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GREAT LAKES
WATER QUALITY BOARD

INTERNATIONAL
JOINT
COMMISSION

GREAT LAKES WATER QUALITY 1974

APPENDIX A
WATER QUALITY OBJECTIVES SUBCOMMITTEE REPORT

GREAT LAKES WATER QUALITY
THIRD ANNUAL REPORT

APPENDIX A

ANNUAL REPORT OF THE WATER QUALITY OBJECTIVES SUBCOMMITTEE

TO THE
IMPLEMENTATION COMMITTEE
GREAT LAKES WATER QUALITY BOARD
JUNE 1975

PREFACE

This Appendix to the 1974 Annual Report on Great Lakes Water Quality is the report of the Water Quality Objectives Subcommittee submitted to the Implementation Committee and the Great Lakes Water Quality Board. The Appendix contains the detailed information and data with respect to water quality objectives for the Boards' Third Annual Report to the International Joint Commission.

The Board has reviewed and approved the Subcommittee's report for publication as an Appendix to its report. However, some of the specific conclusions and recommendations contained in this Appendix may not be supported by the Board in its 1974 Annual Report to the International Joint Commission.

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ACKNOWLEDGEMENTS

In the preparation of this report on water quality objectives for the Great Lakes, the Water Quality Objectives Subcommittee has been fortunate in being assisted by a number of individuals who willingly reviewed pertinent literature, provided constructive comment and suggestions on draft sections of the report, participated in meetings, and contributed unpublished information. Their valuable help significantly lightened the task of the Subcommittee, and contributed, in large measure, to the confidence with which this report is submitted.

We gratefully acknowledge indebtedness to members of the Research Advisory Board's Standing Committee on Scientific Basis for Water Quality Criteria. Dr. W.A. Brungs (U.S. Environmental Protection Agency, National Water Quality Laboratory, Duluth), Dr. J.B. Sprague (University of Guelph, Guelph), Dr. I. Hoffman (National Research Council of Canada, Ottawa), Dr. W.M.J. Strachan (Canada Centre for Inland Waters, Burlington), Dr. A. Robertson (National Oceanographic and Atmospheric Administration, Ann Arbor), and Dr. R. Hartung (University of Michigan, Ann Arbor), participated in many of the Subcommittee meetings, providing extremely valuable expertise, and prepared draft reports on a number of parameters for consideration by the Subcommittee.

We also wish to acknowledge Dr. P.V. Hodson (Great Lakes Biolimnology Laboratory, Canada Centre for Inland Waters, Burlington) for his significant efforts in the preparation of supportive rationales for a number of parameters.

The following individuals also provided advice and participated in the preparation of summaries of pertinent literature for consideration by the Subcommittee, and their efforts are acknowledged:

Dr. G. Leduc, and Mr. M. Speyer (Sir George Williams University, Montreal)

Dr. R.A. Schoettger (U.S. Fish and Wildlife Service, Columbia, Missouri)

Dr. P.G. Wells (Environment Canada, Halifax)

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Mr. B.S. Dobrindt, Mr. J.A. Rackley, Mr. T.G. Spark, Mr. H.H. Stone, and Ms. J.L. Watson (Department of Zoology, University of Guelph, Guelph)

While acknowledging the efforts of others in the preparation of this report, the Water Quality Objectives Subcommittee was responsible for its final preparation, and collectively accepts responsibility for the recommendations in the reports and any errors of ommission or commission.

I INTRODUCTION

The development of common water quality objectives for the Great Lakes is recognized as one of the primary program elements of the Canada-United States Great Lakes Water Quality Agreement of 1972. These common objectives will provide for all water quality surveillance programs and will be of critical importance in evaluating the success of remedial programs. This should provide protection for designated uses. They should ensure against future losses of the beneficial uses which the parties desire to secure and protect when implemented in concert with limitations on the extent of mixing zones or zones of influence and localized areas as designated by regulatory agencies.

The responsibility of the International Joint Commission to develop common water quality objectives was assigned to the Water Quality Board's Water Quality Objectives Subcommittee. This Subcommittee was charged to assess the adequacy of, and refine where necessary, the general objectives in the Agreement and the specific objectives in Annex 1, as well as to recommend specific objectives for other water quality parameters.

Metals have not been comprehensively covered in this first report. Conspicuous by their absence are specific objectives for mercury, cadmium, copper, nickel, lead, silver, zinc and the organometallics. Although the metals work group prepared several drafts and revisions, the Subcommittee did not agree that the objectives proposed were scientifically defensible. The work group has been enlarged, charged to expand the data base and to report to the Subcommittee in July for submission of objectives to the Water Quality Board in September.

In addition to the metals mentioned above, specific objectives for non-persistent toxic substances will be completed for Subcommittee review in July and subsequent submission to the Board along with the metals objectives.

The Water Quality Objectives Subcommittee has been effectively aided in its task of assessing existing specific objectives and developing specific objectives by members of the IJC Research Advisory Board's Standing Committee on Scientific Basis for Water Quality Criteria. (See Acknowledgements). Several joint meetings were held.

II APPROACH TO THE ESTABLISHMENT AND USE OF WATER QUALITY OBJECTIVES

As considered by the Subcommittee, water quality objectives describe, in part, a minimum quality of water which will not only provide for but protect any designated use. However, establishment of water quality objectives alone may not ensure against future losses of the beneficial uses which the Parties desire to secure and protect. The objectives should be implemented in concert with limitations on the extent of mixing zones or zones of influence and localized areas as designated by the regulatory agencies.

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 water quality where it is better than the prescribed objectives. The Subcommittee believes these definitions are inadequate to prevent excessive areas of the Great Lakes from remaining in non-compliance or to prevent excessive areas from being downgraded to the objectives in the future. Each objective alone should provide protection from 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 (specific numerical objectives) occur simultaneously that protection of use is assured. Antagonistic, additive or synergistic effects may occur. Considering the infinite combinations of water quality characteristics we will never be able to predict the effects of these combinations even for adult organisms, much less for their life history stages and processes.

The Agreement describes a mixing zone, in part, 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 in most cases, a loss of use, a loss of value, a trade off. The Subcommittee was extremely reluctant to propose specific water quality objectives when no well-defined international-interstate mechanism existed for limiting the present and future loss of value to mixing zones, not only locally but on a waterbody - wide scale.

The Subcommittee recognized that it was not charged with recommending a framework within which water quality objectives can be used to protect against undefined losses of the beneficial uses the Parties desire to secure and protect. However, in the process of assessing, refining and recommending objectives which would accomplish what the Subcommittee interprets as the intention of the Parties, a scientifically defensible framework evolved. The proposed objectives are predicated on this framework which is drawn partly from the Agreement, partly from the recommended revisions to the Agreement, and partly from an allocation plan which the Subcommittee suggests is worthy of further consideration and study and is described in Chapter V. To facilitate development of objectives by lending confidence to the Subcommittee that the objectives would be protective of uses, adoption of the framework was assumed. The Subcommittee believes its adoption would aid the jurisdictions in protecting against future losses of the beneficial uses which the Parties desire to secure and protect.

In accordance with Articles IV, V and X dealing with regulatory requirements, remedial programs and implementation the objectives should serve as a minimum target wherever water quality objectives currently are not met.

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

Carrying the present non-degradation philosophy a step further, the Subcommittee agrees that "all reasonable and practicable measures" should be taken not only to maintain existing water quality which is better than the objectives, but that the potential for and the desirability of enhancement should be recognized and provided for. This small alteration in approach encourages further improvement, particularly in the open water areas of the lakes.

The Subcommittee recognizes that any jurisdiction could move toward a more positive non-degradation policy than that provided by taking "all reasonable and practicable measures". To encourage such policies the assumed framework includes 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 enhanced.

Specific water quality objectives were designed to be met at the periphery of mixing zones. This assumes water quality conditions better than the objectives will result beyond the mixing zones.

For those contaminants which are non-point source related, are the result of human activity, and do not meet objectives, regulation of the activity itself should be considered in remedial programs.

Water quality criteria on which the present objectives are based were drawn from a data bank which is in a constant state of flux. As new data are developed they are added to this data bank. Because new data may lead to modified recommendations, the objectives should be subject to continual review.

Local biota and local natural or ambient water quality characteristics coupled with a particular objective can result in a different response than assumed by the Subcommittee. The objective may be more restrictive than necessary and, conversely, regulatory agencies should not accept naively that meeting the general and specific objectives guarantees protection of uses. The need for studies of the aquatic environment and effects of conditions on related organisms and uses is not negated by adoption of objectives.

An inadequate scientific data base exists to permit the establishment of scientifically-justifiable numerical objectives for certain unspecified 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, important local species, and apply a stipulated application factor to toxicity data so derived. Such criteria may be termed procedural objectives.

The definition of specific water quality objective in the Agreement includes "---the level of a substance or physical effect --- recognize(d) as a maximum or minimum desired limit---". The definition should either exclude the word "physical" so all effects are recognized or "biological effects" should be included. There is precedence for addition of biological effects since existing objectives include microbiological water quality characteristics and prevention of nuisance growths of algae, weeds and slimes. The Subcommittee assumed the Parties intended originally to consider the level of biological effect on the common resource which may be tolerated without damage to the system. Inclusion would permit development of objectives to protect against mortality of passive organisms, especially fish larvae, as the result of entrainment at water intakes. This phenomenon has been identified by the Subcommittee as potentially of great significance as the use of nearshore waters of the Great Lakes for cooling purposes increases.

The preamble to the Agreement specifically identifies serious concern for trans-boundary effects of water quality deterioration and calls for development and implementation of new and more effective cooperative actions to restore and enhance water quality in the Great Lakes System. The Subcommittee's assumed framework includes recognition of biological effect levels as well as the concentration of a substance or level of physical effect. An objective for a substance or physical effect is designed to protect uses, for example, aquatic organism communities, by a limitation on acceptable levels. An objective for biological effects also should be designed to protect uses, for example, aquatic organism communities, by recognition of "a maximum or minimum desired limit."

The value of the Great Lakes most vulnerable to encroachment by mixing zones is biological because of the fragility and interdependency of the interlocking parts which make up the whole of the Great Lakes ecosystem and the ecosystem of each waterbody. It is obvious to even the casual observer that there is a limit to loss of fish spawning sites, nursery areas, and feeding grounds before ecosystem imbalance and ultimate collapse of a population occur. Ecosystems are not compartmentalized by jurisdictional boundary lines. If excessive encroachment upon an ecosystem is allowed by one jurisdiction, the loss may impact neighboring jurisdictions which share the ecosystem.

The Subcommittee has thoughtfully considered a concept designed to limit biological effects by allocation of biological value loss in mixing zones in such a manner that the biological integrity of the system should be protected (See Chapter V). The "desired limit" of biological effect agreed upon should be worked out by the Parties, provinces and states. A high degree of international and interagency cooperation is required and the first reaction of agencies may be to brush it aside as unworkable and too complicated. Of those who have this reaction, the Subcommittee asks, "What other scientifically justifiable alternative do we have?" The method is simplistic when compared with the complexity of the ecosystem.

The Subcommittee is not recommending adoption of this concept which is in the development stage, but strongly encourages further study for possible adoption in the future. The institutional framework of the IJC provides a forum in which decisions can be made which are critical to the success of this cooperative system to recognize desired limits to biological effects on a water body or portion thereof.

To further encourage consistency in management by the various enforcement agencies, the Subcommittee has developed broad guidelines for mixing zones based upon principles of good water management, which describe desirable conditions within and desirable locations for these zones.

This concludes description of the assumed framework within which the Subcommittee believes water quality objectives can be employed to accomplish what the Subcommittee interprets as the intent of the Agreement.

Deferred Objectives for Raw Public Water Supply

The intent of the Water Quality Board is to provide for protection of 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 the intent of the Board to provide protection of Great Lakes waters for domestic use without treatment. Objectives are not designed to protect this untreated domestic use.

In recommending objectives to protect raw public drinking water supplies, it should be assumed that a minimum level of treatment is provided before distribution to the public for consumption. This minimum level of treatment includes coagulation, sedimentation, rapid sand 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) there is inadequate information on the effect of the defined treatment process on contaminant removal; or

2) the defined treatment process is inconsistent in contaminant removal; or
3) the defined treatment process is ineffective in contaminant removal.

The Canadian Drinking Water Standards are presently under review by a National Working Group composed of Federal and Provincial environmental health and environmental water quality officials. This working group is charged with the responsibility of a complete update of the standards for release by January 1, 1976.

The U.S. Congress passed the Safe Drinking Water Act (PL 93-523) in December 1974. Under the Act, the U.S. Environmental Protection Agency must publish by March 14, 1975, National Interim Primary Drinking Water Regulations. In September 1975 these must be promulgated, incorporating modifications developed from comments, to take effect in March, 1977. During this period the National Academy of Sciences will develop and report on recommended maximum contaminant levels for drinking water in January, 1977. Following review and modification, the National Primary Drinking Water Regulations (Health) are to be promulgated in October 1978. The National Secondary Drinking Water Regulations (Aesthetics) are undergoing an initial schedule which is less stringent.

The Subcommittee did not make recommendations on many objectives to protect raw water supplies because of the pending activities described above and extensive expertise in this area is not represented in the Subcommittee. At present we have no basis for recommending changes in the existing standards of the Parties nor have we examined them in detail.

Jurisdictions are currently protecting their raw public water supplies by adopted state, provincial or federal standards. Until the recommendations of the Parties' work groups are known, existing regulations represent the best information currently available. For purposes of surveillance and monitoring to establish indications of non-compliance, the Subcommittee recommends use of the most restrictive of the raw public water supply standards of each country.

III RECOMMENDED MODIFICATIONS TO THE WATER QUALITY AGREEMENT

The Subcommittee recommends changes in Articles I, II and III of the Water Quality Agreement. The changes pertain to water quality considerations so that the Agreement is consistent with the conceptual framework assumed by the Subcommittee in designing water quality objectives.

Amending Articles of the Agreement may be a difficult political task. The Subcommittee feels that incorporation of the changes would clarify and improve portions of the Articles, but acknowledges the recommended changes are not essential to successful implementation of the Agreement.

The Subcommittee encourages the Parties and jurisdictions to interpret the Agreement with the intent expressed in the recommended changes. The changes are underlined and deletions indicated by parentheses.

ARTICLE I - DEFINITIONS

RECOMMENDATION

It is recommended that the following revised definition for a specific water quality objective be adopted to replace the existing definition stipulated in Article I, paragraph (i) in the Water Quality Agreement, and that the following new definition for a general water quality objective be adopted for inclusion in Article I, as new paragraph (m).

1. Specific Water Quality Objective

   Article I (i) Revised definition

   "Specific water quality objective" means the concentration of a substance or physical or biological effect, that the Parties agree, after investigation, to recognize as a maximum or minimum desired limit for a defined body of water, or portion thereof, taking into account the beneficial uses of the water that the Parties desire to secure and protect.

   Article I (i) Existing definition

   "Specific water quality objective" means the level of a substance or physical effect that the Parties agree, after investigation, to recognize as a maximum or minimum desired limit for a defined body of water, or portion thereof, taking into account the beneficial uses of the water that the Parties desire to secure and protect.

2. General Water Quality Objective

   Article I, proposed new paragraph (m).

   "General water quality objectives" are broad

descriptions of water quality conditions which will protect the boundary waters of the Great Lakes System for the beneficial uses that the Parties desire to secure and which provide overall water management guidance and a framework for the development of the specific water quality objectives.

RATIONALE

Specific Water Quality Objectives

The definition of a specific water quality objective was refined by including reference to "biological effects", recognizing the precedent that objectives were previously established for microbiological water quality characteristics and to prevent nuisance growths of algae, weeds and slimes. This inclusion permits the joint institutions to consider the level of biological effect on the common resource which may be tolerated without damage to the system. Further, this permits consideration to protect against mortality of passive organisms, especially fish larvae, as the result of entrainment at water intakes. This latter concern has been identified by the Subcommittee as being of potential great significance as the use of the nearshore waters of the Great Lakes for cooling purposes increases.

The Subcommittee considered further modification of the definition to include "designated methods for determining such levels" of "physical or biological effect" because for a number of water quality characteristics defensible numerical objectives cannot be established due to a lack of information on their significance in the environment. In addition, development of specific objectives to protect against the environmental effects of complex waste discharges by identification of the critical toxic component is extremely difficult.

In these instances, a standard criterion (i.e. a designated method for determining acceptable levels) by which a water quality objective can be developed for local situations, should be established. Such a criterion would recommend that the local jurisdiction conduct bioassay tests, using a standardized, specified testing methodology, a local, important sensitive species and apply a defensible application factor to derived acute toxicity data. Objectives developed through use of such a criterion would apply at the boundary of the mixing zone, and should provide an adequate level of protection for aquatic life in local situations.

Use of such a specified criterion has been recommended for the definition of objectives for unspecified nonpersistent toxic substances and complex wastes. However, the Agreement encourages development of such techniques and inclusion of this concept in the specific objective definition appears unnecessary.

General Water Quality Objectives

The existing general water quality objectives may be interpreted as minimum conditions which apply within mixing zones, or as comprehensive, ideal goals for the Great Lakes System. The definition of a general water quality objective was prepared for inclusion in Article I to clarify the intent, and to ensure that they are utilized in a consistent fashion.

It was agreed within the Subcommittee that the general water quality objectives represent a broad statement of goals, or desirable conditions which are amplified and implemented by enforcement of the specific water quality objectives. Acceptance of this concept means that the general objectives will not necessarily apply within mixing zones, which are exempt from compliance with the specific water quality objectives. The definition adopted for the general water quality objectives reflects this philosophy, however the recommended quidelines for mixing zones include many, but not all, limitations expressed in the general water quality objectives.

