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New and Revised Specific Water Quality Objectives Proposed for the 1972 Agreement Between the United States and Canada on Great Lakes Water Quality by the Great Lakes Water Quality Board: Full Version

Great Lakes Water Quality Board

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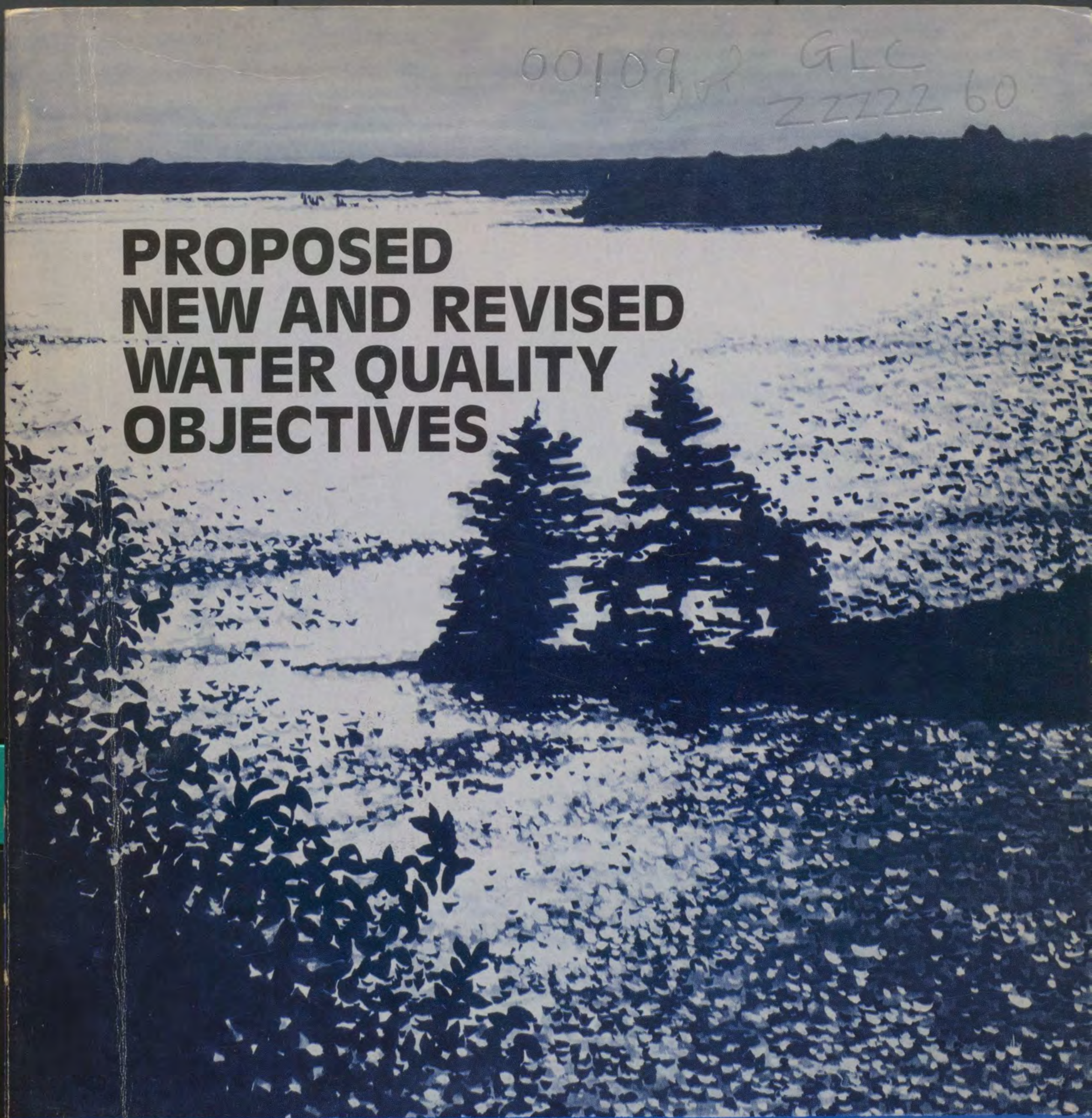

PROPOSED NEW AND REVISED WATER QUALITY OBJECTIVES

TO THE
INTERNATIONAL JOINT COMMISSION
BY THE
GREAT LAKES WATER QUALITY BOARD

NEW AND REVISED

SPECIFIC WATER QUALITY OBJECTIVES

PROPOSED FOR THE
1972 AGREEMENT BETWEEN
THE UNITED STATES AND CANADA
ON GREAT LAKES WATER QUALITY
BY THE
GREAT LAKES WATER QUALITY BOARD

[Full Version]

INTERNATIONAL JOINT COMMISSION
UNITED STATES AND CANADA
SEPTEMBER 1976

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I INTRODUCTION

Water quality objectives are a statement of the goals of the 1972 Great Lakes Water Quality Agreement. Canada and the United States, concerned about the grave deterioration of water quality of the Great Lakes, agreed that the best means to achieve improved water quality in the Great Lakes System is through the adoption of common objectives, the development and implementation of cooperative programs and other measures, and the assignment of special responsibilities and functions to the International Joint Commission.

Canada and Ontario have agreed that the specific water quality objectives of the Agreement shall be the least stringent target used by them in establishing water quality standards or other regulatory requirements for the boundary waters of the Great Lakes System. The states in the Great Lakes Basin generally consider the Agreement's specific water quality objectives in establishing federally approved state water quality standards for the boundary waters within their jurisdiction.

Under Article VI of the Agreement, the International Joint Commission was designated to assist in the implementation of the Agreement. Among the responsibilities given to the Commission was the "Tendering of advice and recommendations to the Parties and to the State and Provincial Governments on problems of the quality of the boundary waters of the Great Lakes System, including specific recommendations concerning the water quality objectives...". Further, the Commission was directed to establish a Great Lakes Water Quality Board to assist it and serve as principal advisor to the Commission with regard to the exercise of the powers and responsibilities (other than assistance in the coordination of research) assigned to it under the Agreement.

The Water Quality Board formed a Water Quality Objectives Subcommittee to assess the adequacy of the objectives in the Agreement and develop new or revised objectives. This Subcommittee, assisted by the Research Advisory Board's Standing Committee on the Scientific Basis for Water Quality Criteria, has been developing specific water quality objectives for a range of parameters, which if not exceeded will protect the most sensitive beneficial use of the boundary waters. However, it is recognized that there must be thorough public discussions on the social and economic implications, and the desirability of attempting to secure and protect all the waters of the Great Lakes for the most sensitive beneficial use.

In its 1974 and 1975 Annual Reports to the Commission the Great Lakes Water Quality Board recommended new and revised specific water quality objectives.

The Commission now has the responsibility of recommending to the Governments whether or not the objectives recommended to it by the Water Quality Board should be incorporated into the Agreement. Prior to making such recommendations, the Commission desires to have the benefit of public comment on the objectives. This document is designed to outline to interested groups and individuals the specific water quality objectives that are being proposed.

Before the Water Quality Objectives Subcommittee could develop new water quality objectives, it was necessary to agree upon a definition of water quality "objectives" and a framework or philosophy for their establishment and use. This conceptual framework is summarized in Section II of this report.

It should be recognized that the Agreement signed in 1972 contained general objectives and a limited number of specific water quality objectives. For ease of reference, the existing general and specific water quality objectives in the Agreement (Article II, Article III and Annex 1) are reproduced in Section III. Although the Agreement calls for a refined objective for radioactivity, this is currently being reviewed by the Canadian and United States Governments and will be considered by the International Joint Commission at a later date.

Section IV presents a proposed reorganization of Annex 1 of the Agreement listing all the existing and proposed new or revised specific water quality objectives.

The recommended new or revised objectives are specified in Section V. Recommendations are also presented for changes in the wording of the Agreement to clarify the ideas presented therein and to reinforce the intent of the Agreement to "maintain or enhance" existing water quality where it is better than that described by the objectives.

In addition to the new objectives which have been recommended by the Board, the Water Quality Objectives Subcommittee has developed objectives for several other parameters which are still under review by the Board. These are listed in Section VI along with a list of parameters which will be considered in the near future.

The "rationale" and scientific basis for each of the recommended new or revised specific water quality objectives are presented in Section VII. These rationales consist of a compendium of two year's work by the Water Quality Objectives Subcommittee (See Section VIII for list of Members) of the Great Lakes Water Quality Board and the Standing Committee on the Scientific Basis for Water Quality Criteria (see Section IX) of the Great Lakes Research Advisory Board. The best scientific data available were used in the formulation of the arguments presented and were previously published in the 1974 and 1975 Appendix "A" - Water Quality Objectives Subcommittee Reports of the Annual Reports of the Great Lakes Water Quality Board.

II APPROACH TO THE ESTABLISHMENT AND USE OF WATER QUALITY OBJECTIVES

What are the Objectives?

Article IV of the 1909 Boundary Waters Treaty between the United States and Canada states, among other things, that "boundary waters and waters flowing across the boundary shall not be polluted on either side to the injury of health or property of the other". The 1972 Great Lakes Water Quality Agreement is a specific application of this principle. Articles II and III of the 1972 Agreement set out the general objectives and some specific objectives to be met to ensure that pollution of the boundary waters does not occur. Articles IV, V and X described standards and other regulatory requirements, remedial programs and other measures to be implemented to meet the objectives.

In order to develop additional specific water quality objectives it was first necessary to agree upon a general framework or philosophy as a basis for developing the objectives. This framework and philosophy was published in the Water Quality Board's 1974 Annual Report and its Appendix "A". It is presented here to provide the necessary background for a comprehensive understanding of the proposed objectives and their intended use.

Water Quality Criteria and Objectives

Water quality objectives describe a minimum quality of water which, by protecting the most critical use, will provide for any specific use of the water. These objectives are to be achieved by remedial programs in all waters of the Great Lakes System used for various purposes, such as for drinking water, recreational activities, as fish habitat, and industrial and agricultural uses. However, the Agreement recognized that adjacent to sewer outfalls and other effluent discharges, relatively small mixing zones, in which water is not used for beneficial purposes, should be delineated. In these mixing zones the objectives would not be met. In addition, the Agreement recognized that some "localized areas", such as harbours, will take a long time to be restored to good water quality due largely to non-controllable sources of pollution. Governments around the lakes were to designate such mixing zones and other areas under agreed guidelines, and none of these were to extend across the international border.

In developing specific water quality objectives, the philosophy of protecting the most sensitive use was employed. In most cases, the objectives are recommended to protect aquatic life. Protection of public water supply is employed next in frequency. Aesthetic and/or recreational uses are most sensitive for a few parameters.

Local biota and local natural or ambient water quality characteristics can result in a different response than that assumed in the establishment of a particular objective. The objective may be more restrictive than necessary or conversely, meeting the general and specific objectives may not guarantee protection of uses.

Water quality criteria on which the proposed objectives are based were drawn from a bank of information which is constantly being updated. As new studies are completed they add to this information bank. Because new data and information may lead to modified recommendations, the objectives are subject to continual review.

An inadequate scientific data base exists to permit the establishment of numerical objectives for certain non-persistent toxic substances and complex wastes. To provide a reasonable degree of protection from the potential effects of such substances and discharges, criteria are recommended by which an objective can be developed for local situations. These criteria recommend that the local jurisdiction conduct specified bioassay tests on the most sensitive and important local aquatic species, and apply an appropriate application factor to toxicity data so derived. Such criteria may be termed procedural objectives.

Numerical objectives for metals were established with the knowledge that natural conditions might cause some areas of the lakes to be out of compliance. The objectives were determined on the basis of total metal concentrations and not upon the concentration of the most toxic form of the metal. At present, there is insufficient data to enable the setting of objectives on the basis of a toxic metal species. Research into the toxicity-speciation problem is needed, as well as the development of routine analytical techniques for surveillance purposes to identify metal species.

Protection of Public Health

The objectives are intended to protect the Great Lakes waters as a raw public water supply which will produce a safe, clear, potable and aesthetically pleasing water after treatment. It is not intended to provide protection of Great Lakes waters for domestic use without treatment and objectives have not been designed to protect for untreated domestic use.

The minimum level of water treatment prior to human consumption includes coagulation, sedimentation, filtration and disinfection. Often a numerical objective specified for a contaminant to protect raw public water supplies is the same as an established drinking water standard because:

1) information is inadequate on the effect of the defined treatment process on contaminant removal; or

2) the defined treatment process in inconsistent in contaminant removal; or

3) the defined treatment process is ineffective in contaminant removal.

Mixing Zones

The Agreement describes a mixing zone as an area within which specific water quality objectives shall not apply. Since specific water quality objectives describe the minimum quality of water which will provide for and protect any designated use, it follows that a mixing zone represents encroachment on useable waters in most cases and implies a loss of use or a loss of value; in essence some form of trade off.

In its present form the Agreement restricts mixing zones to the "vicinity" of outfalls, urges keeping localized areas to a "minimum" and establishes a non-degradation philosophy of taking "reasonable and practicable measures" to maintain or enhance water quality where it is better than the prescribed objectives. These definitions are not considered by the Board to be adequate to prevent excessive areas of the Great Lakes from remaining in non-compliance or to prevent excessive areas of exceptionally high quality from being downgraded in the future.

To further encourage consistency in management by the various enforcement agencies, guidelines for mixing zones have been developed. These were based upon principles of good water management and include descriptions of desirable conditions within, and desirable locations for, these zones.

Each objective alone should provide protection from the effects of that specific condition; however, the safety factor is very small for some conditions and unknown for others. It cannot be assumed that when two or more minimum conditions as defined by specific numerical objectives occur simultaneously that protection for each of the uses is assured. Antagonistic, additive or synergistic effects may occur. Considering the infinite combinations of water quality characteristics, it will never be possible to predict all of the effects of these combinations even for adult organisms, much less for their life history stages and processes. However, the proposed objectives are based on the best scientific knowledge presently available.

Specific water quality objectives are to be met at the periphery of mixing zones and therefore water quality outside the mixing zone should at all times meet the objectives.

Non-Degradation

In those areas where water quality is better than that proposed by the objectives, the Agreement calls for "all reasonable and practicable measures" to prevent degradation in these high quality waters. Carrying this nondegradation philosophy a step further, it is proposed that the countries also recognize and provide for the potential for enhancement. This small alteration in approach encourages further improvement, particularly in the open water areas of the lakes.

Federal, State and Provincial jurisdictions have the authority to adopt a more aggressive non-degradation policy than that currently provided. To encourage such policies, the assumed framework included the concept of jurisdictionally designated areas which have outstanding natural resource value and existing water quality better than the objectives within which the existing water quality should be maintained or further enhanced.

III

EXISTING WATER QUALITY OBJECTIVES

1972 GREAT LAKES WATER QUALITY AGREEMENT

Article II - GENERAL WATER QUALITY OBJECTIVES
Article III - SPECIFIC WATER QUALITY OBJECTIVES
Annex 1 - SPECIFIC WATER QUALITY OBJECTIVES

ARTICLE II

GREAT LAKES WATER QUALITY OBJECTIVES

The following general water quality objectives for the boundary waters of the Great Lakes System are adopted. These waters should be:

(a) Free from substances that enter the waters as a result of human activity and that will settle to form putrescent or otherwise objectionable sludge deposits, or that will adversely affect aquatic life or waterfowl;

(b) Free from floating debris, oil, scum and other floating materials entering the waters as a result of human activity in amounts sufficient to be unsightly or deleterious;

(c) Free from materials entering the waters as a result of human activity producing colour, odour or other conditions in such a degree as to create a nuisance;

(d) Free from substances entering the waters as a result of human activity in concentrations that are toxic or harmful to human, animal or aquatic life;

(e) Free from nutrients entering the waters as a result of human activity in concentrations that create nuisance growths of aquatic weeds and algae.

ARTICLE III

SPECIFIC WATER QUALITY OBJECTIVES

1. The specific water quality objectives for the boundary waters of the Great Lakes System set forth in Annex 1 are adopted.

2. The specific water quality objectives may be modified and additional specific water quality objectives for the boundary waters of the Great Lakes System or for particular sections thereof may be adopted by the Parties in accordance with the provisions of Articles IX and XII of this Agreement.

3. The specific water quality objectives adopted pursuant to this Article represent the minimum desired levels of water quality in the boundary waters of the Great Lakes System and are not intended to preclude the establishment of more stringent requirements.

4. Notwithstanding the adoption of specific water quality objectives, all reasonable and practicable measures shall be taken to maintain the levels of water quality existing at the date of entry into force of this Agreement in those areas of the boundary waters of the Great Lakes System where such levels exceed the specific water quality objectives.

ANNEX 1

SPECIFIC WATER QUALITY OBJECTIVES

1. Specific Objectives. The specific water quality objectives for the boundary waters of the Great Lakes System are as follows:

(a) Microbiology. The geometric mean of not less than five samples taken over not more than a thirty-day period should not exceed 1,000/100 millilitres total coliforms, nor 200/100 millilitres fecal coliforms. 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.

(b) Dissolved Oxygen. 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 be not less than necessary for the support of fishlife, particularly cold water species.

(c) Total Dissolved Solids. In Lake Erie, Lake Ontario and the International Section of the St. Lawrence River, the level of total dissolved solids should not exceed 200 milligrams per litre. In the St. Clair River, Lake St. Clair, the Detroit River and the Niagara River, the level should be consistent with maintaining the levels of total dissolved solids in Lake Erie and Lake Ontario at not to exceed 200 milligrams per litre. In the remaining boundary waters, pending further study, the level of total dissolved solids should not exceed present levels.

(d) Taste and Odour. Phenols and other objectionable taste and odour producing substances should be substantially absent.

(e) pH. Values should not be outside the range of 6.7 to 8.5.

(f) Iron (Fe). Levels should not exceed 0.3 milligrams per litre.

(g) Phosphorus (P). Concentrations 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.

(h) Radioactivity. Radioactivity should be kept at the lowest practicable levels and in any event should be controlled to the extent necessary to prevent harmful effects on health.

2. Interim Objectives. Until objectives for particular substances and effects in the classes described in this paragraph are further refined, the objectives for them are as follows:

(a) Temperature. There should be no change that would adversely affect any local or general use of these waters.

(b) Mercury and Other Toxic Heavy Metals. The aquatic environment should be free from substances attributable to municipal, industrial or other discharges in concentrations that are toxic or harmful to human, animal or aquatic life.

(c) Persistent Organic Contaminants. Persistent pest control products and other persistent organic contaminants that are toxic or harmful to human, animal or aquatic life should be substantially absent in the waters.

(d) Settleable and Suspended Materials. Waters should be free from substances attributable to municipal, industrial or other discharges that will settle to form putrescent or otherwise objectionable sludge deposits, or that will adversely affect aquatic life or waterfowl.

(e) Oil, Petrochemicals and Immiscible Substances. Waters should be free from floating debris, oil, scum and other floating materials attributable to municipal, industrial or other discharges in amounts sufficient to be unsightly or deleterious.

3. Non-degradation. Notwithstanding the adoption of specific water quality objectives, all reasonable and practicable measures shall be taken in accordance with paragraph 4 of Article III of the Agreement to maintain the levels of water quality existing at the date of entry into force of the Agreement in those areas of the boundary waters of the Great Lakes System where such levels exceed the specific water quality objectives.

4. Sampling Data. The Parties agree that the determination of compliance with specific objectives shall be based on statistically valid sampling data.

5. Mixing Zones. The responsible regulatory agencies may designate restricted mixing zones in the vicinity of outfalls within which the specific water quality objectives shall not apply. Mixing zones shall not be considered a substitute for adequate treatment or control of discharges at their source.

6. Localized Areas. There will be other restricted, localized areas, such as harbours, where existing conditions such as land drainage and land use will prevent the objectives from being met at least over the short term; such areas, however, should be identified specifically and as early as possible by the responsible regulatory agencies and should be kept to a minimum. Pollution from such areas shall not contribute to the violation of the water quality objectives in the waters of the other Party. The International Joint Commission shall be notified of the identification of such localized areas, in accordance with Article VIII.

7. Consultation. The Parties agree to consult within one year from the date of entry into force of the Agreement, for the purpose of considering:

(a) Specific water quality objectives for the following substances:

Ammonia
Arsenic
Barium
Cadmium
Chloride
Chromium
Copper
Cyanide
Fluoride
Lead
Mercury
Nickel
Oil
Organic chemicals
Phenols
Selenium
Sulphate
Zinc

(b) Refined objectives for radioactivity and temperature; for radioactivity the objective shall be considered in the light of the recommendations of the International Commission on Radiation Protection.

8. Amendment.

(a) The objectives adopted herein shall be kept under review and may be amended by mutual agreement of the Parties.

(b) Whenever the International Joint Commission, acting pursuant to Article VI of the Agreement, shall recommend the establishment of new or modified specific water quality objectives, this Annex shall be amended in accordance with such recommendation on the receipt by the Commission of a letter from each Party indicating its agreement with the recommendation.

IV

PROPOSED ANNEX 1

OF THE

GREAT LAKES WATER QUALITY AGREEMENT

PROPOSED ANNEX 1 - OF THE GREAT LAKES WATER QUALITY AGREEMENT

1. Specific Objectives
   - A. Chemical Characteristics
     - (1) Persistent Toxic Substances
       - (a) Organic
         - (i) Pesticides
           - Aldrin/Dieldrin (2)
           - Chlordane (2)
           - DDT and Metabolites (2)
           - Endrin (2)
           - Heptachlor (2)
           - Lindane (2)
           - Methoxychlor (2)
           - Toxaphene (2)
         - (ii) Other Compounds
           - Phthalic Acid Esters (2)
           - Polychlorinated Biphenyls (2)
           - Other Organic Contaminants (2)
       - (b) Inorganic
         - (i) Metals
           - Arsenic (2)
           - Cadmium (2)
           - Chromium (2)
           - Copper (3)
           - Iron (3)
           - Lead (2)
           - Mercury (2)
           - Nickel (3)
           - Selenium (2)
           - Zinc (2)
         - (ii) Others
           - Fluoride (2)
           - Total Dissolved Solids (1)
     - (2) Non-Persistent Toxic Substances
       - (a) Organic
         - (i) Pesticides
           - General Objective (1)
           - Diazinon (2)
           - Guthion (3)
           - Parathion (3)

(Continued)

(ii) Other Compounds

Cyanide (3)
Oil and Petrochemicals (2)
Unspecified Non-Persistent Toxic Substances and Complex Effluents (2)

(b) Inorganic

Ammonia (3)
Chlorine (3)
Hydrogen Sulfide (3)

(3) Other Substances

(a) Dissolved Oxygen (1)

(b) pH (2)

(c) Nutrients

(i) Phosphorus (1)

(d) Tainting Substances (2)

B. Physical Characteristics

(1) Settleable and Suspended Solids and Light Transmission (2)

(2) Temperature (3)

(3) Asbestos (2)

(4) Radioactivity (1)

C. Microbiological Characteristics (1)

2. Non-degradation (2)

3. Enhancement (2)

4. Sampling Data (1)

5. Mixing Zines (Guidelines for Designation) (2)

6. Localized Areas (1)

7. Amendment (1)

NOTE:

(1) Existing specific water quality objective for which no change is recommended at this time - See Section III.

(2) New or revised specific water quality objective being recommended for adoption - See Section V.

(3) New water quality objective under development.

V

NEW AND REVISED SPECIFIC WATER QUALITY OBJECTIVES RECOMMENDED FOR ADOPTION

BY THE

GREAT LAKES WATER QUALITY BOARD

SPECIFIC WATER QUALITY OBJECTIVES RECOMMENDED FOR ADOPTION

PESTICIDES (PERSISTENT)

	Rationale Reference
NEW *Aldrin/Dieldrin* *The sum of the concentrations of aldrin and dieldrin in water should not exceed the recommended quantification limit of 0.001 micrograms per litre. The sum of concentrations of aldrin and dieldrin in the edible portion of fish should not exceed 0.3 micrograms per gram for the protection of human consumers of fish.* Note: Based on U.S. Food and Drug Administration guidelines.	34
NEW *Chlordane* *The concentration of chlordane in water should not exceed 0.06 micrograms per litre for the protection of aquatic life.*	37
NEW *DDT and Metabolites* *The sum of the concentrations of DDT and its metabolites in water should not exceed the recommended quantification limit of 0.003 micrograms per litre. The sum of the concentration of DDT and its metabolites in whole fish (wet weight basis) should not exceed 1.0 micrograms per gram for the protection of fish consuming aquatic birds.*	39
NEW *Endrin* *The concentration of endrin in water should not exceed the recommended quantification limit of 0.002 micrograms per litre. The concentration of endrin in the edible portion of fish should not exceed 0.3 micrograms per gram for the protection of human consumers of fish.* Note: Based on U.S. Food and Drug Administration guidelines.	41

SPECIFIC WATER QUALITY OBJECTIVES RECOMMENDED FOR ADOPTION

Rationale Reference

PESTICIDES (Cont'd)

NEW *Heptachlor*

The sum of the concentrations of heptachlor and heptachlor epoxide in water should not exceed the recommended quantification limit of 0.001 micrograms per litre. The sum of the concentrations of heptachlor and heptachlor epoxide in edible portions of fish should not exceed 0.3 micrograms per gram for the protection of human consumers of fish. 43

Note: Based on U.S. Food and Drug Administration guidelines.

NEW *Lindane*

The concentration of lindane in water should not exceed 0.01 micrograms per litre for the protection of aquatic life. The concentration of lindane in edible portions of fish should not exceed 0.3 micrograms per gram for the protection of human consumers of fish. 45

Note: Based on U.S. Food and Drug Administration guidelines.

NEW *Methoxychlor*

The concentration of methoxychlor in water should not exceed 0.04 micrograms per litre for the protection of aquatic life. 47

NEW *Toxaphene*

The concentration of toxaphene in water should not exceed 0.008 micrograms per litre for the protection of aquatic life. 49

SPECIFIC WATER QUALITY OBJECTIVES RECOMMENDED FOR ADOPTION

		Rationale Reference
	OTHER TOXIC PERSISTENT COMPOUNDS	
NEW	*Phthalic Acid Esters* *The concentrations of dibutyl phthalate and di(2-ethylhexyl) phthalate in water should not exceed 4.0 micrograms per litre and 0.6 micrograms per litre, respectively, for the protection of aquatic life. Other phthalic acid esters should not exceed the recommended quantification limit of 0.2 micrograms per litre in waters for the protection of aquatic life.*	51
NEW	*Polychlorinated Biphenyls (PCBs)* *The concentration of total polychlorinated biphenyls in fish tissues (whole fish, calculated on a wet weight basis), should not exceed 0.1 micrograms per gram for the protection of fish consuming birds and animals.*	55

Note:

The detection limit for PCBs in water samples is not low enough to permit setting a water quality objective for concentrations in water. Therefore the proposed objective is based on levels detectable in fish tissue. It is believed that water concentrations less than 0.001 micrograms per litre would be required to preclude significant bioaccumulation of PCBs.

The U.S. Food and Drug Administration has set an administrative guideline of 5 micrograms per gram of PCB as the maximum levels acceptable in the edible portion of fish for human consumption. The Canadian Department of National Health and Welfare has set a similar guideline at 2 micrograms per gram of PCB. The Board is recommending a more stringent objective for the Great Lakes to protect birds and animals whose main diet consist of fish from the lakes.

SPECIFIC WATER QUALITY OBJECTIVES RECOMMENDED FOR ADOPTION

		Rationale Reference
	OTHER TOXIC PERSISTENT SUBSTANCES	
NEW	*Other Organic Contaminants* *For other organic contaminants, the levels of which are not specified but which can be demonstrated to be persistent and are likely to be toxic, it is recommended that the concentrations of such compounds in water or aquatic organisms be limited to the detection level as determined by the best scientific methodology available at the time.*	60
	METALS	
NEW	*Arsenic* *Concentrations of total arsenic in an unfiltered water sample should not exceed 50 micrograms per litre to protect raw waters for public water supplies.*	76
NEW	*Cadmium* *Concentrations of total cadmium in an unfiltered water sample should not exceed 0.2 micrograms per litre to protect aquatic life.*	80
NEW	*Chromium* *Concentrations of total chromium in an unfiltered water sample should not exceed 50 micrograms per litre to protect raw waters for public water supplies.*	91
NEW	*Lead* *Concentrations 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.*	95

SPECIFIC WATER QUALITY OBJECTIVES RECOMMENDED FOR ADOPTION

		Rationale Reference
	METALS (Cont'd)	
NEW	*Mercury* *Concentrations of total mercury in a filtered water sample should not exceed 0.2 micrograms per litre nor should the concentration of total mercury in whole fish exceed 0.5 micrograms per gram (wet weight basis) to protect aquatic life as well as fish-consuming birds.*	101
NEW	*Selenium* *Concentrations of total selenium in an unfiltered water sample should not exceed 10 micrograms per litre to protect raw water for public water supplies.*	108
NEW	*Zinc* *Concentrations of total zinc in an unfiltered water sample should not exceed 30 micrograms per litre to protect aquatic life.*	117
	OTHER INORGANICS	
NEW	*Fluoride* *Concentrations of total fluoride in an unfiltered water sample should not exceed 1.2 milligrams per litre to protect raw waters for public water supplies.*	122

SPECIFIC WATER QUALITY OBJECTIVES RECOMMENDED FOR ADOPTION

Rationale Reference

PESTICIDES (NON-PERSISTENT)

NEW *General Objective*

Concentrations of unspecified, non-persistent pesticides should not exceed 0.05 of the median lethal concentration in a 96-hour test for any sensitive local species. 134

NEW *Diazinon*

The concentration of Diazinon in an unfiltered water sample should not exceed 0.08 micrograms per litre for the protection of aquatic life. 136

OTHER NON-PERSISTENT ORGANIC SUBSTANCES

REVISED

Oil and Petrochemicals

Oil and petrochemicals should not be present in concentrations that: 140

1) *can be detected as visible film, sheen or discolouration on the surface;*
2) *can be detected by odour;*
3) *can cause tainting of fish or edible invertebrates;*
4) *can form deposits on shorelines and bottom sediments that are detectable by sight or odour, or deleterious to resident aquatic organisms.*

EXISTING

Oil and Petrochemicals

Oil, Petrochemicals and Immiscible Substances. Waters should be free from floating debris, oil, scum and other floating materials attributable to municipal, industrial or other discharges in amounts sufficient to be unsightly or deleterious.

Oil or petrochemicals should not be present in concentrations that:

1) can be detected as visible film, sheen or discolouration on the surface;
2) can be detected by odour;
3) can cause tainting of fish or edible invertebrates;
4) can form deposits on shorelines and bottom sediments that are detectable by sight or odour, or deleterious to resident aquatic organisms.

SPECIFIC WATER QUALITY OBJECTIVES RECOMMENDED FOR ADOPTION

Rationale Reference

OTHER NON-PERSISTENT ORGANIC CONTAMINANTS (Cont'd)

NEW *Unspecified Non-Persistent Toxic Substances and Complex Effluents*

Unspecified non-persistent toxic substances and complex effluents of municipal, industrial or other origin should not be present in concentrations which exceed 0.05 of the median lethal concentration (96-hour LC50) for any sensitive local species to protect aquatic life. 146

OTHER SUBSTANCES

REVISED

pH

Values of pH should not be outside the range of 6.5 to 9.0, nor should discharges change the pH at the boundary of the designated mixing zone more than 0.5 units from the ambient. 149

EXISTING

pH

Values should not be outside the range of 6.7 to 8.5.

REVISED

Tainting Substances

1) Raw public water supply sources should be essentially free from objectionable taste and odour for aesthetic reasons. 152

2) Substances entering the waters as a result of human activity that cause tainting of edible aquatic organisms should not be present in concentrations which will lower the acceptability of these organisms as determined by organoleptic tests.

EXISITNG

Taste and Odour

Phenols and other objectionable taste and odour producing substances should be substantially absent.

SPECIFIC WATER QUALITY OBJECTIVES RECOMMENDED FOR ADOPTION

Rationale Reference

PHYSICAL CHARACTERISTICS

REVISED

Settleable and Suspended Solids and Light Transmission 161

For the protection of aquatic life, waters should be free from substances attributable to municipal, industrial or other discharges resulting from activity that will settle to form putrescent or otherwise objectionable sludge deposits or that will alter the value of the Secchi disk depth by more than 10 percent.

EXISTING

Settleable Suspended Materials

Waters should be free from substances attributable to municipal, industrial or other discharges that will settle to form putrescent or otherwise objectionable sludge deposits, or that will adversely affect aquatic life or waterfowl.

NEW *Asbestos* 167

Asbestos should be kept at the lowest practicable levels and in any event should be controlled to the extent necessary to prevent harmful effects on health.

