A REVIEW
OF THE
AQUATIC EFFECTS
OF METALS

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Ministry
of the
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J. Bishop, Director
Water Resources Branch

A REVIEW OF THE AQUATIC EFFECTS OF METALS 1987

Prepared for the Water Resources Branch
Ontario Ministry of the Environment

by

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PREFACE

The Ontario Ministry of the Environment's Water Quality Criteria Development Working Group is pleased to present the following report entitled "A Review of the Aquatic Effects of Metals".

This review, conducted by Dr. Dennis Trotter of Monenco Consultants Limited under the direction of Ministry staff, has two principal objectives:

1. To determine whether existing Provincial Water Quality Objectives (PWQO) for metals require revision based on recent research; and,

2. To review other metals to determine if sufficient information exists to develop PWQO's.

Provincial Water Quality Objectives are set to protect all forms of aquatic life and all aspects of the aquatic life cycle. Other factors such as bioaccumulation, the protection of recreational uses and aesthetics are also considered.

As well as laying out recommendations for water quality criteria, this report provides a thorough review of aquatic toxicological information; a discussion of physicochemical factors affecting toxicity; information on bioavailability, acclimation and accumulation; and, a listing of water quality objectives from other jurisdictions. The report, therefore, should be of general interest and use to water resource managers.

Normally, Ontario's water quality criteria development documents are subjected to international peer review. Since this report was not prepared to recommend any specific objective, it was not subjected to such review. However, a well recognized Canadian specialist in the aquatic toxicology of metals, Dr. J. B. Sprague, was engaged during the project to review the report for thoroughness and accuracy. His review (Appendix A) was most favourable.

The advice and guidance of Dr. Christine Neville of the Water Resources Branch and Mr. Prem Vijan of the Laboratory Services Branch, Ontario Ministry of the Environment were most helpful during the preparation of this report. Their participation is greatly appreciated.

We hope that the report is of some value to you and we would be most interested in any comments or suggestions that you might have.

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SUMMARY

BACKGROUND

In 1979, the Ontario Ministry of the Environment published its rationale for the establishment of the provincial water quality objectives (PWQOs) for eleven elements for the protection of aquatic organisms (MOE 1979). Generally, the scientific information referenced in this publication was published prior to 1977.Since that time additional information has become available concerning the toxicity, physicochemical factors affecting toxicity, bioavailability, tolerance and accumulation of these elements in aquatic organisms.

The objective of this report is to review the more recent information (i.e. 1977 and later) to determine if the existing PWQOs for these individual elements still offer protection to the aquatic organisms in the waters of Ontario.

In addition, the Ministry of the Environment selected eleven other elements as candidates for the establishment of new PWQOs. The readily available scientific literature concerning the aquatic toxicity, fate and effect of these elements in the aquatic environment is reviewed.

ONTARIO MINISTRY OF THE ENVIRONMENT OBJECTIVES AND RATIONALE

The mandate of the Water Resources Branch, Aquatic Biology Section is to ensure the protection of all forms of aquatic life and all aspects of their aquatic life cycles.

The PWQOs established in 1979 were specific numerical values which the Ministry of the Environment based on a variety of documented information including:

- sensitivity of reproduction in aquatic species;
- mortality, both acute and chronic;
- differences in water hardness; and
- previously established objectives from other agencies.

These objectives were derived using the best scientific evidence available at the time concerning acceptable levels of these metals in the aquatic environment.

The objectives and rationales of the Ontario Ministry of the Environment are compared to other provinces and countries.

EXISTING PROVINCIAL WATER QUALITY OBJECTIVES (PWQOs)

For each of the existing eleven PWQOs the following types of information are discussed:

- Aquatic toxicity: For each element, short-term (i.e. less than or equal to 96 hr) and long-term (i.e. greater than 96 hr) toxicity values (i.e. LC_{50}s, EC_{50}s, or other defined endpoints) are tabulated to give an indication of the range of information available and the lowest concentration causing an observed effect. Relative sensitivities of various groups (i.e. vertebrates, invertebrates, plants) to a particular element are sometimes apparent from this information.

- Physicochemical factors affecting toxicity: The known influence of other water quality parameters (e.g. water hardness, alkalinity, organic carbon, presence of chelators, temperature, pH, dissolved oxygen, etc.) on the toxicity of each element is briefly reviewed.

- Bioavailability, tolerance and accumulation: Aqueous forms of the elements are discussed in relation to their ability to (iv) enter aquatic organisms either

through gill or gastrointestinal surfaces. The ability of aquatic organisms to become acclimated to elevated levels of the individual elements is discussed along with the possible mechanisms for this increased tolerance. Available information concerning the degree to which each element accumulates in aquatic organisms and the known potential for transfer to higher trophic levels is briefly discussed.

- Other agency Water Quality Objectives: Water quality objectives, criteria or guidelines from other provinces, countries and international agencies for the protection of aquatic life are tabulated for comparison with Ontario's objective for each element.

- Other factors affecting PWQOs: Existing water quality objectives for other water uses (drinking water supplies, agricultural water supplies, recreation and aesthetics and industrial water supplies) as set by Environment Canada are described relative to the objective for the protection of aquatic life as defined by Ontario.

Based on the above information recommendations are made to either maintain the existing PWQO or revise the existing PWQO for each element. Table 1 summarizes the recommendations.

CANDIDATE ELEMENTS FOR PWQOs

For each of the candidate elements the following types of information is discussed:

- Aquatic toxicity: Readily available data on the aquatic toxicity of each candidate element is tabulated. Where possible, acute and chronic information is separated into two tables.

TABLE 1. Existing Provincial Water Quality Objectives for Metals and Recommendations.

Element	Objective	Recommendation
Be	11 µg/L for water hardness less than 75 ppm 1100 µg/L for water hardness greater than 75 ppm	Revise PWQO
Cd	0.2 µg/L	Revise PWQO
Cr	100 µg/L (total chromium)	Revise PWQO
Cu	5 µg/L	Maintain existing PWQO, but relate level(s) to water hardness
Fe	300 µg/L (total iron)	Maintain existing PWQO
Pb	5 µg/L for alkalinity of 0 to 20 ppm 10 µg/L for alkalinity of 20 to 40 ppm 20 µg/L for alkalinity of 40 to 80 ppm 25 µg/L for alkalinity of 80 ppm	Revise PWQO
Hg	0.2 µg/L as total Hg in filtered water 0.5 µg/g as total mercury in whole fish	Revise PWQO
Ni	25 µg/L	Maintain existing PWQO
Se	100 µg/L	Revise PWQO
Ag	0.1µg/L	Maintain existing PWQO
Zn	30 µg/L	Maintain existing PWQO but relate level(s) to water hardness.

- Fate and effect in the aquatic environment: Information relating to the forms of the candidate element in the aquatic environment, its fate and effects are briefly discussed.

Based on the above information, the sufficiency of data available for each element for the establishment of a PWQO is assessed and a recommendation is made.

A summary of these recommendations is given in Table 2.

TABLE 2. Candidate Elements for PWQO Establishment *and* Recommendations (for protection of aquatic life).

Element	Recommendation
Antimony	Do not establish PWQO; insufficient information.
Barium	Do not establish PWQO; insufficient information.
Boron	Do not establish PWQO; insufficient information.
Cesium	Do not establish PWQO for stable element; however, review existing drinking water PWQO for cesium-137 with regard to fish consumption.
Cobalt	Do not establish PWQO; insufficient information.
Manganese	Do not establish PWQO; insufficient information.
Molybdenum	Do not establish PWQO; insufficient information.
Strontium	Do not establish PWQO for stable element; however, review existing drinking water PWQO for strontium-90 with regard to fish consumption.
Thallium	Do not establish PWQO; insufficient information.
Tin	Establish preliminary or interim PWQO for organotins as a general class of compounds. Do not establish PWQO for inorganic tin; insufficient information.
Vanadium	Establish PWQO with the provision that future testing of invertebrates and plants may require revision of this PWQO.

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PART 1.0

INTRODUCTION

1.0 INTRODUCTION

The Province of Ontario has established a set of numerical and narrative criteria designed for the protection of recreation water uses (including aesthetics) and public health. These criteria are also designed for the protection of all forms of aquatic life and all aspects of their aquatic life cycles (Ontario Ministry of the Environment (MOE) 1979).

Since these criteria were developed and published in 1979 more information has become available in the published scientific literature concerning the fate and effects of metals in the aquatic environment. It is the purpose of this document to review this new information and determine if the Provincial Water Quality Objectives (PWQOs) for metals still ensure the "protection of all forms of aquatic life and all aspects of their aquatic life cycles" given the new information available.

The metals under review are:

Beryllium	Mercury
Cadmium	Nickel
Chromium	Selenium
Copper	Silver
Iron	Zinc
Lead	

The Ministry also realized that important information concerning the fate and effect of other elements not addressed by PWQOs has also become available within the last few years. A secondary purpose of this document is to review this information for the following elements:

Antimony	Molybdenum
Barium	Strontium
Boron	Thallium
Cesium	Tin
Cobalt	Vanadium
Manganese	

If sufficient information exists, recommendations will be made for their inclusion in the PWQOs. Otherwise, information requirements (toxicity studies, fate studies, etc.) will be briefly described to provide the necessary data for their inclusion in the PWQOs.

TERMINOLOGY

In the Aquatic Toxicity Review sections of Parts 3 and 4 of this document a decision was made to divide the available toxicity data into two categories:

- Acute: referring to the results of toxicity tests conducted for 96 hr or less; and

- Subacute and chronic: referring to the results of toxicity tests (or tests with some non-lethal end-point) conducted with sub-lethal concentrations for a time period greater than 96 hours.

This decision, although arbitrary, assisted in using the data tabulated in the USEPA ambient water quality criteria documents.

The use of the term "acute" (meaning fast or immediate) generally implies something on the order of 4 to 7 days. "Chronic" could be considered to be 10% of the organism lifetime or more.

The above terms are not to be confused with "lethal" and "sub-lethal" which are defined as:

- Lethal: causing death by direct action.

- Sub-lethal: below the concentration that directly causes death. Exposure to sub-lethal concentrations of a material produces non-lethal responses such as changes in behaviour, biochemical and/or physiological function and histology.

Generally, the two tables in the Aquatic Toxicity Review Sections of Part 3 give:

- LC_{5O}s (i.e. acute lethal responses) in the first table labelled with the section number followed by "-1".

- Subacute LC_{50}s, subacute, chronic and sub-lethal responses in the second table labelled with the section number followed by "-2".

The amount of toxicity data for the elements reviewed in Part 4 was very limited (except for vanadium) and usually of the sub-acute, chronic and sub-lethal types. This information was generally tabulated in one table (labelled "-1").

PART 2.0

REVIEW OF ONTARIO MINISTRY OF THE ENVIRONMENT OBJECTIVES AND RATIONALE

2.0 REVIEW OF ONTARIO MINISTRY OF THE ENVIRONMENT OBJECTIVES AND RATIONALE

To establish criteria for the protection of all forms of aquatic life and all aspects of their aquatic life cycles, the staff of the Ministry of the Environment (MOE) reviewed and compared water quality objectives, criteria and standards established by Canadian, American and other agencies. In addition, guidance toward specific numerical criteria was obtained from the published scientific literature and data. The majority of the PWQOs adopted and subsequently published were derived from the work of the Water Quality Objectives Subcommittee of the International Joint Commission and the U.S. Environmental Protection Agency.

The 1979 PWQOs for metals and the basis or rationale for the specific numerical value are given in Table 2.0-1. It can be observed from this table that a wide variety of information was used for establishing a specific PWQO. These rationales include:

- sensitivity of reproduction in aquatic species;
- mortality, both acute and chronic;
- differences in water hardness; and
- previously established objectives by other agencies.

These objectives were derived using the best scientific evidence concerning acceptable levels of these metals at the time.

TABLE 2.0-1. Existing Provincial Water Quality Objectives for Metals and Basis for Objective (for unfiltered raw water unless otherwise stated).

Element	Objective	Basis for Objective
Be	11 µg/L for water hardness less than 75 ppm	Application factor of 0.1 and 96 hr LC_{50} value for fathead minnows.
	1100 µg/L for water hardness greater than 75 ppm	Reported100-fold increases in acute fish toxicity in soft water over that in hard water.
Cd	0.2 µg/L	Extreme sensitivity of trout and zoo-plankton reproduction.
Cr	100 µg/L (total chromium)	Algal growth response and mortality of chinook salmon
Cu	5 µg/L	Sensitivity of *Gammarus pseudolimnaeus* young
Fe	300 µg/L (total iron)	Canada-U.S. Agreement on the Great Lakes for protection of raw potable water supplies and aquatic life.
Pb	5 µg/L for alkalinity of 0 to 20 ppm 10 µg/L for alkalinity of 20 to 40 ppm 20 µg/L for alkalinity of 40 to 80 ppm 25 µg/L for alkalinity of 80 ppm	IJC Objectives for total lead In Great Lakes
Hg	0.2 µg/L as total Hg in <u>filtered</u> water 0.5 µg/g as total mercury in whole fish	Hatchability of Zebra fish eggs; bi-concentration of organic mercury.
Ni	25 µg/L	Unclear, but apparently an application factor of 0.001and lowest 96 hr LC_{50} value for fathead minnows, or use of IJC recommendation.
Se	100 µg/L	Acute toxicity to Zebra fish and goldfish.
Ag	0.1 µg/L	Long-term chronic studies demonstrating no effect levels at 3 to 9 months and recommendations of "safe levels".
Zn	30 µg/L	Chronic tests in soft water demonstrating "safe concentration".

2.1 COMPARISON WITH OTHER OBJECTIVES AND RATIONALES

2.11 ALBERTA

The Province of Alberta has determined that the basis for the derivation of water quality objectives will be the minimum value of a pollutant which would allow the "most sensitive use" of each body of water. Although "maximum concentrations" are given for eight elements, the rationale or basis for these numbers is not given. Further, these numerical values represent a goal which should be achieved even though it is recognized that natural conditions within the province will make these goals unattainable in certain areas of the province.

2.12 SASKATCHEWAN

The multipurpose objectives of this province are based on the most sensitive use. The specific surface water quality objectives are intended to be a means by which administrative authorities can assess the quality of water and municipal and industrial wastewater effluents. It is recognized by the province that, in many instances, the natural quality of a lake or river will not meet these objectives. In these cases, the objectives simply do not apply. Eight metals are listed under "Toxic Chemicals" and a maximum concentration is given for each metal. There is, however, no information presented regarding the rationale behind these maximum concentrations.

2.13 BRITISH COLUMBIA

This province is unusual in that it has two sets of numerical values for establishing desirable water quality. The first are the water quality criteria. These apply province-wide and are derived from a critical review of current guidelines from other agencies and the scientific literature. The specific numerical values are then tailored to local conditions within the province in the form of water quality

objectives. British Columbia is, at the time of this writing, in the process of finalizing criteria for specific pollutants. Metals have not yet been addressed.

2.14 UNITED STATES

Like the Province of Ontario, the United States formulated criteria based on the best scientific evidence for the protection of all aquatic life and its uses. The earliest U.S. national criteria document (published in 1968) provided for the formulation of criteria that, if not exceeded, would protect aquatic life. Rationales for these criteria were:

- use-specific and site-specific considerations;
- use of application factors and bioassay data;
- use of a maximum allowable concentration and a 24-hour average concentration;
- a standardized testing or bioassay method; and
- the use of a group or cluster of species for criteria derivation.

Subsequent revisions of these criteria lead to the incorporation of other toxic end points such as bioaccumulation factors and embryo mortality for deriving criteria.

In 1980, the basic objective of protecting all aquatic species at all times was rejected. Because aquatic ecosystems can tolerate some stress and occasional adverse effects, it was not deemed necessary to protect all species all the time to provide overall protection to the aquatic community. If acceptable data are available for a large number of appropriate taxa from an appropriate variety of taxonomic and functional groups, a reasonable level of protection will probably be provided if all except a small fraction of the taxa are protected, unless a commercially or recreationally-important species is very sensitive.

2.15 EUROPEAN INLAND FISHERIES ADVISORY COMMISSION (EIFAC)

The EIFAC is an intergovernmental organization with a current membership of 24 countries. The commission is responsible for the establishment of water quality criteria for European freshwater fish. This is accomplished by a critical examination of the literature (and where necessary experimentation to resolve contradictions and fill in gaps of knowledge) followed by recommendations as to desirable requirements for various aquatic organisms or groups of aquatic organisms with respect to the various qualities of water. The final criteria (as determined by the EIFAC Working Party on Water Quality) are then published and given wide distribution.

The criteria derived for specific metals are based upon:

- direct lethal action on fish;
- sub-lethal effects on fish;
- field observations on fish;
- the effects of specific metals on algae and invertebrates; and
- antagonistic, synergistic and additive actions of other dissolved substances.

The recommendations are published as EIFAC Technical Papers.

PART 3.0

EXISTING PROVINCIAL WATER QUALITY OBJECTIVES (PWQOs)

3.0 EXISTING PROVINCIAL WATER QUALITY OBJECTIVES (PWQOs)

In the following sections of this report, the existing PWQOs are reviewed for:

Beryllium	Mercury
Cadmium	Nickel
Chromium	Selenium
Copper	Zinc, and
Iron	Silver
Lead	

The major emphasis of this review concerned data published since 1980 (inclusive). Ambient water quality criteria documents for cadmium, chromium, copper, lead and mercury were published by the United States Environmental Protection Agency (USEPA) in January 1985 and are used as the starting point for the review of those metals. With the exception of iron, the remaining elements were last reviewed by the USEPA in 1980.Although somewhat outdated, these form the basis for the review of these metals with as much 1980-1985 data incorporated as time allows.

Technical reports, produced by the Water Research Centre in Stevenage, England (August 1984) addressing proposed environmental standards for chromium, copper, lead, nickel and zinc are also extensively used in reviewing these metals. Exposure and risk assessment reports for silver, nickel and zinc published by the USEPA (USEPA 1981, Little 1980, 1981) contain information on the aquatic environment and were also used in this review.

Computerized literature searches with the key words of "aquatic", "water", "toxicity" and the specific element were conducted and used to ascertain as much recent data as possible.

The toxicity data extracted from the USEPA 1985 Ambient Water Quality Criteria publications and presented in tables in each of the following sections had previously been screened so that data were not used if:

- tests were conducted with species not resident to North America;
- species were too atypical to be used in deriving national criteria;
- the element under review was a component of a mixture;
- results were only presented graphically;
- organisms were not exposed to cadmium in water;
- there was no pertinent adverse effect;
- materials, methods or results were insufficiently described;
- high mortalities occurred in all except one test;
- reproductive interactions made data questionable;
- organisms were not tested in the same water in which they were reared;
- the acceptability of the test water was questionable; or
- inappropriate test conditions or test organism treatments were used.

Any additional data used in the report was screened according to the MOE guidelines for toxicity data used in criteria development.

The review of information for each metal is not exhaustive due to the time constraints. The amount of information presented in each of the various subsections is a direct reflection of the information readily available. Some metals have had more attention (in terms of aquatic toxicity) focused on them than others. As a result the depth of information presented will vary from metal to metal.

3.1 BERYLLIUM

3.11 AQUATIC TOXICITY REVIEW

Table 3.1-1 presents selected acute toxicity data (i.e. less than or equal to 96 hr) from the USEPA (1980a) Ambient Water Quality Criteria Document (for beryllium) and later (i.e. 1980 1984) toxicity data from the published and unpublished literature. There is a relatively small amount of aquatic toxicity data available for beryllium. As the latest reference used by the MOE rationale document (MOE 1979) was 1975, it was decided to use aquatic toxicity data (cited by the USEPA) published as far back as 1976 for this section. A cross-check of these *references* showed that the 1976 and later data was not used in the 1979 MOE rationale document (MOE 1979). Acutely toxic values for 50% of the vertebrate test populations range from between 80 and 200 µg/L to greater than 5,090 µg/L. Acute invertebrate toxicity data is limited to two LC_{50}'s of 7,900 and 18,000 µg/L.

Table 3.1-2 presents selected chronic toxicity data from the USEPA (1980a) Ambient Water Quality Criteria Document (for beryllium) and Birge *et al.* 1979.For the reasons stated above, information published as early as 1976 and cited by USEPA (1980a) was used in Table 3.1-2. The lowest value in Table 3.1-2 (7.0 µg/L) is below the Ontario PWQO for water of hardness less than 75 ppm (i.e. 11 µg/L).

Available data indicates large differences between acute and chronic toxicity for this element.

The very limited data describing the effects of beryllium on freshwater plants *seem* to indicate that these organisms are less sensitive to beryllium than aquatic animals and will be protected by objectives designed to protect the latter group.

TABLE 3.1-1. Selected Acute (i.e. less than or equal to 96 hr) Lethality Data for Waterborne Beryllium.

Species	Method	Results In ppb	Test Water	Reference
VERTEBRATES				
Carassius auratus Goldfish	LC_{50}, FT, M	4,800	Hardness:147	USEPA 1980e
Pimephales promelas Fathead minnow	LC_{50}, FT, M	3,250	Hardness:140	As above
Jordanella floridae Hagfish	LC_{50},FT, M	4,440	Hardness:140	As above
As above	LC_{50}, FT, M	3,530	Hardness:140	As above
As above	LC_{50}, FT, M	3,530	Hardness:140	As above
Salvelinus fontinalis Brook trout	LC_{50}, FT, M	GT 5,090	Hardness:140	As above
Ictalurus punctatus Channel catfish	LC_{50}, FT, M	GT 5,090	Hardness:140	As above
Cyprinus carpio Common carp (embryos)	LC_{50}, R, M	GT 80, LT 200	Spring water (soft)	Hildebrand and Cushman 1978
INVERTEBRATES				
Daphnia magna Cladoceran	LC_{50}, S, U	7,900	Hardness:180	USEPA 1980a
As above	LC_{50}, S, U	18,000		As above

LT = Less Than
GT = Greater Than
S = static test
R = static test with renewal
FT = flow through test
M = concentrations of metal measured during test
U = concentrations of metal not measured during tests

TABLE 3.1-2. Effects of Subacute and Chronic (i.e. greater than 96 hr) Exposures to Waterborne Beryllium.

Species	Duration of Test	Exposure Concentration (ppb)	Result	Reference
VERTEBRATES				
Carassius auratus Goldfish	240 hr	3,300	Lethal to 50% of test population	USEPA 1980a
As above	3 days	GT 200	No hatching of eggs	As above
Pimephales promelas Fathead minnow	336 hr	2,200	Lethal to 50% of test population	As above
Salmo gairdneri Rainbow trout (Embryos, Larvae)	28 days	380	Lethal to 50% of test population	Birge *et al.* 1979
As above	28 days	42.0	Lethal to 10% of test population	As above
As above	28 days	7.0	Lethal to 1% of test population	As above

3.12 PHYSICO-CHEMICAL FACTORS AFFECTING TOXICITY

Hardness is known to influence beryllium toxicity with the element being more acutely toxic in soft water. Whether this antagonism is due to the calcium and magnesium ions' contribution to hardness or to the associated anions (i.e. HCO_3^- and CO_3^{-2}) is unknown. This will be discussed further in Section 3.13 below. Little, if any, information seems to be available on the effects of other water quality parameters on beryllium toxicity in the aquatic environment. The chemical properties of beryllium are similar to those of aluminum, zinc and manganese (USEPA 1984b). Thus physicochemical factors affecting the toxicity of zinc (Section 3.11 of this document) may influence the toxicity of beryllium.

The pH of the aqueous solution containing beryllium causes the hydrated complex to behave like a cation (at acidic pHs) or an anion (at pHs greater than 8) (USEPA 1980a).

3.13 BIOAVAILABILITY, ACCLIMATION AND ACCUMULATION

.1 Bioavailability

In aqueous solutions, beryllium does not exist as the divalent Be^{+2} ion, but rather as hydrated complexes. As a hydroxide, beryllium is limited in solubility to a maximum of 2,000 µg/L. Other common beryllium compounds (e.g. sulphate, chloride) are readily soluble; however, pH will determine whether the hydrated complex behaves as cation or anion.

Two possibilities appear to exist in terms of bioavailability and water hardness. As the amount of calcium and magnesium increases in the water, competitive inhibition between those cations and the cationic beryllium complex may cause a change in bio-availability. Similarly, at pHs of approximately eight and above, the anionic beryllium complex could be altered in its bioavailability by the presence of bicarbonate, carbonate and hydroxide ion.

There seems to be few, well-documented investigations concerning the bioavailability of beryllium to aquatic organisms. Although health assessment documents prepared by the USEPA Environmental Criteria and Assessment Office normally contain information on the aquatic environment, the draft Health Assessment Document for Beryllium (USEPA 1984a) did not deal with the aquatic environment.

.2 Acclimation

Information relating to the tolerance of beryllium by terrestrial or aquatic organism was not found. Certain beryllium compounds have been shown to be carcinogenic in various experimental animals under differing routes of exposure.

.3 Accumulation

Available information on accumulation indicates that the bioconcentration of beryllium from water by fish is on the order of 20X. Body burden half-life may be as short as one day. Mammalian studies indicate the liver and skeleton to be major sites of beryllium accumulation (USEPA 1984a).

3.14 OTHER AGENCY WATER QUALITY OBJECTIVES

Table 3-1.1 is a comparison of water quality objectives or criteria as established by other agencies. Only Ontario and the USEPA considered the presence of beryllium in water to be of sufficient concern to establish limits on its presence.

Ontario's 1100 µg/L objective (for hard water) is based on the 96 hr LC_{50} value for fathead minnows and the use of a 0.1 application factor. The 100-fold decrease in the objective for soft water (i.e. 11 µg/L) is based on a report of a 100-fold increase in the acute toxicity of beryllium in soft water (MOE 1979).

TABLE 3.1-3 Comparison of Beryllium Water Quality Objectives from Ontario and Other Agencies (for the Protection of Aquatic Life).

Agency	Objective or Criterion
Ontario (1979)	11 µg/L at hardness less than 75 ppm 1100 µg/L at hardness greater then 75 ppm
US EPA	
On an acute basis On a chronic basis (1980)	130 µg/ 5.3 µg/L
Manitoba (1983 Provisional)	No objective
Quebec (1984)	No objective
Alberta (1977)	No objective
Saskatchewan (1983)	No objective
Environment Canada (1979)	No objective
International Joint Commission	No objective

The USEPA (1980a) criteria are based on observed acute and chronic toxicity reactions at 130 and 5.3 µg/L, respectively. USEPA admits in their criteria rationale that acute and chronic toxic reactions will also occur at levels lower than the stated criteria (i.e. 130 and 5.3 µg/L) among species more sensitive than those tested (i.e. fathead minnow, guppy, bluegill, cladoceran). However, these "more sensitive" species are not defined.

The lack of criteria or objectives in other provinces can generally be ascribed to a level of concern appropriate to the potential for input of beryllium compounds to surface waters regulated by that agency or a lack of understanding of this potential.

3.15 OTHER FACTORS AFFECTING PWQOs

Objectives have not been established by Environment Canada for beryllium in;

- Raw public water supplies;
- Agricultural water (i.e. livestock watering and irrigation);
- Recreational water; and
- Industrial water supplies.

In 1980 the USEPA determined that a beryllium concentration of "zero" in water was preferable for the protection of human health. It was determined that a lifetime cancer risk of 1 in100,000 results from exposure to a concentration of 0.037 µg/L (Sittig 1985).

Animal studies have demonstrated that dietary beryllium intake levels of 5-500 ppm do not produce toxic effects. If insoluble beryllium particles (ores, compounds, etc.) are ingested, the majority of beryllium passes through the gastrointestinal tract unadsorbed. Soluble beryllium salts are available for absorption in the stomach

depending on the availability of acid gastric secretions. However, stomach absorption is small in mammals (USEPA1984a).

At levels of 0.6-6.6 µg/day intake in the drinking water of rats, over 80% of the beryllium passed the gastrointestinal tract unadsorbed. Upon entering the alkaline environment of the intestine, the beryllium became precipitated (probably as a phosphate) and was excreted in the feces (USEPA 1984a).

3.16 STATUS OF EXISTING PWQO

The work of Birge *et al.* (1979) found lethal effects in the test populations of fish at beryllium concentrations of 380, 42 and 7 µg/L (reported in Table 3.1-2). These long-term exposures (28 days) of rainbow trout embryos and larvae occurred at water hardnesses of 92-100 ppm. Under the Ontario PWQO for water of hardness greater than 75 ppm (i.e. 1100 µg/L), the aforementioned lethal concentrations of beryllium would be permissible.

Although there seems to be very little other data available since 1980 concerning beryllium toxicity in the aquatic environment, it is recommended that the Ontario PWQO for beryllium be revised. Given the lack of data, it is also recommended that additional laboratory studies be conducted on beryllium under conditions of temperature and hardness, which reflect the known variations of these water quality parameters within the Province of Ontario.

3.2 CADMIUM

3.21 AQUATIC TOXICITY REVIEW

Table 3.2-1 presents selected acute toxicity data (i.e. less than or equal to 96 hr) from the USEPA (1985a) Ambient Water Quality Criteria Document (for cadmium) for the years 1980-1984. The USEPA survey of toxicity data was conducted in May 1984. Acutely toxic values for 5O% of the vertebrate test populations range from 1.1 to 12,100 µg/L. For invertebrates the range is 30 to 2,130 µg/L.

Table 3.2-2 presents selected (i.e. 1980 and later) data from the USEPA (1985a) report concerning long-term effects of exposure to low levels of cadmium. Two studies have demonstrated that a concentration of 0.2 µg/L (the PWQO) caused reduced survival in a cladoceran (exposed for 20 days) and rainbow trout (exposed for 18 months). With the exception of these two studies, the remaining concentrations are well above the PWQO of 0.2 µg/L.

Of the 44 genera (vertebrate and invertebrate) for which cadmium toxicity data are available in the 1985 report, the genus *Salmo* (i.e. trout) is the most sensitive. This agrees with the MOE rationale of basing the permissible level of cadmium in water on trout reproduction. In addition, the PWQO for cadmium of 0.2 µg/L is 5.5 times lower than the 96 hr LC_{50} of 1.1 µg/L for juvenile chinook salmon (*Oncorhynchus tshawytscha*).

The available data for aquatic plants show this group to be much less sensitive to aquatic cadmium with adequate protection derived from animal toxicity data.

TABLE 3.2-1. Selected Acute (i.e. less than or equal to 96 hr) Lethality Data for Waterborne Cadmium (from USEPA 1985a).