ARTICLE II - GENERAL WATER QUALITY OBJECTIVES

RECOMMENDATION

It is recommended that Article II, General Water Quality Objectives, be revised as follows:

a. No change proposed in existing objective "a" which states: "Free from substances that enter the waters as a result of human activity and that will settle or form putrescent or otherwise objectionable sludge deposits, or that will adversely affect aquatic life or waterfowl;"

b. Amended objective proposed:
Free from flotsam and other floating materials such as oil, scum, and immiscible substances resulting from human activities in amounts that are unsightly or deleterious;

Existing objective:
"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. Amended objective proposed:
Free from materials and heat entering the waters as a result of human activity that alone or in combination with other materials will produce color, odour, taste, or other conditions in such a degree as to interfere with any beneficial use;

Existing Objective:
"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. Amended objective proposed:
Free from materials and heat entering the waters as a result of human activity that along, or in combination with other materials, will produce conditions that are toxic or harmful to human, animal, or aquatic life:

Existing Objective:
"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. Amended objective proposed:
Free from nutrients entering the waters as a result of human activity in amounts that create growths of aquatic plants that interfere with beneficial uses:

Existing objective:
"Free from nutrients entering the waters as a result of human activity in concentrations that create nuisance growths of aquatic weeds and algae."

RATIONALE

General objective (b) was expanded to include immiscible substances. While such substances have a specific gravity less than one, and would float similarly to oil, they would not necessarily be defined as oils. Because the environmental effects of immiscible substances is imperfectly known, they are included in the General Water Quality Objectives as well as in the specific water quality objectives, within the category of unspecified toxic materials. For added water quality protection, the term "debris" was replaced by the more comprehensively descriptive term "flotsam". Debris is defined by Webster (1969) as the remains of something broken down or destroyed. Aparently this would not include items such as discarded glass bottles, plastic containers, tires, etc. The Webster definition of flotsam, in its broader sense, includes all miscellaneous trifles and worthless things and as such would be more appropriate than the term debris.

Objectives (c) and (d) were expanded to included heat, a non-material entity, and also to include protection against synergistic effects. Objective (c) was further expanded and edited to protect against taste impairment with the criteria for regulation being changed from that creating a nuisance to one interferring with any beneficial use. In addition objective (d) was reworded to more closely define the WQOS interpretation of the intent of the Parties to the Agreement.

In the report entitled Water Quality Criteria 1972, (NAS/NAE, 1974) it was stated (page 123) that "when two or more toxic materials are present at the same time in a receiving water, it should be assumed, unless proven otherwise, that their individual toxicities are additive and that some reduction in permissible concentrations is necessary". Moreover the same additive effects can produce undesirable conditions of color, odour, and taste, conditions that would not necessarily be present as a result of a single contaminant. Heat was added to these objectives because it is a known biological and chemical controlling factor, following the law of Van Hoff, and as such will hasten or enlarge upon a synergistic effect. Furthermore, gross heat inputs are biologically detrimental of themselves and their control should be initially stimulated through recourse to the general objectives. Protection against taste impairment was added to objective (c) since odour and taste adversely affect not only the consumer of water, but also the consumer of fish produced in that water. The present nuisance criterion for regulation is public health oriented and was inspired by local legislative and administrative codes that are used primarily to protect the public from garbage dump odours, vermin, general air pollution, etc. The criterion for regulation of interference with a beneficial use complements modern water quality requirement trends and comprehensively expands protection of the public health oriented nuisance criterion to include insults to the entire aquatic environment. The Subcommittee interprets that the intent of the Parties to the Agreement was not to exclude toxic materials completely, but to exclude from the Great Lakes and connecting waterways, conditions that are toxic or harmful.

General objective (e) was refined by changing aquatic weeds and algae to aquatic plants. The popular term weeds, which would require administrative and legally provocative decision making was changed to the inclusive taxonomic term of plants. This change of course made the term algae redundant, since all algae are plants; hence its deletion from the recommended amendment.

LITERATURE CITED

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Webster's Seventh New Collegiate Dictionary, 1969. Thomas Allen and Son Ltd., Toronto. 1221 pp.

ARTICLE III - SPECIFIC WATER QUALITY OBJECTIVES-NON-DEGRADATION

RECOMMENDATION

It is recommended that paragraph 4, Article III regarding non-degradation, be amended as follows:

> *Notwithstanding the adoption of specific water quality objectives, all reasonable and practicable measures shall be taken to maintain and enhance 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) water quality is better than that prescribed by the specific water quality objectives. In areas designated by the appropriate jurisdiction as having outstanding natural resource value and which have existing water quality better than that prescribed by the specific water quality objectives, that water quality should be maintained or enhanced.*

EXISTING OBJECTIVE

The above statement is recommended to replace the existing statement on non-degradation in paragraph 4, Article III, of the Water Quality Agreement which states:

> "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."

COMMENT

This statement promoting preservation of water quality in the Great Lakes System is reiterated in Annex 1, paragraph 3 of the Agreement. It should be noted that in printing the Agreement the non-degradation statement appears to be the second sentence of Article III, paragraph 3. The Subcommittee believes it should be paragraph 4 of Article III.

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 <u>maintain</u> the chemical, physical and biological integrity of the Nation's waters" (emphasis added). Similarly, "Guidelines and Criteria for Water Quality Management in Ontario" state

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*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.

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. Therfore, 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 sepcial 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.

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 propagation 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 <u>or</u> upgrading the existing water quality.

IV RECOMMENDED REVISIONS AND NEW SPECIFIC WATER QUALITY OBJECTIVES (ANNEX 1)

- Toxic Substances
  - Persistent Compounds
    - Persistent Organic Contaminants
      - Phthalic Acid Esters
      - Polychlorinated Biphenyls
      - Aldrin/Dieldrin
      - Chlordane
      - DDT and Metabolites
      - Endrin
      - Heptachlor
      - Lindane
      - Toxaphene
      - Methoxychlor
      - Mirex
    - Metals
      - Aluminum
      - Arsenic
      - Fluoride
      - Iron
      - Selenium
  - Non-persistent Compounds
    - Ammonia
    - Chlorine
    - Hydrogen Sulfide
    - Oil and Petrochemicals
    - Unspecified Toxic Substances and Complex Effluents
- Microbiological Characteristics
- Physical Characteristics
  - Asbestos
  - Settleable and Suspended Solids and Light Transmission
  - Temperature

Chemical Characteristics

- Dissolved Oxygen
- pH
- Phosphorus
- Tainting Substances
- Total Dissolved Solids

Radioactivity

Non-degradation

Mixing Zones

Localized Areas

TOXIC SUBSTANCES - PERSISTENT COMPOUNDS

PERSISTENT ORGANIC CONTAMINANTS

RECOMMENDATION

It is recommended that the following numerical objectives for persistent organic contaminants be adopted to replace the existing interim objectve in Annex 1, paragraph 2 (c) of the Water Quality Agreement:

> *Persistent organic contaminants should nowhere in the Great Lakes system exceed the water and tissue concentrations specified below for the protection of aquatic organisms and consumers of fish.*

Compounds	*Specified concentrations* *Water* *µg/l*	 *Tissue* *µg/g*
Phthalate esters		
Dibutyl phthalate	*4.0*	*U**
Di-(2- ethylhexyl phthalate	*0.6*	*U**
Other phthalate esters	*0.2#*	*U**
Total P.C.B.'s	*U**	*0.1*
Total D.D.T./D.D.E.	*.003#*	*1.0*
Total Aldrin/Dieldrin	*.001#*	*0.3+*
Total Heptachlor/Heptachlor epoxide	*.001#*	*0.3+*
Endrin	*.002#*	*0.3+*
Toxaphene	*.008*	*U**
Chlordane	*.060*	*U**
Lindane	*.010*	*0.3+*
Methoxychlor	*.040*	*U**

*U** - *undetermined at present*

- *recommended quantification limit*

+ - *based upon U.S.F.D.A. guidelines for edible portions of fish.*

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 <u>all</u> 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 arbitrarily 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 work '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 organochlorine, 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 many 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 under-taken 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 factory 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 quidelines 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 1.

Table 1 - 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 determinations, 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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PERSISTENT ORGANIC CONTAMINANTS

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, 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-octylphthalate (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 the 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 0.3 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. McKim (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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PERSISTENT ORGANIC CONTAMINANTS

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 PCB's 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 (PCB's) 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, PCB's 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.

PCB's In Great Lakes Waters

Contamination of the Great Lakes by PCB's 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 for 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 PCB's in water of .035 -.095 µg/l and 0.2 - 10.1 µg/g in sediments (Berg et al., 1974)

PCB's In Biota

Fish 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 PCB's in eggs of four fish-eating bird species are given below in Table 2 (Gilbertson and Reynolds, 1974).

Table 2 - 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 PCB's 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 these forms of edema, increased porphyrin synthesis but not liver necrosis. These signs were 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 PCB's 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 PCB's On Biota

PCB's 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 3×10^5. The factor for bluegills with Aroclors 1248 and 1254 has been estimated at 7.1×10^4 (Stalling and Mayer, Jr., 1972) while large Lake Michigan coho salmon have mean tissue levels of about 15 μg/g (Veith, 1973) which is 1.5×10^6 times greater than the maximum open water concentration of around 0.010 μg/l (Lake Michigan Toxic Substances Committee Report).

Two µg/g PCB's 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 1254 (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 PCB's 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 PCB's 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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PERSISTENT ORGANIC CONTAMINANTS

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) and 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/l 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/l (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/l and use of the arbitrary safety factor of 0.2 results in a concentration of 0.25 µg/l. 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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PERSISTENT ORGANIC CONTAMINANTS

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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PERSISTENT ORGANIC CONTAMINANTS

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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PERSISTENT ORGANIC CONTAMINANTS

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 quidelines 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.

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PERSISTENT ORGANIC CONTAMINANTS

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/l 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 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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PERSISTENT ORGANIC CONTAMINANTS

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 toxicites 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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PERSISTENT ORGANIC CONTAMINANTS

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 by 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 was 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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PERSISTENT ORGANIC CONTAMINANTS

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 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, indicating 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 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 0.04 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 Eisle, 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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PERSISTENT ORGANIC CONTAMINANTS

MIREX

RECOMMENDATION

No recommendation for a "safe" concentration of this compound can be given at this time.

RATIONALE

Mirex, the common name for Dodechachloro-octahydro - 1, 3,4 - metheno - 2H - cyclobuta (c,d) - pentalene, has found use as active ingredient in fire ant bait in several states, and, in combination with other substances, in the production of flame retardant compounds. The chemical is extremely persistent and may have an environmental half life which far surpasses that of any previously studied insecticide (Mehendale et al., 1972). No biologically derived metabloites have yet been observed. Under ultraviolet irradiation, the compound transforms to photodecomposition products of as yet unresolved structure (Alley et al., 1972). Although mirex is not used as insecticide in the Great Lakes region, it has been reported in fish tissues from Lake Ontario (Kaiser, 1974) and should therefore be of concern.

Effects on Aquatic Biota

Little information exists on the toxicity of mirex to freshwater biota. Ludke et al., (1971) studied the response of juvenile crayfish (Procambarus blandingi and Procambarus hayi) to mirex. At an exposure of 5 μg/l mirex in water for six hours, no dead crayfish were observed. However, the same animals, placed in clean water, showed 26% mortality 10 days after the exposure. At an exposure concentration of

5 μg/l mirex for 58 hours, 5% mortality was recorded at the termination of the exposure and 98% mortality after an additional 10 days in clean water. Similarly, a concentration of 1 μg/l mirex for 144 hours resulted in 0% initial mortality and in 95% mortality 10 days after treatment. Procambarus hayi, exposed to 0.5 and 0.1 μg/l mirex for 48 hours, resulted in initial mortalities of 12% and 19%, respectively, and in 71% and 65% mortalities within 4 days after the exposure. In other experiments by Ludke et al., (1971), juvenile crayfish were exposed to water leaching mirex bait granules. At 7 days exposure, 95% mortality was observed, corresponding to a mirex concentration of 0.86 μg/l in the water. The dead crayfish were found to have mirex accumulated to a mean of 1.5 μg/g. At a mirex concentration as low as 0.073 μg/l, 12.5% mortality was observed after the first day of exposure. From this report it appears obvious that mirex is extremely toxic to these species of crayfish. Mortality increases with the time of exposure to the insecticide and, in most cases, significantly delayed toxic action was observed several days after exposure.

In another study Van Valin et al., (1968) exposed bluegills (Lepomis macrochirus) and the goldfish (Carassius auratus) to mirex by feeding a mirex-treated diet or by treating holding ponds with mirex bait. They report no mortality or tissue pathology for the bluegill, however, after 56 days of exposure, gill and kidney breakdown was occuring in the goldfish.

Collins et al., (1973) studied the uptake of mirex by caged and uncaged channel catfish in ponds. The observed residues in uncaged fish were much higher (0.20 to 0.65 μg/g) than those of caged fish (0.0 to 0.03 μg/g) from the same ponds. This indicates a bioconcentration of mirex via the food chain. Residues in cricket frogs were found to be 2.9 μg/g at 6 months after the treatment.

In laboratory or field test systems the reported concentrations were usually between 0.5 and 1.0 μg/l (Van Valin et al., 1968; Ludke, et al., 1971). Although mirex is seldom found above 1 μg/l in the environment, several field studies have shown that the insecticide is accumulated through the food chain. Borthwick et al., (1973) reports the accumulation of mirex in South Carolina estuaries. Their data revealed that mirex was transported from treated land and marsh to the estuary animals and that accumulation, especially in predators, occurred. In the test area, water samples were always <0.01 μg/l. Fish residues varied from 0 to 0.8 μg/g with 15% of the samples containing residues. The amount of mirex and the percent of samples containing mirex increased at higher trophic levels. Mammal residue accumulations ranged from 0. to 4.4 μg/g and 54% occurrence to birds with 0 to 17 μg/g and 78% of the samples containing mirex.

Wolfe and Norment (1973) sampled an area for one year following an aerial application of mirex bait (0.85 g mirex/acre). Crayfish residues ranged from 0.04 to 0.16 μg/g. Fish residues were about 2 to 20 times greater than the controls and averaged from 0.01 to 0.53 μg/g. These values are, in general, similar to those reported by Naovi and De La Cruz (1973) and Borthwick et al., (1973). Naovi and De La Cruz (1973) observed average residues of 0.15 μg/g for molluscs, 0.26 μg/g for fish, 0.29 μg/g for insects, 0.44 μg/g for crustaceans and 0.63 μg/g for annelids.

Effects on Birds and Mammals

The effect of mirex accumulation in terrestrial vertebrates is not known. However, it has been reported that its persistence in bird tissue exceeds all other organochlorine compounds tested, except for DDE. Mirex fed to birds was observed to be slow-acting, causing delayed mortality up to 15 days after dosage ceased (Stickel et al., 1973). Reproduction among penned mallards and bobwhite was not affected when fed diets containing 1 or 10 µg/g mirex (Heath and Spann, 1973), although carcass residues of surviving birds were as high as 287 µg/g. In similar experiments by Medley et al., (1974) roosters were fed diets containing mirex at 0.007 µg/g, 0.006 µg/g, 0.710 µg/g and 7.2 µg/g for periods up to 32 weeks. The highest residue levels observed were 994 µg/g in fat of roosters on a 7.2 µg/g diet. Studies by Hyde et al., (1973) on the reproductive success of mallard ducks fed mirex did not show severe effects on the egg production, shell weight, shell thickness, embryonation, hatchability and duckling survival.

Feeding experiments of Japanese quail, given a single oral dose of ^{14}C - mirex, were studied by Ivie et al. Partial excretion of mirex via feces was initially observed for both sexes, with male quails excreting approximately twice the amount as female birds. However, after the initial excretion, no further residues were found in the feces and male birds had body burdens of more than 50% of the single dose, 84 days after dosing. Egg laying quail hens had eliminated 85% of the single dose via the egg yolks in 84 days. The recoveries of the ^{14}C - mirx from the whole body residues were 97% or greater and the analysis of the extracts revealed unmetabolized mirex only.

A bioassay of mirex for tumorigenicity in mice by Innes et al., (1969), at a diet level of 26 µg/g mirex, resulted in a significantly elevated tumor incidence.

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PERSISTENT COMPOUNDS - METALS

ALUMINUM

RECOMMENDATION

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

Concentrations of aluminum should not exceed 0.10 milligrams per litre to protect aquatic life.

RATIONALE

Aluminum is an abundant element in nature, especially in rocks and ores. The metal is insoluble, but many of the salts are quite soluble. The occurrence of the metal in surface waters is limited because it is precipitated or absorbed into one or more salts. The behavior of aluminum in aqueous solutions is extremely complex, forming a variety of sensitive complexes with water. The solubility of aluminum in natural waters is a direct function of pH, being more soluble at values of pH above and below 5.5.

Aluminum is not considered a public health problem in public water supplies. In fact, aluminum sulfate (alum) is widely used as a coagulant in the treatment of water for public distribution. Water for livestock watering can be used with concentrations of up to 5 mg/l without harm (NAS/NAE, 1974).

The usefulness of water for steam generation can be restricted by the presence of aluminum. Boiler feedwater to be used in high pressure situations may have to be treated to achieve aluminim concentrations of 0.01 mg/l.

Recirculation makeup water may be required to have an aluminum content of no more than 0.1 mg/l. Once-through cooling systems can utilize water as received without its use being restricted by the aluminum concentration (NAS/NAE, 1974). Other industrial processes do not generally have restrictions on the aluminum concentration in the process water. Phytotoxicity from irrigation waters containing aluminum depends largely on soil pH. Alkaline pH values cause the aluminum salts to precipitate in the soil. Low soil pH (less than about 5.5) does not allow this precipitation to occur, thereby creating a toxicity condition thought due to the aluminum ion. On all soils, a maximum aluminum concentration of 5 mg/l is recommended with much higher values allowable for the neutral or alkaline soils (NAS/NAE, 1974).

