

Canadian Water Quality Guidelines for the Protection of Aquatic Life

Guidance on the Site-Specific Application of Water Quality Guidelines in Canada: Procedures for Deriving Numerical Water Quality Objectives

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Acknowledgments

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Acronyms

ACR	Acute-to-chronic ratio
ASTM	American Society for Testing and Materials
BAT-EA	Best available technology - economically-achievable
BCWLAP	British Columbia Ministry of Water, Land and Air Protection
CCME	Canadian Council of Ministers of the Environment
CCREM	Canadian Council of Resource and Environmental Ministers
COPC	Chemical of potential concern
DOE	Environment Canada
EC_{50}	Median effects concentration
Eh	Redox potential
EQG	Environmental quality guideline
FWQO	Final Water Quality Objective
ICP	Inductively coupled plasma
IDZ	Initial dilution zone
Кр	Photolysis of chemicals
Ks	Solubility product
LC_{50}	Median Lethal concentration
LOEL	Lowest observable effects level
NOEL	No observed effect level
PeWQO	Preliminary Water quality objective
QA\QC	Quality assurance \ quality control
SD	Standard deviations
TCe	Toxicity concentration of the effluent
TCwb	Toxicity concentration for the effluent in the water body with complete mixing
TER	Toxicity emission rate
TMDL	Total maximum daily loading
TU	Toxic unit
USEPA	Unites States Environmental Protection Agency
WER	Water effect ratio
WQC	Water quality criterion
WQG	Water quality guideline
WQO	Water quality objective
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1 Introduction

Canada is world renowned for the myriad lakes, rivers, streams, and wetland areas that lie within its boundaries. These freshwater ecosystems deliver many essential goods and services to Canadians, including raw water for drinking water supplies, fish and other aquatic organisms that are used for food, irrigation and livestock water for agriculture, and process water to support various industrial activities. Freshwater ecosystems also support a diversity of recreational pursuits, including both contact (e.g., swimming, wading) and non-contact (e.g., fishing, boating) recreation. Additionally, large streams, rivers, and lakes are used to dispose of a variety of industrial, agricultural, and municipal wastes. Finally, water resources have intrinsic aesthetic value to Canadians, even when they aren't being used directly to support human endeavours. Given the overarching importance of these resources, Canada's freshwater ecosystems represent one of Canada's more important and most valuable assets.

Effective long-term management of Canada's water resources will necessitate a transition toward ecosystembased management. Ecosystem-based management has been defined as the integrated management of natural landscapes, ecological processes, physical and biological components, and, most importantly, human activities to maintain or enhance the integrity of the ecosystem (CCME 1996). Implementation of the ecosystem approach requires a framework in which to develop and implement management policies for the ecosystem. This framework consists of five main elements, including (DOE 1996; CCME 1996):

- Identifying and assessing the issues and collating the existing ecosystem knowledge base;
- Developing and articulating ecosystem health goals and objectives;
- Selecting ecosystem health indicators to gauge progress toward ecosystem health goals and objectives;
- Implementing directed research and monitoring programs; and,
- Making informed decisions on the assessment, conservation, protection, and restoration of natural resources.

Identification of appropriate physical, chemical, and biological indicators of ecosystem health and integrity and the selection of corresponding metrics (i.e., the characteristics of the ecosystem that are measured to obtain information on the status of indicators) and targets (i.e., which identify the acceptable range for each of the variables that will be measured to provide information on the status of the indicator) represent central elements of this framework. Environmental quality guidelines (EQGs) represent an essential element of this process because they provide science-based targets for protecting the designated uses of atmospheric, terrestrial, and aquatic ecosystems. In addition, EQGs provide a scientific basis for developing site-specific

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environmental quality objectives. Such objectives form the basis of water management strategies that effectively integrate social, economic, and environmental interests in a manner that supports long-term sustainability.

1.1 Purpose of Report

In Canada, the Canadian Water Quality Guidelines (WQGs) provide a consistent basis for assessing water quality conditions. These WQGs are derived for the protection of four major water uses (CCREM 1987; CCME 1999), including:

- (i) Drinking water supply;
- (ii) Recreational use and aesthetics;
- (iii) Freshwater and marine aquatic life and wildlife; and,
- (iv) Agricultural water uses (irrigation and livestock watering).

Although WQGs for industrial water supplies had been promulgated previously (CCREM 1987), the CCME (1999) no longer reports WQGs of this water use. Additionally, various provincial jurisdictions have promulgated WQGs to ensure that toxic substances do not bioconcentrate to levels that could adversely affect aquatic-dependent wildlife or human health (Table 1). The Canadian EQGs also include guidelines for the protection of ecological receptors and human health. Together, the guidelines provide basic scientific information regarding the effects of toxic and bioaccumulative substances to support the assessment of water quality issues and concerns and to establish WQOs (CCREM 1987). These guidelines are designed to be conservative and, hence, are likely to be applicable to the vast majority of sites in the country.

The Canadian WQGs are intended to protect the designated uses of aquatic ecosystems throughout the country. Nevertheless, it is possible that the guidelines are over- or under-protective at sites with unique conditions. For example, the most sensitive species that occurs at a site may be more or less sensitive than the most sensitive species represented in the toxicological data set that was used to derive the guidelines. Similarly, a substance may be more or less toxic in site water (i.e., due to factors such as pH, water hardness, complexing agents, etc.) than it is under the range of conditions that is represented in the toxicological data set. In some cases, natural background concentrations of a substance may exceed the guideline without any apparent effect on biota (i.e., if the substance is not present in a bioavailable form). Under these circumstances, it might be necessary to modify the WQGs to account for conditions that occur at the site.

In part, concerns related to the applicability of the guidelines can be addressed by considering information on site characteristics in the development of site-specific WQOs. Using this approach, objectives are developed by identifying the most sensitive water use and adjusting the WQG for that water use to account for the site-

specific factors. While this approach is effective at most sites, atypical conditions exist at certain locations which necessitate further modification of the generic WQGs.

This report was prepared to provide scientific and technical guidance on the development of site-specific water quality objectives WQOs). More specifically, this report was prepared to describe the role of WQGs in the management of Canada's water resources (Chapter 2), to present a framework for developing numerical WQOs (Chapter 3), to identify the factors that could influence the derivation of WQOs (Chapter 4 and Appendix 1), and to describe the recommended methods for deriving such WQOs (Chapter 5). The role of site-specific WQOs in the management of point source effluent discharges is also discussed (Chapter 5).

The procedures recommended in this document apply directly to the development of WQOs for metals and metalloids in freshwater systems. Nevertheless, they are also likely to be generally applicable to organic substances and to marine and estuarine systems, with minor modifications. The recommended procedures are illustrated using two case studies to better enable the reader to understand and apply the recommended methods (Appendix 2 and 3). It is important to note that the methods and procedures recommended in this report are intended to describe the methods that could be used to derive site-specific WQOs in Canada. These recommendations are not intended to prescribe the methods that must be used to derive site-specific WQOs in Canada. Rather, they are intended to assist responsible authorities in the selection of methods that apply most directly to their jurisdiction. The ultimate responsibility for deciding which method, if any, is to be used at specific sites rests with the responsible authorities within each province and territory in the county. Additionally, the potential benefits of deriving site-specific WQOs should be evaluated at the outset, regardless of who undertakes the work.

2 Water Quality Guidelines: A Cornerstone of Water Resources Management in Canada

Effective management of liquid wastes originating from municipal, industrial, agricultural, and other sources represents a formidable challenge, both in Canada and elsewhere worldwide. Resource managers in federal, provincial, and territorial jurisdictions are addressing this challenge using a variety of tools. For example, releases of deleterious substances to fish-bearing waters are prohibited under federal legislation (i.e., *Fisheries Act*). In addition, limits on the releases of toxic and/or bioaccumulative substances have been established for several industrial sectors by the federal government (e.g., Metal Mining Liquid Effluent Regulations; MMLERs). Furthermore, policies have been established by the federal government to reduce or eliminate the risks associated with production, use, and disposal of substances of particular concern (e.g., Environment Canada's Toxic Substances Management Policy). Importantly, programs are in place in every province and territory for licencing or permitting point source effluent discharges to surface waters. Together, these

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strategies provide an administrative basis for managing the releases of liquid wastes into the Canadian environment.

Although the administrative tools available to support water resources management are similar across Canada, the approaches that have been used within the various jurisdictions differ depending on the management goals that have been established. For example, many jurisdictions have applied a technology-based approach to manage releases of liquid effluents. In the technology-based approach, limits on the releases of chemicals of potential concern (COPCs) are frequently established for point source effluent discharges based on the best available technology - economically-achievable (BAT-EA; Song and Marolf 1993). For example, MMLERs specify the maximum concentrations of certain metals and other water quality variables that can be released to the environment in liquid effluents from metal mines. As such, receiving water quality primarily depends on the effectiveness of the existing treatment technology that is being used by a particular facility or industrial sector and the dilution capacity available in the receiving water system. The potential effects of wastewater discharges on designated water uses are generally not considered when discharge limits are established using the BAT-EA approach; however, environmental monitoring (such as that conducted under the Environmental Effects Monitoring Program) provides the information needed to assess the effects associated with point source discharges.

A second approach to the management of liquid effluents is commonly referred to as the use protection approach. Application of this approach involves the establishment of discharge limits for substances of concern (i.e., from one or more point source effluent discharges) based on an understanding of the assimilative capacity of the water body under consideration. In this context, assimilative capacity is defined as quantity of a substance that can be released into a water body during a specific period of time without adversely affecting the designated water uses. This general approach allows environmental managers, in conjunction with stakeholders, to develop broad ecosystem management goals and to assess the benefits and costs of various management options in the context of these goals. Because the use-protection approach accommodates the multiple use of aquatic ecosystems and minimizes conflicts between competing interests, it has been incorporated as a central component of the approach to water management in several Canadian jurisdictions. In applying this approach, all reasonable and preventative measures should be taken to maintain conditions in waters with superior water quality characteristics (i.e., better than the Canadian WQGs; CCME 1999).

The third approach that can be used in water resources management is referred to as the non-degradation approach. Using the non-degradation approach, discharge limits are established based on the natural background levels of substances of concern at the site. Implementation of this approach ensures that environmental receptors are not exposed to elevated levels of environmental contaminants and, hence, have no incremental risk of adverse effects due to discharges from point sources. However, technological limitations and costs are likely to preclude the implementation of this option under most circumstances (USEPA 1988a).

For this reason, the non-degradation approach has generally been applied to waters of high regional, national, or international significance.

Regardless of which of these approaches is applied to support the management of water resources, environmental managers require tools that enable them to evaluate ambient water quality conditions in freshwater, estuarine, and marine waters. In Canada, the *Canadian Water Quality Guidelines* provide the science-based tools to support the conservation and wise management of our shared water resources (CCREM 1987; CCME 1999). This chapter is intended to provide background information relevant to the site-specific application of *Canadian Water Quality Guidelines*. More specifically, this chapter discusses the origins, development, and recommended uses of the *Canadian Water Quality Guidelines*.

2.1 Origins of Canadian Water Quality Guidelines

Environmental managers have recognized the need for numerical WQGs for many years. Although toxicological data linking exposure to toxic substances and associated effects on environmental receptors and human health have been available for hundreds of years, systematic interpretation of such data to support the derivation of numerical WQGs has occurred only relatively recently. In Canada, the development of numerical WQGs began in earnest in the mid 1970's. This work lead to the release of a number of WQGs documents by Environment Canada in the late 1970's and early 1980's (e.g., Reeder *et al.* 1979a; 1979b; Demayo *et al.* 1979a; 1979b; 1980; Taylor *et al.* 1979a; 1979b; 1980a; 1980b) and by various provincial agencies in the early 1980's. In recognition of the advantages of collaborating on the formulation of WQGs, the Canadian Council of Ministers of the Environment (CCME; formerly the Canadian Council of Resource and Environment Ministers; CCREM) appointed a Task Force on WQGs (Task Force) in 1983 to:

- Develop an inventory of water quality criteria (WQC) and guidelines used by governments throughout Canada;
- Review the assembled inventory and make recommendations on the desirability of, and possibilities for, harmonization of WQGs throughout Canada; and,
- Identify emerging water quality issues and assess the ability of the existing WQC and guidelines to address these issues.

Based on the results of its review and evaluation, the Task Force recommended harmonization of Canadian WQGs. The Task Force was subsequently charged with the task of preparing Canadian WQGs.