Species	Method	Results In ppb	Test Water
VERTEBRATES			
Oncorhynchus tshawytscha Chinook salmon (Juvenile)	LC_{50}, FT, M	1.41	Hardness: 25 ppm
As above	LC_{50}, FT, M	1.1	Hardness: 20-22 ppm
Salmo gairdneri Rainbow trout	LC_{50}, S, U	6.0	
As above	LC_{50}, S, M	10.2	Hardness: 55-79 ppm
As above	LC_{50}, S, N	2.3	Hardness: 39-48 ppm
Salmo trutta Brown trout	LC_{50}, S, M	15.1	Hardness: 55-79 ppm
As above	LC_{50}, S, M	1.4	Hardness: 39-48 ppm
Salvelinus fontinalis Brook trout	LC_{50}, FT, M	5,080	Hardness: 47.4 ppm
Pimephales promelas Fathead minnow (Fry)	LC_{50}, S, M	21.5	Hardness: 40 ppm
As above	LC_{50}, S, M	11.7	Hardness: 48 ppm
As above	LC_{50}, S, M	19.3	Hardness: 39 ppm
As above	LC_{50}, S, M	42.4	Hardness: 45 ppm
As above	LC_{50}, S, M	54.2	Hardness: 47 ppm
As above	LC_{50}, S, M	29.0	Hardness: 44 ppm
Pimephales promelas Fathead minnow (Adult)	LC_{50}, S, M	3,060	Hardness: 103 ppm
As above	LC_{50}, S, M	2,900	Hardness: 103 ppm
As above	LC_{50}, S, M	3,100	Hardness: 103 ppm

TABLE 3.2-1 (Cont'd)

Species	Method	Results in ppb	Test Water
VERTEBRATES (Cont'd)			
As above	LC_{50}, S, M	7,160	Hardness: 254-271 ppm
As above	LC_{50}, S, M	3.390	Hardness: 55-79 ppm
As above	LC_{50}, S, M	1,280	Hardness: 39-48 ppm
As above	LC_{50}, FT, M	1,830	Hardness: 55-79 ppm
Ptychochellus oregonensis Northern squawfish	LC_{50}, FT, M	1,092	Hardness: 20-30 ppm
As above	LC_{50}, FT, M	1,104	Hardness: 20-30 ppm
Catostomus commersoni White sucker	LC_{50}, FT, M	1,110	Hardness: 18 ppm
Ictalurus punctatus Channel catfish	LC_{50}, S, M	7,940	Hardness: 55-79 ppm
Lepomis macrochirus Bluegill	LC_{50}, FT, M	21,100	Hardness: 207 ppm
As above	LC_{50}, S, M	3,860	Hardness: 16 ppm
As above	LC_{50}, S, M	2,800	Hardness: 18 ppm
As above	LC_{50}, S, M	2,260	Hardness: 18 ppm
As above	LC_{50}, S, M	8,810	Hardness: 55-79 ppm
INVERTEBRATES			
Branchiura sowerbyi Tubificid oligochaete	LC_{50}, S, M	240	Hardness: 5.3 ppm
Limnodrilus hoffmeisteri Tubificid oligochaete	LC_{50}, S, M	170	Hardness: 5.3 ppm
Quistadrilus multisetasus Tubificid oligochaete	LC_{50}, S, M	320	Hardness: 5.3 ppm
Rhyacodrllus montana Tubificid oligochaete	LC_{50}, S, M	630	Hardness: 5.3 ppm

TABLE 3.2-1 (Cont'd)

Species	Method	Results In ppb	Test Water
INVERTEBRATES (Cont'd)			
Branchiura sowerbyi Tubificid oligochaete	LC_{50}, S, M	240	Hardness: 5.3 ppm
Limnodrilus hoffmeisteri Tubificid oligochaete	LC_{50}, S, M	170	Hardness: 5.3 ppm
Quistedrilus multisetasus Tubificid oligochaete	LC_{50}, S, M	320	Hardness: 5.3 ppm
Rhyacodrilus montana Tubificid oligochaete	LC_{50}, S, M	630	Hardness: 5.3 ppm
Spirosperma ferox Tubificid oligochaete	LC_{50}, S, M	350	Hardness: 5.3 ppm
Spirosperma nikoiskyi Tubificid oligochaete	LC_{50}, S, M	450	Hardness: 5.3 ppm
Stylodrilus heringianus Tubificid oligochaete	LC_{50}, S, M	550	Hardness: 5.3 ppm
Tubifex tubifex Tubificid oligochaete	LC_{50}, S, M	320	Hardness: 5.3 ppm
Varichaeta pacifica Tubificid oligochaete	LC_{50}, S, M	380	Hardness: 5.3 ppm
Aplexa hypnorum Snail	LC_{50}, FT, M	93	Hardness: 45.3 ppm
Daphnia magna Cladoceran	LC_{50}, S, M	66	Hardness: 45 ppm
Cerlodaphnia reticulate Cladoceran	LC_{50}, S, M	129	Hardness: 55-79 ppm
Daphnia papa Cladoceran	LC_{50}, FT, M	58	Hardness: 130 ppm
As above	LC_{50}, R, M	30	Hardness: 100 ppm
As above	LC_{50}, S, M	166	Hardness: 55-79 ppm
As above	LC_{50}, S, M	118	Hardness: 45 ppm

TABLE 3.2-1 (Cont'd)

Species	Method	Results In ppb	Test Water
INVERTEBRATES (Cont'd)			
As above	LC_{50}, S, M	68	Hardness: 45 ppm
Simocephalus serrulatus Cladoceran	LC_{50}, S, M	123	Hardness: 55-79 ppm
As above	LC_{50}, S, M	24.5	Hardness: 39-48 ppm
Simacephalus vetulus Cladoceran	LC_{50}, S, U	24	Hardness: 45 ppm
As above	LC_{50}, S, M	98.3	Hardness: 55-79 ppm
Asellus bicrenata isopod	LC_{50}, FT, M	2,130	Hardness: 220 ppm
Lirceus alabamae isopod	LC_{50}, FT, M	150	Hardness: 152 ppm
Gammarus oseydikunaeys amphipod	LC_{50}, S, M	54.4	Hardness: 55-79 ppm
As above	LC_{50}, S, M	68.3	Hardness: 39-48 ppm
Hyalella azteca Amphipod	LC_{50}, S, M	285	Hardness: 55-79 ppm
Paraleptophlebia praepedita Mayfly	LC_{50}, S, M	449	Hardness: 55-79 ppm
Pectinatella magnifica Bryozoan	LC_{50}, S, U	700	Hardness: 190-220 ppm
Lophopodella carteri Bryozoan	LC_{50}, S, M	150	Hardness: 190-220 ppm
Plumetella emarginata Bryozoen	LC_{50}, S, U	1,090	Hardness: 190-220 ppm

S = static test
FT = flow through test
R = static test with replacement of test solutions
M = concentrations of metal measured during test
U = concentrations of metal not measured during test

TABLE 3.2-2. Effects of Subacute and Chronic (i.e. greater then 96 hr) Exposures to Waterborne Cadmium (from USEPA 1985e unless otherwise noted).

Species	Duration of Test	Exposure Concentration (ppb)	Result
VERTEBRATES			
Salmo gairdneri Rainbow trout	18 months	0.2	Reduced survival
As above (Embryo and larvae)	28 days	140	Death and deformity of 50% of test population
As above (Fingerlings)	4 months	10	Physiological effects
As above	47 days	100	Reduced growth and survival
As above (Embryo, larvae)	62 days	less than 5	Reduced survival
As above (Larvae)	7 days	700	Lethal to 50% of test population
As above	11days	16.0	Lethal to 50% of population at 10°C
As above	178 days	3.6-6.4	Physiological effects
Salmo salar Atlantic salmon	70 days	2	Reduced growth
Pimephales promelas Fathead minnow	7 days	200	Lethal to 50% of test population
Salmo salar Atlantic salmon	92 days	78	Inhibition of skeletal calcification (Rombough and Gerside1984)
Salmo gairdneri Rainbow trout	4 weeks	10	Changes in gill morphology (Karlsson-Norrgren *et al.* 1985)
As above (Eggs to swim-up fry)	27 days	10	increased mortality of eggs, alevins and swim-up fry (Woodworth and Pascoe 1982)

TABLE 3.2-2 (Cont'd)

Species	Duration of Test	Exposure Concentration (ppb)	Result
INVERTEBRATES			
Hydra littoralis Hydra	12 days	20	Reduced growth
Daphnia pulex Cladoceran	21 days	5-10	Maximum acceptable toxicant concentration
Molina macrocopa Cladoceran	20 days	0.2	Reduced survival
Tanytarsus dissimilis Midge	10 days	3.8	Lethal for 50% of the test population
PLANTS			
Plankton	2 weeks	1-3	Reduced abundance of crustacea, zooplankton, and rotifers
Elodea canadensis Vascular plant	28 days	148,000	Phytotoxic to 50% of plants (Brown and Rattigan1979)
Lemna minor Vascular plant	28 days	14,888	As above

3.22 PHYSICO-CHEMICAL FACTORS AFFECTING TOXICITY

It has been recognized for years that water hardness has an antagonistic effect on cadmium toxicity. From the most recent literature regarding this phenomenon (e.g. Wright 1980; Wright *et al.* 1985; Calamari *et al.* 1980), it is apparent that calcium is the main cause of this antagonism. Cadmium is hypothesized to interfere with calcium metabolism by competitive inhibitory processes. Magnesium, the second major ion contributing to water hardness, does not reduce cadmium toxicity with the same effectiveness as calcium.

Recent evidence (i.e. Howell 1985) also points toward zinc as an antagonistic agent in cadmium toxicity.

While dissolved organics generally reduce cadmium toxicity, the uptake of an organic cadmium complex is extremely dependant on the exact type of complexing organic (Part and Wikmark 1984).

Other factors potentially affecting toxicity are:

- physiological stress (e.g. increased toxicity with the advent of parasitism, bacterial infections, etc.);
- temperature (increased toxicity with increased temperature);
- dissolved oxygen (a potential for increasing toxicity at lower dissolved oxygen levels); and
- pH (conflicting data in the literature as to effect, but generally increasing pH is thought to increase toxicity in acute tests (Dave 1985)).

3.23 BIOAVAILABILITY, ACCLIMATION AND ACCUMULATION

.1 Bioavailability

The extent to which a lower uptake of cadmium is attributable to reduced bioavailability of the metal (due to its chemical speciation or to biological factors affecting the epithelial permeability) is not fully understood (Part *et al.* 1985).

Cadmium uptake in freshwater fish occurs mainly via the gills. The rate of uptake is determined by the concentration and permeability of the various chemical forms of the metal. Cadmium forms both soluble and insoluble complexes with the dominating anions in alkaline and saline waters (i.e. OH^-, HCO_3^-, CO_3^{-2}, Cl^-). These inorganic chemical complexes appear to be less available to the fish, offering one explanation for the lower metal uptake and toxicity under such conditions. Part et al. (1985) found that the transfer of cadmium from the water to the gill is, at constant hardness, related to the activity of the Cd^+ ion in the water. Calcium acts to reduce this transfer by changing the gill membrane permeability for cadmium. Concentrations of free metal ion also appear to be the most important control on metal uptake from solutions of cadmium by eukaryotic and prokaryotic algae and invertebrates. In studies concerning this phenomenon, bioavailability was independent of either total metal concentration or the concentration of metals complexed with organic molecules such as EDTA or NTA (Luoma 1983).

Complexation of cadmium by organic compounds is generally thought to decrease bioavailability as it generally decreases toxicity. However, there are two schools of thought concerning this phenomenon. The first is that there is a lower uptake of the organic-metal complex. The second is that while the organic-metal complexes are taken up, they are also rapidly excreted before intracellular damage can manifest itself as toxicity. The ultimate effect of organic complexing agents is extremely dependent on the type of organic compound in question (Part and Wikmark 1984). Natural organic materials of molecular weight less than 500

enhanced the toxicity of cadmium to zooplankton twofold, while larger size fractions of organic material reduced toxicity. The low molecular weight organic material had a cadmium binding capacity comparable to higher molecular weight fractions, suggesting at least some of the cadmium was organically complexed where availability was enhanced. Thus, one or more of the forms of cadmium associated with the low molecular weight material appeared to be biologically available (Luoma 1983). A recent study by Ramamoorthy and Blumhagen (1984) concluded that dissolved organic matter (freeze dried fulvic and humic acids) enhanced the uptake of cadmium from solution.

Laxen (1983) reviewed and collated the data from 33 individual studies of cadmium adsorption on amorphous and crystalline hydrous iron oxides, clays, silica, humic solids, manganese oxides and natural sediments. This information confirms the potentially important role of hydrous oxides of iron and manganese in the adsorption (and removal from bioavailability) of cadmium. Under conditions typical of many freshwaters (i.e. pH 6.5-8.5, suspended sediments 10-100 mg/L) variations over the range 1-90% adsorbed cadmium can be expected.

.2 Acclimation

Acclimation to increased levels of cadmium has been reported by Alabaster and Lloyd (1982) for brown trout, coho salmon, flagfish and rainbow trout previously exposed to sub-lethal levels of cadmium at an earlier life stage. Acclimation of fish can be accomplished at embryonic stage by exposure to levels of 1 to 4 µg/L for periods ranging up to 50 days. Acclimation is also possible at the alevin stage, with a 7 day exposure of rainbow trout alevins to 10 µg/L resulting in the survivors' ability to withstand concentrations of 100 µg/L for 7 days, compared to 2 days for non-acclimated populations.

Duncan and Klaverkamp (1980, 1983) demonstrated that the induced tolerance to cadmium (in white suckers, *Catostomus commersoni*), resulting from sub-lethal exposure of adults to 178, 410 or 730 µg/L, produced an increase in the median survival times of these fish exposed to lethal cadmium concentrations. This acclimation was also non-specific as cadmium tolerance was induced by previous exposure to cadmium as well as zinc, mercury and to a lesser extent selenium.

Survival of rainbow trout fingerlings held in water containing from 0.7 to 0.9 µg/L cadmium for 15 days prior to being exposed to a 140 µg/L cadmium concentration was much longer than rainbow trout survival without pre-exposure (Yamamoto and Inove 1985).

The observed tolerance for cadmium and toxic metals in general is attributable to the induction of the synthesis of a metal binding protein, the so-called metallothioneins. This protein is rich in sulfhydral groups (SH) and serves to bind the toxic metal to such an extent that the metal becomes unavailable for interactions with intracellular receptor sites. Originally, the work on metallothioneins was investigated in mammals, but these same type of protective compounds have been found in fish (Beattie and Pascoe 1979) and Cladocera (Yamamura *et al.* 1983).

.3 Accumulation

A review of over 40 laboratory studies indicates that in the majority of situations, the ability of aquatic organisms to concentrate cadmium from the environment (bioconcentration) is likely to be of little significance. There is also little evidence in the published literature that cadmium is biomagnified (occurs at successively higher concentrations with increasing trophic level) (Taylor 1983). An exception to these studies occurs in the case of marine and freshwater mollusks (Hemelraad *et al.* 1986a,b) and some crustacea where bioaccumulation has been shown to occur leading to relatively high residue levels of cadmium in certain species. It appears likely that these animals are storing the accumulated cadmium

in some complexed form as part of a detoxification process. The toxicological significance of stored complex cadmium compounds to human consumers has not yet been established (Taylor 1983).

3.24 OTHER AGENCY WATER QUALITY OBJECTIVES

Table 3.2-3 is a comparison of water quality objectives or criteria for cadmium as established (or proposed) by other agencies both national and international. There is a general recognition that the limit imposed on the amount of cadmium in water (presumably dissolved) can be related to the hardness of the water. This limit is either in the form of a fixed amount of cadmium for a given hardness or as a formula in which the value of e (2.71828) is raised to an exponent derived from the natural logarithm of the hardness.

3.25 OTHER FACTORS AFFECTING PWQOs

The Environment Canada recommended water quality objectives for cadmium in:

- Raw public water supplies (maximum 10 µg/L as total Cd);
- Agricultural water supplies (maximum 10 µg/L as total Cd);
- Recreation and aesthetics (10 µg/L as total Cd); and
- Industrial water supplies (10 µg/L as total Cd).

are all above the PWQO of 0.2 µg/L for the protection of aquatic life and would be protected by this latter objective.

The working group of the World Health Organization regional office for Europe recommended a maximum cadmium level in drinking water of 5 µg/L (World Health Organization 1984).

TABLE 3.2-3. Comparison of Cadmium Water Quality Objectives from Ontario and Other Agencies (for the Protection of Aquatic Life).

Agency	Objective or Criterion
Ontario (1979)	0.2 µg/L
USEPA (4 day average concentration not to be exceeded more than once every 3 years) (1985)	0.66 µg/L at hardness of 50 ppm 1.1 µg/L at hardness of 100 ppm 2.0 µg/L at hardness of 200 ppm $e^{(0.7852\ [\ln(\text{hardness})]-\ 3.490)}$ for any hardness
USEPA (one hour average concentration not to be exceeded more than once every 3 years) (1965)	1.8 µg/L at hardness of 50 ppm 3.9 µg/L at hardness of 100 ppm 8.6 µg/L at hardness of 200 ppm $e^{(1.128\ [\ln(\text{hardness})]-\ 3.828)}$ for any hardness
Manitoba (1983 Provisional)	0.012 µg/L at hardness of 50 ppm 0.025 µg/L at hardness of 100 ppm 0.051 µg/L at hardness of 200 ppm
Quebec (1984)	$e^{(1.05\ [\ln(\text{hardness})]-\ 8.53)}$ for any hardness (total extractable Cd)
Alberta (1977)	10 µg/L
Saskatchewan (1983)	10 µg/L
Environment Canada (1979)	0.2 µg/L (as total cadmium)
International Joint Commission (1978)	0.2 µg/L (as total cadmium)
EIFAC (1982) (proposed)	0.05 and 0.01 of the annual 50 and 95 percentile, respectively, of concentrations of “soluble” cadmium
The Netherlands (1985) (proposed) (van Leeuwen *et al*.1985a)	0.1 µg/L

The current Ontario PWQO for cadmium for the protection of aquatic life is low enough for the protection of recreational and aesthetic uses of the water.

3.26 STATUS OF EXISTING PWQO

In view of the recent work by van Leeuwen *et al.* (1985) and recent chronic toxicity data demonstrating reduced survival in a cladoceran and rainbow trout exposed to 0.2 µg/L, it is recommended that the PWQO of 0.2 µg/L be reassessed for the protection of aquatic life in the Province of Ontario. This reassessment should consider the effect of hardness on cadmium toxicity.

3.3 CHROMIUM

3.31 AQUATIC TOXICITY REVIEW

The two oxidation states of chromium (i.e. III and VI) exist in various water bodies and either can be converted to the other under the appropriate natural conditions. As the chemical and toxicological properties of the two oxidation states appear to be quite different and the toxicities of the two states have not been shown to be additive, chromium (III) and chromium (VI) acute and chronic toxicities were separated in Tables 3.3-1 and 3.3-2.

Table 3.3-1 presents acute toxicity data (i.e. less than or equal to 96 hr) from the USEPA (1985b) Ambient Water Quality Criteria Document (for chromium) for the years 1980-1984. The USEPA's survey of toxicity data was conducted in May 1984. Acutely toxic values for 50% of the vertebrate test populations range from 4,400 to 29,000 µg/L for chromium (III) and from 32,700 to 132,900 µg/L for chromium (VI). Acutely toxic values for 50% of the invertebrate test populations range from 16,800 to 58,70O µg/L for chromium (III) and from 15.3 to 57,300 µg/L for chromium (VI).

Table 3.3-2 presents selected (i.e. generally 1980 and later) data from the USEPA (1985b) report concerning the long-term effects of exposure to low levels of chromium. Adverse effects on the survival of rainbow trout early life stages were observed at concentrations of chromium (III) as low as 30 µg/L. Adverse effects on survival and reproduction during the life cycle of *Daphnia magna* have been demonstrated at less than 2.5 µg/L for chromium (VI). Both values (for chromium III and VI) are well below the current PWQO of 100 µg/L total chromium.

The most sensitive of 18 genera for chromium (III) is *Ephemerella* (a mayfly).

TABLE 3.3-1. Selected Acute (i.e. less than or equal to 96 hr) Lethality Data for Waterborne Chromium (III E VI) (from USEPA 1985b).

Species	Method	Results in ppb	Test Water
VERTEBRATES		**Chromium III**	
Salmo gairdneri Rainbow trout	LC_{50}, FT, M	4,400	Hardness: 26 ppm
Pimephales promelas Fathead minnow	LC_{50}, FT, M	29,000	Hardness: 203 ppm
As above	LC_{50}, FT, M	27,000	Hardness: 203 ppm
INVERTEBRATES			
Daphnia magna Cladoceran	LC_{50}, S, M	16,800	Hardness: 52 ppm
As above	LC_{50}, S, M	27,400	Hardness: 99 ppm
As above	LC_{50}, S, M	26,300	Hardness: 110 ppm
As above	LC_{50}, S, M	51,400	Hardness: 195 ppm
As above	LC_{50}, S, M	58,700	Hardness: 215 ppm
VERTEBRATES		**Chromium VI**	
Carassius auratus Goldfish	LC_{50}, S, U	110,000	-
Pimephales promelas Fathead minnow	LC_{50}, S, U	39,700	Hardness: 209 ppm
As above	LC_{50}, S, U	32,700	Hardness: 209 ppm
As above	LC_{50}, FT, M	37,700	Hardness: 209 ppm
As above	LC_{50}, FT, M	37,000	Hardness: 209 ppm
As above	LC_{50}, FT, M	35,900	Hardness: 209 ppm
Lepomis macrochirus Bluegill	LC_{50}, FT,M	132,900	Hardness: 20-44 ppm

TABLE 3.3-1 (Cont'd)

Species	Method	Results in ppb	Test Water
INVERTEBRATES			
Cerlodaphnia reticulata Cladoceran	LC_{50}, FT, M	45	Hardness: 45 ppm
Daphnia magna Cladoceran	LC_{50}, S, M	212	Hardness: 213 ppm
As above	LC_{50}, S, M	85.7	Hardness: 196 ppm
As above	LC_{50}, S, M	19.9	Hardness: 50 ppm
As above	LC_{50}, S, M	131	Hardness: 185 ppm
As above	LC_{50}, S, M	73.6	Hardness: 196 ppm
As above	LC_{50}, S, M	21.3	Hardness: 50 ppm
As above	LC_{50}, S, M	13.7	Hardness: 212 ppm
As above	LC_{50}, S, M	66.7	Hardness: 188 ppm
As above	LC_{50}, S, M	15.3	Hardness: 50 ppm
As above	LC_{50}, S, M	164	Hardness: 185 ppm
As above	LC_{50}, S, M	75.8	Hardness: 213 ppm
As above	LC_{50}, S, M	20.6	Hardness: 50 ppm
As above	LC_{50}, S, U	81	Hardness: 240 ppm
As above	LC_{50}, S, U	110	Hardness: 240 ppm
As above	LC_{50}, S, U	35	Hardness: 240 ppm
As above	LC_{50}, FT, M	24.2	Hardness: 45 ppm
As above	LC_{50}, FT, M	22	Hardness: 45 ppm
Daphnia pulex Cladoceran	LC_{50}, S, U	48	Hardness: 45 ppm
As above	LC_{50}, FT, M	36.3	Hardness: 45 ppm

TABLE 3.3-1 (Cont'd)

Species	Method	Results in ppb	Test Water
Simocephalus serrulatus Cladoceran	LC_{50}, FT, M	40.9	Hardness: 45 ppm
Simocephalus vetulus Cladoceran	LC_{50}, S, U	50	Hardness: 45 ppm
As above	LC_{50}, FT, M	32.3	Hardness: 45 ppm
Gammarus pseudolimnaeus Amphipod	LC_{50}, S, M	104	Hardness: 50 ppm
As above	LC_{50}, S, U	94.1	Hardness: 42 ppm
As above	LC_{50}, FT, M	67.1	Hardness: 48 ppm
Hyalella azteca Amphipod	LC_{50}, S, M	630	Hardness: 50 ppm
Tanytarsus dissimilis Midge	LC_{50}, FT, M	57,300	Hardness: 47 ppm
Pectinatella magnifica Bryozoan	LC_{50}, S, U	1,440	Hardness: 205 ppm
Lophopodella carteri Bryozoan	LC_{50}, S, U	1,560	Hardness: 205 ppm
Plumatella emerginata Bryozoan	LC_{50}, S, U	650	Hardness: 205 ppm

S = static test
FT = flow through test
M = concentrations of metal measured during test
U = concentrations of metal not measured during test

TABLE 3.3-2. Effects of Subacute and Chronic (i.e. greater than 96 hour)Exposures to Waterborne Chromium (from USEPA 1985b unless otherwise noted).

Species	Duration of Test	Exposure Concentration (ppb)	Result
		Chromium (III)	
VERTEBRATES			
Salmo gairdneri Rainbow trout	30 days (Early Life Stage)	30-157	Adverse effects on survival
Daphnia magna Cladoceran	21 days	330	Impaired reproduction
As above	21 days	2,000	Lethal for 50% of test population
		Chromium (VI)	
Pimephales promelas fathead minnow	123 days(Life Cycle)	1,000-3,950	As above
Oncorhynchus kisutch (Coho salmon)	14 days	520	Significant mortality after transfer to 30 ppt seawater
As above	14 days	480	As above, except 20 ppt seawater
As above	28 days	230	As above
As above	14 days	500	Decreased resistance to disease (Immunosuppresion)
As above	14 days	470	As above
Salmo gairdneri Rainbow trout (Embryo, larvae)	28 days	190	Death and deformity of 58% of test population
As above	28 days	56.9	Death and deformity of 10% of test population

TABLE 3.3-2 (Cont'd)

Species	Duration of Test	Exposure Concentration (ppb)	Result
As above (Adult)	6 months	200	Decrease of total liver glucides and increase in liver proteolytic activity in males
As above (Eyed embryo, Juvenile)	32 weeks	2,000	No survival at pH 6.5
As above	32 weeks	2,000	32% survival at pH 7.8
As above	32 weeks	200	40% survival at pH 6.5
As above	32 weeks	200	76% survival at pH 7.8
As above (Alevin, Juvenile)	32 weeks	2,000	0% survival at pH 6.5
As above	32 weeks	2,000	44% survival at pH 7.8
As above	32 weeks	200	72% survival at pH 6.5
As above	32 weeks	200	76% survival at pH 7.8
As above (Juvenile)	11days	3,200	Induced hyperplesia
Salmo trutta Brown trout (Yearling)	38 weeks	1,010	Suppression of Immune response
Cyprinus carpio Common carp (Adult)	38 weeks	1,010	As above
Pimephales promelas Fathead minnow (Larvae)	28 days	1,860	Reduced growth (Barron and Adelman 1984)
INVERTEBRATES			
Cerlodaphnia reticulata Cladoceran	7 days (life cycle)	25-64	Adverse effects on survival and reproduction

TABLE 3.3-2 (Cont'd)

Species	Duration of Test	Exposure Concentration (ppb)	Result
Daphnia magna Cladoceran	7 days (life cycle)	less than 2.5	As above
Daphnia palex Cladoceran	7 days (life cycle)	4.7-8.0	As above
Simocephalus serrulatus Cladoceran	7 days (life cycle)	13.9-28.5	As above
Simocephalus vetulus Cladoceran	7 days (life cycle)	4.7-8.0	As above

Of the 27 genera for which acute toxicity information is known, *Daphnia* (a cladoceran) is the most sensitive for chromium (VI).

Data on the effects of chromium (III) to freshwater plants are limited to growth suppression of a freshwater green alga by 397 µg/L in soft water and inhibition of root growth by Eurasian water milfoil at 9,900 µg/L. Green algae are much more sensitive to chromium (VI) with growth inhibition occurring as low as 10 µg/L.

The use of different chromium salts in toxicity testing has lead to the general conclusion that with the oxidation state of +VI, dichromates (i.e. $Cr_2O_7^{-2}$) are more toxic than chromates (i.e. CrO_4^{-2}).The +III oxidation state is generally regarded as being less toxic to aquatic life than the +VI oxidation state, although the available data can be conflicting.

3.32 PHYSIO-CHEMICAL FACTORS AFFECTING TOXICITY

Chromium (VI) reacts strongly with oxidizable organic matter, thereby favouring the generally less toxic chromium (III). If there is very little organic matter in the water, chromium (VI) can remain stable for long periods of time in aerobic natural waters. Under anaerobic conditions, chromium (VI) is reduced to chromium (III). Chromium (III) also has a strong tendency to form stable complexes with negatively charged inorganic or organic species. In neutral solutions chromium (III) can react with water to form colloidal hydrous oxides. Chromium (III), however, is least soluble in the pH range of natural waters.

Although there is much less information for chromium (III), the toxicity of both oxidation states is influenced by hardness. Chromates and dichromates increase in toxicity as hardness and/or alkalinity are decreased. Dichromates are less toxic if the water hardness is the result of a calcium:magnesium ratio of 4:1 than if the same hardness is the result of either calcium or magnesium alone. From the available

data, dichromate toxicity appears to decrease up to one order of magnitude in short-term toxicity when accompanied by a hardness increase from 20 to 300 ppm (EIFAC 1983).

The toxicity of chromates is lowered at higher pH. Part of the reduction may be due to the increasing prevalence of the less toxic CrO_4^{-2} ion (over the more toxic $Cr_2O_7^{-2}$ ion) at higher pHs.

Previous data concerning the effect of temperature on the toxicity of chromium (VI) in hard and soft water demonstrated little difference. Other data show either an insignificant effect of temperature or a reduction in toxicity in warmer water (EIFAC 1983). Recent work by Bryant *et al.* (1984) on the toxicity of chromium (VI) to estuarine animals demonstrated a significant increase in toxicity with increased temperature (i.e. 5 to 15°C).

There is some evidence that larger fish of a given species may be more tolerant of chromium than small fish (EIFAC 1983). Exposure to sub-lethal concentrations of chromium also appears to decrease the exposed population's resistance to bacterial infection (Mance *et al.* 1984a).

3.33 BIOAVAILABILITY, ACCLIMATION AND ACCUMULATION

.1 Bioavailability

In addition to its low solubility in the pH range of natural waters, movement of chromium (III) across biological membranes is highly restricted due to its net charge. Although this charge could be decreased by complexation with organic ligands, work reviewed thus far seems to indicate that organic complexation would not make chromium (III) more bioavailable than the uncomplexed ion. The uptake of radiolabeled chromium (III) from the water by fish was found by Stary *et al.*

(1982b) to be low, with most of the chromium being adsorbed to the outside surface of the fish. By contrast, chromium (VI) crosses biological membranes relatively easily.

A reduction in the cytotoxic potential and influx by chromium (VI) ions across biological membranes might also be the result of a change in the ratio of monovalent to divalent chromate ions (i.e. $HCrO_4^-/CrO_4^{-2}$). The monovalent species are believed to be more readily absorbed and decreases in pH (from 8.0) may favour the increased availability of this ion (Rao and Doughtie 1984).

Investigation of the uptake of radiochromium (chromium-51 as CrO_4^{-2}), by van de Putte *et al.* (1981) has demonstrated that the pH of the water controls the bioavailability of hexavalent chromium. At a pH of 7.8, chromium was able to move freely across the gill membranes without eliciting cytotoxic reactions and accumulate in other organs of the fish.

.2 Acclimation

Stevens and Chapman (1984) conducted early life stage toxicity tests with chromium (III) and steelhead trout (*Salmo gairdneri*). Acute toxicity tests conducted with fish surviving the early life stage exposures showed no acclimation to chromium (III) exposure. Similar studies for chromium (VI) were not found, but as chromium (VI) may be reduced in the intracellular environment to chromium (III) (Mance *et al.* 1984a), the Stevens and Chapman (1984) study must also apply to chromium (VI).

.3 Accumulation

Algae accumulate chromium (III) very rapidly, predominantly by adsorption on the surface of the cell. By contrast, chromium (VI) does not accumulate in or on algal cells (Stary *et al.* 1982a).

Rainbow trout exposed to radioactive chromium (as CrO_4^{-2}) in concentrations ranging from 200 to 50,000 µg/L and at pH's of 7.7 and 6.5 accumulated significantly more chromium at the lower pH. Target organs for chromium accumulation were the gills (especially at low pH), kidney, liver, and digestive tract. The gills were much less of a target organ at high pH.

Once placed in chromium free water, the accumulated chromium was lost at pH dependent rates. Various studies reported by Mance *et al.* (1984a) indicate that chromium (either VI or III) does not accumulate within freshwater organisms to any great extent. Biomagnification upward through increasing freshwater trophic levels is unknown for chromium.

3.34 OTHER AGENCY WATER QUALITY OBJECTIVES

Table 3.3-3 is a comparison of water quality objectives or criteria for chromium as established (or proposed) by other agencies, both national and international.

From these criteria, there seems to be a recognition of the differences in toxicity between chromium (III) and (VI) only by the USEPA, Manitoba and Quebec. The EIFAC recognizes the differences in sensitivity between salmonid and non-salmonid fish and allows a four fold increase in permissible "soluble" chromium levels for this latter group.

Compared to the other provinces, the Ontario PWQO of 100 µg/L is above that for Manitoba, Quebec, Alberta and Saskatchewan. The Ontario PWQO is also above the Environment Canada objective for the protection of aquatic life (i.e. 40 µg/L).