It has been reported that alum at a concentration of 0.1 mg/l as aluminum in swimming pools may cause eye irritation (Capen, 1939).

The toxicity of aluminum to aquatic organisms varies with hardness, turbidity and pH. Symptoms of aluminum poisoning are different for dissolved and suspended aluminum. Acute toxicity is most pronounced when aluminum is dissolved, while chronic effects appear when aluminum is in suspended form. Freeman and Everhart (1971) reported that at pH 7.0 the saturation level of aluminum in water was 0.05 mg/l. At this concentration there were no observed effects on rainbow trout. When the pH was increased to 9.0, at least 5 mg/l of aluminum dissolved and fingerling rainbow trout were killed in 48 hours. These same investigators indicate that an aluminum concentration of 0.52 mg/l did not produce stress symptoms until after a few weeks exposure, and high mortality rates were predicted for continued exposure. Doudoroff and Katz (1953), reporting on the work of Jones

(1939), indicate a lethal threshold concentration of 0.07 mg/l for stickleback using aluminum nitrate of 0.3 mg/l for one day and 0.1 mg/l for one week. These tests were carried out with extremely soft water and at low pH. Other studies reported by Doudoroff and Katz (1953) reveal varying toxicity values with one study reporting no effect on rainbow trout in 48 hours at 1 mg/l. Biesinger and Christensen (1972) reported that impairment of reproduction of Daphnia magna occurred at aluminum concentrations of 0.32 mg/l and three week LC_{50} for the same organism was 1.4 mg/l. The analysis of Freeman and Everhart (1971) concludes with the statement that "If aluminum is present only in anionic and neutral or near neutral precipitated forms, a condition that should hold for most natural waters with pH greater than 5.50, tolerable concentrations of either form probably should not exceed 0.10 mg/l if trout are to survive and grow normally." The objective for aluminum of 0.10 mg/l is based on the protection of freshwater aquatic life.

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PERSISTENT COMPOUNDS - METALS

ARSENIC

RECOMMENDATION

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

> *Concentrations of total arsenic should not exceed 0.05 milligrams per litre for the protection of raw drinking 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, volcanic activity and solubilization 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 mg/kg; shale can yield arsenic concentrations as high as 10 mg/kg while sandstone and limestone contain approximately 1.5 mg/kg of arsenic.

Other important sources of arsenic contamination are the burning of fossil fuels such as coal and oil, 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 mg/kg have been measured (Zwick and Benstock, 1971).

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).

Effects of Arsenic on Aquatic Organisms

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 arsenic trioxide (Hollard, 1960).

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. Tests made to determine the toxicity of sodium arsenite to chum salmon fry (*Oncorhynchus keta*) have a 48-hr. LC_{50} of about 11.0 mg/l (Alderdice and Brett, 1957). Holland (1960) noted 22% initial mortality of young pink salmon exposed to 5.3 mg/l arsenic, but mortality in the survivors continued for an additional 20 days. Lawrence (1958) investigated the effect of arsenic trioxide on fish production using ponds stocked with bluegills. At 4.0 mg/l and 8.0 mg/l reduction of bottom organisms compared to the controls was 34% and 45% respectively. The weight of fish harvested was also substantially reduced in the treated ponds. 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 4.0 mg/l arsenic (a single treatment) maximum tissue residues in fish were 1.3 mg/kg for muscle, 2.4 mg/kg for skin and scales, 17.6 mg/kg for gills and digestive tract, 11.6 mg/kg for liver, 5.9 for kidneys and 8.4 mg/kg for ovary. Recently, Speyer (1974) found 6.0 mg/l arsenic to be the lowest level effecting growth of rainbow trout although the response was increased by the presence of 0.2 mg/l HCN.

Domestic Drinking Water Supplies

With reference to the toxicity of arsenic to man, attention has been focused on levels in drinking water. In 1968 the World Health Organization originally established a permissible limit of 0.2 mg/l; in 1963 the limit was altered to 0.05 mg/l. The United States Public Health Service recommended in 1962 a maximum concentration of 0.01 mg/l and a maximum permissible limit of 0.05 mg/l in water destined for a public drinking supply (Ferguson and Gavis, 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 0.05 mg/l, the same value as in the existing standards. Recently, the National Academy of Sciences (NAS/NAE, 1974) has recommended a maximum level of 0.1 mg/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 0.01 mg/l and a maximum permissible level of 0.05 mg/l.

Summary

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 in keeping with the approved concentration for the protection of human health.

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PERSISTENT COMPOUNDS - METALS

FLUORIDE

RECOMMENDATION

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

> *Concentrations of fluoride should not exceed 1.0 milligrams per litre for the protection of raw water supplies and to protect aquatic life.*

RATIONALE

The existing levels of fluorides in the Great Lakes are generally low. A review of fluoride concentration in water intakes from Wisconsin communities indicates levels in Lake Superior of 0.1 mg/l or less, and in Lake Michigan of 0.3 mg/l or less. Existing fluoride levels in Lake Erie and Lake Ontario are about 0.15 mg/l.

Fluoride has different effects on different organisms. Plants can accumulate fluoride in their tissues by uptake through the root system, but only in extreme cases will the levels be high enough to cause direct damage to plants. McKee and Wolf (1963) indicate that no plant injury is noted by irrigation with water containing 10.0 mg/l fluoride. Water Quality Criteria 1972 (NAS/NAE, 1974) recommends a maximum continuous concentration in irrigation water of 1.0 mg/l for all soil applications and 15.0 mg/l for a 20-year period on neutral and alkaline fine textured soils without accumulating to harmful levels.

Fluoride in drinking water for animals other than man generally have the same effect as in man. Concentrations greater than about 1.0 mg/l generally have no effect on animals other than minor mottling of teeth. Extremely high intakes of fluorides, especially via food, can cause skeletal fluorosis or anemia. The effect of high levels of fluorides in food can be further enhanced by high fluorides in water. There appears to be only a slight transfer to milk, tissue or eggs at normal levels. McKee and Wolf (1963) indicate that 1.0 mg/l is the level at which no harm has been observed for stock and wildlife watering, and recommends that level. NAS/NAE, (1974), recommends an upper limit of 2.0 mg/l for livestock drinking water to prevent excessive mottling of teeth. The Ontario Ministry of the Environment (1974) indicated 2.4 mg/l as permissible and 1.2 mg/l as the desirable level.

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 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 U.S. Public Health Service Drinking Water Standards have recommended the fluoride concentrations, shown in Table 3 based upon annual average of maximum daily air temperature:

Table 3 - RECOMMENDED FLUORIDE LIMITS (USPHS)

Annual Average of Maximum Daily Air Temperatures (°F)	Recommended Control Limits Fluoride (mg/l) Lower	Optimum	Upper
50.0 - 53.7	0.9	1.2	1.7
53.8 - 58.3	0.8	1.1	1.5
58.4 - 63.8	0.8	1.0	1.3
63.9 - 70.6	0.7	0.9	1.0
70.7 - 79.2	0.7	0.8	1.0
79.3 - 90.5	0.6	0.7	0.8

Levels greater than twice the optimum values in the above table constitute grounds for rejection of the supply. The southern latitudes of the Great Lakes have an average maximum daily temperature of about 60°F indicating that 1 mg/l is the optimum fluoride level in drinking water for the region. The Canadian Drinking Water Standards recommend that 1.2 mg/l be maintained as the optimum level in fluoridated supplies, and when fluoride is naturally present in water supply sources, the concentration should not exceed 1.5 mg/l.

Water Quality Criteria 1972 for public water supplies (NAS/NAE, 1974) recommend the following temperature dependent values for Fluoride:

Annual Average of Maximum Daily Air Temperature (°F)	Fluoride Maximum (mg/l)
50 - 54	2.3
55 - 58	2.2
59 - 64	2.0
65 - 71	1.8
72 - 79	1.6
80 - 91	1.4

The WHO European Drinking Water Standards recommends an upper fluoride drinking water limit of 1.5 mg/l.

Waters used for industrial purposes, especially in the food processing industry, can cause fluoride concentrating. Due to this factor, McKee and Wolf (1963) recommend a maximum industrial water supply level of 1.0 mg/l. Water Quality Criteria 1972 (NAS/NAE, 1974), similarly recommends 1.0 mg/l for a portion of the food processing industry and 1.2 mg/l is recommended for supplies for the petroleum refining industry. Ontario also recommends 1.0 mg/l for certain segments of the food processing industry.

The effects of fluoride on aquatic life has not been extensively studied. Neuhold and Sigler (1960) indicate that "At 55^{O}F the LC$_{50}$ (for rainbow trout) varied between 2.7 mg/l fluoride (95 percent confidence level) in a 480-hour experiment with the last recorded mortality occurring at 218 hours." The same reference indicates that for carp "At temperatures ranging between 65^{O} and 75^{O}F, the LC$_{50}$ was between 75 and 91 mg/l flouride (95 percent confidence level)." For rainbow trout eggs, the following LC$_{50}$'s were recorded: at 46^{O}F between 222 and 273 mg/l fluoride (424 hours); at 55^{O}F, between 242 and 261 mg/l (214 hours); and at 60^{O}F, between 237 and 281 mg/l (167 hours).

Angelovic, et.al. (1961) report the following in 240-hour experiments on rainbow trout: "At 45^{O}F, the LC$_{50}$ was estimated between 5.9 and 7.5 mg/l fluorides. At 55^{O}F, the LC$_{50}$ was between 2.6 and 6.0 mg/l fluorides, and at 65^{O}F, the LC$_{50}$ was between 2.3 and 7.3 mg/l fluorides." With respect to time to initial mortality, the same report indicates that the greatest effect appeared between 2 and 4 mg/l fluorides at temperatures between 45^{O} and 55^{O}F. Based on their experiments using fluoride concentrations between 0 and 25 mg/l, these authors conclude that "The over-all effect of fluoride concentration on the mortality of rainbow trout is a direct linear relationship in which an increase in fluoride concentration produces an increase in mortality." The following caveat is included in the discussion of the results of the experiment: "With an increase in fluoride the duration of the mortality period initially increases, and then as the fluoride concentration continues to increase the duration of the mortality period starts to decrease. This may be because the lower concentrations of fluoride are not actually lethal to the rainbow trout and may, at certain low concentrations, act as a deterrent to other causes of mortality such as bacterial or fungal infections. Actually the number of rainbow trout dying in the low concentration was very small and could have been either natural mortality or some other factor such as physiological stress due to space limitation. Since only one or two fish died in the low concentration, and those died at almost the same time, the short duration of the mortality period in the low fluoride concentrations is actually misleading.

Ellis, et.al. (1948) reported that they had observed that the hatching of fish eggs in water containing 1.5 mg/l of fluoride was delayed several days beyond those hatched in unfluoridated water. No specific information is given on the results or procedures that produced this conclusion.

Herbert and Shurben (1964) also reported on the toxicity of fluoride to rainbow trout. Their laboratory tests indicate a 96-hour LC_{50} of about 18 mg/l in very soft water (hardness - 12 mg/l). Use of the normal one-twentieth application factor yeilds a safe level of 0.9 mg/l. The authors conclude that water with a greater hardness significantly reduced the toxicity of fluoride. They further state that 1.0 mg/l of fluoride ". . . is unlikely to kill more than 0.01 percent of a population of trout similar in resistance to those used in present work. Such a low mortality would be negligible by comparison with the natural death rate to which trout populations are subject."

Olson (1975) in a recent study with fathead minnows using Lake Superior water found that fluoride concentrations of 6.8 mg/l and below had no apparent effect on any life stage. The 96-hour LC_{50} in a static exposure was 80 mg/l for 4-day-old larvae and 200 mg/l for 14-week-old minnows. With respect to fluoride uptake in fish, Neuhold and Sigler (1960) report that as the fluoride in water increases, the fluoride in both muscle and bone tissue increases. A similar result was found in experiments with trout eggs. The exact mode of toxicity is not clearly stated in the article and it may or may not be related to this tissue uptake.

Personal communication from some Canadian investigators indicate concern for the accumulation of fluoride in the food chain. Evidence at this time does not conclude that fluoride concentrations in water of greater than 1 mg/l will be detrimental to higher organisms even though potential ecological significance has been noted.

Available information on the effects of fluoride indicate that 1.0 mg/l will be protective of the aquatic population, and will also permit the use of the Great Lakes as a raw water supply.

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PERSISTENT COMPOUNDS - METALS

IRON

RECOMMENDATION

It is recommended that the existing objective for iron specified in Annex 1, paragraph 1 (f) of the Water Quality Agreement be retained. This objective states:

Levels should not exceed 0.3 milligrams per litre.

COMMENTARY

Historically the most sensitive use to be protected by an iron limitation has been water supply. Concentrations above 0.3 mg/l may result in accumulations in distribution systems, staining of basins and toilet bowls and spotting of laundry. The Subcommittee reviewed the recommendation in Water Quality Criteria 1972 (NAS/NAE, 1974) and concluded that on the basis of user preference and because the defined treatment process can remove insoluble iron but may not remove soluble iron, 0.3 mg/l soluble iron should not be exceeded in public water supply sources. On this basis it was originally decided to recommend that the IJC objective of 0.3 mg/l as Fe be modified to read 0.3 mg/l soluble iron. However, a recent draft of proposed water quality criteria by the U.S. EPA indicates that concentrations of iron (chemical form unspecified) were lethal to a variety of benthos and fish between 0.32 and 1.0 mg/l (Warnick and Bell, 1969; Bandt, 1948; Doudoroff and Katz, 1953). EIFAC (1964) recommended that iron concentrations not exceed 1.0 mg/l in waters to be managed for fish life.

The Subcommittee interprets the present objective to mean total iron and concluded that liberalization of the objective from 0.3 mg/l as total iron to 0.3 mg/l soluble iron is not defensible. This objective will be considered for revision in 1976 after further study.

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PERSISTENT COMPOUNDS - METALS

SELENIUM

RECOMMENDATION

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

(1) *Concentrations for selenium in water should not exceed 0.01 mg/1, for the protection of public water supplies.*

(2) *To protect aquatic life, concentrations of selenium in water should not exceed 0.02 of the 96-hour median lethal concentration, as determined through bioassay using a sensitive resident species. This objective applies if it is lower than that given in (1).*

NOTE: The Board express concern for the protection of predatory birds and expresses mammals and notes that concentrations greater than 3 ug/g of selenium in the muscle of fish, dry weight, should be regarded with suspicion. Possible sources of selenium pollution should be investigated and controlled if they exist.

RATIONALE

Selenium is a non-metallic (or "semi-metallic") rare element which usually occurs in nature as sulfide ores of heavy metals. It appears in soils as elemental selenium or in its oxidized forms as salts of selenite (SeO_3^-) or selenate (SeO_4^-). 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 such as the xerox machine. It is also used in steel and in pigments for paints, glass, and ceramics (Cooper, 1967; Lymburner and Knoll, 1973).

Selenium in Water

Selenium is usually present in water as the selenate and selenite salts; 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, bottom and fly ash from a single burner has turned up levels of 2 mg/kg, 3.4 mg/kg and 41.3 mg/kg respectively (Lymburner and Knoll, 1973). Man's burning of fossil fuel puts about 450 tons per year of selenium (SEO_2) into the atmosphere, thus 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. Concentrations in mine tailings were below the detectable limit when measured by the Water Management Branch of the Ontario Ministry of the Environment. Californian sewage had only 0.01 to 0.06 mg/l of selenium, whether it was raw or treated, except for a high value of 0.28 mg/l in an industrial area (Feldman, 1974).

Amounts in water are usually low. The literature has been reviewed in several places (e.g. NAS/NAE, 1974), but many of the older estimates are probably too high because of limitations of chemical methods. Most uncontaminated surface waters have less than 0.05 mg/l of selenium, and most drinking waters contain less than 0.01 mg/l (APHA et al. 1971). Surface waters in a province of Germany average 0.004 mg/l (Heide and Schubert, 1960). The normal concentration in sea water is only 0.0004 mg/l (Chau and Riley, 1965). Even seepages from seleniferous areas do not contain more than 0.5 mg/l, and this content is lost when the seepages empty into ponds or lakes, apparently by coprecipitation with ferric hydroxide (APHA et al. 1971).

Lake sediments seem to act as reservoirs or sinks; in northern U.S.A. they contained from 1.0 to 3.5 mg/kg dry weight of selenium, considerably more than the usual level in soils (Wiersma and Lee, 1971). Small ecosystem experiments showed that of rain-carried selenium which falls on soil, 75% stayed there. Of the 25% which ran off into an aquatic system, 9% of the original amount ended on the sediments, and most of the rest was in the biota (Huckabee and Blaylock, 1974).

As a Toxicant and Required Nutrient for Humans and Domestic Animals

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 1000 mg/kg or more of selenium whereas the chronic type is associated with grains and plants which contain 5 to 20 mg/kg of selenium (Moxon, 1958). The large literature on natural poisoning of livestock from selenium in their food plants agrees in general that 5 mg/kg 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 mg/kg (National Technical Advisory Committee, 1968; NAS/NAE, 1974; McKee and Wolf, 1963). The usual chronic effects in mammals are weakness, visual impairment, paralysis, damage to heart, liver and viscera, stiff joints, and loss of hair and hooves. Additional symptoms in humans are marked pallor, red tainting of fingers, teeth and hair, dental caries, debility, depression, and irritation of nose and throat. In humans, overdoses resulting in acute toxicity are characterized by nervousness, vomiting, cough, dyspnea, convulsions, abdominal pain, diarrhea, hypotension and respiratory failure (Schroeder, 1974; NAS/NAE, 1974; Rodier, 1971).