The CCME published the *Canadian Water Quality Guidelines* in 1987 (CCREM 1987). The *Canadian Water Quality Guidelines* were developed to provide basic scientific information about the effects of water quality variables on uses in order to assess water quality issues and concerns and to establish WQOs for specific sites (CCREM 1987). The existing guidelines from many sources were reviewed and evaluated to support the

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establishment of numerical WQGs. Guidelines that were found to be appropriate for Canadian conditions were adopted directly as *Canadian Water Quality Guidelines*. Guidelines that were found to be less appropriate were modified so that they could be used under Canadian conditions, if sufficient scientific data were available to do so. If no published guidelines were available for a substance or insufficient scientific data were available to facilitate modification of an existing guideline, then no *Canadian Water Quality Guideline* was recommended for that substance. This pragmatic approach enabled the Task Force to recommend numerical WQGs for more than 50 water quality variables, including a substantial number of toxic and/or bioaccumulative substances.

Because water quality requirements differ for various water uses, the CCREM (1987) developed numerical WQGs for a number of water uses. More specifically, the *Canadian Water Quality Guidelines* provided a compilation of WQGs for protecting the following uses of freshwater ecosystems:

- Raw water for drinking water supply;
- Recreational water quality and aesthetics;
- Freshwater aquatic life;
- Agricultural uses; and,
- Industrial water supplies.

Since the original *Canadian Water Quality Guidelines* were published, understanding of the threats to ecosystem health has increased substantially. Canadians have realized that a more holistic approach is needed to protect and manage the various living and non-living components of the ecosystem. In response to concerns regarding the status and trends of aquatic and terrestrial ecosystems in Canada, CCME (1999) expanded the scope of the *Canadian Water Quality Guidelines* to address the protection of other atmospheric, aquatic, and terrestrial resources, including air quality, marine water quality, marine and freshwater sediment quality, tissue quality, and soil quality. The Canadian EQGs that emerged from this initiative represent scientifically-defensible goals for the quality of atmospheric, aquatic, and terrestrial ecosystems. The CCME (1999) defines EQGs as:

Numerical concentrations or narrative statements that are recommended as levels that should result in negligible risk to biota, their functions, or any interactions that are integral to sustaining the health of ecosystems and the designated resource uses they support.

2.2 Procedures for Deriving Canadian Water Quality Guidelines

Although the approach that was used to establish the original *Canadian Water Quality Guidelines* provided an effective means of addressing the immediate need for numerical WQGs, the CCME recognized that a more rigorous process would be required to support the derivation of WQGs for substances for which published guidelines were not yet available. For this reason, the Task Force of WQGs developed a series of protocols to support the derivation of *Canadian Water Quality Guidelines*. The first in the series was *A Protocol for the Derivation of Water Quality Guidelines for the Protection of Aquatic Life* (Appendix IX of CCREM 1987; CCME 1991). This protocol established a number of Guiding Principles for the development of WQGs, provided an overview of the guideline derivation protocol, and discussed the uses of WQGs and WQOs in water quality management. Importantly, the protocol document also established minimum data requirements for deriving WQGs, detailed the methods for evaluating candidate toxicological data, and described the procedures for calculating guidelines from acute and chronic toxicity data.

The Guiding Principles included in the protocol document outline the philosophical underpinnings of the *Canadian Water Quality Guidelines* in terms of the level of protection afforded ecological receptors and interpretation of the resultant guidelines (CCME 1991), including:

- In deriving the *Canadian Water Quality Guidelines* for aquatic life, all components of the ecosystem (e.g., algae, macrophytes, invertebrates, fish) are considered if the data are available. Where data are available but limited, interim guidelines are deemed preferable to no guidelines;
- The approach to the development of guidelines for aquatic life follows that of the International Joint Commission and the Ontario Ministry of Environment. This approach states that guidelines "are set at such values as to protect all forms of aquatic life and all aspects of aquatic life cycles." The goal is to protect all life stages during an indefinite exposure to water. Whether this goal can be realized is a water management issue and does not affect the guideline derivation procedure;
- For most water quality variables, a single maximum value, which is not to be exceeded, is recommended as a *Canadian Water Quality Guideline*. This maximum is based on a long-term no-effect concentration; and,
- Unless otherwise specified, a guideline value refers to a total concentration of a substance in an unfiltered sample. Total concentrations will apply unless it can be demonstrated that: (a) the relationship between the variable fractions and their toxicity is firmly established; and, (b) analytical techniques have been developed that unequivocally identify the toxic fraction of a variable in a consistent manner using routine field-verified measurements.

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In addition to their relevance for deriving *Canadian Water Quality Guidelines*, these Guiding Principles are critically important to the development of site-specific WQOs, which is discussed in the subsequent chapters of this report.

In accordance with the above Guiding Principles, *Canadian Water Quality Guidelines* are derived only if sufficient scientific data are available. The types of information that are collected to support guideline derivation include: physical and chemical properties; environmental levels; environmental fate and behaviour; bioaccumulation; acute and chronic toxicity to aquatic organisms; genotoxicity; and, guidelines from other jurisdictions. The protocol document outlines the minimum environmental fate and effects data for deriving WQGs and interim WQGs (CCME 1991). These minimum data requirements assure that data on the toxicity of a substance to key components of the aquatic ecosystem, including fish, invertebrates, and plants, are included in the guideline derivation process.

Assuming that the requisite environmental fate and effects data are available, numerical WQGs are derived using a straightforward process. Guidelines are preferentially derived from the lowest observed effect level (LOEL) from a chronic study using a nonlethal endpoint for the most sensitive life stage of the most sensitive aquatic species investigated (CCME 1991). However, guidelines may be derived from acute studies if such chronic toxicity data are unavailable. Using appropriate data from a chronic toxicity test, the guideline is derived by multiplying the most sensitive LOEL by a safety factor of 0.1 (CCME 1991). In the absence of an appropriate measured chronic LOEL, such a value can be estimated by multiplying an LOEL from an acute toxicity test by an acute-to-chronic ratio (ACR). An ACR is calculated by dividing a median lethal concentration (LC₅₀) or a median effects concentration (EC₅₀) by the no observed effect level (NOEL) from a chronic exposure test for the same species (i.e., LC_{50}) NOEL). If an acceptable ACR is not available, then the guideline value is derived by multiplying the acute LC_{50} or EC_{50} by an application factor. For nonpersistent substances (i.e., half life in water of <8 weeks), an application of 0.05 is used to derive the WQG. Alternatively, an application of 0.01 is used to derive the WQG for persistent substances (i.e., half life in water of <8 weeks).

The WQG derivation process culminates in the preparation of detailed technical report that summarizes the results of the investigations. These technical reports are reviewed by the members of the Task Force and the resultant guidelines are approved if they are found to be scientifically-defensible. This rigorous process assures the internal consistency and scientific validity of the *Canadian Water Quality Guidelines for the Protection of Aquatic Life*. Protocols for the development of *Canadian Water Quality Guidelines* for irrigation and livestock watering have also been established to assure the consistency and validity of the guidelines of these water uses (CCME 1993).

2.3 Applications of Canadian Water Quality Guidelines

The *Canadian Water Quality Guidelines* are science-based tools for assessing the quality of aquatic ecosystems. As indicated above, the guiding principles and procedures for deriving such WQGs have been documented in a series of national scientific protocols (CCME 1999). Importantly, the use of national protocols ensures consistency, transparency, and scientific defensibility in the guidelines development process (CCME 1999). These characteristics make the *Canadian Water Quality Guidelines* useful in various environmental assessment and management programs. Some of the recommended applications of the *Canadian Water Quality Guidelines* include (CCME 1999):

- National benchmarks to assess potential or actual impairment of socially-relevant water uses;
- The scientific basis for the development of site-specific WQOs and standards;
- Indicators for state-of-the-environment reporting;
- Science-based performance indicators for regional, national, or international management strategies for toxic substances;
- Interim management objectives for persistent, bioaccumulative, and toxic substances to track progress toward virtual elimination;
- Indicators of ecotoxicologically-relevant concentrations of persistent, bioaccumulative, and toxic substances for the purpose of improving analytical detection and quantification capabilities;
- Tools for developing licences and/or permits for point source effluent discharges, in conjunction with the application of best available technology;
- Tools to evaluate the effectiveness of point source controls;
- The scientific basis for environmental regulations;
- Scientific benchmarks or targets in the assessment and remediation of contaminated sites; and,
- Science-based assessments and tools for consideration in the development of Canada-wide standards under the Canada-wide Accord on Environmental Harmonization.

Although the *Canadian Water Quality Guidelines* are broadly used within Canada and elsewhere to assess and manage water quality conditions, they should not be regarded as blanket values for national environmental quality (CCME 1999). Variations in environmental conditions across the country have the potential to influence the applicability of the *Canadian Water Quality Guidelines*. More specifically, factors such as elevated natural background levels of COPCs, the atypical levels of water quality variables that influence the bioavailability and/or toxicity of COPCs, and the sensitivity ranges of resident species can limit the applicability of generic WQGs. Therefore, it may be necessary to establish site-specific WQOs that account for such variations in environmental conditions.

When used in conjunction with robust water quality monitoring data, WQGs and WQOs provide effect tools for assessing ambient water quality conditions in Canada. Interpretation of such data can be further enhanced through the application of the CCME Water Quality Index.

3 Approaches for Developing Site-Specific Water Quality Objectives in Canada

The *Canadian Water Quality Guidelines* provide important information for assessing water quality issues and establishing WQOs (CCREM 1987; CCME 1999). Water quality objectives are science-based tools that provide an effective basis for managing the resources in aquatic ecosystems. These tools describe conditions that environmental managers and stakeholders agree should be met to protect the designated uses of freshwater, estuarine, and marine ecosystems. Water quality objectives are used in conjunction with other management tools, such as permitting processes, technology development, and enforcement, to achieve environmental conditions that support sustainable resource use. This chapter is intended to describe the strategies that can be used for deriving and implementing site-specific WQOs in Canada. In addition, a number of guiding principles are offered to encourage consistency and defensibility in the WQOs development process. Finally, several general approaches to the derivation of site-specific WQOs are recommended.

3.1 Defining Water Quality Objectives

According the CCREM (1987), WQOs are defined as numerical concentrations or narrative statements that establish the conditions necessary to support and protect the most sensitive designated use of water at a specified site. Objectives are typically based on generic WQGs, which may be modified to account for local environmental conditions or other factors. In general, WQOs are prepared only for those water bodies and water quality variables that may be significantly affected by human activities, either now or in the future. (Please note that the terms criteria and guidelines are used interchangeably in this discussion and are considered to be functionally equivalent).

Water quality objectives have no legal standing at this time and, therefore, are not enforced directly. While a formal mechanism has not been established, WQOs are often used in permitting and licensing processes. In addition, the WQOs can be employed to support a broad range of land use management decisions. Furthermore, decisions on the need for habitat restoration and other remedial actions may be based, in part, on WQOs. Importantly, WQOs also provide standards for assessing the performance of water management initiatives in Canada.

3.2 Philosophical Basis for Developing Site-Specific Water Quality Objectives

Two distinct strategies are commonly used to establish WQOs in Canada, including the antidegradation strategy and the use protection strategy. For water bodies with aquatic resources of national or regional significance, the WQOs are established to avoid degradation of existing water quality. For other water bodies, the WQOs are established to protect the designated uses of the aquatic ecosystem. As long as the designated water uses are protected, some degradation of existing water quality may be acceptable in these water bodies, provided that all reasonable and preventative measures are taken to protect water quality conditions.

3.3 Guiding Principles for the Development of Site-Specific Water Quality Objectives

Development of site-specific WQOs is a complicated process. Derivation of such WQOs requires extensive knowledge of the physical, chemical, and biological characteristics of the water body under consideration, as well as the social and economic characteristics of the local area (CCME 1999). Once such information is acquired, WQOs are derived using the national protocols for deriving *Canadian Water Quality Guidelines* (CCME 1991; 1993), considering the species and environmental conditions that are relevant to the site. Social and economic factors may then be considered to determine if the objectives can realistically be attained in the near term (CCME 1999). Information on the social and economic conditions within the watershed under consideration can also be used in establishment of effluent regulations that may provide regulated interests with more time to meet the WQOs in receiving water systems. In some jurisdictions, both acute and chronic objectives may be established for the same substance to support water quality management in the vicinity of effluent discharges. Periodic assessments are conducted to refine the WQOs and pollution control programs, if necessary, to ensure that the desired water quality is maintained.

