels but not in chronic exposures. No single metal tests run simultaneously	8
Jordanella floridae (Flagfish)	Cd & Zn	Cumulative toxicity to reproduction observed but not statistically significant	17
Salmo salar (Atlantic Salmon)	Cu & Zn	Toxic unit concept works for sublethal avoidance response	19

toxicity (9); of subacute toxicity to eggs, alevins, and fry (10,13); and of chronic toxicity during the reproductive stage (17). A less common phenomenon in some mixtures, with some species, is a reduction in toxicity of one metal by the presence of another. For example, copper toxicity was reduced by zinc with one of four algal species tested (4), and cadmium toxicity to algae and mercury toxicity to goldfish (*Carassius auratus*) were reduced by selenium (12,14).

Several models have been used to predict the toxicity of mixtures. One technique is to add together the percent reduction in growth caused by each constituent in single toxicant tests (11,15). This technique will work only if toxicity is relatively low. Another procedure involves summing the toxicant-induced mortality rates or the toxicant-induced increases in the inverse of the growth rates observed during single toxicant exposures (3). Some authors have multiplied survival (as a fraction) in one toxicant by survival in the second to estimate survival in the mixture (e.g. response addition) (1). Also, toxicity of mixtures can be predicted from log probit plots if the slopes of these plots for individual toxicants are similar (e.g. concentration addition) (1). All such models however, require complete concentration-response curves for each toxicant singly in order to predict toxicity at various concentrations of the mixtures. Furthermore, these concentration-response curves will differ between species and between toxicants. The use of such models in water quality evaluation would require excessively complicated mathematical formulas which would vary from one organism to another. A much simpler approach is required for a metals mixture objective.

The toxic unit concept, used initially for lethal studies with fish and reviewed by Sprague (18), provides a useful basis for a mixtures objective. The concentration of a metal may be measured in toxic units, where one toxic unit is the concentration eliciting a defined response (e.g. 50% mortality). In mixtures, the defined response would be expected whenever the total concentration of all metals, each measured in toxic units, was equal to 1.0. Deviations of the observed response from the expected, using the toxic unit concept, have been called synergism or antagonism but the definitions of these terms depend on the type of model used by each author. Therefore the toxic unit concept should not be used indiscriminantly in attempts to measure synergism or antagonism (3).

The toxic unit concept overestimates somewhat (up to 10%) the lethal toxicity of cadmium-zinc mixtures to shrimp (*Paratya tasmaniensis*) (21) but underestimates (up to 35%) the lethality of copper-mercury mixtures to brine shrimp and copepods (6). However, most lethal studies with fish indicate that the concept works fairly well (5,8,20, review by 18). Sprague (18) expressed concern that toxic units might not predict lethality when concentrations of each component were <0.2 toxic units. However, he felt that toxic units might be usefully applied to sublethal responses at these low concentrations, although he had few sublethal data to investigate this possibility.

Some recent publications do, however, provide an indication of its utility at sublethal toxicant concentrations. Growth rates of zooplankton in mixtures of up to five metals can be predicted reasonably well with toxic units (3) as can growth rates of ciliates if the growth rate data of Parker (15) are analyzed in the same way as the data of Borgmann (3). Parker did not use the toxic unit concept to analyze his data. Spehar *et al.* (17) observed that the number of embryos produced per female flagfish (*Jordanella floridae*) in chronic studies on cadmium and zinc mixtures was always much less in any of the mixtures compared to the control and single-metal exposures, although data variability did not permit demonstrations of statistically significant differences between the various treatments. Eaton (8) felt that most of the chronic toxicity to fathead minnows (*Pimephales promelas*) in cadmium, copper, and zinc mixtures was due primarily to zinc. However, he tested only mixtures containing all three metals and compared his results to data on single metals reported by three different sets of authors. Therefore it is not clear whether these two fish studies do or do not support use of the toxic unit concept. In contrast, an avoidance response by Atlantic salmon (*Salmo salar*) to mixtures of copper and zinc at very low concentrations does suggest that the toxic unit concept can be applied to fish (19).

The toxic unit concept may not be scientifically valid in that each metal may have a unique toxic action which does not necessarily add to the action of the other metals in a mixture. However, on a practical basis, the concept does seem to estimate reasonably well the effects on growth of zooplankton of metal mixtures (3), i.e. the overall outcome can be predicted independently of specific toxic actions.