TABLE 3.3-3 Comparison of Chromium Water Quality Objectives from Ontario and Other Agencies (for the Protection of Aquatic Life).

Agency	Objective or Criterion
Ontario 1979 (Total Cr)	100 µg/L
USEPA Chromium (VI) (4-day average concentration not to be exceeded more than once every 3 years) (1985)	50 µg/L
USEPA Chromium (VI) (one hour average concentration not to be exceeded more than once every 3 years) (1985)	1,100 µg/L
USEPA Chromium (III) (4-day average concentration not to be exceeded more than once every 3 years) (1985)	120 µg/L at hardness of50 ppm 210 µg/L at hardness of100 ppm 370 µg/L at hardness of 200 ppm $e^{(0.8190\ [\ln(\text{hardness})]+1.561)}$ for any hardness
USEPA (Chromium (III) (one hour average concentration not to be exceeded more than once every three years) (1985)	980 µg/L at hardness of 50 ppm 1,700 µg/L at hardness of100 ppm 3,100 µg/L at hardness of 200 ppm $e^{(0.8190\ [\ln(\text{hardness})]+\ 3.688)}$ for any hardness
Environment Canada Total Chromium (1979)	40 µg/L
International Joint Commission (1978)	50 µg/L
Manitoba Chromium (VI) (1983 Provisional)	0.29 µg/L
Quebec Chromium (III) (1984)	44 µg/L

TABLE 3.3-3 (Cont'd)

Agency	Objective or Criterion
Alberta (1977)	50 µg/L
Saskatchewan (1983)	50 µg/L
EIFAC Salmonid fish (mean aqueous 'soluble' chromium not to *be* exceeded) (1983)	25 µg/L
(95 percentile of 'soluble' chromium concentrations not to be exceeded) (1983)	100 µg/L
EIFAC Non-salmonid fish (mean aqueous “soluble” chromium not to be exceeded) (1983)	100 µg/L
(95 percentile of “soluble” chromium concentrations not to be exceeded) (1983)	400 µg/L
Water Research Centre* Chromium (III & VI) Salmonid Fish (1984)	5 µg/L at hardness of less than 50 ppm 10 µg/L at hardness of 50-100 ppm 20 µg/L at hardness of 100-200 ppm 50 µg/L at hardness greater than 200 ppm
Coarse Fish (1984)	150 µg/L at hardness of less than 50 ppm 175 µg/L at hardness of 50-100 ppm 200 µg/L at hardness of 100-200 ppm 250 µg/L at hardness greater than 200 ppm
Other Freshwater Life	Same as Salmonid fish

* Mance *et al.* 1984a. Proposed Environmental Quality Standards for List II Substances in Water, Chromium.

3.35 OTHER FACTORS AFFECTING PWQO's

The Environment Canada recommended water quality objectives for chromium in:

- Raw public water supply (100 µg/L as total chromium);
- Agricultural water supply (1,000 µg/L as total chromium for livestock watering and 100 µg/L as total chromium for irrigation);
- Recreation (100 µg/L as total chromium); and
- Industrial water supplies (100 µg/L as total chromium),

all equal or exceed the PWQO of 100 µg/L for the protection of aquatic life.

Thus, all other uses of freshwater within the Province of Ontario are protected by a PWQO of 100 µg/L total chromium.

The Water Research Centre (Stevenage, England) has recommended a 95 percentile concentration of 500 µg/L chromium (both III and VI) as the maximum permissible for freshwater bathing and contact water sports (Mance *et al.* 1984a).

3.36 STATUS OF EXISTING PWQO

The current PWQO for chromium is 100 µg/L as total chromium. New data (i.e. since 1980) has revealed that both chromium III and VI concentrations below the PWQO have the potential to cause adverse effects on reproduction of vertebrates and invertebrates. Thus it is recommended that the PWQO for chromium be reviewed to provide an objective for the protection of aquatic life at all times. This objective should be based on water quality parameters such as hardness and/or dissolved organic carbon.

3.4 COPPER

3.41 AQUATIC TOXICITY REVIEW

Table 3.4-1 presents selected acute toxicity data (i.e. less than or equal to 96 hr) from the USEPA (1985c) Ambient Water Quality Document (for copper) for the years 1980-1984. USEPA's survey of toxicity data was conducted in May 1984. Acutely toxic values for 50% of the vertebrate test populations ranged from 18 to 1940 µg/L. For invertebrates the range was 6.5 to 1690 µg/L. The lowest values for both groups of organisms are greater than the Ontario PWQO of 5 µg/L.

Table 3.4-2 presents selected (i.e. 1980 and later) data from the USEPA (1985c) document concerning long term effects of exposure to low levels of copper. The range of copper concentrations which have been observed to affect aquatic organisms (including plants) during exposures greater than 96 hours ranges from 2.5 to 717 µg/L. The lowest value (2.5 µg/L) was shown to affect periphyton species composition and reduce primary productivity over a period of 12 months. This copper concentration (i.e. 2.5 µg/L) is the only value in Table 3.4-2 below the Ontario PWQO.

A concentration double the PWQO (i.e. 10 µg/L) was shown to reduce primary production in mixed phytoplankton population during a 124 hr exposure.

Of the 41 genera reviewed by the USEPA (1985c) for acute toxicity, the genus *Ptychocheilus* (squawfish) is the most sensitive. *Acroneuria* (stonefly) was the most resistant species. Several of the upper concentrations known to inhibit the growth of various plant species are near or below the chronic values for fish and invertebrate species. However, most concentrations inhibiting plant growth are higher.

TABLE 3.4-1 Selected Acute (i.e. less than or equal to 96 hr) Lethality Data for Waterborne Copper (from USEPA 1985c unless otherwise noted).

Species	Method	Results in ppb	Test Water
VERTEBRATES			
Oncorhynchus tshawytscha Chinook salmon (Juvenile)	LC_{50}, FT, M	33.1	Hardness: 25 ppm
As above	LC_{50}, FT, M	32	Hardness: 21 ppm
Salmo gairdneri Rainbow trout	LC_{50}, FT, M	190	Hardness: 125 ppm
As above	LC_{50}, FT, M	210	Hardness: 125 ppm
As above	LC_{50}, FT, M	80	Hardness: 120 ppm
Cyprinus carpio Common carp (140 mg)	LC_{50}, S, U	117.5	Hardness: 144-188 ppm
As above (3200 mg)	LC_{50}, S, U	530	Hardness: 144-188 ppm
Pimephales promelas Fathead minnow (Adult)	LC_{50}, S, M	210	Hardness: 103 ppm
As above	LC_{50}, S, M	310	Hardness: 103 ppm
As above	LC_{50}, S, M	120	Hardness: 103 ppm
As above	LC_{50}, S, M	390	Hardness: 254-271 ppm
Ptychochellus oregonensis Northern squawfish	LC_{50}, FT, M	18	Hardness: 52-56 ppm

TABLE 3.4-1 (Cont'd)

Species	Method	Results in ppb	Test Water
Gambusia affinis Mosquito fish (female)	LC_{50}, S, U	93	Hardness: 27-41 ppm
As above	LC_{50}, S, U	200	Hardness: 27-41 ppm
Poecilla reticulate Guppy(6.5 mg)	LC_{50}, R, U	160	Hardness: 144-188 ppm
As above (63 mg; females)	LC_{50}, R, U	275	Hardness: 144-188 ppm
As above (60 mg; males)	LC_{50}, R, U	210	Hardness: 144-188 ppm
As above (340 mg; females)	LC_{50}, R, U	480	Hardness: 144-188 ppm
As above (Adult)	LC_{50}, S, U	1,230	Hardness: 230 ppm
As above	LC_{50}, S, U	764	Hardness: 240 ppm
Lepomis gibbosus Pumpkinseed	LC_{50}, FT, M	1,940	Hardness: 125 ppm
As above	LC_{50}, FT, M	1,240	Hardness: 125 ppm
As above	LC_{50}, FT, M	1,660	Hardness: 125 ppm
INVERTEBRATES			
Goniobasis livescens Snail	LC_{50}, S, M	590	Hardness: 154 ppm
As above	LC_{50}, S, M	390	Hardness: 154 ppm
Corbicula fluminea Asiatic clam	LC_{50}, S, U	40	Hardness: 64 ppm

TABLE 3.4-1 (Cont'd)

Species	Method	Results in ppb	Test Water
As above	LC_{50}, FT, U	490	Hardness: 64 ppm
Cerlodaphnia reticulata Cladoceran	LC_{50}, S, U	17	Hardness: 45 ppm
Daphnia magna Cladoceran	LC_{50}, S, M	31.8	Hardness: 100 ppm
As above	LC_{50}, S, M	26	Hardness: 143 ppm
As above	LC_{50}, S, U	6.5	Hardness: 250 ppm
As above	LC_{50}, S, U	54	Hardness: 45 ppm
As above	LC_{50}, S, U	53	Hardness: 45 ppm
Gammarus pulex Amphipod	LC_{50}, R, U	41	Hardness: 104 ppm
As above	LC_{50}, R, U	183	Hardness: 249 ppm
Procambarus clarkii Crayfish (Larvae)	LC_{50}, FT, M	720	Hardness: 17 ppm
Chironomus tentans Midge (1^{st}instar)	LC_{50}, FT, M	298	Hardness: 71-84 ppm
As above (2^{nd} instar)	LC_{50}, FT, M	773	Hardness: 71-84 ppm
As above (3^{rd} instar)	LC_{50}, FT, M	1,446	Hardness: 71-84 ppm
As above (4^{th} instar)	LC_{50}, FT, M	1,690	Hardness: 71-84 ppm
Pectinatella magnifica Bryozoan	LC_{50}, S, U	510	Hardness: 190-220 ppm

TABLE 3.4-1 (Cont'd)

Species	Method	Results in ppb	Test Water
Lophopodelia carteri Bryozoan	LC_{50}, S, U	140	Hardness: 190-220 ppm
Plumatella emarginata Bryozoan	LC_{50}, S, U	140	Hardness: 190-220 ppm
*Daphnia magna** Cladoceran	EC_{50}, S, M	35.6	Hardness: 111 ppm
As above	EC_{50}, S, M	102	Hardness: 111 ppm with algae
As above	EC_{50}, S, M	92.8	Alkalinity:105 ppm
As above	EC_{50}, S, M	55.3	Alkalinity: 95 ppm
As above	EC_{50}, S, M	207	Alkalinity: 105 ppm Tris: 30 ppm
As above	EC_{50}, S, M	146	Alkalinity: 95 ppm Tris: 30 ppm

* Data from Borgmann and Charlton 1984.

S = static test
FT = flow through test
R = static test with replacement of test solutions
M = concentrations of metal measured during test
U = concentrations of metal not measured during test

TABLE 3.4-2 Effects of Subacute and Chronic (i.e. greater than 96 hr) Exposures to Waterborne Copper (from USEPA 1985c unless otherwise noted).

Species	Duration of Test	Exposure Concentration (ppb)	Result
VERTEBRATES			
Oncorhynchus kisutch Coho salmon	100 days	70	Reduced growth rate
As above	168 hr	275	Lethal to 50% of test population
As above (Acclimated for 2 weeks)	168 hr	325-440	Lethal to 50% of test population
Salmo gairdneri Rainbow trout (Embryo, larvae)	28 days	16.5	Lethality and deformity of 10% of test population
As above (Juvenile)	144 hr	246-408	Lethal to 50% of test population
As above	144 hr	274-381	Incipient lethal level
As above (Acclimated at 131-194 µg/L)	144 hr	564-717	incipient lethal level
As above (Juvenile)	85 days	31	Reduced growth
As above	85 days	16 (Intermittent exposure)	Reduced growth
As above	16 weeks	110	Significant Increase in levels of blood neutrophils (Dick and Dixon 1985)
INVERTEBRATES			
Protozoa Mixed species	7 days	167	Reduced colonization rates

TABLE 3.4-2 (Cont'd)

Species	Duration of Test	Exposure Concentration (ppb)	Result
Protozoa Mixed species	15 days	100	Reduced colonization rates
Acanthocyclops and *Diacyclops* sp. Copepods	7 days	42	20% growth reduction
Procambarus clarkii Crayfish (Adult)	1,358 hr	657	Lethal to 50% of test population
Chironomus tentans Midge	20 days	77.5	Lethal to 50% of test population
Tanytarsus dissimilis Midge	10 days	16.3	Lethal to 50% of the test population
Clistornia magnifica Caddisfly	8 months	13.0	Significant reduction in adult emergence
PLANTS			
Cladophora glomerata Green algal	12 months	120	Suppressed growth
Coreoneis placentula Diatom	12 months	120	Suppressed growth
Phytoplankton Mixed species	124 hr	10	Reduced rate of primary production
Periphyton Mixed species	12 months	2.5	Affected species composition; reduced productivity
Selenastrum capricornutum Alga	13 days	400	100% reduction in cell volume (Christensen *et al*.1979)
Chlorella stigmatophora Alga	24 days	400	As above
Lemna minor Vascular plant	28 days	130	Phytotoxic to 50% of plants (Brown and Rattigan 1979)

3.42 PHYSICO-CHEMICAL FACTORS AFFECTING TOXICITY

A number of studies have confirmed that the following factors affect the toxicity of copper:

- Temperature (increases in temperature increase toxicity);
- Hardness (increases in hardness decrease toxicity);
- Total organic carbon (increases in organic carbon decrease toxicity);
- Organisms size (large fish are generally more resistant than smaller fish);
- Dissolved oxygen (decreases in dissolved oxygen generally increase toxicity);
- pH (decreases in pH increase toxicity); and
- Suspended solids (increases in suspended solids have been shown to decrease toxicity in terms of total copper. However the toxicity of soluble copper appears to increase with increasing suspended solids) (USEPA 1985c, Alabaster and Lloyd 1982).

The effect of suspended solids on copper toxicity can be extremely variable depending upon the organic content of the suspended material and its ability to adsorb copper ions and inorganic complexes (Demayo *et al.* 1982).

Total organic carbon, especially if present as dissolved humic substances, can substantially reduce the toxicity of copper.

The effect of pH and hardness have a strong effect on the presence of the dissolved copper ion and its various inorganic soluble complexes. This will be discussed in the next section.

The toxicity of copper and zinc has been shown to be more than additive (i.e. synergistic) while toxicity due to copper and nickel were shown to be additive.

3.43 BIOAVAILABILITY, ACCLIMATION AND ACCUMULATION

.1 Bioavailability

The bioavailability of copper to aquatic organisms depends upon the particular form which copper takes in the natural aquatic ecosystem. Copper may exist in a natural water system as the dissolved cupric ion (Cu^{+2}) or as a complex with inorganic anions (eg. carbonates, chlorides) or organic ligands (eg. humic or fulvic acids). Copper can also exist as particulate or colloidal suspensions of hydroxides, phosphates or sulphides or adsorbed directly to particulate matter. The concentrations of each of the above forms depends on the complex interaction of many other dissolved and suspended substances. In freshwaters with very low organic carbon levels (i.e. 1-2 ppm), hydrolysis and precipitation would be the most important processes governing the availability of copper. Below pH 6, the cupric ion (Cu^{+2}) would be expected to be dominant. Carbonate complexes would be expected to predominant between pH 6 and 9.3 (Mance *et al.* 1984b).

The cupric ion has generally been conceded to be the most bioavailable and toxic form, although studies exist where toxic reactions are explained better by the summation of Cu^{+2}, $CuOH^{+}$, and $Cu(OH)_2$ species as equally toxic species. Chakoumakos *et al.* (1979) found Cu^{+2}, $CuOH^{+}$, $Cu(OH)_2^{\circ}$ to be toxic forms of copper to cutthroat trout. $CuHCO_3^{+}$, $CuCO_3^{\circ}$ and $Cu(CO_3)_2^{-2}$ were non-toxic. Dissolved copper in the form of an undissociated carbonate have also been implicated in toxicity to aquatic organisms (Demayo *et al.* 1982).

The equilibrium between the copper ion and the various inorganic anions can be drastically altered by the presence of dissolved organic carbon. Where dissolved organic carbon is not limited, most of the copper (i.e. between 80 and 98%) becomes organically complexed with the free cupric ion generally comprising less than 10% of the total copper in solution. Generally organic copper complexes are less toxic than the cupric ion, although there are exceptions. Humic acid-copper and

nitrilotriacetic acid-copper complexes are known to be less toxic than the equivalent amount of cupric ion apparently due to a lack of uptake. However, copper complexes with nitrogen substituted aromatic hydrocarbons are more toxic than the equivalent amount of cupric ion (Alabaster and Lloyd 1982).

.2 Acclimation

Acclimation to copper was investigated by Dixon and Sprague (1981). The effect of sub-lethal levels of copper on the subsequent tolerance of lethal concentrations was dependent upon the acclimation concentration. A discrete acclimation threshold of 18% of the control incipient lethal level was found. Rainbow trout acclimated to concentrations above the threshold developed increased tolerance of lethal copper levels whereas those acclimated below the threshold showed reduce tolerance. Significant increases in the incipient lethal level of copper were demonstrated by fish exposed to 94, 131 and 194 µg Cu/L for periods of 7, 14 and 21 days. Exposure to 30 µg Cu/L, however, for 14 and 21 days caused a significantly lower tolerance for lethal copper concentrations.

This research demonstrated the presence of a physiological mechanism operating within fish to mitigate the toxic effects of copper. A minimum level of copper is required to activate this mechanism with the threshold level capable of only sufficient induction to balance the detrimental effect of the previous copper exposure. The reduced tolerance demonstrated by fish acclimated to copper levels below the threshold (sensitization) implied that the physiological mechanism was not induced. The detrimental effects of the acclimation concentration were carried over and added to the impact of the lethal concentrations of copper during subsequent tests for the incipient lethal level.

.3 Accumulation

Uptake of copper by juvenile and adult fish may occur at one rate (as in rainbow trout) or at two rates (i.e. initially fast followed by a slower phase) as in sunfish. The uptake rate corresponds with alterations in respiratory activity resulting from copper exposure. Generally, smaller fish have a larger lamellar surface area to the gills compared to larger fish and thus more sites for copper uptake per unit weight (Demayo *et al.* 1982). The method of exposure also has an effect on accumulation. Fish intermittently exposed to sub-lethal copper concentrations accumulated significantly more copper than a similar group continuously exposed at the same daily mean concentrations (Seim *et al.* 1984). Once exposure to copper has ended, depuration occurs through the gills. Half-lives of copper in fish have been found to vary from 1.6 to 4.8 hours (Demayo *et al.* 1982).

Although almost all the current scientific literature concerning the uptake of copper describes copper accumulation from the water, Lanno *et al.* (1985) documented the dietary uptake of copper in rainbow trout. Juvenile rainbow trout were demonstrated to tolerate a copper level of 664 mg/kg in their diet in 24-week feeding tests. Initially growth was depressed for a period of16 weeks. However, the period of compensatory growth which followed eliminated any differences between treatment and control fish.

Freshwater organisms accumulating the largest concentrations of copper are clams and algae which can produce bioconcentration factors of several thousand. Accumulation by clams is probably a direct result of their filter feeding habits and a well established detoxification system for metals. Accumulation of copper by algae internally may also be supplemented by adsorption of copper to the external cell wall.

3.44 OTHER AGENCY WATER QUALITY OBJECTIVES

Table 3.4-3 is a comparison of water quality objectives or criteria for copper as established (or proposed) by other agencies, both national and international.

There is a general recognition by the USEPA and EIFAC of the effect of water hardness on the toxicity of copper. There is no recognition by any agency of the reduction of copper toxicity by naturally occurring organic carbon.

The Ontario PWQO for copper (5 µg/L) is below other provincial water quality objectives and below the USEPA and EIFAC recommended objectives for water of 50 ppm hardness. The MOE PWQO is above Environment Canada's objectives for the protection of aquatic life (2 µg/L) and ten times greater than the proposed standard for soft waters supporting salmonid fish (Water Research Centre, Stevenage, England).

3.45 OTHER FACTORS AFFECTING THE PWQO

The Environment Canada recommended water quality objectives for copper in:

- Raw public water supply (500 µg/L total copper);
- Water for livestock (1,000 - 5,000 µg/L total copper, depending on type of livestock);
- Irrigation water (200 µg/L - 5,000 µg/L total copper, depending on continuous or intermittent use and type of crops);
- Recreational waters (500 µg/L total copper); and
- Industrial water supplies (500 µg/L total copper),

are all above the objective of 5 µg/L for the protection of aquatic life and are therefore protected by this latter objective.

TABLE 3.4-3 Comparison of Copper Water Quality Objectives from Ontario and Other Agencies (for the Protection of Aquatic Life).

Agency	Objective or Criterion
Ontario (Total Copper) (1979)	5 µg/L
USEPA (4 day average concentration not to be exceeded more than once every 3 years) (1985)	6.5 µg/L at hardness of 50 ppm 12 µg/L at hardness of 100 ppm 21 µg/L at hardness of 200 ppm $e^{(0.8545\ [\ln(\text{hardness})]-1.465)}$ for any hardness
USEPA (one hour average concentration not to be exceeded more than once every 3 years) (1985)	9.2 µg/L at hardness fo 50 ppm 18 µg/L at hardness of100 ppm 34 µg/L at hardness of 200 ppm $e^{(0.9422\ [\ln(\text{hardness})]-1.464)}$ for any hardness
Manitoba (1983 Provisional)	5.6 µg/L
Quebec (1984)	5.6 µg/L
Alberta (1977)	20 µg/L
Saskatchewan (1983)	20 µg/L
Environment Canada (1981)	2 µg/L
International Joint Commission (1978)	5 µg/L
EIFAC Maximum annual median concentrations of "soluble" copper for salmonid species (1982 proposed)	1.0 µg/L at hardness of10 ppm 6.0 µg/L at hardness of 50 ppm 10.0 µg/L at hardness of100 ppm 28.0 µg/L at hardness of 300 ppm
Water Research Centre* for soft waters supporting salmonid fish (1984)	0.5 µg/L

* Mance *et al.* 1984b. Proposed Environmental Quality Standards for List II Substances in water. Copper.

3.46 STATUS OF EXISTING PWQO

Concentrations of copper in the range 1-10 µg/L are usually reported for unpolluted surface waters in the United States (USEPA 1985c). In Canada, the Experimental Lakes Area near Kenora in Ontario had a mean of 2 µg/L for 102 lakes. Offshore waters of the upper Great Lakes generally contained less than 5 µg/L. Onshore water ranged from 2 to 60 µg/L with the high values associated with human activity.

Considering these facts and:

- the bioconcentration of copper by phytoplankton and periphyton with its subsequent transfer to lake sediments;
- the protection from copper toxicity offered by naturally occurring dissolved organics; and
- the values and chronic responses given in Table 3.4-2,

it is recommended that the existing PWQO of 5 µg/L be maintained for the protection of aquatic life. This level should, however, be related to a specific hardness, with increasing water hardness allowing the PWQO to increase in accordance with the known antagonism between these two parameters.

3.5 IRON

3.51 AQUATIC TOXICITY REVIEW

In early studies of iron toxicity, the effects of pH and iron were not possible to separate and the toxicity of the iron solutions was, at times, attributed to the acidity of the test solutions. In more recent studies, the toxic effect of iron at neutral pH has been demonstrated. However, the effect may result more from the iron hydroxide colloids or particles than from iron in true solution. The toxic effect of iron at neutral pH has been attributed to the precipitation of ferric hydroxide on the surface of eggs and gills. In these cases the toxicity is a result of the physical covering or occlusion of respiratory surfaces.

Dave (1985) used buffered solutions to study the effects of pH on iron toxicity, but the occurrence of the hydroxide floc could not be prevented above pH 7.0. Under the test conditions, iron was more toxic at low pH (i.e. greater concentrations of soluble iron).

Transient alterations in the concentrations of serum proteins, glucose, sodium and potassium were observed in common shiners (*Notropus cornutus*) exposed to a 3,000 µg/L ferric hydroxide suspension for two to eight weeks. However, this same concentration did not affect embryonic development, hatchability, survival and maturation of coho salmon (*Oncorhynchus kisutch*) alevins.

The toxicity data presented in Table 3.5-1 from Amelung (1982) apparently resulted from "dissolved" iron salts. However, it is not known whether the Fe^{+2} and Fe^{+3} salts were in true solution or existed in a colloidal form. The same comment could be made concerning the work of Dave (1985) in Table 3.5-1. At the higher pHs he did record a noticeable precipitate occurring in the test chambers.

TABLE 3.5-1 Effects of Subacute and Chronic (i.e. greater than 96 hr) Exposures to Waterborne Iron.

Species	Exposure Concentration (ppb) (Exposure Duration)	Results / Comments
VERTEBRATES		
Salmo gairdneri Rainbow trout (Embryo-Larvae)	5,700 (28 days)	Delay In embryogenesis (Amelung 1982)
As above	1,300	100% lethal to larvae, 3 days after hatching. (Amelung 1982)
Brachydanio rerio Flagfish (Embryo-Larvae)	32,000	Median survival time slightly reduced (Dave 1985)
Notropus cornutus Common Shiner (Adult)	3,000 (2 to 8 weeks)	Transient alterations in concentrations of serum proteins, glucose, sodium and potassium (Dave 1985)
Pimephales promelas Fathead minnow (Adult)	290-1,870	Upper safe limit for Iron between these values (Dave 1985)
As above	63-500	Hatching progressively delayed at pH 6.0-7.4 (Dave 1985)

Given the variation in the physical size of the particles of the Fe^{+3} precipitate, (discussed below) and the lack of information concerning the proportions of Fe^{+3}, $FeOH^{+}_{2}$, $Fe(OH)_2^{+}$ and $Fe(OH)_4^{-}$ in specific solutions used for toxicity testing, it is impossible to pinpoint the specific toxic agent or fraction producing the toxic response.

3.52 PHYSICO-CHEMICAL FACTORS AFFECTING TOXICITY

Iron in aqueous solution can exist in two oxidation states, Fe^{+2} and Fe^{+3}. However, the occurrence of these ions and their hydrated complexes in a true dissolved state is very dependent upon environmental conditions. Generally, the presence of soluble Fe^{+2} ion and its hydrated complexes is favored in environments containing:

- low dissolved oxygen;
- relatively high carbon dioxide concentrations;
- a pH below 7.5; and
- reducing organic compounds (Thurston *et al.* 1979).

In natural waters Fe^{+3} is very insoluble. In the absence of complexing agents other than OH^{-}, the solubility of ferric ion (i.e. the sum of Fe^{+3}, $FeOH^{+2}$, $Fe(OH)_2^{+}$ and $Fe(OH)_4^{-}$) cannot exceed approximately 10^{-8} M (approximately 5.6×10^{-2} µg/L) within the pH range 6 to 9.

Fe^{+3} can also be present as an organic complex. Humic acids can form chelates with Fe^{+3} but it is not certain whether such substances keep iron in true solution at the pH of natural waters. It is possible that Fe^{+3} is present as the insoluble hydroxide (along with the humic acids) but in the form of a highly dispersed colloid. The size of the individual particles making up the $Fe(OH)_3$ precipitate varies with the pH of the solution and can be as small as 100 angstroms (Stumm 1967).

3.53 BIOAVAILABILITY, ACCLIMATION AND ACCUMULATION

.1 Bioavailability

The study by Hesslein *et al.* (1980) in which iron-59 was added to the epilimnion of Lake 224 demonstrated that this element had a strong association with suspended particulate material. This association was complete and immediate, making the introduced iron unavailable to fish via absorption through the gills. The removal rate of iron-59 from the water column was rapid, principally by the settling of particulate material. Iron-59 could not be detected in the water column beyond 37 days after isotope addition and was not present in sufficient quantity to assess its movement through biological pathways over the duration of the experiment.

.2 Acclimation

Tolerance to iron can be considered in terms of two groups:

- tolerance of the dissolved ion or ionic complexes; and
- tolerance of the colloidal or suspended precipitate.

Iron is required for normal metabolism in aquatic organisms and as such is expected to be under some type of regulatory control. Increased intake would be expected to cause increased excretion of iron or iron compounds.

Tolerance of the colloidal or suspended precipitate iron would involve the ability to overcome the covering or abrasive action of this material on respiratory membrane surfaces. Scientific studies detailing these mechanisms of toxicity for iron were not found during the literature search.

.3 Accumulation

A study of iron-59 accumulation in two species of fish from Lake 224 was conducted by Klaverkamp *et al.* (1983c). Although iron-59 was found consistently in the gut contents of the fish during the early stages of the experiment, it was only found in one out of four gut analyses by day 49. Analysis of fish tissues throughout the experiment failed to demonstrate any accumulation of the iron-59 in either of the fish species.

This contrasts with the figure of 190 (given by Williams *et al.* 1974) as the bioconcentration factor of iron in fish. Bioconcentration factors for aquatic macrophytes were reported to be on the order of 3,600 (Williams *et al.* 1974). Aquatic invertebrates were reported to bioconcentrate ^{59}Fe by a factor of 3,200 (Blaylock and Witherspoon 1978).

3.54 OTHER AGENCY WATER QUALITY OBJECTIVES

Table 3.5-2 is a comparison of water quality objectives or criteria as established by other agencies. Objectives are either300 or 1000 µg/L of iron for all agencies having an objective for this element. An additional USEPA criterion of 300 µg/L was not included in Table 3.5-2 because it is specifically for domestic water supplies.

3.55 OTHER FACTORS AFFECTING PWQOs

Objectives have not been established by Environment Canada for iron in:

- Raw public water supplies;
- Agricultural water (i.e. livestock watering and irrigation);

TABLE 3.5-2 Comparison of Iron Water Quality Objectives from Ontario and Other Agencies (for the Protection of Aquatic Life).

Agency	Objective or Criterion
Ontario (1979)	300 µg/L
USEPA (1976)	1,000 µg/L
Manitoba (1983 Provisional)	1,000 µg/L
Quebec	No objective
Alberta (1977)	300 µg/L
Saskatchewan (1983)	300 µg/L
Environment Canada (1983)	No objective
International Joint Commission (1978)	300 µg/L

- Recreational water; and
- Industrial water supplies.

In view of the USEPA's criterion for public water supply (i.e. 300 µg/L) based on aesthetic concerns, and the available toxicity data, it may well be that 300 µg/L as total iron will provide sufficient protection for aquatic organism.

3.56 STATUS OF EXISTING PWQO

Given the small base of toxicity data and the lack of understanding of the exact nature of the toxic agent (i.e. soluble ion, colloidal suspension or precipitate) it is recommended that the existing PWQO of 300 µg/L not be revised.

3.6 LEAD

3.61 AQUATIC TOXICITY REVIEW

Table 3.6-1 presents selected acute toxicity data (i.e. less than or equal to 96 hr) from the USEPA (1985d) Ambient Water Quality Criteria Document (for lead) for the years 1980-1984. The USEPA survey of toxicity data was conducted in May 1984. Acutely toxic values for 50% of the vertebrate test populations range from 12,000 to 400,000 µg/L. For invertebrates the range *was* 140 to224,000 µg/L.

Table 3.6-2 presents selected (i.e. 1980 and later data from the USEPA (1985d) report concerning long-term effects of exposure to low levels of lead. Exposure concentrations which produced effects range from 10.3 to 13,350 µg/L. The value of 10.3 µg/L (which caused death and deformity in 1% of the test population of fish at an alkalinity of 54.6 ppm) is below the PWQO for lead (i.e. 20 µg/L) at that alkalinity.

Of the data collected by the USEPA, amphipods appear to be the most sensitive of all freshwater animals tested. The 96 hr LC_{50} for the amphipod *Gammarus pseudolimnaeus* is 140 µg/L. The effects of lead on various species of aquatic plants have demonstrated adverse effects at concentrations ranging from 500 to 63,000 µg/L. It appears that aquatic plants are less sensitive to lead and would be protected by concentrations protective of chronic effects on freshwater animals.