Site-specific WQOs may be derived by federal, provincial, or territorial agencies, First Nations, regulated interests, or non-governmental organizations. Therefore, it is important to establish a set of guiding principles that enables any guideline user to derive site-specific WQOs that are consistent with the CCME principles. The following guiding principles for the development of numerical WQOs are based on the philosophy established by the CCME (1991; 1993) and B.C. Ministry of the Environment (BCMOE 1986; Water Management Branch 1984; MacDonald 1997):

- Water quality objectives should be developed to protect the most sensitive water use at the site;
- The water uses to be protected include raw water for drinking water supplies, recreation and aesthetics, aquatic life, wildlife, agriculture (including livestock water and irrigation), and tissue quality (i.e., for the protection of aquatic-dependent wildlife and human health);
- The *Canadian Water Quality Guidelines* for the most sensitive water use for each should be adopted as the preliminary WQO (PeWQO) for each water quality variable for a site;

- The approach used to develop WQOs should follow the formal protocols established by the CCME (1991; 1993), appropriate protocols established by provincial or territorial jurisdictions; and the guidance provided in this document;
- At sites which have atypical water quality characteristics or ecological receptors, the Canadian WQGs could be modified to account for these site-specific factors;
- The administrative rules (see Section 5.4) specify the conditions under which the Canadian WQGs could be modified or site-adapted;
- For the purpose of deriving site-adapted WQOs for the protection of aquatic life, information on the aquatic organisms (e.g., algae, invertebrates, fish, and amphibians) that are not relevant to the site under consideration may be omitted from the toxicological data set, provided that the minimum data requirements for deriving guidelines are met (CCME 1991). As degraded sites may have altered communities of aquatic organisms, information from a suitable reference site should also be used for identifying the species that are relevant to the site and, subsequently, refining the toxicological data set for deriving the site-adapted WQOs;
- Chemical (numerical WQOs), toxicological (toxicity test results), and/or biological (aquatic ecosystem community structure, etc.) indicators can be used to evaluate attainment of the management goals at the site under consideration (Table 2); and,
- Technical, social, and economic issues considered in the development of final WQOs should be reviewed and approved by the responsible agency(ies) considering the input provided by relevant stakeholder groups.

3.4 Recommended Approaches for Deriving Site-Specific Water Quality Objectives

There are a number of approaches that can be used to derive site-specific WQOs (See MacDonald and Sobolewski 1993; MacDonald 1997 for descriptions of the various approaches). In Canada, the responsible authorities for managing water resources have the responsibility for deciding which approach, if any, is most appropriate for use in their jurisdiction. The approaches described herein are not intended to be prescriptive; rather, they are intended to provide federal, provincial, and territorial agencies with general guidance on the development of site-specific WQOs.

The use-protection strategy described above provides a consistent scientific basis for establishing WQOs that accommodate multiple water uses of aquatic ecosystems. Using this strategy, ambient WQOs can be derived using three separate approaches, including:

• Direct adoption of *generic* WQGs;

- Derivation of *site-adapted* WQOs (e.g., which involves modification of the generic WQGs using the recalculation or water effect ratio (WER) procedures; see Section 4.2 and 4.3, respectively); and,
- Development of *site-specific* WQOs (e.g., using the resident species procedure; see section 4.4).

At most sites, the generic WQGs can be adopted directly as WQOs. Infrequently, such generic guidelines may require modification before they are directly applicable to certain sites, especially those sites with water quality conditions or assemblages of resident species that are different from those used to develop the guidelines. Alternatively, it may be necessary to develop WQOs on a *de novo* basis (i.e., by utilizing site-specific data only) in some cases, particularly when a high level of accuracy in the resultant objectives is required. Some of the factors that influence the applicability of the generic guidelines are identified and discussed in the following section.

Development of numerical WQOs from the generic WQGs involves a number of steps. The first step in this process involves identification of the designated uses of the aquatic ecosystem. Next, a list of water quality variables of concern (which are also referred to as chemicals of potential concern; COPCs) is prepared using information on the existing and proposed human activities in the basin. Screening the data on wastewater and receiving water quality using the generic WQGs also supports the identification of COPCs. However, it may be necessary to utilize more sophisticated methods to identify the COPCs that represent significant hazards to aquatic organisms when complex mixtures of contaminants are present in wastewaters or receiving waters (e.g., toxicity identification evaluation procedures; Ankley and Thomas 1992). Once the COPCs are identified, the available WQGs for each substance and each water use are compiled and modified to account for the ambient water quality characteristics of the water body (e.g., pH, water hardness, etc.). For each substance, the WQG for the most sensitive water use is then selected as the preliminary WQO. The preliminary WQOs are subsequently compared to the natural background concentrations of each substance, and the higher of the two values is selected as the WQO for that substance.

While adoption of generic WQGs represents the primary procedure for establishing numerical WQOs, the presence of unique water quality characteristics or species assemblages at certain sites may necessitate the derivation of site-adapted WQOs. For example, the receiving water at a site could have high levels of dissolved organic carbon, which has the potential to complex dissolved metals and reduce their toxicity. Alternatively, the receiving water system could contain only a warmwater fish assemblage, which may be less sensitive to certain contaminants than salmon or trout. The presence of endangered species represents a special concern because these species are often highly sensitive to toxic and/or bioaccumulative substances. In each of these situations, the development of site-adapted WQOs would be appropriate. Therefore, procedures are needed for deriving WQOs that consider the sensitivities of resident species and/or the effect of site water characteristics on contaminant toxicity.

At a few sites, it might be necessary to develop very accurate WQOs that are directly applicable to the receiving water system under investigation. For example, it might be necessary to develop such site-specific WQOs when insufficient toxicological data are available to develop generic WQGs for a substance. Alternatively, insufficient information on the physical, chemical, and biological characteristics of the receiving water system may be available to modify the generic WQGs to consider site conditions. The development of manufacturing processes that reduce the production of waste products and improve the performance of wastewater treatment systems are normal research and development activities that are actively pursued by all responsible corporations and government organizations. Nonetheless, it is possible that the costs associated with implementing the remedial measures necessary to comply with the WQOs could be substantial in certain situations. In such cases, more certainty in the WQOs may be required to assure that such expenditures are justified. Such site-specific WQOs should account for both the sensitivities of resident species and the effects of site water on contaminant toxicity simultaneously.

4 Procedures for Deriving Site-Specific Water Quality Objectives

In Canada, the *Canadian Water Quality Guidelines* provide the basic scientific information that is needed to evaluate the effects of water quality variables on the designated uses of water resources (CCREM 1987; CCME 1999). In addition to supporting the assessment of water quality issues and concerns, WQGs can be used to establish WQOs for specific sites throughout the country. However, there are a number of factors that have the potential to affect the site-specific applicability of generic WQGs, including:

- Background levels of the substance under consideration;
- Analytical detection limits for the substance under consideration;
- Levels of the variables that have the potential to alter the toxicity of the substance under consideration; and,
- Sensitivity ranges of resident species to the substance under consideration.

A detailed discussion of the physical, chemical, and biological interactions that occur in freshwater systems, as well as their potential influences on the derivation of WQOs, is provided in Appendix 1. In recognition of the potential influence of these factors, a number of procedures have been developed to provide a basis for deriving WQOs that consider the hazards to aquatic organisms associated with exposure to water-borne contaminants. These procedures include:

- Background concentration procedure;
- Recalculation procedure;
- Water effect ratio procedure; and,

• Resident species procedure.

In this chapter, the available information on these procedures for deriving WQOs is reviewed and summarized to provide the reader with adequate information for assessing their potential applicability for use in Canada.

4.1 Background Concentration Procedure

In the background concentration procedure, the natural background concentrations of a contaminant in water (which is termed the non-reductable background in Quebec) are determined and these levels are used to define acceptable water quality conditions at the site under consideration. Its use is based on the premise that surface water systems with superior water quality (i.e., relative to the Canadian WQGs) should not be degraded (CCREM 1987). This approach has been used most commonly to define WQOs for relatively pristine water bodies, including several river systems in Canada (e.g., Dunn 1989; MacDonald and Smith 1990). It has also been used in somewhat contaminated water bodies, such as Burrard Inlet (Nijman and Swain 1989). In addition to supporting the establishment of site-specific WQOs, the information generated to support this procedure (i.e., data on background levels of water quality variables) is essential for evaluating the suitability of the WQOs derived using other procedures.

Site-specific WQOs, developed using the water background concentration approach, may be established in at least two ways. First, the upper limit of natural background of a substance may be established as the WQO. In general, statistical procedures are used to estimate the upper limit of background. For example, Dunn (1989) defined the upper limit of background for 15 water quality variables as their mean value plus two standard deviations (SDs), while Breidt *et al.* (1991) used the 90th percentile value to establish these limits. In Quebec, the median value is used to estimate non-reductable background levels (Sinotte et al. 1996). Other statistical procedures have also been recommended for analyzing data on background water quality conditions (Warn 1982; Van Hassel and Gaulke 1986). Second, the WOO for a substance may be set at a level which is slightly above the background level. For example, Singleton (1985) suggested that fish and aquatic life in stream systems would be protected if suspended sediment concentrations were elevated by no more than 10% above background levels. For flow- or temperature-dependent water quality variables, the WQO may be set at the upper 95% prediction limit of the regression equation for the dependent and independent variables (i.e., either temperature or flow; Schropp et al. 1990). This approach results in the establishment of WQOs that vary over time and space, in contrast to the single values that are routinely derived. Application of all of these procedures depends on the availability of monitoring data for appropriately selected reference sites (i.e., not influenced by point source discharges). Alternatively, regionally applicable data on background concentrations may be used when site-specific data are not available.

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The background concentration approach is directly applicable to the development of site-specific WQOs for waters of national or regional significance. In addition, the procedures that have been developed to support this approach may be used directly in the process for developing WQOs using the use-protection strategy. Specifically, information on background levels is required to assess the applicability of the preliminary water quality objectives (PeWQOs) that are selected from the available effects-based WQGs. This assessment is needed to ensure that the WQOs represent realistic targets for water management (i.e., the WQOs should not be lower than background concentrations).

Three general approaches have been used to define background concentrations of water quality variables, which involve:

- Utilization of historically-collected water quality data for the site (i.e., prior to the commencement of activities that could have substantially altered water quality conditions);
- Monitoring contemporary water quality conditions at one or more stations located upstream of contaminant sources; and,
- Monitoring contemporary water quality conditions at one or more reference areas, which are generally located nearby the site under consideration but have not been adversely affected by human activities.

Determination of the most appropriate method for establishing natural background concentrations requires consideration of a number of factors related to the water body under study. For example, one of the major difficulties associated with the implementation of the background concentration procedure relates to the variability of water quality over time and space. River systems and estuaries are subject to large variations in water quality on daily, seasonal, and annual bases. In these types of water bodies, extensive sampling effort is required to accurately define background concentrations. In addition, it may be difficult to identify suitable reference sites in areas that have been affected by anthropogenic activities for extended time periods (e.g., in areas affected by mining or urban development; Runnels *et al.* 1992). In such cases, it may be necessary to identify nearby reference areas with similar geological, topographical, physiographical, climatological and ecological features to define background levels of naturally-occurring substances.

4.2 Recalculation Procedure

The recalculation procedure is a method for deriving site-specific WQOs that accounts for any real differences between the sensitivity range of the species of aquatic organisms represented in the complete toxicological data set and that of the species that occur at the site under consideration (USEPA 1983). For example, or more specifically, aquatic species that occur at the site are those species (genera, families, orders, etc) that are:

- Usually present at the site;
- Present at the site only seasonally due to migration;
- Present intermittently because they periodically return to or extend their range into the site;
- Not currently at the site due to degraded conditions;
- Are present in nearby bodies of water; or,
- Were present at the site in the past and are expected to return to the site when conditions improve.

Using this procedure, data on species that are not resident at the site under consideration are eliminated from the data set that was assembled to formulate the generic WQG. Then, a site-adapted WQO is calculated using the same methodology employed to derive the generic WQG. The recalculation procedure may be used to derive site-specific WQOs only if the minimum data requirements established for formulating national WQGs are met (CCME 1991; 1993). Otherwise, additional toxicity testing on resident or appropriate indicator species in laboratory water is needed to generate the information necessary to derive the site-adapted WQOs.

The recalculation procedure is directly applicable to the derivation of site-adapted WQOs in Canada. When used in conjunction with the protocol for the derivation of WQGs for the protection of aquatic life (CCME 1991), the recalculation procedure provides a practical means of modifying the generic WQGs to reflect the sensitivities of the species that are present or ought to be present at the site under investigation. The recalculation procedure is likely to be relevant when the most sensitive species represented in the complete toxicological database does not occur at the site under consideration.