BASIC CONCEPTS

REVISED

Non-degradation 169

Notwithstanding the adoption of specific water quality objectives, all reasonable and practicable measures shall be taken in accordance with paragraph 4 of Article III of the Agreement to maintain the levels of water quality existing at the date of entry into force of the Agreement in those areas of the boundary waters of the Great Lakes System where such water quality is better than that prescribed by the specific water quality objectives.

SPECIFIC WATER QUALITY OBJECTIVES RECOMMENDED FOR ADOPTION

	Rationale Reference
BASIC CONCEPTS (Cont'd) EXISTING Non-degradation Notwithstanding the adoption of specific water quality objectives, all reasonable and practicable measures shall be taken in accordance with paragraph 4 of Article III of the Agreement to maintain the levels of water quality existing at the date of entry into force of the Agreement in these areas of the boundary waters of the Great Lakes System where such levels exceed the specific water quality objectives.	
NEW *Enhancement* *In areas designated by the appropriate jurisdiction as having outstanding natural resource value and which have water quality better than prescribed by the specific water quality objectives, that water quality should be maintained or enhanced.*	169
REVISED *Mixing Zones* *The responsible regulatory agencies may designate restricted mixing zones in the vicinity of outfalls within which the specific water quality objectives shall not apply. Mixing zones shall not be considered a substitute for adequate treatment or control of discharges at their source.* *The following guidelines should be used in the designation of mixing zones.* *1. A mixing zone is an area, contiguous to a point source, where exceptions to water quality objectives and conditions otherwise applicable to the receiving waterbody may be granted.* *2. Specific water quality objectives and conditions applicable to the receiving waterbody should be met at the boundary of mixing zones.*	172

BASIC CONCEPTS (Cont'd)

3. Limitations on mixing zones should be established by the responsible regulatory agency on a case-by-case basis, where "case" refers to both local considerations and the waterbody as a whole, or segment of the waterbody.

4. Mixing zones, by definition, represent a loss of value.

5. Many of the general water quality objectives should apply to discharge-related materials within mixing zones. The zones should be free of:
- *(a) objectionable deposits;*
- *(b) unsightly or deleterious amounts of flotsam, debris, oil, scum and other floating matter;*
- *(c) substances producing objectionable colour, odour, taste, or turbidity; and*
- *(d) substances and conditions or combinations thereof at levels which produce aquatic life in nuisance quantities that interfere with other uses.*

6. No conditions within the mixing zone should be permitted which are either (a) rapidly lethal to important aquatic life (conditions which result in sudden fish kills and mortality of organisms passing through the mixing zone); or (b) which cause irreversible responses which could result in detrimental post-exposure effects; or (c) which result in bioconcentration of toxic materials which are harmful to the organism or its consumers.

7. Concentrations of toxic materials at any point in the mixing zone where important species are physically capable of residing should not exceed the 24 to 96-hour LC50.

8. When designing conditions to protect specific organisms it is necessary to know that the organisms would normally inhabit the area within the mixing zone. Zones of passage should be assured either by location or design of conditions within mixing zones. Mixing zones should not form a barrier to migratory routes of aquatic species or interfere with biological communities or populations of important species, to a degree which is damaging to the ecosystem, or diminish other beneficial uses disproportionately.

BASIC CONCEPTS (Cont'd)

9. Mixing zones may overlap unless the combined effects exceed the conditions set forth in other guidelines.

10. Municipal and other water supply intakes and recreational areas should not be in mixing zones as a general condition, but local knowledge of the effluent characteristics and the type of discharge associated with the zone could allow such a mixture of uses.

11. Areas of extraordinary value may be designated off-limits for mixing zones.

12. The size, shape and exact location of a mixing zone should be specified so that both the discharger and the regulatory agency know the bounds.

13. Existing biological, chemical, physical and hydrological condtions should be known when considering location of a new mixing zone or limitations on an existing one.

EXISTING

Mixing Zones

The responsible regulatory agencies may designate restricted mixing zones in the vicinity of outfalls within which the specific water quality objectives shall not apply. Mixing zones shall not be considered a substitute for adequate treatment or control of discharges at their source.

VI

NEW AND REVISED
SPECIFIC WATER QUALITY OBJECTIVES
UNDER DEVELOPMENT

BY THE
WATER QUALITY BOARD
AND THE
WATER QUALITY OBJECTIVES SUBCOMMITTEE

The Water Quality Objectives Subcommittee has developed specific water quality objectives for the parameters listed below. At this time the Water Quality Board is reviewing these objectives internally before making any recommendations with respect to them to the Commission.

CHEMICAL CHARACTERISTICS		PHYSICAL CHARACTERISTICS
Inorganic	*Organic*	Temperature
Copper	Cyanide	
Iron	Guthion	
Nickel	Parathion	
Ammonia		
Chlorine		
Hydrogen Sulfide		

The Water Quality Objectives Subcommittee will continue its review of the scientific literature for new knowledge on cause/effect relationships which can be used to refine the specific water quality objectives and to develop new water quality objectives. In the immediate future, the Subcommittee plans to consider the parameters listed below, but may not necessarily write objectives for them.

CHEMICAL CHARACTERISTICS

Inorganic

- Manganese
- Phosphorus (elemental)
- Barium
- Boron
- Sulphate
- Aluminum
- Silver
- Vanadium
- Thallium
- Super saturation of dissolved gases
- Nutrients
  - Nitrate
  - Silicate
  - Phosphate

Organic

- Mirex
- Nitrilotriacetic Acid
- Organophosphates
- Carbamates
- Phenols
- Rotenone
- Organo-tin compounds
- Detergents
  - Surfactants
  - Builders
- Polynuclear Aromatic Hydrocarbons
- 3-trifluoromethyl - 4 nitrophenol
- Pulp mill effluent components

PHYSICAL CHARACTERISTICS

- Asbestos

BIOLOGICAL CHARACTERISTICS

- Micro-organisms
- Toxicity units
- Biological effects of intakes
- Chlorophyll-a

VII

RATIONALE AND SCIENTIFIC BASIS

FOR

PROPOSED NEW AND REVISED

SPECIFIC WATER QUALITY OBJECTIVES

A. CHEMICAL CHARACTERISTICS

(i) PERSISTENT TOXIC SUBSTANCES

(a) ORGANIC

(i) PESTICIDES

ALDRIN/DIELDRIN

RECOMMENDATION

It is recommended that the following numerical objective for aldrin/dieldrin be adopted to replace, in part, the existing objective for persistent organic contaminants in Annex 1, paragraph 2 (c) of the Agreement.

> *The sum of the concentrations of aldrin and dieldrin in water should not exceed the recommended quantification limit of 0.001 μg/l. The sum of the concentrations of aldrin and dieldrin in the edible portion of fish should not exceed 0.3 μg/g for the protection of human consumers of fish.*

RATIONALE

Aldrin is readily metabolized to the epoxy form, dieldrin by both aquatic (Gakstatter, 1968; Khan et al., 1972) and nonaquatic organisms (Gianotti et al., 1956; Bann et al., 1956). It has also been shown that the toxicity to aquatic organisms of both aldrin and dieldrin are similar (Jensen and Gaufin, 1966; Henderson et al., 1959) are consequently, the recommendation has been expressed in terms of the total concentrations of dieldrin and aldrin.

The proposed United States drinking water standard (EPA, 1974) was recommended to be 0.00014 μg/1 total aldrin plus dieldrin based upon carcinogenicity studies. This standard is lower than any water levels which can be obtained from acute or chronic effect levels for fresh water aquatic organisms but its status is uncertain at present. The lowest effect levels which have been observed for freshwater species pertain to the stonefly and to the sailfin molly. The stonefly naiad was observed to have a 20-30 day LC_{50} of 0.2 μg/1 (Jensen and Gaufin 1966) but there is no available experimental application factor to obtain "safe" concentrations for this sensitive species. The sailfin molly exhibited chronic effects - inhibition of growth and reproduction (Lane and Livingstone, 1970) - at 0.75 μg/1 and use of the arbitrary safety factor of 0.2 results in a concentration of 0.25 μg/1. This level, however, is inadequate for the protection of the stonefly and possibly other species. Aldrin and dieldrin have recently been shown to be carcinogenic (Walker et al., 1970) and, hence, the recommended concentration is the present recommended quantification limit as based on the lowest three reported values in the laboratory survey.

There are several reports on dietary dosing of aldrin and dieldrin which have led to low level sub-acute responses for different organisms. Rats and dogs (Lehman, 1965) showed no ill effects over 90 days - 2 years at dietary levels of 0.5 µg/g and the Hungarian partridge (Neill, 1969) had adverse effects on reproduction when the dosage in their diet was 1 µg/g. In the aquatic field, 0.36 µg/g in the diet of the rainbow trout affected the biochemical processes of the fish (Mehrle and Bloomfield, 1974). Since the allowable edible fish tissue concentration under the United States Food and Drug Administration guidelines is 0.3 µg/g, this is recommended.

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CHLORDANE

RECOMMENDATION

It is recommended that the following numerical objective for chlordane be adopted to replace, in part, the existing objective for persistent organic contaminants in Annex 1, paragraph 2(c) of the Agreement:

> *The concentration of chlordane in water should not exceed 0.06 µg/l for the protection of aquatic life.*

RATIONALE

Cardwell et al., (1974) conducted long-term flow-through studies on the effects of chlordane including studies on the effect on reproduction of fathead minnows, bluegills and brook trout. "Safe" concentrations ranged from 0.8 to less than 0.3 µg/l, and corresponding 96-hr LC_{50} values ranged from 59 to 37 µg/l. The smallest application factor between acute and "safe" concentrations was less than 0.008 for brook trout. If this factor is applied to the lowest available 96-hr LC_{50} of 7.8 µg/l (Anon., 1965) for rainbow trout, then a derived "safe" concentration would be 0.06 µg/l.

The "safe" level for the midge Chironomus was found to be 0.7 µg/l by Cardwell et al., (1974). No acute toxicity determination could be made for this species. The "safe" chlordane concentrations for Daphnia magna and Hyalella azteca were about 12 and 5 µg/l, respectively.

Reported acute toxicity concentrations of chlordane for invertebrates in general range from less than 1 to more than 1000 µg/l (Cardwell et al., 1974; Konar, 1968, Sanders, 1969; 1972; Sanders and Cope, 1966 and 1968). It is likely that "safe" protection to aquatic invertebrates as well. Therefore it is recommended that the concentration in water should not exceed 0.06 µg/l.

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DDT AND METABOLITES

RECOMMENDATION

It is recommended that the following numerical objective for DDT and metabolites be adopted to replace, in part, the existing objective for persistent organic contaminants in Annex 1, paragraph 2(c) of the Agreement:

> *The sum of the concentrations of DDT and its metabolites in water should not exceed the recommended quantification limit of 0.003 μg/l. The sum of the concentrations of DDT and its metabolites in whole fish (wet weight basis) should not exceed 1.0 μg/g for the protection of fish consuming aquatic birds.*

RATIONALE

Egg shell thinning has been reported in the American Kestrel after chronic experimental feeding with 2.8 μg/g DDE (Wiemeyer and Porter, 1970); Mallard (2.8 μg/g DDE, converted from dry basis) (Health et al., 1969; black duck (3.3 μg/g DDE, converted from dry basis) (Longcore et al., 1971); and other species (Stickel, 1973). It is assumed that similar levels of intake will produce some detrimental effect of reproduction in some species of birds under natural conditions. The lowest experimentally determined level at which egg shell thinning was found was 2.8 μg/g DDE. The effect was considered a subtle effect. As a subtle effect, an arbitrary 0.2 safety factor was applied to estimate the "safe" level. This would produce an estimated "safe" body burden in fish which are consumed by aquatic birds, of 0.56 μg/g DDE. This metabolite has been found to constitute 50-90% of the residue of DDT (Klaassen and Kadoum, 1973; Frank et al., 1974; Reinert and Bergman, 1974). Therefore the permissible body burden in fish was set at 1 μg/g total DDT to protect aquatic birds.

The FDA and FDD administrative action guidelines for DDT in edible portions of fish are set at 5 μg/g. This may be adequate for human consumption, but in the light of the above information, it will not protect aquatic birds.

The concentration of DDT in water which is likely to produce unacceptable body burdens in fish cannot be estimated accurately, because concentration factors for DDT appear to differ among the various Great Lakes, possibly due to other water quality parameters. Water concentrations which are "safe" for fish appear to be higher than those which produce unacceptable body burdens. However, "safe" water concentrations for fish have not been established by chronic experiments measuring subtle effects on fish. Therefore, no "safe" water concentration of DDT can be established and, consequently, the concentration of DDT in water should not exceed the recommended quantification limit of 0.003 μg/l, based on the lower three reported values from laboratory survey.

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ENDRIN

RECOMMENDATION

It is recommended that the following numerical objective for endrin be adopted to replace, in part, the existing objective for Persistent Organic Contaminants in Annex 1, paragraph 2(c) of the Agreement:

> *The concentration of endrin in water should not exceed the recommended quantification limit of 0.002 µg/l. The concentration of endrin in the edible portion of fish should not exceed 0.3 µg/g for the protection of human consumers of fish.*

RATIONALE

While there are considerable data available on the acute toxicity (96-hour LC_{50}) of endrin towards fish at approximately 0.5 µg/l (Mount, 1962; Henderson, 1959; Katz, 1961), there are no experimental data available which would permit the translation of these concentrations to safe levels for aquatic organisms. There is a reported 30-day LC_{50} for the stonefly naiad of 0.035 µg/l (Jensen and Gaufin, 1966), so "safe" levels to protect all aquatic organisms must lie below this value. In addition to the absence of appropriate chronic toxicity data, the guidelines for raw water do not provide protection for all aquatic organisms. Consequently, it is recommended that the concentration of endrin in water should not exceed the recommended quantification limit as derived from the survey of laboratories and mentioned in the general section on persistent organic contaminants. Because it is felt that low levels should be sought in situations where data are inadequate to support a higher level, the quantification limit is set at the mean of the lower three of those reporting in the above survey. The level recommended for water is therefore 0.002 µg/l.

Two values for tissue levels are appropriate for consideration. American kestrels showed adverse effects when fed a diet containing 0.5 µg/g of endrin (Stickel, 1975), however, American kestrels are not fish eating predators. The United States Food and Drug Administration guideline for residues of this compound in edible fish tissue is 0.3 µg/g and the latter is recommended for the protection of consumers of fish.

LITERATURE CITED

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HEPTACHLOR

RECOMMENDATIONS

It is recommended that the following numerical objective for Heptachlor be adopted to replace, in part the existing objective for Persistent Organic Contaminants in Annex 1, paragraph 2(c) of the Agreement:

> *The sum of the concentrations of heptachlor and heptachlor epoxide in water should not exceed the recommended quantification limit of 0.001 µg/l. The sum of the concentrations of heptachlor and heptachlor epoxide in edible portions of fish should not exceed 0.3 µg/g for the protection of human consumers of fish.*

RATIONALE

Epoxidation of heptachlor yields heptachlor epoxide, and this reaction is facile in the aquatic environment (Stickel et al, 1965; Hannon et al., 1970; Wisman et al., 1967; Barthel et al., 1960; Perry et al., 1958). The epoxidized form of heptachlor is at least as toxic as the parent compound, (U.S. - H.E. & W., 1972; Rudd and Genelly, 1956) and as a consequence, heptachlor concentrations are expressed as the sum of heptachlor plus heptachlor epoxide.

One of the basis of available evidence, no experimentally determinable "safe" levels can be set for water. The lowest available LC_{50} of 1.1 µg/l for stoneflies (Sanders and Cope, 1968) cannot be translated into safe levels. The proposed U.S. Drinking Water Standard of 0.1 µg/l may not give a sufficient margin of safety and hence a quantification limit ascertained from the survey of laboratories is recommended. The mean of the lower three reported values in the survey was employed in setting the recommended level of 0.001 µg/l total for water.

For tissues, the minimal or no-effect dietary level for rats and dogs is reported at 0.5 µg/g (Lehman, 1965). The United States Food and Drug Administration guideline for this pesticide as a residue in edible fish tissue is given as 0.3 µg/g and in the absence of aquatic dosing experiments, the latter is the level recommended for edible portions of fish in the Great Lakes.

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LINDANE

RECOMMENDATION

It is recommended that the following numerical objective for lindane be adopted to replace, in part, the existing objective for persistent organic contaminants in Annex 1, paragraph 2(c) of the Agreement:

> *The concentration of lindane in water should not exceed 0.01 μg/l for the protection of aquatic life. The concentration of lindane in edible portions of fish should not exceed 0.3 μg/g for the protection of human consumers of fish.*

RATIONALE

Macek et al., (1975) experimentally determined "safe" water concentrations for bluegills, brook trout, and fathead minnows to range from 8.8 to 9.1 μg/l. The LC_{50} concentrations for the latter three species range from 20 to 54 μg/l which when divided by the respective "safe" concentrations, result in application factors of 0.17 to 0.34 for fish. The brown trout is apparently the fish most sensitive to lindane on an acute basis among those species used in aquatic bioassays. The 96-hour LC_{50} for brown trout is 2.0 μg/l (Macek and McAllister, 1970). Utilizing the lowest experimentally determined application factor for lindane in fish (0.17), a "safe" concentration of 0.34 μg/l would be predicted for brown trout.

Macek et al., (1975) determined the acute and chronic toxicities of lindane to the midge (Chironomus tentans, Daphnia magna, and the scud Gammarus faciatus. The midge was the most sensitive of these species chronically, with 2.2 μg/l being the highest concentration producing no observable adverse effect. Daphnia were least sensitive as 11 μg/l was determined to be "safe" over three consecutive generations of exposure. The midge and Daphnia were significantly different from fish in one respect, however, the application factors for these invertebrates were much less than for fish, namely, 0.01 and 0.02 based on 48-hour. LC_{50} values of 207 and 485 μg/l, respectively.

Two investigators (Snow, 1958; Cope, 1965) have reported 96-hour LC_{50} values of 1 μg/l for stoneflies. Sanders and Cope (1968) reported an acute LC_{50} for stoneflies of 4.5 μg/l lindane. If the experimentally determine application factor for invertebrates for lindane of 0.01 is applied to the lowest reported 96-hour LC_{50} of the most sensitive species, the stonefly, then a predicted "safe" concentration of lindane in water for that species would be 0.01 μg/l. This therefore, is the recommended level for water.

Little information is available on accumulation of lindane in fish tissues. However, Macek et al., (1975) observed whole-body (eviscerated) concentrations (wet weight) that were about 500 times the corresponding water concentrations in fathead minnows that had been exposed for several months. Butler (1967) observed accumulations of up to 250 times exposure concentrations in marine mollusks. Such factors, at present, are not consistent enough to be useful in deriving tissue levels and therefore the recommended criterion is based on the 0.3 µg/g administrative guideline of the United States Food and Drug Administration for lindane in edible portions of fish.

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METHOXYCHLOR

RECOMMENDATION

It is recommended that the following numerical objective for Methoxychlor be adopted to replace, in part, the existing objective for persistent organic contaminants in Annex 1, paragraph 2(c) of the Agreement:

> *The concentration of methoxychlor in water should not exceed 0.04 µg/l for the protection of aquatic life.*

RATIONALE

Chronic exposures of fathead minnows to methoxychlor demonstrated no effects on weight gain below 0.5 µg/l during 4 months of exposure, and no effects on mortality below 0.25 µg/l. The number of eggs laid by fathead minnows was unaffected by a 4-month exposure to 0.125 µg/l, but the hatchability of the eggs was reduced from 69% in controls to 39% (Merna and Eisele, 1973). Yellow perch seem to be less sensitive than fathead minnows.

Merna and Eisele (1973) also did chronic exposures of several invertebrates for 28 days and monitored survival, pupation, and/or emergence. Emergence for Stenonema was unaffected at 0.25 µg/l. Pupation of Cheumatopsyche was unaffected at 0.125 µg/l, but the growth rate of this species was affected by the exposure.

Eisele (1974) dosed a small stream with a 0.2 µg/l methoxychlor continuously for one year. No insect or fish mortalities were observed. No invertebrate species were eliminated, but populations of baetids, stoneflies, and scuds were reduced. Hydropsychids, blackflies, crayfish and dragonflies showed only temporary changes before returning to control levels when exposed to continued dosing. While some species increased, there was no change in the diversity or density of invertebrates. There was however, a slight reduction in biomass. Most effects were sufficiently subtle so that routine ecological surveys would not have uncovered them. Crayfish body burdens rose to approximately 100 µg/g methoxychlor, incidating a concentration factor of 500.

In evaluating the above data, most weight was placed on studies which explored chronic effects under field conditions. The 0.2 mg/l exposure which produced subtle effects on some invertebrate populations. Application of the arbitrary 0.2 safety factor to these subtle effects was used to estimate the "safe" concentration of 0.004 µg/l recommended.

Methoxychlor may not conform to the definition of a persistent compound. It degrades readily and the structure of its probable metabolites would not indicate that they are likely to be persistent either. However, the actual rate of degradation is not indicated in the literature and it has been considered under the category of persistent contaminants due to its organochlorine pesticide nature. If it were classified as non-persistent, consideration would be given to the lowest reported 96-hr LC_{50}

concentrations which pertain to crustaceans (0.8 to 5 μg/l; Sanders, 1969; Sanders and Cope, 1966) and to insects (0.6 to 1.4 μg/l; Sanders and Cope, 1968; Merna and Eisele, 1974). Regardless of application factors, since good experimental and field data exist for deriving "safe" levels for this compound, these should be employed in setting the recommended level.

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TOXAPHENE

RECOMMENDATION

It is recommended that the following numerical objective for toxaphene be adopted to replace, in part, the existing objective for persistent organic contaminants in Annex 1, paragraph 2(c) of the Agreement:

> *The concentration of toxaphene in water should not exceed 0.008 μg/l for the protection of aquatic life.*

RATIONALE

Mayer et al. (1975) report decreased reproduction of brook trout when exposed to concentrations of 0.068 μg/l of toxaphene in water. Body burdens associated with this exposure were 0.6 μg/g. In a chronic bioassay with brook trout, Mayer et al. (1975) found that toxaphene in water, at a level of 0.039 μg/l, affected the growth and development of brook trout fry over an exposure period of 90 days. With the application of the safety factor of 0.2, a "safe" concentration of toxaphene is calculated to be 0.008 μg/l.

Acute toxicity of toxaphene to fish has been reported as 4.3 μg/l for bullheads (Mahdi, 1966). Lawrence (1950) reported the acute toxicity to bluegills as 3.5 μg/l in soft water. Acute toxicities have also been reported for several species of fish be Macek (1970), ranging from 2 μg/l for largemouth bass to 13 μg/l for black bullhead, and by Nagvi and Ferguson (1970) for freshwater shrimp as 24-hr LC_{50}, ranging from 41 to 283 μg/l in four different lakes.

Schoettger and Olive (1961) reported mortality of kokanee salmon when fed Daphnia which were exposed to sub-lethal concentrations of 10 and 20 μg/l of toxaphene over periods of 120 to 312 hours. Hughes (1968) reported that toxaphene treated lakes (40 to 150 μg/l) remained toxic to fish for periods of a few months to five years after treatment. The persistence of toxaphene, and its highly lipophilic character would suggest the potential for bioconcentration and transfer through the food chain to higher trophic levels. Bioconcentration factors of 5,000 to 21,000 for brook trout (Mayer et al., 1975), and 1,000 to 2,000 for aquatic invertebrates (Terriere et al., 1966) were observed. Bioconcentration of toxaphene in fathead minnows were observed to be in the range of 77,000 to 108,000 (Mayer et al., 1975). However, these factors have not been related to deleterious body burdens, and, therefore, no recommendation for tissue concentrations of toxaphene can be set at this time.

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ii) OTHER COMPOUNDS

PHTHALIC ACID ESTERS

RECOMMENDATION

It is recommended that the following numerical objective for phthalic acid esters be adopted to replace, in part, the existing objective for persistent organic contaminants in Annex 1, paragraph 2(c) of the Agreement:

> *The concentrations of dibutyl phthalate and di-(2-ethylhexyl) phthalate in water should not exceed 4.0 µg/l and 0.6 µg/l, respectively, for the protection of aquatic life. Other phthalic acid esters should not exceed the recommended quantification limit of 0.2 µg/l in waters for the protection of aquatic life.*

RATIONALE

It is recognized that the phthalic acid esters (PAE's) are probably non-persistent in water and aerobic sediments. However, there is some evidence that some PAE's may persist in anaerobic sediments, and for that reason they are provisionally included with the persistent organic chemicals. Since they are distinct compounds, not necessarily occuring together, a list of some of the more common ones are indicated.

Phthalic Acid Esters

Di-(2-ethylhexyl) phthalate (DEHP)
Di-iso-cotyplthalate (DIOP)
Di-octylphthalate (DOP)
Di-butylphthalate (DBP)
Di-ethylphthalate (DEP)
Di-methylphthalate (DMP)

The occurrence of PAE residues in North American environments was reviewed at a conference on PAE's sponsored by the National Institute of Environmental Health Sciences (1972), by Mathur (1974) and by Mayer et al (1972). Within aquatic ecosystems, PAE residues have been detected in fish, water and sediments, and sources are most likely municipal and industrial effluents (Mayer, et al., 1972; Stalling et al., 1973; Hites, 1973; Lake Michigan Toxic Substances Committee, 1974). Monitoring surveys by several Great Lakes states showed that effluents of industrial and municipal waste treatment facilities contained PAE's in concentrations ranging from less than 1 to 1,200 µg/l and tributaries to Lake Michigan contained 1 µg/l or less. The fate of PAE's discharged into these tributaries is not well defined, but analyses of settleable solids showed residues ranging from 1 to 75 µg/g (dry wt). These results suggest that PAE's may be adsorbed to particulate materials in streams and ultimately deposited in bottom sediments.

Whether PAE's such as DEHP and DBP are biologically degraded in waste treatment plants or sediments of natural ecosystems has not been fully investigated. Graham (1973) reported that laboratory-scale, activated sludge processes degraded 91% of DEHP within 38 hours. However, analyses of sewage sludge from 54 municipal sewage treatment plants showed DEHP residues of 17 to 884 µg/g (dry wt.) (Lake Michigan Toxic Substances Committee, 1974). Thus, either activated sludge processes are not efficient in degrading PAE's, or raw sewage contains very large amounts of PAE's. Laboratory incubation of DEHP and DBP with pond hydrosoils suggests that natural micro-organisms do, in time, hydrolyze the ester linkage and decarboxylate the phthalic acid moiety (Johnson, 1974). In aerobiosis studies, 98% of DBP was degraded after 5 days at 20°C, but only 50% of DEHP was degraded at 14 days. Under anaerobiosis, degradation of both PAE's was significantly retarded. Thus, although there is laboratory evidence for some biological degradation of PAE's, little is known of the dynamics of PAE residues in natural sediments. These dynamics could be affected by continuous or intermittent input of PAE's, oxidation-reduction state of the sediment, temperature, type of sediment, and probably other factors. In any case, limited monitoring data (Lake Michigan Toxic Substances Committee, 1974) suggest that PAE's may occur in bottom sediments and, therefore, important bottom-dwelling macro- and micro-fauna could be exposed to significant PAE residues.

DBP residues in fish from several areas of North America range from less than detectable concentrations of 0.5 µg/g, and DEHP residues have been found as high as 3.2 µg/g (Mayer, _et al_ 1972; Stalling _et al_. 1973). PAE residues in Great Lakes area fish range from undetected to 1.3 µg/g (Lake Michigan Toxic Substances Committee, 1974). However, one third to one half again as much residue may also be present in fish in the form of the monoester or conjugates of the monoester and phthalic acid (Mayer _et al_., 1972; Mayer and Sanders, 1973). Mayer and Sanders (1973) exposed fathead minnows _(Pimephales promelas)_ to 1.9 µg/l of DEHP for 56 days and found that residues reached an equilibrium concentration of 2.6 µg/g within 28 days. This gave an accumulation factor of nearly 1,400, which agrees well with data for DEHP in bluegills _(Lepomis macrochirus)_ exposed to 0.1 µg/l (Johnson, 1974). However, Mayer and Rogers (1972) found that accumulation factor for DEHP in fathead minnows was reduced to 160 when the fish were exposed to a higher concentration of 60 µg/l.

Accumulation factors for DEHP and DBP in aquatic crustacea and insects are generally between 350 and 3,900 following exposures ranging from 0.08 to 0.03 µg/l (Mayer and Sanders, 1973). When fish and invertebrates containing PAE residues are placed in untreated water, they eliminate 50% of the residue within 3 to 7 days. Residues in fish and invertebrates have not as yet been correlated with untoward biological effects.

Toxicity

The acute 96-hour LC_{50} values for DBP with fathead minnows, channel catfish (Ictalurus punctatus), rainbow trout (Salmo gairdneri), scud (Gamarus pseudolimnaeus) and crayfish (Orconectes nais) fall between 730 and 10,000 µg/l (Mayer and Sanders, 1973). Although the toxicity of DEHP is more difficult to determine in static tests because it is less soluble in water, 96-hour LC_{50} values are estimated to be above 10,000 µg/l. Flow-through tests were used for scud (G. fasciatus) and gave a 9-week LC_{50} value of 210 µg/l (McKim, 1974). The acute toxicities of both DBP and DEHP are considerably below those of most organochlorine insecticides which are usually toxic between 0.1 and 50 µg/l.

The chronic toxicities of DEHP and DBP have not been as well defined as desired. However, the chronic studies so far completed suggest that both DEHP and DBP are biologically active at concentrations well below acutely toxic concentrations. McKin (1974) reported that growth of brook trout (Salvelinus fontinalis) was reduced significantly at a DBP concentration of 300 µg/l, but not at 90 µg/l. However, aquatic invertebrates appear to be more sensitive than fish. Reproduction in daphnids (Daphnia magna) is impaired by DBP and DEHP concentrations of 20 and 3 to 5 µg/l, respectively (Mayers and Sanders, 1973; McKim, 1974). The emergence of adult midges, (Chironomus tentans) is reduced significantly at a DEHP concentration of 14 µg/l (Mayer and Rodgers, 1972).

Employing the chronic data for daphnids and the safety factor of 0.2 recommended maximum levels of 4 µg/l for DBP and 0.6 µg/l for DEHP are obtained. It is further recommended that until such time as chronic data on other PAE's become available, concentrations of other individual PAE's in water be restricted to the recommended quantification level of 0.2 µg/l.

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POLYCHLORINATED BIPHENYLS

RECOMMENDATION

It is recommended that the following new objective for polychlorinated biphenyls be adopted:

> *The concentration of total polychlorinated biphenyls in fish tissues (whole fish, calculated on a wet weight basis), should not exceed 0.1 micrograms per gram for the protection of fish consuming birds and animals.*
>
> Note: The Subcommittee expresses concern that a water concentration objective for this ubiquitous contaminant is unavailable. Based upon poorly defined bioconcentration factors it may be concluded that PCBs in water should not exceed 0.001 micrograms per litre. However, this level may not be adequate to provide protection to certain predators, and could presently not be enforced because of insufficiently sensitive quantification limits.

RATIONALE

In North America polychlorinated biphenyls (PCBs) are manufactured solely by the Monsanto Chemical Company and are distributed under the trade name AROCLOR^{R}. Each Aroclor is a mixture of various isomers of which 210 may occur in theory, the actual number of isomers formed chemically is probably closer to 100. In addition, a significant percentage of these isomers has been predicted to exist in pairs of optically active forms (Kaiser, 1974).

Polychlorinated biphenyls are now known to constitute the third most widely distributed pollutants on Earth, exceeded only by the chlorinated insecticides DDT and dieldrin. Similar to the latter compounds, PCB residues are found in the fat deposits of numerous warm and cold-blooded animals including man. Their persistence is generally considered to be greater than most chlorinated insecticides. In the aquatic environment, PCBs have been detected in water, sediments, invertebrates, fish and waterfowl with highest levels being recorded in predatory organisms high in the food chain. While greater quantities are found in areas close to heavy industrialization, substantial residues have been detected in fish from undeveloped localities suggesting that aerial transport may play a significant role in their distribution.

PCBs In Great Lakes Waters

Contamination of the Great Lakes by PCBs has been, and continues to be, extensive. Fifty-seven percent of water samples from 30 major tributaries analyzed by Michigan Water Resources Commission (1971) contained detectable concentrations of PCB (0.01 µg/l). Mean values determined for Michigan tributaries of Lakes Michigan, Huron, Superior, St. Clair and Erie were .023 µg/l, .228 µg/l, .010 µg/l, .081 µg/l, and .186 µg/l total PCB respectively. The Canada Centre for Inland Waters examined open waters of Lakes Ontario and Erie during 1971 and measurable quantities were found in 60 percent and 63 percent of the samples respectively. Summaries of data from the three basins in each lake are presented in the Report of the IJC Boards to the IJC (1972). The highest mean value was 0.062 µg/l for bottom waters of Lake Ontario (western region), while the lowest was .012 µg/l for the surface of Lake Ontario (eastern region). Lakewide means of surface and bottom samples were .030 µg/l and .032 µg/l respectively for Lake Ontario, and .027 µg/l and .025 µg/l for Lake Erie. Samples taken from Hamilton Harbour (Lake Ontario) by the Ontario Ministry of Environment in 1972 showed ranges of PCBs in water of .035 - .095 µg/l and 0.2 - 10.1 µg/g in sediments (Berg et al., 1974).