It seems certain that selenium is carcinogenic. Schroeder, (1974) reviews his work and that of others, and current controversies. It is documented that 3 mg/kg of selenium in selenite form in the lifetime diet will kill rats and cause tumours in mice. The same amount in the form of selenate did not kill rats, but caused tumours, mostly malignant. Based on such studies, it is against the law in the U.S.A. for selenium to be added to food, even though it might be a remedy for deficiencies in some regions.

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, 1974) or 0.05 to 0.02 mg/kg in the food (Hoffman, et al. 1973). Daily requirements in humans have been similarly stated at 0.1 mg/day (Schroeder, 1974) and at 0.04 to 0.10 mg/kg of food. Schroeder states that 0.1 mg/day is met by usual diets, and NAS/NAE (1974) suggests that the normal dietary intake of selenium is about 0.2 mg/day.

Antagonism between 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 antagonized 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 interrelationship with vitamin E and possible teratogenic effects, (best reviewed in Anonymous (1972).

Criteria for Drinking Water and Stock-watering

There is not a great deal of information on this topic, probably because concentrations in water are generally low, and because cases of toxicity are mostly related to intake with food, not water.

"Water quality criteria 1972" (NAS/NAE, 1974) suggests a limit of 0.01 mg/l of total selenium in drinking water assuming that two litres of water are ingested per person per day. This concentration would increase the normal dietary intake (assumed at 0.2 mg/day) by 10%, or by 20% if it is assumed at 0.1 mg/day (Schroeder, 1974). Considerations about the greater toxicity of selenium in food (organic form) vs selenium in water bring an additional safety factor, so that a 0.01 mg/l criterion for drinking water seems reasonable, being somewhat above most natural levels. This criterion is also accepted by WHO, U.S.A., Canada and U.S.S.R. whereas some European countries such as France use a 0.05 mg/l criterion.

The U.S. National Academy of Sciences (NAS/NAE, 1974) recommends that the upper limit for selenium in livestock waters be 0.05 mg/l. This figure is also used by the Ontario Ministry of the Environment (1974).

These objectives seem reasonable considering the limited toxicity data available. A very high level of 9 mg/l in well-water resulted in human poisoning in 3 months. (Beath, 1962). Rats were killed by 2 mg/l of selenium in selenite form, in their drinking water, although selenate did not kill them (Schroeder, 1967). Mice seem more tolerant, since 3 mg/l of selenium (as sodium selenite and selenate) in the drinking water of mice over their lifetime, did not cause tumours, or affect survival, and caused only slightly shorter life and lower weights in females, and slightly higher weights in males (Schroeder et al. 1972).

Toxicity to Aquatic Life

Most lethal concentrations for aquatic animals reported are in the range of 2 to 20 mg/l with a sub-lethal effect on goldfish at 0.25 mg/l (0.02 of LC_{50}).

Ellis (1937) reported that 10 mg/l of sodium selenite was lethal to goldfish in about 5 days in very soft water. Other work by Ellis et al. (date unknown) showed that 2 mg/l of the same salt killed goldfish in 18 to 46 days, according to a report by Orsanco (1950). Selenium dioxide is 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). Tests with invertebrates (Bringmann and Kuhn, 1959) showed higher thresholds for lethal effects. The highest value was 90 mg/l for the bacterium Escherichia coli. The alga Scendedsmus sp. and waterflea Daphnia sp. had lethal thresholds of 2.5 mg/l in 2 to 4 days, similar to those of fish. Finally, one piece of research on a sub-lethal effect has been recorded (Weir and Hine, 1970). Goldfish showed a 7-day LC_{50} of 12 mg/l, similar to the values above. Fish showed significant impairment of a conditioned response at 0.25 mg/l which is 0.02 LC_{50}.

According to the numbers discussed above, a "safe" level for aquatic life, of selenium in water, would be some what below 0.02 LC_{50}. This would be somewhat less than 0.25 mg/l for certain organisms, and somewhat below 0.04 mg/l for others. Since these concentrations are higher than the objective for drinking water (0.01 mg/l) the concentrations are not given as objectives. However, the application factor of 0.02 LC_{50} is given in case it is required for protection of unusually sensitive local species.

Bioaccumulation

Concentrations of selenium in the tissues of fish range from 0.8 to about 3 mg/kg dry weight in a wide range of locations and conditions in fresh and ocean water. This range holds for Canadian fish from industrial and isolated locations (0.85 to 1.9 mg/kg, Uthe and Bligh, 1971); for a large series of freshwater fish from New York (1.0 to 2.5 mg/kg, Pakkala et al. 1972); for ocean and freshwater fish in Finland (1.0 to 2.9 mg/kg, Sandholm et al. 1973); seafoods (about 1.6 to 2.8 mg/kg, Morris and Levander, 1970); the edible portion of trout (about 1.4 to 3.4 mg/kg, Arthur, 1972); and for samples of marine food fish obtained in Ontario markets (0.8 to 2.0, Dr. D. Arthur, Dept. Nutrition, University of Guelph). In a very large series of fish samples from central Canada, average content was about 1.3 mg/kg, and most fish fell in the range mentioned above (Beal, 1974). However, the total range was wider. From the Great Lakes, values were higher for fish from Georgian Bay and parts of Lake Huron, up to 4.6 mg/kg and slightly lower for some fish from Lake Erie, down to 0.4 mg/kg.

The range of 0.8 to 3 mg/kg is about the same as concentrations found in fish in Europe and elsewhere (Anonymous, 1972), and in muscle of domestic land animals (loc cit.; Hoffman et al. 1973).

Fish mortality in a Colorado reservoir was reported by Barnhart (1958) as being caused by selenium from bottom deposits, passed through the food chain to accumulated levels of 300 mg/kg. This is the single such case known. In a more normal aquatic ecosystem (Sandholm et al., 1973) the animals have higher residues than plants, but there is no pattern of continuing accumulation. Presumably, excretion takes place in the usual ways, similar to that in humans, where a normal 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, 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 very high concentrations of 46 to 134 mg/kg selenium (Koeman et al., 1973). These are much higher than the values of 0.5 to 1.3 mg/kg 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 mg/kg selenium. The topic is not well understood yet; Koeman et al. considered that the high selenium might be protective against high mercury residues.

Nevertheless, the possibility exists that fish-eating birds and mammals including humans, may be subject to 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 there is general agreement that 5 mg/kg in the diet is dangerous (see above) and since a normal range of tissue concentration in fish is up to 3 mg/kg, it is desirable to have a tissue residue objective based on fish. This should protect predators until the question of bio-accumulation is better understood.

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NON-PERSISTENT COMPOUNDS

AMMONIA

RECOMMENDATION

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

> *Concentrations of un-ionized ammonia (NH_3) should not exceed 0.020 milligrams per litre for the protection of aquatic life. Concentrations of total ammonia should not exceed 0.50 milligrams per litre for the protection of public water supplies.*

RATIONALE

Ammonia enters natural water systems from several sources, either directly as ammonia or indirectly by formation from other nitrogenous matter. Direct sources are precipitation of ammonia with rain and snow, gas exchange with the atmosphere and the influx of ammonia containing effluents from urban, industrial and agricultural sources. Indirect sources are the chemical and biochemical transformation of nitrogenous organic and inorganic matter in soil and water, nitrogen fixation processes of dissolved nitrogen gas in water and excretion of ammonia by biota.

Ammonia is consumed by chemical and biochemical processes, some of them resulting in its oxidation to nitrite and nitrate ions, other reactions resulting in its incorporation into organic matter, particularly with the formation of proteins.

Aqueous Ammonia Equilibrium System

At high concentrations, ammonia becomes a significant toxicant to the aquatic biota. The toxicity of ammonia to fish is primarily due to un-ionized ammonia (NH_3) (Chipman, 1973; Wuhrmann et at., 1947; Wuhrmann and Woker, 1948; Hemens, 1966). Ionized ammonia (NH_4^+) is considered non toxic or significantly less toxic than un-ionized ammonia (NH_3) (Tabata, 1962). The percent of un-ionized ammonia in an aqueous ammonia solution is strongly dependent on pH, according to the equilibrium equation:

$$NH_3 + H_2O \rightleftharpoons NH_3 . H_2O \rightleftharpoons NH_4^+ + OH^-$$

The above equation is abbreviated and does not consider the hydrogen bonding of the molecules and ions to adjacent water molecules (Butler, 1964).

The equilibrium of ionized with un-ionzed ammonia is also influenced by the temperature and salinity of the water. As shown in Table 4, the fraction of un-ionized ammonia increases with rising temperature, particularly at low pH levels. The presence of low to moderate amounts of dissolved solids (200-1000 mg/l) will slightly lower the concentration of un-ionized ammonia. In Great Lakes waters, the magnitude of this effect will usually be less than the effect of lowering the temperature by 1°C under otherwise constant conditions. For practical purposes and for the definition of this objective the influence of the salinity will hence be neglected.

Table 4 - PERCENT UN-IONIZED AMMONIA IN AQUEOUS AMMONIA SOLUTION

(Values at zero salinity) (After Thurston et al., 1974)

Temperature	pH Value								
(°C)	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0
5	0.013	0.040	0.13	0.39	1.2	3.8	11.	28.	56.
10	0.019	0.059	0.19	0.59	1.8	5.6	16.	37.	65.
15	0.027	0.087	0.27	0.86	2.7	8.0	22.	46.	73.
20	0.040	0.13	0.40	1.2	3.8	11.	28.	56.	80
25	0.057	0.18	0.57	1.8	5.4	15.	36.	64.	85.
30	0.081	0.25	0.80	2.5	7.5	20.	45.	72.	89.

Conditions under which the objective for total ammonia is limiting.

Conditions under which the objective for un-ionized ammonia is limiting.

Toxicity to Fish

At concentrations above 0.5 mg/l un-ionized ammonia (NH_3) is strongly toxic to many fishes. Comprehensive reviews on the toxicity of ammonia to aquatic biota are published by EIFAC (1973), NAS/NAE (1974), and by McKee and Wolf (1963). A compilation of major studies on fish is given in Table 5. Most of these data on rainbow trout, Atlantic salmon, striped bass, three-spined stickleback, carp and other species are in the form of one to four day LC_{50} concentrations and under pH, temperature and dissolved oxygen conditions as they prevail in the Great Lakes. Two to four day LC_{50} concentrations for rainbow trout range from 0.25 to 0.75 mg/l NH_3 with coarser fishes being slightly less sensitive.

The equilibrium of un-ionized and ionized ammonia, and thus the toxicity of ammonia, is strongly dependent on the pH and temperature, and, to a lesser degree on the salinity of the water. The toxicity of un-ionized ammonia is to a minor degree further dependent on the alkalinity and free carbon dioxide of water, and, to an unknown degree, on other synergistic and antagonistic factors, such as dissolved oxygen levels, biota acclimation, etc.

There are few published data available on chronic sub-lethal effect of ammonia to fish of any species. A three-month test on 200 rainbow trout (Water Pollution Research 1967; 1968) showed a 15% mortality at 0.27 mg/l NH_3 and a 5% mortality at un-ionized ammonia concentrations of 0.13 and 0.07 mg/l NH_3, respecively.

Although no mortality data have been reported at concentrations less than 0.2 mg/l NH_3, deleterious effects of ammonia at comparable concentrations and lower have been observed by

Table 5 - AMMONIA TOXICITY TO FISH

Species	Length (cm.)	pH	Temp. (^{o}C)	NH_3 Concentration (mg/1 NH_3)	Dissolved Oxygen (% saturation)	Mortality (% of total fish)	Exposure Time (days)	Reference
Rainbow trout (salmo gairdnerii RICHARDSON)	15.2	7.86-8.22	10.5-11.6	0.50	≥90	50	2	BALL (1967)
	3-5	8.1 -8.3	12-13	$0.25^{a)}$		50	>4	Water Poll.Res.(1968)
	3-5	8.1 -8.3	2-4	$0.42^{a)}$		50	3	"
		7.8	5	<0.25		50	4	"
		7.8	18	~0.75		50	4	"
				0.27		16	90	"
				0.07		5	90	"
				0.13		5	90	"
	13-14	7.45	13.6	$0.70\ (65)^{b)}$		50	$1^{d)}$	HERBERT &. SHURBEN(1965)
	13-14	7.81	13.6(?)	$0.49\ (37)^{b)}$		50	$1^{e)}$	"
		7.8	17.5	$\sim 0.50\ (24.6)^{c)}$	~100	50	$2^{f)}$	HERBERT &. SHURBEN(1964)
		7.8	17.5	$\sim 0.45\ (30.1)^{c)}$	47	50	$2^{f)}$	"
		6.9	17.7	$\sim 0.65\ (193.)^{c)}$	~100	50	$2^{g)}$	"
	7.3	7.0-8.0	19.8	1.7	~15 to ~90	50	0.01-0.25	DOWNING & MERKENS(1955)
	7.3	7.0-8.0	19.8	1.2	~15 to ~90	50	0.01-0.5	"
	7.3	7.0-8.0	19.8	0.7	~15 to ~90	50	0.01-0.8	"
Atlantic salmon		7.81	13.6(?)	$0.28\ (15)^{b)}$		50	$1^{e)}$	HERBERT & SHURBEN(1965)
Perch	10.1	7.75-8.12	9.4-11.1	0.35	≥92	50	4	BALL (1967)
Roach	8.6	7.86-8.30	10.0-13.2	0.42	≥90	50	4	"
Rudd	11.3	8.05-8.30	12.2-13.2	0.45	≥88	50	4	"
Bream	11.1	7.75-8.12	9.4-14.6	0.50	≥92	50	2 to 6	"
Striped bass	2.0-9.3	7.3-7.9	15	1.4	≥50	50	4	HAZEL,THOMSEN & MEITH (1971)
	2.0-9.3	7.4-8.0	23	0.93	≥50	50	4	"
Stickleback (three spined)	3.2-6.0	6.8-7.2	15	1.0	≥50	50	4	"
	3.2-6.0	7.0-7.3	23	0.88	≥50	50	4	"
Common carp		8.3-8.7	11	1.3		16	10	FLIS (1968a)
		8.3-8.7	11	0.9		18	10	"
		8.05		0.11		8 and 0	35	FLIS (1968b)

a) Water hardness 320 mg/1 $CaCO_3$

b) Values taken from EIFAC (1970), original values (in brackets) as total mg/1 N from NH_4Cl

c) Values calculated from Table , original values (in brackets) as total mg/1 N from NH_4Cl

d) Water hardness 125 mg/1 $CaCO_3$

e) Water hardness 248 mg/1 $CaCO_3$

f) Water hardness 320 mg/1 $CaCO_3$, water alkalinity 240 mg/1 $CaCO_3$

g) Soft water

a number of researchers. Reichenback-Klinke (1967), in a series of one-week tests on 240 fish of 9 species at concentrations of 0.1 to 0.4 mg/l NH_3 observed as well as inflammations and hyperplasia swelling of and diminishing of the number of blood cells. Irreversible blood damage occurred in trout fry at 0.27 mg/l NH_3. He also noted that these low NH_3 doses inhibited the growth of young trout and lessened their resistance to diseases. Flis (1968) reported that a 35-day exposure of carp to a concentration of approximately 0.1 mg/l NH_3 resulted in extensive necrobiotic and necrotic changes and tissue disintegration in various organs.

Reduction in growth rates for rudd has also been observed after 95 days at concentrations greater than 0.1 mg/l NH_3 (Water Pollution Research 1971; 1972) and for rainbow trout at 0.02 mg/l NH_3 after 6 months (Smith and Piper, 1974). Smith and Piper (1974) also reported severe pathological changes in gills and livers of rainbow trout after 12 months exposure at 0.02 mg/l NH_3. On a test of rainbow trout for the 21-day period between egg hatching and swim-up stage, a reduction in development (length and sac absorption) was observed at concentrations of 0.07 mg/l NH_3 and higher (Thurston, 1974). Concentrations as low as 0.002 mg/l NH_3 have been reported to cause gill hyperplasia in fingerling chinook salmon in 6 weeks (Burrows, 1964).

Rainbow trout have successfully spawned in the laboratory at 0.06 mg/l NH_3 and have produced significant numbers of viable fry (Thurston, 1974).

It is common practice, for the establishment of water quality objectives, to muliply 96-hour LC_{50} data by an application factor to arrive at recommendations for those objectives. According to Water Quality Criteria 1972 (NAS/NAE, 1974) application factors range, depending on the compound in question, from 0.1 (e.g. copper) to 0.005 (e.g. zinc). For ammonia, an application factor of 0.05 is recommended. With an average 96-hour LC_{50} value of about 0.50 mg/l NH_3 X 0.05, a safe concentration of 0.025 mg/l NH_3 is calculated. This value appears to be a safe concentration of un-ionized ammonia for the survival of rainbow trout fry and fingerlings. However, judging from the comparison of trout and salmon sensitivities by Herbert & Shurben (1965), salmon appear to be almost twice as sensitive to ammonia as trout. Therefore, with an application factor of 0.05 a limit of about 0.015 mg/l NH_3 could be calculated.

Both values of 0.025 and 0.015 mg/l NH_3 are in close proximity to the experimentally observed threshold for sub-lethal effect of ammonia on rainbow trout, reported as 0.02 mg/l NH_3 by Water Pollution Research (1971; 1972) and Smith and Piper (1974). Extreme deviations of the "mean" of 0.02 mg/l NH_3 may be represented by the value of 0.06 mg/l NH_3 for the successful spawning and apparently normal fry development of rainbow trout (Thurston, 1974) and by the observations of sub-lethal effect at un-ionized ammonia concentrations of 0.002 mg/l NH_3 to fingerling chinook salmon by Burrows (1964). Until it can be shown that exposure of biota to un-ionized ammonia concentrations of less than 0.02 mg/l NH_3 is indeed resulting in long term sub-lethal effect, and in view of the acute toxic levels of 0.2 mg/l NH_3 or higher, it is recommended that un-ionized ammonia should not exceed 0.02 mg/l NH_3.