The principal advantage of the recalculation procedure is that it provides a simple, but defensible, basis for deriving site-adapted WQOs. For many substances (trace metals, toxic compounds of nitrogen, certain pesticides), the data required to derive the site-adapted WQOs are likely to be available in the toxicological data set that was used to develop the generic WQGs. Notwithstanding the associated costs, missing data may be generated by conducting toxicity tests on resident species or appropriately selected resident species. Hence, it should be possible to derive the site-adapted WQOs for many substances.

Several limitations of the recalculation procedure were identified by USEPA (1983). First, additional field investigations may be needed to comprehensively identify resident species within the water body under consideration. In addition, elimination of information on non-resident species from the data set may necessitate the generation of additional toxicological information on resident species to support the derivation of site-adapted WQOs. Depending on the number of species and chemicals for which data are required, this process could be costly and time-consuming.

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4.3 Water Effect Ratio Procedure

The WER procedure represents a powerful tool for modifying generic WQGs to account for the unique characteristics of the site under investigation. This procedure is based on the assumption that the physical and/or chemical characteristics of water can vary among sites and can influence the bioavailability and, hence, toxicity of environmental contaminants. In many cases, the factors that influence the toxicity of xenobiotic substances have been identified. For example, relationships between water hardness and acute toxicity to fish have been established for several metals (e.g., cadmium, copper, lead, nickel, and zinc; CCREM 1987; Nagpal 1997). Likewise, the toxicity of ammonia to fish is known to be a function of pH and temperature (MacDonald *et al.* 1987). The presence of other contaminants and other factors (such as suspended particulate matter) at a site can also affect the bioavailability of the substance under consideration. Therefore, consideration of the factors that could influence the toxicity and/or bioavailability of a substance at a site is likely to improve the applicability of the resultant WQO.

Using the WER procedure, acute and/or short-term chronic toxicity tests are conducted with indicator and/or resident species using both site water and laboratory water (i.e., standard reconstituted laboratory water). Indicator species are acceptable non-resident species that are used as surrogates for resident species. Typically, rainbow trout (*Onchorynchus mykiss*), fathead minnows (*Pimephales promelas*), the water flea, (*Ceriodaphnia dubia*), and the alga, *Selenastrum capricornutum* are used to assess the influence of site water quality conditions on the toxicity of COPCs because they are easy to culture, widely available, and consistently generate reliable data (Willingham 1988; MacDonald *et al.* 1989). Moreover, they either occur or are representative of the species that occur at sites in Canada (i.e., they are good surrogates for resident species).

The information generated in these toxicological investigations is used to determine the ratio of the toxicity of the substance in water from the site to its toxicity in laboratory water, which is known as the *water effect ratio*. The calculated WER is then used directly to convert the generic WQG to a site-adapted WQO. For example, if a substance is twice as toxic in site water as it is in laboratory water, then the generic WQG would be divided by a factor of two to obtain the site-adapted value. Toxicity data on at least one fish and one invertebrate species are required to calculate the geometric mean WER, which is then used to modify the generic WQG (USEPA 1994).

The WER procedure is likely to be directly applicable to the derivation of site-adapted WQOs in Canada, particularly for COPCs such as ammonia and certain metals. The methods for assessing the acute and short-term chronic toxicity of water-borne substances have been well established (see USEPA 1993a; 1993b; DOE 1990a; 1990b; 1990d; 1992a; 1992b; 1992c). These methods provide a reliable basis for determining WERs for priority substances and, hence, for modifying the generic WQGs for the protection of aquatic life. This type of information can also be used to derive site-specific objectives on a *de novo* basis, provided that the minimum data requirements identified in the protocol document have been met (CCME 1991).

The WER procedure is an extremely useful tool for modifying generic WQGs to account for unique characteristics of the site under investigation. By explicitly considering the toxicity of a substance in the site water, this procedure supports the development of WQOs that are reliable and relevant to the site. In addition to this significant advantage, this procedure is supported by toxicity tests that are easy to run, reasonably inexpensive, and available at most biological testing facilities. The quality of these tests is easily evaluated using the results of the positive (reference toxicant) and negative (solvent only) controls that must be run simultaneously. Furthermore, the bioassays may be performed on site (both flow-through or static tests) or site dilution water can be shipped to a laboratory for off-site testing (static tests only), which adds a considerable level of flexibility to the process.

Perhaps the major limitation of the procedure is that it does not consider the temporal variability of water quality at the site (USEPA 1983). In general, the acute toxicity tests are conducted over a discrete time interval (usually about a week). As such, the WER that is calculated for the site is, necessarily, specific to the sampling program that was used to obtain the site water. It is important to explicitly recognize this limitation because this procedure provides very precise results which tend to generate a great deal of confidence in the WQOs derived. Nevertheless, the WQOs might not be applicable under other circumstances, such as during periods of elevated streamflow. Therefore, information on the variability of water quality conditions at the site is needed to design a representative toxicity testing program. Diurnal variability in water quality may be accommodated by conducting flow-through bioassays, while seasonal changes in the characteristics of the site water may be assessed by performing tests at key periods throughout the year (e.g., under high flow and base flow conditions). Another limitation of the procedure is associated with the complexity of the implementation guidance that is currently available (i.e., USEPA 1983; 1994). Many of the practitioners that were contacted found the guidance documents to be highly complicated and confusing. Finally, care must be taken to ensure that potentially confounding factors (such as differences in Ca:Mg ratios, alkalinity, and pH between site water and laboratory water) are adequately controlled during toxicity testing (Welsh *et al.* 2000).

4.4 Resident Species Procedure

The resident species procedure is designed to account for both of the major factors affecting the derivation of site-specific WQOs: the sensitivity of the species that occur at the site; and, the influence of site water characteristics on toxicity (USEPA 1983). This procedure involves the generation of a complete data set on the toxicity of the substance under consideration using site water and resident species (i.e., the data set must satisfy the minimum data requirements for deriving WQGs). In accordance with the CCME (1999) protocol, at least six species of aquatic organisms that are resident at the site must be represented in this data set, including three fish species, two invertebrate species, and one algae or aquatic vascular plant species. Following their generation, these site-specific toxicity data are used directly to establish the final WQOs for the substance at the site (i.e., using the procedures outlined in the national protocol documents; CCME 1991; 1993).

The resident species procedure provides a very effective tool for deriving site-specific WQOs when the applicability of generic WQGs to the site is questionable or when such WQGs are not available. WQOs derived using this highly specific data set are likely to be very accurate and, hence, a great deal of confidence may be placed on them.

The most serious drawback of this procedure is the cost of conducting the extensive suite of bioassays required to support the derivation of site-specific WQOs. These costs may be even higher than anticipated if significant daily or seasonal variability in water quality is evident at the site. Likewise, costs could escalate if difficulties are encountered in culturing and testing resident species. Many of the limitations discussed for the recalculation and WER procedures also apply to this procedure (USEPA 1983).

Due to the costs associated with the implementation of this procedure, the resident species procedure is likely to have only limited application in Canada. Nevertheless, the procedure provides a consistent and reliable basis for deriving *de novo* WQOs when generic WQGs are not available and insufficient toxicological information is available to support their derivation. Implementation of this procedure may also be warranted at sites where a high degree of confidence in the WQO is required (e.g., at contaminated sites that are slated to be remediated). Likewise, it may be desirable to use this procedure when the costs associated with remediation are expected to be high.

4.5 Summary

Four distinct procedures were reviewed to identify methods that could be used to derive numerical WQOs in Canada. Evaluation of these procedures indicated that no single method can adequately address all of the potential requirements for objectives development (Table 3). For this reason, the most useful elements of each procedure were identified and integrated into the recommended methods for deriving numerical WQOs (Figure 1). A series of administrative rules were also developed to assist practitioners in applying these methods in a consistent manner at sites throughout the country (see Section 5.4).

5 Recommended Methods for Deriving Site-Specific Water Quality Objectives for Freshwater Aquatic Life in Canada

The review and evaluation of the approaches that have been used in Canada and elsewhere for deriving WQGs provide a scientific basis for recommending methods for deriving WQOs in Canada. In total, three general approaches are recommended for deriving site-specific WQOs, including adoption of the generic WQGs, modification of these WQGs to reflect site conditions, or derivation of *de novo* WQOs using site-specific information (See Section 3.4 of this report). In addition, a total of four specific procedures (i.e., background concentration procedure, recalculation procedure, WER procedure, and the resident species procedure) are recommended for deriving site-specific WQOs in Canada (See Chapter 4 of this report). This chapter is intended to provide further guidance on the application of these approaches and procedures by recommending more specific methods for deriving site-specific WQOs. These recommendations are not intended to prescribe the methods that must be used to derive site-specific WQOs. Rather, they are intended to assist the responsible federal, provincial, and territorial authorities in the selection of methods that apply most directly to their jurisdiction.

5.1 Adoption of Generic Water Quality Guidelines and Criteria

Canadian WQGs are developed to provide a high level of protection for designated water uses. More specifically, the WQGs for freshwater aquatic life are set at such values as to protect all forms of aquatic life and all aspects of the aquatic life cycles (CCME 1991). In addition, Canadian WQGs are developed to be broadly applicable to surface water and groundwater systems in this country. Therefore, these guidelines are likely to be appropriate for establishing WQOs at most sites in Canada.

Direct adoption of Canadian WQGs is a simple and direct procedure for deriving WQO. This process involves three major steps, including:

- Assemble the generic WQGs for each water use;
- Establish PeWQOs for each substance; and,
- Evaluate the applicability of the PeWQO for each substance.

The first step in this process is to assemble the generic WQC for each of the designated water uses within the water body under consideration. If the generic criteria are expressed in terms of the factors that influence toxicity, then the appropriate value(s) for the site should be determined. For example, the Canadian WQC for cadmium, applicable to the protection of aquatic life, are 0.01, 0.03, 0.05, and 0.06 :g \cong L⁻¹ at water hardnesses of 30, 90, 150, and 210 mg \cong L⁻¹, respectively (Porter *et al.* 1995). If the site under investigation has an average water hardness of 30 mg \cong L⁻¹, then the lowest of these values would be applicable and would be identified as

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the WQG for the protection of aquatic life. The WQGs for other water uses would also be assembled at this stage of the process.

The second step in this process is to establish a PeWQO. In general, the lowest of the guidelines for the designated uses of water at the site is adopted as the PeWQO for each priority contaminant. For example, a stream in the immediate vicinity of an abandoned aldicarb pesticide manufacturing facility might be used for a variety of purposes. If this facility were located in a rural area, this water source might be used as a raw drinking water supply, for fish culture in a trout farm, for livestock watering at a sheep farm, and/or for irrigation of market garden crops. The recommended WQGs for each of these water uses are 9.0, 1.0, 0.4, and $15.0 : g \cong L^{-1}$, respectively (MacDonald 1991). In this example, the recommended WQG for livestock watering, which is the lowest of the four WQGs, would be adopted as the PeWQO.

Once the PeWQO has been selected for each priority substance, its applicability to the site under consideration must be evaluated (Figure 2). At least four factors should be considered in the evaluation of the PeWQO (BCMOE 1986; Parkerton *et al.* 1989; Miller *et al.* 1988), including:

- (i) The background levels of the contaminant;
- (ii) The limit of quantification (i.e., analytical detection limit) for the substance;
- (iii) The applicability of the toxicological information that was used to derive the generic WQG to the site under consideration; and,
- (iv) The levels of substances that could affect the bioavailability of the contaminant (if these were not accounted for in the derivation of the generic WQG).

Information on background concentrations of metals and certain organic contaminants (e.g., petroleum hydrocarbons) at the site under investigation is essential for evaluating the applicability of the PeWQO. A number of techniques have been used to estimate background levels of contaminants and other water quality variables in surface water systems. Typically, historical information collected at or near the site is used to define background water quality conditions (Runnels *et al.* 1992; Dunn 1989). However, if historical data are not available, it may be possible to collect the necessary information at appropriate reference sites, which are considered to be indicative of water quality conditions at the site under consideration. In river systems, reference sites are generally established immediately upstream of known contaminant sources (MacDonald and McDonald 1987; MacDonald *et al.* 1988). However, a nearby stream system, that drains an area with similar geological, topographical, physiographical, climatological, and ecological characteristics, may also be used as a reference site if the upstream reaches of the river under investigation are known or thought to be affected by contaminant inputs from other developments (Valiela *et al.* 1987). Similar methods would also be appropriate for selecting reference sites in lacustrine, estuarine, and marine systems.