PCBs In Biota

The contamination is also widespread. The U.S. Food and Drug Administration guideline of 5 µg/g in edible tissue has been exceeded in numerous species in Lake Michigan including lake trout, coho salmon, chinook salmon and chub. In Lake Huron, walleye, whitefish, and catfish are above the tolerance level and likewise smelt and coho salmon in Lake Ontario. PCB concentrations in Lake Erie fish are generally below 5 µg/g with the exception of white bass (Report of the IJC Boards to the IJC, 1972). Recent analyses by the Ontario Ministry of the Environment on fish from the St. Clair River revealed muscle concentrations of 4.3 - 12.3 µg/g in white bass, 0.1 - 6.8 µg/g in pike, 0.1 - 2.8 in white suckers and 1.5 - 4.7 µg/g in coho salmon. Perch from Lake St. Clair showed levels of 0.1 - 0.25 µg/g and in the same area walleye contained 0.2 - 3.0 µg/g (Berg et al., 1974).

A serious situation exists with respect to populations of fish eating birds in the vicinity of the lower Great Lakes. Severe reproductive failure has been identified in herring gull colonies around Lake Ontario. While eggshell thinning has been correlated with DDE content of the eggs there is a positive correlation between early embryonic mortality and PCB contamination (Gilbertson and Fox, 1975). Geometric means for PCBs in eggs of four fish-eating bird species are given below in Table 1 (Gilbertson and Reynolds, 1974).

TABLE 1 - PCB RESIDUES IN BIRD EGGS

(µg/g, dry weight basis)

Location	Herring gull	Ring-billed gull	Common tern	Double-crested cormorant
Lake Nipigon				77.5(52)
Lake Huron	368(5)	113(2)	81.7(8)	140.0(55)
Detroit River	520(2)			
Lake Erie	300(6)	243(4)	156(15)	63.7(18)
Hamilton Harbour			258(71)	
Lake Ontario	565(16)	379(4)	268(20)	114(7)

The major effect of PCBs on young birds is to produce symptoms of chick edema disease. The symptoms are subcutaneous pericardial and abdominal edema, prophyria, liver necrosis and high mortality (Gilbertson, 1974; Gilbertson and Hale, 1974; Gilbertson and Fox, 1975). In herring gull chicks from Lake Ontario colonies poor hatching success is associated with levels of PCB's of over 900 µg/g on a dry matter basis in the liver - amongst the highest levels in the world. Less severe signs were seen in Lake Erie chicks at about 600 µg/g, but were not completely absent in a control group from outside the Great Lakes at about 35 µg/g. Clearly, even the Lake Erie group is contaminated by more than an order of magnitude above these.

In summary there can be little doubt that the existing state of PCB contamination in the Great Lakes system is excessive. Of particular concern must be the higher forms of life in which the process of bioconcentration causes the greatest residues to be accumulated. At present, there are insufficient data to estimate water concentrations of PCBs which will assure protection of predatory fish, fish eating birds and other predators; this will require greater understanding of the correlation of dietary intakes and bioconcentration factors.

Effects of PCBs On Biota

PCBs are toxic to aquatic life by direct exposure and are hazardous also to consumers of contaminated fish. Reproduction of midges and *Daphnia magna* was reduced at 0.45 µg/l (Aroclor 1254) and 1.3 µg/l respectively (Nebeker and Puglisi, 1974). The highest concentration of Aroclor 1248 having no effect on the fathead minnow was about 0.3 µg/l (National Water Quality Laboratory, 1974), a concentration which resulted in tissue residues of about 90 µg/g or 18 times the guideline for human consumption recommended by U.S. and Canadian federal health authorities. This indicates a bioconcentration factor for fathead minnows of approximately 3 x 10^5. The factor for bluegills with Aroclors 1248 and 1254 has been estimated at 7.1 x 10^4 (Stalling and Mayer, Jr., 1972) while large Lake Michigan coho salmon have mean tissue values of about 15 μg/g (Veith, 1973) which is 1.5 x 10^6 times greater than the maximum open water concentration of around 0.010 μg/l (Lake Michigan Toxic Substances Committee Report).

Two μg/g PCBs in fish flesh has been shown to prevent survival of newborn commercial ranch mink (Ringer et al., 1972) while reproduction was eliminated in mink fed a beef diet containing 0.64 μg/g Aroclor 1253 (Platonow and Karstad, 1973). While this is not a subtle effect, it is the lowest dietary concentration observed to produce a deleterious biological effect. The safety factor of 0.2 applied to this results in the recommended tissue level of 0.1 μg/g.

The recommendation for PCBs is designed to protect the aquatic biota as well as the consumer of aquatic life. A conservative bioconcentration factor of 10^5 could be used to calculate a water concentration for total PCBs which should prevent tissue levels greater than 0.1 μg/g. This would result in a PCB concentration in water of less than 0.001 μg/l, a concentration which would be beyond the present routine analytical sensitivities and therefore impossible to monitor or enforce. It is therefore recommended that the regulatory agencies undertake fish and bird monitoring programs to determine compliance with the recommendation regarding tissue levels.

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OTHER ORGANIC CONTAMINANTS

For other organic contaminants, the concentrations of which are not specified but which can be demonstrated to be persistent and are likely to be toxic, it is recommended that the concentrations of such compounds in water or aquatic organisms be limited to the detection level as determined by the best scientific methodology available at the time.

Note: Such a compound for which concentrations cannot be specified is Mirex, a rationale for which appears along with those for compounds specified above.

Note: Where waters are found to be contaminated as defined by exceeding the appropriate objective, all reasonable and practicable measures should be taken by the regulating agencies to reduce the input of the persistent organic contaminant to any part of the Great Lakes System.

EXISTING OBJECTIVE

The recommended numerical objectives are intended to replace the existing interim objective in Annex 1, paragraph 2(c) of the Agreement which states:

> "Persistent Organic Contaminants. Persistent pest control products and other persistent organic contaminants that are toxic or harmful to human, animal or aquatic life should be substantially absent in the waters."

RATIONALE

Synthetic organic contaminants entering surface waters may be broadly divided into persistent and non-persistent compounds. The distinction is important since the organic contaminants known to present the greatest hazard to human, animal and aquatic life are those which are resistant to degradation and which are thus available for dispersion in the environment and for incorporation into biological tissues. Concentrations of persistent organic contaminants in the aquatic environment seldom achieve acutely-toxic proportions except in localized situations due to accident or misuse. Of much greater concern are effects due to long-term exposure at sub-lethal levels and bio-concentration of residues resulting in tissue accumulations of increasing magnitude with each higher level in the aquatic food chain. For these reasons it is necessary to consider persistent contaminants separately from those which are readily decomposed to non-toxic constituents.

Persistent organic contaminants are, according to the Canada-U.S. Agreement, to be "substantially absent" from Great Lakes waters. While the Water Quality Objectives Subcommittee would like to interpret this as completely absent from the aquatic ecosystem, it is constrained by the need to justify selected levels based upon protection of all potential uses.

Consequently, it recommends levels based upon (1) protection of all aspects of aquatic life and human health as measured by water and tissue levels, (2) quantification limits for water concentrations, and (3) drinking water and food standards when these levels are limiting. Recreational effects of persistent organic compounds in water, with the possible exception of oil (covered under a separate objective), do not present any limitations to the introduction of such material into the water system. Agricultural use levels also are not likely to provide adequate protection for aquatic life.

Persistence

A persistent compound is defined as one which either (a) by itself or as its transformation product, has a half-life for degradation under natural environmental conditions of more than eight weeks, or (b) by itself or as its transformation product, on entering surface waters may bioconcentrate in the biota of the receiving system.

Persistence is the property of chemical compounds, measured in units of time, which describes their ability to resist structural alteration under specific physical and chemical conditions. Under similar environmental conditions, different compounds exhibit different persistences depending on their molecular configuration. No standard test of persistence has yet been developed and, consequently, the term lacks precise definition. This is reflected in the common practice of arbitrarily classifying environmental contaminants as persistent when their presence can be demonstrated in different substrates several days or weeks after release.

The development of a standard test of persistence is a desirable precursor to the introduction of an objective for persistent contaminants in water. However, such a test cannot be artibrarily selected, will require careful research and evaluation, and must be generally acceptable to the scientific community before its application for regulatory purposes. Whereas such research should be stimulated at the earliest opportunity, there is no possibility that an acceptable test for 'persistence' can be developed for incorporation into the impending revision of the U.S. - Canada Agreement on the Great Lakes' Water Quality. Thus, if the word 'persistence' is to appear in the objectives it must include the present broad meaning indicated in (a) of the above definition.

A laboratory study of eight organochlorines, ten organophosphorus and seven carbamate compounds showed marked differences in persistence in river water over an eight week period (Eichelberger and Lichtenberg, 1971). The results indicated, however, that 50% or more of the initial concentrations (10 µg/l) of all major environmental contaminants studies remained at the termination of the study. Thus a halflife of eight weeks would appear to be a reasonable criterion for the separation of persistent and non-persistent compounds in water.

In keeping with the intent of the objectives that persistent organic contaminants be substantially absent, the definition has been modified to include the property of bioconcentration potential so as to provide for the distinct possibility that levels in tissue may accumulate from water concentrations below those which can be detected. This effect is provided for in part (b) of the definition.

While the problem of bioconcentration is real and is the reason for the inclusion of tissue levels in the objectives, bioconcentration factors are not standardized, sometimes combining dietary and direct water uptake, and sometimes being acquired from systems considerably above the solubility of the compound under examination. As a consequence of these, and other difficulties in determining this factor, no defensible objective can presently be made based primarily upon this influence. It is hoped that future work in this area may allow the situation to change.

Aquatic Life

Body burdens of persistent organic contaminants in aquatic biota and those of their predators may become limiting for species survival. Most of such compounds are classified by organic chemists as "non-polar" and as such they are very insoluble and are liable to occur predominantly as adsorbed material on the particulate load. From there it may be ingested along with the particulates, thus entering the food chain, or it may be deposited in the sediment from where it can enter via benthic organism. Fish may also absorb these compounds directly through the gills. In higher trophic organisms, the persistent material usually ends up in the liver or in the adipose tissue due to its preferential solubility in fats and oils over that in aqueous fluids. In amny cases, bioconcentration occurs as well since the material then may not readily be excreted by the organism. As a consequence of these considerations, sediments, plankton, fish tissue and predators of fish are probably better indicators of the presence of persistent organic contaminants than is water. Predators are of concern since avian and other non-aquatic predators feed on aquatic life and their body burdens may accumulate to toxic levels as a result. Since fish are the food source of concern for these predators, levels are largely set for fish tissue, but where it can be shown that detrimental effects occur in the predators the tissue level objective should be extended to include the predators.

The dynamics of adsorption also give rise to increased levels of persistent organic contaminants in the sediments. However, sediments are prone to movements over large distances through current action and additionally, present technology does not permit the determination of their deposition rates on a useful time scale for these monitoring purposes. Hence, they presently can only give indications of the presence of the contaminants but cannot easily be related to detrimental effects. It is recommended that studies be undertaken into such sampling methods as would permit the use of sediment levels for measuring contamination but for the present, criteria are not recommended for this compartment of the ecosystem.

Specific recommendations have been made for those cases where significant studies have determined "safe" levels for representative fish and invertebrate species by chronic toxicity experiments. In cases where subtle and deleterious effects were noted at the lowest chronic dose level (e.g. a partial reduction in hatchability of eggs), an arbitrary safety factor of 0.2 was applied to estimate the "safe" level. In cases where the acute toxicity studies indicated that some species of fish were more sensitive than those actually investigated, an experimentally determined application factor for fish for the compound in question was utilized to estimate a "safe" level for the more sensitive species of fish. Data for invertebrate studies were handled in the same fashion.

When chronic field studies were available which documented water concentrations and used intensive ecological analyses, these were given greater weight than laboratory studies. Concentration factors for pesticides from water to aquatic life were found to be too variable (often greater than an order of magnitude) to utilize meaningfully in the establishment of water quality criteria. Therefore, body burdens of various persistent chemicals in fish were utilized directly, when appropriate information existed. Protection of wildlife which consumes aquatic life, is based on chronic feeding studies of sensitive species and calls for restrictions on body burdens.

It is the intent of the Agreement to protect boundary waters of the Great Lakes System as a raw public water supply which will produce a safe drinking water after treatment. In addition, the use of fish for human consumption should be protected. Existing standards for most of the toxic persistent organic contaminants are inadequate to protect aquatic life. Protection of fish as a resource is provided by guidelines of the U.S.F.D.A. for three persistent organics. (See recommendations). As new standards related to raw water supplies or drinking water which are lower than recommended water concentrations are developed and adopted by Canadian or U.S. federal agencies. They should be adopted as part of the specific objectives, as should new edible tissue guidelines from U.S. Food and Drug Administration or the Canadian Food and Drug Directorate.

Quantification Limits

The water quality objectives proposed for persistent organic contaminants have been based on the intent expressed within the existing Agreement which is that such materials should be "substantially absent" within the boundary waters of the Great Lakes. The assumed philosophy, which is perpetuated here, is that danger exists in allowing persistent materials of unknown fate or biological significance to be added to surface waters within arbitrarily established limits because there is no assurance that bioconcentration will not occur and reach unacceptable levels. Corrective action may come too late to offset serious environmental consequences. Therefore, the philosophy of substantial absence of these substances is endorsed. In a practical sense, this is that concentration which is below that which can be quantified. That such quantification limits should be the objective for compounds without "safe levels" is indicated in the preceeding, but it should be particularly so for proven carcinogens. In a survey of some ten laboratories in the Great Lakes region which are currently doing routine determinations of pesticides and other persistent organic contaminants, the following means and ranges of quantification limits were reported, Table 2.

TABLE 2

PERSISTENT ORGANIC CONTAMINANTS QUANTIFICATION LIMITS

Compound	Mean µg/l	Range µg/l	Recommended Quantification Limit µg/l
Lindane	.004	.001-.010	.001
Heptachlor	.004	.001-.010	.001
Heptachlor Epoxide	.004	.001-.010	.001
pp'-DDD	.012	.001-.050	.002
pp'-DDE	.011	.001-.050	.002
pp'-DDT	.011	.001-.125	.003
op'-DDT	.014	.001-.045	.003
Aldrin	.004	.001-.010	.001
Dieldrin	.008	.001-.025	.001
Endrin	.008	.001-.020	.002
Chlordane	.005	.002-.010	.002
Total PCB	.035#	.020-.100#	.010
pp' Methoxychlor	.020	.010-.050	.010
Phthalate esters	.6	.1 -1.5	.2

\# does not include a single high value of 1.5 µg/l.

* the mean of the lowest three values reported.

The third column is the mean of the lowest three quantification limits reported. Since it is desired to provide incentive to the development of more sensitive procedures, and not to condone insensitive determination, it is these means which are recommended. They are employed, where appropriate, for specification of concentrations for which experimental data are not available to produce "safe" water levels but where there are data to establish "safe" tissue levels.

Where an organic compound can be demonstrated to be persistent and likely to be toxic and for which data are unavailable to establish either "safe" water or tissue concentrations, it is recommended that its concentration in water or aquatic organisms be limited to the detection level as determined by the best scientific methodology available at the time.

These quantification and detection limits, however, should not be accepted as permanent substitutes for experimentally determined "safe" concentration - rather it is intended that they should stimulate research on safety evaluations and analytical methods, plus provide a mechanism for action in the case of newly observed contaminants.

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b) INORGANIC

i) Metals

INTRODUCTION

It can be generally stated that all natural elements, (metals, metalloids and non-metallic elements) are present in all natural waters, in sediments, and in most living matter. For the majority of these elements, their occurrence is in minute concentrations, much below analytical detection limits of sophisticated monitoring (less than μg/l concentrations). Obviously for most of these elements, no environmental concern is valid unless they are discharged at concentrations greater than present in the receiving waters.

Metals, such as sodium, potassium, calcium and magnesium are found in mg/l concentrations in most waters. They are essential to all forms of life as basic components of skeletal systems and for many biological processes in general. Ions of such metals are not lethal by themselves unless at very high concentrations (> 1,000 mg/l). On the other hand, metals, in particular aluminum, selenium and arsenic, are common to all natural aquatic systems in the μg/l range. In trace quantities, some of these elements are essential for certain biological processes while others have no known functions. Whether essential or not, these elements are lethal to biota at high concentrations (> 100 mg/l) and, in a few cases, their natural background levels are approaching toxic concentrations. To protect the aquatic ecosystem, these elements should not be allowed to increase in their concentrations, through man's activities.

Sources for all elements in surface waters are the result of weathering of rocks and soils (Table 3), industrial and municipal effluents and precipitation of airborne matter. In fact, it has been calculated that some large lakes with comparatively little human activity in the drainage basin may derive the major part of their metals from precipitation. Lake sediments especially in shallow lakes, may also be an important source of trace metals. Such a recycling has been observed for mercury and is well known for the element phosphorus.

Chemistry

Dissolved Metals

In distilled water, dissolved metals largely exist in "free" ionic form, that is, as very weakly complexed hydroxy or aquo complexes. Because of their low complex formation constants, these elements are readily available for any chemical reaction and for biological uptake. Consequently, any uptake by organisms of such ionic metals from water will be rapid and proportionate to their concentration.

TABLE 3

AVERAGE CONCENTRATIONS OF METALS IN ROCKS IN mg/kg (Bowen, 1966)

METAL	IGNEOUS ROCK	SHALES	SANDSTONES	LIMESTONES	SOILS	COAL
Al	82,300	80,000	25,000	4,200	71,000	----
As	1.8	13	1	1	6	25
Cd	.2	.3	.05	.035	.06	.25
Cr	100	90	35	11	100	60
Cu	55	45	5	4	20	300
Fe	56,300	47,200	9,800	3,800	38,000	----
Hg	.08	.4	.03	.04	.03	----
Pb	13	20	7	9	10	5
Ni	75	68	2	20	40	35
Se	.05	.6	.05	.08	.2	< 7
Ag	.07	.07	.05	.05	.1	.1
Zn	70	95	16	20	50	40

However, natural waters always contain a significant amount of dissolved organic material including human acids, lignin derivatives, fatty acids, amino acids, many other compounds from plant and animal origin, as well as increasing amounts of synthetic chemicals. Most of these compounds have one or more functional groups, such as hydroxy-, carboxy, sulfo- and amino- groups, which may combine with "free" metal ions to form metal-ligand complexes. Depending on the detailed structures of such ligands and the chemical characteristics of the metal ions, complexation can completely mask the availability of the metal ions for common reactions. Of course, any two ligands will act differently on a given set of metal ions and, as a result, the biological effects of a mixture of metal ions and organic compounds is extremely difficult to predict. If, as in the case of certain synthetic chemicals, the complex formation is very strong and no other physical, chemical or microbial degradation of the complex took place, quite high concentrations of toxic metal ions could be present without immediate harmful effects to aquatic life.

Organo-metallic Compounds

Chemical compounds of organo-metallic nature, that is with directcarbon-metal bonds, have been known to chemists for a long time. Recently it has been found that certain metals (for example mercury,) can be methylated by microbial action in sediments and these compounds can enter the aquatic food chain. Because of their partially organic nature, such compounds are likely to be associated with fatty tissues, where they may be stored and accumulated. At the same time, these compounds may produce strong toxic effects on the accumulator organism.

There is still comparatively little understanding of the biological and environmental behaviour and effects of organo-metallic compounds. Studies to determine which elements can be methylated or transformed to organo-metallic forms in aquatic ecosystems are presently underway. So far, in addition to mercury and arsenic, the elements lead, tin, cadmium and selenium may be able to undergo such reactions.

Particulate and Colloid Metals

Trace metals may also be found in water in forms such as hydroxides, oxides, silicates, phosphates or carbonates which are commonly part of the particulate matter from either biological or mineral origin. Metals which become absorbed or chemically bound by particulate organic matter are sedimented with the organic matter thereby providing a major route for their removal from aquatic systems.

Additionally, trace metals may be found as hydroxides and their dehydrated forms in very finely dispersed particulate matter of a few hundred to a few thousand molecular units. These aggregates or colloids are usually formed by precipitation of dissolved metals as a result of pH changes, oxidation or through biological action. Processes of that nature occur primarily in effluents entering water of different quality. Because of the very small size of colloids and their inherently large surface area and high chemical and biological activity, they may be toxic to biota to a much higher degree than large size particulate matter of a similar chemical composition.

Analysis and Great Lakes Concentrations

Present analytical methods for the quantitative determination of metals in water, sediments and biota include the following: atomic absorption spectrometry, neutron activation analysis, polarography, anodic stripping, voltammetry, specific ion electrodes, titration with specific reagents and spectrophotometry.

As previously discussed, metals are found in dissolved, complexed and particulate forms in water. Consequently, analyses are performed for dissolved, suspended, extractable and total metals. At present, most analyses are for total metal, which may include dissolved and adsorbed or suspended metals irrespective of their oxidation state or form of complexation.

Many metals occur in natural waters at concentrations below direct routine analytical detectability. In such cases concentration procedures, usually by solvent extraction, have to be applied in order to obtain reliable quantitative results at these low levels.

Water samples for metal analyses are generally preserved by adding acid to pH 2 or less. At this pH all metals become available for solvent extraction except those very strongly bound by ligands.

Difficulty was experienced in obtaining accurate data on concentrations of metals in Great Lakes waters. Unpublished raw data from monitoring often contained incorrect values due to sample contamination at some stage between collection and analysis. Since analyses are generally quite accurate, the problem is one of sample collection and storage. Consequently, metal concentrations in offshore Great Lakes waters in Table 4 include only summary statistics derived from well-screened raw data on specific metals from the upper lakes. Similar statistics are not available for Lakes Michigan, St. Clair, Erie and Ontario. Other data on concentrations of metals in waters is from published sources and the accuracy of the data has not been assessed.

Biological Effects and Monitoring Problems

Sprague (1970) in his review of the utility of bioassay results indicated that for fish at different times and places, "precipitated" zinc was less toxic, equally as toxic or more toxic than "ionic" zinc. This ambiguity was probably the result of the inability of various authors to measure the various forms

Table 4

Concentrations (μg/l) of metals in filtered water samples from the epilimnion of the Upper Great Lakes. These statistics represent values from many stations within a lake sampled several times within a year. The statistics are derived from an unpublished draft of the 1975 Report of the Upper Lakes Reference Group, IJC. Data on Lake Huron, Georgian Bay and the North Channel are from Vol. II, Chapter 5.3 and the data for Lake Superior, are from Vol. III, Chapter 5.3

	LAKE SUPERIOR, - 1973				NORTH CHANNEL, LAKE HURON - 1974			
	Detection Limit (D.L.)	Percent of Samples below D.L.	Modal Conc'n.	95 percentile Concentration	Detection Limit	Percent of Samples below D.L.	Modal Conc'n.	95 percentile Concentration
Cadmium	0.2	72	≤0.2	0.6	0.2	100	≤0.2	0.2
Chromium	0.2	63	≤0.2	0.4	0.2	95	≤0.2	0.2
Copper	0.5	5	2.0 - 2.5	5.0	0.5	5	1.0	4.0
Iron	0.5	3	1.0 - 1.5	7.0	0.5	3	1.5 - 2.5	4.5
Lead	1.0	63	≤1.0	3.0	1.0	98	≤1.0	1.0
Mercury	0.05	7	0.1 - 0.15	0.25	-	-	-	-
Nickel	1.0	46	≤1.0	5.0	1.0	10	2.0 - 5.0	6.0
Zinc	1.0	72	7 - 10	40	1.0	2	3.0	6.0

	GEORGIAN BAY, LAKE HURON - 1974				LAKE HURON, - 1971			
	Detection Limit (D.L.)	Percent of Samples Below D.L.	Modal Conc'n.	95 percentile Concentration	Detection Limit	Percent of Samples Below D.L.	Modal Conc'n.	95 percentile Concentration
Cadmium	0.2	96	≤0.2	0.2	0.2	98	≤0.2	0.2
Chromium	0.2	94	≤0.2	0.4	0.1	70	≤0.1	0.6
Copper	0.5	25	1.0	4.5	0.25	28	≤0.25	*
Iron	0.5	5	1.5	3.5	0.25	12	1.0	2.0
Lead	1.0	90	≤1.0	1.0 - 2.0	0.5	38	≤0.5	1.5
Mercury	-	-	-	-	-	-	-	-
Nickel	1.0	10	2.0	5.0	0.5	87	≤0.5	5.0
Zinc	1.0	20	2.0	9.0	0.5	54	≤0.5	*

***Could not be determined from the data available.**

of zinc. On the other hand, toxicity of copper has been related, with reasonable success, to measurement of specific forms.

As a working method for some metals, fairly good correlations with biological availability and hence toxicity, have been obtained by assuming that soluble toxic forms pass a 0.45 μ filter while insoluble non-toxic forms do not. It is recognized however, that the actual separation of these forms is not that simple. Forms which were retained by the filter could be a reservoir of potentially toxic forms which may readily redissolve under changing conditions. Pulse polarography has been used to measure "labile" and "non-labile" forms of copper, but lability has not been directly related to toxicity to algae (Gächter et al., 1973). Specific ion electrodes were used to measure ion activity of copper (Zitko et al., 1973). While the measured ion activity was roughly related to copper toxicity to salmon, an ion activity below 200 μg/l could only be determined by extrapolation. Shaw and Brown (1974) also correlated copper toxicity to trout with ion activity as well as with estimated concentrations of carbonate-complexed and NTA-complexed copper. They concluded that toxicity was best characterized by the total of copper (II) (≃ ion activity) and copper carbonate and not by a single form alone.

The standard chemical procedure of acidifying samples to pH 2 solubilizes many loosely-bound forms of copper (= "acid extractable"). While this may be undesirable when carrying out toxicity tests, it is an essential procedure for assessing loadings and for assessing the potential harm of toxic forms and reservoirs of copper, as well as temporarily inactive forms of copper.

Removal of phyto- and zooplankton from a sample is probably unnecessary because their metal concentrations are low and their contribution to total metal concentrations in water samples is minor. For example, copper concentrations in Lake Michigan phyto- and zooplankton were 6 and 5 mg/kg wet weight respectively (Copeland and Ayers, 1972). Assuming a Lake Erie seasonal maximum density of phytoplankton of 14 mg/l (Vollenweider et al., 1974) and of zooplankton of 1 mg/l (Watson, 1974), the total copper in plankton would be equivalent to 0.089 μg/l of copper in the water. Copper concentrations in Lake Michigan water average 5 μg/l (Copeland and Ayers, 1972). Thus in whole-water the maximum error in the metal concentration of the sample during plankton blooms would be about 2%. This value may be too high since plankton in a bloom might deplete the metal ions in the water being sampled rather than adding metal ions. There is also a possibility of zooplankton "swarms" with densities approaching one gram per litre. Such "swarms" might contribute significantly to metal concentrations but the problem could be avoided by not sampling under such extreme conditions. In addition, filtration to remove micro-organisms could be another problem -- the filter may add or remove ionic copper (Marvin et al., 1970). A further problem may be anomalously high concentrations of metals in samples obtained from turbid inshore waters affected by shoreline erosion. These concentrations should be interpreted with caution. The measurement of metals in a sample that has been allowed to settle or that has been filtered could also give erroneous results if metals which are easily dissolved from particulate matter were removed.

Stiff (1971) has assembled a variety of methods and has outlined an analytical routine for differentiating various forms of copper. However, results of this approach have yet to be correlated to toxicity tests in a variety of waters and are not suitable for application to routine monitoring. However, it is hoped that future developments in the methodology for identifying the various forms of metals will allow for refinements of objectives. Obviously any such refinement in the determination of the chemical and physical specification of an element will also require more elaborate sampling and storage procedures.

Therefore, until the relationship between metal forms and their toxicity is firmly established, and until there are reliable methods for monitoring such forms, water quality objectives for metals will refer to total concentrations of each metal in an unfiltered, (whole water), digested sample.

Setting Objectives for Metals for Aquatic Biota

Concentrations of metals that are above the level required for the nutrition of aquatic organisms but which are below their lethal level may produce subtle detrimental effects to their organisms. These effects may range from the inhibition of a single enzyme to failure in reproduction. The inhibition of a single enzyme may be of minor consequence or it may contribute to reproductive failure. If an aquatic organism is affected in some way by a metal so that it fails to reproduce, the population of that organism may disappear without evident direct mortality. Reductions in growth or in the efficiency of various physiological functions, changes in behaviour, or occurrence of physical abnormalities may all reduce the probability of successful reproduction of an organism. In particular, avoidance of sublethal concentrations of pollutants may be harmful to populations of fish by preventing migration to spawning areas or favourable feeding areas.

Thus, the objectives for metals are set at safe concentrations for aquatic species. Safe concentrations are determined as the maximum concentrations shown to have no harmful effect on any or all aspects of an aquatic organism's reproduction, physiology, behaviour, growth or any other function or activity essential for the maintenance of its population. In addition there should be no detrimental effect on a fishery based directly or indirectly on that organism. An unsafe concentration is any concentration having a harmful effect.

Safe concentrations are usually developed by laboratory measurements of sublethal toxicity. A measurement of concentrations inhibiting reproduction or producing mortality of a sensitive life stage provides a direct measurement of the unsafe concentration. Measurements of concentrations inhibiting physiological processes are most useful when the relevance to maintaining a population of the test organism is defined.

Safe concentrations may be derived from three measurements:

(a) The Maximum Acceptable Toxicant Concentration (MATC) as defined by Mount and Stephan (1967) consists of two numbers: (1) the lowest concentration of a toxicant having a harmful effect on an organism (unsafe) and (2) the highest concentration not producing that effect (safe). The threshold of response occurs somewhere between these two concentrations.

(b) A direct measurement of the threshold concentration causing the harmful effect. These data may be less useful if there are no limits given to the range of threshold concentrations.

(c) The application factor concept provides the third source of data for objectives since it is the ratio of MATC's to 96-hour LC_{50}'s. Consequently, an application factor can estimate the MATC for a particular species after a simple 96-hour LC_{50} measurement. Since there are error limits to both the application factor and the 96-hour LC_{50}, a direct estimation of the MATC by experimentation is preferable.

It is the intent of the Water Quality Board to provide a quality of water in the Great Lakes that will protect all water uses. Therefore, the proposed objectives for the metals that follow are based on the most sensitive of the defined uses of these Great Lakes waters.

Table 5

Concentrations (μg/l) of metals in filtered Great Lakes water
sampled from municipal water intakes between 1962 and 1967 (Kopp and Kroner, 1970).

	Detection Limits[8]	Lake Superior				Lake Michigan				Lake Huron		Lake St.Clair		Lake Erie		St. Lawrence R.	
		at Duluth		at St. Mary's R.		at Milwaukee		at Gary		at Port Huron		at Detroit		at Buffalo		at Massena	
Metal	(μg/l)	Mean[1]	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Aluminum	40	11	ND[5]-26	6	ND-10	Not measured		21	ND-58	24	ND-65	29	ND-68	31	ND-66	39	ND-148
Arsenic	100	Not measured		—	—	—	—	—	—	—	—	—	—	—	—	38	ND-58
Cadmium	20	Not measured		—	—	—	—	—	—	—	—	—	—	7	ND-12	Not measured	
Chromium	10	9	ND-20	3	ND-7	—	—[4]	10	ND-19	5	ND-8	8	ND-13	7	ND-10	26	ND-112
Copper	10	3	3-36	5	2-28	13	ND-34	4	ND-7	10	4-20	8	6-13	24	10-56	7	ND-23
Iron	10	23	2-83	19	ND-168	20	ND-37	49	ND-114	16	ND-53	23	ND-62	19	4-84	22	ND-171
Lead	40	—	—[2]	6	ND-12	13	ND-20	34	ND-55	14	ND-28	21	ND-53	Not measured		22	ND-48
Nickel	20	—	—[3]	11	ND-28	ND	ND	ND	ND	ND	ND	—	—[6]	—	—[7]	7	ND-10
Silver	2	Not measured		—	—	—	—	—	—	—	—	—	—	—	—	2.6	ND-6.0
Zinc	20	9	ND-17	41	2-406	13	ND-23	25	10-55	12	ND-20	24	ND-69	178	64-423	41	ND-210

1. Mean of concentrations above limits of detection in extracted samples.
2. Only two detections: 7 and 20 μg/l.
3. Only one detection: 2 μg/l.
4. Only two detections: 2 and 4 μg/l.
5. ND = not detected at limits of analytical method.
6. Only two detections: 5 and 20 μg/l.
7. Only two detections: 13 and 21 μg/l.
8. Extraction methods allow the measurement of concentration below normal detection limits.