Unlike other toxic metals, there are no dramatic changes in locomotor activities when fish are exposed to concentrations of lead approaching toxic levels (Ellgaard and Rudner 1982).

TABLE 3.6-1 Selected Acute (i.e. less than or equal to 96 hr) Lethality Data for Waterborne Lead (from USEPA 1985d unless otherwise noted).

Species	Method	Results in ppb	Test Water
VERTEBRATES			
Pimephales promelas Fathead minnow	LC_{50}	27,000	Hardness: 44 ppm
As above	LC_{50}	12,000	Hardness: 44 ppm
Ictalurus punctatus Channel catfish	LC_{50}, S, U	GT 100,000	Hardness: 45 ppm
Lepomis macrochirus Bluegill	LC_{50}, S, U	400,000	pH: 6.5
As above	LC_{20}, S, U	300,000	pH: 6.5
INVERTEBRATES			
Aplexa hypnorum Snail	LC_{50}, FT, M	1,340	Hardness: 61 ppm
Daphnia pulex Cladoceran	LC_{50}, S, U	5,100	Hardness: 45 ppm
Simocephalus vetulus Cladoceran	LC_{50}, S, U	4,500	Hardness: 45 ppm
Gammarus pseudolimnaeus Amphipod	LC_{50}, FT, M	140	Hardness: 48 ppm
Tanytarsus dissimilis Midge	LC_{50}, FT, M	224,000	Hardness: 48 ppm

GT = greater than
FT = flow through tests
S = static test
M = concentration of metal measured during test
U = concentration of metal not measured during test

TABLE 3.6-2 Effects of Subacute and Chronic (i.e. greater than 96 hr) Exposures to Waterborne Lead (from USEPA 1985d unless otherwise noted).

Species	Duration of Test	Exposure Concentration (ppb)	Result
VERTEBRATES			
Salmo gairdneri Rainbow trout	32 weeks	120	Black-tails in 3 of10 remaining fish
As above	29 weeks	87	All fish had black-tells and decrease of delta-aminolevulinic acid dehydratase in blood
As above	20 days	25	45% inhibition of delta-aminolevulinic acid activity
As above (Embryo, larva)	28 days	220	Death and deformity in 50% of test population
Cyprinus carpio Common carp	6 days	13,350	50% reduction In hatch
Salmo gairdneri Rainbow trout	8 days	100	Greater uptake of lead by opercular bone In small fish than in larger fish (Hodson *et al*.1982)
As above (Sac fry stage)	14 *weeks*	543	Rate of Intoxication by lead increased with growth rate (Hodson *et al.* 1982)
As above (6.5 g body weight)	30 weeks	120	Development of black-tails and spinal curvature in 30% of test population (Sippel *et al*.1983)
INVERTEBRATES			
Natural copepod assemblages	7 days	2,320	Reduced growth rate
Tanytarsus dissimilis Midge (Embryo - 3rd instar)	10 days	258	Lethal to 50% of test population

TABLE 3.6-2 (Cont'd)

Species	Duration of Test	Exposure Concentration (ppb)	Result
PLANTS			
Selenastrum capricornutum Alga	13 days	10,000	100% reduction in total cell volume (Christensen *et al.* 1979)
Chlorella stigmatophora Alga	24 days	10,000	As above
Elodea canadensis Vascular plant	28 days	136,000	Phytotoxic to 50% of plants (Brown and Rattigan1979)
Lemna minor Vascular plant	28 days	16,300	As above

The existing PWQO's for dissolved lead in water (i.e. 5 to 25 µg/L depending on alkalinities) appear to be within the range of values established as the maximum acceptable toxicant concentration for lead in soft and hard water (4.1 to 7.6 µg/L and 18.2 to 21.7 µg Pb/L, respectively).

3.62 PHYSICO-CHEMICAL FACTORS AFFECTING TOXICITY

Hardness (representing a number of interrelated ions such as hydroxide, carbonate, calcium and magnesium) has been shown to have a major influence on lead toxicity. Cladocera are three times more sensitive to lead in soft than in hard water. This increase in sensitivity may be as much as seven times for rainbow trout.

As with other metals, the most toxic component of aquatic lead is the free, uncomplexed ion and/or simple inorganic complexes. Thus, natural organic ligand concentrations, pH and precipitation reactions will have some effect on toxicity. Freedman et al. (1980) demonstrated a detoxifying effect of increasing soluble phosphate concentrations (0.095 to 95 mg/L) on lead toxicity to an amphipod.

Other physiochemical factors (e.g. temperature, physiological well being of test organism, interaction with other metals) may also affect the toxicity of aquatic lead, however, these factors do not appear to have been adequately examined for lead as they have for other toxic metals.

3.63 BIOAVAILABILITY, ACCLIMATION AND ACCUMULATION

.1 Bioavailability

As previously stated in Section 3.62, the most available form of lead appears to be the ionic (Pb^{+2}, $PbCl^{+}$, $PbOH^{+}$) form.

Lead in the ionic state increases with decreases in pH. Organic lead compounds are generally more toxic than inorganic lead compounds presumably because of their more rapid uptake and lipid soluble properties of the complex (Wong *et al.* 1981). The primary organo-lead compounds of interest are man-made (i.e. tetramethyl and tetraethyl lead). Naturally occurring methylated lead, while postulated to occur, cannot be substantiated in laboratory investigations despite intensive investigations into this phenomenon since 1981 (Jarvie *et al.* 1983). A recent article by Craig and Rapsomanikis (1985) examined the feasibility of environmental methylation of tin and lead. While the case for methylation of tin in the environment was established, the case for lead methylation was much weaker. This work has yet to be confirmed by other investigators.

.2 Acclimation

While some acclimation to lead by microorganisms has been reported in the scientific literature, these effects might well have been caused by the interaction of the nutrient media components with lead making it unavailable to the organisms until relatively high concentrations of lead are reached (Wong *et al.* 1978).

In their review of metallothionein and acclimation to heavy metals in fish, Klaverkamp *et al.* (1984) state that the synthesis of this protein (i.e. metallothinein) is induced by exposure to metals in Groups IB and IIB (of the periodic chart). Lead is a member of group IVA and thus does not appear to possess the ability to induce metallothionein. Support for this conclusion is given by Klaverkamp *et al.*'s (1984) summary of investigations on acclimation to metals by fish from 1937 to 1983. Not one of these investigations studied acclimation of fish to lead.

.3 Accumulation

Generally invertebrate aquatic species accumulate lead to a greater extent than aquatic vertebrates. Bioconcentraton factors for aquatic invertebrates range from 500 to 1,700, whereas the same factors for fish are in the order of 40 to 50 (USEPA 1985d). The pH of the water plays the most important role in accumulation of lead by fish. Investigations of lead accumulation by freshwater fish showed almost three times more lead was accumulated at pH 6.0 than at pH 7.5.The sites of lead accumulation within the body (i.e. fins, gills and liver) were not altered by the change in pH.

3.64 OTHER AGENCY WATER QUALITY OBJECTIVES

Table 3.6-3 is a comparison of water quality objectives or criteria for lead as established (or proposed) by other agencies both national and international. There is a recognition by most agencies that hardness has a dramatic effect on the toxicity of lead. Hardness in natural water is imparted by divalent cations, mainly calcium and magnesium. Since the main species of lead dissolved in natural waters are Pb^{+2}, $PbOH^{+}$ and $PbCl^{+}$, antagonism with the divalent cations producing hardness is highly probable. Ontario's PWQO for lead is related to alkalinity (i.e. the amount of the anionic species HCO_3^-, CO_3^{-2} and OH^- in the water). Indirectly, HCO_3^- and CO_3^{-2} are related to the amount of calcium and magnesium in natural waters. However, HCO_3^- and CO_3^{-2} probably do not play as important a role in reducing lead toxicity as do the divalent cations. Thus, lead objectives based on hardness are more closely related to the modifiers of toxicity than objectives based on alkalinity.

TABLE 3.6-3 Comparison of Lead Water Quality Objectives from Ontario and Other Agencies (for the Protection of Aquatic Life).

Agency	Objective or Criterion
Ontario (1979)	5 µg/L at alkalinities 0 to 20 ppm 10 µg/L at alkalinities 20 to 40 ppm 20 µg/L at alkalinities 40 to 80 ppm 25 µg/L at alkalinities greater than 80 ppm
USEPA (4 day average concentration not to be exceeded more than once every 3 years) (1985)	1.3 µg/L at hardness of 50 ppm 3.2 µg/L at hardness of100 ppm 7.7 µg/L at hardness of 200 ppm $e^{(1.273\ [\ln(\text{hardness})]-\ 4.705)}$ µg/L for any hardness
USEPA (one hour average concentration not to be exceeded more than once every 3 years) (1985)	34 µg/L at hardness of 50 ppm 82 µg/L at hardness at 100 ppm 200 µg/L at hardness at 200 ppm
Manitoba (1983 Provisional)	0.75 µg/L at hardness of 50 ppm 3.8 µg/L at hardness of100 ppm 20 µg/L at hardness of 200 ppm
Quebec (1984)	$e^{(2.35\ [\ln(\text{hardness})]-\ 9.45)}$ µg/L for any hardness
Alberta (1977)	50 µg/L
Saskatchewan (1983)	50 µg/L
Environment Canada (1979)	5 µg/L at hardness of less than 95 ppm 10 µg/L at hardness greater than 95 ppm 30µg/L for waters where sensitive fish (e.g. rainbow trout) are absent
International Joint Commission (1978)	10 µg/L in Lake Superior 20 µg/L in Lake Huron 25 µg/L In all remaining Great Lakes

TABLE 3.6-3 (Cont'd)

Agency	Objective or Criterion
Water Research Centre* (1984)	For protection of salmonid fish 4 µg/L at hardness less than 50 ppm 10 µg/L at hardness of 50-150 ppm 20 µg/L at hardness greater than 150 ppm For protection of other fish 50 µg/L at hardness less than 50 ppm 125 µg/L at hardness of 50-150 ppm 250 µg/L at hardness greater than150 ppm For protection of other freshwater life 4 µg/L at hardness less than 75 ppm 60 µg/L at hardness greater than 75 ppm

* Brown *et al.* 1984. Proposed Environmental Quality Standards for List II Substances in Water. Inorganic Lead.

3.65 OTHER FACTORS AFFECTING PWQO's

The Environment Canada recommended water quality objectives for lead in:

- Raw public water supply (50 to 250 µg/L depending on treatment);
- Livestock water (500 to 1,000 µg/L depending on presence or absence of horses):
- Irrigation water (500 to 10,000 µg/L depending on continuous or intermittent use);
- Recreational waters (50 µg/L); and
- Industrial water supplies (50 to 250 µg/L depending on treatment),

are all above the maximum PWQO of 30 µg/L for protection of aquatic life where sensitive species of fish are absent.

The Water Research Centre (Stevenage, England) has recommended a 95 percentile concentration of 500 µg/L lead as the maximum permissible for freshwater bathing and contact water sports (Brown et al. 1984).

All other uses of freshwater within the province of Ontario are protected by the PWQO of 30 µg/L.

3.66 STATUS OF EXISTING PWQO

The existing Ontario PWQO should be revised in accordance with the current scientific knowledge concerning the fate and toxicity of inorganic lead in the aquatic environment. This revision should use as a basis for a numerical objective the hardness and alkalinity of the water in which the objective is to be applied.

Methylation of lead in the natural environment in significant quantities is apparently still open to debate. Consideration of methyl lead in relation to any revision of the PWQO should be made by contacting specific research groups who are currently investigating this phenomenon.

3.7 MERCURY

3.71 AQUATIC TOXICITY REVIEW

Two forms of mercury exist in the aquatic environment, inorganic and organic. As an inorganic ion (i.e. mercury II) mercury generally displays the characteristics of other potentially toxic metals. Methylation of inorganic mercury to an organic form (principally monomethyl mercury) produces a much more mobile and toxic compound. Methylation occurs in a variety of micro-environments within the general aquatic environment. In addition, organic mercurial compounds have also been produced for industrial and agricultural *uses* and have found their way into the aquatic environment.

As the two types of mercury in the aquatic environment exhibit different toxicities, they were separated in Tables 3.7-1 and 3.7-2.In addition, the chemical tested was judged to be of more importance than the test water conditions (especially in regard to organic mercury) and thus the former information is presented in Table 3.7-1.

Table 3.7-l presents acute toxicity data (i.e. less than or equal to 96 hr) from the USEPA (1985e) Ambient Water Quality Criteria Document (for mercury) for the years 1980-1984. The USEPA's survey of toxicity data was conducted in May 1984. Acutely toxic values for 502 of the vertebrate test populations range from 30 to 420 µg/L for vertebrates and from 4.4 to 370 µg/L for invertebrates for inorganic mercury (i.e. mercury II).

Table 3.7-2 presents selected (i.e. generally 1980 and later) data from the USEPA (1985e) report concerning the long-term effects of exposure to low levels of mercury. Adverse effects on a population of rainbow trout embryos and larvae have been reported to occur at less than 0.1 µg/L of inorganic mercury. As well, 0.05

TABLE 3.7-1 Selected Acute (i.e. less than or equal to 96 hr) Lethality Data for Waterborne Mercury (from USEPA 1985e).

Species	Method	Results in ppb	Test Chemical
	MERCURY (II)		
VERTEBRATES			
Salmo gairdneri Rainbow trout	LC_{50}, FT, U	420	Mercuric Chloride
Salmo gairdneri Rainbow trout (Juvenile)	LC_{50}, FT, M	275	Mercuric Chloride
Pimephales promelas Fathead minnow	LC_{50}, FT, M	168	Mercuric Chloride
As above	LC_{50}, FT, M	150	Mercuric Chloride
Gambusia affinis Mosquito fish (Female)	LC_{50}, S, U	180	Mercuric Chloride
Poecilla reticulata Guppy (116-157 mg)	LC_{50}, R, U	30	Mercuric Chloride
Poecilla reticulata Guppy (362-621 mg)	LC_{50}, R, U	53.5	Mercuric Chloride
INVERTEBRATES			
Branchlura sowerbyi Tubificid oligochaete	LC_{50}, R, U	80	Mercuric Chloride
Limnodrilus hoffmeisteri Tubificid oligochaete	LC_{50}, R, U	180	Mercuric Chloride
Quistadrilus multisetosus Tubificid oligochaete	LC_{50}, R, U	250	Mercuric Chloride
Rhyacodrilus montana Tubificid oligochaete	LC_{50}, R, U	240	Mercuric Chloride

TABLE 3.7-1 (Cont'd)

Species	Method	Results in ppb	Test Chemical
Spirosperma ferox Tubificid oligochaete	LC_{50}, R, U	330	Mercuric Chloride
Spirosperma nitroistryi Tubificid oligochaete	LC_{50}, R, U	500	Mercuric Chloride
Stylodrlius heringianus Tubificid oligochaete	LC_{50}, R, U	140	Mercuric Chloride
Tubifex tubifex Tubificid oligochaete	LC_{50}, R, U	140	Mercuric Chloride
Varichaeta pacifica Tubificid oligochaete	LC_{50}, R, U	100	Mercuric Chloride
Aplexa hypnorum Snail	LC_{50}, S, U	370	Mercuric Chloride
Daphnia magna Cladoceran (6 hr old)	LC_{50}, S, U	4.4	Mercuric Chloride
Daphnia magna Cladoceran (24 hr old)	LC_{50}, S, U	4.4	Mercuric Chloride
Daphnia magna Cladoceran (1-9 days old)	LC_{50}, S, U	5.2 to 14.8	Mercuric Chloride
Faxonella clypeatys Crayfish (Male, mixed ages)	LC_{50}, R, M	20	Mercuric Chloride
	OTHER MERCURY COMPOUNDS		
Salmo gairdneri Rainbow trout (Juvenile)	LC_{50}, FT, M	24	Methyl mercuric Chloride
Cyprinus carpio Common carp	LC_{50}, R, U	139	2-Methoxy Ethyl Mercuric Chloride

TABLE 3.7-1 (Cont'd)

Species	Method	Results in ppb	Test Chemical
Pimephales promelas Fathead minnow	LC_{50}, S, M	40	Mercuric Acetate
As above	LC_{50}, S, M	115	Mercuric Thiocyanate
Gambusia affinis Mosquito fish (Female)	LC_{50}, S, U	910	Methoxyethyl Mercuric Chloride
As above	LC_{50}, S, U	37	Phenylmercuric Acetate
As above	LC_{50}, S, U	44	Phenylmercuric Acetate (Ceresan)

S = static test
R = static test with replacement
FT = flow through test
M = concentrations of metal measured during test
U = concentrations of metal not measured during test

TABLE 3.7-2 Effects of Subacute and Chronic (i.e. greater than 96 hr) Exposures to Waterborne Mercury (from USEPA 1985e unless otherwise noted).

Species	Duration of Test	Exposure Concentration (ppb)	Result
		MERCURY (II)	
VERTEBRATES			
Salmo gairdneri Rainbow trout	1 week	100	Effected osmoregulation
As above (Embryo, larva)	28 days	4.7, 5.0	Death and deformity In 50% of test population
As above	28 days	LT 0.1	Death and deformity in 50% of test population
As above	28 days	0.9	Death and deformity in10% of the test population
		OTHER MERCURY COMPOUNDS	
Salmo gairdneri Rainbow trout	1 *week*	5	Effected osmoregulation
Cyprinus carpio Common carp	16 days	0.05	Reduced protein synthesis
Ephydatia fluviatilis Sponge	30 days	1	Malformed gemmoscleres
As above	30 days	100 to 500	Lethal to 50% of test population
		MERCURY (II)	
INVERTEBRATES			
Diaphanosoma sp. Cladoceran	3 weeks	2.8	Reduced population density
Daphnia galeata mendotae Cladoceran	3 *weeks*	2.2	Reduced population density

TABLE 3.7-2 (Cont'd)

Species	Duration of Test	Exposure Concentration (ppb)	Result
Bosmina longirostris Cladoceran	3 *weeks*	2.8	Reduced population density
Natural copepod Assemblages	7 days	28.3	Reduced growth rate
PLANTS			
Ankistrodesmus braunli Alga	24 days	74	inhibited growth
Ankistrodesmus sp. Alga	10 days	5	More toxic at pH 5 than pH 7
Elodea canadensis Vascular plant	28 days	7,400	Phytotoxlc to 50% of plants (Brown and Rattigan1979)
Leona minor Vascular plant	28 days	1,000	Phytotoxlc to 50% of plants (Brown and Rattlgan1979)

LT = less than

µg/L organic mercury (methyl mercuric chloride) has been reported to reduce protein synthesis in the common carp after 16 days exposure. Both of these values are below the current PWQO of 0.2 µg/L.

The most sensitive organism to inorganic mercury toxicity are invertebrates (i.e. the genus *Daphnia*).The most resistant (*Acroneuria*) is also an invertebrate (i.e. a stonefly). Both early life-stage and life cycle tests with mercuric chloride found adverse effects on the fathead minnow at 0.23 µg/L (USEPA 1985e).

Freshwater plants are relatively insensitive to inorganic mercury and sensitive to methylmercury. Generally, however, they do not appear to be more sensitive to organic mercury than freshwater animals and will be protected by objectives for the protection of this latter group (USEPA 1985e).

3.72 PHYSICO-CHEMICAL FACTORS AFFECTING TOXICITY

The following factors are thought to affect the acute and chronic toxicity (as well as bioaccumulation) of the various forms of mercury:

- Alkalinity;
- Hardness;
- Ascorbic acid (vitamin C);
- Chloride;
- Dissolved oxygen;
- Organic complexing agents;
- pH;
- Sediment chemistry; and
- Temperature (USEPA 1985e).

The production of an antagonistic effect by hardwater to mercury toxicity has been reported in some studies but not others. Low levels of dissolved oxygen generally increase the toxicity of heavy metals due to an increase in rate of water

flow over the gills. A negative correlation between the pH of the water and mercury levels in fish has been reported. Thus, increased pH would appear to make mercury less available for uptake. Increases in temperature can increase mercuric ion toxicity as much as threefold. The presence of copper has also shown to be antagonistic to mercury toxicity. Selenium also can reduce the body burdens of mercury by pre-exposure to the former element. However, other studies using selenium and mercury in combination seemed to demonstrate a synergistic toxic effect (Reeder *et al.* 1979).

In addition to the above mentioned abiotic factors, biological factors such as fish growth rate, metabolic rate, and fish size also affect the uptake and toxicity of mercury (Wren and MacCrimmon 1983).The study by Ramamoorthy and Blumhagen (1984) demonstrated that the uptake of mercury (both inorganic and organic) was more than doubled in the presence of zinc and cadmium.

3.73 BIOAVAILABILITY, ACCLIMATION AND ACCUMULATION

.1 Bioavailability

Inorganic mercury in natural waters has been shown to be rapidly and efficiently transferred to the sediment in both aerobic and anaerobic situations. The uptake phenomena are surface area dependent with the surface 0.1 cm depth of sediment being the most affected. The sediment uptake rate for methylmercury ions is higher than that for inorganic mercury. The formation of insoluble sulphides by both inorganic and organic mercury are the most important reactions leading to the reduced bioavailability of mercury.

Methylation of inorganic mercury (by both aerobic and anaerobic bacteria and humic substances) in the sediment or liver, intestine and slime coat of fish can produce an extremely mobile, lipophilic compound, easily available to fish and other aquatic animals. The increased bioavailability of organic mercury was shown by

Biesinger *et al.* (1982) when *Daphnia magna* accumulated approximately 20 times more mercury when exposed to methyl mercuric chloride than when exposed to inorganic mercury.

.2 Acclimation

The synthesis of metallothionein by killifish as a mechanism of increased mercury tolerance *was* investigated by Weis (1984).The results of his work suggest that metallothionein production by this fish (which was collected from metal polluted areas) was not a significant factor in mercury tolerance in adults and had a questionable role in embryonic and larval tolerance to inorganic mercury. Metallothionein is considered by some investigators not to react with methylated mercury, which generally forms the largest portion of the body burden of aquatic animals.

.3 Accumulation

Uptake of mercury through the gills and digestive tract is significant for fish and some information suggests that tissue residues are higher in organisms exposed via both routes than via either separately. The form of mercury is also important in the pattern of trophic accumulation. The digestive tract wall represents a barrier to inorganic mercury and acts as a preferential site of accumulation for this form. Methylmercury, however, easily passes through the intestinal wall and into the blood stream making possible the contamination of all organs (Boudou and Ribeyre, 1985).

Direct accumulation from the water is directly attributable to absorption by the gills with the more lipid soluble methylmercury having an advantage over inorganic mercury in passage through membrane surfaces.

The accumulation of mercury in an aquatic organism is a function of uptake and depuration rates. Bioconcentration factors for fish are relatively high because uptake is fast and depuration is very low. The biological half-life of mercury in fish is 2 to 3 years. Generally, less than 60% of the total body burden of mercury is methylated in invertebrates. By contrast, usually more than 70% is methylated in adult fish (USEPA 1985e).

Accumulation plays an important part in the determination of the Ontario PWQO for mercury as it is the only metal which considers the concentration of mercury in whole fish as a factor in the establishment of the objective. For the purpose of setting a numerical value, the total amount of mercury in a filtered water sample is arbitrarily considered to be methylmercury (MOE 1979). Bioconcentration factors for methylmercury range from 4,000 to 85,000 (USEPA 1985e). Given these bioconcentration factors and the 0.5 µg/g limit of total mercury in whole fish, the range of values for water quality objectives could be 0.125 to 0.0058 µg/L. Both values are below the current PWQO of 0.2 µg/L.

3.74 OTHER AGENCY WATER QUALITY OBJECTIVES

Table 3.7-3 is a comparison of water quality objectives or criteria for mercury as established (or proposed) by other agencies. Ontario's PWQO is the only objective which gives a numerical value for whole fish concentrations of total mercury as a guideline for the objective as well as a numerical water concentration. Both of the USEPA criteria (i.e. four day and one-hour averages) have incorporated bioconcentration factors in their derivation, with the stipulation that if the criterion of 0.012 µg/L is exceeded more than once in a three year period, the edible portion of consumed species should be analyzed to determine whether the concentration of methylmercury exceeds the U.S. Food and Drug Administration action level for this metal.

TABLE 3.7-3 Comparison of Mercury Water Quality Objectives from Ontario and Other Agencies (for the Protection of Aquatic Life).

Agency	Objective or Criterion
Ontario (1979)	0.2 µg/L as total Hg in filtered water, or 0.5 µg/L as total Hg in whole fish
USEPA (4 day average concentration not to be exceeded more than once every 3 years) (1985)	0.012 µg/L
USEPA (one hour average concentration not to be exceeded more than once every 3 years) (1985)	2.4 µg/L
Manitoba (1983 Provisional)	0.00057 µg/L
Quebec (1984)	0.00057 µg/L
Alberta (1977)	0.1 µg/L
Saskatchewan (1983)	0.1 µg/L
Environment Canada (1979)	0.1 µg/L as total Hg to protect consumers of fish 0.2 µg/L as total Hg where fish are not eaten
International Joint Commission (1978)	0.2 µg/L as total Hg in filtered water, or 0.5 µg/L as total Hg in wholefish

The Ontario PWQO for mercury is in the same order of magnitude as those objectives for Environment Canada, Alberta, Saskatchewan and Manitoba. The USEPA four day average criteria is an order of magnitude lower' while the one hour average is an order of magnitude higher. Quebec has the lowest objective of any surveyed (i.e. 0.00057 µg/L) and is similar to an objective derived from a bioconcentration factor of 85,000 and a maximum permissible concentration of 0.5 µg/g mercury in whole fish.

3.75 OTHER FACTORS AFFECTING PWQO's

The Environment Canada recommended water quality objectives for mercury in:

- Raw public water supplies (1 µg/L as total mercury);
- Livestock water supplies (3 µg/L as total mercury);
- Recreational water (except for fishing) (l µg/L as total mercury); and
- Industrial water supplies (l µg/L as total mercury),

are all above the PWQO of 0.2 µg/L for the protection of aquatic life and thus would be protected by this latter objective.

The World Health Organization's guideline value for total mercury in drinking water is 1 µg/L (World Health Organization 1984).

3.76 STATUS OF EXISTING PWQO

If the requirement for the protection of all forms of aquatic life and all aspects of their aquatic life cycles remains in effect, then a revision of the PWQO is recommended. The basis for this recommendation results from:

- Chronic toxicity tests demonstrating adverse effects at 0.23 µg/L;
- The additional information concerning the bioaccumulation and fate of mercury in the aquatic environment; and
- The order of magnitude lower criteria set by the USEPA (as a four day average) considering bioaccumulation effects.

It cannot be determined at this stage which water quality parameter has the most influence on mercury toxicity. Inorganic mercury can be methylated in such a wide variety of aquatic micro environments that the primary concern should be water quality parameters which reduce the uptake of waterborne organic mercury.

3.8 NICKEL

3.81 AQUATIC TOXICITY REVIEW

Table 3.8-1 presents selected acute toxicity data (i.e. less than or equal to 96 hr) from USEPA (1980c) Ambient Water Quality Criteria Document (for nickel) and Nebeker *et al.* (1985). This information was published (or in manuscript form) between the years 1978 and 1985' inclusive. Acutely toxic values for 50% of the vertebrate test populations range from 2,400 to 17,700 µg/L. For invertebrates the range is 645 to 4,960 µg/L.

Table 3.8-2 presents selected (i.e. 1978 and later) data from various sources concerning the long term effects of exposure to low levels of nickel. The data from Birge and Black (1980) demonstrate that concentrations of nickel between 3.0 and 10.6 µg/L will be lethal to between one and 10% of rainbow trout, channel catfish, and largemouth bass embryos and larvae for exposure periods of 32 days. The survival of amphibian embryos is also affected in this range. These values (i.e. 3.0 to 10.6 µg/L) are below the Ontario PWQO of 25 µg/L.

Of the acute toxicity data for 22 species examined by the USEPA (1980c), both the most sensitive and least sensitive organisms were invertebrates. The invertebrates of the genus *Daphnia* seem to be more sensitive to long term chronic exposures than vertebrates (USEPA 1980c).

The concentrations of nickel which are known to reduce the growth of several freshwater algae species are generally higher than the chronic exposures producing effects in fish and invertebrate species. Thus, water quality objectives designed to protect the aquatic fauna will also protect freshwater plants.

TABLE 3.8-1 Selected Acute (i.e. less than or equal to 96 hr) Lethality Data for Waterborne Nickel.

Species	Method	Results In ppb	Test Water	Reference
VERTEBRATES				
Pimephales promelas Fathead minnow	LC_{50}, FT, M	5,210	Hardness: 45 ppm	USEPA 1980c
As above	LC_{50}, FT, M	5,160	Hardness: 44 ppm	As above
As above	LC_{50}, FT, M	2,920	Hardness: 29 ppm	As above
As above	LC_{50}, FT, M	12,400	Hardness: 77 ppm	As above
As above	LC_{50}, FT, M	17,700	Hardness: 89 ppm	As above
As above	LC_{50}, FT, M	8,620	Hardness: 91 ppm	As above
As above	LC_{50}, FT, M	5,380	Hardness: 86 ppm	As above
Ambiopiltes rupestris Rock bass	LC_{50}, FT, M	2,400	Hardness: 26 ppm	As above
Salmo gairdneri Rainbow trout (3 months old)	LC_{50}, FT, M	10,000	Hardness: 27-30 ppm	Nebeker *et al.* 1985
As above	LC_{50}, FT, M	10,900	Hardness: 27-30 ppm	As above
As above (12 months old)	LC_{50}, FT, M	8,900	Hardness: 27-30 ppm	As above
Cyprinus carpio Common carp (Embryo)	LC_{50}, S, U	6,100	Hardness:128 ppm	USEPA 1980c
As above (Larvae)	LC_{50}, S, U	8,460	Hardness:128 ppm	As above
INVERTEBRATES				
Daphnia magma Cladoceran	LC_{50}, S, M	1,810	Hardness: 51 ppm	USEPA 1980c
As above	LC_{50}, S, M	1,810	Hardness: 48 ppm	As above

TABLE 3.8-1 (Cont'd)

Species	Method	Results in ppb	Test Water	Reference
INVERTEBRATES (Cont'd)				
As above	LC_{50}, S, M	1,840	Hardness: 44 ppm	As above
As above	LC_{50}, S, M	1,900	Hardness: 44 ppm	As above
As above	LC_{50}, S, M	3,160	Hardness: 94 ppm	As above
As above	LC_{50}, S, M	3,830	Hardness:144 ppm	As above
As above	LC_{50}, S, M	2,470	Hardness: 244 pm	As above

S = static test
FT = flow through test
M = concentrations of metal measured during test
U = concentrations of metal not measured during test

TABLE 3.8-2 Effects of Subacute and Chronic (i.e. greater than 96 hr)Exposures to Waterborne Nickel.