Determination of natural background levels of water quality variables is complicated due to the inherent variability in water quality conditions. Water quality conditions in surface waters may vary on both spatial (i.e., depth, cross-sectional, longitudinal, etc.) and temporal (i.e., daily, seasonal, annual) bases (Valiela and Whitfield 1988; MacDonald and Smith 1990). Therefore, sampling programs to establish baseline or background conditions must be designed to characterize this variability and the site-specific WQOs should reflect this variability.

As indicated previously, historical data or data from reference sites that are deemed to have acceptable water quality must be assembled and evaluated to determine background conditions at the site. These data should then be analyzed to determine if the concentration of the substance under consideration is dependent on other ecosystem characteristics (e.g., suspended sediment levels are dependent on discharge, dissolved oxygen levels are often dependent on temperature, etc.; Breidt *et al.* 1991). For these variables, background levels may be expressed as a regression equation with confidence intervals (Valiela and Whitfield 1988). For example, suspended sediment concentrations in Howell Creek in British Columbia have been described by the following equation (Valiela *et al.* 1987):

$$Log C = 1.742 \cdot log Q - 0.553$$

where:

C = suspended sediment concentration (in mg \cong L⁻¹); and Q = streamflow (in m³ \cong second⁻¹). (r² not reported).

For substances whose concentrations are apparently independent of other variables, statistical descriptors of central tendency and variability provide a means of defining background levels at sites that currently support designated water uses. Dunn (1989) recommended the use of average concentrations plus two SDs, calculated for both open water and ice cover conditions, for defining the upper limit of background levels for water quality variables in river systems in the prairie provinces. However, alternate statistical procedures can also be used to estimate background levels, such as monthly means plus two SDs or various percentiles (50th, 90th or 95th).

If the PeWQO is greater than the natural or non-reductable background concentration, then the preliminary value should be further evaluated to determine its applicability to the site under consideration. Conversely, if the PeWQO is lower than the estimated background level of a contaminant, then the generic WQG is not directly applicable to the site. In this circumstance, the upper limit of the background concentration should be adopted as the PeWQO. Alternatively, site-adapted or site-specific WQOs could be derived for the site and subsequently evaluated.

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Monitoring to assess attainment of the WQOs is an essential component of the overall environmental management process. However, effective attainment monitoring is dependent on the availability of accurate and precise methods for quantifying contaminant concentrations. The analytical limits of quantification that are achieved using these methods must be below the level defined by the PeWQO, preferably by a factor of two or more. If the PeWQO is lower than the analytical limit of quantification that is routinely achieved using the best available methods, then it will be difficult to reliably evaluate compliance with the PeWQO. In this case, chemical laboratories should be asked to refine the available methods to improve detection limits.

There are several other circumstances under which the generic WQG would not be directly adopted as the WQO. Specifically, modification of the generic WQG would be justified if information were available that indicated that the toxicity of a substance could be influenced by the unique conditions at the site. For example, generic WQGs have been derived from studies in which adequate environmental conditions for the test organisms have been maintained (e.g., minimum dissolved oxygen levels must have been present). However, the existing conditions at the site (i.e., low dissolved oxygen, the presence of other contaminants, etc.) may represent additional stressors on resident species. Where such conditions occurred, the applicability of the generic guideline to the site would be questionable, possibly necessitating modification of the generic WQG.

A number of factors have the potential to affect the bioavailability of water-borne chemicals and, hence, the applicability of the generic WQG. For example, Zitko *et al.* (1973) demonstrated that the toxicity of copper was mitigated by adding humic acids to tests systems. These results and those obtained by other investigators (e.g., Brown *et al.* 1978; Shaw and Brown 1974; Black 1974) indicate that the presence of organic chelators can significantly reduce copper toxicity. Therefore, the generic WQG for copper may not be directly applicable at sites with high levels of humic acids or other organic chelators. This example illustrates the need to evaluate the applicability of the PeWQOs and to take appropriate steps to establish the final WQOs.

The sensitivity of resident species is also an important consideration in the assessment of the PeWQO. Typically, Canadian WQGs for aquatic life are derived to protect the most sensitive life stage of the most sensitive species in aquatic ecosystems. As such, data on coldwater and warmwater fish, amphibians, several classes of invertebrates, vascular aquatic plants, and algae are considered in the guideline derivation process, if they are available. However, a much more limited aquatic community may have been historically present at some sites (e.g., warmwater fishes may have been historically absent from the system). In such cases, the generic WQG might not be directly applicable to the site under investigation. At such sites, it may be appropriate to derive site-specific WQOs.

5.2 Modification of Generic Water Quality Criteria

As indicated above, the presence of unique conditions at the site under investigation may necessitate modification of the generic WQGs. Four procedures are recommended to modify the PeWQO to reflect site-specific conditions, including:

- Background concentration procedure;
- Analytical limit of quantification procedure;
- Recalculation procedure; and,
- Water effect ratio procedure.

Each of the recommended procedures for modifying the generic criterion will result in the derivation of a new PeWQO, which must be evaluated to assess its applicability to the site under consideration. If this new PeWQO satisfies all of the evaluation criteria (i.e., background concentrations, analytical limits of quantification, assemblage of aquatic organisms, and the presence of factors that influence bioavailability), then it should be adopted as the final WQO. However, the PeWQO will require adjustment if one or more of the evaluation criteria are not satisfied.

When the PeWQO is lower than the natural or non-reductable background concentration of the contaminant under consideration, then it will be necessary to revise the PeWQO upward using the water background procedure. In this situation, the upper limit of background for the site could be adopted as the PeWQO. The various methods that have been used to define background concentrations have been described previously. Alternatively, one of the other procedures for modifying the generic WQGs could be used to establish an alternate PeWQO. However, any PeWQO derived using alternate procedures would have to be evaluated relative to background levels at the site under investigation.

Monitoring to assess attainment of the PeWQOs is challenging when the PeWQO is lower than the best available analytical limit of quantification for that substance using best available laboratory technology. The analytical limits of quantification that are typically achieved at Environment Canada's National Water Quality Laboratory (Burlington, Ontario) could be used as the benchmarks for comparison to the PeWQOs. Alternatively, the analytical limits of quantification that are typically achieved by regional laboratories could be used if they are lower than those of the National Water Quality Laboratory. When the PeWQO is lower than the benchmark analytical limit of quantification, the feasability of applying or developing more sensitive analytical methods could be evaluated or an alternate procedure could be used to generate the PeWQO.

Modification of the generic criteria is also permissible at sites with atypical assemblages of aquatic organisms (i.e., the species that occur, or that potentially occur, at the site include only a proportion of those that are represented in the complete toxicological data set). At these types of sites, the recalculation procedure can be

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used to derive site-adapted WQOs (USEPA 1983). The first step in the application of this procedure is to assemble a list of the families of organisms that occur at the site and/or that occur at a similar reference site. Usually, development of such a list will require extensive sampling at the site or at nearby sites in order to evaluate temporal and spatial variability in distribution of aquatic organisms. Then, all of the toxicological data on the families or life stages that are not expected to occur at the site should be eliminated from the toxicological data set. This reduced data set should then be examined to determine if the minimum data set requirements for deriving WQGs are met (see CCME 1991). If sufficient data are available, then a site-adapted WQO should be calculated using the procedure outlined in the formal protocol. If the minimum data requirements are not met, then additional biological testing may be conducted to obtain the necessary information. These tests would be performed on resident species or relevant indicator species in laboratory water.

The presence of atypical environmental conditions at the site under consideration could necessitate the modification of the PeWQO for certain substances. Under these circumstances, the WER procedure developed by the USEPA (1983) is recommended to modify the generic WQGs because it provides a basis of evaluating the toxicity of a substance in site water. Hence, this procedure accounts for the factors that could influence the bioavailability of a substance at a site. Using this procedure, bioassays would be conducted with at least two indicator species (e.g., rainbow trout, fathead minnows, and water fleas are commonly used) using site water and standard laboratory water. These species should be chosen based on their applicability to the system under consideration (i.e., warmwater vs. coldwater species), availability, and ease of culture and maintenance. The results of these bioassays would then be used to calculate a '*water effect ratio (WER)*' for each test (see Table 2 for a list of recommended toxicity tests; MacDonald 1997), as follows:

WER = Site Water LC₅₀) Laboratory Water LC₅₀

If the WERs for the two species are similar (i.e., within a factor of 3; USEPA 1994), then the geometric mean of the two values would be calculated (Note: the geometric mean is calculated, rather than the arithmetic mean, because the distribution of the WERs is unknown; i.e., the WERs are not necessarily normally distributed) and used to modify the generic guidelines, as follows:

$WQO = WQG \bullet WER$

If the two ratios are not similar, then it is necessary to conduct additional paired (i.e., using laboratory and site water) indicator species bioassays to confirm or refute the results of the initial tests. More specific guidance for conducting bioassays to support the derivation of WERs is provided in MacDonald (1997).

5.3 Derivation of de novo Water Quality Objectives

For certain substances, the requisite toxicological and/or environmental fate data for deriving generic WQGs will not be available in the literature. However, it may be possible to supplement the information that is available with the results of bioassays conducted at the site (and/or a nearby reference site). In these cases, the WER procedure is recommended to derive the site-specific WQO (USEPA 1983). Briefly, this would involve a review of the available data to identify specific data gaps. Then, a suite of bioassays using resident and/or indicator species that would fill the data gaps previously identified would be conducted at the site. This suite of bioassays would include paired tests using site water and laboratory reconstituted water. The results of the tests conducted in the laboratory water would be used to derive the generic criteria. The results of the tests conducted in site water would be used, in conjunction with the laboratory results, to establish a WER for the site.

Derivation of *de novo* WQOs would also be justified if the available toxicological data did not adequately reflect the species composition and water quality conditions at the site. In this case, the resident species procedure could be used to derive site-specific WQOs. This procedure is described in Section 4.4 and in USEPA (1983).

5.4 Recommended Rules for Developing Site-Specific Water Quality Objectives

Derivation of site-adapted and site-specific WQOs are complex processes that require detailed information on the site under investigation, on the contaminants present at the site, and on potential exposure of human and environmental receptors. To ensure that these processes can be implemented in a fair and consistent manner, a series of rules has been recommended to simplify the derivation of WQOs. These following rules outline when it is appropriate to adopt the generic WQGs directly, to modify the generic WQGs, and to develop WQOs on a *de novo* basis.

- (i) Generic WQGs should be adopted as WQOs at all sites unless the generic WQG for a substance is lower than the upper limit of background at the site under investigation.
- (i) The analytical limits of quantification for chemical substances vary depending on the extraction and quantification techniques used, the medium sampled, and the laboratory considered. For the purposes of WQOs derivation, the analytical limits of quantification that are typically achieved at the National Water Quality Laboratory (Burlington, Ontario) and/or a relevant regional laboratory should be used to evaluate the applicability of PeWQO.
- (iii) Generic WQGs should be adopted as WQOs at all sites unless it can be demonstrated that the toxicity of a substance is dependent on an environmental factor (e.g., water hardness, pH, etc.) that was not considered in the derivation of the generic WQG and that the site under investigation has atypical levels of that factor. For example, the generic WQG for copper accounts for water hardness (CCREM 1987). However, this guideline does not account for

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the potential influence of high levels of humic acids on copper toxicity. Therefore, it would be appropriate to evaluate the applicability of the generic copper guidelines at sites with high levels of humic acids and, if necessary, modify it to reflect site-specific water quality characteristics.