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ARSENIC

RECOMMENDATION

It is recommended that the following new objective for arsenic be adopted:

Concentrations of total arsenic in an unfiltered water sample should not exceed 50 micrograms per litre to protect raw waters for public water supplies.

RATIONALE

There are several forms of arsenic found in fresh water; the most common are the arsenic and arsenious acids, the oxides of arsenic (As_2O_3), and some sulphur compounds (realgar and orpiment). The form in which one finds arsenic in fresh water is largely dependent upon the eH and pH values of the water (Ferguson and Gavis, 1972). Arsenic is also found in water in a variety of salt forms, such as sodium arsenite and sodium arsenate.

Physical forces such as weathering represent pathways by which arsenic may enter the aquatic ecosystem. It has been found that some igneous rocks have an arsenic content of about 2 μg/g; shale can yield arsenic concentrations as high as 13 μg/g while sandstone and limestone contain approximately 1 μg/g of arsenic (Table 3).

Other important sources of arsenic contamination are the burning of fossil fuels such as coal and oil, and various pesticides such as herbicides applied directly to water (Wiebe, 1930; Gilderhus, 1966). Arsenic also comes from various cleansing compounds in which levels as high as 35 μg/g have been measured (Zwick and Benstock, 1971). About 91,000 kg of arsenic were used in the Great Lakes basin in 1968, primarily as As_2O_3, for metallurgy (Fenwick, 1972).

Arsenic levels in surface waters, from natural or man made contamination vary considerably. Ferguson and Gavis (1972) report levels between 0 and 10 μg/l in freshwater; in Germany levels of 2 to 3 μg/l are normally found (Hutchinson, 1957, p. 563). Concentrations of arsenic in the Great Lakes are uniformly 1 μg/l or less in offshore waters (CCIW, unpublished data) but were found to be as high as 58 μg/l in a water intake at Massena, New York (Table 3). The Moira River, flowing into the Bay of Quinte, contains high levels of arsenic due to mining activity in its watershed. Concentrations of arsenic in the water of this river are normally greater than 10 μg/l but values as high as 300 μg/l have been recorded (OME, 1971).

Arsenic has no known nutritive value for plants (Bowen, 1966) and its essentiality for animals has not been proven. However, arsenic in the form of arsanilic acid, 4-nitrophenylarsonic acid, 3-nitro-4-hydroxyphenylarsonic acid and phenyl-arsenoxide are proven growth stimulants for pigs and poultry (Underwood, 1971).

Arsenic is classified by Bowen (1966) as moderately toxic to plants (toxic effects appear at concentrations between 1 and 100 mg/l in the nutrient solution). Arsenic is highly toxic to animals and it is a cumulative poison. Acute poisoning produces intestinal pain, vomiting and can lead to death. Chronic symptoms include cramps, nausea and liver damage (Fenwick, 1972).

In accordance with the "Safe Drinking Water Act", (PL-93-523), the U.S. Environmental Protection Agency proposed interim drinking water standards in the Federal Register on March 14, 1975. The maximum contaminant level for arsenic is proposed to be 50 µg/l, the same value as in the existing standards. Recently, the National Academy of Sciences (NAS/NAE, 1973) has recommended a maximum level of 100 µg/l total arsenic "because of adverse physiological effects on humans and because there is inadequate information on the effectiveness of defined (water) treatment procedures in removing arsenic." The existing guidelines for raw water in Canada (1968 Canadian Drinking Water Standards and Objectives - under review) specify an acceptable arsenic level of 10 µg/l and a maximum permissible level of 50 µg/l. For livestock an upper limit of 200 µg/l of arsenic in water is recommended (NAS/NAE, 1973)

The presence of arsenic in the aquatic environment has been shown in some cases to have deleterious effects on organisms. Some workers have used sodium arsenite to determine the lethality of arsenic on test organisms (Gilderhus, 1966), while others have used arsenite as arsenic trioxide (Holland, 1960). The lethal concentrations of both arsenate and arsenite for some algae fall between 2,000 and 10,000 µg/l (Wong, 1975).

The three week LC_{50} of sodium arsenate to Daphnia magna was 2,850 µg/l while the concentrations causing 50 and 16% impairment of reproduction were 1,400 and 520 µg/l, respectively (Biesinger and Christensen, 1971). Little is known about the effects of sodium arsenite on invertebrate and fish physiology. It is mainly used as a herbicide, but it may also be used as a deterrent to Toredo infestation of wooden structures in salt water. The 48-hour LC_{50} of sodium arsenite to chum salmon (Oncorhynchus keta) is about 11,000 µg/l (Alderdice and Brett, 1957). Holland (1960) noted 22% initial mortality of young pink salmon exposed to 5,300 µg/l arsenic, but mortality in the survivors continued for an additional 20 days. Recently, Speyer (1974) found 6,000 µg/l arsenic to be the lowest level affecting growth of rainbow trout although the response was increased by the presence of 200 µg/l HCN. Lawrence (1958) investigated the effect of arsenic trioxide on fish production using ponds stocked with bluegills. At 4,000 µg/l and 8,000 µg/l, reduction of bottom organisms as compared to the controls was 34% and 45%, respectively. The weight of fish harvested was also substantially reduced in the treated ponds. Conditioned avoidance behaviour of goldfish was significantly impared by 100 μg/l arsenic as sodium arsenate but not by 50 μg/l (Weir and Hine, 1970).

Gilderhus (1966) studied the uptake of sodium arsenite by bluegills in outdoor pools containing invertebrates, vegetation and sediments. He noted that much of the arsenic applied ended up in the sediment. At 4,000 μg/l arsenic (a single treatment) maximum tissue residues in fish were 1,300 μg/kg for muscle, 2,400 μg/kg for skin and scales, 17,600 μg/kg for gills and digestive tract, 11,600 μg/kg for liver, 5,900 μg/kg for kidneys and 8,400 μg/kg for ovary. Average residues in Great Lakes fish vary from 3-43 μg/kg on a whole weight basis (Lucas et al., 1970), < 50-700 μg/kg on a dressed fish basis (Uthe and Bligh, 1971) and 6-80 μg/kg on a liver basis (Lucas et al., 1970). These values are considerably below those observed on an experimental basis.

Concentrations of arsenic considered safe for public drinking water supplies are substantially lower than those required to protect aquatic life. Consequently, the objective for arsenic should be 50 μg/l in keeping with the approved concentration for the protection of human health. However, to protect aquatic life, the Province of Ontario, specifies that "an environmental level of 10 μg/l should not be exceeded under any circumstances" (OWRC, 1970). This guideline is not well supported by scientific evidence.

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CADMIUM

RECOMMENDATION

Concentrations of total cadmium in an unfiltered water sample should not exceed 0.2 micrograms per litre to protect aquatic life.

RATIONALE

Cadmium is a divalent metal that occurs mostly as a sulphide, usually in association with other metal sulphides, especially of lead and zinc. There is no mining activity specifically for cadmium; it is obtained principally as a by-product of zinc mining (Lymburner, 1974).

The properties of cadmium make it important in electroplating, in solders, as a pigment, as a catalyst, in photography, lithography and the electronics industry, and in the manufacturing of glass, alloys, biocides, lubricants and storage batteries (Lymburner, 1974, Cheremisinoff and Habib, 1972). In the Great Lakes Basin, cadmium is a by-product of zinc refining in Port Maitland, Ontario and cadmium-containing ores are mined in the Lake Superior region (Lymburner, 1974). There is considerable use associated with the automotive and metallurgical industries of the lower Great Lakes region. Therefore, cadmium may enter Great Lakes waters as a result of these processes. Additional inputs are derived from the weathering of rocks and the fallout from airborne cadmium originating in fossil fuels.

In water, cadmium may be complexed with soluble inorganic or organic materials as well as adsorbed to particulate matter. Hem (1972) derived theoretical limiting equilibrium solubilities for the carbonate and hydroxide complexes of cadmium in specific waters. He found that cadmium concentrations in surface waters of the United States, as reported by various authors, were much lower than the maximum permitted by the solubility product of the carbonate, the least soluble salt. He attributed the difference to the action of other complexing and adsorbing materials. Hahne and Kroontje (1973) also showed theoretically that, at high pH's or chloride concentrations, a high proportion of cadmium was mobilized as hydroxy or chloride complexes. However, their data show that at pH 7-8 and at chloride concentrations of 35 mg/l, the bulk of cadmium would occur as Cd^{++}. Using a cadmium specific ion electrode, Gardiner (1974a) measured the degree of complexation of cadmium in synthetic solutions and natural river waters containing varying amounts of carbonate, sewage effluent and humic acids. He found that a large proportion of cadmium occurred as Cd^{++} although the amount decreased with increasing pH, sewage effluent concentration or humic acid concentration. Humic substances accounted for most of the complexation. In natural waters, Gardiner (1974a) found that, of 1,000 µg/l added cadmium, 29-89% occurred as Cd^{++}, and the proportion was generally in excess of 50%. Suspended solids originating from bottom muds will also adsorb cadmium (Gardiner, 1974b). The degree of adsorption depended on the type of solid, state of subdivision, concentration of metal ion, time of contact and concentration of other complexing ligands. Humic materials again appeared to be the major component of mud that is important. Gardiner (1974b) however, after these laboratory studies, was unable to satisfactorily explain the high proportion of measured free cadmium after adding cadmium to the effluent from a percolating filter. In a study of two streams in Tennessee, Perhac (1972) measured the metal content of coarse particulate suspended solids (Svedberg coefficient* (S) > 20000), in colloidal particulate suspended solids (100 < S <20000) and in dissolved solids. The mean cadmium concentrations in these fractions were 18, 519 and 12 µg/gm respectively. While the greatest concentration of cadmium was in colloidal solids, this represented the smallest proportion of heavy metal in water because colloids occurred only in trace amounts. The highest proportion of cadmium (≃98%) occurred in the dissolved solids. Presumably these materials would include humic acids, carbonates, chlorides, etc. Total cadmium in these waters ranged from 2-3 µg/l. Therefore, assessment of the impact of cadmium in water will probably be most concerned with free cadmium and soluble complexes.

Cadmium concentrations in the Upper Great Lakes are almost always less than 0.2 µg/l offshore (Table 4). In Lake Superior a small proportion of concentrations are between 0.2 and 0.6 µg/l. In Lake Erie, concentrations of cadmium in offshore filtered water never exceeded 1 µg/l, the detection limit at that time (Chawla and Chau, 1969; MWRC, 1972) but in a water intake at Buffalo, concentrations ranged as high as 12 µg/l and the mean was 7 µg/l (Table 5). In Lake Michigan, concentrations never exceeded 1 µg/l in 1970 although some tributaries were slightly higher (MWRC, 1972). In a 1974 survey of American nearshore waters, cadmium was always less than 2 µg/l (detection limit) in Lake Superior and Lake Huron (MWRC, 1975).

Cadmium is extremely toxic to mammals. Acute toxicity to humans includes severe nausea, salivation, vomiting, diarrhea, abdominal pains and myalgia. Liver and/or kidney damage may follow acute poisoning and respiratory distress may also occur (Flick et al., 1971). Chronic toxicity includes damage to liver, kidney, hematopoietic tissue and the respiratory tract (Flick et al., 1971). Cadmium has been implicated in bone degeneration in Japan although these findings are controversial (Dr. E. Sandi, personal communication). Epidemiological and experimental evidence suggests that cadmium may also cause hypertension. In experimental animals cadmium causes testicular damage, kidney damage, increased incidence of tumours and reduced growth (Flick et al., 1971). The biochemical bases for these effects may be the interaction of cadmium with thiol groups of enzymes or with phosphatidylethanolamine and phosphatidylserine monolayers (Vallee and Ulmer, 1972). As a result, many enzymatic reactions are inhibited by cadmium, and toxic effects occur in mitochondria, kidney tubules and nerve membranes (Vallee and Ulmer, 1972). The daily uptake of cadmium by an adult human from drinking water has been estimated as 15 µg, as compared to 200 µg in food and 1 µg in air (Nilsson, 1970). Of the total cadmium taken in,

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* Svedberg coefficient is a numerical value related to the settling velocity of a spherical particle.

only 1-2% is retained and the rest is excreted in faeces and urine. To limit intake from water to 200 μg/day, a drinking water limit of 10 μg/l cadmium has been recommended (NAS/NAE, 1974). In Canada, the maximum permissible concentration of cadmium in drinking water is 10 μg/l while the acceptable concentration is less than 10 μg/l (DNHW, 1969). A recommendation of 50 μg/l is given to protect livestock (NAS/NAE, 1973).

Cadmium is not a nutrient for plants and is classified as highly toxic by Bowen (1966), (toxic at concentrations less than 1,000 μg/l in the nutrient solution). Since crop growths may be reduced at concentrations as low as 10 μg/l, recommendations for irrigation water are 10 μg/l for continuous use on all soils and 50 μg/l on neutral and alkaline fine textured soils for a 20-year period (NAS/NAE, 1973).

Low concentrations of cadmium are harmful to algae. Growth of *Scenedesmus quadricauda* in the laboratory was significantly inhibited at concentrations as low as 6 μg/l (Klass *et* al., 1974). *Selenastrum capricornutum* is somewhat less sensitive since 80 μg/l caused complete growth inhibition while 50 μg/l caused a slight inhibition (Bartlett *et al.*, 1974). In a comparative study, Burnison *et al.* (1975) found that the concentrations of cadmium in Lake Ontario water causing 70% inhibition of primary productivity of *Scenedesmus quadricauda*, *Chlorella pyrenoidosa*, *Ankistrodesmus falcatus* and *Chlorella vulgaris* were 20, 100, 1,000 and 1,000 μg/l respectively. A macrophyte, *Najas quadulepensis*, was also affected by cadmium. Severe effects were observed at 90 μg/l while 7 μg/l caused reduced chlorophyll, turgor and stolon development (Cearley and Coleman, 1973).

The acute toxicity of cadmium to zooplankton varies considerably with the species tested. In water from Lake Monate, the 48-hour LC_{50}'s for *Cyclops abyssorum prealpinus*, *Eudiaptomus padanus padanus* and *Daphnia hyalina* were 3,800, 550 and 55 μg/l respectively (Baudouin and Scoppa, 1974). The 48-hour LC_{50} for *Daphnia magna* in Lake Superior water was 65 μg/l (Biesinger and Christensen, 1972), a value close to that of *Daphnia hyalina*. The 3-week LC_{50} for *Daphnia magna* was 5 μg/l while 0.17 μg/l caused 16% impairment of reproduction (Biesinger and Christensen, 1972). The 96-hour LC_{50} of the freshwater shrimp *Paratya tasmaniensis* at 10 mg/l hardness was 60 μg/l (Thorp and Lake, 1974). A 96-hour exposure of these shrimp to 30 μg/l cadmium caused a change in the ultrastructure of the gills (Lake and Thorp, 1974).

Aquatic insects are less sensitive than zooplankton. At a hardness of 44 mg/l, the 96-hour LC_{50}'s of cadmium for *Acroneuria lycorias* (stonefly), *Ephemerella subvaria* (mayfly) and *Hydropsyche betteni* (caddisfly) were >32,000, 2,000 and >32,000 μg/l respectively (Warnick and Bell, 1969). At 50 mg/l hardness, the 96-hour LC_{50}'s of a caddisfly, a damsel fly, and a midge (*Chironomus* sp.) were 3,400, 8,100, and 1,200 μg/l respectively (Rehwoldt *et al.*, 1973). The species of caddisfly was unidentified and appeared 10 times more sensitive than that tested by Warnick and Bell (1969). The 96-

hour LC$_{50}$'s of a caddisfly, a damsel fly and a mayfly of Tasmania in water of 10 mg/l hardness was 2,000, 250,000 and 840 µg/l respectively (Thorp and Lake, 1974). Amphipods are much more sensitive since the 96-hour LC$_{50}$ of *Australochiltonia subtennis* was 40 µg/l (Thorp and Lake, 1974), while that of a scud (*Gammarus* sp.) was 70 µg/l (Rehwoldt *et al.*, 1973).

The 96-hour LC$_{50}$'s for a gastropod snail were 3,800 µg/l for eggs and 8,400 µg/l for adults (Rehwoldt *et al.*, 1973). In contrast, the snail *Helisoma* sp. had a 14-day LC$_{50}$ of 50 µg/l, and 20 µg/l reduced rates of survival and hatching of eggs (Heidel and McLaughlin, 1973). No effect was observed at 10 µg/l cadmium. Another benthic organism, the bristle worm (*Nais* sp.) had a 96-hour LC$_{50}$ of 1,700 µg/l (Rehwoldt *et al.*, 1973), while that for the rotifer *Philodina* sp. was about 100 µg/l (Sullivan *et al.*, 1973). *Tetrahymena pyriformis*, a protozoan, showed a growth depression at 15,000 µg/l cadmium and slower swimming at 1,000 µg/l (Bergquist and Bovee, 1973).

The acute toxicity of cadmium to fish varies with species and the time of exposure. The 96-hour LC$_{50}$ for fathead minnows (*Pimephales promelas*) at 200 mg/l hardness was 4,500 µg/l while the 8-day LC$_{50}$ was 450 µg/l (Pickering and Gast, 1972). Similarily, the 96-hour LC$_{50}$ for rainbow trout in hard water (290 mg/l) was about 2,000 µg/l while the 7-day LC$_{50}$ was 8-10 µg/l (Ball, 1967). Kumada *et al.* (1972) observed a similar 10-day LC$_{50}$ for rainbow trout of 5-7 µg/l cadmium. The 96-hour LC$_{50}$'s for bluegills (*Lepomis macrochirus*), Florida flagfish (*Jordanella floridae*, dace (*Triborodon hakonensis*) and striped bass (*Morone saxatilis*) were 17,200-24,200, 2,500, 56-100, and 2 µg/l respecitvely (Eaton, 1974; Spehar, unpubl. man.; Kumada *et al.*, 1972; and Hughes, 1973).

The sublethal effects of cadmium on fish include lingering mortality and inhibition of reproduction. In hard water (200 mg/l) 57 µg/l of cadmium decreased the survival of fathead minnow larvae, the most sensitive stage. No effect was observed at 37 µg/l (Pickering and Gast, 1972). At a hardness of 120 mg/l, a mixture of cadmium, zinc and copper reduced the spawning of fathead minnows when the concentrations were 7.1, 42.3 and 6.7 µg/l respectively (Eaton, 1973). No effect was seen when the concentrations of cadmium, zinc and copper were 3.9, 27.3 and 5.3 µg/l respectively. It is not known whether the apparent increase in toxicity of cadmium is due to a change of water hardness or to the presence of the other metals. Since the toxic effects (larval mortality and reduced spawning) differed, it was probably the effect of the other metals.

Eaton (1974) showed that, at a hardness of 200 mg/l, bluegill survived and spawned successfully at 31 µg/l cadmium. Lingering mortality of adults occurred at 80 µg/l and bluegill appear as sensitive as fathead minnows at this hardness. In water of 180 mg/l hardness, Cearley and Coleman (1974) found that bluegill survival was not affected at 80 µg/l cadmium but 100%

mortality occurred at 850 µg/l after 5 months. The principal difference between Eaton's (1974) study and that of Cearley and Coleman (1974) is that the latter used water of low alkalinity (49 mg/l) compared to the former (152 mg/l). In addition the chloride content of the water used by Cearley and Coleman (1974) was 193 mg/l. Largemouth bass (Micropterus salmoides) were more sensitive than bluegills. Significant mortality occurred at concentrations of 80 µg/l cadmium and behaviour was affected at 8 µg/l (Cearley and Coleman, 1974).

Survival of flagfish larvae in water of 44 mg/l hardness was affected at 8 µg/l cadmium and was normal at 4 µg/l. When the embryos were exposed to cadmium before hatching, the hatched larvae were less sensitive to cadmium (Spehar, Unpub. man.).

The reproductive physiology of brook trout (Salvelinus fontinalis) is also affected by cadmium. Exposures to 25 µg/l for 24 hours or 10 µg/l for 21 days at 20 mg/l hardness caused extensive hemorhagic necrosis of the testes of male trout (Sangalang and O'Halloran, 1972, 1973). After about 4 months exposure, 1 µg/l cadmium caused changes in testosterone and 11-ketotestosterone metabolism of male fish. There was no effect on secondary sexual characteristics and spermatogenesis, but testes regressed at least 2 weeks earlier than controls (Sangalang and Freeman, 1974). Brook trout alevins showed a decreased wet weight, increased protein content and increased acetylcholinesterase activity at 0.70 µg/l cadmium in water of 45 mg/l hardness (Christensen, 1975). These results correspond fairly well with the effects of cadmium on reproduction and survival of brook trout measured by Benoit et al. (1975). Survival of adult males during spawning and growth of juveniles were reduced at 3.4 µg/l while no adverse effects were noted at 1.7 µg/l cadmium.

Cadmium up to 100,000 µg/kg in the food of fish was not toxic to rainbow trout or dace after 18 weeks exposure (Kumada et al., 1972).

Cadmium residues in fish are fairly uniform. Lovett et al. (1972) measured cadmium concentrations in dressed fish from Lake Erie, Lake Ontario and the St. Lawrence River. Concentrations were generally between 10 and 30 µg/kg although a few had less than 10 µg/kg (the detection limit) and Gizzard shad from Lake Erie had 72 µg/kg. In another survey of dressed fish, from Lakes Erie and Ontario, cadmium concentrations were uniformly less than 50 µg/kg, the detection limit, with one exception - 60 µg/kg in rainbow smelt from Lake Erie (Uthe and Bligh, 1971). Using neutron activation, Lucas et al. (1970) measured cadmium concentrations of 62-140 µg/kg in whole fish from Lake Erie, Michigan and Superior. In fish livers, concentrations ranged from 60 to 1,400 µg/kg with most values around 400 µg/kg. This suggests that the liver concentrates cadmium. In Lake Michigan, fish (presumably whole) contained 100-300 µg/kg cadmium and there was no variation with feeding habits of the fish (MWRC 1972).

In experimental systems, bass and bluegills had total body accumulations of 8-15 and 6-20 times the concentration in water, depending on that concentration (Cearley and Coleman, 1974). Uptake and concentration in tissues levelled off within 2 months and the greatest accumulation occurred in internal organs. Kumada et al. (1972) found that cadmium concentrations in rainbow trout exposed to cadmium in water reached a plateau in 10-20 weeks and maximum concentrations were found in the kidneys. Concentrations in whole fish were about 10-80 μg/kg in control fish and increased only at cadmium concentrations above 1 μg/l. Concentrations in whole fish reached a maximum of 960 μg/kg after 30 weeks in 4.8 μg/l and declined to 440 μg/kg after 10 weeks in clean water. Similar increases in cadmium content were seen in rainbow trout and dace fed food containing up to 100,000 μg/kg of cadmium. Concentrations in whole trout fed this concentration reached 1,600 μg/kg after 12 weeks and declined dramatically to 70 μg/kg after 6 weeks on a clean diet (Kumada et al., 1972). The dramatic decrease was seen at all concentrations and indicates that cadmium taken in with the food is cleared faster than cadmium taken in from water. This could be illusory if the gills of fish exposed to cadmium in water contain high concentrations that are slowly released to the rest of the body after transferral to clean water.

White catfish (Ictalurus catus) given an intragastric dose of radioactive cadmium regurgitated 39-56% of the dose (Rowe and Massaro, 1974). Within one hour, 75% of the cadmium in the body was contained within the GI tract and 23% was in the gills. The fact that 2% was in the skin suggests that the gill load may have been picked up from the water after regurgitation. Over a period of 21 days, cadmium gradually moved down the intestine and concentrations gradually increased in both the liver and kidneys. By day 21, 34% of the cadmium was in the kidneys, 5% in the liver, about 56% still remained in the intestine and the rest was spread among other organs at low concentrations. Therefore, the total transfer from cadmium in the gut to other organs appears rather low.

Despite accumulation of cadmium, there is little evidence for bioconcentration up food chains. Mathis and Cummings (1973) found that mean concentrations of cadmium in Illinois River bottom sediments, worms, clams, omnivorous fish, carnivorous fish and water were about 2,000 μg/kg, 1,100 μg/kg, 600 μg/kg, 30 μg/kg and 0.6 μg/l respecitvely. Similarily, in eutrophic Wintergreen Lake, the concentrations of cadmium in bottom sediments, zooplankton, aquatic macrophytes, fish and water were 1,100 μg/kg, 500 μg/kg, 200 μg/kg, 40 μg/kg, and 0.9 μg/l respectively (Mathis and Kevern, 1975). Surprisingly, faeces from large flocks of migrating Canada geese contained up to 600 μg/kg cadmium.

A food chain model has been developed that predicts cadmium will bioconcentrate in Western Lake Erie food chains (Thomann et al., 1974). The model may not be useful since data on all trophic levels below fish are inadequate. However, future use of such models, based on adequate data, may give a clearer indication of the potential for bioconcentration.

Therefore, because of the extreme sensitivity to cadmium of trout and zooplankton reproduction, an objective for cadmium in the Great Lakes of 0.2 μg/l is recommended.

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CHROMIUM

RECOMMENDATION

It is recommended that the following new objective for chromium be adopted:

> *Concentrations of total chromium in an unfiltered water sample should not exceed 50 micrograms per litre to protect raw waters for public water supplies.*

RATIONALE

Chromium as Cr(VI) can enter aquatic ecosystems from the production and use of explosives, paper, dyes, paints, plated materials and tanning. As Cr(III), chromium is present in glass, ceramics, photography processes and textile dying mordants (Cheremisinoff and Habib, 1972). Up to 1,700 mg/l of chromium as dichromate, are also added to cooling tower waters to prevent corrosion and this amount is discharged directly to water courses (Shepherd and Jones, 1971). Chromium occurs at very low concentrations in Great Lakes waters. Offshore, the average recorded concentrations are less than 0.2 µg/l, the detection limit, and 95% of samples contain less than 0.6 µg/l (Table 4). At water intakes, average concentrations are shown to be less than 10 µg/l and maxima less than 20 µg/l (Table 3). However, concentrations of chromium in water intakes in the St. Lawrence River appear much higher, (Table 5). Since Cr (III) is probably complexed as an insoluble hydrated oxide above pH 5 (NAS/NAE, 1973), most dissolved chromium in Great Lakes waters is probably in the Cr(VI) valence state. However, Schroeder and Lee (1975) have clearly demonstrated that Cr(III) added to natural lake waters is converted very slowly to Cr(VI) and that the conversion is slower at low temperatures. Consequently, significant concentrations of Cr(III) could exist in lake water for many days. Cr(VI) can potentially be reduced by H_2S at the interface of aerobic and anaerobic waters (Schroder and Lee, 1975). However, in aerobic lake waters Cr(VI) is not reduced and is removed principally by physical processes. For example, Cr(VI) is sorbed effectively by $Fe(OH)_3$. The result is a significant positive, linear correlation of chromium with iron in lake sediments (Schroder and Lee, 1975).

Chromium at low concentrations may be a nutrient for plants and animals. Although not proven to be essentialy for plants, low concentrations in soil and water appear to stimulate growth of terrestrial and aquatic species (NRCUS, 1974). In mammals, chromium interacts with insulin to increase glucose tolerance, and some diabetic conditions are alleviated by chromium treatment (Bowen, 1966; Underwood, 1971). A United States National Research Council panel on chromium concluded that: "Chromium deficiency can be produced in experimental animals but it can be prevented and cured by appropriate chromium supplementation. Its symptoms are reproducible and consist of a general decrease in the tissue response to insulin. On this basis, chromium must be considered an essentialy element" (NRCUS, 1974).

At high concentrations, chromium in air causes respiratory damage and cancer to mammals and contact with the skin can cause ulcers, scars and allergic effects (NRCUS, 1974). The effects on humans of chromium in drinking water are unknown but a standard of 50 μg/l total chromium has been set in the U.S. to limit total daily intake (NAS/NAE, 1973). In Canada, the maximum permissible concentration is 50 μg/l as Cr(VI) and the acceptable limit is less than 50 μg/l (DNHW, 1969).

The toxicity of chromium to aquatic biota is quite variable and depends on the species tested. Hervey (1949) used a subjective measurement of unicellular algal growth inhibition to demonstrate that some diatoms were sensitive to 320 μg/l but not to 32 μg/l of chromium. WiumAnderson (1974), using ^{14}C fixation to estimate growth, estimated that 650 μg/l of Cr(VI) caused 50% inhibition of photosynthesis by the diatom, *Nitzschia palea*. Patrick *et al*. (1968) indicated that 208 μg/l of Cr(III) also caused 50% reduction of photosynthesis of *N. palea*. Based on cell counts, 150 μg/l allowed very little growth after 4 days exposure at low cell densities (Wium-Anderson 1974). *Daphnia magna* reproduction and activity were inhibited by 330 and 320 μg/l chromium, respectively (Biesinger and Christensen, 1972; Anderson, 1946). Another invertebrate, *Philodina roseola* was shown to be 10 times less sensitive than *Daphnia magna* since its life cycle was affected between 3,400 and 4,600 μg/l (Schaeffer and Pipes, 1973).

A series of unpublished studies by Benoit and Pickering, reported in Water Quality Criteria, 1972 (NAS/NAE, 1973), demonstrated "safe" concentrations, based on reproduction, of 300, 600 and 1,000 μg/l of hexavalent chromium for rainbow trout (*Salmo gairdneri*), brook trout (*Salvelinus fontinalis*), and fathead minnow (*Pimephales promelas*), respectively. The "safe" concentration of trivalent chromium for fathead minnows was 1,000 μg/l. Therefore, both valence states of chromium appear equally toxic on a sublethal basis. However, Olson (1958) observed that chinook salmon fingerlings (*Oncorhynchus tshawytscha*), after 12 weeks exposure, had higher mortality rates (>50%) and lower growth rates in 200 μg/l Cr(VI) than in 200 μg/l Cr(III) or in control tanks. The fish in Cr(III) had mortality and growth rates identical to those of the control fish. Therefore, on an acute basis, Cr(III) appears less toxic than Cr(VI).

Chromium concentrations in fish tissue are low. Lucas and Edgington (1970) measured chromium by neutron activation and found that average whole body concentrations in alewife, spottail shiner and trout perch ranged from 0.9-1.6 μg/g. Chromium was also measured by neutron activation in dressed samples of whitefish, northern pike, smelt and perch. The concentrations ranged from <0.017 μg/g to 0.034 μg/g wet weight (Uthe and Bligh, 1971). These results are quite low compared to those in whole fish, suggesting that chromium is not retained by muscle. In addition, there was no variation in the chromium concentration in the fish within species from Lake Erie and from Moose Lake, Manitoba. Moose

Lake is a lake free of industrial activity. Experimental exposures indicate that Cr(VI) was taken up from water at concentrations as low as 1 µg/l (Fromm and Stokes, 1962). At 2,500 µg/l, uptake was via the gills and the metal occurred in the spleen, posterior gut, pyloric caeca, stomach and kidney (Knoll and Fromm, 1960). Little occurred in muscle and uptake across the stomach was minimal. It does not appear that chromium contamination of fish represents a problem since oral toxicity to mammals is low (NRCUS, 1974). Also, the residues reported in the uptake experiments were not associated with any damage to the fish. Therefore, no objective for chromium concentrations in fish tissues is recommended at this time.

The data presented on toxicity suggest an objective for chromium in water somewhat greater than the guideline for drinking water, to protect aquatic life. Since the U.S. and Canadian guidelines for drinking water are 50 µg/l, the objective for total chromium is 50 µg/l.

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LEAD

RECOMMENDATION

It is recommended that the following new objective for lead be adopted:

Concentrations 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.

RATIONALE

Lead is released to aquatic ecosystems from the production and use of lead in gasolines, paints, glazes, pipes, roofing materials and ammunition (especially shotgun pellets). Lead is also released during metal mining and refining processes, recycling of used lead products, burning of fuels and recycling or disposal of used motor oils (NRCC, 1973).

Lead generally occurs in very low concentrations in water due to its low solubility. Since carbonate, hydroxide, phosphate, chloride, etc. form insoluble salts with lead, any dissolved lead can be converted to an insoluble form and precipitated to the sediments. In Lake Ontario water, for example, it has been found that at concentrations above 100 mg/l lead, more than 98% is precipitated after 24 hours. Above 10 mg/l, 70% is precipitated and above 1 mg/l, 10% is precipitated. The precipitate does not appear to redissolve upon agitation (Hodson, unpublished data). Below 1 mg/l, lead may be in an insoluble form but not precipitated, perhaps due to particle size. The proportion in an undissolved form varies with water hardness (Davies and Everhart, 1973). At a hardness of 24.0 mg/l, alkalinity of 22.8 mg/l and pH of 6.91, about 100% of lead below 100 µg/l is in a dissolved form. In water with a hardness of 353 mg/l, alkalinity of 243 mg/l and pH of about 7.9, dissolved lead was only 2% of a total of 3,240 µg/l. As the total concentration decreased, dissolved lead increased to 27% of a total of 40 µg/l lead (Davies and Everhart, 1973). Lead solubility is strongly influenced by pH, and above pH 8.0 the solubility is less than 10 µg/l, regardless of alkalinity (Hem and Durum, 1973).