Ammonia in Raw Water Supplies

In water treatment, (total) ammonia interferes with the water chlorination. If ammonia is present, chlorine will react with it first, producing chloramines. On continued chlorination, oxidation of intermediate chloramines to HCl and N_2 will occur. Chloramines also have bactericidal properties but are slower acting than free chlorine. In the past, chloramines, intentionally produced by adding ammonia to raw water, were used to prevent the reaction of chlorine with phenols. To destroy ammonia occurring in raw water, about 10 parts of chlorine to 1 part of ammonia nitrogen is required (Matheson, 1973). Because of these unwanted effects, the level of total ammonia for raw water supplies is desired to be less than 0.01 mg/l NH_3 (total). However, for practical purposes WHO (1963), NAS/NAE (1974), and Ministry of the Environment (1974), recommend 0.5 mg/l NH_3 (total) as the upper limit for raw water supplies. At concentrations above this value, problems associated with disinfection, and taste and odor are experienced.

In accordance with above recommendations and for the protection of the use of Great Lakes water as raw water supply, it is recommended that the objective for total ammonia should not exceed 0.5 mg/l NH_3 (total).

The conditions under which either the objective for un-ionized ammonia, for the protection of aquatic life, or the objective for total ammonia, for protection of public water supplies, becomes the limiting parameter is indicated in Table 4. At a low pH, the value for total ammonia is limiting; at a high pH, the value for un-ionized ammonia is the limiting parameter.

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NON-PERSISTENT COMPOUNDS

CHLORINE

RECOMMENDATION

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

Total residual chlorine, as measured by the amperometric (or equivalent) method, should not exceed:

1. *0.002 milligrams per litre in order to protect trout, salmon, and sensitive fish food organisms.*
2. *0.01 milligrams per litre in order to protect warmwater fish and most fish food organisms.*

RATIONALE

Elemental chlorine is a gas that is highly soluble in water and reacts readily with many inorganic substances and all plant and animal tissues. Liquified chlorine gas assumes two principal forms in wastewater: hypochlorous acid (HOCl) and monochloramine, the dominant form in wastewater. Sodium hypochlorite (NaOCl) is being used increasingly, for safety reasons, as a disinfectant and is as effective as chlorine gas and assumes the same chemical forms. Total residual chlorine (TRC) is the sum of free available chlorine (HOCl or hypochlorite ion) and combined available chlorine (chloramines and other chloro derivatives). Free available chlorine is seldom found in treated wastewaters because chlorine is added in an amount less than the chlorine demand before discharge to a surface water.

Toxicity of Chlorinated Wastewaters

There is an extensive data base on the toxicity of TRC on freshwater aquatic life and these data have been adequately summarized (Isom, 1971; McKee and Wolf, 1963; Doudoroff and Katz, 1950; Brungs, 1973; and Michigan Dept. of Natural Resources, 1971). The following discussion is limited to those studies that have involved chlorinated wastewaters and does not include numerous studies of TRC in clean waters.

The Michigan Department of Natural Resources (1971) reported the effects on caged fish in several receiving streams below wastewater discharges. Fifty percent of the rainbow trout died within 96 hr (96-hr LC_{50}) at TRC concentrations of 0.014 to 0.029 mg/l; some fish died as far as 0.8 mile (1.3 km) below the outfall. These same discharges were studied when chlorination was temporarily interrupted, and no mortality was observed. In addition, dechlorination with sodium thiosulfate eliminated toxicity in 4-day tests with undiluted effluent.

Tsai (1973) studied the effects on fish of 156 wastewater treatment plants in Maryland, northern Virginia, and southeastern Pennsylvania. All the plants discharged chlorinated municipal wastes into small streams containing fish. In most of the plants in Maryland and Virginia, 0.5 to 2.0 mg/l residual chlorine is maintained in the effluents, and Pennsylvania requires 0.5 mg/l in effluents prior to discharge to natural surface water. Tsai (1973) studied principally fish, but observed typically a clean bottom without living organisms in the area immediately below the chlorinated outfalls. Unchlorinated discharge areas were typically characterized by abundant growths of wastewater fungi. No fish were found in water with a TRC above 0.37 mg/l, and the species diversity index reached zero at 0.25 mg/l. A 50 percent reduction in species diversity index occurred at 0.10 mg/l. Of the 45 percent species of fish observed in the study areas, the brook trout and brown trout were the most sensitive and were not found at concentrations above approximately 0.02 mg/l. Ten species were not found above 0.05 mg/l.

Arthur et al (1975) has studied the effect of chlorinated secondary wastewater treatment plant effluent containing only domestic sewage effluent on reproduction of fathead minnows, Daphnia magna, and the scud (Gammarus pseudolimnaeus). Daphnia magna apparently was the most sensitive invertebrate species and died at a TRC concentration of 0.014 mg/l, and acceptable reproduction occurred at 0.003 mg/l and below. Scud reproduction was reduced at concentrations above approximately 0.012 mg/l (1.2 percent effluent). No effects on any life cycle stage, including reproduction, of the fathead minnow was observed at a concentration of 0.014 mg/l; adverse effects were observed at 0.042 mg/l. Acute toxicity studies with eight species of fish, crayfish (Orconectes virilis), scud (Gammarus pseudolimnaeus), snails (Physa integra and Campeloma decisum), and stoneflies (Acroneuria lycorias) indicated that the crayfish, snails, and caddisfly larvae were least sensitive (7-day LC_{50} values greater than 0.55 mg/l. Seven-day LC_{50} values for the other organisms were between 0.083 and 0.261 mg/l; coho salmon and brook trout were the most sensitive. Nearly 50 percent of these observed mortalities occurred in the first 12 hr of the acute tests indicating that the lethal effect of TRC occurs rapidly. Comparible acute and chronic tests with the effluent dechlorinated with sulfur dioxide indicated that most, if not all, of the toxicity of the chlorinated effluent was eliminated. Esvelt et al (1971; 1973) and Krock and Mason (1971) completed an extensive study on the toxicity of chlorinated municipal wastewaters entering San Francisco Bay and surrounding areas. They observed a significant increase in toxicity following chlorination. Chlorine toxicity was still significant in aged (up to 3 days) chlorinated wastewater, in which TRC concentrations were as high as 25 percent of the initial level. Rainbow trout was the most sensitive of the species tested, followed by the golden shiner and three-spined stickleback. A calculated chlorine residual of 0.03 mg/l, based on dilution of a measured concentration of 2.0 mg/l, reduced plankton photosynthesis by more than 20 percent of the value obtained with a dilution of effluent having no chlorine residual. Dechlorination with sodium bisulfite also eliminated chlorine-related toxicity. One of the conclusions of the California study was that chlorination may be the largest single source of toxicity in San Francisco Bay.

Martens and Servizi (1974) and Servizi and Martens (19740 observed mortality of salmon in receiving streams at TRC concentrations as low as 0.02 mg.l. Determinations of the effect of time on chlorine residuals were made by sample storage and lagoon retention. Lethal concentrations persisted in undiluted effluent for at least 50 hours. Twenty to one dilutions resulted in the chlorine residual declining to a non-detectable concentration after 22 hours. Studies with live cages at points downstream of the effluent demonstrated acutely lethal conditions that did not persist during periods when the chlorinator was inoperable.

An ongoing project sponsored by the U.S. Environmental Protection Agency at the Grandville, Michigan treatment plant has also studied the chronic effects of various disinfection techniques on the fathead minnow. While the results are incomplete and statistically untested, it appears that the toxicity of this chlorinated effluent is similar to that observed earlier (Arthur et al., 1975).

Methodology

Many wastewater treatment plants are required to maintain a residual chlorine concentration of 0.5 to 2.0 mg/l. Most plant operators use the orthotolidine method which has been frequently shown to be inaccurate resulting in much higher concentrations than necessary for adequate disinfection. This compounds toxicity problems in receiving waters. Total residual chlorine concentrations in 20 Illinois effluents ranged from 0.98 to 5.17 mg/l (Snoeyink and Markus, 1974). A similar study at 22 plants in southern Wisconsin resulted in observed concentrations of TRC between 0.18 to 10.3 mg/l (McKersie, 1974). Both studies demonstrated that the orthotolidine methods provided the poorest results when compared against better methods such as the amperometric titration technique. Other studies (Martens and Servizi, 1974; Servizi and Martens, 1974) reached the same conclusion that the commonly used orthotolidine method is inadequate to determine TRC in wastewaters or receiving streams.

Criteria

Several reviewers of chlorine toxicity have recommended numerical criteria for continuous concentrations of TRC that would not adversely effect aquatic populations. Basch and Truchan (1974) recommended maximum concentrations of 0.02

and 0.005 mg/l for warmwater and coldwater intolerant fish, respectively. EIFAC (1973) has suggested criteria dependent upon pH and temperature with an acceptable upper limit of 0.004 mg HOCl/l (TRC from 0.004 mg/l at a pH of 6.0 and 5^o C to 0.121 mg/l at a pH of 9.0 and 25^o C). A third review by Brungs (1973) has recommended criteria of 0.01 mg/l for warmwater fish and 0.002 mg/l for coldwater species and the most sensitive fish food organisms.

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NON-PERSISTENT COMPOUNDS

HYDROGEN SULFIDE

RECOMMENDATION

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

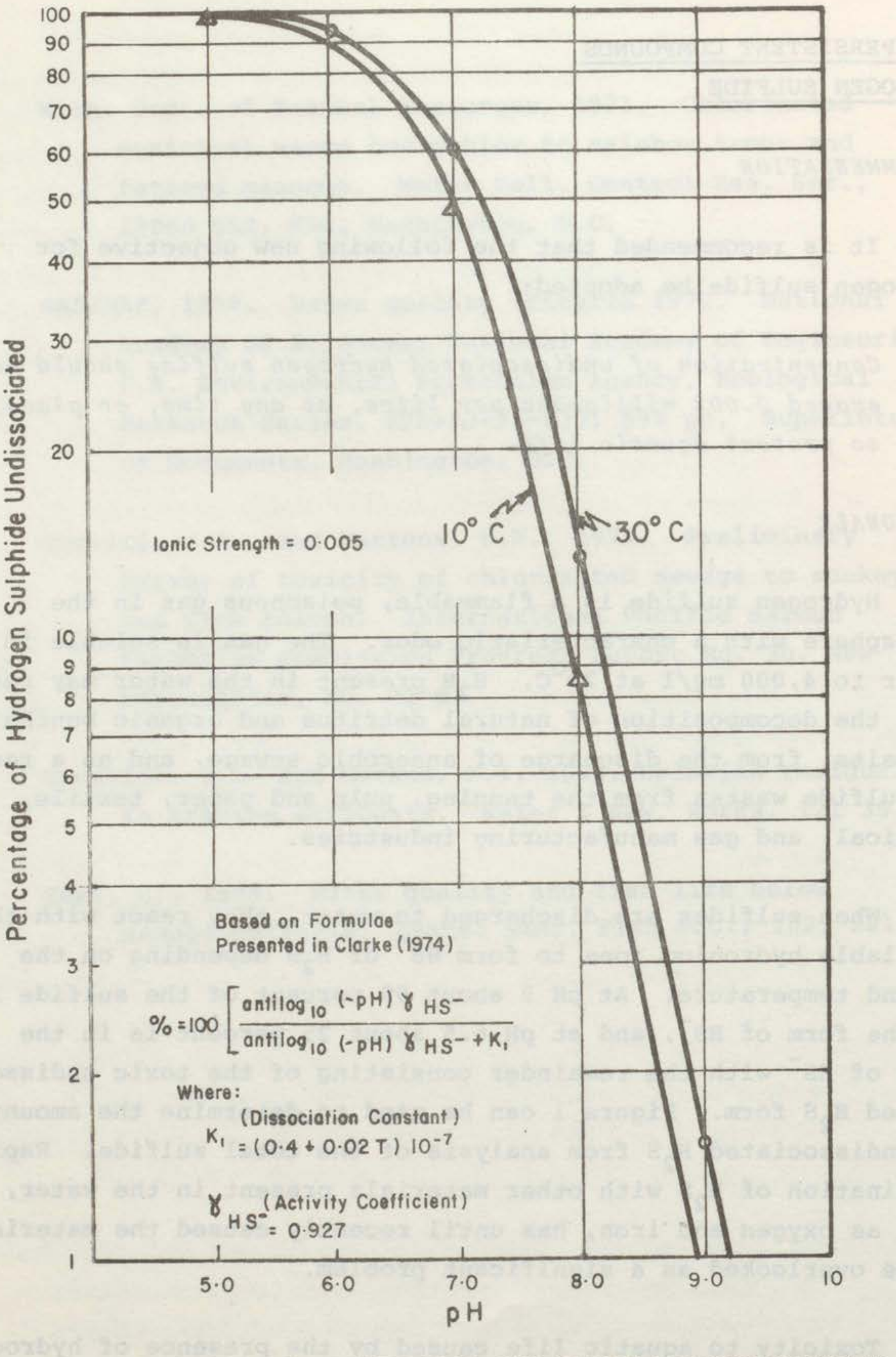
> *Concentration of undissociated hydrogen sulfide should not exceed 0.002 milligrams per litre, at any time, or place, to protect aquatic life.*

RATIONALE

Hydrogen sulfide is a flammable, poisonous gas in the atmosphere with a characteristic odor. The gas is soluble in water to 4,000 mg/l at 20°C. H_2S present in the water may result from the decomposition of natural detritus and organic benthal deposits, from the discharge of anaerobic sewage, and as a result of sulfide wastes from the tanning, pulp and paper, textile, chemical, and gas manufacturing industries.

When sulfides are discharged to water, they react with the available hydronium ions to form HS^- or H_2S depending on the pH and temperature. At pH 9 about 99 percent of the sulfide is in the form of HS^-, and at pH 6.5 about 25 percent is in the form of HS^- with the remainder consisting of the toxic undissociated H_2S form. Figure 1 can be used to determine the amount of undissociated H_2S from analysis of the total sulfide. Rapid combination of H_2S with other materials present in the water, such as oxygen and iron, has until recently caused the material to be overlooked as a significant problem.

Toxicity to aquatic life caused by the presence of hydrogen sulfide is dependent on the temperature, pH and dissolved oxygen



PERCENTAGE OF HYDROGEN SULPHIDE UNDISSOCIATED
AS A FUNCTION OF pH

Figure 1

present. At a lower pH the amount of the toxic form (H_2S) will be greater. When temperatures are low, fish life exhibit a greater tolerance to H_2S. The presence of high dissolved oxygen levels promotes rapid conversion of the H_2S to sulfates, and therefore, maintaining high D.O, levels reduces the likelihood of H_2S toxicity problems. Fish also exhibit a strong avoidance reaction to sulfide, and it is hypothesized that such a reaction would occur before they were harmed (Jones, 1964).

Most recent investigations into H_2S toxicity have been as it relates to the presence near the sediment-water interface especially near organic sludge deposits. In this zone, within a few centimeters of the bottom, significant concentrations of H_2S can occur if the benthal material is undergoing anaerobic decomposition. It should be noted that certain types of sludge deposits, notably those from pulp and paper mills, are more likely to cause H_2S formation than others.

Colby and Smith (1967) report that walleye eggs held in trays in zones where H_2S levels were commonly 0.1 to 0.02 mg/l did not hatch. The same study reports a 96-hour LC_{50} of 0.05 mg/l for walleye fry in a laboratory bioassay. Adelman and Smith (1970) report that "The maximum possible safe level of H_2S for (northern pike) eggs is between 0.014 and 0.018 mg/l and for sac fry between 0.004 and 0.006 mg/l for 96 hour exposure." Smith and Oseid (1973) report the 96-hour LC_{50} for juvenile brook trout, goldfish and walleye as 0.017, 0.090 and 0.020 mg/l respectively. They also indicated that the no-effect level for the growth of juveniles is also reported as 0.002 mg/l for bluegills, 0.004 mg/l for walleye and 0.003 mg/l for the fathead minnow.

On the basis of chronic tests evaluating growth and survival, the safe level for bluegill juveniles and adults was 0.002 mg/l and for fathead minnows was between 0.002 and 0.003 mg/l (NAS/NAE, 1974). Safe levels for various arthropods were between 0.002 and

0.003 mg/l (Smith, 1971). Oseid and Smith (1972) indicate that depending on other environmental factors H_2S levels of 0.0015 mg/l can reduce the physical capability of fish.

Oseid and Smith (1974) report that the maximum safe H_2S concentration for Gammarus is 0.002 mg/l in hard water. The mean 96-hour LC_{50} for the same test was 0.022 mg/l indicating an approximate application factor of 10.

Clarke (1974) states that "A molecular (undissociated) H_2S concentration of 0.01 mg/l would appear to be an approximate safe level for sensitive fish development stages in water with a dissolved oxygen concentration of about 10-12 mg/l, and for periods of exposure of 100-200 hours." This proposed level is based on a slightly different method of calculating the undissociated H_2S from the total and is about 1.5 to 2 times greater than that reported in other works.

It should be noted that H_2S will occur in lakes where natural organic bottom material is decomposing. Under summer conditions the elevated levels will be limited to the hypolimnion, while in winter unsafe levels could spread throughout the profile. It is unlikely that this will occur in other than small lakes with little circulation. The primary area where H_2S may create problems in the Great Lakes is in relatively unmixed bays which received industrial wastes such as those from pulp and paper mills. Care must be exercised in interpreting H_2S data collected in the field, because a fish population could be thriving in the water overlying an area where the H_2S level at the mud-water interface is high. Where these H_2S levels are high near the decomposing benthal deposit, it is likely that dissolved oxygen conditions would also be low, thereby aggravating the problem. Although zones of elevated H_2S can occur, a transient fish population could be present, but the survival of eggs in the area is unlikely. The criterion proposed for H_2S will, as a secondary benefit, protect against the discharge of decomposable and settleable materials.