Species	Duration of Test	Exposure Concentration (ppb)	Result	Reference
VERTEBRATES				
Salmo gairdneri Rainbow trout(Embryo)	28 days	50	Lethal to 50% of test population	USEPA 1980c
As above (no life stage given)	56 days	650	Lethal to 50% of test population	Mance and Yates 1984a
Carassius auratus Goldfish (Embryo)	7 days	2,140	Lethal to 50% of test population	USEPA 1980c
Cyprinus carpio Common carp (Larvae)	257 hours	750	Lethal to 50% of test population	As above
Micropterus salmoides Largemouth bass (Embryo)	8 days	2,020	Lethal to 50% of test population	As above
Gastrophryne carolinensis Toad (Embryo)	7 days	50	Lethal to 50% of test population	As above
Pimephales promelas Fathead minnow	32 days	120	Significant mortality compared to control population	Birge *et al.* 1984
As above	32 days	733	Significant reduction in mean standard length of test population	As above
As above	32 days	57	Highest no observed effect level based on frequency of mortalities and teratogenicity	As above
Salmo gairdneri Rainbow trout (Eyed Eggs)	38 days	431	Significant effects on growth and weight	Nebeker *et al.* 1985

TABLE 3.8-2 (Cont'd)

Species	Duration of Test	Exposure Concentration (ppb)	Result	Reference
VERTEBRATES (Cont'd)				
As above	38 days	1,680	Significant mortality in test population	As above
As above (Pre-Swim Up Larvae)	38 days	700	Significant effects on growth	As above
As above	38 days	134	No-effect-level	As above
Salmo gairdneri Rainbow trout (Embryo, Larvae)	32 days	50	Lethal to 50% of test population	Birge and Black 1980
As above	32 days	10.6	Lethal to 10% of test population	As above
As above	32 days	3.0	Lethal to 1% of test population	As above
Ictalurus punctatus Channel catfish (Embryo, Larvae)	32 days	710	Lethal to 50% of test population	As above
As above	32 days	38.4	Lethal to 10% of test population	As above
As above	32 days	3.6	Lethal to 1% of test population	As above
Micropterus salmoides Largemouth bass (Embryo, Larvae)	32 days	2,060	Lethal to 50% of test population	As above
As above	32 days	113.1	Lethal to 10% of test population	As above
As above	32 days	10.6	Lethal to 1% of test population	As above
Carassius auratus Goldfish (Embryo, larvae)	32 days	2,780	Lethal to 50% of test population	As above

TABLE 3.8-2 (Cont'd)

Species	Duration of Test	Exposure Concentration (ppb)	Result	Reference
VERTEBRATES (Cont'd)				
As above	32 days	414.4	Lethal to 10% of test population	As above
As above	32 days	87.7	Lethal to 1% of test population	As above
Gastrophyne carolinensis Toad (Embryo, Larvae)	32 days	50	Lethal to 50% of test population	As above
As above	32 days	4.1	Lethal to 10% of test population	As above
As above	32 days	0.5	Lethal to 1% of test population	As above
Ambystoma opacum Salamander (Embryo, Larvae)	32 days	410	Lethal to 50% of test population	As above
As above	32 days	60.4	Lethal to 10% of test population	As above
As above	32 days	12.7	Lethal to 1% of test population	As above
Bufo fowleri Toad (Embryo, Larvae)	32 days	11,030	Lethal to 50% of test population	As above
As above	32 days	407.4	Lethal to 10% of test population	As above
As above	32 days	27.7	Lethal to 1% of test population	As above
Ambystoma opacum Salamander(Embryo)	8 days	420	Lethal to 50% of test population	USEPA 1980c

TABLE 3.8-2 (Cont'd)

Species	Duration of Test	Exposure Concentration (µg/L)	Results	Reference
INVERTEBRATES				
Daphnia magna Cladoceran	9 days	500	Lethal to 50% of test population	USEPA 1980c
As above	9 days	100	Growth Inhibition	As above
Clistoronia magnifica Caddisfly	Greater than 25 days (life cycle)	250	Adult emergence significantly less than control	Nebeker *et al.* 1984
As above	Greater than 25 days (life cycle)	66	No observed effect level	As above

3.82 PHYSICO-CHEMICAL FACTORS AFFECTING TOXICITY

It is well established that water hardness affects nickel toxicity. Toxicity will generally decrease by one order of magnitude with a 20 fold increase in hardness. Other factors affecting toxicity are not well studied. From the limited data available, it does not appear that temperature affects nickel toxicity (Little 1981). Increases in both pH and suspended solids appear to decrease the toxicity of nickel in solution. Both water quality parameters (i.e. increased pH and suspended solids) remove dissolved nickel from solution making it less available to biological organisms (Environment Canada 1979).

Although little specific data is available concerning the interaction of naturally occurring organics and dissolved nickel, (USEPA 1980c) microbial studies have demonstrated that the presence of an extracellular polymer appeared to inhibit the uptake of nickel by *Klebsiella aerogenes* (Rudd *et al.* 1983). Cytotoxicity studies using cultured mammalian cells also report that blood serum constituents (mainly albumin) can effectively bind nickel and prevent its cellular uptake (Fischer and Skreb 1984).

3.83 BIOAVAILABILITY, ACCLIMATION AND ACCUMULATION

.1 Bioavailability

Mainly due to the lack of available data, the free ion (Ni^{+2}) is assumed to be the prevalent form of nickel in water with low concentrations of suspended solids and low total organic carbon. There are few known reactions which would be expected to occur between nickel and anions such as sulphate, chloride, and carbonate in freshwater systems, because of the relatively low concentrations of these substances. The effect on bioavailability of complexation by naturally occurring organic substances is poorly understood (USEPA 1980c).

Like other divalent metals, nickel uptake can be competitively inhibited by the presence of calcium and magnesium. Both of these latter ions appear equally effective in reducing the biological effect of nickel to aquatic organisms.

.2 Acclimation

Although previous investigations have compiled evidence that distinct metal acclimated plant ecotypes have developed over time in metal contaminated (copper and nickel) aquatic environments, McNaughton *et al.* (1974) found no evidence of this occurrence. Similar work by Taylor and Crowder (1983) confirmed this latter work.

Personal communication with researchers in the area of metal toxicity to aquatic organisms at the University of Kentucky revealed that little or no information is available on the acclimation of aquatic organisms to nickel.

.3 Accumulation

Accumulation of nickel varies widely among aquatic plants with bioconcentration factors of 120 for *Sagittaria sagittifolia* to 19,667 in algal periphyton. Bioconcentration factors for zooplankton, clams, and fish have been reported as 643, 262 and 329, respectively (Environment Canada 1979). Despite the information cited by Environment Canada (1979), bioconcentration factors for fish usually appear to be on the order of 30-60 (Birge and Black 1980, USEPA 1980c). Among 48 fish from 11 New York State waters (decapitated and eviscerated) analyzed for nickel (range 0.03 to 0.19 µg/g), the predacious species generally had the highest concentrations.

Bivalves, due to their filter feeding mode of life, tend to show the highest accumulations of nickel and may attain bioconcentration factors of 14,000 in the marine environment. Similarly, benthic organisms exposed to nickel contaminated

sediments may have higher accumulation factors for this metal (Birge and Black 1980).

Several other studies have indicated the absence of nickel biomagnification through the food web. The most *recent* confirmation of this is the report of Watras et al. (1985). While *Scenedesmus obliquus* accumulated nickel to concentrations 30 to 300 times the ambient water concentrations, *Daphnia magna* (in the same system) concentrated nickel to levels only slightly above the ambient water concentration. For *Daphnia*, direct uptake of nickel from solution (as opposed to uptake of ingested nickel) was the primary accumulation vector.

3.84 OTHER AGENCY WATER QUALITY OBJECTIVES

Table 3.8-3 is a comparison of water quality objectives or criteria for nickel as established by other agencies, both national and international. There is a general recognition by most agencies of the effect of hardness on nickel toxicity. This recognition is incorporated into the objective either in the form of a fixed amount of nickel for a given hardness or as a formula in which the value e (2.1828) is raised to an exponent derived from the natural logarithm of the hardness.

Ontario's PWQO of 25 µg/L (unrelated to hardness) is generally more conservative (i.e. lower) than other agencies which attempt to deal with both hardness and nickel toxicity.

The World Health Organization (1984) has determined (based on available toxicological data) that a guideline is not required at present for nickel in drinking water.

TABLE 3.8-3 Comparison of Nickel Water Quality Objectives from Ontario and Other Agencies (for the Protection of Aquatic Life).

Agency	Objective or Criterion
Ontario (1979)	25 µg/L
USEPA (24-hour average not to be exceeded)	56 µg/L at hardness of 50 ppm 96 µg/L at hardness of 100 ppm 160 µg/L at hardness of 200 ppm $e^{(0.76\ [\ln(\text{hardness})]+1.06)}$ for any hardness
(Not to be exceeded at any time) (1980)	1,100 µg/L at hardness of 0 ppm 1,800 µg/L at hardness of 100 ppm 3,100 µg/L at hardness of 200 ppm $e^{(0.76\ [\ln(\text{hardness})]+4.02)}$ for any hardness
Manitoba (1983 Provisional)	56 µg/L at hardness of 50 ppm 96 µg/L at hardness of 100 ppm 160 µg/L at hardness of 200 ppm
Quebec (1984)	$e^{(0.76\ [\ln(\text{hardness})]+1.06)}$
Alberta (1977)	No objective
Saskatchewan (1977)	No objective
Environment Canada (1979)	25 µg/L in soft water 250 µg/L at hardness greater than 150 ppm
International Joint Commission (1978)	25 µg/L
Water Research Centre* Freshwater Fish	50 µg/L at hardness of less than 50 ppm 100 µg/L at hardness of 50 to 100 ppm 150 µg/L at hardness of100 to 200 ppm 200 µg/L at hardness of greater than 200 ppm

TABLE 3.8-3 (Cont'd)

Agency	Objective or Criterion
Other Freshwater Life (1984)	8 µg/L at hardness of less than 50 ppm 20 µg/L at hardness of 50 to 100 ppm 50 µg/L at hardness of 100 to 200 ppm 100 µg/L at hardness of greater than 200 ppm

* Nance and Yates.1984a. Proposed Environmental Quality Standards for List II Substances in Water. Nickel.

3.85 OTHER FACTORS AFFECTING PWQOs

The Environment Canada recommended water quality objectives for nickel in:

- Raw public water supplies (250 µg/L for waters subject to conventional treatment);
- Livestock water (5,000 µg/L);
- Irrigation water (200 to 2,000 µg/L depending on continuous or intermittent use);
- Recreational water (200 µg/L); and
- Industrial water supplies (200 µg/L),

are all above the current Ontario PWQO of 25 µg/L for the protection of aquatic life and will be protected by this latter objective.

3.86 STATUS OF EXISTING PWQO

The data of Birge and Black (1980) demonstrate that nickel concentrations of between 3 and 10 µg/L have the potential to adversely affect the development of fish embryos. However, a major problem exists in relating the laboratory study which produced these values to the real world. The potential importance of removal or detoxification reactions in a real world situation is usually much greater than in laboratory studies. Given the already conservative objective of 25 µg/L, it is recommended that no action be taken to revise this objective. The current scientific literature does not include sufficient information concerning the interaction of nickel with other environmental variables (except hardness) to permit a revision.

3.9 SELENIUM

3.91 AQUATIC TOXICITY REVIEW

Table 3.9-1 presents selected acute toxicity data (i.e. less than or equal to 96 hr) from the USEPA (1980b) Ambient Water Quality Criteria Document (for selenium) and later (i.e. 1980-1985) toxicity data from the published scientific literature. Acutely toxic values for 50% of the vertebrate test populations range from 1,000 to 82,000 µg/L. For invertebrate test populations the range is 100 to 42,400 µg/L.The lower value for invertebrates (i.e.100 µg/L) is the Ontario PWQO.

Table 3.9-2 presents selected chronic toxicity data from the USEPA (1980b) Ambient Water Quality Document (for selenium) and later (i.e. 1980-1985) data from the published scientific literature. The lowest concentration causing an effect was 47 µg/L (for 41 days exposure).This value is approximately half the PWQO of100 µg/L.

Laboratory studies have generally concluded that invertebrate species were more sensitive to selenium (as selenite) than fish. In addition to laboratory studies of chronic selenium toxicity, two chronic selenium pollution episodes in the environment have been dealt with extensively in the published literature.

Chronic selenium exposure in a power plant cooling reservoir in North Carolina, U.S.A., was detailed by Lemly (1985). Selenium entered the reservoir by way of an effluent from a coal ash disposal basin which contained 100-200 µg Se/L. Concentration of selenium in the lake water averaged 10 µg/L. Two years after the initial operation of the plant, 16 of the original 20 species of fish initially present in the reservoir were eliminated. Two species were rendered sterile, but persisted as adults; one species was eliminated but managed to recolonize from a relatively

TABLE 3.9-1 Selected Acute (i.e. less than or equal to 96 hr) Lethality Data for Waterborne Selenium.

Species	Method	Results in ppb	Test Chemical	Reference
VERTEBRATES				
Salmo gairdneri Rainbow trout	LC_{50}, FT, M	7,200	Sodium selenite	USEPA1980b
As above	LC_{50}, FT, M	8,200	As above	As above
As above	LC_{50}, FT, M	8,800	As above	As above
Pimephales promelas Fathead minnow	LC_{50}, FT, M	1,000	As above	As above
Cyprinus carpio Common carp	TLm, S, R	72,000	As above	Sato *et al.* 1980
As above	TLm, S, R,	50,000	As above	As above
As above	TLm, S, R,	35,000	As above	As above
Esox lucius Northern pike	LC_{50}, FT, M	11,000	As above	Kiaverkamp *et al.* 1983b
Catostomus commersoni White sucker	LC_{50}, FT, M	29,000	As above	As above
Pimephales promelas Fathead minnow	LC_{50}, S, U	82,000	Sodium selenate	Watenpaugh and Beitinger 1985
INVERTEBRATES				
Daphnia magna Cladoceran	LC_{50}, FT, M	710	Sodium selenite	USEPA 1980b
As above	LC_{50}, FT, M	430	As above	As above
Hyalella azteca Scud	LC_{50}, FT, M	340	As above	As above
Tanytarsus dissimilis Midge	LC_{50}, FT, M	42,400	Selenium oxide	As above

TABLE 3.9-1 (Cont'd)

Species	Method	Results In ppb	Test Chemical	Reference
Daphnia pulex Cladoceran (Juveniles)	LC_{50}, S, U	600	Sodium selenite	Schultz *et al*.1980
As above	LC_{50}, S, U	100	As above	As above
As above (Adults)	LC_{50}, S, U	1,300	As above	As above
As above	LC_{50}, S, U	500	As above	As above
As above	LC_{50}, S, U	3,870	As above	Reading and Bulkema 1983

S = static test
FT = flow through test
M = concentrations of metal measured during test
U = concentrations of metal not measured during test

TABLE 3.9-2 Effects of Subacute and Chronic (i.e. greater than 96 hr) Exposures to Waterborne Selenium (chemical tested Is sodium selenite, unless otherwise noted).

Species	Duration of Test	Exposure Concentration (ppb)	Result	Reference
VERTEBRATES				
Salmo gairdneri Rainbow trout	9 days	5,400	Lethal to 50% of test population	USEPA 1980b
As above	9 days	6,900	As above	As above
As above	9 days	7,000	As above	As above
As above	41 days	47	Reduction of hatch of eyed embryos	As above
As above	50 weeks	53	Iron content of blood decreased	As above
Pimephales promelas Fathead minnow	14 days	600	Lethal to 50% of test population (Se as selenium dioxide)	As above
Lepomis macrochirus Bluegill (Juveniles)	120 days	10 µg/L	Accumulation of selenium In spleen, heart, liver, kidney, erythrocytes, gill, plasma, white muscle, gonad, intestine, stomach and brain. Possible pathologic enhancement.	Lemly 1982
Salmo gairdneri Rainbow trout (Embryo, larvae)	28 days	5,170	Lethal to 50% of test population	Birge *et al.* 1979
As above	28 days	786	Lethal to 10% of test population	As above
As above	28 days	169	Lethal to 1% of test population	As above
As above (Sac Fry)	90 days	47	Reduced survival and weight; calcium content of bones significantly decreased	Hunn *et al.* 1987
As above	30 days	47	Significant reduction in length	As above

TABLE 3.9-2 (Cont'd)

Species	Duration of Test	Exposure Concentration (µg/L)	Result	Reference
INVERTEBRATES				
Daphnia magna Cladocera	14 days	430	Lethal to 50% of test population	USEPA 1980b
Hyallela azteca Scud	14 days	70	Lethal to 50% of test population	As above
Daphnia pulex Cladoceran	28 days	400-600	Number of live young per brood was depressed	Reading and Bulkema 1983
As above	28 days	800	Appreciable mortality; growth depressed during pre-adult Instars	As above

S = static test
FT = flow through test
M = concentrations of metal measured during test
U = concentrations of metal not measured during test

uncontaminated headwater area and persisted in the reservoir as sterile adults. One species was unaffected. The abundance and diversity of biota other than fishes was not affected.

A second chronic exposure episode occurred in an east Texas reservoir receiving selenium-containing wastes from an electrical generating station operation. Studies documenting the response of individual fish species in the reservoir were documented by Sorensen *et al.* (1982, 1984), Sorensen and Bauer (1984a,b) and Sorensen and Bauer (1983). Histopathological conditions in the fish species examined from the selenium contaminated discharge site included:

- Hyperlobulation of the hepatopancreas;
- Hypoxic vacuolation in proximity to central hepatopancreas veins;
- Proliferative glomerulonephritis in the kidney;
- In situ degeneration of maturing follicles in ovaries;
- Changes in the cellular structure of the gill lamellae and myocardium;
- Hematological abnormalities;
- Significantly higher pancreas cell to liver cell ratios than uncontaminated fish;
- Significantly reduced condition factors compared to uncontaminated fish; and
- Smaller hepatopancreas-weight-to-body-weight ratios than uncontaminated fish.

The average selenium concentration of the reservoir was reported to be 5 µg/L.

Selenium at low levels in a warm water aquatic environment will first manifest itself in fish reproductive aberrations as a result of selenium accumulation through the food chain. This point is reached at water concentrations between 2 and 5 µg/L in soft water. Whether or not this applies to cold, hardwater environments is unknown (A.D. Lemly, personal communication).

A dietary selenium concentration of 13 µg/g dry weight of food has caused elevated mortality, reduced feeding, slower growth, high feed:gain ratios and liver paleness in trout within four weeks of first feeding. The small difference between dietary selenium concentrations which are toxic (i.e. 10-13 µg Se/g dry weight of food) and normal dietary selenium concentrations found in food chain organisms (0.1 to 4.7 µg Se/g) indicates a potential for serious environmental problems (Hodson and Hilton 1983) arising from even small discharges of this element.

The effects of selenium on freshwater plants is less documented than for aquatic animals. Given the work of Lemly (1985), however, it appears that aquatic plants will be protected by objectives derived for the protection of fish.

3.92 PHYSICO-CHEMICAL FACTORS AFFECTING TOXICITY

An evaluation of the available data by the USEPA in 1980 concluded that information was inadequate to evaluate the influence of hardness, alkalinity or pH on the toxicity of selenium. Judging from its known chemistry, however, the aforementioned water quality characteristics were not expected to have much influence on the solubility or toxicity of selenium.

Acute selenium toxicity has been shown to be increased approximately three to five times by a temperature increase of 12°C (USEPA 1980b).

Conversations with Dr. A.D. Lemly (the leading U.S. researcher in the ecological effects of selenium toxicity) revealed that very little is known concerning the effect of water quality parameters such as hardness, alkalinity and pH on selenium toxicity. Much of what is known is documented in private reports to electric power generating companies in the southern U.S. A large study to examine the ecological effects of selenium contamination in the Kesterson National Wildlife Refuge (California) will attempt to answer many of the questions regarding the

ecotoxicology of selenium. This study is slated to begin in 1986.

Selenium toxicity is alleviated by antimony, arsenic, copper, germanium and tungsten (Marier and Jaworski 1983).

3.93 BIOAVAILABILITY, ACCLIMATION AND ACCUMULATION

.1 Bioavailability

As with other elements, oxidation state affects the availability of selenium to organisms. Selenium exists in four oxidation states (-2, 0, +4, and +6). Heavy metal selenides (-2) are insoluble and are removed from the water by precipitation, as is the elemental form (Se°). Inorganic selenites (i.e. SeO_3^{-2}) have an affinity for iron and aluminum oxides forming stable absorption complexes. Alkaline and oxidizing conditions favour the formation and stability of selenates (i.e. SeO_4^{-2}) which have less of an affinity for iron and aluminum oxides (USEPA 1980b).

Although selenates would appear to represent a greater hazard than selenites, the majority of toxicity studies have used selenites. Comparison of the available selenite and selenate toxicity data presented by USEPA (1980b) do not show dramatic differences. Luoma (1983) states that selenite is more available to marine mussels than is selenate.

Chemically, selenium is very similar to sulphur and can easily be converted (or ionically bonded to) various organic compounds (e.g. proteins). While the seleno-organic compounds might be more biologically available, there is little known concerning their toxicity.

Aquatic microorganisms play an important role in reducing the availability of selenium in two ways:

- microbial reduction of selenite; and
- microbial methylation of inorganic selenium.

Several species of microorganisms are able to reduce selenite. In some cases the proceeds through elemental selenium to selenide; in other instances microbial reduction stops at elemental selenium. Both reductions allow the biologically available selenite to be converted to compounds which precipitate from solution. Selenate, however, has not been shown to be microbially reduced.

Biological methylation has been demonstrated to occur in lake sediments under both aerobic and anaerobic conditions. Using inorganic or organic selenium as a substrate, methylation was shown to produce volatile dimethyl selenides.In additional to itspotential for volatilization, dimethyl selenide is also about one five-hundredth as toxic as selenite. Also there is no evidence for its accumulation in the food chain (Faust and Aly 1981).

.2 Acclimation

Selenium is not known to induce tolerance among aquatic organisms by the production of metallothioneins.Its chemicalsimilarity to sulphur and membership in group VIA of the periodic chart (along with oxygen, sulphur and tellurium) would seem to preclude tolerance by any mechanism.Very little information isavailable concerning selenium tolerance and that which is available is not well documented (A.D. Lemly, personal communication).

.3 Accumulation

Waterborne selenium is taken up rapidly by all trout life stages with equilibrium being reached within 96 hr. A marked decrease (15 to 60 fold) occurs in

bioconcentration factors as waterborne concentrations increase from background (0.4 µg/L) to 50 µg/L. A less efficient uptake or more efficient elimination of selenium at higher exposure concentrations may explain this phenomenon. The rate of excretion of selenium absorbed from water is directly proportional to the exposure concentration, which indicates a passive diffusion operation driven by the concentration gradient. Half-lives appear to be a constant (approximately 29 days) regardless of the original exposure concentration (Hodson and Hilton 1983).

Linear increases in selenium trout tissue concentrations are caused by increasing dietary selenium concentrations. Absorption of ingested selenium appears to be very efficient. However, tissue bioconcentration factors (tissue concentration divided by dietary concentration) were found to decrease by 3 to 7 times as dietary concentration increased (from 0.07 to 13.1 µg Se/g). This indicates either a progressively less efficient uptake or a more efficient elimination as dietary concentrations increase (Hodson and Hilton 1983). The major uptake pathway appears to be erythrocyte transport mediated by active oxo-groups on the selenium anion with subsequent exchange at preferential sites (e.g. spleen, heart, liver, kidney, etc.) (Lemly 1982).

The chemical form of selenium bioaccumulating in fish tissue has not as yet been identified. In addition, few attempts have been made in previous studies to differentiate selenium species in tissues and the biologically active forms of the element remain speculative. It has been suggested that enzyme systems may not be able to discriminate between sulphur and selenium at high selenium concentrations. The resulting selenium analogs of various proteins may then find their way into various tissues (e.g. ovary) during normal biological processes. Proof of this would require analytical methods for identifying these selenium analogs both in the diet and body fluids of fish known to bioaccumulate selenium. Unfortunately these analytical methods are either not proven or do not exist (Huhn *et al.* 1987).

3.94 OTHER AGENCY WATER QUALITY OBJECTIVES

Table 3.9-3 is a comparison of water quality objectives or criteria as established (or proposed) by other agencies. Ontario's PWQO (100 µg/L) is well above the objectives for the other provinces and that set by Environment Canada. Only the USEPA's 1980 criterion of 260 µg/L (never to be exceeded) is above Ontario's PWQO. The USEPA is currently revising its criteria for selenium with a draft document due in June 1986.Preliminary indications are that the 260 µg/L criteria will be revised downward.

3.95 OTHER FACTORS AFFECTING PWQOs

The Environment Canada recommended water quality objectives for selenium in:

- Raw public water supplies (50 to 250 µg/L depending on treatment);
- Water for livestock (maximum of 50 µg/L);
- Irrigation water (20-50 depending on continuous or intermittent use);
- Recreational water (50 µg/L); and
- Industrial water supplies (50 to 250 µg/L depending on treatment),

are all generally below the PWQO of 100 µg/L for protection of aquatic life. Thus, some uses (i.e. recreation, livestock watering, raw public supply with simple treatment) would not be protected by a PWQO of 100 µg/L.

The World Health Organization's (1984) guideline for selenium in drinking water is 10 µg/L.

TABLE 3.9-3 Comparison of Selenium Water Quality Objectives from Ontario and Other Agencies (for the Protection of Aquatic Life).

Agency	Objective or Criterion
Ontario (1979)	100 µg/L as total Selenium
USEPA 24 hour average concentration not to be exceeded Not to be exceeded at any time (1980)	 35 µg/L 260 µg/L
Manitoba (1983 Provisional)	35 µg/L (Total Selenite)
Quebec (1984)	10 µg/L
Alberta (1977)	10 µg/L
Saskatchewan (1983)	10 µg/L
Environment Canada (1979 Preliminary)	10 µg/L
International Joint Commission (1981)	1 µg/L

3.96 STATUS OF EXISTING PWQO

New information related to the sub-lethal effects of selenium (both waterborne and dietary) on fish require that the existing PWQO be revised. Currently, the authors of the 1986 USEPA Water Quality Criteria Document for selenium (draft due in June 1986) are attempting to make the new criteria as ecologically meaningful as possible (A.D. Lemly, personal communication). Any revision of the PWQO should place heavy emphasis on this document and ongoing research on the ecotoxicity of selenium.

3.10 SILVER

3.101 AQUATIC TOXICITY REVIEW

Table 3.10-1 presents selected acute toxicity data (i.e. less than or equal to 96 hr) from the USEPA (1980e) Ambient Water Quality Criteria Document (for silver) and later (i.e. 1980-1985) toxicity data from the published scientific literature. Acutely toxic values for 50% of the vertebrate test populations range from 4.9 to 84.4 µg/L. For invertebrate test populations, the range is 0.6 to 4,500 µg/L.

Table 3.10-2 presents selected chronic toxicity data from the USEPA (1980e) Ambient Water Quality Criteria Document (for silver) and later (i.e. 1982-83) data from the published scientific literature. The lowest concentration causing an effect on a vertebrate population would appear to be in the range 0.03-0.06 µg/L (the chronic limit for eyed embryos at 13 month exposure). This value is only slightly below the Ontario PWQO of 0.1 µg/L.

Fish are generally sensitive to silver over a much narrower range of concentrations than are invertebrates (mainly cladocerans). However, the various silver compounds used in laboratory toxicity tests also differ in their toxicity. Silver nitrate, which is an excellent source of free, soluble silver ions, is the most toxic silver compound. Silver chloride, which can yield free silver ions apparently can also form a soluble chloride complex which is less toxic. Silver thiosulphate and both forms of silver sulphide are even less toxic (USEPA 1980e).

Although adverse reactions in plants have been observed at silver concentrations ranging from 30 to 7,500 µg/L, it appears that plants will be protected by objectives derived from animal data (USEPA 1980e).

TABLE 3.10-1 Selected Acute (i.e. less than or equal to 96 hr) Lethality Data for Waterborne Silver.

Species	Method	Results in ppb	Test Water	Reference
VERTEBRATES				
Salmo gairdneri Rainbow trout	LC_{50}, FT, M	5.3	Hardness: 31 ppm	USEPA 1980e
As above	LC_{50}, FT, M	6.2	Hardness: 20 ppm	As above
As above	LC_{50}, FT, M	8.1	Hardness: 26 ppm	As above
As above	LC_{50}, FT, M	13	Hardness: 350 ppm	As above
Pimephales promelas Fathead minnow	LC_{50}, FT, M	11	Hardness: 48 ppm	As above
As above	LC_{50}, FT, M	16	Hardness: 38 ppm	As above
Rhinichthys osculus Speckled dace	LC_{50}, FT, M	4.9	Hardness: 30 ppm	As above
As above	LC_{50}, FT, M	14	Hardness: 250 ppm	As above
Jordanella floridae Flagfish	LC_{50}, FT, M	9.6	Hardness: 48 ppm	As above
Lepomis macrochirus Bluegill	LC_{50}, S, U	64	Hardness: 40 ppm	As above
Pimephales promelas Fathead minnow	LC_{50}, FT, M	12.9	Hardness: 44.4 ppm	Holcombe *et al.* 1983
As above	LC_{50}, FT, M	9.5	Hardness: 44.4 ppm	As above
As above	LC_{50}, FT, M	7.2	Hardness: 44.4 ppm	As above
As above	LC_{50}, FT, M	6.7	Hardness: 44.4 ppm	As above
As above	LC_{50}, S, M	14.0	Hardness: 44.8 ppm	As above
As above	LC_{50}, S, M	14.0	Hardness: 44.8 ppm	As above
As above	LC_{50}, S, M	14.0	Hardness: 44.8 ppm	As above
As above	LC_{50}, S, M	14.0	Hardness: 44.8 ppm	As above

TABLE 3.10-1 (Cont'd)

Species	Method	Results In ppb	Test Water	Reference
Ictalurus punctatus Channel catfish	LC_{50}, FT, M	18.4	Hardness: 44.4 ppm	As above
As above	LC_{50}, FT, M	17.3	Hardness: 44.4 ppm	As above
Pimephales promelas Fathead minnow (No acclimation)	LC_{50}, FT, M	30.0	Hardness: 141 ppm	Birge *et al.* 1984
As above	LC_{50}, FT, M	36.6	Hardness: 141 ppm	As above
As above	LC_{50}, FT, M	37.2	Hardness: 141 ppm	As above
As above (Acclimated to 1.5 µg/L for 7 days)	LC_{50}, FT, M	42.6	Hardness: 141 ppm	As above
As above (Acclimated to1.5 µg/L for 14 days)	LC_{50}, FT, M	41.3	Hardness: 141 ppm	As above
As above (Acclimated to1.5 µg/L for 14 days; de-acclimated for 7 days)	LC_{50}, FT, M	24.5	Hardness: 141 ppm	As above
As above (Acclimated to 15 µg/L for 7 days)	LC_{50}, FT, M	45.6	Hardness: 141 ppm	As above
As above (Acclimated to 15 µg/L for 14 days)	LC_{50}, FT, M	46.4	Hardness: 141 ppm	As above
As above (Acclimated to 15 µg/L for 14 days; deacclimated for 7 days	LC_{50}, FT, M	29.1	Hardness: 141 ppm	As above

TABLE 3.10-1 (Cont'd)

Species	Method	Results in ppb	Test Water	Reference
As above (Acclimated to 15 µg/L for 14 days; deacclimated for 14 days)	LC_{50}, FT, M	31.0	Hardness: 141 ppm	As above
Pimephales promelas Fathead minnow	LC_{50}, FT, M	15.2	Hardness: 44.3 ppm	Lima *et al*. 1982
As above	LC_{50}, FT, M	11.6	Hardness: 44.3 ppm	As above
As above	LC_{50}, FT, M	10.7	Hardness: 44.3 ppm	As above
As above	LC_{50}, FT, M	10.7	Hardness: 44.3 ppm	As above
Jordanella floridae Flagfish	LC_{50}, FT, M	43.7	Hardness: 44.3 ppm	As above
As above	LC_{50}, FT, M	25.9	Hardness: 44.3 ppm	As above
As above	LC_{50}, FT, M	15.8	Hardness: 44.3 ppm	As above
As above	LC_{50}, FT, M	9.2	Hardness: 44.3 ppm	As above
Salmo gairdneri Steelhead trout (0.2 g)	LC_{50}, FT, M	9.2	Hardness: 36 ppm Temperature: 12°C	Nebeker *et al.* 1983
Salmo gairdneri Rainbow trout (6.6 g)	LC_{50}, S, M	72.9	Hardness: 40 ppm Temperature: 10°C	As above
As above	LC_{50}, S, M	84.4	Hardness: 37 ppm Temperature: 9°C	As above
As above (0.2 g)	LC_{50}, S, M	10.9	Hardness: 26 ppm Temperature: 12°C	As above
As above (0.3 g)	LC_{50}, S, M	8.5	Hardness: 35 ppm Temperature: 12°C	As above
As above (0.2 g)	LC_{50}, FT, M	8.6	Hardness: 29 ppm Temperature: 12°C	As above
As above (0.4 g)	LC_{50}, FT, M	9.7	Hardness:42 ppm Temperature:12°C	As above

TABLE 3.10-1 (Cont'd)

Species	Method	Results in ppb	Test Water	Reference
Pimephales promelas Fathead minnow	LC_{50}, S, M	9.4	Hardness: 38 ppm Temperature: 20°C	As above
As above (0.1g)	LC_{50}, S, M	9.7	Hardness: 39 ppm Temperature: 21°C	As above
As above	LC_{50}, FT, M	5.6	Hardness: 40 ppm Temperature: 22°C	As above
As above	LC_{50}, FT, M	7.4	Hardness: 36 ppm Temperature; 22°C	As above
INVERTEBRATES				
Daphnia magna Cladoceran	LC_{50}, S, U	1.5	Hardness: 40 ppm	USEPA 1980e
Gammarus pseudolimnaeus Scud	LC_{50}, FT, M	4,500	Hardness: 48 ppm	As above
Tanytarsus dissimilis Midge	LC_{50}, FT, M	3,200	Hardness: 48 ppm	As above
Daphnia pulex Cladoceran	LC_{50}, S, U	14		Mount and Norbeg 1984
Cerlodaphnia reticulata Cladoceran	LC_{50}, S, U	11		As above
Simocephalus vetulus Cladoceran	LC_{50}, S, U	15		As above
Aplexa hypnorum Snail	LC_{50}, R, M	241	Hardness: 50.4	Holcombe *et al.* 1983
Gammarus pseudolimnaeus Scud	LC_{50}, FT, M	4.7	Hardness: 44.3 ppm	Lima *et al*. 1982
As above	LC_{50}, FT, M	4.7	Hardness: 44.3 ppm	As above
As above	LC_{50}, FT, M	4.5	Hardness: 44.3 ppm	As above
As above	LC_{50}, FT, M	4.5	Hardness: 44.3 ppm	As above

TABLE 3.10-1 (Cont'd)

Species	Method	Results in ppb	Test *Water*	Reference
Tanytarsus dissimulis Midge	LC_{50}, S, M	5,030	Hardness:44.3 ppm	As above
As above	LC_{50}, S, M	3,160	Hardness:44.3 ppm	As above
Daphnia magna Cladoceran	LC_{50}, S, M	1.1	Hardness:38 ppm Temperature: 20°C	Nebeker *et al.* 1983
As above	LC_{50}, S, M	0.6	Hardness:40 ppm Temperature:20°C	As above
As above	LC_{50}, S, M	1.1	Hardness:33 ppm Temperature: 20°C	As above
As above	LC_{50}, S, M	12.5	Hardness:33 ppm Temperature:20°C	As above

S = static test
R = static test with renewal
FT = flow through test
U = concentrations of metal not measured during test
M = concentration of metal measured during test

TABLE 3.10-2 Effects of Subacute and Chronic (I.e. greater than 96 hr) Exposures to Waterborne Sliver.