Modal lead concentrations in the Upper Great Lakes waters are less than 1.0 µg/l offshore, and 95% of all samples contain less than 3.0 µg/l (Table 4). At water intakes, mean lead concentrations are as high as 34 µg/l with maxima at 55 µg/l or less (Table 5). The higher inshore concentrations probably reflect local inputs to the lakes.

Lead is not essential for plant and animal growth and is, in fact, quite toxic. Bowen (1966) has rated lead as being very toxic to plants, i.e. toxic effects may be seen below 1 mg/l in the nutrient solution.

Lead shot is also toxic to wildlife. Poisoning of diving and dabbling ducks, as well as swans and geese is a major problem of wetlands management (NRCC, 1973). Birds may die by feeding off bottom material heavily contaminated with lead shot from hunting. One lead pellet ingested by a mallard can cause elevated blood lead levels for up to three months (Dieter and Finley, 1975). The same exposure also caused marked changes in enzyme activity of brain and liver tissue (Dieter and Finley, 1975). The lethal dose of lead pellets is estimated as 5-6 for a mallard and 15-25 for a Canada Goose (NRCC, 1973) and toxicity varies with diet.

Lead toxicity to mammalian wildlife has not been reported but some domestic animals and humans are quite susceptible to lead. Domestic animals are exposed through ingestion of solid waste (e.g. lead-acid batteries) or contaminated drinking water. Chronic toxic effects include digestive problems, renal damage, neural damage and eventually death. Embryotoxicity due to transplacental lead transfer has been observed but teratogenicity has not been proven conclusively (NRCC, 1973). Many of these results are from experimental poisonings. The recommendation for lead in water for livestock in the U.S. is 100 µg/l (NAS/NAE, 1973).

Man is exposed to lead through food, water and air. Sources of lead include burning of fossil fuels, smoking, drinking water, non-food items such as paint chips, illicit liquor, containers improperly glazed with lead silicates and industrial operations (NRCC, 1973). Lead poisoning or plumbism, has three aspects: (1) mild or severe dysfunction of the alimentary tract; (2) neuromuscular atrophy; and (3) encephalopathy. Therefore, it has been recommended that total lead intake be limited to 0.6 mg/day by adults (NRCC, 1973; NAS/NAE, 1973) and 0.3 mg/day by children (NRCC, 1973). The recommendation for lead in drinking water in the U.S. is 50 µg/l (NAS/NAE, 1973) while in Canada, the maximum permissible limit is 50 µg/l, less than 50 µg/l is acceptable, and the objective is "not detectable" (DNHW, 1969).

Lead appears to be relatively non-toxic to algae. Concentrations reducing growth as determined by cell numbers, CO_2 fixation, chlorophyll production, etc. are generally between 1 and 100 mg/l and occasionally as high as 1,000 mg/l (Wong _et al._, in preparation). Toxicity varies considerably between species and between growth media. The growth media factor is of considerable importance since toxicity of lead in natural waters is much greater than in artificial media. Growth of _Ankistrodesmus falcatus_, a green alga of the Great Lakes, was reduced 50% by about 10,000 µg/l lead in Chu 10 medium. In Lake Ontario water, a similar effect was seen between 10 and 100 µg/l (Wong _et al._, in preparation). Temperature must also be considered, since toxicity increases with temperature (Wong _et al._, in preparation) and most laboratory studies are conducted at 20 C.

Daphnia magna reproduction was inhibited by 30 μg/l lead (Biesinger and Christensen, 1972). Conditioned behaviour of goldfish (*Carassius auratus*) was affected by 70 μg/l lead (Weir and Hine, 1970) but the importance of this change is unknown. Growth of brook trout (*Salvelinus fontinalis*) was reduced by periodic high concentrations of lead between 15,000 and 25,000 μg/l (Dorfman and Whitworth, 1969) while growth of guppies (*Lebistes reticulatus*) was reduced by continuous exposure to 1,250 μg/l (Crandall and Goodnight, 1962; 1963).

Prolonged lead exposure of rainbow trout (*Salmo gairdneri*), starting as fingerlings, caused black tails and lordosis (dorso-ventral spinal curvature) plus scoliosis (bilateral spinal curvature) (Davies and Everhart, 1973). These effects are probably due to neural damage and they occurred between 13.3 and 20 μg/l total lead at 27 mg/l hardness and 23 mg/l alkalinity. At 354 mg/l hardness and 243 mg/l alkalinity, the effects occurred between 120 and 360 μg/l total lead. When the results from hard water were expressed as "free" lead as measured by pulse polarography, the effects occurred between 18 and 32 μg/l. *Therefore, a safe concentration based on total lead varies considerably with hardness while that based on "free" lead varies only slightly.* In soft water, for trout exposed from the egg stage onwards and from parents exposed to lead for one year, the safe-unsafe range was 6-12 μg/l.

Interpolating from Davies and Everhart's (1973) results, safe-unsafe concentration ranges for total lead in the Great Lakes are as follows:

	Hardness (mg/l)	Alkalinity (mg/l)	Safe-unsafe range based on hardness (μg/l of lead)	Safe-unsafe range based on alkalinity (μg/l of lead)
Lake Superior	44	41	15 - 24	16 - 25
Lake Huron	94	75	21 - 37	22 - 38
Lake Michigan	119	--	25 - 46	--
Lake Erie	123	91	25 - 46	26 - 48
Lake Ontario	135	90	27 - 52	26 - 48

These results have been confirmed by Goettl *et al*. (1973) using the same dilution water. They found that lordosis plus scoliosis developed in young rainbow trout at lead concentrations between 8.0 and 14.0 μg/l. A third study of brook trout in water of 44 mg/l hardness gave similar results between 58 and 119 μg/l total lead (Holcombe *et al*., unpub.man.) On a dissolved basis, this represented 39 and 84 μg/l. It would appear that brook trout are not as sensitive as rainbow trout.

Some lead accumulation occurs in aquatic biota. Phytoplankton accumulate large quantities, perhaps due to adsorption by the relatively large surface areas of algal cells, or to ion exchange (Shukla and Leland, 1973). Leland and McNurney (1973) showed that concentrations of lead were always highest in periphyton of streams and decreased with increasing trophic level. Herbivorous fish had higher concentrations of lead than did carnivorous fish. All concentrations of lead in fish were less than 5.0 μg/g.

Lead concentrations in fillets of Great Lakes fish were found to be uniformly less than 0.5 μg/g, the detection limit, regardless of species or sample location (Uthe and Bligh, 1971). However, in a more recent survey, Brown and Chow (1975) reported that fish from Baie du Dore, Lake Huron, contained 0.19 μg/g lead in muscle while those from Toronto harbour contained 1.78 μg/g. Since only the values from Toronto Harbour appear elevated, muscle lead concentrations may reflect local contamination. Higher concentrations of lead occur in other organs of fish. In trout from a stream, concentrations of lead were higher in bone than in liver or gills (Pagenkopf and Neuman, 1974). In addition, there was a significant difference in lead content of bone between fish from a hatchery and fish from a river containing 2.65-2.93 μg/l lead, twice as much as in hatchery water. Lead may also occur in blood and accumulate in kidney tissue (Hodson, unpublished data). The significance of these residues to fish health has not yet been determined.

The criteria for lead for aquatic biota require a more stringent objective than for drinking water. Therefore, to account for the variation with water hardness of the response of rainbow trout to total lead in water, the objective for total lead is recommended as 10 μg/l in Lake Superior, 20 μg/l in Lake Huron and 25 μg/l in all other lakes.

Since lead may be methylated to tetramethyl lead by lake sediments (Wong et al., 1975), these objectives should be re-evaluated when the significance of methylation is defined.

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MERCURY

RECOMMENDATION

It is recommended that the following new objective for mercury be adopted:

> *The concentration of total mercury in filtered water should not exceed 0.2 micrograms per litre nor should the concentration of total mercury in whole fish exceed 0.5 micrograms per gram (wet weight basis) for the protection of aquatic life and fish-consuming birds.*

RATIONALE

The biologically significant form of mercury is methylmercury. The bulk of the mercury found in fresh water fish occurs in the form of methylmercury (Johnels et al. 1967; Kamps et al. 1972).

Various forms of mercury may be methylated by at least two mechanisms (Wood et al., 1968; Ladner, 1971). The extent and rates of methylation are affected by many factors, among them are: concentration of mercury ions, availability of mercury ions, growth rate or metabolic activity of the methylating organisms, temperature, and pH (Bisogni and Lawrence, 1975). Methylmercury may also be demethylated by bacteria in sediments (Spangler et al., 1973). Thus the amount of methylmercury found in the environment at any one time is dependent on the combined reaction kinetics of the methylating and the demethylating processes. As a consequence, the combination of the available mercury concentrations and the operations of both transformation processes are significant. Since fish concentrate methylmercury preferentially over other forms of mercury, and since they excrete methylmercury very slowly, they provide a good indicator of long-term trends of the net methylation rate in an environment. Crayfish also accumulate significant amounts of methylmercury (Armstrong and Hamilton, 1973). Because of their shorter life cycles, they may be suitable to measure intermediate term trends in the net methylation rate in an aquatic environment.

The present administrative guideline for fish for human consumption promulgated by the U.S. Food and Drug Administration as well as the Canadian Food and Drug Directorate is 0.5 μg/g mercury in edible portions of fish. Natural background concentrations of mercury in fish are generally below this level, but may locally exceed it in some species. There is no evidence that concentrations of 0.5 μg/g in fish have any effect on them. Concentrations of mercury in fish that have been killed by chronic exposure to methylmercury ranged from 9.5 to 23.5 μg/g (McKim et al., 1975).

It is nearly impossible to correlate environmental concentrations of total mercury in unfiltered water with concentrations of methylmercury which accumulate in fish. There appear to be several reasons for this: in aquatic ecosystems the vast majority of the total mercury is located in the sediments, where the highest concentration is associated with the smallest particles (Armstrong and Hamilton, 1973 and Walter and Wolery, 1974). The mercury associated with these small particles in the water sample would be included in unfiltered samples so that the turbidity of a sample significantly affects the mercury determination. The biological availability of mercury associated with these samples is probably significantly lower than that of any methylmercury in solution. In addition to mercury compounds adsorbed onto or incorporated into particles, an unfiltered water sample will contain mercury compounds chelated by dissolved organic substances such as fulvic acids (Andren and Harriss, 1975), and dissolved mercury compounds. The proportion of methylmercury in this complex mixture is probably variable, and is not readily determined by presently available techniques. Indirect evidence indicates that the amount of methylmercury in water constitutes a minor proportion of the total mercury content in unfiltered samples. Experimental exposure of brook trout to 0.03 μg/l of methylmercury has resulted in an accumulation of 0.96 μg/g after 239 days of exposure (McKim et al., 1975). Equilibrium concentrations were not reached during this exposure and were estimated to be significantly higher (>3 μg/g) by Hartung (1975). However, background levels of total mercury in water have been reported to range from 0.05 to 0.1 μg/l (N.A.S. Water Qual. Criteria 1972), and these have been associated with concentrations of 0.01 to 0.2 μg/g mercury in fish. Thus there is a significant discrepancy between bioaccumulation data derived from experimental exposures to methylmercury when compared with those derived from experimental data. As a consequence it must be concluded that measurements of total mercury in unfiltered water have only marginal usefulness in deriving environmental quality criteria, and therefore the measurement of mercury accumulated in biological organisms represents a significantly more persuasive criterion.

A series of toxicity studies is summarized in Table 6. It demonstrates that most organic mercury compounds are more toxic than inorganic mercury salts. No effects were noted in a three generation exposure of brook trout to 0.29 μg/l methylmercury. A slight reduction in the hatchability of eggs of zebrafish was noted at 0.2 μg/l. However, while this level should protect aquatic life, it will result in accumulations of methylmercury in aquatic life in excess of 0.5 μg/g. For the purpose of setting an objective to protect aquatic life, the total amount of mercury in filtered water samples is arbitrarily considered to be methylmercury. Concentrations of 0.2 μg/l of total mercury in filtered water should therefore protect aquatic life with a more than adequate safety margin.

Table 6

MERCURY TOXICITY STUDIES

Organism	Compound	Effect	Lowest Conc. Producing Effect	Highest No. Effect Conc.	Remarks	Reference
Gammarus sp.	Hg^{++}	24hr LC_{50} 96hr LC_{50}	90 µg/l 10 µg/l			Rehwoldt *et al.*
Nais sp.	Hg^{++}	24hr LC_{50} 96hr LC_{50}	1900 µg/l 1000 µg/l			
Caddis fly	Hg^{++}	24hr LC_{50} 96hr LC_{50}	5600 µg/l 1200 µg/l			
Damsel fly	Hg^{++}	24hr LC_{50} 96hr LC_{50}	3200 µg/l 1200 µg/l			
Chironomus sp.	Hg^{++}	24hr LC_{50} 96hr LC_{50}	60 µg/l 10 µg/l			
Amnicola sp.	Hg^{++}	24hr LC_{50} 96hr LC_{50}	1100 µg/l 80 µg/l			
Brook trout						
embryos	CH_3Hg^+	GOT(decreased)	1.03 µg/l	0.08 µg/l	adults exposed 7 mo. before spawning; offspring maintained at same conc.	Christensen
alevins	CH_3Hg^+	GOT(enhanced)	0.93 µg/l	0.08 µg/l		
Rainbow trout	CH_3Hg^+	Decreased Hematocrit	10 µg/l		12 weeks exposure	O'Connor & Fromm
		Plasma electrolytes		10 µg/l	"	
		in vitro O_2 metabol.		10 µg/l	"	
Brook trout	CH_3Hg^+	Cough response	3 µg/l		5 day exposure	Drummond *et al.*
Zebrafish	Phenyl mercuric acetate	No. eggs spawned	1 µg/l	0.2 µg/l	19-25 day exposures	Kihlstrom *et al.*
		% hatching	0.2 µg/l			
Rainbow trout	Hg^{++}	decreased activity	50 µg/l		4-6 day exposure	Alexander
Brook trout	CH_3Hg^+	deformities, deaths in 2nd gen.	0.93 µg/l	0.29 µg/l	3 generation exposure	McKim *et al.*

Table 6 cont'd.

Organism	Compound	Effect	Lowest Conc. Producing Effect	Highest No. Effect Conc.	Remarks	Reference
Cat	CH_3Hg^+	C.N.S. deaths	0.25 mg/kg/ day		55-96 feeding of synthetic or "natural" CH_3Hg^+	Charbonneau *et al*.
Japanese quail	$HgCl_2$	Egg shell thinning	1 µg/g (diet)	2 µg/g (diet)		Stoewsand *et al*.
Mallard	N-(ethyl mercury) -p-toluene-sulfonanilide	Egg shell thinning		200 µg/g	85 day exposure (contains 3.1% Hg)	Haegele *et al*.
American kestrel	CH_3Hg^+	Egg shell thinning		10 µg/g (diet)	3 months exposure	Peakall & Lincer
Ring dove	CH_3Hg^+	Egg shell thinning		10 µg/g	intramuscular	"
		decreased egg laying	10 µg/g		"	"
Mallard	CH_3Hg^+	Decreased hatchling survival	3 µg/g (diet)	0.5 µg/g(diet)	21 week exposure	Heinz
Mallard duckling	CH_3Hg^+	enhanced avoidance response	0.5 µg/g (diet)		hens fed prior to and during reproductive phase	Heinz

Protection of organisms which consume aquatic life cannot be based on water concentrations, but must be based on an evaluation of the amounts of mercury accumulated in aquatic organisms.

On Lake St. Clair in 1970, great blue herons were found with mercury levels up to 23 µg/g in their flesh, and terns up to 7.5 µg/g in their flesh. Fish recovered from their stomachs contained up to 3.8 µg/g mercury (Dustman <u>et al</u>., 1972). No mortalities or population effects were noted in these species. Keith and Gruchy (1971) also reported finding gulls with elevated mercury residues in their eggs without finding effects on reproduction. The levels found in these instances are close to or identical to levels associated with mercury poisoning in some species of seed eating birds. It is therefore evident that species differences exist, and at least some fish-eating birds appear to be more resistant than some seed eating species.

Table 6 also lists the effects of feeding methylmercury to birds. Eggshell thinning was reported to occur in one study in Japanese quail at 1 µg/g of mercuric chloride in the diet. However, studies with organic mercury including methylmercury have not confirmed this in other species, even at higher dose levels. The most sensitive effects found, have been effects of hatchling survival in mallards at 3 µg/g, but not at 0.5 µg/g. The avoidance response of ducklings was enhanced slightly at 0.5 µg/g methylmercury fed to ducks prior to and during the reproductive phase. Since this effect was slight and may not be harmful, it is likely that the safe level for methylmercury in the diet of birds is close to 0.5 µg/g.

Therefore, fish-eating birds should be protected if the concentration of total mercury in whole fish does not exceed 0.5 µg/g. Since not all species of fish accumulate mercury equally, this provides an additional margin of safety. Also, since concentrations of 0.5 µg/g in fish produce no deleterious effects to fish, this limitation assures long-term protection of fish. Therefore, the simultaneous application of the proposed objectives for water and for bioaccumulated mercury in fish should protect aquatic life as well as the consumers of aquatic life.

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SELENIUM

RECOMMENDATION

It is recommended that the following new objective for selenium be adopted:

> *Concentrations of total selenium in an unfiltered water sample should not exceed 10 micrograms per litre to protect raw water for public water supplies.*

NOTE: The effect of high dietary selenium concentrations on fish-eating birds and wildlife is unknown. Based on the response of laboratory mammals, concentrations of selenium approaching 3 μg/g, wet weight, in whole fish should be regarded with concern.

RATIONALE

Selenium is a common element appearing in the earth's crust at approximately 7 X 10^{-5}%. It is present largely as heavy metal selenides (together with sulphide minerals) but also occurs as selenates and selenites. In soils, excluding seleniferous soils not normally found in the Great Lakes region, it has been variously reported to be present at levels ranging from 0.1 μg/g to less than 2 μg/g (Cooper et al., 1974). Elevated levels of selenium are found in some sedimentary rock formations and their derived soils in central areas of Canada and the United States. There are no known mining activities for selenium and its production comes mostly as a by-product of copper and lead refining.

Commercial use of selenium was about 500 metric tons per year in 1968, mostly in the elemental form as red crystals or grey powder. It is used in electronics for rectifiers, photocells, and xerography. It is also used in steel and in pigments for paints, glass, and ceramics (Cooper, 1967; Lymburner and Knoll, 1973).

Selenium is usually present in water as selenate and selenite; the elemental form is insoluble but may be carried in suspension. Weathering of rocks and soil erosion is a major source of selenium in water. On a world basis, approximately 10,000 metric tons yearly are weathered and carried downstream to the sea. Of this, 140 tons is in solution but only 16 tons remains dissolved in the sea. The rest of it goes into sediments (Schroeder, 1974). The burning of fossil fuels is another source of soluble selenium. Analysis of coal and bottom and fly ash from a single burner has turned up levels of 2 μg/g, 3.4 μg/g and 41.3 μg/g, respectively (Lymburner and Knoll, 1973). Man's burning of fossil fuel puts about 450 tons per year of selenium (SeO_2) into the atmosphere, about 4.5% of the amount eroded naturally (Schroeder, 1974).

Disposal of waste containing selenium could be another source, although levels in effluents seem to be low. Sewage in California (both raw and treated) was found to have only 10 to 60 μg/l of selenium, except for a high value of 280 μg/l in an industrial area (Feldman, 1974).

Concentrations in water are usually low. The literature has been reviewed in several places (e.g. NAS/NAE, 1973), but many of the older estimates are probably too high because of the limitations of chemical methods. Most uncontaminated surface waters have less than 50 μg/l of selenium, and most drinking waters contain less than 10 μg/l (APHA *et al.*, 1971). Surface waters in a province of Germany averaged 4 μg/l (Heide and Schubert, 1960). The normal concentration in sea water is only 0.4 μg/l (Chau and Riley, 1965). Even seepages from seleniferous areas do not contain more than 500 μg/l and this content is lost when the seepages empty into ponds or lakes, apparently by coprecipitation with ferric hydroxide (APHA *et al.*, 1971). Selenium concentrations in the Great Lakes are below 1 μg/l offshore and mean concentrations are 0.2 μg/l or less (Table 4).

Lake sediments seem to act as reservoirs or sinks; in the northern United States they contained from 1.0 to 3.5 μg/g dry weight of selenium, considerably more than the usual concentration in soils (Wiersma and Lee, 1971). Small experimental ecosystem experiments showed that of the total amount of selenium in rain which fell on soil, 75% stayed in soil and 25% ran off into an aquatic system. Thirty-six percent of the amount of selenium that entered the aquatic system ended in the sediments and most of the rest was in the biota (Huckabee and Blaylock, 1974).

Deficiency of selenium in the soil and in grass eaten by livestock, leads to "white muscle disease". Dietary needs of livestock are in the vicinity of 0.1 to 0.2 mg/day (NAS/NAE, 1973) whereas the daily selenium requirement of humans has not been accurately determined. It would appear to be in the range of 0.1 to 0.2 mg/day (Levander, 1975), an amount normally found in an adequate diet (NAS/NAE, 1973).

Selenium poisoning of livestock has been divided into two classes: the acute type called blind staggers and the chronic type called alkali disease. The acute type is associated with ingestion of highly seleniferous plants containing 1,000 μg/g or more of selenium whereas the chronic type is associated with grains and plants which contain 5 to 20 μg/g of selenium (Moxon, 1958). The extensive literature on natural poisoning of livestock from selenium in their food plants agrees, in general, that 5 μg/g or more can lead to death in the herbivore, and that such levels in plants result from soil concentrations in the range 0.5 to 6 μg/g (National Technical Advisory Committee, 1968; NAS/NAE, 1973; McKee and Wolf, 1963). Also, a diet containing 3 μg/g of selenium in selenite form, in a lifetime study killed rates (Schroeder, 1967). The usual chronic effects in mammals may include weakness, visual impairment, paralysis, damage to heart, liver and viscera, stiff joints, and loss of hair and hooves. Additional symptoms in humans are marked pallour, red tainting of fingers, teeth and hair, dental caries, debility, depression and irritation of nose and throat. In humans, overdoses resulting in acute toxicity may be characterized by nervousness, vomiting, cough, dyspnea, convulsions, abdominal pain, diarrhea, hypotension and respiratory failure (Schroeder, 1974; NAS/NAE, 1973; Rodier, 1971). No recognized cases of non-industrial chronic selenium poisoning in man have been reported (Sakurai and Tsuchiya, 1975).

The carcinogenic potential of selenium has been widely investigated (Schroeder, 1974). Recent critical evaluations made of these early studies leads to the conclusion that there are insufficient high quality data to allow evaluation of the carcinogenicity of selenium compounds (WHO, 1975; Palmer and Olsen, 1974). No suggestion that selenium is carcinogenic in man can be found in the available data (WHO, 1975).

Antagonism between toxicity of selenium and other metals has been pointed out; Levander (1973) reviewed the action of arsenic in counteracting selenium toxicity. Several cases in which cadmium poisoning is decreased by selenium are listed by Pakkala _et_ _al_. (1972) and Anonymous (1972). The action against mercury toxicity has been mentioned by Koeman _et_ _al_. (1973). There are other aspects such as the interrelationship with vitamin E and possible teratogenic effects (Anonymous, 1972).

Toxicity due to selenium in drinking water is not common, probably because concentrations in water are generally low, and cases of toxicity to livestock are usually related to intake with food. However, a level of 9,000 µg/l in well water resulted in human poisoning in 3 months (Beath, 1962).

Water Quality Criteria 1972 (NAS/NAE, 1973) suggests a limit of 10 µg/l of total selenium in drinking water assuming that two litres of water are ingested per person per day. This recommendation is also accepted by WHO, U.S.A., Canada and U.S.S.R. whereas some European countries such as France use a 50 µg/l limit on selenium in potable water.

The U.S. National Academy of Sciences (NAS/NAE, 1973) recommends that the upper limit for selenium in water given to livestock be 50 µg/l. This figure is also used by the Ontario Ministry of the Environment (1974).

Bowen (1966) has described selenium as moderately toxic to plants (toxic effects at concentrations between 1 and 100 mg/l in the nutrient solution). This appears to apply to freshwater algae as well. The concentrations of selenite causing 95% growth inhibition of _Anabaena_ _variabilis_ and _Anacystis_ _nidulans_ were 20 and 70 mg/l, respectively (Kumar and Prakash, 1971). Selenate produced the same results with these species at 30 and 50 mg/l, respectively. Kumar (1964) showed that growth of _Anacystis_ _nidulans_, a bluegreen alga was also completely inhibited by 20 mg/l of selenate. However, a culture of this alga at increasing concentrations of selenate, over several generations, produced a tolerant strain that could grow in 250 mg/l of selenate. _Scenedesmus_ sp. however, was more sensitive since 2.5 mg/l was lethal (Bringman and Kuhn, 1959).

Little information is available on the toxicity of selenium to invertebrates, but *Daphnia* sp. has been found to be as sensitive as *Scenedesmus* sp. with a lethal threshold of 2.5 mg/l. (Bringman and Kuhn, 1959).

Niimi and LaHam (1975, 1976) have published the most comprehensive studies to date on toxicity of selenium to fish. Acute studies (Niimi and LaHam, 1976) indicated that lethality of selenium to zebrafish larvae (*Brachydanio rerio*) varied with the selenium salt used. The 96-hour and 10-day LC_{50}'s (Table 7) indicate that selenate salts are less toxic than selenite salts.

Table 7

Acute toxicity of selenium salts to zebrafish larvae (from Niimi and LaHam, 1976).

	96-hr. LC_{50} (mg/l)	10-day LC_{50} (mg/l)
selenium dioxide	20	5
sodium selenite	23	4
potassium selenite	15	≃2
sodium selenate	82	40
potassium selenate	81	50

These salts are the most common forms normally occurring in freshwaters. The selenides, selenomethionine and selenocystine, were also shown to be toxic. Selenocystine was about as toxic as the selenates and selenomethionine was more toxic. Reliable LC_{50}'s for selenides could not be calculated, however, due to a loss of compounds from the solution perhaps due to biological action. Biological action was also a problem in early experiments with inorganic compounds. It was noticed that bacterial slimes in test containers could produce a highly toxic, unidentified organic selenium compound. Daily cleaning alleviated the problem but it suggested that hazardous transformations of inorganic to organic selenium compounds might occur in aquatic systems.

Niimi and LaHam (1975) have also studied the toxicity of selenium dioxide to zebrafish embryos. Embryos were quite resistant and concentrations up to 10 mg/l had no effect on hatching. This was probably due to the extremely low permeability of the egg membrane. Larvae, by comparison, were quite sensitive and high mortality was observed at concentrations as low as 3 mg/l after 10 days. No effect was observed at 1 mg/l.

The acute toxicity of selenium to goldfish is similar to that of zebrafish. In very soft water, the 5day LC_{50} of sodium selenite for goldfish was 10 mg/l (Ellis et al., 1937). Other work by Ellis et al. (1937) showed that 2 mg/l of the same salt killed goldfish in 1846 days. Weir and Hine (1970) found a 7day LC_{50} for goldfish of 12 mg/l in water of 50 mg/l $CaCO_3$. Using a conditioned avoidance response as an index, Weir and Hine (1970) also found that 0.25 mg/l could significantly affect learning behaviour as compared to controls. A concentration of 0.15 mg/l had no significant effect.

Selenium dioxide was also lethal to six species of fish in 4 days to 2 weeks, at concentrations between 2 and 20 mg/l, (Cardwell et al., no date).

Concentrations of selenium in the tissues of fish range from 0.16 to about 0.6 µg/g, wet weight, in a wide range of locations in fresh and ocean water. This range holds for Canadian dressed fish from industrial and isolated locations (0.17 to 0.38 µg/g, Uthe and Bligh, 1971); for a large series of freshwater fish from New York (0.2 to 0.5 µg/g, Pakkala et al., 1973); for ocean and freshwater fish in Finland (0.2 to 0.58 µg/g, Sandholm et al., 1973); seafoods (about 0.32 to 0.56 µg/g, Morris and Levander, 1970); the edible portion of trout (about 0.28 to 0.68 µg/g, Arthur, 1972); and for samples of marine food fish obtained in Ontario markets (0.16 to 0.4 µg/g, Dr. D. Arthur, Dept. Nutrition, University of Guelph). In a very large series of fish from central Canada, concentrations in muscle sample averaged about 0.26 µg/g, and most of the fish fell in the range mentioned above (Beal, 1974). However, the total range was wider. In the Great Lakes, concentrations of selenium in fish from the North Channel of Lake Huron, Georgian Bay, Lake Erie and Lake Ontario ranged from 0.56-2.00, 0.42-1.15, 0.10-0.75 and 0.06-0.96 µg/g, respectively.

Fish mortality in a Colorado reservoir was reported by Barnhart (1958) as being caused by selenium from bottom deposits which had passed through the food chain to accumulated levels of 300 µg/g. This is the single known case. In a less contaminated aquatic ecosystem, the animals were shown to have higher residues than the plants, but there was no pattern of continuing accumulation. Also, fish from pond culture where the artificial food was low in selenium, contained less selenium than those from a natural system (Sandholm et al., 1973). In an experimental system, Sandholm et al. (1973) also found that Scenedesmus dimorphus could actively concentrate selenomethionine but showed no active or passive uptake of inorganic selenium. Daphnia pulex, however, could absorb selenium from selenite. Fish (Puntius arulius) absorbed selenium principally from food and showed little uptake from inorganic and organic forms in water. Copeland (1970) reported that concentrations of selenium from Lake Michigan zooplankton were highest downwind of industrialized areas, although this was not reflected in the sediments. Concentrations in the sediments were uniformly less than 0.5 μg/g, whereas, concentrations in zooplankton increased from 1 μg/g in uncontaminated areas to 7 μg/g in contaminated waters. Elimination of selenium by fish has not been studied but there appears to be no correlation of selenium with size, sex or age of fish (Pakkala et al., 1974). Therefore, selenium may be excreted in a similar fashion as determined in humans. A normal human intake of 0.06 to 0.15 mg/day is balanced by an output of 0.03 mg in faeces, 0.05 mg in urine, and 0.08 mg in sweat, air and hair (Schroeder et al., 1970).

A serious cause for concern may exist in the discovery that livers of some seals contain from 46 to 134 μg/g selenium (Koeman et al., 1973). These are much higher than the values of 0.5 to 1.3 μg/g found in the livers of land animals. Also, the single sample of tissue from a northern Canadian beluga whale showed a high level of 14.3 μg/g selenium. The topic is not well understood yet, Koeman et al. (1973) considered that the high selenium might be protective against high mercury residues.

Nevertheless, the possibility exists that fish-eating birds and mammals may be subject to a dangerous accumulation of selenium. The difference between optimal and toxic intake levels in the food is comparatively narrow (25 to 40 times, Hoffman et al., 1973). The fish mortality in Colorado indicates that accumulation can take place.

Since 3 μg selenium per gram of diet is toxic to rats over their lifetime and since the toxicity of selenium to fish-eating birds or wildlife is unknown, any accumulation of selenium in whole fish approaching 3 μg/g wet weight should be regarded with concern.

In summary, the recommendations for selenium in drinking water are more stringent than those for aquatic biota. Therefore, the recommended objective for selenium is 10 μg/l to protect raw drinking water supplies.

Selenium is known to be methylated biologically and Chau et al. (1976, in press) have recently demonstrated methylation of sodium selenite, sodium selenate, selenocystine, selenourea and seleno-DL-methionine by microbial action in lake sediments. All sediments that demonstrated microbial action were capable of methylating selenite and/or selenate. Three compounds, mono, and dimethyl selenide, and an unknown were produced. Since the bacterial action may have produced an unknown selenium compound of high toxicity to fish (Niimi and LaHam, 1976), the selenium objective should be reviewed when the environmental significance of selenium methylation is more completely understood.

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ZINC

RECOMMENDATION

It is recommended that the following new objective for zinc be adopted:

> *Concentrations of total zinc in an unfiltered water sample should not exceed 30 micrograms per litre to protect aquatic life.*

RATIONALE

Zinc, in various forms is used in metallurgy, metal fabricating, metal coatings, batteries, paint and varnish, industrial chemicals, rubber, soaps, medicines and pulp and paper production. In 1968, over 1,356 million pounds were used for these purposes in the Great Lakes basin (Fenwick, 1972). Zinc may enter the Great Lakes as a result of these uses in addition to inputs from mining and smelting of zinc ore, corrosion of metallic zinc and fallout from atmospheric contamination resulting from the burning of zinc-containing fossil fuels.