There is no criterion established for H_2S for either public or agricultural water supplies, because the unpleasant taste and odor would preclude use of that water at hazardous concentrations. The allowable levels of hydrogen sulfide in water for industrial use are greater than those necessary to sustain aquatic life.

Based upon the protection of a balanced population of complete aquatic life cycles, it is recommended that the maximum undissociated H_2S concentration be 0.002 mg/l.

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NON-PERSISTENT 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 I 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 water-birds and aquatic mammals. The mortality of water-birds 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 insulation 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 water-birds.

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 sub-lethal 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 than 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 aromatics 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 $\frac{0.72}{13} = 0.55$, 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 aviation 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 metric tons per year, almost equivalent to one "Arrow" sized 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 tones 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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NON-PERSISTENT COMPOUNDS

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 of 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 non-persistent 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 on 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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MICROBIOLOGY

RECOMMENDATION

It is recommended at this time that the following existing objective for microbiology which appears in Annex 1, paragraph 1 (a) in the Water Quality Agreement, be retained:

> "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".

RATIONALE

There is widespread contention among scientists whether total and fecal coliform standards in use by regulatory agencies throughout the Great Lakes System to protect swimmers are over-restrictive. Many beaches adjacent to large population centers, where swimming could be a major source of recreation, are closed to this activity. Water Quality Criteria 1972 (NAS/NAE, 1974) includes a review of the relationships between bacteriological water quality and health of swimmers which concluded, "No specific recommendation is made concerning the presence or concentrations of micro-organisms in bathing water because of the paucity of valid epidemiological data".

The U.S. EPA (Cabelli and McCabe, 1974) responded to the needs by inaugurating a very carefully designed study at ocean beaches after extensive critical analysis of the methods of preceding investigators. Pretesting of the first years trial study (1973) are encouraging.

Canada Centre for Inland Waters (CCIW) has an on-going research program to improve the specificity of microbiological techniques and relate the incidence and abundance of organisms to water quality. Mr. B. Dutka, CCIW, is chairman of a massive committee approach organized by the American Society of Testing and Materials (ASTM) to improve and standardize microbiological techniques.

The opinion of the Research Advisory Board's Standing Committee on Health Effects is that the total coliform objective has continued value in tracing water quality trends, as has the fecal coliform objective. They feel that fecal coliform measurements should be coupled with not more than one or two other yet-to-be decided specific organisms to provide a more accurate criterion for protection of swimmers. Various organisms have been suggested but there is no unanimity. Perhaps the ASTM committee activity will provide the necessary forum for agreement. Research on epidemiological relationships must be encouraged at freshwater beaches if we are to make more effective use of our recreational resources. In the meantime, since the existing objective appears to be protecting swimmers, it should be retained.

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PHYSICAL CHARACTERISTICS

ASBESTOS

RECOMMENDATION

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.

RATIONALE

Asbestos is a generic name for several fibrous silicates. The reported background level of asbestiform fibre concentration in the Great Lakes varies from less that 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 needed 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 Center 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 fibers; 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 equal 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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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 purtescent 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 purtescent 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 direct 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 percent from its seasonally 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 processess. 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 an 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/l
Moderate protection	80 mg/l
Low Level of protection	400 mg/l
Very low level of protection	over 400 mg/l

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 whose effect occurs in the water column and those whose 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/l, 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/l upstream vs. 390 mg/l 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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PHYSICAL CHARACTERISTICS
TEMPERATURE

RECOMMENDATION

It is recommended that the following, revised objective for temperature be adopted to replace the interim objective in Annex 1:

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

2) *At the boundary of the mixing zone, the following upper temperature limits, should apply"*
   (a) *in the warmer months, (April through October), the maximum weekly average temperature during any month should not exceed the optimum plus one third of the range between the optimum for growth and the ultimate upper incipient lethal temperature for the most sensitive important species or appropriate life stage that is normally found at the location at that time, or'*
   (b) *during reproductive seasons, (e.g., April - June and September - November for fish), weekly average temperatures should meet site specific requirements for successful maturation, migration, spawning, egg incubation, fry rearing and other reproductive functions for the local sensitive important species.*

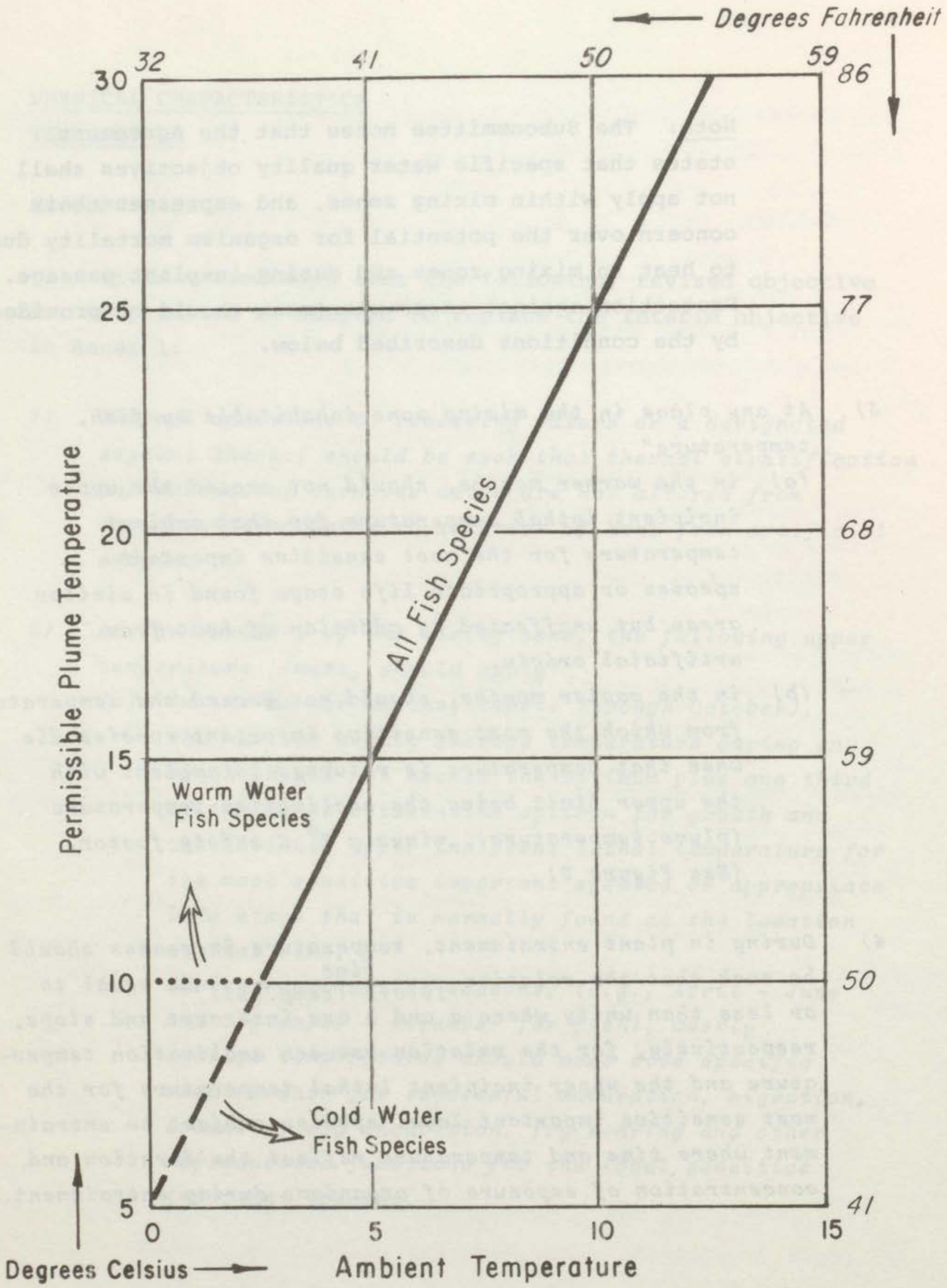
Note: The Subcommittee notes that the Agreement states that specific water quality objectives shall not apply within mixing zones, and expresses their concern over the potential for organism mortality due to heat in mixing zones and during in-plant passage. Protection against these phenomena should be provided by the conditions described below.

3) At any place in the mixing zone inhabitable by fish, temperature"

(a) in the warmer months, should not exceed the upper incipient lethal temperature for that ambient temperature for the most sensitive important species or appropriate life stage found in similar areas but unaffected by addition of heat from artificial origin.

(b) in the cooler months, should not exceed the temperature from which the most sensitive important species die when that temperature is returned to ambient with the upper limit being the acclimation temperature (plume temperature), minus a 2° C safety factor. (See Figure 2)

4) During in plant entrainment, temperature increases should be such that the relation $\frac{time}{10(a+b\ (temp.+2))}$ *is equal to or less than unity where a and b are intercept and slope, respectively, for the relation between acclimation temperature and the upper incipient lethal temperature for the most sensitive important local species subject to entrainment where time and temperature reflect the duration and concentration of exposure of organisms during entrainment.*



MAXIMUM PERMISSIBLE WEEKLY AVERAGE PLUME TEMPERATURE vs AMBIENT TEMPERATURE

Figure 2

Note: Detailed discussion of the above terminology and concepts are available (NAS/NAE 1974; USEPA 1975) in a form compatible with the above recommendations.

EXISTING OBJECTIVE

The above objective is recommended to replace the existing interim objective for temperature stipulated in Annex 1, para. 2 (a) of the Water Quality Agreement. This interim objective states:

> "There should be no change that would adversely affect any local or general use of these waters."

RATIONALE

The large volumes of water required for cooling purposes necessitates the involvement of the Water Quality Objectives Subcommittee not only in the water quality of receiving waters but also in the fate of organisms inhabiting the waters used for cooling. The normal contribution of heat to aquatic systems is essentially through solar radiation but when that contribution is augmented by the increasing development of urban and industrial complexes requiring cooling water, the potential alteration of thermal structure, local or lake-wide becomes of concern. Since it has been predicted that by 1980 (Picton, 1960) one-fifth of the total freshwater runoff for the United States will be required as cooling water, it is apparent that the potential for alteration of thermal structure, and probability of exposure to in-plant effects, will increase. The magnitude of the problem is placed in perspective by Krenkel and Parker's (1969) statement that 70% of the process water withdrawn is for cooling purposes and Acre's (1970) prediction of an elevenfold increase in this source of heat input by the year 2000.

Assuming, therefore, that man-made heat inputs to the Great Lakes are largely from the use of water for cooling purposes, effects can be simplified by categorization into far field, (Part 1 of the recommendation), near field (Part 2 and 3), or in-plant (Part4) in nature. Although the Water Quality Objectives Subcommittee focuses largely (Parts 1, 2 and 3) on the far-field effect at edge of mixing zone and beyond in establishing specific water quality objectives, the magnitude of the water volume required (Mihursky and Kennedy, 1967) necessitates involvement in the three areas of effect in order to maintain the integrity of Great Lakes biological systems. Specific water quality objectives should also be sufficient in scope so as to include the particular communities of organisms and their critical life stages which tend to vary between and within lakes.

In general, the composition of aquatic communities depends largely on the temperature characteristics of their environment. Biota occuring naturally in each body of water, or a portion of it, compete with varying degrees of success depending upon habitat characteristics. Consequently, alteration in temperature may disturb natural balances. In order to safeguard against wholesale changes in aquatic communities, it is recognized that natural behaviour of the water mass must be preserved (Part 1 of the objective). Furthermore, since the nearshore environment may behave and function with varying degrees of interaction with the rest of the water body, alterations to this sensitive portion of the water body must be considered separately at least to some degree (Part 2 of the objective).

To further facilitate allocating areas of protection prior to formulating the recommendation, components of the resource have been categorized and related to their potential for exposure to the three levels of effect indicated above. For this purpose, biota have been sub-divided into mobile (prone to near-field and far-field effects) and passive (prone to in-plant, near-field and far-field effects) organisms.

Mobile organisms demonstrate habitat preference to varying degrees. For these organisms not only the increase in temperature above ambient must be considered, but also the downward trend position. The effects of directional shifts in temperature depend upon species and acclimization. Research indicates that fish, contradictorily, may inhabit discharges for extended periods, or may avoid these areas, (Coutant, 1970; Neill and Magnuson, 1974; Kelso, 1974; Ontario Ministry of Natural Resources, personal communication), based in part on their temperature preference and/or their reaction to current. Although association with the discharge canal and mixing zone is noticeably variable, association with elevated temperatures beyond the mixing zone may also be ephemeral unless no other suitable habitat is available. Consequently, a temperature objective must be created to protect those that inhabit areas of elevated temperature and those that visit and provide maximum habitat for their use. Furthermore, temperature restrictions must envelop the effects of both upward and downward shifts as well as the possibility of general increase in temperature in the nearshore area, epilimnion or the lake as a whole.

Passive biota, on the other hand, have three possible exposures to elevated temperatures: 1) they may be entrained at the intake, exposed abruptly to elevated temperatures during the cooling process, then reintroduced to the receiving water where they will return to ambient conditions at some later time; 2) they may be entrained at the discharge structure (through addition of tempering water), in the mixing zone or in the plume and consequently have lower exposures than (1); or 3) there may be no exposure to increased temperature (providing no general warming trend has occurred in any portion of the epilimnion). If a specific water quality objective for temperature is derived by considering the entrainment process, conditions will be sufficiently restrictive so as to protect organisms entrained later in the process. Should objectives apply only at the boundary of the mixing zone, the stage of maximum stress would be ignored. Both passive and mobile forms, existing naturally in the Great Lakes system form communities whose composition and performance depend largely upon the temperature characteristics of their environment. Although the normal annual cycle in temperature may not always be optimum for these communities, the changes are frequently required to trigger spawning activities, hatching, egg or larval development, metamorphosis or migration. Consequently the normal temperature levels and seasonal trends must be maintained to ensure that neither the communities composition nor its well-being are adversely affected by temperature.

It seems obvious that no single temperature rise limitation can be applied uniformly to continental or large regional areas; the requirements must be closely related to each body of water and to its particular community of organisms. A temperature objective should consider invertebrates, plankton, or other plant and animal life that may be of importance to food chains or otherwise interact with species of direct interest to man. Since thermal requirements of various species differ, the social choice of the species could allow for different "levels of protection" among water bodies. Such decisions, however, clearly transcend the scientific judgements needed in establishing thermal criteria. If it is desirable to attempt preservation of an existing ecosystem, then the most sensitive species or life stage dictates the objective selected.

The recommended objectives for temperature consider both the multiple thermal requirements of aquatic species and requirements for balanced communities. The number of distinct requirements and the values yielded from each require periodic reexamination as knowledge of thermal effects on aquatic species and communities increases. Currently, definable requirements are available (for selected species populations or communities) or can be obtained for:

1. Maximum sustained temperatures that are consistent with maintaining desirable levels of productivity (growth minus mortality);

2. Maximum levels of thermal acclimation that will permit return to ambient winter temperatures should artificial sources of heat cease;

3. Temperature limitations for survival of brief exposures to temperature extremes, both upper and lower;

4. Restricted temperature ranges for various stages of reproduction, including (for fish) gonad growth and gamete maturation, spawning migration, release of gametes, development of the embryos and larvae, commencement of independent feeding (and other activities) by juveniles; and temperatures required for metamorphosis, emergence, and other activities of lower forms;

5. Thermal limits for diverse compositions of species of aquatic communities, particularly where reduction in diversity creates nuisance growths of certain organisms, or where important food sources or chains are altered;

6. Thermal requirements of downstream aquatic life where upstream warming of cold water sources will adversely affect downstream temperature requirements.

Available data for temperature requirements for growth and reproduction, lethal limits for various acclimation temperature levels, and various temperature-related characteristics of many of the more desirable freshwater fish species have been summarized (NAS/NAE, 1974; USEPA, 1975).

The foregoing rationale provides the basis for deriving water quality objectives to safeguard against adverse temperature conditions in the far-field (parts 1 and 2 of the objective), near-field (part 3 of the objective) and in-plant (part 4 of the objective), areas of effect (see NAS/NAE, 1974 for elaboration of the proposed objectives). In considering recommendations for resource protection, variability in habitat, biota, and history of the biota must be considered. It must be recognized, however, that the biotic resource may be perturbed not only by temperature; but also by physical stresses from pump action, high velocities and other mechanical stresses imposed during in-plant entrainment. Thus, siting and plant design, (in terms of intake placement and construction; pumping system, discharge mechanism) may in many cases minimize effect in terms of temperature and physical loss. Effects from altered temperature per se may also be lessened by improved design e.g. deflection of heated water offshore by deflectors which would lessen effect on sensitive nearshore organisms. Consequently, it must be recognized that although the proposed objective for temperature can be used to lessen effects from temperature, protection of biological integrity of Great Lakes systems could best be achieved through control of siting, plant design, plant operation and temperature alterations.

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CHEMICAL CHARACTERISTICS

DISSOLVED OXYGEN

NOTE TO THE WATER QUALITY BOARD

The Subcommittee voted their approval of the DO objective as recommended below. The Implementation Committee reviewed the rationale and did not feel there was sufficient justification for adoption of Part 1 of the recommendation. If the Board, following review of the rationale and its supporting documents (particularly Davis, 1974; Doudoroff and Shumway, 1970; and NAS/NAE, 1974), shares this viewpoint, the Subcommittee will withdraw the dissolved oxygen recommendation in its entirety and reconsider the matter. The existing objective is satisfactory pending further review.