At the present time, the toxic unit concept appears to be the only convenient method available for predicting the safe concentrations of metals in mixtures. One overall metal objective which could be defined is:

$$\Sigma \left[\frac{Mi}{Oi} \right] \leq 1.0$$

where Mi is the observed concentration of metal "i" and Oi is the objective for metal "i", if present singly.

One example of a test of this objective is available. Wong *et al.* (22) showed that a mixture of ten metals (concentrations in µg/L: As = 50, Cd = 0.2, Cr = 50, Cu = 5, Fe = 300, Pb = 25, Hg = 0.2, Ni = 25, Se = 10, Zn = 30) at the concentrations set as objectives in the 1978 Great Lakes Water Quality Agreement reduced primary production by algae by 68% from control levels in culture medium and by 78% in Hamilton Bay water. Even if each metal is present at *one tenth* the concentration of the objective, thereby just meeting the mixture objective proposed above, primary production was still reduced by 40% in growth medium and 21% in Hamilton Bay water. More recent research to fully evaluate this phenomenon has demonstrated that mixtures containing zinc are the most toxic and that the "safe" concentration of zinc alone for algae is less than the Agreement objective of 30 µg/L (23).

Although the zinc toxicity does not explain the entire degree of toxicity in mixtures, it reduces the apparent synergism somewhat and indicates the need for sound criteria for realistic single metals and mixtures objectives.

These results show that the proposed mixtures objective may not necessarily provide complete protection against toxicity of metal mixtures, but will nevertheless provide considerably more protection than strict reliance on the single metal objectives. This objective will also not protect against some specific metal mixtures which may be extremely toxic to some species (e.g. the synergistic toxicity of zinc and arsenic mixtures to copepods) (3).

In summary, although it is recognized that an overall mixtures objective based on the toxic unit concept will not always be 100% accurate in predicting safe levels of metals for aquatic organisms, it will provide at least some protection not afforded by the single metals approach. The reliability of both the mixtures and single metals objectives will also depend on whether the single metals objectives are appropriate to protect aquatic biota.

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TERMS OF REFERENCE
AQUATIC ECOSYSTEM OBJECTIVES COMMITTEE

The Aquatic Ecosystem Objectives Committee (AEOC) of the Science Advisory Board will:

1. Develop aquatic ecosystem objectives. Where feasible, these should be in the form of use effect curves, for various uses, and always including the most sensitive use.
2. Regularly review objectives and recommend amendment or introduction, based upon all available criteria.
3. Establish task forces to develop position papers on which to base the development of new or altered objectives.
4. Set general guidelines under which the objectives will be developed and define some minimum levels of scientific information at which an objective can be defined.
5. Develop an approach for the selection and ordering of parameters to be addressed.
6. Identify gaps in the knowledge needed to develop objectives and recommend the research required to fill the gaps.

MEMBERSHIP

AEOC will consist of eight members: two aquatic toxicologists, three water quality specialists (one each from the provincial, state, and one of the federal governments), a limnologist, an aquatic chemist, and a human health aspects expert.

SUBMISSION OF PROPOSED OBJECTIVES

"Since the Science Advisory Board has the responsibility for advising on scientific matters, and since the Water Quality Board will deal with the policy implications of proposed objectives on an *ad hoc* basis, the Commission plans to advise the Science Advisory Board to take the initiative in the study of new or revised water quality objectives, in consultation with the Water Quality Board as required, and to forward reports simultaneously to the Commission and the Water Quality Board. Thus, the study of objectives will not be dependent on actions of the Water Quality Board, but there will be an opportunity for the Board to advise the Commission on the practicability of the objectives under consideration or on the need for additional study from the Water Quality Board perspective." (Excerpt from a letter dated May 13, 1980, from the International Joint Commission to the Secretary of the Water Quality Board).

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The example of an aquatic ecosystem objective is still under development. Nonetheless, AEOC has received assistance in the form of presentations and discussions, to help develop the ecosystem concept, some of the directions which such an objective might take, and how it might be applied. AEOC gratefully acknowledges assistance from:

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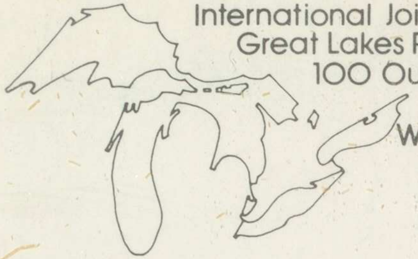

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