Zinc is quite soluble in water and weathering of rocks containing zinc contribute soluble forms to water (Fenwick, 1972). Offshore in the Great Lakes, modal concentrations of zinc are less than 10 µg/l, and 95% of samples contain less than 40 µg/l (Table 4). However, the mean zinc concentrations range from 1.8 to 28.2 µg/l. At water intakes, the mean zinc concentrations are generally less than 45 µg/l except in Lake Erie at Buffalo, where the mean is 178 µg/l. High concentrations have been observed at the St. Mary's River, the outlet of Lake Superior, at Buffalo (Lake Erie) and at Massena (outlet of Lake Ontario) (Table 5). At Buffalo, consistently high values suggest local zinc outputs near the water intake. Because zinc use is so widespread, sample contamination may be a problem.

Zinc is an essential element for both plants and animals. It is a constituent of many metalloenzymes and of several proteins of unknown function (Bowen, 1966). Zinc is necessary for reproduction, growth, formation of DNA and RNA, formation of the eye, and prevention of a fatal skin disease of pigs. It also promotes wound healing and prevents symptoms of poor blood supply in the legs that results from hardening of the arteries (Schroeder, 1974).

Zinc toxicity to land plants is rare and is usually observed on soils enriched with zinc as a result of mining operations (Bowen, 1966). Zinc is relatively non-toxic to man. However, when zinc metal is heated, zinc oxide fumes may be evolved that can cause "brass chills" or "brass founders ague". Direct doses of soluble zinc salts can cause nausea and vomiting (Fenwick, 1972). However, prolonged consumption of water containing up to 40,000 µg/l zinc has been reported with no harmful effects on humans (NAS/NAE, 1973). Consequently, the U.S. drinking water recommendation is based on taste and has been set at 5,000 µg/l (NAS/NAE, 1973). The maximum permissible limit in drinking water in Canada is also 5,000 µg/l but the objective is less than 1,000 µg/l (DNHW, 1969).

Concentrations of zinc inhibiting growth of freshwater algae generally range between 1,000 and 10,000 µg/l (Wong, 1975). However, growth inhibition of more sensitive species such as Oedogonium sp., Cladophora glomerata and Selenastrum capricornutum has occurred at 220, 240 and 700 µg/l, respectively (Whitton, 1970;Barlett et al., 1974).

Aquatic invertebrates are more sensitive to zinc than algae. Daphnia magna exposed to zinc for three weeks exhibited 50% mortality at 158 µg/l and 50% and 16% inhibition of reproduction at 102 µg/l and 70 µg/l, respectively (Biesinger and Christensen, 1972). Water hardness and alkalinity were 45.3 and 43.3 mg/l, respectively. In Lake Erie water, with a hardness and alkalinity of 123 and 91 mg/l, respectively, the 64-hour EC_{50} for immobilization of Daphnia magna was less than 150 µg/l (Anderson, 1948).

Fish are more sensitive to zinc than other aquatic organisms. Sublethal exposures of zinc for fathead minnows in Lake Superior water (hardness 45 mg/l, alkalinity, 42 mg/l) caused reduced egg production during spawning at 180 µg/l. No effect was observed at 30 µg/l (Brungs, 1969). In similar water, flagfish (Jordanella floridae) were more sensitive than fathead minnows. Eighty percent mortality of larvae of flagfish occurred at 85 µg/l zinc and only 10% at 51 µg/l. However, if the larvae had been pre-exposed as embryos to the test concentrations of zinc, they were more tolerant of the zinc. Complete mortality occurred at 267 µg/l, 20-30% occurred at 139 µg/l and 0-20% occurred at 75 µg/l or less (Spehar, unpublished manuscript). Rainbow trout fry also die at low concentrations. In water of 26 mg/l hardness and 25 mg/l alkalinity, unacclimated trout had a 120-hr LC_{50} of 135 µg/l while those pre-exposed as eggs had an LC_{50} greater than 526 µg/l. Based on lingering mortality of pre-exposed trout, the safe-unsafe concentrations were 135-251 µg/l (Goettl, et al., 1973). Reproduction of bluegills was affected by zinc. Decreased spawning and complete mortality of fry occurred at 235 µg/l, while no effect was seen at 76 µg/l. Hardness and alkalinity were 51 and 41 mg/l, respectively (Sparks et al., 1972).

Avoidance of zinc may prevent reproduction of Atlantic salmon. In the laboratory, juvenile salmon avoided 54 µg/l zinc, while in the field, migration of adults was prevented by about 240 µg/l (Sprague et al., 1965) In the field, there were also 19 µg/l copper in the water. The higher effective concentration of zinc could be due to the age of the fish or to the interaction between zinc and copper or some other constituent of natural waters. Growth of Phoxinus phoxinus in water with 63 mg/l alkalinity was reduced at 130 µg/l zinc but not at 50 µg/l (Bengtsson, 1974).

Sublethal toxicity to zinc may be enhanced when in combination with copper and cadmium. At a hardness of 207 mg/l, alkalinity of 154 mg/l, copper of 6.7 μg/l, and cadmium of 7.1 μg/l, 42.3 μg/l of zinc was associated with reduced spawning of fathead minnows. When copper, cadmium and zinc were 5.3, 3.9 and 27.3 μg/l, respectively, reproduction was unaffected (Eaton, 1973). Therefore, a safe concentration of zinc for fathead minnows was 30 μg/l in soft water (Brungs, 1969) and 27.3 μg/l in hard water in the presence of added copper and cadmium (Eaton, 1973). However, in Eaton's (1973) study, it cannot be stated that the effects observed were solely due to zinc. Nevertheless, concentrations of zinc causing sublethal harm to aquatic biota do not appear to vary significantly with hardness or alkalinity.

The average zinc content of Great Lakes fish ranged from 11-20 μg/g in fish fillets (Uthe and Bligh, 1971) and from 11-48 μg/g in fish livers (Lucas et al., 1970). From these data there appeared to be little variation in zinc content in fish with location within species. In contrast, Brown and Chow (1975) showed that the average concentration of zinc in fish muscle across 7 species of fish from Baie du Dore, Lake Huron, was 4.69 μg/g while the average across 11 species from Toronto Harbour was 36.02 μg/g. This suggests that levels may be influenced by local contamination. Experimental exposures of fish to ^{65}Zn in water indicated maximum accumulation in the gills and kidney. Following injection, maximum accumulation occurred in body tissues, such as kidney, hepatopancreas, heart, intestine, gill and scales (Saiki and Mori, 1955). Therefore, the route of uptake will affect distribution. Saiki and Mori (1955) did not follow concentration or location beyond 48 hours of exposure, nor after transferral to clean water. Mount (1968) found that the ratio of zinc in gills to zinc in bones was relatively constant in fish exposed to low levels of zinc. This indicated equal rates of deposition in these tissues. In fish exposed to lethal zinc concentrations, the ratio increased dramatically as the gills took up zinc quickly. In fish killed by zinc, the ratio exceeded a definite threshold. For fish subject to sublethal zinc intoxication, there is, as yet, no data relating tissue concentrations to particular toxic effects.

Therefore, in view of the great sensitivity of fish to low concentrations of zinc, an objective of 30 μg/l zinc is recommended for the Great Lakes.

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ii) OTHERS

FLUORIDE

RECOMMENDATION

It is recommended that the following new objective for fluoride be adopted:

> *Concentrations of total fluoride in an unfiltered water sample should not exceed 1.2 milligrams per litre to protect raw waters for public water supplies.*

RATIONALE

Fluorine, chemically bound as fluoride, is the 17th most abundant element in the earth's crust. It occurs in both igneous and sedimentary rocks and enters surface waters mainly through the weathering process of these rocks (Kilham and Hecky, 1973). The main fluorine-containing minerals are fluorspar (CaF_2), cryolite (Na_3AlF_6) and fluorapatite [$Ca_5F(PO_4)_3$].

The fluoride cycle involves passage to and from the atmosphere, hydrosphere, lithosphere and biosphere. It has been estimated that 6,000 tons of fluoride are contained in the 30 million tons of soil distributed in the atmosphere each year in the United States (NAS/NRC 1971). Industrial sources to the atmosphere and surface waters have been steadily increasing over the past hundred years with the processing of new materials from the earth's crust. These industrial sources include manufacture of aluminum; steel; brick and tile products; phosphorus fertilizer and coal fired electric power generation. Fluoride is also used as a pesticide and for many other commerical purposes. It has been estimated that approximately 120,000 tons of fluoride were emitted to the atmosphere in the United States in 1968 from industrial operations. A large portion of these particulates and gases are removed from modern plants practising good emission control by the use of filters, electrostatic precipitators and various wet-scrubbing systems (NAS/NRC, 1971).

Groth (1975) estimated that the phosphate and aluminum industries discharge between 10,000 to 35,000 tons of fluoride into United States surface waters annually. He also estimates that fluoridation practices in municipal water supplies add another 20,000 tons each year.

Fluoride in Water

In general, most fluoride salts formed with mono-valent cations are water soluble (e.g., NaF, AgF and KF) but those formed with di-valent cations are usually quite insoluble (e.g., CaF_2 and PbF_2), (Sienko, 1957).

Natural or "background" fluoride levels in most freshwater streams have less than 0.2 mg/l (Neuhold and Sigler, 1960; Groth, 1975). Concentrations of 13 mg/l are present in the Firehole and Madison Rivers in Yellowstone National Park and in Pyramid and Walker Lakes in Nevada (Sigler and Neuhold, 1972). Many East African lakes contain more than 1,000 mg/l, the highest natural concentrations found anywhere (Kilham and Hecky, 1973). A 1970 "background" water quality survey of 23 streams in the urbanized S.E. portion of Michigan's lower peninsula compared to 32 streams in the upper peninsula showed mean fluoride concentrations of 0.40 and 0.18 mg/l, respectively (Michigan DNR, 1970).

Fluoride concentrations in the upper Great Lakes are below those predicted by the equilibrium constants of Kramer (1964). This was based on the calcium-carbonate-phosphate-fluoride system which is believed to regulate the concentrations of fluoride in inland lakes. This regulating system was postulated as the explanation for the observation of uniform concentrations of fluoride (0.46 mg/l) at different depths and even in the interstitial water of 14 foot deep core samples from a meromictic lake (Brunskill and Harriss, 1969). Comparisons of actual concentrations in the Great Lakes to Kramer's model (1964) are as follows:

Table 8

Comparison of Kramer's predicted fluoride levels
for the Great Lakes with concentrations actually observed
(in mg/l).

Lake	Predicted Levels	Average fluoride concentrations		
		1961 to 1963*	1968**	1971***
Lake Superior	0.23	0.15	0.032	0.05
Lake Michigan	0.18	0.1	0.1	--
Lake Huron	0.43	--	0.074	0.08
Lake Erie	0.4	0.1	0.110	0.12
Lake Ontario	0.35	0.2	0.116	0.14

* Kramer 1964

** Weiler and Chawla 1969

*** CCIW 1975

Fluoride concentrations have been observed to increase with high river flows (Baker and Kramer, 1971), below municipal wastewater discharges (Bahls, 1973), and in the vicinity of phosphate-mining operations (Moore, 1971).

It is also interesting to note that fluoride is considered one of the main ligands responsible for keeping beryllium, aluminum, scandium, niobium, tantalum, iron and tin in solution in natural waters (Pitwell, 1974).

Drinking Water Supplies

Fluoride in drinking water for domestic animals generally has the same effect as in man. Concentrations less than 2 mg/l generally have no effect. Levels higher than this can cause mottling of teeth and extremely high intakes can cause skeletal fluorosis. Since food is the major source of fluoride intake by domestic animals, it has been suggested that concentrations in forage averaging 40 μg/g or less will not cause significant fluorosis (NAS/NRC, 1971). It has been reported that 4 to 5 mg/l of fluoride in drinking water resulted in observable effects in cattle in the form of dental lesions, mottling, staining and abnormal wearing of the teeth. Thorough examination, however, established that these effects were insignificant in the health, vitality, reproduction or milk production of the animals (Neeley and Harbaugh, 1954). Even when cattle receive large amounts of fluoride neither their flesh nor their milk pass it along the food chain to man. The body burden they do accumulate is almost entirely in their bones (NAS/NRC, 1974). NAS/NAE (1973) recommends an upper limit for fluoride in livestock drinking water of 2 mg/l for prevention of excessive teeth mottling.

Fluoride is often added to domestic water supplies to a level in the distribution system of 1.0 mg/l to prevent dental caries. Water containing less than about 1 mg/l will seldom cause mottling of teeth even in the most susceptible children. Levels sufficient to cause other health problems will not be encountered in a water supply fit to drink, but could only be accumulated through a large intake of drinking water.

The World Health Organization European Drinking Water Standards recommend an upper fluoride drinking water limit of 1.5 mg/l.

The United States Public Health Service Drinking Water Standards (1962) specify the same standard for drinking water as does Ontario, Canada (1974). These standards, for the Great Lakes Basin, are 1.3 mg/l in each case. The Canadian Drinking Water Standards (DNHW, 1969) specify a fluoride concentration in drinking water of 1.2 mg/l.

Effects on Vegetation

All vegetation contains some fluoride due to uptake from soil and water. The normal range for terrestrial plants is 2 to 20 µg/g (dry weight). Plants can also absorb soluble fluoride salts through their leaves. Information on the amount of fluoride in plant tissue derived from irrigation water is limited. One investigation showed that irrigation water containing 6.2 mg/l of fluoride increased the fluoride content of forage crops from 11 µg/g to 15 to 25 µg/g (Rand and Schmidt, 1952). A U.S. group of experts recently recommended a maximum of 1.0 mg/l for continuous use in irrigation water for all general soil applications and 15 mg/l for use over a 20-year period on neutral and alkaline fine textured soils (NAS/NAE, 1973).

Apparently no plant injury occurs by irrigation water containing 10-15 mg/l fluoride (Bower and Hatcher, 1967; McKee and Wolf, 1963). No reduction in carbon dioxide uptake occurred in terrestrial mosses incubated in aqueous solutions containing 820 mg/l fluoride for 24 hours. Uptake was effectively stopped by 8,200 mg/l after 24 hours (Inglis and Hill, 1974). They concluded that fluoride was relatively non-toxic to mosses.

Aquatic plants have been found to contain higher concentrations of fluoride than terrestrial plants. The terrestrial plants contained 33.8 µg/g compared to 40.5 µg/g in the aquatics (Danilova, 1944). However, no bioaccumulation was observed in either Cladophora or diatoms experimentally exposed for 72 days to fluoride concentrations of 52 mg/l (Hemens and Warwick, 1972). Suppression of growth was observed by Smith and Woodson (1964) in a bioassay using the alga Chlorella pyrenoidosa at all levels between 4.2 to 4,200 mg/l of fluoride. They concluded that this antimetabolite has its greatest effect between 420 and 4,200 mg/l where 86 and 98% inhibition occurred after 72 hours. Fluoride concentrations of 4.2 and 42 mg/l had equal inhibitory effects of 19% after 72 hours. Using the same algal species, but measuring respiration instead of growth, Sargent and Taylor (1972), however, did not detect inhibition at high levels of fluoride (1,680 mg/l). They did find that copper sulfate and fluoride acted more than additively in inhibiting respiration.

Kilman and Hecky (1973) observed that the sedge Cyperus papyrus was absent in African lakes containing 5.4 and 6.6 mg/l of fluoride but was abundant in lakes with 0.95 mg/l of fluoride.

Effect on Aquatic Animals

Recently Groth (1975) reviewed the available literature and concluded that there was a fairly compelling case for dealing with fluoride as a pollutant with a great capacity to do ecological harm. As part of the evidence supporting this concern he cited the fact that downstream concentrations of 0.5 to 3 mg/l fluoride can result from both industrial sources and municipal sewage. Concentrations are highest during summer months when biological activity is also at its peak. No ecological effects were correlated with these fluoride levels (Bahls, 1973). Groth (1975) states that much additional research is needed on the effects of fluoride and indicates that adverse effects on aquatic life may have been masked in the past by far more severe effects of untreated sewage, industrial effluents and other major pollutants.

Bacterial species commonly associated with municipal wastewaters were unaffected by concentrations up to 800 mg/l fluoride during a 48-hour bioassay. No changes in growth or morphology were observed in Escherichia coli, Pseudomonas fluorescens and Enterococcus species grown in nutrient broth and mineral media with the above-mentioned concentration of fluoride. No changes in viability were observed in these species after 4 months storage in the fluoride solution (Vajdic, 1966). Paramecia, Euglena and rotifers continued to live, reproduce and were active in fluoride concentrations of 2 to 1,000 mg/l (Wantland, 1956).

Using Lake Erie water as the diluent and fluoride as the toxicant, Anderson (1946) found a 48-hour EC_{50} of 504 mg/l for Daphnia magna. The measure of acute toxicity used was the 48-hour median effective concentration (48-hour EC_{50}) based on immobilization.

Indigenous populations of copepods were found in East African lakes containing 437 mg/l fluoride but not in lakes with 1,064 mg/l (Kilham and Hecky, 1973).

Studies with marine invertebrates indicate that only high fluoride concentrations were toxic to the bluecrab, Callinectes sapidus, (greater than 20 mg/l, (Moore, 1971)) and to oysters, (greater than 128 mg/l, (Moore, 1969)). However, Hemens and Warwick (1972) found a 30% mortality in brown mussels Prena perna after 5 days exposure to approximately 7.2 mg/l, and 60% mortality at 41.6 mg/l. No mortality was observed in 3 species of estuarine fish after 96 hours in 100 mg/l fluoride test solution. Stewart and Cornick (1964) found that exposure to 5 mg/l in sea water did not harm the lobster Homarus americanus at 2C, for 10 days.

Reliable bioassay data for freshwater fish are very limited and some researchers have used soft water as a diluent. Since calcium is antagonistic to fluoride toxicity it may not be valid to apply bioassay data from low calcium water, (less than 3 mg/l) to the Great Lakes which contain from 13 to 46 mg/l calcium (Vallin, 1968; Weismann, 1974; Sigler and Neuhold, 1972).

Neuhold and Sigler (1960) determined a 20-day LC_{50} for rainbow trout Salmo gairdneri of 2.7 to 4.7 mg/l fluoride (95% confidence level) using softened dilution water (calcium less than 3 mg/l). They concluded that this is much lower than would occur in high calcium water. They also subjected rainbow trout to 30 different combinations of fluoride and calcium concentrations ranging from 0 to 25 mg/l fluoride and 0 to 25 mg/l calcium. From these bioassays they determined the antagonistic relationship between fluoride and calcium and expressed it in an equation. Applying their equation for calcium/fluoride antagonism to Lake Superior water with a calcium concentration of 13 mg/l the LC_{50} for rainbow trout is 26 mg/l fluoride (Appendix I, page 132). The LC_{50} they determined for rainbow trout eggs (237 to 381 mg/l) was very high compared with earlier observations by Ellis et al. (1948) indicating that 1.5 mg/l delayed hatching and caused a poorer hatch. Neuhold and Sigler (1960) also found that rainbow trout embryos and fry are more sensitive than eggs to fluoride. The 34-day LC_{50} was between 61 and 85 mg/l. In bioassays of the more tolerant carp they found an LC_{50} between 71 and 91 (95% confidence level) at temperatures ranging between 18 and 24C. The carp ranged from 10 to 33 cm in size.

Bioassays by Herbert and Shurben (1964) using rainbow trout showed a 96-hour LC_{50} of about 18 mg/l in very soft water (hardness 12 mg/l). However, the authors concluded that waters with a greater hardness significantly reduced the toxicity of fluoride. They further stated that 1.0 mg/l fluoride would have only a negligible toxic effect on a trout population.

Wallen et al. (1957) found the mosquitofish *Gambusia affinis* survived fluoride concentrations of 560 mg/l and lower in turbid water with an alkalinity of less than 100 mg/l. The 96-hour LC_{50} was 925 mg/l. Ellis (1937) reported that goldfish *Carassius auratus* survived in a concentration of 100 mg/l in hard water for four days (termination of experiment).

In a review, Sigler and Neuhold (1972) indicate that the response of fish to moderate fluoride concentrations (1.5 to 5 mg/l) is related to acclimation, environmental variables such as calcium concentrations and temperature, and is species dependent. They state that fish populations vary with respect to their resistance to fluoride toxicity giving as examples the healthy growing populations of trout in the Firehold River in Yellowstone National Park, Pyramid and Walker Lakes in Nevada where fluoride concentrations reach 13 mg/l. Yet their earlier tests showed that trout raised in low fluoride concentrations displayed LC_{50} of approximately 3 mg/l.

Bioaccumulation in Aquatic Animals

Fluoride concentrations in fish range from less than 0.1 to 24 µg/g (NAS/NRC, 1974). Most of the data available deal with marine fish and potential problems with high fluoride concentrations in fish flour (Farkas, 1974). Fish-protein concentrate made in the United States was found to contain 169 µg/g fluoride (Hadjimarkos, 1964). Hoskins and Loustaunau (1974) analyzed fish-protein concentrate made from two marine species and one freshwater species and found that all were less than the F.D.A.'s 100 µg/g limitation and many were less than 25 µg/g.

Bioassays using fluoride concentrations ranging from 0.5 to 128 mg/l showed accumulations occurred at 2 mg/l and above in oyster tissues. Maximum levels in tissue, which were obtained after the first five days of exposure, were 100 µg/g exposed to solutions of 32 mg/l fluoride while 18 µg/g was found after the 2 mg/l exposure (Moore, 1969). The blue crab similarly reached a concentration of 50 µg/g in muscle after 90 days exposure to 20 mg/l fluoride while the control (0.1 - 1.5 mg/l fluoride) contained 10 µg/g (Moore, 1971).

Generally potential problems occur only at high exposures of fluorides or when the total fish is consumed (including bone) as in fish-protein concentrate.

In summary, since most of the fluoride toxicity studies on aquatic life have involved either the use of low calcium dilution waters or marine organisms, it is not practical to set an objective based on the protection of aquatic life. Therefore, it is recommended that the objective for fluoride be: 1.2 mg/l total fluoride in an unfiltered water sample to protect raw waters for public water supplies.

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APPENDIX I - FLUORIDE OBJECTIVE

EXTRAPOLATION OF LC_{50} USING CALCIUM CONTENT OF LAKE SUPERIOR WATER AND NEUHOLD'S EQUATION FOR CALCIUM/FLUORIDE ANTAGONISM

$$y = 2.33 + 2.03\ X$$

where y = probits - use 5, which is LC_{50}

$$x = (\text{Log } F - \text{Log } Ca + 1)$$

$$5 = 2.33 + 2.03\ (\text{Log } F - \text{Log } Ca + 1) \qquad Ca\ (\text{ppm}) = 13$$

$$(\text{Log } F = 1.11 + 1) \qquad \text{Log } 13 = 1.11$$

$$5 = 2.33 + 2.03\ (\text{Log } F - .11)$$

$$5 - 2.33 = 2.03\ (\text{Log } F) - .11\ X\ 2.03$$

$$2.67 = 2.03\ (\text{Log } F) - .22$$

$$2.89 = 2.03\ (\text{Log } F)$$

$$2.89 \div 2.03 = \text{Log } F$$

$$1.42 = \text{Log } F$$

$$26.0 = F \text{ conc. in mg/l}$$

APPENDIX I - FLUORIDE OBJECTIVE (cont'd)

CALCIUM

The relationship between the concentrations of calcium and fluoride ions and the LC_{50} of rainbow trout subjected to varying combinations of calcium and fluoride was ~~determined~~ determined by plotting the log of the ratio of fluoride to calcium against the probit of responses to the varying combination of calcium and fluoride. A straight line relationship from which the LC_{50} can be determined was found (Figure 1). The LC_{50} was determined between 1.01 and 4.22 [fluoride] / [calcium] at the 95 percent confidence

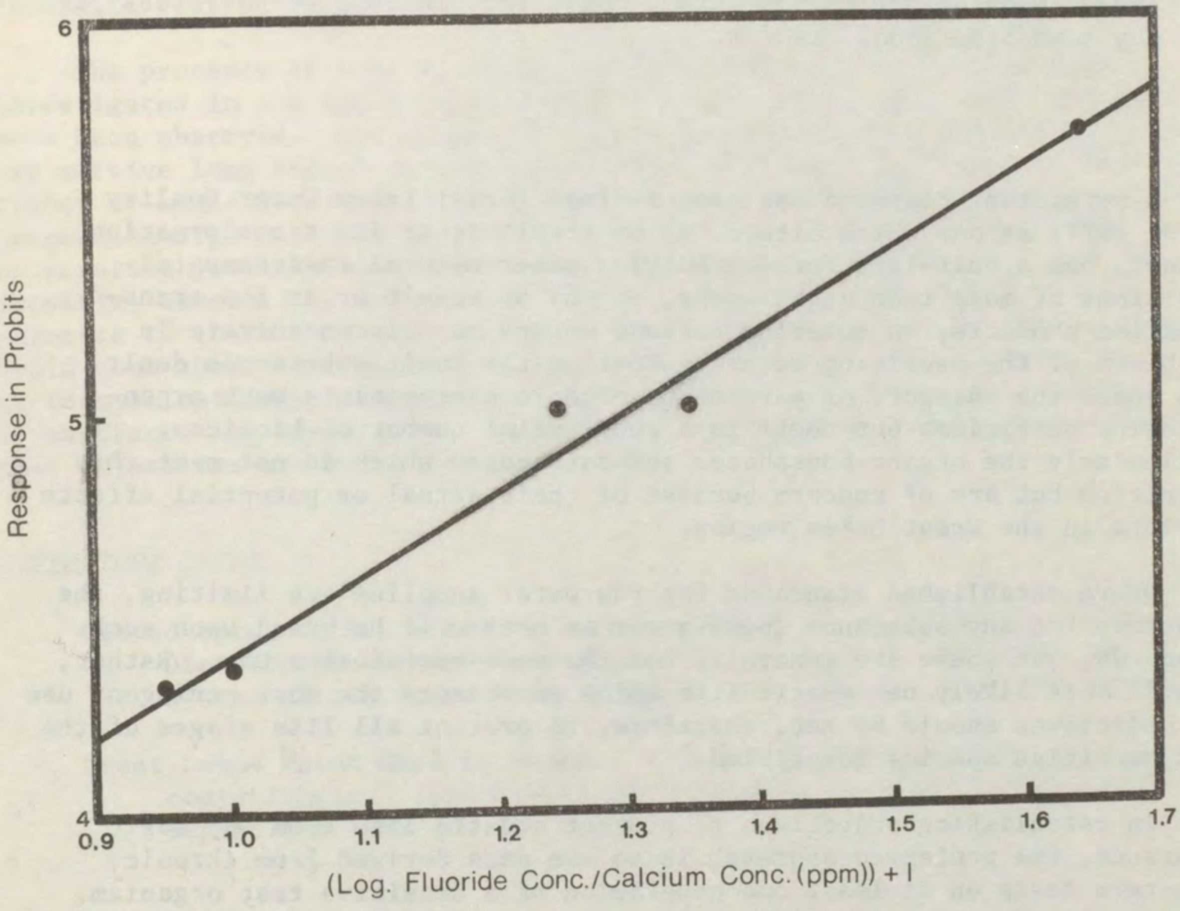

Figure 1. The response of rainbow trout to combinations of fluoride and calcium in the medium (expressed as the ratio between fluoride and calcium).

level. The sensitivity of the rainbow trout to the ratio of fluoride to calcium was between 1.71 and 2.35 probits of response per unit change in the log of the ratio. The relationship between the response and the log of the fluoride/calcium ratio (Figure 1) is expressed by the formula,

$$Y = 2.33 + 2.03X$$

where Y is the response in probits and X is the logarithm of the ratio between the fluoride concentration and the calcium ion concentration plus one unit characteristic.

(2) NON-PERSISTENT TOXIC SUBSTANCES

(a) ORGANIC

(i) PESTICIDES

GENERAL OBJECTIVE

RECOMMENDATION

Concentrations of unspecified, non-persistent pesticides should not exceed 0.05 of the median lethal concentration in a 96-hour test for any sensitive local species.

A persistent compound has been defined (Great Lakes Water Quality Board, 1974) as one which either a) by itself or as its transformation product, has a half-life for degradation under natural environmental conditions of more than eight weeks, or b) by itself or as its transformation products, on entering surface waters may bioconcentrate in the biota of the receiving waters. Most of the toxic substances dealt with under the category of persistent organic contaminants were organochlorine pesticides but there is a substantial number of biocides, particularly the organo-phosphates and carbamates which do not meet this definition but are of concern because of their actual or potential effects on biota in the Great Lakes region.

Where established standards for raw water supplies are limiting, the objective for any substance (persistent or not) will be based upon such standards, but these are generally not the most restrictive use. Rather, it will more likely be aquatic life which represents the most stringent use and objectives should be set, therefore, to protect all life stages of the most sensitive species identified.

In establishing objectives to protect aquatic life from any toxic substance, the preferred approach is to use data derived from chronic, long-term tests on at least one generation of a sensitive test organism. Accordingly, the approach adopted here is to establish objectives for those specific pesticides for which low level, long-term chronic testing has been conducted. Where scientifically determined "no-effect" levels are available, these levels shall be recommended as the specific numerical objective; but where such levels have not been determined, objectives will be established by applying an arbitrary safety factor of 0.2 to the lowest concentration which produced a subtle effect (e.g., reduction in reproductive success) on an appropriate test organism. This latter approach should provide a realistic estimate of "safe" levels, and is consistent with the philosophy established earlier for the establishment of objectives for persistent substances. Where neither the "no-effect" nor the estimated "safe" levels have been determined and where there are indications of potential and significant inputs to the Great Lakes basin, it is recommended that protection be afforded aquatic life through the use of a 0.05 safety factor applied to the 96-hour LC_{50} for the pesticide for sensitive local species.

It should be recognized that the preceding approach will significantly restrict the number of specific pesticides regulated within this category of substances, as an inadequate scientific data base exists for most of them to permit the establishment of defensible numerical objectives. For this reason, the use of the arbitrary safety factor of 0.05 times the 96 hour LC_{50} is employed. Objectives based on this latter procedure may be inadequate to protect aquatic life from a variety of deleterious sublethal effects or conversely, it may be unduly restrictive. Such a procedural objective is intended only as a temporary measure and not as a substitute for the requisite testing necessary to establish scientifically defensible objectives.

The presence of some of the organophosphorus pesticides has been investigated in the upper Great Lakes (Glooschenko et al., 1976) but none have been observed. While many of the compounds are not "persistent", they may survive long enough in localized areas to cause deleterious effects - either at acute levels or through accumulation of biological effects. The usage/discharge patterns are unknown for most of these substances and, to date, no pressing problems have been noted, at least on a basin basis. It is possible, however, to conceive of changing patterns such that localized exposure to these compounds might lead to undesirable levels. Such exposure could come about through direct application in spraying programmes and accidental spillage, via surface runoff or leaching, and with discharges in manufacturing operations. It is to protect against these eventualities that objectives are being formulated here.

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DIAZINON

RECOMMENDATION

The concentration of Diazinon in an unfiltered water sample should not exceed 0.08 micrograms per litre for the protection of aquatic life.

RATIONALE

Diazinon is the common name for the organo-phosphate pesticide diethyl-2-isopropyl-6-methyl-4-pyrimidyl phosphorothionate. It is commonly used to protect fruit trees, corn, tobacco and potatoes from sucking and leaf-eating insects. Diazinon is only slightly soluble in water (40 milligrams/litre at room temperature), and is stable in alkaline media, but is readily hydrolyzed in water (Martin, 1971).

Available data indicate that the persistence of diazinon in aquatic ecosystems is greatly influenced by pH. Cowart et al. (1971) demonstrated that the half-life of diazinon in water at a pH of 6.0 was 14 days. Miller et al. (1966) reported that 320 µg/l applied to a cranberry bog disappeared completely within 6 days. Gomaa et al. (1969) have indicated that the half-life of diazinon at pH values of 7.4, 9.0 and 10.4 was 184, 136 and 24 days, respectively. As pH values of 7.4-9.0 are normally encountered in waters of the Great Lakes system, it is possible that diazinon has the capability of persisting for up to several months in aquatic ecosystems. Because of the apparently conflicting data on its persistence, and as organophosphate compounds are generally non-persistent (i.e. half-life less than 8 weeks), diazinon is considered under the category of non-persistent pest control products.

Investigations of the accumulation rate of diazinon indicate that this compound does not appreciably accumulate in biological tissue. The Mummichog (Fundulus heteroclitus) concentrated diazinon to a level of approximately ten times the concentration in the surrounding water, but that 50% of tissue residue was lost in less than one week (Miller et al., 1966). Allison and Hermanutz (manuscript) reported that the accumulation factor for diazinon in fish is low (compared to that observed for most organochlorine pesticides), and that the tissue concentration is directly proportional to water concentrations.