Species	Duration of Test	Exposure Concentration (ppb)	Result	Reference
VERTEBRATES				
Salmo gairdneri Rainbow trout	28 days	10	Lethal to 50% of test population	USEPA 1980e
As above (Eyed embryos)	13 months	0.03-0.06	Chronic limits	As above
As above (Green embryos)	10 months	0.18-0.40	Chronic limits	As above
Micropterus salmoides (Largemouth bass)	B days	110	Lethal to 50% of test population	As above
Ambystoma opacum (Salamander)	8 days	240	Lethal to 50% of test population	As above
Salmo gairdneri Rainbow trout	18 months	0.09-0.17	Long term no effect level	Davies *et al.* 1978
INVERTEBRATES				
Daphnia magna Cladoceran	7 days	1.6-4.1	Chronic limit	Nebeker 1982
As above	7 days	8.8-19.4	Chronic limit	As above
As above	7 days	3.4-8.0	Chronic limit	*As* above
As above	7 days	2.7-3.9	Chronic limit	Nebeker *et al.* 1983
As above	7 days	10.5-21.2	Chronic limit	*As* above
As above	7 days	19.8-41.2	Chronic limit	*As* above
PLANTS				
Lemna minor Vascular plant	28 days	270	Phytotoxlc to 50% of plants	(Brown and Rattlgan 1979)

3.102 PHYSICO-CHEMICAL FACTORS AFFECTING TOXICITY

Although some contradictory evidence exists, water hardness is considered to reduce silver toxicity. Unlike other antagonistic metal-water hardness interactions, reduction in silver toxicity is thought to be the result of increased anion complexation and precipitation with increased hardness (i.e. increased anionic strength) (USEPA 1981). The effect of organics (particulate and dissolved) on the toxicity of silver was demonstrated by side-by-side test of the effect of added food on *Daphnia* toxicity tests. The presence of the food decreased toxicity by three times in one comparison (USEPA 1980e).

Other factors affecting the aquatic toxicity of silver are:

- temperature (increased temperature increases toxicity);
- dissolved oxygen concentration (decreased oxygen increases toxicity);
- pH (decreasing pH increases toxicity);
- the form of the silver (inorganic and organic complexes are less toxic than the free ion); and
- fish size and species (smaller fish are more sensitive than larger fish) (USEPA 1981).

3.103 BIOAVAILABILITY, ACCLIMATION AND ACCUMULATION

.1 Bioavailability

In natural water, the monovalent ion (Ag^+) is the most readily available form and is of chief environmental concern. in addition, the monovalent ion may also exist in various degrees of association with a large number of inorganic ions such as sulphate, bicarbonate, nitrate and chloride. From the various laboratory tests using different silver compounds, it is inferred that inorganic complexation reduces

bioavailability. Sorption also appears to be a dominant process in reducing the bioavailability of silver. Manganese dioxide, iron compounds and clay minerals allhave some degree of adsorptive affinity for silver and are involved in its transport (by settling) to aquatic sediments. Silver sulfides are extremely insoluble and in the presence of oxidizing conditions remove silver from availability to biological organisms. Silver may also exist as a dissolved metal-organic complex. Although this form of silver is generally considered to be less available for uptake by aquatic organisms, definitive studies have not been conducted.

.2 Acclimation

Birge *et al.* (1984) found that pretreatment of laboratory populations of fathead minnows for seven and 14 days with 1.5 and 15 µg Ag/L resulted in an increased tolerance of silver in acute toxicity tests. The change appears to be minimal, however, and of doubtful statistical significance. Similar small changes in tolerance were reported for the very low and the very high pre-exposures, and the results may in fact represent the usual variation in within-lab testing. Upon return to clean water, the LC_{50} descended below the control value by a proportion that was as great as the reported increase following pre-exposure.

.3 Accumulation

Algae can accumulate silver from the water on the order of 100 times the water concentration (Taylor *et al.* 1980). This mechanism of accumulation appears to be the result of polyfunctional weakly-acidic cation exchangers on the algal cell wall surface (Stary and Kratzer 1984). The silver accumulated by the algae is not transferred to primary consumers such as *Daphnia*. Both invertebrates and fish can accumulate silver from the water, however, organisms at higher trophic levels accumulate less per unit weight then organisms at lower trophic levels. There is no evidence for the biomagnification of silver through the food web.

Typical bioconcentration factors for silver in fish accumulated from water range from 15 to 240.

3.104 OTHER AGENCY WATER QUALITY OBJECTIVES

Table 3.10-3 is a comparison of water quality objectives of criteria as established (or proposed) by other agencies. Ontario's PWQO (0.1 µg/L) is equal to or lower than all other objectives presented in Table 3.10-3. The Ontario PWQO is an order of magnitude lower than the USEPA's criterion for silver in soft water (i.e. 50 ppm as calcium carbonate).

3.105 OTHER FACTORS AFFECTING PWQOs

The Environment Canada recommended water quality objectives for silver in:

- Raw public water supplies (50 to 200 µg/L depending on treatment);
- Recreational water (50 µg/L); and
- Industrial water supplies (50 to 200 µg/L depending on treatment),

are all above the Ontario PWQO for the protection of aquatic life and these uses are protected by the 0.1 µg/L objective. Insufficient information was available to Environment Canada for establishing water quality objectives for silver in water used for livestock watering and irrigation.

TABLE 3.10-3 Comparison of Silver Water Quality Objectives from Ontario and Other Agencies (for the Protection of Aquatic Life).

Agency	Objective or Criterion
Ontario (1979)	0.1 µg/L
USEPA Not to be exceeded at any time (1980)	1.2 µg/L at hardness of 50 ppm 4.1 µg/L at hardness of 100 ppm 13 µg/L at hardness of 200 ppm $e^{(1.72\ [\ln\ (\text{hardness})]\ -\ 6.52)}$
Manitoba (1983 Provisional)	0.1µg/L
Alberta (1977)	50 µg/L
Saskatchewan (1983)	50 µg/L
Environment Canada (1979 Preliminary)	0.1 µg/L
International Joint Commission (1982)	0.1µg/L

3.106 STATUS OF EXISTING PWQO

The existing Ontario PWQO for silver of 0.1 µg/L is within the range of concentrations for the long-term no effect level for 18 months exposure (i.e. 0.09-0.17 µg/L) using rainbow trout. More recent data has not shown significant effects below this concentration of silver in water. In addition, silver has the ability to be taken up by adsorption to algal cell walls and other particulate material occurring in natural waters thereby reducing its bioavailability. For these reasons, it is recommended that the existing PWQO for silver remain in effect without revision.

The USEPA is scheduled to revise their water quality criterion for silver in September 1986.

3.11 ZINC

3.111 AQUATIC TOXICITY REVIEW

Table 3.11-l presents selected acute toxicity data from the USEPA (1980d) Ambient Water Quality Criteria Document (for zinc) and additional published scientific data. A review of the toxicity data demonstrated comparatively little was published after 1980. It was very apparent, however, that a great deal of toxicity information was published in 1978. As the latest publication referenced in the MOE rationale document (MOE 1979) was 1975, it was decided to include the 1978 data cited by the USEPA (1980d) in their Ambient Water Quality Document. Generally, this acute data is for toxicity tests of 96 hours duration or less. An exception is the data cited from Bradley and Sprague (1985b) in which toxicity tests (for LC_{50}'s) were conducted for 96 to 120 hours. Acutely toxic values for 50% of the vertebrate test populations range from 93 to 103,000 µg/L. For invertebrate test populations, the range is 68 to 2,300 µg/L. The current Ontario PWQO for zinc (30 µg/L) is approximately four tenths of the lowest acutely toxic value.

Table 3.11-2 presents selected chronic toxicity data from the USEPA (1980d) Ambient Water Quality Criteria document (for zinc). For the same reason stated above, information published in 1978 and later in the USEPA document was used in Table 3.11-2. The lowest value in Table 3.11-2 causing an effect (i.e. 173 µg/L for 40 days exposure) is almost six times higher than the Ontario PWQO of 30 µg/L. The value 173 µg/L is also above the previously mentioned acutely toxic values of 93 and 68 µg/L. These latter values were obtained under conditions of low water hardness.

Although the most recent data (i.e. 1978 and later) does not demonstrate an increased sensitivity of aquatic plants over that of animals, the USEPA (1980d) states that zinc concentrations ranging from 30 to 21,600 µg/L have been shown to reduce growth in various plant species.

TABLE 3.11-1 Selected Acute (i.e. less than or equal to 96 hr) Lethality Oates *for* Waterborne Zinc.

Species	Method	Results In ppb	Test Water	Reference
VERTEBRATES				
Oncorhynchus kisutch Coho salmon	LC_{50}, FT, M	905	Hardness:25 ppm	USEPA 1980d
Oncorhynchus nerka Sockeye salmon	LC_{50}, FT, M	749	Hardness:22 ppm	As above
As above (Zn acclimated)	LC_{50}, FT, M	1,660	Hardness:22 ppm	As above
Oncorhynchus tshawytscha Chinook salmon (Swimup)	LC_{50}, FT, M	97	Hardness:24 ppm	As above
As above (Parr)	LC_{50}, FT, M	463	Hardness:22 ppm	As above
As above (Smolt)	LC_{50}, FT, M	701	Hardness:24 ppm	As above
Salmo gairdneri Rainbow trout (Alevin)	LC_{50}, FT, M	815	Hardness:22 ppm	As above
As above (Swim up)	LC_{50}, FT, M	93	Hardness:22 ppm	As above
As above (Parr)	LC_{50}, FT, M	136	Hardness:24 ppm	As above
As above (Juvenile)	LC_{50}, FT, M	370	Hardness:47 ppm	As above
As above	LC_{50}, FT, M	517	Hardness:47 ppm	As above
As above	LC_{50}, FT, M	756	Hardness:44 ppm	As above
As above	LC_{50}, FT, M	2,510	Hardness:178 ppm	As above
As above	LC_{50}, FT, M	2,960	Hardness:179 ppm	As above

TABLE 3.11-1 (Cont'd)

Species	Method	Results in ppb	Test Water	Reference
Salvelinus fontinalis Brook trout	LC_{50}, FT, M	2,120	Hardness: 47 ppm	As above
As above	LC_{50}, FT, M	2,420	Hardness: 44 ppm	As above
As above	LC_{50}, FT, M	6,140	Hardness: 178 ppm	As above
As above	LC_{50}, FT, M	6,980	Hardness: 179 ppm	As above
As above	LC_{50}, FT, M	4,980	Hardness: 170 ppm	As above
Agosia chrysogaster Longfin dace	LC_{50}, R, M	790	Hardness: 217 ppm	As above
Pimephales promelas Fathead minnow	LC_{50}, FT, M	600	Hardness: 46 ppm	As above
Ptychochellus oregonensis Northern squawfish	LC_{50}, FT, M	3,498	Hardness: 20-30 ppm	Andros and Garton 1980
As above	LC_{50}, FT, M	3,693	Hardness: 20-30 ppm	As above
Lepomis macrochirus Bluegill	LC_{50}, FT, M	3,600	Hardness: 21-59 ppm	Thompson *et al.* 1980
As above		3,000	Hardness: 21-59 ppm	As above
Salmo gairdneri Rainbow trout (Juvenile)	LC_{50}, FT, M	880	Hardness: 31.4 ppm Alkalinity: LT 1.0 ppm, pH:5.56	Bradley and Sprague 1985
As above	LC_{50}, FT, M	11,100	Hardness: 389 ppm Alkalinity: LT T.0 ppm, pH:5.59	As above
As above	LC_{50}, FT, M	9,950	Hardness: 394 ppm Alkalinity: LT 1.0 ppm, pH:5.46	As above
As above	LC_{50}, FT, M	170	Hardness: 30.2 ppm Alkalinity: 8.1ppm pH:7.00	As above
As above	LC_{50}, FT, M	190	Hardness: 31.8 ppm Alkalinity: 23.8 ppm pH:7.04	As above

TABLE 3.11-1 (Cont'd)

Species	Method	Results In ppb	Test Water	Reference
As above	LC_{50}, FT, M	110	Hardness: 31.3 ppm Alkalinity: 10.8 ppm pH:6.97	As above
As above	LC_{50}, FT, M	4,460	Hardness: 387 ppm Alkalinity: 8.6 ppm pH:6.99	As above
As above	LC_{50}, FT, M	5,160	Hardness: 389 ppm Alkalinity: 24.3 ppm pH:7.05	As above
As above	LC_{50}, FT, M	4,530	Hardness: 30.9 ppm Alkalinity: 23.7 ppm pH:9.01	As above
As above	LC_{50}, FT, M	2,800	Hardness: 40 ppm Temperature:15°C	USEPA 1980d
As above	LC_{50}, FT, M	1,560	Hardness: 40 ppm Temperature:15°C	As above
As above	LC_{50}, FT, M	2,100	Hardness: 40 ppm Temperature:30°C	As above
Carassius auratus Goldfish	LC_{50}, FT, M	103,000	Hardness: 40 ppm Temperature:5°C	As above
As above	LC_{50}, FT, M	40,000	Hardness: 40 ppm Temperature:15°C	As above
As above	LC_{50}, FT, M	24,000	Hardness: 40 ppm Temperature:30°C	As above
Notemigonius crysoleucus Golden shiner	LC_{50}, FT, M	11,400	Hardness: 40 ppm Temperature: 5°C	As above
As above	LC_{50}, FT, M	7,760	Hardness: 40 ppm Temperature:15°C	As above
As above	LC_{50}, FT, M	8,330	Hardness: 40 ppm Temperature:30°C	As above
Lepomis macrochirus Bluegill	LC_{50}, FT, M	23,000	Hardness: 40 ppm Temperature:5°C	As above

TABLE 3.11-1 (Cont'd)

Species	Method	Results in ppb	Test Water	Reference
As above	LC_{50},FT, M	19,100	Hardness:40 ppm Temperature:15°C	As above
As above	LC_{50}, FT, M	8,850	Hardness:40 ppm Temperature:30°C	As above
INVERTEBRATES				
Daphnia magna Cladoceran	LC_{50}, S, U	2,300	Hardness:45 ppm Temperature:5°C	USEPA 1980d
As above	LC_{50}, S,U	1,700	Hardness:45 ppm Temperature:10°C	As above
As above	LC_{50}, S, U	1,100	Hardness:45 ppm Temperature:15°C	As above
As above	LC_{50}, S,U	560	Hardness:45 pm Temperature:25°C	As above
Daphnia pulex Cladoceran	LC_{50}, S, M M	1,600	Hardness:45 ppm Temperature:5°C	As above
As above	LC_{50}, S, M	1,200	Hardness:45 ppm Temperature:10°C	As above
As above	LC_{50}, S, M	940	Hardness:45 ppm Temperature:15°C	As above
As above	LC_{50}, S, M	280	Hardness:45 ppm Temperature:25°C	As above
As above	LC_{50}, R, M	107	-	Mount and Norberg 1984
Daphnia magna Cladoceran	LC_{50}, R, M	68	-	As above
Cerlodaphnia reticulate Cladoceran	LC_{50}, R, M	76	-	As above

S = Static test
R = Static test with renewal
FT = Flow through test
M = Concentrations of metal measured during test
U= Concentrations of metal not measured during test

TABLE 3.11-2 Effects of Subacute and Chronic (i.e. greater than 96 hr) Exposures to Waterborne Zinc.

Species	Duration of Test	Exposure Concentration (ppb)	Result	Reference
VERTEBRATES				
Oncorhynchus nerka Sockeye salmon	115 hr	447	Lethal to 50% of test population	USEPA 1980d
As above (Zn acclimated)	115 hr	GT 630	Lethal to 50% of test population	As above
Salmo salar Atlantic salmon	21 days	1,450	Lethal to 50% of test population	As above
As above	21 days	1,600	Lethal to 50% of test population	As above
As above	21 days	510	Lethal to 50% of test population	As above
As above	21 days	1,460	Lethal to 50% of test population	As above
As above	21 days	340	Lethal to 50% of test population	As above
As above	21 days	350	Lethal to 50% of test population	As above
Poecilla reticulata GUPPY	134 days	607	Reduced wet weight of females by 40%	Pierson 1981
As above	70 days	173	Significantly fewer females reach maturation	As above
As above	70 days	607	Significantly fewer females give birth	As above
Pimephales promelas Fathead minnow	56 days	152-294 (Avg. 223)	84% mortality	Spear1981
As above	30 days	480	Growth reduction in test population	As above

TABLE 3.11-2 (Cont'd)

Species	Duration of Test	Exposure Concentration (ppb)	Result	Reference
INVERTEBRATES				
Chilomonas paramecium	163 hr	LT 5,000	Lethal to 50% of test population	Spear 1981
Acroneuria lycoris Stonefly	11 days	32,000	Lethal to 50% of test population	Mance and Yates 1984b
Pteronarcys californica Stonefly	14 days	GT 13,900	Lethal to 50% of test population	As above
PLANTS				
Chlamydomonas sp. Algae	5 days	15,000	Reduced growth rate by 65%	USEPA 1980d
Scenedesmus quadricauda Alga	5 days	20,000	Reduced growth rate by 25%	As above
Cyclotella meneghiniana Alga	5 days	20,000	Reduced growth rate by 65%	As above
Lemna minor Duckweed	28 days	67,700	Lethal to 50% of test population	As above
Elodea canadensis Vascular plant	28 days	22,500	Lethal to 50% of test population	As above

GT = Greater than
LT = Less than

Algae appears to be more sensitive than macrophytes, with *Selenastrum capricornutum* being the most sensitive of the algal species tested. The USEPA considers the potential for growth inhibition at low zinc levels to be of ecological importance.

3.112 PHYSICO-CHEMICAL FACTORS AFFECTING TOXICITY

The following factors are known to influence the toxicity of zinc:

- Hardness;
- Temperature;
- Dissolved Solids; and
- pH.

Water hardness is the most well documented of the above factors. This water quality parameter may produce variations in zinc toxicity by a factor of over 50 in vertebrate species. The influence of hardness on invertebrate toxicity is not as well documented and suggests a smaller effect. The calcium ion has been indicated as the agent responsible for the reduction of zinc toxicity, apparently by reducing the permeability of cell membranes or by directly protecting the biochemical processes with which zinc interferes (Little 1980).

Several studies have investigated the relationship between temperature and zinc toxicity. Less resistance to zinc was found in the goldfish and bluegill as the temperature of water was successively raised from 5 to 15 to 30°C. Rainbow trout and the golden shiner, however, did not show similar reactions. Other research in the temperature-toxicity relationship with Hudson River fish did not find significant differences in zinc sensitivity with changes in temperature (USEPA 1980d). These conflicting results confirm the general conclusion of Sprague (1985) that temperature effects on toxicity may cause either increased or decreased toxicity and in general are not major if fish are acclimated to the temperature at which exposure

takes place.

The relationship between temperature and zinc toxicity was well defined for Atlantic salmon by Hodson and Sprague (1975). Differences on threshold LC_{50}'s were not great for fish tested at their own acclimation temperature of 3, 11 or 19°C. Zinc was slightly more toxic at the cold temperature than at the warmest temperature. Fish were less tolerant of zinc if tested at a temperature lower than their acclimation temperature. They were more tolerant if tested at a temperature higher than their acclimation temperature.

Increased dissolved solids (primarily the mono and divalent cations and anions) electrostatically inhibit the ability of zinc to approach the absorption or binding sites of the organism (USEPA 1980d).

There is conflicting information in the scientific literature regarding the influence of pH on zinc toxicity, with reports of both increasing and decreasing toxicity with increasing pH (i.e. 6 to 8). Two competing mechanisms appear to be operating with respect to zinc toxicity and pH. Dissolved zinc becomes increasingly toxic as the pH rises. However, at higher pH the dissolved zinc tends to precipitate from solution as very fine particulate material. This precipitate is also toxic to fish.

There is some data to support an inverse relationship between dissolved oxygen levels and zinc toxicity. Lower dissolved oxygen levels generally increase fish respiration thereby increasing dissolved zinc contact with the gills and lowering the LC_{50} value.

Sensitivity to zinc generally decreases among salmonid species from the swim-up fry stage to the parr stage.

Several types of interaction between zinc and other metals are reported in the literature and some data is conflicting. Zinc is known to suppress the toxicity of lead. The relationship between copper and zinc is less clear. Some investigations report a synergy of copper and zinc toxic reactions while others report antagonism or additivity. Finlayson and Verrue (1982) reported that a decrease in the copper:zinc ratio of 1:3 to 1:2 decreased the toxicity of the mixtures as a result of greater antagonism between the metals. Additional studies with copper-zinc-cadmium mixtures indicated either independent or antagonistic behaviour.

The toxicity of phenol was also additive when in combination with zinc and copper. Chronic exposures of aquatic organisms to zinc reduced the survival time when subsequently exposed to acute concentrations of a second toxicant (both organic and inorganic) (Environment Canada 1980).

Natural chelating agents such as humic acid apparently have little or no effect on the acute toxicity of zinc to fish in soft water. Whether this is due to the antagonistic behaviour of other divalent ions (e.g. calcium) or simply the inability of zinc to form a stable zinc-humic acid complex is unknown. The presence of man-made chelating agents (i.e. NTA and EDTA) has been demonstrated to decrease the toxicity of zinc.

3.113 BIOAVAILABILITY, ACCLIMATION AND ACCUMULATION

.1 Bioavailability

In aqueous solution, zinc exhibits amphoteric properties, dissolving in acids to form hydrated zinc (II) cations and under very alkaline conditions, exhibiting the properties of an anion (e.g. $Zn(OH)_4^{-2}$). Zinc forms complexes with a variety of organic and inorganic ligands which are readily soluble under the conditions of most natural waters producing a bioavailable hydrated Zn(II) cation.

Reduction in bioavailability is accomplished mainly by adsorption to particulate surfaces and precipitation. Most of the zinc introduced into the aquatic environment is partitioned between soluble and particulate phases. Adsorption of zinc by hydrous metal oxides (e.g. magnesium, manganese and iron hydroxides), clay minerals, and particulate organic material (e.g. algal cell walls) is probably the dominant direction of the partitioning. The degree of adsorption is dependent on the nature of the sorbent as well as the pH of the water.

Precipitation of zinc as a sulfide, hydroxide or carbonate (in reducing environments or those with hard or high pH water) might also reduce the availability of zinc to biological organisms.

While precipitation might make the zinc less bioavailable, one published report showed an increased toxicity of zinc as a suspended solid by gill abrasion and increased mucosis.

.2 Acclimation

Rainbow trout previously exposed to 2,090 µg/L zinc had an increased tolerance of the metal (as measured by LC_{50}'s) by a factor of 2.5. The induction of the tolerance occurred within seven days. The results of studies on tolerance induction suggests the synthesis of metallothionein (a heat-stable, sulphydral-rich protein) by the gill and liver tissue of the organism. Although metallothioneindoes not appear to bind and store excess zinc, it may increase the ability of the fish to regulate internal zinc concentrations resulting in a reduced rate of zinc accumulation (Bradley *et al.* 1985).

Rahel's (1981) work with zinc tolerance of laboratory population of flagfish suggested that acute zinc exposure did not cause genetic changes specifically related to zinc tolerance. A population of common shiners (*Notropis cornutus*) inhabiting a zinc-polluted stream were found to be as tolerant to zinc as the same species from

two nearby unpolluted streams.

Tolerance is also influenced by fish size. Tolerance of zinc was reduced by a factor of 3.2 when accompanied by an increase in weight from 1.7 to 29.0 g (Bradley and Sprague 1985a).

.3 Accumulation

The major route of zinc accumulation is via the gills with accumulation rates of about 40 µg/g-hr reported for a variety of different fish sizes (Bradley and Sprague 1985a). Bioconcentration factors for zinc determined with two freshwater fish and two invertebrate species were 51 and 432 (for fish) and 107 and 1,130 (for invertebrates) (USEPA 1980d).

Zinc accumulation by aquatic organisms depends on the trophic level. Benthic insects generally have higher concentrations than fish, and omnivorous fish accumulate more zinc than piscivorous species.

Zinc concentrations in algae reflect the relative concentrations of zinc in the water but some algal species may accumulate zinc by a factor of 2,900.

3.114 OTHER AGENCY WATER QUALITY OBJECTIVES

Table 3.11-3 is a comparison of water quality objectives or criteria as established (or proposed) by other agencies, both national and international. There is the recognition by most agencies of the part water hardness plays in reducing zinc toxicity. Ontario's PWQO of 30 µg/L is the lowest (with the exception of one objective by the EIFAC) of all the objectives or criteria.

TABLE 3.11-3 Comparison of Zinc Water Quality Objectives from Ontario and Other Agencies (for the Protection of Aquatic Life).

Agency	Objective or Criterion
Ontario (1979)	30 µg/L
USEPA 24 hour average concentration not to be exceeded (1980)	180 µg/L at hardness of 50 ppm 320 µg/L at hardness of100 ppm 570 µg/L at hardness of 200 ppm $e^{(0.83\ [\ln(\text{hardness})]+1.95)}$ for any hardness
Manitoba (1983 Provisional)	47 µg/L
Quebec (1984)	47 µg/L
Alberta (1977)	50 µg/L
Saskatchewan (1983)	50 µg/L
Environment Canada (1980)	50 µg/L at hardness 0 to 120 ppm 100 µg/L at hardness 120 to 180 ppm 200 µg/L at hardness 180 to 300 ppm 300 µg/L at hardness of greater than 300 ppm
International Joint Commission (1978)	30 µg/L
EIFAC Salmonid fish (95 percentile concentration of 'soluble' zinc) (1982)	30 µg/L at hardness of10 ppm 200 µg/L at hardness of 50 ppm 300 µg/L at hardness of100 ppm 500 µg/L at hardness of 500 ppm
Coarse fish except minnows (95 percentile concentration of 'soluble' zinc) (1982)	300 µg/L at hardness of 10 ppm 700 µg/L at hardness of 50 pm 1,000 µg/L at hardness of100 ppm 2,000 µg/L at hardness of 500 ppm

TABLE 3.11-3 (Cont'd)

Agency	Objective or Criterion
Water Research Centre*	8 µg/L at hardness of 10 ppm
Salmonid fish	50 µg/L at hardness of 50 ppm
(1984)	75 µg/L at hardness of 100 ppm
	125 µg/L at hardness of 500 ppm
Coarse fish	75 µg/L at hardness of 10 ppm
(1984)	175 µg/L at hardness of 50 ppm
	250 µg/L at hardness of 100 ppm
	500 µg/L at hardness of 500 ppm

* Mance and Yates. 1984b. Proposed Environmental Quality Standards for List II Substances in Water. Zinc.

In view of the objectives and criteria established by other agencies, 30 µg/L might be considered over-protective. However, Ontario's PWQO's are specifically designated for the protection of all aquatic organisms at all times. Thus, reports of zinc concentrations as low as 30 µg/L affecting algal growth must be considered in any evaluation of the objective.

3.115 OTHER FACTORS AFFECTING PWQOs

Environment Canada recommended water quality objectives for zinc in:

- Raw public water supplies (5,000 to 10,000 µg/L depending in pre-distribution treatment);
- Livestock water (50,000 µg/L);
- Irrigation water (l,000 to 5,000 µg/L depending on soil pH);
- Recreational water (5,000 µg/L); and
- Industrial water supplies (5,000 to 10,000 µg/L depending on pre-distribution treatment),

are all much larger than the PWQO for the protection of aquatic life and are protected by this letter objective.

3.116 STATUS OF EXISTING PWQO

A great deal of information concerning zinc in the aquatic environment has become available since 1975 (the latest reference cited by the MOE rationale document). This information serves to reinforce MOE's 1979 conclusion that a maximum concentration of 30 µg/L will protect all aquatic organisms. While individual species of algae in the laboratory might be affected by a concentration of 30 µg/L, phytoplankton and periphyton assemblages in nature are extremely plastic and resilient. In addition, the redundancy of organism types in phytoplankton and

periphyton assemblages make the effect of reduced growth on one species insignificant in comparison to the overall function of the algal community.

Thus, it is recommended that the PWQO for zinc of 30 µg/L not be revised. Consideration should be given to relating the PWQO of 30 µg Zn/L to a specific water hardness or water hardness range and specifying other concentrations of zinc for other levels of water hardness.

PART 4.0

CANDIDATE ELEMENTS FOR PWQ0s

4.0 CANDIDATE ELEMENTS FOR PWQOs

In the following sections of this report, 11 candidate elements are reviewed for the possibility of establishing a PWQO for each individual element. These candidate elements are:

- Antimony;
- Barium;
- Boron;
- Cesium;
- Cobalt;
- Manganese;
- Molybdenum;
- Strontium;
- Thallium;
- Tin; and
- Vanadium.

This review describes the readily available toxicity data and information concerning the fate and effect of these elements in the aquatic environment. Generally, published reviews of these elements in the aquatic environment were not available and individual scientific papers and documents had to be used as sources of information.