- (iv) Generic WQGs should be adopted as WQOs at all sites unless it can be demonstrated that the species represented in the toxicological data set used to derive the generic guidelines are not representative of the species that occur at the site under investigation.
- (v) Generic WQGs must be available for each of the designated water uses at the site before selecting a PeWQO, unless it can be demonstrated that the available guidelines include the most sensitive water uses (protection of fish and aquatic life is generally the most sensitive water use).
- (vi) If generic WQGs are not available for one or more water uses at the site, these guidelines may be derived using the appropriate protocols. However, these generic guidelines should be reviewed on a priority basis by the responsible authority and/or CCME Water Quality Task Group (as applicable) before they are implemented as WQOs at the site under consideration.
- (vii) If generic WQGs are not available for one or more water uses at the site and insufficient data are available to support their derivation, then the additional toxicological and/or environmental fate data needed to support the derivation of the necessary WQG may be generated. Alternatively, site-specific WQOs may be derived using the resident species approach.
- (viii) If insufficient data are available to determine background concentrations of priority substances in water at a site, an appropriate reference site should be designated and the data necessary to determine these levels should be collected.
- (ix) The sampling design, collection, and laboratory analytical procedures used to determine background concentrations of priority substances in water at a site must be approved by the responsible authority within the jurisdiction.
- (x) The PeWQO may be recalculated using only the toxicological information that is applicable to the site under investigation (i.e., a subset of the toxicological data set that was used to derive the generic WQG). However, the following rules apply when assessing the applicability of the information in the complete toxicological data set to the site:
 - (a) Toxicity data on representative species that are known to occur or have the potential to occur at the site may not be excluded from the toxicological data set. Representative species are defined below;
 - (b) In assessing the potential for a species to occur at a site, information should be consulted on the historic and contemporary distribution of the species in Canada. For example, *Freshwater Fishes of Canada* (Scott and Crossman 1973) and *Pacific Fishes*

of Canada (Hart 1973) provide excellent information on the distribution of fish species. Information on the distribution of freshwater fish is also available on the World Wide Web (www.bcfisheries.gov.bc.ca/ fishinv/ and www.fishbase.org). Data from field studies conducted at and nearby the site may also be used to identify site receptors if the data are considered to be appropriate by the responsible authority;

- (c) If a member of a family of freshwater fish occurs or could occur at a site (e.g., rainbow trout from the family Salmonidae), then the toxicity data on any of the fish species within that family (e.g., rainbow trout, coho salmon, mountain whitefish, arctic grayling, arctic char, etc.) must be included in the site-specific toxicological data set. In some cases, include the available toxicological data on coldwater fish species or warmwater fish species in the site-specific toxicological data set;
- (d) If a member of a family of amphibians occurs or could occur at a site (e.g., bullfrog from the family Ranidae), then the toxicity data on any of the amphibian species within that family (e.g., bullfrog, green frog, leopard frog, etc.) must be included in the site-specific toxicological data set;
- (e) If a member of a class of freshwater invertebrates occurs or could occur at a site (e.g., water flea from the family Bosminidae), then the toxicity data on any of the invertebrate species within that class (e.g., water fleas, copepods, ostracods, etc.) must be included in the site-specific toxicological data set;
- (f) If a member of a phylum of freshwater algae occurs or could occur at a site (e.g., *Chlamydomonas debaryana* from the phylum Chlorophyta), then the toxicity data on any of the algal species within that phylum (e.g., *Chlamydomonas debaryana*, *Chlorella variegata*, *Stichococcus bacillaris*, etc.) must be included in the site-specific toxicological data set; and,
- (g) If a life stage of an aquatic organism does not occur and is not expected to occur at the site (e.g., eggs and alevins of rainbow trout are not expected to occur at sites with soft bottom sediments), then the toxicity data on that life stage may be excluded from the site specific toxicological data set, provided that the data point is not the sole entry for a species or family that is know or expected to occur at the site.
- (xi) To implement the recalculation procedure, the information in the site-specific toxicological data set must satisfy the minimum toxicological data set requirements for deriving Canadian WQGs (CCME 1991; Singleton *et al.* 1995). Additional toxicity testing, using appropriate methods, may also be conducted to verify the toxicological data available on the most sensitive species.
- (xii) If insufficient data are available in the site-specific toxicological data set to support the derivation of WQGs, supplementary data may be generated by conducting toxicity tests using indicator or resident species. However, these tests must be supported by adequate quality

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assurance/quality control (QA/QC) procedures, including acceptable control and reference toxicant tests. For additional information on bioassay procedures, see ASTM (1994a; 1994b; 1994c), DOE (1990a; 1990b; 1990c; 1992a; 1992b; 1992c; 1990d), and USEPA (1993a; 1993b).

- (xiii) The PeWQO may be modified to account for levels of the factors that are considered to affect the bioavailability and/or toxicity of a substance that are different than those that were used in the development of the generic guidelines. For example, the PeWQO for copper could be modified to account for high levels of humic acids at a site. In these cases, detailed sciencebased rationale should be provided to the responsible authority for approval prior to pursuing this option.
- (xiv) The WER procedure provides a direct means of modifying the PeWQO to account for sitespecific water quality characteristics. Using this procedure, WERs for each priority substance at the site would be calculated and used to modify the PeWQO. However, other procedures for assessing bioavailability at the site (e.g., bioaccumulation tests) may be used under some circumstances, subject to approval by the responsible authority.

6 Role of Site-Specific Water Quality Objectives in Managing Point Source Discharges

Site-specific WQOs can be established using three main approaches, including adoption of generic WQGs, modification of generic WQGs, and derivation of *de novo* WQOs (see Chapter 5 for more information). Water quality objectives, so derived, have a number of important applications in Canada, including but not limited to: supporting the design of environmental quality monitoring programs; evaluating the status and trends in environmental quality conditions (including state-of-the-environment reporting); assessing and managing contaminated sites; designing and conducting ecological and human health risk assessments; developing and evaluating watershed management plans; and, supporting the licencing and permitting of effluent discharges.

This chapter provides a discussion of the role of WQOs in managing point source effluent discharges. In Canada, licencing and permitting activities have largely relied on technology-based approaches to establish effluent limits for wastewater discharges (i.e., the maximum permissible concentrations of COPCs in wastewaters that are discharged to the environment). Because point source effluent discharges have the potential to significantly alter water quality conditions in receiving water systems and, in so doing, adversely affect one or more designated water uses, transitioning toward a use-protection approach is likely to improve the management of liquid effluents. Water quality objectives (and the WQGs upon which they are based) provide the science-based tools needed to support such a transition. While the information included in this chapter provides specific guidance on the development of science-based effluent quality criteria, it is recognized that there are other methods for establishing the limits on the discharge of COPCs from point sources. Decisions on which method is the most appropriate for use at specific sites will be made by the responsible authorities in each jurisdiction.

6.1 Overview of the Process for Deriving Effluent Quality Limits using the Use-Protection Approach

In Canada, freshwater, estuarine, and marine ecosystems support a variety of water uses (see Section 2.1). In addition, these aquatic ecosystems often receive wastewater discharges from a variety of industrial, municipal, agricultural, and other sources. Such discharges are typically prohibited unless authorized by the responsible authority within a province or territory. Such wastewater discharges may also be subject to various federal, provincial, or territorial regulations. The licences or permits which are issued to authorize such discharges often specify the maximum concentrations of COPCs that may be discharged (i.e., effluent quality criteria). This approach to the management of liquid wastes is premised on the assumption that receiving water systems have some capacity to assimilate anthropogenic wastes without adversely affecting designated water uses.

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In the past, effluent quality criteria were primarily established using information on best available treatment technology. That is, the effluent quality criteria were set at levels that could be readily achieved by regulated interests (e.g., metal mines, pulp mills) using existing wastewater treatment technologies. This approach tacitly assumed that other water uses would not be adversely affected by ongoing wastewater discharges and/or that the benefits associated with the operation of the regulated interest outweighed the benefits associated with the water uses that might be adversely affected by such wastewater discharges. Today, many stakeholders believe that protection of existing water uses is a fundamental element of defensible water management strategies. For this reason, environmental managers need to consider ways and means of managing liquid wastes in a manner that assures the protection of the existing and future uses of aquatic ecosystems.

The use-protection approach offers a scientifically-defensible basis for establishing effluent quality criteria for the protection of existing and/or future uses of aquatic ecosystems. Implementation of this approach involves several steps, including:

- Identification of the physical, chemical, and/or biological variables of concern with respect to an existing or proposed wastewater discharge;
- Establishment of ambient WQOs for the receiving water system under consideration (see Chapter 5 for more details);
- Determination of the areal extent of the initial dilution zone (IDZ) for wastewater discharge (note: IDZs must be established in accordance with the guidance provided by the responsible authority); and,
- Development of use-protection-based effluent quality limits that ensure that the ambient WQOs will be met at the edge of the IDZ (i.e., using dispersion modelling and/or other appropriate techniques). It is important to remember that effluent quality criteria derived in this manner cannot be higher than those that are developed based on BAT-EA.

In addition to developing use-protection-based effluent quality limits (which are termed water quality based effluent limits in Quebec), it is important to determine if they are likely to be achieved using the proposed (i.e., in the case of new projects) or in-use (i.e., in the case of existing facilities) wastewater treatment technologies. At this stage of the process, it is also useful to evaluate the efficacy of other readily-available or readily-adaptable wastewater treatment technologies. Such information is likely to be useful in discussions with regulated interests regarding the practicality of establishing effluent quality criteria that are designed to protect the existing and future uses of the aquatic ecosystem. This information is also likely to be useful for identifying and evaluating various alternatives for regulating the wastewater discharge, if it is determined that it is not possible or practicable to attain the use-protection-based effluent quality criteria in the near-term. In some cases, this situation will necessitate phasing in the use-protection-based effluent quality criteria over a

period of time or, in the case of proposals for new developments, postponing the project until the necessary wastewater treatment technology is available and cost-effective.

Increasingly, jurisdictions within Canada are involving stakeholders in the management of aquatic ecosystems (i.e., through involvement in watershed planning processes, monitoring and assessment initiatives, and other processes). Therefore, it is important to establish and maintain an open and transparent process in the development of effluent quality criteria. Although the authority to specify the effluent quality criteria that are included in licences and/or permits is vested in the responsible authority, involving stakeholders in the process (or, at minimum, keeping them fully informed) will help build the trust needed to keep them engaged in other aspects of the water management process.

6.2 Determination of the Areal Extent of the Initial Dilution Zone

During the course of licensing or permitting wastewater discharges, responsible authorities may establish an IDZ (i.e., which is also referred to as the mixing zone) in the vicinity of existing or proposed outfall. Although the definition of an IDZ differs among jurisdictions, the following definition is generally applicable:

An initial dilution zone is the area contiguous with a point source (effluent) where the effluent mixes with ambient water and where concentrations of some substances may not comply with water quality guidelines or objectives.

The concept of the IDZ is based on the understanding that it is often possible to allow somewhat elevated concentrations of COPCs to occur within relatively small areas of a receiving water body, without significantly affecting the integrity of the water body as a whole. Such IDZs are typically established when wastewater discharges are known or predicted to contain elevated levels of COPCs, the COPCs in the wastewater discharge have the potential to adversely affect the designated water uses in the receiving water system, and responsible authorities wish to limit the geographic area that could potentially be affected by the discharge. Importantly, establishment of an IDZ enables the regulated interest to utilize the dilution capacity of the receiving water system such that it is not necessary to achieve the water quality objectives at the end of pipe.

Because authorization of IDZs has the potential to adversely affect existing and/or potential water uses, many jurisdictions have established a set of guiding principles to ensure that important water management interests are duly considered in the process. The following guiding principles, which have been abstracted from various sources (BCMOE 1986; MENVIQ 1991; Sinotte *et al.* 1996; CCME WQGs Task Force and Kemper and Associates 2001), are intended to identify some of the factors that ought to be considered in the establishment of IDZs:

- The dimensions of an IDZ should be restricted to avoid adverse effects on the designated uses of the receiving water system (i.e., the IDZ should be as small as possible);
- The IDZ should not impinge on critical fish or wildlife habitats (e.g., spawning or rearing areas for fish; overwintering habitats for migratory water fowl);
- Conditions outside the IDZ should be sufficient to support all of the designated uses of the receiving water system;
- Wastewaters that are discharged to the receiving water system must not be acutely toxic to aquatic organisms;
- Conditions within the IDZ should not cause acute or short-term chronic toxicity to aquatic organisms;
- Conditions within an IDZ should not result in bioconcentration of COPCs to levels that are harmful to the organism, aquatic-dependent wildlife or human health;
- A *zone of passage* for migrating aquatic organisms must be maintained;
- Placement of mixing zones must not block migration into tributaries;
- Mixing zones for adjacent wastewater discharges should not overlap with each other;
- Mixing zones should not unduly attract aquatic life or wildlife, thereby causing increased exposure to COPCs;
- Mixing zones should not be used as an alternative to reasonable and practical pollution prevention, including wastewater treatment (pollution prevention principle);
- Mixing zones must not be established such that drinking water intakes are contained therein;
- Accumulation of toxic substances in water or sediment to toxic levels should not occur in the mixing zone; and,
- Adverse effects on the aesthetic qualities of the receiving water system (e.g., odour, colour, scum, oil, floating debris,) should be avoided.