There is currently no standard in use in either Canada or the United States which specifies maximum permissible concentrations of diazinon in raw public water supplies.

Exposure of the green alga Scenedesmus quadricaudata to diazinon concentrations of 100 and 1,000 µg/l produced no effect on cell number, photosynthesis, or biomass over a ten-day study (Stadnyk and Campbell, 1971).

Studies of the toxicity of diazinon to fish are limited, and generally report the results of acute exposures. The 24-hour LC_{50} for rainbow trout (Salmo gairdneri) to diazinon was determined to be 380 µg/l at 13°C (Cope, 1965). Cope (1966) reported that the 48-hr. LC_{50} for rainbow trout at 13°C and bluegills (Lepomis macrochirus) at 24°C was 170 µg/l and 96 µg/l, respectively. Mean 96-hr LC_{50} values for diazinon were reported to be 7,800, 460, 770 and 1,600 µg/l for fathead minnows (Pimephales promelas), bluegills, brook trout (Salvelinus fontinalis), and flagfish (Jordanella floridae) respectively (Allison and Hermanutz, manuscript).

The chronic effects of diazinon on fathead minnows and brook trout were studies by Allison and Hermanutz (manuscript). Statistically significant reductions in production rate for fathead minnows and brook trout were observed at 3.2 and 0.55 µg/l (lowest concentrations tested). Exposure of brook trout for 6-8 months to concentrations of diazinon varying from 0.55 - 9.6 µg/l resulted in equally reduced growth rates for progeny as well as adults. For fathead minnow, the hatch of progeny was reduced by 30% at a concentration of 3.2 µg/l. There is evidence that these effects on the progeny were the result of parental exposure alone, and not diazinon levels to which progeny were exposed following fertilization.

Available data indicate that the aquatic invertebrates are much more acutely sensitive to diazinon than are fish. The 48-hour EC_{50} (immobilization value at 15°C) for water fleas (Simocephalus serrulatus and Daphnia pulex) exposed to diazinon was 1.8 µg/l and 0.90 µg/l, respectively (Sanders and Cope, 1966). Sanders (1969) has reported that the 96-hr LC_{50} for Gammarus lacustris was 200 µg/l. The 48-hour LC_{50} for the stonefly (Pteryonarcys californica) has been demonstrated to range from 6 µg/l (FWPCA, 1968) to 7.5 µg/l (Cope, 1966). The 96-hr. LC_{50} of diazinon for Acroneuria lycorias has been reported to be 1.7 µg/l (NAS/NAE, 1973).

A number of studies have been conducted to determine the long-term acute toxicity of diazinon to aquatic invertebrates. These data are summarized in Table 9 (NAS/NAE, 1973).

Table 9 - Toxicity of Diazinon to Aquatic Invertebrates (NAS/NAE, 1973)

Organism	30-day LC_{50} (µg/1)	30-day no effect (µg/1)
Gammarus pseudo-limnaeus	0.27	0.20
Daphnia magna	-	0.26
Pteronarcys dorsata	4.6	3.29
Acroneuria lycorias	1.25	0.83
Ophiogomphus rupinsulensis	2.2	1.29
Hydropsyche bettoni	3.54	1.79
Ephemerella subvaria	1.05	0.42

No studies have been conducted to evaluate the chronic effects of diazinon on reproduction and behaviour of invertebrates. Similarly, there have been no complete life cycle studies to establish a "no-effect", or safe concentration of diazinon for aquatic invertebrates.

Results from studies of the long-term acute toxicity of diazinon to aquatic invertebrates indicate that an objective less than 0.20 µg/1 would protect invertebrates from exposure to concentrations which are directly lethal. The unpublished work of Allison and Hermanutz would indicate that 0.55 µg/1 of diazinon is sufficiently high to exert a negative effect on brook trout productivity. In the absence of "no effect" concentrations established through the conduct of complete life-cycle studies, and information on the chronic toxicity of diazinon to invertebrates, it is recommended that the objective for diazinon be derived by application of a safety factor of 0.05 to the 96-hour LC_{50} for the most sensitive species. A review of the data presented here indicates that Acroneuria lycorius (96-hr LC_{50} of 1.7 µg/1) is the most sensitive organism. Accordingly, it is recommended that concentrations of diazinon in water not exceed 0.08 µg/1 to ensure protection of aquatic life. Available data on the long-term acute toxicity, and studies of the chronic effect of diazinon on brook trout, would indicate that this objective should protect sensitive species of fish and aquatic invertebrates.

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ii) Other Compounds

OIL AND PETROCHEMICALS

RECOMMENDATION

It is recommended that the following revised objective for Oil and Petrochemicals be adopted:

Oil or petrochemicals should not be present in concentrations that:

(a) can be detected as a visible film, sheen, or discolouration on the surface (generally any amounts equal to or greater than 15 millilitres per 100 square metres);

(b) can be detected by odour;

(c) can cause tainting of edible aquatic organisms;

(d) can form deposits on shorelines and bottom sediments that are detectable by sight or odour, or are deleterious to resident aquatic organisms;

(e) can cause concentrations in water which exceed 0.09 of the lethal concentration (96-hr LC_{50}) for any important sensitive local organism.

EXISTING OBJECTIVE

The above objective is recommended to replace the existing objective for oil, petrochemicals and immiscible substances presently stipulated in Annex 1 of the Water Quality Agreement. This existing objective states:

> "Oil, Petrochemicals and Immiscible Substances. Waters should be free from floating debris, oil, scum and other floating materials attributable to municipal, industrial or other discharges in amounts sufficient to be unsightly or deleterious."

RATIONALE

Amenities, Waterfowl and Health

The first four objectives are self-evident on the basis of general knowledge. To protect aesthetic values, water and shoreline recreation, all four objectives are required.

The amount of oil required to produce a visible slick will vary with type of oil and weather conditions. However, the American Petroleum Institute has estimated that the first trace of irridescence or colour is formed when about 15 millilitres of oil is spread over 100 square metres (= 100 U.S. gallons over one square mile, or a film about 0.15 microns thick) (NAS/NAE, 1974).

Surface slicks must also be prevented to protect waterbirds and aquatic mammals. The mortality of waterbirds as a result of severe oil pollution is direct and immediate, and in major oil spills, deaths have been measured in the thousands. Birds that feed from the water or settle on it are vulnerable; diving ducks especially so. Plumage matted with oil allows water to displace air, causing the bird to lose both insultation and buoyance. Oil ingested during preening can have toxic effects. Less obvious, but long-continued small slicks such as from sewered oil, will in the end have similar debilitating effects on resident waterbirds.

Available information on occupational health and industrial hygiene indicates that any tolerable health concentrations for petroleum-derived substances far exceeds the limits of taste and odour. Thus, any hazards to humans from drinking oil-polluted water will not arise because such substances become objectionable at concentrations far below their chronic toxicity levels. Oils of animal or vegetable origins are usually non-toxic to humans and aquatic life.

Aquatic Organisms

The toxicity of crude oils and their derived substances to aquatic life cannot be stated in simple terms because they contain many different organic compounds and inorganic elements. The major components of crude oil are a series of hydrocarbons from paraffins and napthenes to aromatics, resins, asphaltenes, heterocyclic compounds and metallic compounds. The hydrocarbons make up the major group of acutely toxic compounds and there is agreement that their toxicity increases along the series paraffins, napthenes, and olefins to aromatics. Within each series of hydrocarbons, the smaller molecules are more toxic than the larger molecules. However, the high carbon number aromatics are the more persistent (Butler and Berkes, 1972).

Among freshwater organisms some information is available for fish. Lethal levels of oils are in the hundreds or thousands of µl/l. Bunker oil is lethal to American shad at 2400 µl/l (Tagatz, 1961) and Atlantic salmon at 1700 µl/l (Sprague and Carson, 1970). Crude oil slicks exceeding concentrations equivalent to 500 mg/l killed young coho and sockeye salmon in laboratory tests (morrow, 1974). Diesel oil kills shad at 167 µl/l (Tagatz, 1961). Some petroleum products appear to contain no soluble poisonous substances but when emulsified by agitation with water they prove deadly to fish. Agitated solutions of automobile gasoline and jet aviation fuel have been found to be lethal to fingerling salmon at concentrations of 100 and 500 mg/l respectively (EPA, 1974). Long-term effects would not be expected from these two fuels since they are volatile and would not remain in water for more than short periods, but short-term sublethal damage could occur.

An excellent set of tests has recently been reported in a provisional report by the U.S. National Water Quality Laboratory (Hedtke et al., 1974). Used crankcase oil was used in their tests, and this is probably a major source of oil in the Great Lakes. Floating oil killed fathead minnows at 11,000 µl/l, but mixed into the water it killed these fish at 1,600 µl/l, and flagfish at 1,000 µl/l. In chronic tests with flagfish (Jordanella floridae), 338 µl/l affected reproduction, while 93 µl/l did not. These are all nominal or "added" concentrations. We may take the ratio of proven "safe" level to the LC_{50}, = 93/1,000 = 0.093, as an application factor which is potentially useful in other situations.

Toxicity to marine animals (i.e. living in sea water), seems to have been studied more extensively that toxicity to freshwater forms. Marine invertebrate larvae seem particularly sensitive to oils. About 100 µl/l of various crude oils were lethal to planktonic stages of crab larvae and several other invertebrates (mironov, 1969a,b), shrimp (Mills and Culley, 1972). The same concentration of No. 2 fuel oil killed kelp crab larvae (Lichatovich et al., 1971), while 10 µl/l of "oil" killed a copepod in 4 days (Mironov, 1968). Lobster larvae were killed in 4 days by 13 mg/l of dispersed crude oil, and in 30 days by only 0.78 mg/l. Those were nominal concentrations and the acutal concentrations of oil estimated by measurement of the aromtics by u.v. spectrophotometry were only 18% of those values. That is, measured concentrations in the lobster experiments were 4-day LC_{50} = 2.3 mg/l and 30-day LC_{50} = 0.14 mg/l (Wells, in preparation).

Some sub-lethal effects have also been documented in marine animals. Crude oil at 100 µl/l caused inactivity and lack of survival over 2 weeks of Neopanope (Katz, 1973). For lobster larvae, the safe concentration of dispersed oil for rate of development and moulting was 0.72 mg/l nominal concentration, about the same as the 30-day LC_{50}. The measured concentration would be 0.13 mg/l (Wells, in preparation). The ratio of this "safe" concentration to the 4-day LC_{50} is $\frac{0.72}{1.3}$ = 0.55, a value which may be used as an application factor. For floating crude oil, the 4-day LC_{50} for lobster larvae was 150 mg/l, moulting was slowed at 12.5 mg/l, yielding a similar application factor of 0.083. For floating No. 2 fuel oil, the same values were 60 and 12.5 mg/l yielding an application factor of 0.21 (Wells, in preparation).

It is probable that the safe level of crude oils for sensitive Great Lakes crustaceans would be in the vicinity of 2 - 4 µl/l, as is the case for their marine cousins. However, such experiments have apparently not been done for freshwater invertebrates, and thus it is not warranted to use these low concentrations as criteria in the Great Lakes.

Use of application factors does seem warranted. The three application factors obtained for a marine crustacean are close to the one calculated for flagfish in fresh water. The median of the four application factors is 0.088, or close to 0.09. Applying this to the average lethal concentrations mentioned for freshwater fish, we may estimate "safe" levels for fish as follows:

Bunker oil	180 µl/l
Used crankcase oil	120 µl/l
Crude oil slicks	45 µl/l
Jet avaiation fuel	45 µl/l
Diesel oil	15 µl/l
Automobile gasoline	9 µl/l

Those concentrations are nominal (added) ones, and would have to be related to the measured concentrations in the water, according to the chemical procedures used in any individual situation.

The approximate "safe" concentrations listed above, are higher than those which would be expected to cause problems of odour, amenities, etc. under objectives (a) to (d). Therefore the safe concentrations for aquatic life have not been listed in the objectives, since other uses are more restrictive. The application factor has been put into the objectives. It seems likely that future research with sensitive organisms will show that in some situations, objective (e) will be the most restrictive.

Control

The eventual fate of oil in water depends on the basic processes of weathering, dispersion and degradation. The removal of hydrocarbons from water is accomplished by its breakdown into carbon dioxide and water. The natural processes that bring about the disappearance of oil in water include evaporation, solution, formation of emulsions, and sinking but none of these processes render the oil harmless to the aquatic environment. The ultimate destruction of oil depends upon its oxidation which is mainly by bacteria, although some photo-oxidation takes place.

There have been numerous corrective measures derived to clean up spilled oil, such as mechanical means and the use of detergents. Mechanical means have proven quite successful, but the use of detergent to disperse the oil has in many instances produced considerably more toxicity to aquatic life than the oil proper. The toxicity effects of detergent-oil mixtures are covered by the section on Unspecified Toxic Substances.

The only effective measures for the control of oil pollution of water is prevention of all spills and releases.

In this connection it is not generally recognized that much more oil enters world waters from routine operations and dumping, than from spills. For example, the International Lake Erie Water Pollution Board (1969, page 252) has estimated that the input of oil and grease to the Detroit and St. Clair Rivers is in excess of about 1,100 barrels per day. This is in the vicinity of 64,000 metric tons of oil per year. Such a "normal" operation is equivalent to the amount of oil from 3 or 4 major tanker wrecks, every year, each the size of the "Arrow" disaster on the Canadian east coast. Similarly, the International Niagara River Pollution Board, (IJC, 1971, p. 28) reported that 29 million pounds of oils were discharged to the Upper Niagara River. This is about 13,000 metrics tons per year, almost equivalent to one "Arrow" size wreck. Furthermore, the Board estimated that 40% of the oil came from municipal treatment plants. Large quantities of oil are also contained in dredging spoils. Dredging operations in Cleveland harbour in 1966 and 1967 resulted in the disposal of over 16,000 metric tons of oil and grease to Lake Erie (International Lake Erie Water Pollution Board et al, 1969). Again, that is just about equal to the amount of oil in the wrecked "Arrow". It is evident that as much pollution-control effort should be devoted to these routine sources as to spills.

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UNSPECIFIED NON-PERSISTENT TOXIC SUBSTANCES AND COMPLEX EFFLUENTS

RECOMMENDATION

It is recommended that the following new objective for unspecified non-persistent toxic substances and complex effluents be adopted:

> *Unspecified non-persistent toxic substances and complex effluents of municipal, industrial or other origin should not be present in concentrations which exceed 0.05 of the lethal concentration (96-hour LC_{50}) for any approved test species to protect aquatic life.*

RATIONALE

This procedural objective is developed to limit the effects of: (1) unspecified non-persistent substances toxic to aquatic life but which are not presently identified by a specific objective within Annex I of the Agreement, and (2) complex industrial and municipal effluents which are toxic to aquatic life and are discharged directly to the Great Lakes.

A large number of specialty chemicals are presently utilized in industrial processes, in agriculture and in the home. They include chemical reagents, disinfectants, pest control products, preservatives, emulsifiers, defoamers, floatation and chelation agents. In some cases treatment systems are either not utilized or are inadequate to reduce the toxicity of these materials before they are discharged to surface waters. Some of these substances combine with others in ways which have not been defined, analytical procedures necessary for their identification and quantification have not been developed and toxicity testing sufficient to permit establishment of a specific water quality objective has not been conducted. These substances may be discharged as components of complex effluents and their effects within the receiving water will be indistinguishable from the combined effects of the total discharge. In view of the unspecified nature and the lack of an adequate toxicological data base for these substances the objective recommends use of an application factor with acute toxicity data derived for approved test species.

Acute toxicity refers to 96 - hour concentrations lethal to half of the test organisms (96-hour LC_{50}) the median lethal concentration) derived in accordance with "Methods for Acute Toxicity with Fish, Macroinvertebrates and Amphibians", U.S. Environmental Protection Agency (in press); or published acute toxicity data expressed as the median lethal concentration for a 96-hour exposure during which test conditions were such that chemical and physical characteristics of the dilution water are comparable to existent water quality conditions at the boundary of the mixing zone.

Approved test species means any sensitive, locally important Great Lakes species or life history stage selected by the regulatory agency on the basis of appropriateness, or those species which have been used successfully in freshwater toxicity tests which are representative of sensitive important Great Lakes species.

To ensure that aquatic life within the receiving waters are afforded adequate protection from acute toxicity of these materials, it is necessary to perform bioassays to establish the toxicity of individual substances or mixtures and to use an application factor which should, in the majority of cases, reduce the concentration to that which is non-lethal for chronic exposure. The use an application factor will not preclude the possibility of sub-lethal effects occurring, but, since by definition these substances are non-persistent, exposure times will tend to be of short duration and effects outside mixing zones would not normally be expected. Where effects outside established mixing zones are demonstrated it should be evident that the application factor was inadequate to derive an objective which would provide for and protect the designated use.

The test species utilized for the establishment of an objective should ideally correspond to the most sensitive important species existing in the locality where the objective is to apply. This is the recommendation currently proposed in Water Quality Criteria 1972 (NAS-NAE, 1974). While this is scientifically sound, it presents a serious difficulty in practice. In order to determine which local species is most sensitive to a given introduced toxicant, it is necessary to evaluate a large number of organisms. Consequently, the objective recommends a choice of locally important test species which are known to tolerate laboratory test conditions. Selection of the approved test species should include representatives of cold and warmwater fish species as well as an important benthic invertebrates.

Recognition should be given to the large volume of acute toxicity data available from the scientific literature since it is unreasonable to require additional testing of those substances previously bioassayed by reputable laboratories. The objective permits use of such data where a) the species tested conforms to the requirements for species selection accompanying the objective and b) where dilution water quality utilized in the test was comparable to that which exists at the intended point of application of the objective (boundary of a mixing zone).

The choice of application factor is based on the recommendation put forward by (NAS-NAE, 1974) for determining acceptable concentrations of toxicants for which comprehensive toxicological data are lacking. This recommendation for nonpersistent and non-cumulative materials is a concentration not exceeding 0.1 of the 96-hour LC_{50} at any time or place after mixing with the receiving waters, while the 24 - hour average should not exceed 0.05 of the LC_{50} after mixing. Since the boundary of a mixing zone may be located further from the source than the point at which rapid mixing is completed, and since monitoring by regulatory agencies will more likely involve spatial sampling an irregular schedule rather than intensive sampling during a 24-hour period, it is recommended that the objective be 0.05 of the 96-hour LC_{50} at the mixing zone boundary. Based on a broad assessment of the scientific literature relative to the differences between LC_{50} values and incipient lethal concentrations for a diverse array of toxicants, and between lethal and sub-lethal concentrations, it is considered that an application factor of 0.05 (1/20th) will, apart from specialized cases, provide adequate protection to the aquatic community. Notwithstanding this recommendation, it is strongly advised that where two or more unspecified toxicants are discharged simultaneously, that the potential for synergistic or additive effects be established through bioassay testing and that the acceptable concentration be based on 1/20th of the net toxicity of the mixture.

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(3) OTHER SUBSTANCES

pH

RECOMMENDATION

It is recommended that the following, revised objective for pH be adopted to replace the existing objective stipulated in Annex 1 of the Water Quality Agreement:

> *Values of pH should not exceed the range 6.5 - 9.0, nor should discharges change the pH at the boundary of the designated mixing zone more than 0.5 units from the ambient.*

EXISTING OBJECTIVE

The above objective is recommended to replace the existing objective in Annex 1, paragraph 1(e) in the Water Quality Agreement, which states:

"Values should not be outside the range of 6.7 to 8.5."

RATIONALE

pH is a measure of hydrogen ion concentration, and in natural waters, results from the equilibrium achieved by the various dissolved compounds, salts and gases. The primary system regulating pH in natural waters is the carbonate system. Its role has been described in some detail by Stumm and Morgan. (1970)

Public Water Supplies

The pH of a raw water supply is significant because it may adversely affect water treatment process and contribute to corrosion of water works structures, distribution lines, and household plumbing fixtures, adding such constituents as iron, copper, lead, zinc and cadmium to the water (NAS/NAE, 1974). Adjustment of pH within the range of 5.0 - 9.0, the common range of pH values in natural waters, is relatively simple. "Water Quality Criteria 1972": (NAS/NAE, 1974) recommends that since "the defined treatment process can cope with natural waters within the pH range of 5.0 to 9.0, but becomes less economical as this range is extended, it is recommended that the pH of public water supplies be within 5.0 to 9.0." The "defined treatment process" includes sedimentation, rapid sand filtration, and disinfection with chlorine.

Primary Contact Recreation

"Water Qulity Criteria 1972" states that "for most bathing and swimming waters, eye irritation is minimized and recreational enjoyment enhanced by maintaining the pH within the range of 6.5 and 8.3 except for those waters with a low buffer capacity where a range of pH between 5.0 and 9.0 may be tolerated" (NAS/NAE, 1974). The principle author of that section is Dr. E. Mood, Yale University. Subsequent investigations on the level of protection afforded recreational users of Great Lakes waters indicated that the characteristics of water in the Great Lakes are such that no eye irritation would be expected if the pH did not exceed 9.0. (E. Mood, personal communication)

Fresh Water Aquatic Life

Based upon present evidence (EIFAC, 1969; NAS/NAE, 1974), a pH range of 6.5 - 9.0 will provide adequate protection for the life processes of fresh water fish and bottom dwelling invertebrates. Outside of this range, most aquatic organisms suffer adverse physiological affects of increasing severity as the degree of deviation increases.

Fluctuation of pH may be harmful not only by producing acid or alkaline conditions, but also by increasing the toxicity of various components in the waters. Reductions in pH caused by the addition of acids can liberate dissolved CO_2 in amounts which may be toxic (Doudoroff and Katz, 1950). Furthermore, acidification of water may increase the toxicity of various components in the waters. The acute toxicity of a metallocyanide complex increased by a factor of a thousand when pH values where reduced by approximately 1.5 units (Doudoroff et al, 1966).

Conversely, increases in pH can cause concentrations of unionized ammonia to increase to toxic levels. Unionized ammonia has been demonstrated to be ten times as toxic at pH 8.0 as at pH 7.0 (EIFAC, 1973).

Because of such effects, pH changes of more than 0.5 pH units should be avoided.

Aesthetic Consideration

The solubility of calcium carbonate in natural waters is influenced by levels of pH. Where levels of dissolved calcium carbonate exceed saturation, a pH approaching 9.0 may cause precipitation of this compound, creating a milky tinge.

However, as the recommended upper pH limit of 9.0 will protect all other designated users of the water, the range of 6.5 - 9.0 has been endorsed, and, the objective for suspended solids should be used to control local situations where precipitation of calcium carbonate may aesthetically degrade water quality.

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TAINTING SUBSTANCES

RECOMMENDATION

It is recommended that the following, revised objective for tainting substances be adopted to replace the existing objective in Annex 1 of the Water Quality Agreement:

1) *Raw public water supply sources should be essentially free from objectionable taste and odour for aesthetic reasons.*

2) *Levels of phenolic compounds should not exceed 0.001 milligrams per litre in raw public water supplies to protect against taste and odour in domestic water.*

3) *Substances entering the water as the result of human activity that cause tainting of edible aquatic organisms should not be present in concentrations which will lower the acceptability of these organisms as determined by organoleptic tests.*

EXISTING OBJECTIVE

The above objectives are recommended to replace the existing specific objective in Annex 1, paragraph 1 (d) in the Water Quality Agreement, which states:

> "Phenols and other objectionable taste and odour producing substances should be substantially absent."

RATIONALE

Raw Water Supply

Municipal wastewater discharges, especially those serving urban areas, and an array of industrial discharges have the capacity to impart objectionable taste and odour to water. There are also a number of naturally occurring materials in aquatic environments, as well as the metabolic by-products of micro-organisms that create tast and odour problems at water treatment plants. Taste and odour are primary factors which influence a consumer in determining acceptability of water for domestic use. Since these factors cannot be directly correlated with the safety of the water supply, protection from objectionable odour and taste is based on aesthetics.

The defined water treatment process is inconsistent in effect on removal of taste and odour producing properties of raw water, and data identifying threshold levels of individual materials are extremely variable. The objective, therefore, is narrative rather than numerical, with the exception of the objective for phenolic compounds.

For more specific information on taste and odour in raw public water supplies see Silvey, 1953; Silvey et al. 1950; Rosen 1966; and American Water Works Association 1970 and 1971.

Phenolic compounds are defined (Standard Methods, 1971) as hydroxy derivatives of benzene and its condensed nuclei. Local major sources of phenolic compounds to the water environment include municipal wastewaters and a variety of industrial wastes, especially those of oil refinery and chemical plants. Phenolic compounds may also occur naturally in aquatic ecosystems. Some phenolics are sufficiently resistant to degradation to be transported long distances in the water environment.

Major problems associated with phenolic compounds are their taste and odour producing properties in water and edible aquatic animals. (See Tables 13 and 14). Threshold odour levels in water are often below 1 mg/l: e.g. 0.555 mg/l p-cresol; 0.25 mg/l m-cresol; and 0.26 mg/l o-cresol (Rosen et al. 1962). Generally, phenolic compounds are not removed efficiently by the defined treatment process, which includes chlorination. If phenolic compounds are present in waters chlorinated for disinfection prior to distribution to consumers chlorophenols can be formed. The odour treshold concentrations for chlorophenols are generally much lower than the unchlorinated phenols: e.g. 4.2 mg/l phenol (Rosen, et al. 1962); 0.002 mg/l 2-chlorophenol (Burtschell, et al. 1959).

Water Quality Criteria 1972 (NAS/NAE, 1974) states that development of criteria for specific phenolic compounds is hampered by the lack of sensitive standard analytical techniques for their detection. However there is a widespread conclusion that protection against taste and odour due to phenolic compounds in water treated by the defined process requires that no more than 0.001 mg/l (1 μg/l) phenolic compounds be present. Variations of this recommendation incorporating the same number appear in California Water Quality Criteria (McKee and Wolf, 1963), European Standards for Drinking Water (WHO, 1970), Water Quality Criteria, 1972 (NAS/NAE, 1974), and the U.S. Drinking Water Standards (USPHS, 1962). The Canadian Water Quality Standards establish a limit of 2 μg/l in the raw water supply unless reduced to this limit by applied treatment.

Water quality criteria for toxic effects of phenol and phenolic compounds to aquatic life reveal that requirements for protection of water supplies are considerably more stringent. See EIFAC (1973) for a review.

TABLE 10

WASTEWATERS FOUND TO HAVE LOWERED THE PALATABILITY OF FISH FLESH (NAS/NAE, 1974)

Wastewaters	Concentration in water affecting palatability of fish	Species	Reference
2,4-D mfg. plant	50-100 ml/l	Trout	Shumway 1966
Coal-coking	0.02-0.1 ml/l	Freshwater fish	Bandt 1955
Coaltar	0.1 ml/l	Freshwater fish	Bandt 1955
Kraft process (untreated)	1-2% by vol.	Salmon	Shumway and Chadwick 1971
Kraft process (treated)	9-12% by vol.	Salmon	Shumway and Palensky 1973
Kraft and neutral sulfite process	----------	Trout	Newton 1967
Municipal dump runoff	----------	Channel catfish	Thomas & Hicks 1971
Municipal untreated sewage (2 locations)	----------	Channel catfish	Thomas & Hicks 1971
Municipal wastewater treatment plants (4 locations)	----------	Channel catfish	Thomas & Hicks 1971
Municipal wastewater treatment plant (Primary)	11-13% by vol.	Freshwater fish	Shumway and Palensky, unpublished data
Municipal wastewater treatment plant (Secondary)	20-26% by vol.	Freshwater fish	Shumway and Palensky, unpublished data
Oily wastes	----------	Trout	Zillich 1969
Refinery	----------	Trout	Fetterolf 1962
Sewage containing phenols	0.1 ml/l	Freshwater fish	Bandt 1955
Slaughterhouses (2 locations)	----------	Channel catfish	Thomas & Hicks 1971

TABLE 11

CONCENTRATIONS OF CHEMICAL COMPOUNDS IN WATER FOUND TO CAUSE TAINTING OF THE FLESH OF FISH

(Modified from NAS/NAE, 1974)

Chemical	Estimated threshold level in water (mg/l)	Reference*
acetophenone	0.5	d
acrylonitrile	18	g
cresol	0.07	g
m-cresol	0.2	g
o-cresol	0.4	g
p-cresol	0.12	g
cresylic acid (meta para)	0.2	d
N-butylmercaptan	0.06	g
o-sec. butylphenol	0.3	d
p-tert. butylphenol	0.03	d
o-chlorophenol	0.0001 to 0.015	b,d,e
p-chlorophenol	0.01 to 0.05	d,g,e
2,3-dichlorophenol	0.084	g
2,4-dichlorophenol	0.001 to 0.014	d,f,g
2,5-dichlorophenol	0.023	g
2,6-dichlorophenol	0.035	g
2-methyl, 4 chlorophenol	0.075	g
2-methyl, 6 chlorophenol	0.003	g
o-phenylphenol	1	d
2,4,6-trichlorophenol	0.003 to 0.05	g
phenol	1 to 10	d,e
phenols in polluted river	0.02 to 0.15	a
diphenyloxide	0.05	d
B,B-dichlorodiethyl ether	0.09 to 1.0	d,g
o-dichlorobenzene	0.25	d
ethylbenzene	0.25	d
ethanethiol	0.24	g
ethylacrylate	0.6	g
formaldehyde	95	g
gasoline	.005	j
kerosene	0.1	d
kerosene plus kaolin	1	i
isopropylbenzene	0.25	d
naphtha	0.1	d
naphthalene	1	a
naphthol	0.5	a
2-naphthol	0.3	g
dimethylamine	7	g
a-methylstyrene	0.25	d

TABLE 11 continued ...

oil, emulsifiable	15	d
pyridine	5 to 28	a,g
pyrocatechol	0.8 to 5	a,g
pyrogaliol	20 to 30	a
quinoline	0.5 to 1	a
p-quinone	0.5	a
styrene	0.25	d
toluene	0.25	d
outboard motor fuel, as exhaust	2.6 gal/acre-foot	c,h
guaiacol	0.082	g

*Reference key:

a Bandt 1955
b Boetius 1954
c English et al. 1963
d Fetterolf 1964 published the results of A.W. Winston, Jr. of the Dow Chemical Company. The data are also available in an undated mimeographed release of the company.
e Schulze 1961
f Shumway 1966
g Shumway, D. L. and J. R. Palensky, 1973
h Surber, et al. 1965
i Westman and Hoff 1963
j Boyle 1967

Protection of Aquatic Life

Edible portions of aquatic life or wildlife whose flavour, odour, colour or appearance has been tainted to a degree which lowers the desirability and acceptability of the organism for use as determined by organoleptic (sensory) tests represents damage to a resource. Commercial and recreational harvest and their associated economic roles have been negatively impacted by tainting (Thomas, 1973).

Many of the same compounds and wastes which cause objectionable taste and odour in domestic water supplies can be taken up by aquatic organisms and detected by the consumer. In addition, the appearance, colour and consistency of an organism or its edible portions can become less acceptable through exposure to a variety of contaminants and conditions. Such tainting can occur in waters with concentrations of the offending material lower than those recognized as being harmful to the organism. Water Quality Criteria 1972 (NAS/NAE, 1974) reviews the subject in detail and summarizes the literature on concentrations of wastewaters found to have lower the palatability of fish flesh and concentrations of chemical compounds in water than can produce identifiable taste in fish flesh. (Table 13 and 14).

These numbers should not be used as specific objectives. Chemical analytical techniques were not described in many of the reports, many of the sensory tests were conducted in uncontrolled environments, and the nature of the tests was often subjective. There is great variability in the threshold of sensory detection. In many cases the purposes of the tests were not to define a threshold level or nondetection level, but simply to provide information to a discharger on potential or existing problems associated with operation of the facility. The numbers should be used as guidelines in identifying possible sources when tainting problems are investigated.

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PHYSICAL CHARACTERISTICS

SETTLEABLE AND SUSPENDED SOLIDS AND LIGHT TRANSMISSION

RECOMMENDATION

It is recommended that the following revised objective for settleable and suspended solids and light transmission be adopted to replace the existing interim objective in Annex 1, paragraph 2 (d) of the Water Quality Agreement:

> *For the protection of aquatic life, waters should be free from substances attributable to municipal, industrial or other discharges resulting from human activity that will settle to form putrescent or otherwise objectionable sludge deposits or that will alter the value of the Secchi disk depth by more than 10 percent.*

EXISTING OBJECTIVE

The above objective is recommended to replace the existing interim objective for "Settleable and Suspended Materials" which is specified in Annex 1, paragraph 2 (d) of the Agreement, which states:

> "Waters should be free from substances attributable to municipal, industrial or other discharges that will settle to form putrescent or otherwise objectionable sludge deposits, or that will adversely affect aquatic life or waterfowl.