4.1 ANTIMONY

4.11 AQUATIC TOXICITY REVIEW

Table 4.1-1 summarizes the limited acute toxicity data for antimony. The lowest acutely toxic value (for 50% of the test population) is 21,900 µg/L. The acutely toxic values for invertebrates range from 9,000 to 19,800 µg/L. Available data for aquatic plants (i.e. algae) seem to indicate that these organisms are much more sensitive to antimony than aquatic animals.

Table 4.1-2 presents selected chronic toxicity data for vertebrates and invertebrates. Although there is not enough invertebrate data to draw any conclusions, the vertebrate data show a wide range of values producing a toxic response in some portion of the test population. Embryonic stages can be affected at concentrations of antimony as low as 3.8 µg/L. There is no information regarding chronic toxicity to plants.

4.12 FATE AND EFFECT AND THE AQUATIC ENVIRONMENT

Antimony is a brittle, silvery metal or metalloid which has a variety of industrial uses, principally as a flame retarding agent. It is a naturally-occurring element with reported mean concentration of 1.1 µg/L in freshwaters. This concentration may be anomalous, in as much as it reflects older measurements which may not be completely accurate.

The limited amount of material available for this review provided insufficient data to assess possible effects of water quality on toxicity to aquatic life. A single study reported no detectable bioconcentration of antimony by bluegills over a 28-day exposure.

TABLE 4.1-1 Selected Acute (i.e. less than or equal to 96 hr) Lethality Date for Waterborne Antimony (from USEPA 1980g).

Species	Method	Results In ppb
VERTEBRATES		
Pimaphales promelas Fathead minnow	LC_{50}, FT, M	21,900
Lepomis macrochirus Bluegill	LC_{50}	530,000
INVERTEBRATES		
Daphnia magna	LC_{50}, S, U	9,000
Cladoceran	LC_{50}, S, M	19,800
PLANTS		
Selenastrum capricornutum	LC_{50} (Chlorophyll inhibition)	610
Alga	LC_{50} (Cell number)	630

S = static test
FT = flow through test
M = concentration of metal measured during test
U = concentration of metal not measured during test

TABLE 4.1-2 Effects of Subacute and Chronic (i.e. greater than 96 hr) Exposures to Waterborne Antimony (from EPA 1980g unless otherwise noted).

Species	Exposure Concentration (ppb) (Exposure Duration)	Results/Comments
VERTEBRATES		
Pimephales promelas Fathead minnow (Embryo-Larvae)	1100 - 2300 (Early-life stage)	Chronic effects
Salmo gairdneri Rainbow trout (Embryo-Larvae)	660 (28 days)	Lethal to 50% of test population (Birge *et al*.1979)
As above	157 (28 days)	Lethal to 10% of test population (Birge *et al*.1979)
As above	48.9 (28 days)	Lethal to 1% of test population (Birge *et al.* 1979)
As above	580 (28 days)	Lethal to 50% of test population (Birge 1978)
As above	28.6 (28 days)	Lethal to 1% of test population (Birge 1978)
Carassius auratus Goldfish (Embryo)	11,300 (7 days)	Lethalto 1% of test population (Birge1978)
As above	111 (7 days)	Lethal to 1% of test population (Birge 1978)
Gastrophryne carolinensis Toad (Embryo)	300 (7 days)	Lethal to 5% of test population (Birge 1978)
As above	3.8 (7 days)	Lethal to 1% of test population (Birge 1978)
INVERTEBRATES		
Daphnia magna Cladoceran	4200 - 7000 (Life Cycle)	Chronic effects

USEPA (1980g) suggests that antimony may undergo microbial methylation in the natural environment, producing organometallic compounds which may be more mobile. There is no direct evidence to date that biological methylation of antimony does occur or is of importance in the cycling of this element.

4.13 SUFFICIENCY OF DATA FOR ESTABLISHING PWQO

Although limited toxicity data is available for fish, there is a general lack of both acute and chronic toxicity data for aquatic invertebrates and plants. This, plus the complete *lack* of information concerning cycling within the aquatic environment and the possible influence of methylation on movement and toxicity make the overall data base insufficient for producing a PWQO.

The USEPA (1980g) established criteria for the presence of antimony in water to protect aquatic organisms on an acute (9,000 µg/L) and chronic (1,600 µg/L) basis. However, the data of Birge (1978) and Birge *et al.* (1979) as reported in Table 4.1-2 indicate that the USEPA criteria would not protect all life-stages of aquatic organisms.

4.14 RECOMMENDATIONS

It is the recommendation of this report that no attempt be made to establish a PWQO for antimony until a much more extensive data base for this metal is developed.

4.2 BARIUM

4.21 AQUATIC TOXICITY REVIEW

Table 4.2-1 presents the limited aquatic toxicity data available for barium.

4.22 FATE AND EFFECT AND THE AQUATIC ENVIRONMENT

In aqueous solution, barium exists as the divalent cation Ba^{+2}. Barium acetate, nitrate, chloride, and hydroxide are soluble in water whereas barium sulphate, carbonate and fluoride are insoluble. The amount of soluble barium in surface waters is controlled by the amount of sulphate and carbonate in the water. Usually, the latter anions are present in such large concentrations relative to the barium ion that precipitation removes much of the metal from solution.

Divalent barium is a physiological antagonist of potassium and interacts with cellular membranes to decrease the outward passive flux of potassium.

4.23 SUFFICIENCY OF DATA FOR ESTABLISHING A PWQO

Insufficient data are available on which to base a PWQO for barium for the protection of aquatic organisms.

The limited data available for characterizing the human intake of barium from drinking water appears to indicate that public water supplies (surface and subsurface) generally contain below 200 µg/L barium. The current maximum contaminant level is 1000 µg/L (Life Systems 1985).

TABLE 4.2-1 Effects of Subacute and Chronic (i.e. greater than 96 hr)Exposures to Waterborne Barium.

Species	Exposure Concentration (ppb) (Exposure Duration)	Result/ Comments
VERTEBRATES		
Salmo gairdneri Rainbow trout (Embryo-Larvae)	42,700 (28 days)	Lethal to 50% of test population (Birge *et al*.1979)
As above	9,543 (28 days)	Lethal to 10% of test population (Birge *et al.* 1979)
As above	2,813 (28 days)	Lethal to 1% of test population (Birge *et al.* 1979)
PLANTS		
Myriophylium spicatum Vascular plant	41,200 (32 days)	50% inhibition of root growth (by weight)(Stanley 1974)
As above	103,000 (32 days)	50% inhibition of shoot growth (by weight)(Stanley1974)
As above	113,000 (32 days)	50% inhibition of root growth (length)(Stanley 1974)
As above	83,800 (32 days)	50% inhibition of shoot growth (length)(Stanley1974)
Chlamdomonas eugametos Alga	5,000 (7 days)	25% growth inhibition (Hutchinson 1973)
Chlorella vulgaris Alga	5,000 (7 days)	62.2% growth inhibition (Hutchinson1973)
Haematococcus capensis Alga	5,000 (7 days)	381 growth inhibition (Hutchinson 1973)

4.24 RECOMMENDATIONS

Due to the lack of toxicity data and the very small solubility products of barium carbonate and barium sulphate, it is recommended that a PWQO not be developed for barium.

4.3 BORON

4.31 AQUATIC TOXICITY REVIEW

Table 4.3-1 presents the available data on boron toxicity to aquatic organisms. Most of the literature concerning boron toxicity deals with terrestrial plants and irrigation waters. Very little new information is readily available concerning boron toxicity to aquatic organisms. Older literature concerning boron toxicity is generally for very short exposures (generally less than 96 hr) and gives 24 to 96 hr LC_{50}'s in the 100,000-1,000,000 µg/L range (Thurston *et al.* 1979).

4.32 FATE AND EFFECT AND THE AQUATIC ENVIRONMENT

There is a considerable amount of information available about the boron content of natural waters, especially irrigation waters. In trace quantities, boron is an essential element forplant growth. Excessively high amounts are harmful and even toxic to some plants. This element is considered to be anionic in aqueous solution because the ortho- and tetraboric acids protolyze into $H_2BO_3^-$, HBO_3^{-2}, and BO_3^{-3} and into $HB_4O_7^-$ and $B_4O_7^{-2}$, respectively.

The average concentration of boron in the surface waters of the United States is approximately 0.1 mg/L, ranging from a low of 0.02 mg/L to a high of 5.0 mg/L. The major significance of boron lies in its occurrence in irrigation waters in parts of Western North America. Criteria have been proposed for the boron content of irrigation waters (Faust and Aly, 1981).

Information relating to the bioavailability of the various cationic and anionic forms was not found during the literature survey.

TABLE 4.3-1 Effects of Subacute and Chronic (i.e. greater than 96 hr) Exposures to Waterborne Boron.

Species	Exposure Concentration (ppb) (Exposure Duration)	Results/Comments
VERTEBRATES		
Salmo gairdneri Rainbow trout (Embryo-larvae)	70,100 (28 days)	Lethal to 50% of test population (Birge *et al*.1979)
As above	21,826 (28 days)	Lethal to 10% of test population (Birge *et al*.1979)
As above	3,887 (28 days)	Lethal to 1% of test population (Birge *et al.* 1979)
Gambusia affinis Mosquitofish	215,000 (144hr)	Lethal to 50% of test population (Mallen *et al*.1957)
PLANTS		
Myriophyllum spicatum Vascular plant	143,000 (32 days)	50% inhibition of root growth (by weight) (Stanley 1974)
As above	214,000 (32 days)	50% inhibition of shoot growth (by weight) (Stanley1974)
As above	152,000 (32 days)	50%inhibition of root growth (length) (Stanley 1974)
As above	171,000 (32 days)	50% inhibition of shoot growth (length) (Stanley1974)

4.33 SUFFICIENCY OF DATA FOR ESTABLISHING A PWQO

In 1976, the USEPA set a criterion for boron at 750 µg/L based on its toxicity to irrigated crops. In their critique of the 1976 USEPA criterion, Thurston *et al.* (1979) stated that the USEPA criterion rationale lacked the presentation of up-to-date information on the effect of boron on aquatic life. The same charge could be made today. Thurston *et al.'s* (1979) recommendations included a value of 10,000 µg/L for water discharged to the freshwater environment.

In 1977, the USEPA suggested an ambient water limit of 43 µg/L based on health effects (Sittig 1985).

While aquatic toxicity information does exist for boron, only the more recent data (i.e. Birge *et al.* 1979) can be considered credible due to the extended exposure times used in testing the effects of this relatively non-toxic element in the aquatic ecosystem. There is also a general lack of understanding of boron cycling in the aquatic environment.

4.34 RECOMMENDATIONS

Based on the lack of recent data for chronic exposures and a lack of understanding of the effect of water quality on boron toxicity, it is recommended that a PWQO not be determined for this element.

4.4 CESIUM

4.41 AQUATIC TOXICITY REVIEW

Available aquatic toxicity data for cesium are presented in Table 4.4-1, Although these data are very limited, they do show that the concentrations required to produce an effect on the survival of rainbow trout embryos is much greater (i.e. 3,887 µg/L) than other metals reviewed in this document. The chemical toxicity of cesium to a wide variety of aquatic organisms is largely unknown, but the information which does exist suggests that it is relatively low (Hakonson *et al.* 1971).

4.42 FATE AND EFFECT AND THE AQUATIC ENVIRONMENT

Cesium is a chemical analogue of potassium and behaves in a similar manner and its uptake is inhibited by potassium. The primary form of cesium in freshwater appears to be Cs^{+}. While radiocesium bioconcentrates in fish tissue, laboratory experiments concerning the radiation effects on aquatic organisms of various radionuclides (e.g. cesium-137) demonstrate that no deleterious effects are observed until radionuclide concentrations in water or tissue are at least six orders of magnitude greater than those presently found in the waters or biota in Canada (NRCC 1983).

Almost all of the work with cesium in the aquatic environment has dealt with the radioactive isotopes of the element (e.g. cesium-137). Input of this isotope into the aquatic environment is the result of atmospheric fallout from nuclear testing and the operation of nuclear *reactors* using natural surface waters for cooling (Beasley and Jennings 1984).

Cesium-137 is generally considered to be potentially hazardous to man for several reasons:

TABLE 4.4-1 Effects of Subacute and Chronic (i.e. greater than 96 hr) Exposures to Waterborne Cesium.

Species	Exposure Concentration (ppb) (Exposure Duration)	Result/Comments
VERTEBRATES		
Salmo gairdneri Rainbow trout (Embryo- larvae)	181,000 (28 days)	Lethal to 50% of test population (Birge *et al*.1979)
As above	21,826 (28 days)	Lethal to 50% of test population (Birge *et al*.1978)
As above	3,887 (28 days)	Lethal to 1% of test population (Birge *et al*.1979)
INVERTEBRATES		
Gammarus sp Scud	10,000 (5 days)	Lethal to 50% of test population (Hakonson *et al.* 1971)

- it is a significant component of fallout from nuclear testing;
- it is present in leakage from nuclear powered reactors;
- it has a long physical half-life (30.5 years);
- it emits both beta particles and gamma radiation; and
- it is known to be biologically active.

Variation between cesium-137 concentrations in natural populations of largemouth bass (*Micropterus salmoides*) in six southern Michigan lakes was studied by Kevern and Spigarelli (1971).The lakes selected provided a wide range of limnologicalconditions. Simple correlation coefficients indicated inverse relationships between the cesium-137 activity of the fish and total cesium, sodium, potassium and specific conductance of the lake water. Multiple regression analysis altered the relative importance of each water quality parameter and resulted in the deletion of sodium and specific conductance from the equation for the prediction of cesium-137 in large mouth bass.

A laboratory study conducted by Gallegos and Whicker (1971) implied that the maximum cesium-137 intake and retention by rainbow trout (*Salmo gairdneri*) would be achieved at water temperatures optimal for food consumption and fish growth. As well, Rickard and Eberhardt (1971) found that the body burdens of cesium-137 in cutthroat trout (*Salmo clarkii*) inhabiting a mountain bog were derived from their diet.

While Spigarelli (1971) agreed that the diet was the major factor affecting the accumulation of cesium-137 by fish, his data also demonstrated a increasing accumulation of cesium-137 in largemouth bass weighing over 1.1 kg. This suggested that physiological changes within the fish influenced the equilibrium cesium-137 body burden. It appears that young, actively growing fish tend to accumulate less cesium-137 in body tissues than do older fish. Under such conditions, maximum body burdens of cesium-137 would occur in large fish that experience reduced metabolic rates but continue to feed actively.

Cesium-133 was introduced into a small lake in 1970 in Colorado to determine the behaviour and distribution of cesium in this environment (Hakonson *et al.* 1971). Detectable quantities of cesium-133 were measured in zooplankton and *Gammarus* samples at 1.5 and 4 hours, respectively, after introduction of the radiocesium into the lake. Concentrations of cesium-133 increased rapidly in both zooplankton and *Gammarus* populations and appeared to peak at about two weeks after radiocesium introduction. Fish muscle followed the same general pattern, but at a much slower rate.

Thirty-nine days after introduction of the radiocesium, fish muscle concentrations still appeared to be increasing. Levels of radiocesium in the *water* exhibited a decrease with time, being reduced by 60% after five days.

The fate of cesium-134 in Lake 224 (of the Freshwater Institute's Experimental Lakes Area) *was* studied by Hesslein *et al.* (1980) and Klaverkamp *et al.* (1983c). After introduction into the epilimnion, the half-life of cesium-134 was 28.1 days. This isotope showed no affinity for the particulate phase. However, direct adsorption to the sediments from the aqueous phase seemed to explain the relative abundance of this metal in the epilimnetic sediments over the hypolimnic sediments. Mass balance calculations 350 days after addition of the isotopes show 22% of the cesium-134 remaining in the water column.

Cesium-134 activity in the gut contents of white suckers increased throughout the 247 day observation period. Cesium-134 was not detected in gill tissue until 14 days after introduction of the radionuclide and generally increased to a plateau at day 49. Cesium-134 activity in the spleen was approximately equal to the gut activity of this radionuclide. Blood had the lowest accumulation of cesium-134 at day 49. Direct uptake of cesium-134 from water by the gills of white suckers was not a major route for entrance of this metal into fish tissues.

Typical concentration factors for cesium isotopes in freshwater organisms are:

- Aquatic plants: 80;
- Molluscs: 600;
- Crustaceans: 4,000; and
- Fish muscle: 3,000.

However, typical successive trophic level concentration of cesium-144 is less than 0.1 (Whicker and Schultz 1982).

Long-term availability of cesium in the aquatic environment depends heavily on ecosystem characteristics (i.e. concentrations of cations, especially potassium) and in particular the properties of the sediments.

4.43 SUFFICIENCY OF DATA FOR ESTABLISHING A PWQO

Insufficient data exist for the establishment of a cesium PWQO for the protection of aquatic life on the basis of its toxicity to aquatic organisms.

However, concern has been expressed in the published literature about the transfer of cesium-137 to man from the aquatic ecosystem. Thus, a PWQO for cesium-137 should be based on the transfer of this radionuclide through the food chain to man through the consumption of fish. A precedent for the establishment of a PWQO based on the level of a contaminant in fish and its potential transfer to man has already been established in the case of mercury.

4.44 RECOMMENDATIONS

Given the concern expressed over the transfer of cesium-137 to man via the aquatic food chain, and the operation of nuclear power plants in Ontario, it is recommended that a PWQO for cesium-137 be reviewed based on the potential for accumulation of the radionuclide in fish and transfer to man.

4.5 COBALT

4.51 AQUATIC TOXICITY REVIEW

The limited amount of data concerning the toxicity of cobalt to aquatic organisms is presented in Table 4.5-1. Aquatic vertebrate embryos can apparently be affected by concentrations of aqueous cobalt of less than one µg/L.

4.52 FATE AND EFFECT AND THE AQUATIC ENVIRONMENT

The predominant cobalt species in water are Co^{+2} (dissolved) and the particulate $CoCO_3$, $Co(OH)_3$ and CoS. Little is known concerning the weathering process of cobalt and its natural introduction into surface waters (Merian 1984). Introduction of cobalt-60 into Lake 224 of the Experimental Lakes Area by Hesslein *et al.* (1980) showed that cobalt was immediately and strongly associated with particulate material. After 350 days, 23% of the cobalt-60 remained in the water column (associated with particulate material). The remaining 77% had been transported to the sediment by settling particles.

Klaverkamp *et al.* (1983c) reported on the investigation of cobalt-60 accumulation in slimy sculpins (*Cottus cognatus*) and white suckers (*Catostomus commersoni*) in Lake 224 from the original additions in 1976 by Hesslein *et al.* (1980). Since cobalt-60 was immediately and completely bound to filterable particulates at the beginning of the experiment in 1976, this element was essentially not bioavailable to the fish at that point. However, alterations in the chemical speciation or changes in binding apparently occurred later as this element was detected in sucker internal organs seven weeks after addition of the element to the lake. The general relationships between movement and distribution of isotopes in water and their accumulation in slimy sculpins and white suckers indicate that

TABLE 4.5-1 Effects of Subacute and Chronic (i.e. greater than 96 hr) Exposures to Waterborne Cobalt.

Species	Exposure Concentration (ppb) (Exposure Duration)	Result /Comments
VERTEBRATES		
Salmo gairdneri Rainbow trout (Embryo-Larvae)	470 (28 days)	Lethal to 50% of test population (Birge 1978)
As above	34.2 (28 days)	Lethal to 1% of test population (Birge 1978)
As above	490 (28 days)	Lethal to 50% of test population (Birge *et al*.1979)
As above	120 (28 days)	Lethal to 10% of test population (Birge *et al* 1979)
As above	38.2 (28 days)	Lethal to 1% of test population (Birge *et al*.1979)
Carasslus auratus Goldfish (Embryo)	810 (7 days)	Lethal to 50% of test population (Birge 1978)
As above	6.8 (7 days)	Lethal to 1% of test population (Birge 1978)
Gastrophryne carolinensis Toad (Embryo)	50 (7 days)	Lethal to 50% of test population (Birge 1978)
As above	0.9 (7 days)	Lethal to 1% of test population (Birge 1978)
INVERTEBRATES		
Daphnia magna Cladoceran	10 (3 weeks)	16% reproductive impairment (Kaiser 1980)

direct accumulation from water was not a major route for the uptake of this element. Unfortunately, not enough information was available on the gut contents or feeding behaviour of the species studied to verify food uptake as a major route of accumulation.

Ophel and Fraser (1971) studied cobalt-60 partitioning in a small lake (Perch Lake) which had received small, relatively constant inputs of this radioisotope over a period of seven years. The concentration factors for ten species of aquatic plants ranged from 20 to 2790 apparently depending on the physical morphology and habitat of the individual species. Fish species inhabiting the lake had bioconcentration factors for cobalt-60 ranging from 9 to 130 depending on fish species and fish age. Of the three large species of fish sampled, the carnivorous adult yellow perch (*Perca flavescens*) contained, on average, much lower concentrations of the element than the omnivorous brown bullhead (*Ictalurus nebulosus*) and sunfish (*Lepomis gibbosus*). In contrast to the large carnivorous adult yellow perch, young individuals of the same species had the highest concentration of this element of all the fish surveyed. While the young perch are also carnivorous, their food is largely zooplankton and insect larvae in contrast to that of adults which is predominantly small fish. Crayfish collected from Perch Lake showed concentration factors of 1,600. Snails showed concentration factors of 4,400.

The resulting analysis of the food web in Perch Lake demonstrated that the highest cobalt-60 concentrations were in herbivores and plant detritus feeders. Generally speaking, the concentrations of cobalt-60 decreased in organisms with increases in trophic level.

One question unanswered by the cobalt-60 studies was the relation between the bioavailability of the radiocobalt and the naturally occurring element.

4.53 SUFFICIENCY OF DATA FOR ESTABLISHING A PWQO

Although ecological studies have been conducted using radiocobalt, insufficient information is available concerning its relative bioavailability and biological reactivity compared to the normally occurring element. In addition, the toxicity data base for cobalt is insufficient to provide a firm basis for a PWQO.

Because the maximum no-adverse-health effect concentration is more than an order of magnitude greater than that found in any natural-water or drinking water supply, there appears to be no reason at present to regulate this element in drinking water (Sittig 1985).Despite this, the USSR has set a limit of 1,000 µg/L for cobalt in water. The USEPA has suggested a permissible ambient goal of 0.7 µg/L based on health effects (Sittig 1985).

4.54 RECOMMENDATIONS

It is recommended that a PWQO for cobalt not be determined based on the lack of available aquatic toxicity data.

4.6 MANGANESE

4.61 AQUATIC TOXICITY REVIEW

The limited amount of aquatic toxicity data available for manganese is presented in Table 4.6-1. Although manganese is not normally thought of as a toxic metal, it is obvious from the data in Table 4.6-1 that it does have that potential. The lowest concentration producing an effect on a vertebrate test population is 3.0 µg/L.

4.62 FATE AND EFFECT AND THE AQUATIC ENVIRONMENT

The aqueous chemistry of manganese is complex, as manganese can be present in the II, III, IV, VI and VII oxidation states. Mn (II) and Mn (IV) are the oxidation states most commonly found. In neutral and acid aqueous solutions, the II state exists as the hexaquo ion, $[Mn(H_2O)_6]^{+2}$, which is unstable with respect to oxidation by O_2 over the entire pH range of natural water. The maximum concentration of soluble Mn^{+2} in many natural waters is limited by the solubility product of $MnCO_3$. With low alkalinities and reducing conditions in fresh waters, solubility may be restricted by high sulphide concentrations.

The possible chelating influence of natural organic compounds in natural waters was studied on a hypothetical multi-metal, multi-ligand system. Calculations were performed simultaneously by two independent investigators and both concluded that a free manganese ion may be present as a predominant species even if complex-forming organic matter is present.

In water of pH 8 or 9, the soluble divalent manganese ion is chemically oxidized to the insoluble tetravalent form. At pH 5.5, chemical reduction of the tetravalent form takes place.

TABLE 4.6-1 Effects of Subacute and Chronic (i.e. greater than 96 hr)Exposures to Waterborne Manganese.

Species	Exposure (Concentration (ppb) (Exposure Duration)	Results/ Comments
VERTEBRATES		
Salmo gairdneri Rainbow trout (Embryo-Larvae)	2,910 (28 days)	Lethal to 50% of test population (Birge 1978)
As above	388 (28 days)	Lethal to 1% of test population (Birge 1978)
As above	958 (28 days)	Lethal to 10% of test population (Birge *et al.* 1979)
Carasslus auratus Goldfish (Embryo)	8,220 (7 days)	Lethal to 50% of test population (Birge 1978)
As above	21.5 (7 days)	Lethal to 1% of test population (Birge 1978)
Gastrophryne carolinensis Toad (Embryo)	1,420 (7 days)	Lethal to 50% of test population (Birge 1978)
As above	3.0 (7 days)	Lethal to 1% of test population (Birge 1978)
PLANTS		
Selenastrum capricornutum Alga	10 00 (13 days)	11% reduction In total cell volume (Christensen *et al*.1979)
As above	10,000 (13 days)	76% reduction In total cell volume (Christensen *et al.* 1979)
Chlorella stigmatophora Alga	10,000(13 days)	34% reduction in total cell volume (Christensen *et al.* 1979)
As above	10,000 (13 days)	52% reduction In total cell volume (Christensen *et al.* 1979)

However, the interconversion of these forms, which is commonly observed at intermediate pH, occurs only by microbial mediation (USEPA 1984b).

Bacteria are important agents in determining the form and distribution of manganese in the environment. Several processes can occur:

- release of inorganic manganese ions during decomposition of organic material;
- immobilization of ions by incorporation into microbial tissue;
- oxidation of manganese to a less available form;
- direct, enzymatic reduction of oxidized manganese; or
- indirect transformation (especially reduction) through changes in pH or oxidation-reduction potential.

Manganese usually enters a surface water in the insoluble oxidized form, which settles to the sediment. Manganese-reducing bacteria may be active in the sediments, or manganese may be reduced by the lowering of pH resulting from general microbial activity (i.e. O_2 consumption or the production of acidic metabolites). In the first case the reduction is enzymatic; in the second it is non-enzymatic. Reduced manganese then diffuses upward in the sediment or into the water column. In Lake Pannus-Yaryl of the Karelian Isthmus (USSR), iron- and manganese-reducing bacteria are present in the upper 10 cm of the sediments. Reduced manganese in the bottom waters of the profundal zone reaches 1.4 mg/L, whereas the total manganese concentration in the rest of the lake is only 0.01 mg/L.

Several types of bacteria have been found capable of oxidizing manganese. The first are included among the "iron bacteria," or that group of aerobic bacteria which appear to utilize the oxidation of ferrous and/or manganous ions as an essential component in their metabolic functioning. These have been assumed to be chemoautotrophs, utilizing energy from the reduction of manganese to carry out synthetic processes, although this conclusion has been questioned by others. A second group consists of heterotrophs possessing a slime capsule that can absorb

divalent manganese. Oxidation then occurs within the sheath, which becomes impregnated with the hydroxide. Manganese-oxidizing ability has been shown to occur in a wide variety of freshwater bacterial genera, comprising from 1 to 69% of the heterotrophic bacterial population of two freshwater lakes studied. Divalent manganese entering the water column from the sediments is precipitated by microorganisms, usually in the form of hydroxides. This leads to a repetition of the oxidation-reduction cycle (USEPA 1984b).

Accumulation of manganese has been studied through the use of the radionuclide ^{54}Mn. Using laboratory microcosms, Kearns and Vetter (1982) determined that the steady state concentration factors were 4,230, 17,000 and 11 for *Chlorella* sp., *Daphnia magna* and yellow perch (*Perca flavescens*), respectively. The biological half-lives for ^{54}Mn in these organisms were 1.6, 1.2 and 8.3 days for *Chlorella, Daphnia* and yellow perch, respectively. This and other studies of manganese accumulation in estuarine organisms demonstrate that biomagnification of manganese with increasing trophic level does not occur. Organisms in the upper trophic levels of aquatic environments appear capable of regulating their internal concentration of manganese (USEPA 1984b).

Compared with organisms, the accumulation factor of manganese by sediment is relatively high (i.e. 2,900) (Hubel *et al.* 1979).Like many other metals which cycle in the aquatic environment, sediments are the ultimate repository for manganese.

4.63 SUFFICIENCY OF DATA FOR ESTABLISHING A PWQO

Although there is an extensive literature data base on the cycling and forms of manganese in the aquatic environment, there is a relatively small amount of information concerning the toxicity of the free metal ion to aquatic organisms. This is possibly due to its low solubility in most natural waters and/or its existence as a hydroxide precipitate or colloid in most surface waters.

The USEPA has no manganese criterion for the protection of aquatic life but suggests that domestic water supplies not exceed 50 µg/L. In most natural waters, the concentration of manganese is less than 20 µg/L, with higher activities usually associated with human activities (USEPA 1984b).

4.64 RECOMMENDATIONS

Due to the relatively small data base concerning the toxicity of dissolved manganese, it is recommended that a PWQO not be developed for this metal. However, there is some concern in the scientific community about the role of this element in acid lakes, particularly as it affects the bones of fish. On-going investigations of acid lakes by the Ontario Ministry of the Environment should follow this element with a view toward establishing an objective in the future.

4.7 MOLYBDENUM

4.71 AQUATIC TOXICITY REVIEW

Table 4.7-1 presents the available vertebrate aquatic toxicity data for molybdenum. Potentially harmful levels of this element are associated with mining and milling operations for both molybdenum and uranium ores (Colborn 1982). However, analyses of water samples collected upstream and downstream of an old, abandoned molybdenum mine failed to detect molybdenum in the water (i.e. it was 1 µg/L or lower).

Apparently the element does bioaccumulate since the molybdenum content was found to be elevated in various benthic invertebrates at locations near to the abandoned mine compared to upstream controls.

Molybdenum (as discussed in Section 4.72, below) is a micronutrient that is effectively removed from water by iron hydroxide. Judging from the available literature, it has never received much attention as a toxic element.

4.72 FATE AND EFFECT AND THE AQUATIC ENVIRONMENT

Molybdate ions readily form aggregates in aqueous solution and various polyions are formed as a result of polymerization and condensation reactions. Their nature depends on the pH and the concentration of the molybdenum (VI) compound. The study of molybdenum (IV) and (V) in solution under a variety of conditions has been the subject of numerous reports. As far as is known, MoO_4^{-2} ions are the main form in the aqueous phase above pH 7. At lower pH values, polymeric compounds ($Mo_7O_{24}^{-6}$) are formed (Busev 1964).

TABLE 4.7-1 Effects of Subacute and Chronic (i.e. greater than 96 hr)Exposures to Waterborne Molybdenum.

Species	Exposure Concentration (ppb) (Exposure Duration)	Results/Comments
VERTEBRATES		
Salmo gairdneri Rainbow trout (Embryo-Larvae)	790 (28 days)	Lethal to 50% of test population (Birge *et al*.1979)
As above	125 (28 days)	Lethal to 10% of test population (Birge *et al*.1979)
As above	27.8 (28 days)	Lethal to 1% of test population (Birge *et al.* 1979)
As above	730 (28 days)	Lethal to 50% of test population (Birge 1978)
As above	22.3 (28 days)	Lethal to 1% of test population (Birge 1978)
Carasslus auratus Goldfish (Embryo)	60,000 (7 days)	Lethal to 50% of test population (Birge 1978)
As above	39.3 (7 days)	Lethal to 50% of test population (Birge 1978)
Gastrophryne carolinensis Toad (Embryo)	960 (7 days)	Lethal to 50% of test population (Birge 1978)
As above	3.1 (7 days)	Lethal to 1% of test population (Birge 1978)

Molybdenum is essential for plant growth and nitrogen fixation. A deficiency of this element in the phytoplankton of several lakes has been demonstrated by increased growth of this community upon molybdenum additions. The amount added to produce enhanced growth varied with the season, and above 25 µg/L inhibition of phytoplankton primary production has been observed. Molybdenum appears to cycle in lakes with depletion from the water in the winter, followed a quick liberation in the spring and a gradual lowering in the summer.