RECOMMENDATION

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

1) *For the protection of aquatic life, dissolved oxygen concentration at any time or place should not be less than given by the formula:* *Dissolved Oxygen (mg/l)* $= 1.41M - 0.0476M^2 - 1.11$, *where M is the natural seasonal minimum concentration and is assumed to be saturation unless scientific data show that natural levels were less than saturation in the absence of man-made effects. (See Table 6 and Figure 3).*

2) *Notwithstanding the water quality objective in 1) above, dissolved oxygen should not be less than 6 milligrams per litre at any time or place.*

Table 6 PERMISSABLE DISSOLVED OXYGEN CONCENTRATIONS

(Derived from: $DO\ mg/l = 2.41 - 0.0476M^2 - 1.11$)

Natural Seasonal Minimum (M) dissolved oxygen (mg/l)	*Temperature (°C) at which M is 100% saturation*	*Permissible D.O. concentration for that value of M (mg/l)*	*% saturation*
8.0	25.9	7.1	89
9.0	19.0	7.7	86
10.0	13.9	8.2	82
11.0	9.7	8.6	79
12.0	6.2	9.0	75
13.0	3.1	9.2	71
14.0	0.4	9.3	66

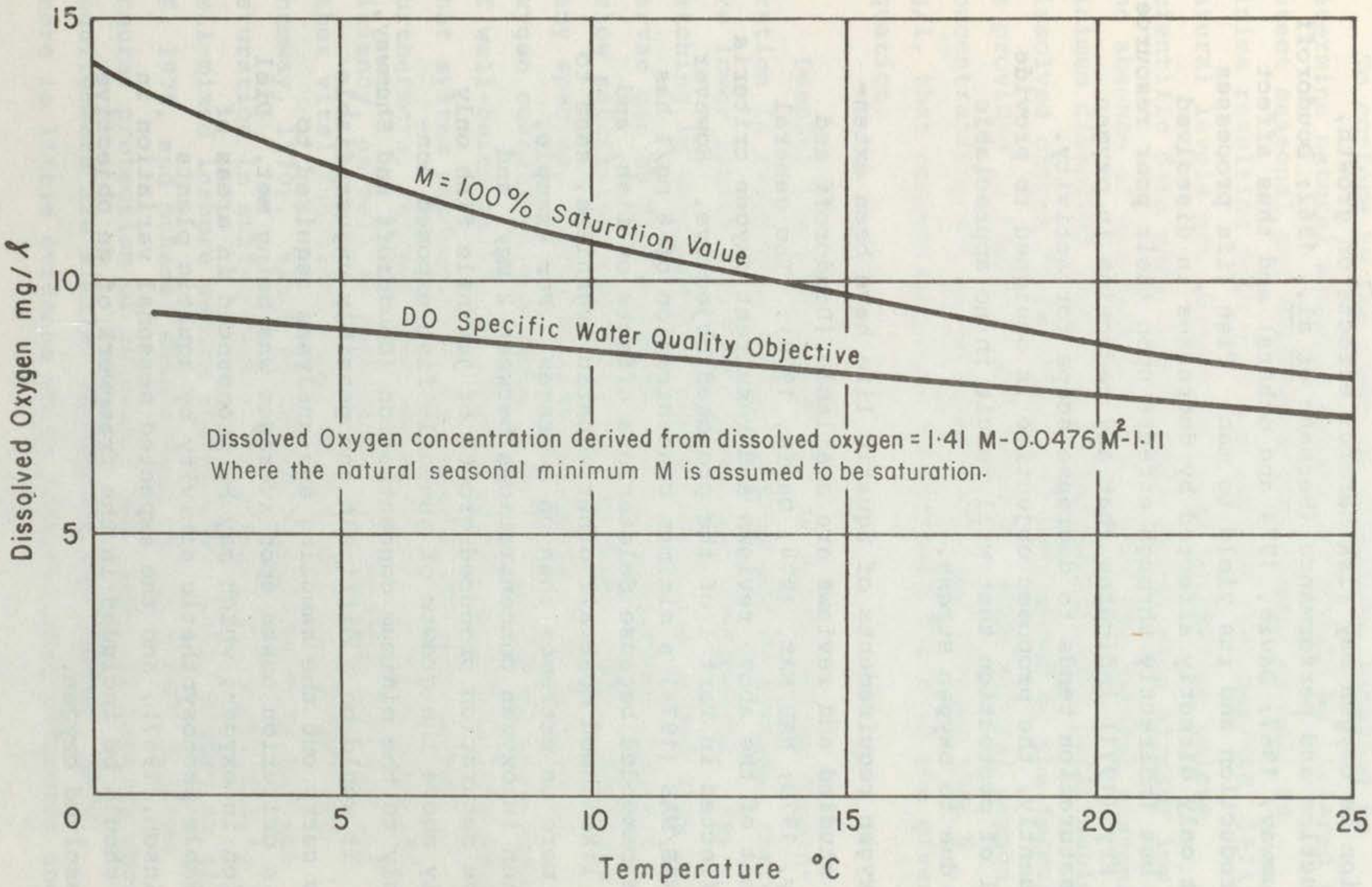
EXISTING OBJECTIVE

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

> "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 support of fishlife, particularly cold water species."

RATIONALE

No single absolute recommendation can be set for dissolved oxygen concentrations that is favourable for all aquatic species under all circumstances. Evidently, any



SPECIFIC WATER QUALITY OBJECTIVE AND SATURATION VALUE FOR DISSOLVED OXYGEN

Figure 3

reduction in oxygen may risk harmful effects on growth, reproduction and performance (Hermann et al., 1962; Doudoroff and Shumway, 1967; Davis, 1974 and others) and thus affect fish production and its yield to man. Fish life processes are not only directly affected by decreases in dissolved oxygen but indirectly through effects upon their poor resource base. Fry (1971) indicates that any reduction in oxygen below saturation tends to decrease scope for activity. Consequently, the proposed objective is designed to provide a level of protection that will result in no appreciable damage due to oxygen stress.

Oxygen requirements of aquatic life have been extensively studied and reviews are available (Doudoroff and Shumway, 1970; NAS/NAE, 1974; Davis, 1974). The general agreement of the above reviews and resultant oxygen criteria are reflected in Part 1 of the proposed objective. However as in NAS/NAE (1974) a minimum concentration of 6 mg/l has been recommended because deleterious effects on fish, and in all likelihood most all other aquatic organisms, seem to depend more on extremes than on averages. For example, variation in oxygen concentrations between 2 mg/l and at/above saturation produced growth of juvenile fish only slightly above the growth of juvenile fish exposed continuously to the minimum concentration (Doudoroff and Shumway, 1970). It would be a difficult and possibly unjustifiable task to carry out the sampling and analyses required to decide a criterion based upon averages was being met. Diel variation in oxygen, which may be pronounced in areas of appreciable photosynthetic activity by aquatic plants (Hutchinson, 1957), and the expected seasonal variation in minima should be included in the framework of an objective for dissolved oxygen.

To conform to the proposed objective, sampling to determine natural seasonal minima (m) should be tailored to detect seasonal and depth-relative changes as well as minima resulting from diel variability (see NAS/NAE, 1974). Natural levels are assumed to be at saturation unless scientific data show that natural levels were already low in the absence of man-made effects. When the natural seasonal minimum dissolved oxygen is at saturation, the permissable dissolved oxygen concentration as determined by the formula is provided in Figure 3 and Table 6. When natural oxygen concentrations are below saturation, but greater than 6 mg/l, that concentration is substituted for M in the given equation.

Despite the indication that no single oxygen concentration is favourable to all species and ecosystems, there are lower limits which are definitely detrimental. Fry hatching is considerably reduced below 5 mg/l and size of larvae can be decreased even at concentrations slightly below saturation (Doudoroff and Shumway, 1970). Although many species, including some salmonids, can survive at oxygen concentrations below 2 mg/l, significant impairment of well-being exists at lowered oxygen concentrations such that system productivity and success are threatened. Furthermore, reduced food consumption and conversion efficiency, as well as alteration in schooling ability and other vital functions occur at 5-6 mg/l (Doudoroff and Shumway, 1970). Since dissolved oxygen tends to be near saturation in surface waters in general and particularly in well-mixed inshore waters (Hutchinson, 1957; Kramer <u>et</u> al. MS, 1970, and others) maintenance of the 6 mg/l minimum ensures protection of coldwater and warmwater species whose requirements are similar (Doudoroff and Shumway, 1970). There is little evidence which suggests that warmwater and coldwater oxygen-sensitive fish species differ in their oxygen requirements and therefore the proposed objective should be protective of both.

Although extensive information describing oxygen requirements of aquatic invertebrates is unavailable, it is likely that protection of fish should ensure protection to other communities using that habitat. It does appear, however, that any reduction in oxygen concentration appears to affect benthic production as well as fish well-being (NAS/NAE, 1974). Since some important benthic invertebrates and eggs and early life processes of fish are noticeably sensitive to decreases in dissolved oxygen (Doudoroff and Shumway, 1970; NAS/NAE, 1974; Davis, 1974) the proposed objective must apply to the sediment/water interface as well as the water column normally used by fish.

Strong indications exist that decreases in hypolimnetic oxygen result in deterioration of coregonid and salmonid fisheries (Colby <u>et al</u>. 1972). Control of both nutrients and oxygen consuming wastes from sewage treatment plants have resulted in increases in hypolimnetic oxygen and subsequent increase in fish production (Numann, 1972). Inclusion of hypolimnetic waters in the proposed objective should protect against increase in areas affected by hypolimnetic oxygen deficits (F.E.J. Fry, personal communication) and will provide a means of measuring the success of remedial programs.

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CHEMICAL CHARACTERISTICS

pH

RECOMMENDATION

It is recommended that the following, revised objective for pH be adopted to replace the existing objective stipulated in Annex I 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 I, 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 processes 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 Quality 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 Considerations

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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CHEMICAL CHARACTERISTICS

PHOSPHORUS

RECOMMENDATION

It is recommended that the existing objective for Phosphorus, as stipulated in Annex 1, paragraph 1 (g) in the Water Quality Agreement be retained at this time. This objective states:

> "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."

COMMENTARY

The existing specific objective is in narrative form because the variable response of aquatic organisms dependent in part on phosphorus to produce nuisance conditions makes selection of a defensible single number very difficult. The Research Advisory Board Standing Committee on Eutrophication has considered the single number concept for all Great Lakes waters. They are considering a water body (or segment of) objective, but have not reached a conclusion.

At this Subcommittee's request they also considered chlorophyll a as an objective. No conclusion was reached on chlorophyll a nor on sulfate as a factor in eutrophication.

The Water Quality Objectives Subcommittee will request the Eutrophication Standing Committee to consider a procedural objective involving stimulation response criteria in local situations as an alternative.

CHEMICAL CHARACTERISTICS

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 taste 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 7 and 8). 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 threshold 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 ug/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.

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 lowered the palatability of fish flesh and concentrations of chemical compounds in water than can produce identifiable taste in fish flesh. (Tables 7 and 8).

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 non-detection 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.

TABLE 7

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	50-100ml/l	Trout	Shumway 1966
Coal-coking	0.02-0.1ml/l	Freshwater fish	Bandt 1955
Coaltar	0.1ml/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 and Hicks 1971
Municipal untreated sewage (2 locations)	....	Channel catfish	Thomas and Hicks 1971
Municipal waste-water treatment plants (4 locations)	....	Channel catfish	Thomas and Hicks 1971
Municipal waste-water treatment plant (Primary)	11-13% by vol.	Freshwater fish	Shumway and Palensky, unpublished data
Municipal waste-water treatment plant (Secondary)	20-26% by vol.	Freshwater fish	Shumway and Palensky, unpublished data

TABLE 7 Cont'd

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 and Hicks 1971

TABLE 8

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 8 Cont'd

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
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CHEMICAL CHARACTERISTICS

TOTAL DISSOLVED SOLIDS

RECOMMENDATION

It is recommended that the existing objective for Total Dissolved Solids stipulated in Annex 1, paragraph 1(c) of the Water Quality Agreement be retained. This objective states:

> "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."

RATIONALE

The existing objective for total dissolved solids (TDS) which is recommended for retention at this time, is based upon a philosophy of non-degradation, and does not comply with the Subcommittees' definition of a specific water quality objective as the level of a substance which will provide for and protect a designated water use. There is no scientific evidence to demonstrate that the specified numerical objectives will interfere with any designated water use.

A review of the scientific literature on the potential effects of TDS on a variety of water uses indicated that a numerical objective far in excess of existing TDS levels would result if a defensible objective were to be established. The Subcommittee was reluctant to pursue such a course, as it would mock the non-degradation philosophy, and provide an incorrect perspective to surveillance programs.

While existing levels of TDS in the Great Lakes do not directly threaten any use of the waters, routine monitoring of levels of TDS has traditionally proven to be valuable to surveillance programs to assess trends in water quality. For this reason, and to comply with the non-degradation provisions in the Water Quality Agreement, the existing objective is endorsed to encourage the continued use of TDS as a monitoring tool.

On the basis of a recent report on the relationship of TDS and conductivity in the Great Lakes, the Great Lakes Water Quality Board's Surveillance Subcommittee has recommended that the existing objective for TDS be replaced by an objective for conductivity. Using a standard conversion factor of 0.65, the numerical conductivity objective for the lower lakes would be 308 µmhos/cm. The Water Quality Objectives Subcommittee has no objection to the measurement of TDS by conductivity methods. However, it is anticipated that as the importance of individual components of TDS are identified, measurement of those individual components will be required.

The following commentary on TDS has been compiled and is presented here to provide an overview of the significance of TDS in the Great Lakes.

COMMENTARY

The existing objective in the Water Quality Agreement is consistent with that suggested in Chapter XII - "Remedial Measures" of a report on Pollution of Lake Erie, Lake Ontario and the International Section of the St. Lawrence River (International Joint Commission, 1969). The report (pg. 99) indicates that TDS levels of Lakes Erie and Ontario have increased from approximately 145 mg/l in 1910 to 185 mg/l in 1970. Furthermore, these lakes have experienced in that time frame a three fold increase in chlorides and a two fold increase in sulfates as well as sodium plus potassium. The report (IJC, 1969) also states that "the build-up of TDS is not in itself at this time, a serious problem but indicates large accumulations of materials."

Dissolved Solids and Aquatic Life

Hart et al (1945) has indicated that among the inland waters of the United States supporting a good mixed fish fauna, 95% have a dissolved solids concentration of under 400 mg/l. The main concern of TDS with respect to aquatic life is its effect on the ability of an organism to regulate the intake and elimination of water in such a manner so as to neither dilute nor concentrate its body fluids. In freshwater fish, the intake of water occurs through the mucous membranes of the gills, which act like a semi-permeable membrane. The dilution of body fluids of freshwater organisms is the result of osmosis. Nearly all freshwater and terrestrial plants, by virtue of their cellulose walls and active plasma membranes, maintain their cellular-fluid constituents, particularly their vacuolar sap, at concentrations higher than those of the fluids which bathe their tissues (Prosser and Brown, 1966). The cells are continually more concentrated than the tissue fluids and hence turgid.

The range of environmental osmotic conditions tolerated by animals is great, whereas the tolerated range of internal osmotic conditions is much less. Typical values of osmoconcentrations for the freshwater aquatic environment and animal cells, expressed in terms of degrees Celsius lowering of the freezing point of water, are given in Table 9 (Prosser and Brown, 1966).

Table 9 - TOTAL DISSOLVED SOLIDS: OSMOCONCENTRATIONS

Environment	AT°C	Animal	OT°C
Freshwater	-0.01	Mussel	-0.08
		Pelomyxa (a)	-0.14
		Fish	-0.05 to -0.55
		Frog	-0.45
		Crayfish	-0.82
		Earthworms	-0.3 to -0.4

(a) A large amoeboid protozoan

The concept of freezing point reduction is used primarily because of its applicability to the determination of the molecular weights of non-volatile dissolved substances in dilute solutions such as body fluids. 9A water solution of a uni-valent salt such as sodium chloride at a concentration of 0.1 molality (5800 mg/l) would cause a freezing point lowering of 0.35° C(b). Table 10 shows the equivalent body fluid concentrations, expressed as sodium chloride, for the above listed freshwater animals.

Table 10 - TOTAL DISSOLVED SOLIDS AS NaCl: BODY FLUID

Animal	mg/l	Milliosmoles
Mussel	1365	25
Pelomyxa	2388	41
Fish	8530-9380	147-162
Frog	7680	132
Crayfish	13.990	241
Earthworm	5118-6824	88-117

(b) For dilute solutions of an electrolyte the osmotic concentration exceeds the molal concentration by a factor slightly less than 2 for univalent salts, and slightly less than 3 for bi-valent salts based on activity co-efficients.

According to the report of the National Technical Advisory Committee (U.S. Dept. of the Interior, 1968) diatoms are extremely sensitive to changes in chlorides or other dissolved solids and a TDS limit of 50 milliosmoles for the protection of aquatic life is recommended.

In studies on the toxicity of brine waters from oil wells, Clemens and Jones (1954) found that the 96-hr median toxicity thresholds (equivalent to a 96-hr LC_{50}) of TDS to 10 varieties of fish to be as listed in Table 11.