RATIONALE

Materials present in a lake absorb, scatter, and reflect light as it passes through the water (Hutchinson, 1957). Dissolved materials absorb light but substantial reduction in light transmission more commonly results from the presence of suspended particles. In areas where such particles are high in concentration, their influence can be noted by the human eye and the water is called turbid. Moreover, the effect of the particles on the light depends not only on concentration but also on size, shape, color, refractive index, and specific gravity.

The turbidity of the water can have a great effect on the types and quantities of algae that grow in a lake by altering the quality and quantity of light available for photosynthesis (Brylinsky and Mann, 1973; Hutchinson, 1967; and Pechlaner, 1970). This has been clearly demonstrated in the Great Lakes by Chandler's work in western Lake Erie.

Chandler shows that the algal productivity is high when turbidity is low and vice versa (Chandler 1940; 1945). His studies indicate that the composition, size, duration and emergence of phytoplankton pulses in this area are influenced by turbidity (Chandler, 1942a; 1942b; 1944; 1945). As the light energy fixed into organic matter by phytoplankton is the basis of almost all aquatic life, the turbidity-induced effects on these plants have ramifications throughout the ecosystem.

The ecological effects due to turbidity may be entirely natural. Such mechanisms as wave induced shoreline erosion and resuspension of bottom sediments, and the bloom of algal cells under favorable conditions may decrease light transmission to such an extent that the magnitude of photosynthesis is substantially curtailed. In addition, human activities may greatly alter turbidity and increase its fluctuations, thus having a large and usually unfavorable effect on the ecosystem. Besides the obvious effects on turbidity from direction addition of particulates, human activities can indirectly increase turbidity by adding nutrients that cause increased production and abundance of aquatic plants. In special circumstances human activities can also decrease turbidity by adding substances that cause the existing particles to aggregate and settle out of suspension faster than otherwise would occur. Even this effect could be detrimental to beneficial uses of the water by allowing much greater than usual algal production and by smothering benthic organisms and fish eggs. Large blooms of algae can lead to taste and odor problems in public water supplies as well as making the water aesthetically less suitable for such recreational activities as boating, water skiing, fishing, etc. Thus alterations in the ability of Great Lakes water to transmit light need to be strictly controlled.

This need was recognized for all aquatic environments in the U.S. by the National Academy of Sciences in its recommendations on water quality criteria (NAS/NAE, 1974). The Academy recommends "The combined effect of color and turbidity should not change the compensation point more than 10 percnet from its seasonlly established form, nor should such a change place more than 10 percent of the biomass of photosynthetic organisms below the compensation point." The term compensation point signifies the depth at which the amount of light energy fixed by algae is balanced by the energy used during normal metabolic processes. At depths greater than this point more energy is used than the algal cells fix. As a result the algae must use metabolic reserves in order to survive. This recommendation is intended to protect the naturally occurring photosynthetic capacity in the upper waters where photosynthesis takes place. The only problem with a criterion based on compensation point and biomass is the difficult and time-consuming nature of the measurement. For this reason, and objective upon light extinction as measured by Secchi Disk, an easy and problem-free procedure, is being recommended. Furthermore, it is generally accepted that the Secchi Disk measurement bears an approximately constant relation to the lower limit at which the necessary light to carry on photosynthesis is available (e.g., Holmes, 1970).

The value of 10% recommended in this criterion is somewhat arbitrary in that any alteration in turbidity will affect light transmission and consequently photosynthesis. Small changes in turbidity are difficult to detect, however, and will usually have only a minor effect on photosynthesis. Thus, the 10% value has been chosen as a level that can be detected quite easily and at which appreciable changes in algal production may begin to occur.

The United States Environmental Protection Agency in a late draft of a report to be published in Spring of 1975 has adopted the recommendation of the NAS. The complete NAS recommendation includes (NAS/NAE, 1974):

"Aquatic Communities should be protected if the following maximum concentrations of suspended solids exist:"

High level of protection	25 mg/1
Moderate protection	80 mg/1
Low level of protection	400 mg/1
Very low level of protection	over 400 mg/1

The rationale as presented below was taken primarily from the U.S. EPA late draft.

Fish and other aquatic life requirements concerning suspended solids can be divided into those who effect occurs in the water column and those who effect occurs following sedimentation to the bottom of the water body. Noted effects are similar for both fresh and marine waters.

EIFAC (1966) identified four categories of concern as suspended solids affect fish and fish food populations, namely:

> "(1) by acting directly on the fish swimming in water in which solids are suspended, and either killing them or reducing their growth rate, resistance to disease, etc.;
>
> (2) by preventing the successful development of fish eggs and larvae;
>
> (3) by modifying natural movements and migrations of fish;
>
> (4) by reducing the abundance of food available to the fish;..."

While indicating that no sharp boundaries exist for inert suspended solids whereby fisheries are not damaged above that level, the EIFAC review yielded the following conclusions assuming inert solids and otherwise satisfactory water quality:

> "(a) there is no evidence that concentrations of suspended solids less than 25 ppm (parts per million) have any harmful effects on fisheries;
>
> (b) it should usually be possible to maintain good or moderate fisheries in waters which normally contain 25 to 80 ppm suspended solids. Other factors being equal, however, the yield of fish from such waters might be somewhat lower than from those in category "a";
>
> (c) waters normally containing from 80 to 400 ppm suspended solids are unlikely to support good freshwater fisheries, although fisheries may sometimes be found at the lower concentrations within this range; and
>
> (d) at the best, only poor fisheries are likely to be found in waters which normally contain more than 400 ppm suspended solids".

However, available evidence indicates that the death rate for fish living in water containing 200 ppm or more of suspended solids for long periods of time will be greater than for similar fish living in clear water, and that suspended material from industrial discharges (e.g., coal washings and pulp wastes) may be substantially more toxic (EIFAC, 1965).

The committee added a caveat that although exposure to several thousand parts per million for several hours or days may not kill fish, such excessive concentrations should be prevented in waters reserved for maintenance of good fisheries.

Settleable materials which blanket the bottom of water bodies damage the invertebrate populations, block gravel spawning beds, and if organic, remove dissolved oxygen from overlying waters (EIFAC, 1965; Edberg and Hofsten, 1973). In a study downstream from the discharge of a rock quarry where inert suspended solids were increased by 80 mg/1, the density of macroinvertebrate populations also decreased by 60 percent regardless of the suspended solid concentrations (Gammon, 1970). Similar effects have been reported downstream from an area which was intensively logged. Major increases in stream suspended solids (25 mg/1 upstream vs. 390 mg/1 downstream) caused smothering of bottom invertebrates, reducing organism density to only 7.3 per square foot versus 25.5 per square foot upstream (Tebo, 1955).

When settleable solids block gravel spawning beds which contain eggs, high mortalities result although there is evidence that some species of salmonids will not spawn in such areas (EIFAC, 1965).

It has been postulated that silt attached to the eggs prevents sufficient exchange of oxygen and carbon dioxide between the egg and the overlying water. The important variables are particle size, stream velocity and degree of turbulence (EIFAC, 1965).

Deposition of organic materials to the bottom sediments can cause imbalances in stream biota by increasing bottom animal density, principally worm populations, and diversity is reduced as pollution sensitive forms disappear (Mackenthun, 1973). Algae likewise flourish in such nutrient rich areas although forms may become less desirable (Tarzwell and Gaufin, 1953).

Identifiable effects of suspended solids on irrigation use of water include the formation of crusts on top of the soil which inhibits water infiltration, plant emergence and impede soil aeration; the formation of films on plant leaves which block sunlight and impede photosynthesis and which may reduce the marketability of some leafy crops like lettuce; and finally the adverse effect on irrigation reservoir capacity, delivery canals and other distribution equipment (NAS/NAE, 1974).

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ASBESTOS

RECOMMENDATION

> *Asbestos should be kept at the lowest practicable levels and in any event should be controlled to the extent necessary to prevent harmful effects on health.*

RATIONALE

At this time there is insufficient information to recommend a meaningful or defensible numerical asbestiform fibre objective for protection of aquatic organisms, raw public water supply or drinking water.

Asbestos is a generic name for several fibrous silicates. The reported background level of asbestiform fibre concentration in the Great Lakes varies from less than one million to ten million fibres/litre. Sources of asbestiform fibres are natural erosion, mining and processing operations, and man's use of the manufactured products. That inhaled asbestos is related to an increased incidence of cancer is reasonably well known, but the effects of ingested asbestiform fibres have only recently come under study and the demonstrable hazard to health is not defined. A major Lake Superior source is the Reserve Mining Company operation at Silver Bay, Minnesota. Eighty-seven and two hundred fifty million fibres/litre have been reported from Lake Superior water in the Beaver Bay and Duluth, Minnesota areas, respectively. These elevated levels have focused attention on the desirability of defining threshold effect and safe levels for various water uses. The reader is referred to "Asbestos in the Great Lakes Region" (IJC, 1975), the source of the above text, for more detailed information.

Research on health effects of ingested asbestiform fibres is ongoing through animal feeding studies conducted under the aegis of the Environmental Protection Agency and the U.S. Food and Drug Administration.

Very little is known concerning the effects of asbestiform fibres on aquatic organisms. Concern has been expressed over possible effects from: (1) ingestion by fish with water need for osmoregulation; (2) inadvertent ingestion by particulate feeders; (3) decrease in buoyancy of planktonic organisms caused by accumulations on their surfaces; and (4) decreased gill-function efficiency.

Filter feeders, such as the fingernail clams, appear especially vulnerable to direct ingestion of asbestiform particles. Halsband (1974) investigated the short term effects of asbestos intake on the mussel (Mytilus edulis), a marine mollusk filter feeder. He exposed mussels to the fine fraction of tailings from a process which separates asbestos fibres from ore whose source is the Ungava Peninsula of Canada on the northeastern shore of Hudson Bay. Mussels were exposed for 5 days in extremely high concentrations of 100 mg/l and 10 mg/l. Some were removed after exposure and prepared for tissue examination while others were placed in "unpolluted" water for 7 days to provide an opportunity for purging before tissue examination. Examination showed clearly that asbestos fibres penetrated the epithelial tissue of the stomach and intestinal tract of mussels in the variations of exposure and post-exposure. Apparently some mussels were allowed longer purging periods for Halsband states, "After several weeks exposure ... to unpolluted seawater these foreign bodies were not disposed of". He concluded that tissue damage had occurred, but offered no evaluation of effects.

The Canada Centre for Inland Waters reports they do not know of experimental work in Canada dealing with effects of asbestos on aquatic organisms. The U.S. EPA National Water Quality Laboratory at Duluth has commenced a $644,000 project extending to 1979 entitled "Environmental Impact of Asbestos on Freshwater Organisms". This project will: determine the extent to which environmental contamination has occurred in the U.S. by extensively surveying all existing data; employ tracer, autoradiographic and other refined techniques to identify target organs and tissues in important fish species; develop better methods to determine asbestos content in water and tissue; develop response data relating effects of freshwater organisms exposed to asbestos fibres; and determine the extent to which previous water quality criteria data was affected by the laboratory's water supply contamination by asbestiform minerals.

Examination of the research plan suggests the emphasis will be on fish and larger invertebrate animals. Effects on plankters may be of aquatic or greater importance and might be more easily detected. Tests with these smaller organisms should be conducted.

The IJC Research Advisory Board's Standing Committees on Health Effects and Scientific Basis for Water Quality Criteria have established lines of communication with personnel on the research projects and will remain alert to findings appropriate to establishment of objectives.

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NON-DEGRADATION AND ENHANCEMENT

RECOMMENDATION

It is recommended that the following statements regarding non-degradation and enhancement be adopted to replace the existing statement which appears in paragraph 3, Annex 1 of the Water Quality Agreement:

> *Non-degradation*
> *Notwithstanding the adoption of specific water quality objectives, all reasonable and practicable measures shall be taken in accordance with paragraph 4 of Article III of the Agreement to maintain the levels of water quality existing at the date of entry into force of the Agreement in those areas of the boundary waters of the Great Lakes System where such water quality is better than that prescribed by the specific water quality objectives.*
>
> *Enhancement*
> *In areas designated by the appropriate jurisdiction as having outstanding natural resource value and which have water quality better than prescribed by the specific water quality objectives, that water quality should be maintained or enhanced.*

EXISTING OBJECTIVE

The above statements are recommended to replace the existing non-degradation statement in Annex 1, paragraph 3 of the Agreement, which states:

> "Notwithstanding the adoption of specific water quality objectives, all reasonable and practicable measures shall be taken in accordance with paragraph 4 of Article III of the Agreement to maintain the levels of water quality existing at the date of entry into force of the Agreement in those areas of the boundary waters of the Great Lakes System where such levels exceed the specific water quality objectives."

COMMENTARY

The existing statement is drawn from Article III, paragraph 4 of the Agreement and it should also be amended as above.

RATIONALE

A water quality objective as defined by the Water Quality Objectives Subcommittee is "that minimum quality of water which will provide for and protect any designated use". A primary purpose for establishing water quality objectives is to upgrade and enhance water quality that is already deteriorated from the objective. In many areas, however, depending on the assigned use, the existing level of water quality is significantly better than the objective stated for that use. It becomes equally important then, that in order to maintain existing water uses, the water quality not be deteriorated from present levels.*

The Congress of the United States in the first sentence of the 1972 Amendments to the Federal Water Pollution Control Act stated: "the objective of this Act is to restore and maintain the chemical, physical and biological integrity of the Nation's waters" (emphasis added). Similarly, "Guidelines and Criteria for Water Quality Management in Ontario" state in part that "water of a higher quality than that required by the standard will be maintained at that high quality..." These statements clearly indicate the importance placed on preserving existing water quality, and are the basis on which non-degradation policies must be established with respect to the boundary waters of the Great Lakes System.

The Water Quality Agreement in Article III and again in Annex 1 presents a statement of non-degradation. There are provisions in this statement which can result in technical misinterpretation of non-degradation, and water quality degradation of even sensitive areas of the Great Lakes.

Technical misinterpretations of the stated non-degradation policy center upon the word "exceed". The statement indicates that water quality must be maintained at existing levels where such levels "exceed" the specific water quality objectives. It is generally understood that the drafters of the Agreement intended that water quality should be maintained at existing levels when those levels are within the limits of the stated objective. In a majority of cases, water quality objectives are concentrations of contaminants above which water uses will be restricted. In other cases, the objective is the lowest concentration which should be maintained to assure the stated use. Therefore, a strict interpretation of the word "exceed" could mean that if a particular parameter concentration was greater than the objective, maintenance at that level would be appropriate when actually the water quality objective was being violated. Maintaining water quality which is "better" than the stated objective more properly states the intent of the non-degradation policy.

Under current policies, degradation of the water quality of the boundary waters of Great Lakes system can occur provided that "all reasonable and practicable measures" are taken to maintain that quality. The implied intent of the Agreement is not to allow water quality degradation except in special circumstances and under very tight restrictions. That such deterioration should be allowed under warranted conditions may be necessary to preserve a resource of higher value.

* Conformance with a non-degradation policy assumes a knowledge of baseline water quality. Other committees and study groups within the International Joint Commission are assigned the task of ascertaining existing levels of water quality. Concurrence with respect to the results of these activities will necessarily be the basis from which non-degradation is required.

The National Resource Defence Council recognized that fact when in 1973 they adopted a policy on non-degradation. That policy states in part:

> "After public hearings, all water segments in the state should be divided into two categories. Category I would be segments which should be kept in their present condition because they constitute an outstanding natural resource, e.g., rivers in parks and other waters of great recreational or ecological significance. No degradation in these segments would be allowed.
>
> Category II would be all other segments. Water quality here would be allowed to degrade by a small predetermined percentage. The percentage would vary depending on the water quality parameter but in no case would the percentage be large enough to allow the waters to degrade significantly. Moreover, if existing water quality meets the 1983 interim standard expressed in Sections 101 (s) (2) and 302 of the Federal Water Pollution Control Act, the quality should in no case fall below that standard. The water quality required by 1983 is that which provides for the protection and propogation of fish, shellfish, and wildlife and which provides for recreation in and on the water."

There are within the boundary water of the Great Lakes System areas which are of special natural resource significance. These areas must receive the maximum amount of protection that current technology and legislation can provide. A non-degradation policy should reflect this protectionist philosophy for those unique areas of the Great Lakes that deserve this special attention. In order to assure that these areas are recognized an effort must be made to designate areas of "outstanding natural resource value". The intent is not to prohibit all use, development, or discharge into such areas, but rather to assure that water quality is at least maintained at existing levels. The recommended revision provides management with a basis for maintaining or upgrading the existing water quality.

MIXING ZONES (GUIDELINES FOR DESIGNATION)

The following concepts are recommended as non-numerical mixing zone guidelines which reflect good water management principles:

1. *A mixing zone is an area, contiguous to a point source, where exceptions to water quality objectives and conditions otherwise applicable to the receiving waterbody may be granted.*

It is not prudent to provide blanket exemption from all water quality objectives within mixing zones. Therefore, exemption should be at the discretion of the regulatory authority on the basis of local conditions.

2. *Specific water quality objectives and conditions applicable to the receiving waterbody should be met at the boundary of mixing zones.*

It is important to recognize that this concept allows the plume of the effluent to be identifiable outside the mixing zone. It does not limit the extent of the plume, only that portion of the plume that is not required to meet water quality objectives.

3. *Limitations on mixing zones should be established by the responsible regulatory agency on a case-by-case basis, where "case" refers to both local considerations and the waterbody as a whole, or segment of the waterbody.*

Guidelines cannot be substituted for knowledge of local areas or common sense but they can assist in identifying critical factors on which to base decisions. Mixing zones should be tailored to the characteristics of receiving systems, recognizing not only the local effect, but the cumulative effect of all mixing zones on the waterbody or segment thereof.

4. *Mixing zones, by definition, represent a loss of value.*

Because specific water quality objectives define minimum conditions to provide for and protect a use and because exemption to objectives may be granted within mixing zones, it is apparent that certain values are lost. There is a gradation of loss of values from greatest at the end of the pipe to least at the periphery. Mixing zones may increase recreation potential or production of desirable organisms in some instances and losses may occur only seasonally. However, in allocation of loss of biological value it may be assumed that areas within mixing zones represent a potential total loss of the most sensitive value identified as being affected adversely.

5. *Many of the general water quality objectives should apply to the discharge-related materials within mixing zones. The zones should be free of:*

(a) *objectionable deposits;*

(b) *unsightly or deleterious amounts of flotsam, debris, oil, scum and other floating matter;*

(c) *substances producing objectionable colour, odour, taste, or turbidity; and*

(d) *substances and conditions or combinations thereof at levels which produce aquatic life in nuisance quantities that interfere with other uses.*

Objections of people to a point source discharge are often related to the impact on their aesthetic sensitivities. Aesthetically acceptable mixing zones create goodwill among the discharger, the public and the regulatory agency.

6. *No conditions within the mixing zone should be permitted which are either (a) rapidly lethal to important aquatic life (conditions which result in sudden fish kills and mortality of organisms passing through the mixing zone); or (b) which cause irreversible responses which could result in detrimental post-exposure effects; or (c) which result in bioconcentration of toxic materials which are harmful to the organism or its consumers.*

Rapid changes in water quality cause stress in aquatic life through shock effect, thus changes should be guarded against in the operational regime. Rapid dilution in mixing zones is desirable so that weak swimmers, such as planktonic organisms entrained in the plume at the discharge, will be exposed to the higher concentrations of constituents for short periods only.

7. *Concentrations of toxic materials at any point in the mixing zone where important species are physically capable of residing should not exceed the 24 to 96-hour* LC_{50}.

The mixing zone should be considered as a region in which organism response to water quality characteristics is time-dependent. Therefore, if organisms are exposed for short periods only, a greater concentration can be considered. Conversely, when it is known, or can be demonstrated, that the discharge is attracting and holding organisms for long periods, a reduction of concentrations of toxic materials to below the 96-hour LC_{50} should be considered.

8. *When designing conditions to protect specific organisms it is necessary to know that the organisms would normally inhabit the area within the mixing zone. Zones of passage should be assured either by location or design of conditions within mixing zones. Mixing zones should not form a barrier to migratory routes of aquatic species or interfere with biological communities or populations of important species to a degree which is damaging to the ecosystem, or diminish other beneficial uses disproportionately.*

To prevent blocks to passage, less than half the stream width should be used as a mixing zone. Since dischargers may wish to use the other half in the future, good practice suggests limiting individual mixing zones to one-third of the width.

9. *Mixing zones may overlap unless the combined effects exceed the conditions set forth in other guidelines.*

10. *Municipal and other water supply intakes and recreational areas should not be in mixing zones as a general condition, but local knowledge of the effluent characteristics and the type of discharge associated with the zone could allow such a mixture of uses.*

11. *Areas of extraordinatory value may be designated off-limits for mixing zones.*

12. *The size, shape and exact location of a mixing zone should be specified so that both the dischargers and the regulatory agency know the bounds.*

13. *Existing biological, chemical, physical and hydrological conditions should be known when considering location of a new mixing zone or limitations on an existing one.*

There are many advantages to be gained by designing with nature and severe penalties for working against nature.

VIII

MEMBERSHIP

OF

WATER QUALITY OBJECTIVES SUBCOMMITTEE

OF

THE GREAT LAKES WATER QUALITY BOARD

MEMBERSHIP LIST

WATER QUALITY OBJECTIVES SUBCOMMITTEE (1974-75)

William H. Anderl*
Minnesota Pollution Control Agency
1935 West Country Road B2
ROSEVILLE, Minnesota 55113

George C. Becking*
Chief
Environmental Toxicology Division
Bureau of Health Hazards
Health and Welfare Branch
OTTAWA, Ontario K1A 0L2

Gerald P. Brezner*
Chief
Water Quality Standard Section
Department of Environmental Conservation
State of New York
50 Wolf Road
ALBANY, New York 12201

Tom Brydges*
Ontario Ministry of the Environment
Box 213
REXDALE, Ontario

Patrick S. Chamut*
Environment Canada
Fisheries & Marine Service
615 Booth Street
OTTAWA, Ontario

George B. Garrett*
Chief
Division of Water Quality Standards
Ohio Environmental Protection Agency
P. O. Box 1049
COLUMBUS, Ohio 43216

Peter V. Hodson*
Canada Centre for Inland Waters
Great Lakes Biolimnology Laboratory
P. O. Box 5050
BURLINGTON, Ontario L7R 4A6

James B. Park
Supervisor Standards Unit
Division of Water Pollution Control
Illinois EPA
2200 Churchill Road
SPRINGFIELD, Illinois 62706

Chris P. Potos*
Environmental Protection Agency
230 South Dearborn Street
CHICAGO, Illinois 60604

Stewart W. Reeder* (Chairman)
Coordinator, Water Quality Objectives
Water Quality Branch
Inland Waters Directorate
Environment Canada
Place Vincent Massey
HULL, Quebec

John Robinson*
Chief
Water Quality Appraisal Section
Michigan Department of Natural Resources
Stevens T. Mason Building
LANSING, Michigan

Kenneth E. Schoener
Lake Erie-Ohio River Basin Engineer
Division of Water Quality
Dept. of Environmental Resources
Commonwealth of Pennsylvania
P. O. Box 2063
HARRISBURG, Pennsylvania 17120

Duane H. Schuettpelz*
Wisconsin Dept. of Natural Resources
P. O. Box 450
MADISON, Wisconsin

J. Arthur Terreault
Services de Protection de L'Environment
Centre D'Achate Innovation
2360 Chemin Ste-Foy
STE-FOY, Quebec G1V 4H2

*Denotes Active Member

EX-OFFICIO MEMBERS

M. G. Johnson
Director
Great Lakes Biolimnology Laboratory
Canada Centre for Inland Waters
P. O. Box 5050
BURLINGTON, Ontario L7R 4A6

N. A. Berg
Associate Administrator
Soil Conservation Service
U.S. Department of Agriculture
12th & Independence St. S. W.
Room 5103
WASHINGTON, D. C. 20250

Secretariat Responsibilities:

H. Shear*
Biologist
Great Lakes Regional Office
International Joint Commission
100 Ouellette Avenue
WINDSOR, Ontario N9A 6T3

*Denotes Active Member

G. K. Rodgers
Chief
Applied Research Division
Canada Centre for Inland Waters
P. O. Box 5050
BURLINGTON, Ontario L7R 4A6

alternate:

Klaus L. E. Kaiser*
Toxic Substance Section
Process Research Division
Canada Centre for Inland Waters
P. O. Box 5050
BURLINGTON, Ontario L7R 4A6

C. Timm
Deputy Director
Surveillance & Analysis Division
U.S. EPA, Region V
230 South Dearborn
CHICAGO, Illinois 60604

Official Observer

William E. Fox*
Physical Scientist
U.S. Environmental Protection Agency
4th & M St., S.W.
WASHINGTON, D. C. 20460

WATER QUALITY OBJECTIVES SUBCOMMITTEE (1975-76)

C. M. Fetterolf* Chairman
Chief Environmental Scientist
Bureau of Water Management
Mich. Dept. of Natural Resources
Stevens T. Mason Building
LANSING, Michigan 48926

Stewart W. Reeder* (Vice-Chairman)
Coordinator, Water Quality Objectives
Water Quality Branch
Inland Waters Directorate
Environment Canada
Place Vincent Massey
HULL, Quebec

Carl T. Blomgren
Manager
Standards Section
Division of Water Pollution Control
Illinois E.P.A.
2121 West Taylor Street
CHICAGO, Illinois 60612

George B. Garrett*
Ohio Environmental Protection Agency
P. O. Box 1049
COLUMBUS, Ohio 43216

John R. M. Kelso*
Great Lakes Biolimnology Laboratory
Canada Centre for Inland Waters
Environment Canada
P. O. Box 5050
BURLINGTON, Ontario L7R 4A6

William H. Anderl* (Jan. 1/75)
Minnesota Pollution Control Agency
1935 West County Road B2
ROSEVILLE, Minnesota 55422

Christopher P. Potos*
Environmental Protection Agency
230 South Dearborn Street
CHICAGO, Illinois 60604

Donald B. Stevens* (Resigned Dec. 31/75)
Department of Environmental Conservation
State of New York
50 Wolf Road
ALBANY, New York 12201

J. Arthur Terreault*
Services de Protection de L'Environment
Centre D'Achate Innovation
2360 Chemin Ste-Foy
STE-FOY, Quebec G1V 4H2

Kenneth E. Schoener
Lake Erie-Ohio River Basin Engineer
Division of Water Quality
Dept. of Environmental Resources
Commonwealth of Pennsylvania
P. O. Box 2063
HARRISBURG, Pennsylvania 17120

Duane H. Schuettpelz*
Wisconsin Department of Natural Resources
P. O. Box 450
MADISON, Wisconsin

Russel Mt. Pleasant (Jan. 1/75)
Department of Environmental Conservation
State of New York
50 Wolf Road
ALBANY, New York 12201

alternate:

Ronald E. Maylath* (Jan. 1/75)
Chief, Water Quality Surveillance
Dept. of Environmental Conservation
State of New York
50 Wolf Road
ALBANY, New York 12201

R. G. V. Boelens* (Resigned Jan.31/75
Head, Toxicity Unit
Water Resources Branch
Ontario Ministry of the Environment
P. O. Box 213
REXDALE, Ontario M9W 5L1

John Pegors (Resigned Dec. 1974)
Minnesota Pollution Control Agency
1015 Torrey Building
DULUTH, Minnesota 55802

EX-OFFICIO MEMBERS

M. G. Johnson*
Director
Great Lakes Biolimnology Laboratory
Canada Centre for Inland Waters
P. O. Box 5050
BURLINGTON, Ontario L7R 4A6

R. K. Lane
Chief
Scientific Operations Division
Canada Centre for Inland Waters
P. O. Box 5050
BURLINGTON, Ontario L7R 4A6

alternate:

K. L. E. Kaiser*
Environmental Quality Co-ordination Unit
Canada Centre for Inland Waters
P. O. Box 5050
BURLINGTON, Ontario L7R 4A6

Secretariat Responsibilities:

P. S. Chamut** (resigned April 18/75)
Biologist
Great Lakes Regional Office
International Joint Commission
100 Ouellette Avenue
WINDSOR, Ontario N9A 6T3

W. R. Drynan (temporary duty)
Senior Engineer
Great Lakes Regional Office
International Joint Commission
100 Ouellette Avenue
WINDSOR, Ontario N9A 6T3

* Denotes Active Member

** Current Address

P. S. Chamut
Environment Canada
Fisheries and Marine Service
Aquatic Contaminants Unit
615 Booth Street
OTTAWA, Ontario

N. A. Berg
Associate Administrator
Soil Conservation Service
U.S. Department of Agriculture
South Agriculture Building
12th & Independence St. S.W.
Room 5103
WASHINGTON, D. C. 20250

alternate:

J. G. Konrad
Supervisor of Special Studies
Dept. of Natural Resources
MADISON, Wisconsin 53701

C. Timm
Deputy Director
Surveillance & Analysis Division
U.S. Environmental Protection Agency
Region V
230 South Dearborn Street
CHICAGO, Illinois 60604

alternate:

D. C. Kraus
Great Lakes Surveillance Branch
U.S. Environmental Protection Agency
1819 W. Pershing Road
CHICAGO, Illinois 60609

IX

MEMBERSHIP

OF

STANDING COMMITTEE ON SCIENTIFIC BASIS

FOR WATER QUALITY

OF

THE GREAT LAKES RESEARCH ADVISORY BOARD

MEMBERSHIP LIST

STANDING COMMITTEE ON SCIENTIFIC BASIS FOR WATER QUALITY CRITERIA

William Brungs (Chairman - resigned Dec. 1975)
U.S. Environmental Protection Agency
6201 Congdon Boulevard
DULUTH, Minnesota 55804

Rolf Hartung*
School of Public Health I
University of Michigan
ANN ARBOR, Michigan 48104

Stewart W. Reeder*
Coordinator, Water Quality Objectives
Water Quality Branch
Inland Waters Directorate
Environment Canada
Place Vincent Massey
HULL, Quebec

W. M. J. Strachan*
Toxic Substance Section
Process Research Division
Canada Centre for Inland Waters
P. O. Box 5050
BURLINGTON, Ontario L7R 4A6

C. M. Fetterolf, Jr.*
Executive Secretary
Great Lakes Fishery Commission
1451 Green Road
ANN ARBOR, Michigan 48105

I. Hoffman*
National Research Council of Canada
Association Committee on Scientific
Criteria for Environmental Quality
OTTAWA, Ontario K1A 0R6

Andrew Robertson* (Acting Chairman)
Great Lakes Environmental Research
Laboratory, NOAA
2300 Washtenaw Avenue
ANN ARBOR, Michigan 48104

John Sprague (Resigned January, 1976)
Associate Professor
Department of Zoology
University of Guelph
GUELPH, Ontario

Secretariat Responsibilities:

Dennis E. Konasewich
Research Scientist
Great Lakes Regional Office
International Joint Commission
100 Ouellette Avenue
WINDSOR, Ontario N9A 6T3

*Denotes Active Member

Please attach this Errata Sheet to your copy of "Proposed, New and Revised Water Quality Objectives", the Great Lakes Water Quality Board's recent report to the International Joint Commission.

Page 47	Last line of paragraph 4 under *RATIONALE*: 0.004 μg/l should be 0.04 μg/l.
Page 51	Compounds list: di-iso-cotyphlthalate should be di-iso-octylphthalate.
Page 52	Last paragraph, line 3: 0.03 μg/l should read: 0.3 μg/l...
Page 56	Under PCBs in Biota line 1 should begin: Fish...
Page 57	Paragraph 1 end of line 5, after associated with add: ...these forms of edema, increased porphyrin synthesis but not liver necrosis. These signs were...
Page 58	First full paragraph, end of line 3, compound should be: Aroclor 1254
Page 60	Line 1, concentrations should read levels
Page 65	Line 1 should read: These quantification and detection limits, however, should not be accepted...
Page 101	Line 1 under *RECOMMENDATIONS* should read: The concentration of total mercury in a filtered water sample should not
Page 140	Delete paragraph (e) under OIL AND PETROCHEMICALS
Page 147	Paragraph 2, line 6 should read: ...exposure. The use of...
Page 152	End of line 5 under Raw Water Supply should read: ...taste and odour...
Page 153	Paragraph 4 line 8 should read: be formed. The odour threshold...
Page 157	Paragraph 2, line 10 should read: wastewaters found to have lowered...
Page 163	Fifth full paragraph, lines 2 and 3: who should be whose
Page 168	Second full paragraph, line 3 should begin: equal...
Page 171	Line 1 should read: The Natural Resources Defense Council...
Page 176	Date should be (1975-76)
Page 178	Date should be (1974-75)