Molybdenum concentrations in freshwater lakes have been found to range from less than 0.06 µg/L to 100 µg/L (the latter case attributed to water of geothermal origin). The normal cycling of molybdenum in lakes can be temporarily altered by inputs to the water from decaying algal blooms. Sediment and iron hydroxide adsorption-desorption reactions are hypothesized to govern the seasonal cycle of molybdenum in lakes, along with uptake of the element by actively growing phytoplankton and its subsequent release on death or senescence (Dumont 1972).

Sakaguchi *et al.* (1981) studied the uptake of molybdenum by *Chlorella regularis* and found that the initial uptake of the metal is mainly dependent on physico-chemical adsorption at the cell surface. However, after 20 hours some of the absorbed molybdenum (VI) had been reduced to molybdenum (III) by a metabolic process within the algal cell.

Bioconcentration factors for molybdenum-54 in invertebrates and fish are 40,000 and 100 respectively (Blaylock and Witherspoon 1978).

4.73 SUFFICIENCY OF DATA FOR ESTABLISHING A PWQO

There is insufficient data upon which to base a PWQO for molybdenum. Although a great deal of information is available for this element as a micronutrient, the toxicity aspect of its impact on the aquatic environment is much less known. If

mining activity within the Province of Ontario is expected to produce molybdenum bearing wastes which could affect adjacent aquatic environments, then additional laboratory toxicity data will have to be generated prior to establishing an objective for this metal.

4.74 RECOMMENDATIONS

It is recommended that a PWQO for molybdenum not be established at this time.

4.8 STRONTIUM

4.81 AQUATIC TOXICITY REVIEW

Table 4.8-1 presents the readily available aquatic toxicity data for strontium. Aquatic vertebrate embryos appear to be affected at concentrations as low as 2.4 µg/L. From the very limited data, invertebrates appear to be less sensitive than vertebrates.

4.82 FATE AND EFFECT AND THE AQUATIC ENVIRONMENT

Much of the work dealing with strontium in the environment has concerned the radioisotopes ^{89}Sr and ^{90}Sr which received great notoriety and study during the era of atmospheric nuclear testing in the 1950s and early 1960s. Strontium-90 is produced in high yields from nuclear fission and is persistent in the biosphere because of its 28 year half-life. As well, strontium forms relatively soluble compounds and because of its chemical similarity to calcium, strontium and its isotopes are comparatively mobile in ecosystems. These properties allow strontium in general and strontium-90 in particular to deposit in calcium-bearing structures such as bones and shells where it can remain for years with the radioactive isotopes posing potential danger to living tissues.

Owing to its metabolic control by calcium, strontium uptake by organisms has often been expressed as an "observed ratio", which is defined as the Sr/Ca ratio in an organism divided by the Sr/Ca ratio in the diet (or water in the case of aquatic organisms). Observed ratios for soil to plants are usually close to unity, suggesting little discrimination between strontium and calcium by plants. On the other hand, observed ratios describing food-to-animal tissue transfers are usually less than unity, indicating discrimination against strontium in favour of calcium.

TABLE 4.8-1 Effects of Subacute and Chronic (i.e. greater than 96 hr) Exposures to Waterborne Strontium.

Species	Exposure Concentration (ppb) (Exposure Duration)	Results/Continents
VERTEBRATES		
Salmo gairdneri Rainbow trout (Embryo-Larvae)	250 (28 days)	Lethal to 50% of test population (Birge *et al*.1979)
As above	49.0 (28 days)	Lethal to 10% of test population (Birge *et al*.1979)
As above	13.0 (28 days)	Lethal to 1% of test population (Birge *et al.* 1979)
As above	200 (28 days)	Lethal to 50% of test population (Birge 1978)
As above	6.0 (28 days)	Lethal to 1% of test population (Birge 1978)
Carassius auratus Goldfish (Embryo)	2,140 (7 days)	Lethal to 50% of test population (Birge 1978)
As above	68.8 (7 days)	Lethal to 1% of test population (Birge 1978)
Gastrophryne carolinensis Toad (Embryo)	160 (7 days)	Lethal to 50% of test population (Birge 1978)
As above	2.4 (7 days)	Lethal to 1% of test population (Birge 1978)
INVERTEBRATES		
Daphnia magna Cladoceran	42,000 (3 weeks)	16% reproductive impairment (Kaiser 1980)

Many studies have demonstrated that factors such as soil composition, diet, and age can substantially modify observed ratios. Therefore, the observed ratio is not a predictive panacea. Observed ratios describing Sr/Ca transport from water to fish muscle and bone also suggest discrimination against strontium. Nevertheless, concentration factors for strontium in aquatic organisms can be very high. Although strontium isotopes in the environment readily enter food chains, tissue concentrations do not appear to increase with trophic level. High available calcium budgets in ecosystems tend to reduce the bioaccumulation of strontium. Calcium and strontium-90 measured in brown trout (*Salmo trutta*) and water from various locations in the United Kingdom exhibited an inverse correlation between ^{90}Sr concentration factors and the calcium content of the water (Whicker and Schultz 1982).

Typical bioconcentration factors for strontium-90 in freshwater organisms are:

- Fish muscle: 200;
- Crustaceans: 200;
- Molluscs: 600; and
- Algae: 100 (Whicker and Schultz 1982, Stary and Kratzer 1984)

4.83 SUFFICIENCY OF DATA FOR ESTABLISHING A PWQO

There is a general lack of both acute and chronic aquatic toxicity data for the formulation of a PWQO. Much more information appears to be available on the movement and compartmentalization of strontium-90 in the aquatic environment, although toxicity data are also lacking on this isotope.

4.84 RECOMMENDATIONS

Currently, the Ontario maximum acceptable concentration for strontium-90 in water (related to human health) is 10 Bq/L. It is recommended that this guideline be reviewed based on:

- the relatively high mobility of this radionuclide in the aquatic environment;
- the operation of nuclear power plants in Ontario; and
- the potential for adverse human health effects due to ingestion of this radionuclide.

It is realized that insufficient acute and chronic toxicity data exist for this element on which to base a PWQO for the protection of aquatic life. However, the necessity to protect human health from significant exposure to this radionuclide via the aquatic environment is surely justification for a review of the isotope.

4.9 THALLIUM

4.91 AQUATIC TOXICITY REVIEW

The limited amount of data presented by USEPA (1980f) and summarized in Tables 4.9-1 and 4.9-2 indicates that acute and chronic toxicity to freshwater aquatic life occurs at concentrations as low as 1400 and 2.4 µg/L, respectively. *Daphnia magna* and fathead minnows had similar acute sensitivities, with LC_{50}'s in the range from 910 to 2,180 µg/L, while values for bluegills were two orders of magnitude greater. Algae may be affected by aqueous thallium concentrations as low as 100 µg/L. It is lethal to aquatic invertebrates at concentrations between 2,000 and 4,000 µg/L. Fish have been reported to be killed slowly at concentrations of 1,000 to 60,000 µg/L. Thallium has been reported to be lethal to tadpoles at 400 µg/L (Wallwork-Barber *et al.* 1985). Zitko *et al.* (1975) suggests that thallium is as acutely toxic as copper on a weight basis, and 3 to 4 times as toxic on a molar basis.

4.92 FATE AND EFFECT AND THE AQUATIC ENVIRONMENT

Thallium is a soft heavy metal which has a variety of industrial uses. While thallium compounds show a wide range of solubilities in water, no scientific work has apparently been carried out on its distribution and cycling in the aquatic environment. Zitko *et al.* (1975) noted that thallium differs from other metals in its apparent general lack of complex formation, making its toxicity independent of water hardness.

Microcosm (i.e. water, sand, vegetation, fish) experiments of 220 hours duration demonstrated that thallium introduced into the water *was* taken up by vegetation and fish (by 10 fold) while it decreased slowly in the water. At the end of the experiment, thallium movement out of the water had begun to stabilize, but

TABLE 4.9-1 Selected Acute (i.e. less than or equal to 96 hr) Lethality Data for Waterborne Thallium (from USEPA 1980f Unless Otherwise Noted).

Species	Method	Results In ppb
VERTEBRATES		
Pimephales promelas Fathead minnow	LC_{50}, FT, M	1,800
Lepomis macrochirus Bluegill	LC_{50}, S, U	121,000 - 132,000
INVERTEBRATES		
Daphnia magna	LC_{50}, S, U	2,180
Cladoceran	LC_{50}, S, M	910
PLANTS		
Selenastrum capricornutum Alga	LC_{50} (Chlorophyll Inhibition)	110
	LC_{50} (Cell number)	100

S = static test
FT = flow through test
U = concentration of metal not measured during test
M = concentration of metal measured during test

TABLE 4.9-2 Effects of Subacute and Chronic (i.e. greeter than 96 hr) Exposures to Waterborne Thallium (from USEPA 1980f Unless Otherwise Noted).

Species	Exposure Concentration (ppb) (Exposure Duration)	Result /Comments
VERTEBRATES		
Pimephales promelas Fathead minnow (Entryo-Larvae)	LT40-81 (Early life stage test)	Chronic limits
As above	800 (7 days)	Lethal to 50% of test population
Salmo salar Atlantic salmon (Juveniles)	20 45 (2600 hr exposure)	Lethal to 40% of test population Lethal to 70% of test population
Salmo gairdneri Rainbow trout (Embryo-Larvae)	180 (28 days)	Lethal to 50% of test population (Birge *et al*.1979)
As above	36.3 (28 days)	Lethal to 10% of test population (Birge *et al*.1979)
As above	9.9 (28 days)	Lethal to 1% of test population (Birge *et al.* 1979)
As above	170 (28 days)	Lethalto 50% of test population (Birge 1978)
As above	8.4 (28 days)	Lethal to 1% of test population
Caressius auratus Goldfish(Embryo)	7,000 (7 days)	Lethal to 50% of the test population (Birge 1978)
As above	52.5 (7 days)	Lethalto 1% of test population (Birge 1978)
Gastrophyne carolinensis Toad (Embryo)	110 (7 days)	Lethal to 50% of test population (Birge 1978)

TABLE 4.9-2 (Cont'd)

Species	Exposure Concentration (ppb) (Exposure Duration)	Result/Comments
As above	2.4 (7 days)	Lethal to 1% of test population (Birge 1978)
INVERTEBRATES		
Daphnia magna Cladoceran	100-181 (over life cycle)	Chronic limits
PLANTS		
Elodea canadensis Vascular plant	2,000 (28 days)	Phytotoxic to 50% of plants (Brown and Rattigan 1979)
Lemna minor Vascular plant	8 (28 days)	As above

LT = Less than

thallium concentrations in vegetation and fish were apparently still increasing (Wallwork-Barber *et al.* 1985).

Bioconcentration of thallium is reported to be greater for freshwater fishes than for marine fauna, with Atlantic salmon (juveniles) accumulating thallium in muscle tissue to 130 times that of water, and bluegill (whole body) to 34 times.

4.93 SUFFICIENCY OF DATA FOR ESTABLISHING A PWQO

Based on an experimental study, Krasousky *et al.* (1980) determined that the maximum allowable concentration of thallium in water (based on the toxicology of the element) should be 0.1 µg/L. However, other than this Russian language report, there is very little information on which to base a PWQO.

The USEPA (1980f) criteria for the protection of aquatic life on an acute basis is 1,400 µg/L. On a chronic basis the value is 40 µg/L. These values were based on 10 scientific documents covering both the marine and freshwater environments dating from 1926 to 1978.

The data of Birge (1978) demonstrate that thallium concentrations as low as 8.4 µg/L can affect the survival of rainbow trout embryos.

4.94 RECOMMENDATION

There are insufficient data available on the aquatic chemistry, environmental fate and effect, and toxicity on which to base a firm rationale for a PWQO. More chronic toxicity data should be acquired before the decision is made to establish a PWQO for thallium.

4.10 TIN

4.101 AQUATIC TOXICITY REVIEW

Table 4.10-1 presents the limited available aquatic toxicity data for both inorganic and organic tin. It is very apparent that the organotins are much more toxic than the inorganic tin compounds.

The available data indicate that trialkyltin compounds are toxic to freshwater organisms at micromolar concentrations over short periods of time. What is not known is the effect of even lower concentrations of these compounds over prolonged periods of time.

4.102 FATE AND EFFECT AND THE AQUATIC ENVIRONMENT

Little information could be found regarding the form or forms of inorganic tin in the aquatic environment. Discussions by Craig and Rapsomanikis (1985) seem to indicate that tin can exist in the aquatic environment in the oxidation states Sn^{+4}, Sn^{+2} or Sn°. However, the hydrolysis products of tin are highly insoluble and as a result, low levels (i.e. less than 500 µg/L) are usually found in surface waters. The oxidation state Sn^{+4} is more stable than Sn^{+2} and, with the exception of some anaerobic sediments, will be the oxidation state found in various aquatic ecosystem components (i.e. water, sediments, organisms, etc.) Tin (IV) does not exist as the free aqueous cation Sn^{+4}, but most likely as the hydroxide $Sn(OH)_4$, or the hydroxyoxides $SnO(OH)_2$ and $SnO(OH)_3^-$. Speciation is dependent on oxidation-reduction potential and pH (Thompson *et al.* 1985).

Organic tin, by contrast, can be present in the aquatic environment in a wide variety of formulations, chiefly as a result of it wide industrial and agricultural

TABLE 4.10-1 Effects of Subacute and Chronic (i.e. greater than 96 hr) Exposures to Waterborne Tin.

Species	Duration of Test	Exposure Concentration (ppb)	Result	Reference
		INORGANIC TIN		
VERTEBRATES				
Salmo gairdneri Rainbow trout (Embryo-Larva)	28 days	420	Lethal to 50% of test population	Birge *et al.* 1979
As above	28 days	75.5	Lethal to 10% of test population	As above
As above	28 days	18.6	Lethal to 1% of test population	As above
As above	28 days	400	Lethal to 50% of test population	Birge 1978
As above	28 days	15.5	Lethal to 1% of test population	As above
Carasslus auratus Goldfish (Embryo)	7 days	2,140	Lethal to 50% of test population	As above
As above	7 days	68.8	Lethal to 1% of test population	As above
Gastrophryne carolinensis Toad (Embryo)	7 days	90	Lethal to 50% of test population	As above
As above	7 days	1.7	Lethal to 1% of test population	As above
		ORGANIC TIN		
VERTEBRATES				
Salmo gairdneri Rainbow trout (Yolk Sac Fry)	12 days	5	Lethal to 100% of test population	Thompson *et al.* 1985

TABLE 4.10-1 (Cont'd)

Species	Duration of Test	Exposure Concentration (ppb)	Result	Reference
		Organic Tin (Cont'd)		
VERTEBRATES (Cont'd)				
As above	110 days	0.2	Significant retardation of growth; diminished glycogen storage	As above
Lebistes reticulatus Guppy	7 days	21-39	Lethal to 50% of test population	As above
INVERTEBRATES				
Biomphalaria glabrata Snail	-	10	100% inhibition of oviposition	As above
As above	-	1	Greater than 90% inhibition of oviposition	As above
As above	-	0.1	50% inhibition of oviposition	As above

applications. These applications may include:

- stabilizers and catalysts; and
- biocides and preservatives

The main organotin compounds which are likely to be released to the environment in Canada as a result of these applications are:

- triphenyl tin;
- tricyclohexyl tin;
- tri-n-butyl tin;
- di-n-butyl tin;
- di-n-octyl tin; and
- dimethyl tin (Thompson *et al.* 1985)

Inorganic tin may also be methylated to form both di-and trimethyl tin. However, very little work has been performed to determine the chemical speciation of organotins in the natural waters.

Methyl tin compounds can be sequentially demethylated to inorganic tin by photolysis; however, estimates of the environmental half-life are uncertain.

Most of the information available on environmental persistence and fate of organotins concerns butyl tin compounds. These compounds are apparently stable in the dark and are not lost by volatilization. There is evidence for their strong binding to sediments, non-extractable residue formation, and microbial dealkylation.

Estimates of photolytic half-life of butyl tin compounds have been given as 18 days and greater than 89 days. This variation may have been due to the different kinds and concentrations of naturally occurring photosensitizer used in the experiments from which the numbers were derived.

Tributyl tin appears to be at least moderately persistent in aquatic environments. Adsorption to sediments may be an important pathway, but the strength of adsorption and the biological availability of sediment associated tributyltin requires further investigation.

Methylation plays an important role in making both inorganic tin and organic tin more available to aquatic organisms. Tributylmethyl tin and dibutyldimethyl tin have been found in sediments from several harbours in Canada. In general, the larger the number and molecular weight of the organic groups attached to the tin atom, the higher the compound's octanol:water partition coefficient and the higher its potential for bioaccumulation.

Few workers have studied the uptake, distribution and bioconcentration of organotin compounds in aquatic organisms and almost no work has been done concerning the metabolic degradation of these compounds. Organotin compounds are known to accumulate in certain aquatic organisms and can be bioaccumulated to different extents in different tissues. Unfortunately more information is required before a detailed assessment of the effects of these activities can be made.

4.103 SUFFICIENCY OF DATA FOR ESTABLISHING A PWQO

Limited toxicity data are available concerning the toxicity of inorganic and organic tin to freshwater organisms. Much of the research into tin toxicity, cycling, methylation / demethylation, aquatic transfer and compartmentalization, bioaccumulation and biomagnification is on-going.

4.104 RECOMMENDATION

Given the available evidence, organotin compounds present a potentially serious threat to the aquatic environment. Although much of the toxicity work has been conducted with marine organisms, some attempt should be made to establish a preliminary or interim objective for organotin (either as total tin or organotin). This interim objective should incorporate provisions for later revision as new data becomes available.

4.11 VANADIUM

4.111 AQUATIC TOXICITY REVIEW

Table 4.11-1 presents selected acute toxicity data (i.e. less than or equal to 96 hr) from the published literature. While there are data available for fish, very little is available for invertebrates and plants. Acutely toxic values for 50% of the vertebrate test populations range from 4,800 to 118,000 µg/L. Available data for invertebrates appears to show a greater sensitivity by these organisms.

Table 4.11-2 presents selected chronic toxicity data from the published literature. The apparent *safe* concentration of vanadium in water for the protection of fish is 41 µg/L. This value was established by long-term (i.e. 96 day) exposures of flagfish (*Jordanella floridae*) fry to maturity and production of a second generation. This value is almost an order of magnitude lower than the lowest reported value causing an effect (i.e. 170 µg/L) in the same test situation. The value of 41 µg/L is considerably above the 9.0 µg/L concentration shown to be toxic to one percent of a test population by Birge *et al.* (1979).

4.112 FATE AND EFFECT AND THE AQUATIC ENVIRONMENT

Fate and effect of vanadium in the aquatic environment is poorly known. Concern over this element arises from its presence as a contaminant in fossil fuels, and its possible release to the environment during mining or processing of these materials.

Studies by Holdway *et al.* (1983) indicated that vanadium bioconcentration by fish posed little danger to fish. Flagfish were exposed to a range of vanadium concentrations from age 10 days to maturity, spawning and subsequent development of second generation for a total period of 96 days.

TABLE 4.11-1 Selected Acute (i.e. less than or equal to 96 hr) Lethality Data for Waterborne Vanadium.

Species	Method	Results in ppb	Test Water	Reference
VERTEBRATES				
Pimephales promelas Fathead minnow	LC_{50}, S, U	4,800	Softwater	Bakker and Jaworski1980
As above	LC_{50}, S, U	30,000	Hardwater	As above
As above	LC_{50}, S, U	13,000	Softwater	As above
As above	LC_{50}, S, U	15,000	Hardwater	As above
Lepomis macrochirus Bluegill	LC_{50}, S, U	6,000	Softwater	As above
As above	LC_{50}, S, U	55,000	Hardwater	As above
Salmo gairdneri Rainbow trout (Eyed eggs)	LC_{50}, R, M	118,000	Hardness:90 ppm	Giles and Klaverkemp 1982
As above (Fingerlings)	LC_{50}, FT, M	34,890	Hardness:90 ppm pH:7	Giles *et al.* 1979
As above	LC_{50}, FT, M	34,990	Hardness:90 ppm pH:8	As above
As above	LC_{50}, FT, M	20,430	Hardness:90 ppm pH:7	As above
As above	LC_{50}, FT, M	24,680	Hardness:90 ppm pH:8	As above
As above	LC_{50}, FT, M	31,830	Hardness:90 ppm pH:9	As above
As above	LC_{50}, FT, M	36,910	Hardness:90 ppm pH:6	As above
As above	LC_{50}, FT, M	13,700	Hardness:90 ppm pH:7	As above
As above	LC_{50}, FT, M	16,730	Hardness:90 ppm pH:8	As above

TABLE 4.11-1 (Cont'd)

Species	Method	Results In ppb	Test Water	Reference
As above	LC_{50}, FT, M	18,090	Hardness:90 ppm pH:9	As above
As above	LC_{50}, FT, M	21,750	Hardness:90 ppm pH:6	As above
As above	LC_{50}, FT, M	8,150	Hardness:90 ppm pH:7	As above
As above	LC_{50}, FT, M	11,430	Hardness:90 ppm pH:8	As above
As above	LC_{50}, FT, M	15,730	Hardness:90 ppm pH:9	As above
As above	LC_{50}, FT, M	6,430	Hardness:90 ppm pH:8.0	As above
As above (Juveniles)	LC_{50}, FT, M	6,570	Hardness:31 ppm pH:6.60	Sprague *et al.* 1978
As above	LC_{50}, FT, N	5,870	Hardness:30 ppm pH:7.70	As above
As above	LC_{50}, FT, M	6,830	Hardness:29 ppm pH:8.80	As above
As above	LC_{50}, FT, M	11,650	Hardness:101 ppm pH:5.51	As above
As above	LC_{50}, FT, M	5,690	Hardness:105 ppm pH:6.66	As above
As above	LC_{50}, FT, M	6,160	Hardness:103 ppm pH:7.72	As above
As above	LC_{50}, FT, M	10,000	Hardness:101 ppm pH:7.71	As above
As above	LC_{50}, FT, M	5,160	Hardness:98 ppm pH:7.66	As above
As above	LC_{50}, FT, N	13,200	Hardness:368 ppm pH:6.61	As above

TABLE 4.11-1 (Cont'd)

Species	Method	Results In ppb	Test Water	Reference
As above	LC_{50}, FT, M	7,210	Hardness:355 ppm pH:7.70	As above
As above	LC_{50}, FT, M	8,690	Hardness:335 ppm pH:8.75	As above
INVERTEBRATES				
Daphnia magna	LC_{50}, S, U	LT160	-	Giles *et al*.1979

LT = Less than
S = Static test
FT = Flow through test
M = Concentration of metal measured during test
U = Concentration of metal not measured during test

TABLE 4.11-2 Effects of Subacute and Chronic (i.e. greeter than 96 hr) Exposures to Waterborne Vanadium.

Species	Duration of Test	Exposure Concentration (ppb)	Result	Reference
VERTEBRATES				
Salmo gairdneri Rainbow trout	7 days	2,500	Lethal to 50% of test population	Stendahl and Sprague 1982
As above	7 days	2,400	Lethal to 50% of test population	As above
As above	7 days	1,900	Lethal to 50% of test population	As above
As above	7 days	2,100	Lethal to 50% of test population	As above
As above	7 days	5,100	Lethal to 50% of test population	As above
As above	7 days	4,300	Lethal to 50% of test population	As above
As above	7 days	3,400	Lethal to 50% of test population	As above
As above	7 days	4,100	Lethal to 50% of test population	As above
As above	7 days	6,000	Lethal to 50% of test population	As above
As above	7 days	3,300	Lethal to 50% of test population	As above
As above	7 days	2,500	Lethal to 50% of test population	As above
As above	7 days	4,200	Lethal to 50% of test population	As above
As above	7 days	5,400	Lethal to 50% of test population	As above

TABLE 4.11-2 (Cont'd)

Species	Duration of Test	Exposure Concentration (ppb)	Result	Reference
Jordanella floridae Flagfish (Embryo to adult)	28 days	1,500	Lethal to over 50% of test population	Holdway and Sprague 1979
As above	30 days	1,500	Lethal to over 50% of fry of 2nd generation	As above
As above	96 days	170	Significantly lower dry weight in off-spring from initial test population	As above
As above	96 days	480	"Slow" recently hatched 2nd generation of test population	As above
As above	96 days	41	Apparent safe concentration	As above
Carassius auratus Goldfish	144 hr	8,100	Lethal to 50% of test population	Bakker and Jaworski 1980
As above	144 hr	3,000	Lethal to 50% of test population	As above
As above	144 hr	3,800	Lethal to 50% of test population	As above
As above	144 hr	2,500	Lethal to 50% of test population	As above
Poecilla reticulata Guppy	144 hr	1,100	Lethal to 50% of test population	As above
As above	144 hr	400	Lethal to 50% of test population	As above
As above	144 hr	1,500	Lethal to 50% of test population	As above
As above	144 hr	500	Lethal to 50% of test population	As above
Salmo gairdneri Rainbow trout (Embryo-larvae)	28 days	170	Lethal to 50% of test population	Birge *et al*.1979

TABLE 4.11-2 (Cont'd)

Species	Duration of Test	Exposure Concentration (ppb)	Result	Reference
As above	28 days	33.8	Lethal to 10% of test population	As above
As above	28 days	9.0	Lethal to 1% of test population	As above
PLANTS				
Chlorella pyrenoidosa Alga	6 days	20	Cell division stopped at three days, many giant cells incapable of dividing were observed at six days	Bakker and Jaworski (1980)

Exposure concentrations were 41, 170, 480 and 1,500 µg/L. Fish exposed to the higher concentrations (i.e. 480 and 1500 µg/L) accumulated more vanadium than fish exposed to the lower concentrations. Bioconcentration factors ranged from 2 to 28 and were up to three orders of magnitude lower than the factors for zinc and cadmium. They appeared to be at the low end of the range of bioconcentration factors known for metals in fish.

Results of long term exposure tests are limited in number, with Stendahl and Sprague (1982) providing the most detailed information available. They found that vanadium was unusual in showing no threshold for acute lethality, at least up to 11 days. The response for vanadium was fairly even over the various hardness/pH combinations tested. They summarized lethal levels for trout as being 1,900 to 6,000 µg/L, based on 7 day exposures, indicating moderate toxicity as compared to other metals (more toxic than nickel but less toxic than copper).

4.113 SUFFICIENCY OF DATA FOR ESTABLISHING PWQO

There appears to be sufficient information available to support a PWQO for the protection of freshwater fish. However, insufficient information is available concerning the long-term effects of vanadium on aquatic plants and invertebrates to support the objective of protection of all aquatic species.

The USEPA has not issued a criterion for the maximum permissible concentration in water for the protection of aquatic life, but has suggested a permissible ambient goal of 7 µg/L based on health effects.

4.114 RECOMMENDATIONS

A PWQO should be developed for vanadium for the protection of freshwater fish. This PWQO should be developed with the provision that not enough is known about the toxicity of this element or its cycling in aquatic systems to ensure that invertebrates and freshwater plants will be equally protected.

PART 5.0

CONCLUSIONS REGARDING EXISTING PWQOs FOR METALS

5.0 CONCLUSIONS REGARDING EXISTING PWQOs FOR METALS

Based on the literature published since the adoption of Ontario's Provincial Water Quality Objectives (MOE 1979), it is recommended that revisions be made to the PWQOs for the following metals and trace elements:

- Beryllium;
- Cadmium;
- Chromium;
- Lead;
- Mercury; and
- Selenium.

A review of the published literature has demonstrated that the PWQOs for the following metals are sufficiently low for the protection of all aquatic life:

- Copper;
- Nickel;
- Iron;
- Silver; and
- Zinc.

While these PWQOs need not be revised, some of them (e.g. zinc, copper) should be related to specific water quality parameters (e.g. water hardness) with the view toward providing a sliding scale related to the effect of water quality on the toxicity.

PART 6.0

CONCLUSIONS REGARDING CANDIDATE ELEMENTS FOR PWQ0s

6.0 CONCLUSIONS REGARDING CANDIDATE ELEMENTS FOR PWQOs

After a review of the published scientific literature for data concerning the aquatic toxicity and the fate and effect of the candidate elements in the aquatic environment, it was concluded that insufficient data was available to establish PWQOs for:

- Antimony;
- Barium;
- Boron;
- Cobalt;
- Manganese;
- Molybdenum; and
- Thallium

The isotopes cesium-137 and strontium-90 posed a special problem in this review. Although sufficient toxicity data was not available to establish a PWQO for their respective stable elements (for the protection of aquatic life), there *was* concern expressed in the published literature concerning the effects on human health of the consumption of fish containing these isotopes. PWQOs (based on drinking water requirements) already exist for cesium-137 and strontium-90.These PWQOs should be reviewed with the intent of including human exposure via fish consumption.

The review of tin also posed a problem. There is, currently, insufficient information on the aquatic toxicity of inorganic tin to establish a PWQO. However, within the last few years organotin compounds have come to be realized as a serious threat to aquatic and marine environments. Although much of the toxicity data regarding organotins has used marine species, there appears to be enough information to set an interim guideline. The low levels of organotin already known

to cause aquatic environmental perturbation require that some objective be established pending further investigations into this group of compounds.

Vanadium toxicity to freshwater fish has received sufficient attention to merit the development of a PWQO. It was noted in the literature review, however, that while the data base for fish is comparatively large, little work has been completed with other aquatic organisms. As well, the cycling of vanadium in the aquatic environment is not understood. While a PWQO for vanadium is recommended, it must be stated that it is based almost completely on fish toxicity data.

PART 7.0

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APPENDIX A

J. B. SPRAGUE ASSOCIATES LTD.
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March 28, 1986

Mr. John Ralston, P. Eng.
Water Resources Branch
Ontario Ministry of the Environment
1 St. Clair Ave. West, 4th Floor
Toronto, Ontario
M4V 1P5

Dear Mr. Ralston,

Dr. Dennis M. Trotter of Monenco Consultants Ltd. has asked that I write you, giving my impressions of fulfilment of the contract to review the existing Ontario water quality objectives for metals, and to document recent research. I have now seen drafts of sections for all the metals, and am pleased to report very favourable reactions to the work which has been done.

I am most impressed with the quantity and quality of the material, particularly considering the short time allowed for completion of the contract. I am also impressed with Dr. Dennis Trotter who did most of the work; you have had the services of a professional who is fully conversant with the field of aquatic toxicology. It is my understanding that this report is to be taken as an initial appraisal, and it is a good one. The Ministry has obtained sound advice and extremely good value in the contract, especially considering the modest level of funding for the large number of metals to be evaluated. Finally, I was very pleased with the way Monenco brought me into the project, providing full background information, and sending draft sections as soon as they were available.

In general I agreed with the interpretations and Judgements for the individual metals. I made technical suggestions, of varying importance, for a few metals.

In addition, I passed on to Dr. Trotter some advice on general approaches, for example on the merits of considering chemical species of metal, the importance of eventually Juxtaposing the earlier literature, and the vital need to address the question of mixtures of toxicants. And of course as a professor, I could not resist numerous suggestions on wording, and on definitions of terms, such as misuse of the word "tolerance".

It would appear that the contract would not allow time for Monenco to incorporate many of these suggestions into the report, if it were decided that some were worthwhile. Perhaps the opportunity will arise as the Ministry continues its examination of water quality objectives.

May I take this opportunity to say that I much appreciate the philosophy and the specifics of the Ministry booklet on "Water Management...". I teach water pollution biology to graduating students in the Fisheries and Marine programs at the University of Guelph, and key sections of the booklet are required reading in the course, every semester. I wish you success in your continuing evaluation of the objectives.

Yours sincerely,
John B. Sprague