Table 11 - TOTAL DISSOLVED SOLIDS: 96 HR. LC_{50} VALUES FOR FISH

Fish	TDS-mg/1	
Plains Killifish	23,000	
Gambusia	15,240	
White Crappie	12,570	
Bluegill	11,330	
Green Sunfish	11,330	Median 11,200
Channel Catfish	11,120	
Black Bullheads	10,300	
Red Shinner	10,506	
Largemouth Bass	9,476	
Fathead Minnows	8,858	

In addition, 96 hour median toxicity treshold of TDS for invertebrates based on dilution of brine waters, was reported to be as follows, Table 12, (Clemens and Jones, 1954):

Table 12 - TOTAL DISSOLVED SOLIDS: 96 HR. LC_{50} VALUES FOR INVERTEBRATES

Organism	TDS-mg/1
Cambarus	17,900

Libellulida	14,800	
Coenargrionidae	14,800	
Hexagenia	10,500	
Tubificidae	10,100	Median 8,950
Hyalella	7,830	
Baetidae	1,410	
Diaptomus	6,590	
Physa	6,400	
Daphnia	3,710	

A review of the above indicated a median value of 11,200 mg/l for fish and 8,950 mg/l for invertebrates. Since the major salt was calcium chloride, these values are equivalent to 101 and 81 milliosmoles respectively, as calcium chloride. These data in addition to that given in Table 2 TDS for body fluids tend to support the general belief that the toxicity of TDS to freshwater aquatic life is that level which has a osmoconcentration equal to that of the body fluids of the organism. It should be noted, however, that the osmoconcentrations of body fluids may differ for various species, as well as for life cycle, age, nutrition, and acclimation. The fact that fathead minnows did not spawn successfully in waters with a TDS level of 2,000 mg/l as observed by McCarthy and Thomas (1968) in Nebraska, tend to support this concept. The value given in Table 4 - TDS for Daphnia is equivalent to 33.4 milliosmoles or some what lower than the 50 milliosmoles value recommended in the report of the National Technical Advisory Committee (U.S. Dept. of the Interior, 1968).

In studies pertaining to the discharge of wastewaters from a soda ash manufacturer, the bioassay laboratory of Ohio EPA found the 96-hr LC$_{50}$ for fathead minnows to be approximately 8,800 mg/l, whereas that for Daphnia was approximately 4,500 mg/l. Based on current knowledge, the laboratory recommended a safety factor of 0.3 to 0.5 be applied to derive appropriate level for full life cycle protection of warm-water aquatic life in an inland stream.

In view of the foregoing and the relatively low levels of dissolved solids in the Great Lakes, it appears that there is no scientific basis for establishing an objective for TDS for the protection of aquatic life that is any way as low as existing or projected TDS levels.

Existing low level of dissolved solids in the Great Lakes limits their buffering capacity. In order to preserve this capacity there should be no significant change in the general chemical composition of the TDS levels.

Historical Trends: Their Value and Implications

Measurements of the TDS levels of the Great Lakes have been made along with their makeup in terms of major cation and anion by many investigators for nearly 100 years. This information has been collated by Beeton and Chandler (1963), Kramer (1964) and updated by Weiler and Chawala (1969). Kramer (1964) has shown that a significant portion of the present TDS levels of each of the lakes is the result of natural chemical equilibria between the water and the sediments. Lake Superior is considerably lower in dissolved solids and alkalinity because it lies outside of, or along the edge of a Paleozoic carbonate belt and its sediments have a lower concentration of carbonates. In contrast, the other four lakes lie entirely within this belt.

A review of the data presented by Kramer (1964) and Weiler and Chawala (1969) demonstrates that the TDS levels have significantly increased for Lakes Erie and Ontario since 1900, whereas only a moderate increase has taken place for lakes Michigan and Huron. In contrast, a slight decrease in TDS levels has taken place in Lake Superior.

Chlorides

By examining the trends for the chloride ion concentration it will be noted that the levels of the lower lakes have increased from 8 mg/l in 1900 for both lakes to nearly 25 mg/l for Erie, and about 28 mg/l for Ontario in 1970. During the same period a minimal increase has taken place in the other three lakes, ranging from zero for Lake Superior to 4 mg/l for Lakes Huron and Michigan.

Based on an average outflow of 196,000 cfs for Lake Erie, a 1 mg/l increase is equivalent to the addition of 1.06×10^6 lbs. per day. Thus the increase from 8 mg/l to 25 mg/l represents an addition of 18.1×10^6 lbs. per day or 9050 tons per day of chlorides as Cl. The daily addition of chlorides to Lake Erie by human wastes along with an indication of impact of this load to the total load may be estimated for 1970 as follows:

Per capita contribution of Cl = 0.0154 lbs/day
(Meridith et al, 1974)
Chloride load 11,000,000 x 0.0154 = 169,400 lbs/day
Per cent of total load 169,400/18,100,000 x 100 = 0.92%

The use of salt for deicing purposes and its impact on Lake Erie has been investigated by FWPCA (Annon, 1966), the Three Rivers Watershed District (the Cleveland and Akron Area) in 1969-70 (private communication), the State University of New York at Buffalo in 1972-73 (private communication) as well as Owenby and Kee (1964).

The FWPCA study indicated that in 1966, 3.12×10^6 lbs/day on an annual basis was used for deicing purposes in the Lake Erie Basin. During the winter of 1969-70, the Three Rivers Watershed District estimated 1.05×10^6 lbs/day of salt as chlorides were used on annual basis in an area with a population of 2.5 million persons. In the Greater Buffalo area which has a population of nearly 500,000, approximately 15,000 tons of salt as chloride was used for deicing purposes during the winters of 1971-72 and 1972-73. In summarizing the above, the per capita use of salt for deicing purposes expressed as chloride varied from 0.312 to 0.420 lbs/day with a weighter average of 0.336 lbs/day. Using this weighted average the estimated total chloride load to Lake Erie is 1.52 x 10^6 lbs/day on an annual (150 day) average.

Another significant source of chloride loads to Lake Erie is an Ohio Manufacturer of Soda Ash which discharges nearly 2,000 tons/day of chlorides in an approximately equal portions of sodium and calcium chloride. Several other manufacturers of Soda Ash located along the Detroit River plus other discharges contribute nearly 3,450 tons/day. Table 13 summarizes the chloride loads to Lake Erie.

Table 13 - CHLORIDE LOADINGS TO LAKE ERIE

Source	Tons/day	% Total
Upper lakes	2120	23.4
Human wastes	9	0.9
Deicing	760	8.4
Industrial	5450	60.2
Others	711	7.8

The foregoing percentages compare favorably with those of Owenby and Kee (1964).

Sulfates

Human wastes contribute nearly 2.6 g of sulfates per capita per day (Anon, 1975). Again based on the Lake Erie drainage basin population of 11 x 10^6 persons, the total load of sulfates from human wastes would amount to 28.6 x 10^6 grams per day or (28.6 x

10^3 kg/day or 62,900 lbs/day). Such a load would cause only an increase of 0.05 mg/l in the sulfate concentration in Lake Erie. This increase is minor compared with the long term increase of 11 mg/l as reported by Beeton and Chandler (1963). In appraising the long term increase for Lake Erie it should be noted that a very significant portion of this increase is the result of the 12 mg/l increase observed by Beeton and Chandler (1963) in Lake Michigan.

In summary it should be noted that the mole percent increase in chlorides in the Great Lakes is at the expense of the mole percentage of alkalinity. This increase is accompanied with a large mole percentage increase in sodium at the expense of the calcium ion.

Recognizing that the proposed water quality objectives may be adopted as standards by the regulatory jurisdictions, it is recommended that the objective for TDS not be translated into a standard but that it be retained as an objective, for use as a monitoring tool.

The Subcommittee plans to approach the design of defensible objectives for TDS in two ways:

1. Investigation of the influence of TDS on species composition of phytoplankton communities; and

2. Investigation of effects of individual components of TDS such as sulfate in eutrophication and chlorides and sodium in drinking water.

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RADIOACTIVITY

RECOMMENDATION

It is recommended that the existing objective for Radioactivity as stipulated in Annex 1, paragraph 1 (h) of the Water Quality Agreement be retained. This objective states:

> "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."

RATIONALE

Recognizing the need for a refined objective, according to Annex 1, paragraph 1 (h), the Parties agreed:

> "to consult within one year from the date of entry into force of the Agreement, for the purpose of considering ....refined objectives for radioactivity....considered in the light of the recommendations of the International Commission on Radiation Protection."

The Parties, at their meeting of January 29-30, 1973, in assessing the progress of implementing the Water Quality Agreement, agreed:

> "to establish a joint working group of experts to explore the possibilities for the objective for radioactivity..."

The Canadian and the U.S. Advisory Groups, thus formed, have defined the essential background upon which to base a refined objective, describing three possible bases:

health, nondegradation, and as low as practicable. The Advisory Groups are expected to agree upon a basis and present a refined objective for radioactivity during the latter half of 1975.

NON-DEGRADATION

RECOMMENDATION

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

> *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 or enhance the 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. 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 statement is 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. The supportive rationale for the recommendation is included in the section of this report dealing with Article III.

MIXING ZONES

RECOMMENDATION

The Subcommittee recommends no change in existing objective, acceptance of guidelines and conceptual framework, and initiation of a joint institution to develop a procedure within the framework to limit the effects of mixing zones so that protection of resources will be achieved on a waterbody-wide scale.

EXISTING OBJECTIVE

"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 sources."

COMMENTARY

Water quality objectives describe, in part, a minimum quality of water which will not only provide for but protect any designated use. However, establishment of water quality objectives alone may not ensure against future losses of the beneficial uses which the Parties desire to secure and protect. The objectives should be implemented in concert with limitations on the extent of mixing zones or zones of influence and localized areas as designated by the regulatory agencies. Therefore, to protect uses the Subcommittee predicted the recommended objectives on the basis that adoption of a scientifically-sound procedure will be achieved for limiting the biological effects of mixing zones not only locally, but on a waterbody-wide scale. A mechanism for limiting loss of beneficial uses through the allocation of biological value and guidelines for the designation of mixing zones compatible with that mechanism as presented in Chapter V and VI respectively.

LOCALIZED AREAS

Recognizing that certain waters of the Great Lakes will not meet water quality objectives as a result of land drainage, land use, certain natural phenomena or geographical location, the Water Quality Agreement exempts such "Localized Areas" from compliance with the objectives. Guidelines for the identification of Localized Areas in the Great Lakes have been prepared, and adopted by the Water Quality Board. Identification of the location and extent of Localized Areas in the Great Lakes by the appropriate jurisdictions is now in progress.

V A PROPOSED MECHANISM TO LIMIT LOSS OF BENEFICIAL USES THROUGH ALLOCATION OF BIOLOGICAL VALUE

Previous methods of establishing mixing zones have resulted in arbitrarily limiting mixing zone sizes (i.e. -- an area equivalent to a circle with a radius of 1000 feet) without a logical basis. The mechanism proposed below, on the other hand, limits loss of beneficial uses in the present and future through allocation of biological value. Thus, the size of a mixing zone is fixed by its impact on ecosystem function rather than by some predetermined arbitrary decision.

There is a finite limit to encroachment on areas of biological value such as fish spawning sites, nursery areas, food production areas and living space before ecosystem imbalance and ultimate collapse of population occur. To protect against imbalance and collapse, a mechanism to restrict the encroachment and subsequent loss of biological value is essential. Such a mechanism is provided by the framework outlined below. Implementation requires a high degree of international and interstate cooperation.

A. Agreement on the Biological and Other Uses to be Protected

The acceptable limits to loss of biological value will vary with the biota to be protected and the biological replacements potential of the waterbody or segment thereof. Restrictions or allowances established by one regulatory agency can impact the resource value in the portion of the waterbody governed by another. Therefore, agreement on uses to be protected is essential so that the purpose of limitations and management programs will be directed toward the same goal.

B. Identification of Important Species

Within each ecosystem there are many species which may be important for a variety of reasons: e.g. sport fishing; commercial fishing; as a food chain organism to support sport or commercial species; or for normal community function and ecosystem maintenance. Designing a mechanism to protect every species could be an infinite job. There are logical reasons to assume that the important species are identifiable and if the limitation mechanism is designed for their protection, then other species of lesser ecological importance will be protected and management objectives will be achieved.

At the lower trophic levels it may be impossible to select the important species and protection of the trophic level community may be necessary.

C. Selection of representative important species whose protection assures protection of the ecosystem to support the management objective.

Many of the important species have habits or life history requirements which are sufficiently similar that conditions assuring the natural completion of the life cycle of a representative species assure protection to the species with similar requirements.

D. Biological mapping of the waterbody, supported by chemical and physical mapping, to establish biotic zones of the important species or representative important species

Much of this information is available in published literature and unpublished information of various natural resource management agencies. However, it has not been assembled in such a manner that the location and areal extent of biotic zones are known for a waterbody. Such a map, or series of maps on a seasonal basis, would immediately identify areas important to ecosystem maintenance and also provide insight into availability of habitat which is limiting to management objectives by its scarcity.

This map can help dischargers and regulatory agencies select locations for, configurations of, and conditions within mixing zones which minimize loss of biological value. An example of site-selection aid occurred in the St. Clair River where a consultant for a power company demonstrated a great difference in the numbers of fish fry on opposite sides of the river.

E. Assignment of Numerical Value to the Biotic Zones

It is obvious that certain areas within a waterbody have higher biological value than others. To generalize, an acre of spawning ground has a higher biological value than an area of off-shore living area. The beach zone of a rocky protected bay may be very productive, but a sandy, wind-swept exposed beach zone may be very unproductive. The mouth of a spawning stream may be extremely valuable, but the current-swept, deep navigation channel of large rivers is probably of less value.

Recreational use of nearshore waters can also be included in assigning biological value.

In a well-known ecosystem, biological values could be assigned as:

Open water greater than 100 feet deep	1
Exposed sandy shores to 20 feet deep	2
Waters between 20-100 feet deep high in food production	3
Nursery areas	7
Protected rocky shores	5
Spawning grounds	10
Unique spawning ground	Infinite

It may be that mixing zones should not be permitted in unique spawning grounds and other areas of extreme biological value.

Common sense indicates that mixing zones should be located in the less valuable biotic zones, or biotic zones which are not limiting to productivity. Assignment of value encourages dischargers to locate in areas least likely to be damaged.

F. Selection of a Level of Protection for the Waterbody or Segment

The nature of the ecosystem and the management objectives are primary factors in determining the level of protection necessary. Fragile ecosystems with low productivity require a high level of protection; perhaps only one percent of biological value should be assigned to mixing zones. For ecosystems with high capactiy for regeneration and ability to withstand insults, a lower level of protection would be permissible; perhaps from 4 to 8 percent of the biological value could be assigned to mixing zones.

G. Calculation of Available Biological Value for Allocation

Once the level of protection is decided, biological values established, and areal extent of biotic zones known, the value available for allocation can be determined. While limitation is decided on loss of biological value, size is also related. For physical reasons, a large volume discharge should received a larger mixing zone than a low volume discharger. However, mixing zones should not be considered a substitute for adequate waste treatment or control of contaminants at their source, nor should their conditions of establishment encourage excessive use of water for dilution.

The permissible size depends on the availability of area within a biotic zone. The larger the zone and the lower its biotic value, the greater may be the size of the mixing zone. The acceptable size for a mixing zone depends also on the number of mixing zones in a waterbody or segment or biotic zone. The greater the number, the smaller each must be if the limit for allocation of biological value is not to be exceeded.

If a given discharger was allocated a biological value of x units, the size of mixing zone could be 1000 acres in a biotic zone of value 1, or 500 acres in a biotic zone of value 2, or 143 acres in a biotic zone of value 7, or zero in a biotic zone of infinite value.

H. Allocation to Present Dischargers and Reservation for Future Dischargers

By comparison of loss of biological value to existing mixing zones with the biological value available for allocation, the regulatory authority will learn either that there is a major reserve for future use, that the allocation has already been exceeded, or the situation rests somewhere in between. On the basis of this information the fraction of biological value to be allocated to present dischargers and that reserved for future discharges must be decided. In reaching a decision, available projections on future municipal-industrial growth can be evaluated to estimate the potential need for future mixing zones. The planned plant closures due to obsolescence, and the trend towards more efficient use of industrial waters and advances in waste treatment technology should be considered.

Plume Rose Concept

Under the fairly uniform conditions found in connecting channels of the Great Lakes, establishment of fixed points to designate mixing zones is relatively simple. Along shorelines where plume directions and configuration vary greatly with wind and current conditions, establishment of a biologically defensible boundary is more difficult. A semi-circle or rectangle may be appropriate. However, one purpose of establishing mixing zones is to limit their biological effect. Since specific water quality objectives are based on chronic effects of exposure, it is probable that a location impacted only briefly or occasionally by water quality slightly less than objectives will not have a measurable biological effect.

The vectors of wind, currents and discharge inertia produce plume behavior that can be mapped over time as a plume rose. Within a plume rose, mixing zone boundaries can be established which reflect the plume rose shape. Mathematical models to develop mixing zone boundaries based on presence of water quality below objectives 20% or more of the time may delineate the boundary of biological effect. If sufficent field measurements were made by the discharger and regulatory agency to verify the model, and changes did not occur in quality, quantity, or mode of discharge, there would be little need for regular field monitoring to determine if the discharger was in compliance with the mixing zone boundary.

Conclusions

Given the above information, a formula (USEPA, 1974) can be applied to provide scientifically-defensible mixing zone limitations on individual discharges and all discharges in combination on a waterbody or segment. The Subcommittee concludes that this framework of guidelines and concepts can produce a mechanism acceptable to the governments, industries, and people of the Parties to the Agreement which will protect and secure the beneficial uses of the waters of the Great Lakes. The Subcommittee recommends further study of this mechanism under the aegis of IJC for refinement and evaluation of the procedure for possible adoption in the future.

LITERATURE CITED

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VI MIXING ZONE GUIDELINES

In line with the charge from the Water Quality Board to propose non-numerical mixing zone guidelines which reflect good water management principles, the Subcommittee recommends the following concepts as guidelines.

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 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 such 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 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 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.