Certain jurisdictions in Canada have published guidance on the establishment of IDZs. In British Columbia, for example, the existing guidance indicates that an IDZ may extend up to 100 m downstream from a discharge and may not encompass an area greater than 25% of the stream width (extending from the bed to the surface; BCMOE 1986). In Quebec, the physical boundaries of this zone are described in *Method for Calculating Water Quality-Based Effluent Objectives for Aquatic Pollutants* (MENVIQ 1991; as revised in Sinotte *et al.* 1996). It should be noted that discharges of certain hazardous substances are either not allowed or severely restricted (e.g., PCBs, organochlorine pesticides); IDZ would not be appropriate for such substances.

6.3 Consideration of Contaminant Loadings in the Management of Point Source Discharges

For substances that are readily degraded in aquatic ecosystems (e.g., nitrite, ammonia), regulation based on concentrations alone is likely to be sufficient to achieve the water management goals and objectives that have been established for the water body under consideration. In addition, this approach may be relevant to water bodies that receive wastewater discharges from only one facility. However, protection of existing and future water uses is more challenging when more persistent substances are discharged from a facility and/or when a water body receives discharges from multiple point and non-point sources. In these situations, it may be necessary to establish total maximum daily loadings (TMDLs) for each COPC that is released or is likely to be released into the receiving water system from all sources. In this way, effluent quality criteria and other measures to control or prevent contaminant releases can be established based on an understanding of the assimilative capacity of the water body. Guidance on the determination of TMDLs is currently being prepared by the USEPA.

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Tables and Figures

Table 1. Application of water quality guidelines (modified from ME
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Water or Resource Use	Protected Organism	Environmental Compartment	
Drinking water	Human health (ingestion of water and aquatic organisms)	Raw water supplies, recreational waters	
Body-contact recreation	Recreational activities	Use-specific site in fresh, brackish or salt waters	
Health of aquatic life	Aquatic life	All fresh, brackish and salt waters, as appropriate All fresh, brackish and salt waters (or organoleptic guidelines related to the flesh of organisms)	
Fish consumption	Human health (ingestion of aquatic organisms only)	All fresh, brackish and salt waters	
Fish consumption	Piscivorous wildlife	All fresh, brackish and salt waters	
Health of agricultural plants or animals	Irrigation, livestock watering	Use-specific in fresh water	

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Tool	Capabilities	Limitations
Substance-specific quality guidelines for objectives	* Define level of protection for aquatic life, human health and piscivorous wildlife.	* Take into account only those contaminants that are known and that were analyzed.
	* Cover a wide range of species and effects for a given contaminant.	 * Do not take contaminants bioavailability into account.
	* Integrate the contaminant's fate (bioaccumulation, sedimentation).	 * Do not take possible interactions in mixtures into account.
	* Direct treatment technologies by identifying a substance.	* Do not directly measure biotic effects; the cause-effect relation is uncertain.
	 * Not very costly if a limited number of contaminants are analyzed. * Are preventative 	 May involve considerable costs if there are a number of contaminants to analyze.
Whole effluent (or ambient water) toxicity tests	* Integrate and measure the toxic effec of several substances at a time.	ts * Do not protect human health or pisivorous wildlife.
	* Take contaminant bioavailability into account.	 * Represent incomplete toxicology (only test some species and some effects).
	* Limit toxicity measurement to a sing analysis.	le * Ignore persistency (bioaccumulation) and sedimentation.
	 * Measure the exact toxicity of effluen ambient waters. * Are preventative. 	t or * Are not always representative of actual receiving water conditions when used solely on effluent.
		* Provide incomplete data on the causative contaminant.
		* Do not orient treatment technologies since no substance is identified.
Bioassessments	* Measure receiving water effects.* Integrate effects over time and define	* Do not protect human health or piscivorous wildlife.
	historical trends.* Integrate the effects of all sources,	 * Do not assess effects during critical flow periods.
	 mixtures of pollutants, including unknown ones. 	* Do not isolate a single cause for an observed effect.
	* Integrate the effects of all other possistresses (degradation of the physical environment, parasitism) in addition those linked to toxics.	* Measure effects (not preventive).

Table 2 Tools for assessing water and effluent quality (modified from MENV, 2001).

Table 3. Evaluation of the various procedures for deriving water quality objectives

Evaluation Criteria	Background Concentration Procedure	Recalculation Procedure	Water Effect Ratio Procedure	Resident Species Procedure
Scientific Defensibility				
Based on biological effects data?	No	Yes	Yes	Yes
Considers potential for bioaccumulation?	No	No	No	No
Considers site-specific conditions?	Yes	Yes	Yes	Yes
Applicable to all classes of chemicals?	Yes	Yes	Yes	Yes
Applicability				
Degree of site-specificity	High	Moderate	High	Very High
Uncertainty in the applicability of the WQOs	Low	Moderate	Low	Very Low
Acceptability to stakeholders	Unknown	Unknown	Unknown	Unknown
Practicality				
Supports the development of numerical WQOs?	Yes	Yes	Yes	Yes
Level of Complexity	Moderate	Low	High	High
Timeliness	Moderate	High	Moderate	Low-Moderate
Cost Effectiveness				
Expensive to implement?	Moderate	Low	High	Very High
Requires generation of new data?	Often	No	Yes	Yes
Most Appropriate Applications	Pristine waters	Sensitivity range of	Factors present	Unique sensitivity
	High value waters	resident species differs	which could influence	range of resident
	Waters with threatened	from that of	the bioavailability	species and presence
	or endangered species	complete toxicological	of contaminants	of factors influencing
	-	data set		bioavailability

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Figure 1. An overview of the recommended process for deriving numerical water quality objectives (WQOs).

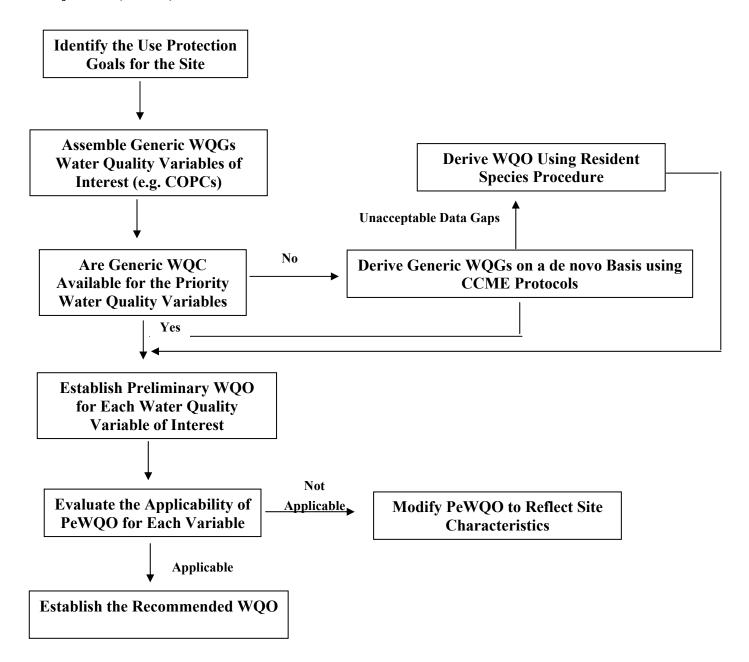
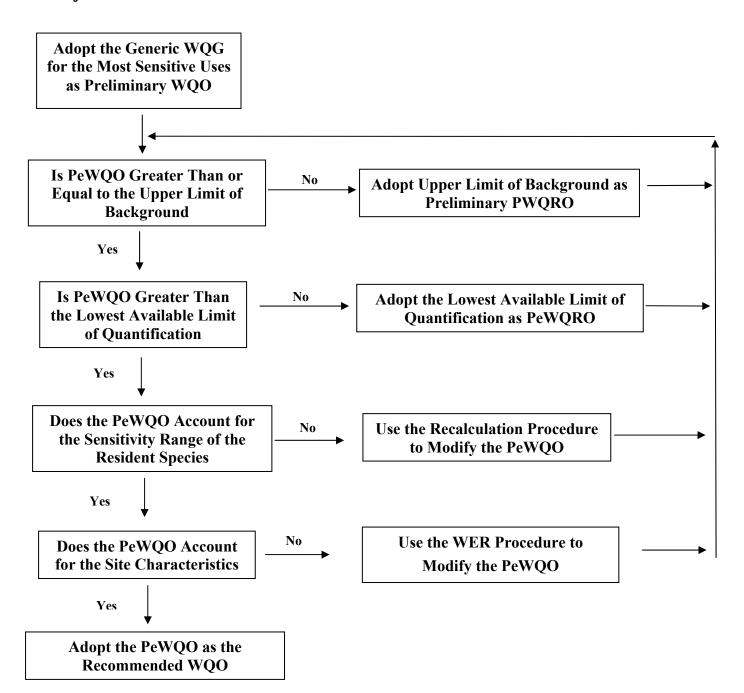


Figure 2. Recommended process for evaluating and modifying preliminary water quality objectives



Appendix 1 Physical, Chemical, and Biological Factors Influencing the Development of Water Quality Objectives

Modification of WQGs to support the establishment of site-specific WQOs requires an understanding of the chemical, physical and biological characteristics of the water body and the behaviour of a substance in the aquatic environment. Some of the factors that can influence the application of the guidelines include:

- (1) The general characteristics of lakes, rivers and reservoirs;
- (2) The effect of local environmental conditions on water quality;
- (3) Processes affecting the concentration of parameters in water; and
- (4) Factors that modify toxicity to aquatic organisms.

This appendix does not present a detailed or comprehensive review of all the information related to the application of the guidelines. Rather, it is intended to provide a greater appreciation of the complex chemical, physical and biological interactions that take place in freshwater, estuarine, and marine ecosystems that have the potential to influence the development of WQOs. Not all of the factors discussed will apply in every situation.

A1.1 Differences Between Water Bodies

Differences in the nature of rivers, reservoirs and lakes is important in developing WQOs because of the fundamental physical attributes of these types of water bodies. Most temperate lakes are stratified on a seasonal basis. During the winter, the lakes are covered with ice. Winter stagnation can develop with water temperatures of 0°C directly below the ice and uniformly low temperatures at, or slightly above, 4°C in the deeper waters. After ice break-up, wind action on the surface results in mixing of the entire water mass (spring overturn). The lake becomes isothermal and chemically homogeneous (Birge and Juday 1921).

In summer, density gradients are formed in sufficiently deep lakes through the accumulation of heat. A boundary layer (thermocline) develops between the mixed surface layer (epilimnion) and the cooler and less mixed water mass (hypolimnion; Birge 1910). In the autumn, cooler temperatures result in changes in water density and the breakdown of thermal stratification. By late autumn, isothermal conditions develop and the lake is mixed again (autumn overturn). The thermocline is very important to the biology of a lake. It acts as a barrier to the movement of dissolved oxygen, solutes, toxicants and the distribution of heat between the epilimnion and the hypolimnion (Reid and Wood 1976).

Tributaries control the water regime of many lakes. They connect a lake both geo-chemically and biologically with its catchment area. Tributaries influence lake conditions as a function of their inflow rate relative to the water budget of the lake and the degree of mixing of the incoming waters with the lake waters.

The character of rivers and streams is influenced to a significant extent by current velocity. The velocity depends on the width, depth and gradient of the stream or river; the roughness of the bed; and, seasonal variations in the flow rate. Velocity also plays a major role in influencing the distribution of dissolved substances, the quantity of sediment (silt, sand, clay and organic matter) in suspension and in the process of settling, the bed composition, and the development, distribution and stability of the biotic community (Reid and Wood 1976). Dissolved substances move at the velocity of water, whereas colloidal and particulate matter are subject to additional transport processes, such as sedimentation or re-suspension at higher velocities.

The chemical content of flowing waters varies greatly from one area to another, and is a reflection of local geography, season runoff, and biological processes (Bowen 1979). The relative concentration, composition and longitudinal distribution of dissolved solids in rivers will differ from those in lakes because of differences in water volume, surface-to-volume ratio and mixing characteristics, which are subject to changes in flow rather than stratification (Horne 1978).

The oxygenation of flowing waters occurs primarily by physical aeration and photosynthesis. The importance of each process varies depending on the time of day, the season, current velocity, bed morphology, temperature, and biological factors. The rate of physical aeration in rivers is largely determined by temperature, degree of turbulence, depth, and oxygen demand. A discharge of organic matter, for example, will cause a decrease in dissolved oxygen concentrations as a result of increased microbial respiration. Replenishment occurs by absorption of atmospheric oxygen at the air-water interface. Photosynthetic contributions to dissolved oxygen concentrations are more noticeable under less turbulent conditions, where algae and higher order plants have an opportunity to produce oxygen. Photosynthetic processes, however, are subject to diurnal and seasonal fluctuations (Reid and Wood 1976).

The temperature in streams is determined by factors such as current velocity, volume, depth, shading, water source, and seasonal and diurnal variations. Vertical thermal stratification is not generally observed in rivers largely because turbulent streamflow assures good vertical mixing (Hynes 1970).

Reservoirs are intermediate water bodies between lakes and rivers. The characteristics of inflowing rivers and the residence time of water in the reservoir determine their chemistry. Outlet structures and their location have a significant effect on downstream water quality since hypolimnetic waters are withdrawn from basal outlets, with surface water being drawn off by high level outlets and spillways. In temperate climates, the thermal effect of hypolimnetic withdrawals of 4° C water during winter can have a pronounced effect on community structure below reservoirs. The effects of streamflow and the potential removal of high discharge flushing flows are significant to benthic invertebrates and many fish species.

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The physical attributes of water bodies are important in the development of WQOs due to their influence on the chemical and biological characteristics of aquatic ecosystems. Such attributes are particularly important when evaluating the secondary effects of COPCs. For example, WQOs for ammonia or nitrite might be established based on the potential for toxic effects associated with exposure of aquatic organisms to these substances. However, these substances can also serve as aquatic plant nutrients or be converted to other nutrients, such as nitrates. In certain aquatic systems the secondary effects of these substances may not represent a concern (i.e., in large, turbid rivers). However, releases of nutrients into other types of water bodies (i.e. oligotrophic lakes) could lead to problematic levels of aquatic plant growth (eutrophication). Therefore the nature of the receiving water system is an important consideration in WQOs development.

A1.2 Water Quality Characteristics

The water quality characteristics of receiving water systems is of fundamental importance in the development of site-specific WQOs. Such characteristics are important because certain water quality variables can have both direct and indirect effects on water uses. For example, most aquatic organisms have specific ranges of pH that they can tolerate. However, pH can also modify the toxicity of various substances (e.g., ammonia). Therefore, ambient water quality conditions must be considered in the derivation of site-specific WQOs.

pН

The pH of water approximates the activity of free hydrogen ions in water. It is defined as the negative logarithm of the hydrogen ion concentration. The major influence on hydrogen ions and the parameters affecting alkalinity and acidity is the geology of the watershed. Dissolution processes take place because of the thermodynamic instability of many minerals in the presence of water and the atmosphere. Biological processes (e.g., photosynthesis and respiration), as well as turbulence and aeration, influence pH by varying the concentrations of dissolved carbon dioxide. The pH is likely to increase and decrease in response to photosynthetic and respiratory processes, respectively (McNeely *et al.* 1979).

The pH of water affects transformation processes among the various forms of nutrients and metals, and influences the toxicity of pollutants consisting of acids and bases because of the effects of ionization on these compounds. When in the molecular form, these substances usually penetrate the membranes of fish and other aquatic life more easily (Sprague 1985).

The toxicity of ammonia is strongly influenced by pH. More specifically, pH influences the equilibrium between unionized ammonia (NH_3) and the ammonium ion (NH_4^+) in receiving waters. Because the unionized ammonia form is much more toxic than the ammonium ion, total ammonia tends to be more toxic at elevated pHs (i.e., low pHs favour formation of the ammonium ion).

The pH of water plays a major role in the chemical speciation of many metals, their water solubility, and their bioavailability. At high pH, many metals form hydroxides or carbonates that are relatively insoluble and

usually precipitate. Metallic hydroxides of iron and manganese, for example, act as scavengers for many heavy metals. Decreases in pH alter the surface charges and attractive forces of these hydroxides and result in the release of sorbed metal ions (Faust and Aly 1981; Eichenberger and Chen 1982). This is because some metal ions hydrolyze at low pH; the hydrogen ion thus produced will interfere with adsorption and ion exchange by competing for active sites (Pagenkopf 1978; Eichenberger and Chen 1982). Because the adsorption process is reversible and depends on pH, it raises concerns about the potential effects of increased acidity in terms of releasing metals from sediments (Faust and Aly 1981; Eichenberger and Chen 1982).

The direct effects of pH on organisms become more severe as the pH tends away from the natural range (6.5-9.0). Alabaster and Lloyd (1984) provide a summary of these effects. In general, few fish can acclimate to pH 3.5-4.0. While some fish species, such as perch and pike, can acclimate to this pH range, they are unlikely to be able to successfully reproduce under such conditions. The tolerance level for many fish is approached in alkaline waters at pH 9.0-9.5, but most invertebrates are unaffected by elevated pHs. A pH ranging from 9.5 to 10.0 may be lethal to salmonids over a long period of time (Sprague 1985).

Alkalinity

Total alkalinity is, in general, the sum of all the components in the water system that act to buffer the water against changes in pH (e.g., bicarbonates, carbonates, hydroxides, sulphides, silicates and phosphates). The species composition of alkalinity depends on pH, mineral composition, temperature and ionic strength. Because the major buffering system in natural waters is the carbonate system, alkalinity is customarily expressed in terms of equivalent bicarbonate or carbonate.

In brown water acid systems, organic acids and complex colloids replace the normal carbonate buffering mechanisms. Under these conditions, the toxicity of certain chemicals may be altered in unpredictable ways. Site-specific toxicity testing, such as that conducted using the Water-effects Ratio approach can resolve uncertainties regarding the application of generic WQG under such conditions.

Hardness

The levels of calcium and magnesium salts largely regulate the hardness of a water body. The presence of other constituents, such as iron, manganese and aluminum can also contribute to hardness, but are not usually present in appreciable concentrations (Wetzel 1975). Hardness is usually expressed as an equivalent of calcium carbonate (CaCO₃), and is used as an indication of water type, buffering capacity, and productivity of a water body (Borgmann 1983; O'Donnel *et al.* 1985).

Increasing hardness in water mediates the toxicity of many metals to aquatic life, largely due to the formation of metal-carbonate complexes and calcium antagonism. The complex and equivocal interrelationship of hardness, pH and alkalinity is documented with studies on copper toxicity. It is reported that the ionic form of the metal is very toxic, as are ionized hydroxides of copper; but possibly not its un-ionized carbonates. If

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hardness is kept constant and alkalinity changed, the toxicity changes. Furthermore, for the same hardness, the toxic forms of the metal are greater at higher than at lower pH (Sprague 1985). Some guidelines for metals take hardness into account, so that a site-specific objective can be calculated if the hardness of a receiving water body is known. Water hardness also influences the toxicity of fluoride.

Organic Carbon

Organic carbon in waters has the ability to bind some fractions of metals. Hence, the presence of elevated levels of dissolved and/or particulate organic carbon can result in reduced toxicity of metals. The results of recent investigations suggest that the type of organic carbon present may also be important in evaluating the toxicity of metals and other substances that sorb to organic carbon.

Chloride

Increasing chloride concentrations ameliorates the toxicity of nitrite in freshwater systems.

Metals

The development of WQOs for metals is complex because their toxicity is affected by a number of sitespecific factors. Advances in knowledge of metal toxicity indicate that the following factors should be carefully considered during the preparation of site-specific objectives:

- Chemical composition of the effluent and the valence state of the metal(s);
- Fate and transport of metal between environmental components (i.e., water, sediment, particles, etc.);
- Monitoring and associated quality assurance data (i.e., the use of ultra clean metal procedures); and,
- Total versus dissolved metals levels.

The speciation and bioavailability of trace metals in water is important with respect to evaluating their hazards to aquatic life. For some metals, like mercury, bioaccumulation and associated hazards to human health are controlled by physical and chemical interactions and equilibria. These interactions are affected by many factors, including pH, redox, temperature, hardness, CO_2 concentrations, the type and concentration of available ligands and chelating agents, and the type and concentrations of metal ions (Mullins 1977; Connell and Miller 1984; Westman 1985).

Metals may exist in the soluble form as simple or complex free metal ions, ion pairs, coordination compounds, or un-ionized organometallic chelates or complexes. Complexes may be formed with anionic species (e.g., OH^- , Cl^- , $SO_4^{2^-}$, HCO_3^- , organic acids and amino acids); associations with colloid and particulate material include clays, organic matter, and hydrous iron and manganese oxides. Dissolved metals may be removed

from the water column by adsorption, precipitation, and co-precipitation processes. Lead, for example, is strongly adsorbed to particles and can be removed from the water column and concentrated in sediments. Cadmium, which complexes with organics, is likely to remain largely in the water column (Laxen 1983).

Of particular concern is the apparent toxicity of some ionic metals to fish due to desorption of the metal at the gill surface. Particulate bound forms of the same metal have much reduced toxicity. This is important when comparing the laboratory toxicity results with field situations where more metal binding agents are likely to be present, thereby usually reducing the toxicity of the metal. Conversely, fish tested in the laboratory are usually not fed and do not ingest particulate metals.

Determining metal bioavailability requires information on the physical form and chemical speciation of the metal and the interactions among the various forms (Laxen 1983). Studies show, for example, that non-complexed ions, such as Cd^{2+} , Cu^{2+} , Pb^{2+} and Zn^{2+} , are usually more readily available to aquatic biota than are complexed forms (Leland and Kuwabara 1985). The effects of metal exposure on physiological processes are complex and variable (Connell and Miller 1984). Furthermore, metals usually occur in combination in nature, and therefore, the overall toxicity to aquatic biota may change (Mullins 1977).

When defining effluent quality criteria based on site-specific WQOs, the total recoverable metal values and not the dissolved metal values should be used since:

- Total recoverable includes dissolved metals and that fraction of solid metals that can easily become soluble in ambient conditions (USEPA 1993a; 1993b). Ambient physico-chemical conditions often differ greatly from effluent conditions and there is no guarantee that the particulate fraction of the effluent will not dissolve under ambient conditions;
- Total recoverable allows concentrations affecting both the water column and sediments to be taken into account. The mass balance must be calculated using total recoverable metal since, by considering only the dissolved fraction, large amounts of particulate metal could be released and the effect of their accumulation in the sediment would not be evaluated; and,
- While the toxicity of the particulate fraction of a metal is lower than the dissolved fraction, it is not zero (USEPA 1992).

Total Dissolved Solids

The term total dissolved solids (TDS) refers to the concentration of dissolved matter in water. The principal anions comprising TDS include carbonates, bicarbonates, chlorides, sulphates, phosphates, and nitrates. The major cations comprising TDS include calcium, magnesium, sodium, potassium and iron. The concentration of total dissolved solids is of interest primarily because:

- TDS concentration determines the electrolyte characteristics or ionic strength of the solution (the ionic strength is related to the activity coefficient and, therefore, to the solubility of solutes); and,
- Anions participate along with cations in complexing and precipitation processes with many trace metals (Mullins 1977; Pagenkopf 1978).

In natural waters, carbonates, sulphates, chlorides, phosphates, and nitrates affect metal speciation by forming ionizable salts. Insoluble carbonate formation is one of the most important processes for removing metals from solution (Stumm and Morgan 1970; Pagenkopf 1978).

The composition and concentration of total dissolved solids are important in determining the diversity and abundance of plants and animals in aquatic ecosystems. The chemical density of the aquatic environment influences the osmotic regulation of metabolism and biotic distribution. Furthermore, dissolved solids constitute the sole source of nutritionally important ions to phytoplankton (Wetzel 1975). A major change in the quantity or composition of total dissolved solids can affect the structure and function of the aquatic ecosystem under investigation.

Suspended Solids

Turbidity is a measure of water clarity. It can provide an estimate of the concentrations of suspended materials, such as clay, sand, silt, finely divided organic and inorganic matter, and plankton and other microorganisms in water (McNeely *et al.* 1979). Increases in turbidity and colour, by limiting light penetration, can reduce photosynthesis and directly influence the amount of biological production occurring within a water body. Greater absorption of solar energy also results in warmer surface water.

Radionuclides, organics and metals tend to accumulate on the surface of colloids and particles and, hence, their biological effects may be modified by increasing levels of total suspended solids (TSS; Kranck 1980). The complexing and adsorptive behaviour of colloids and particles changes as they are carried from one location to another and encounter different physical and chemical conditions.

Suspended solids can adversely affect aquatic organisms in several ways, including:

- Clog the filtering apparati of some immature stages of insects (e.g., caddisfly larvae) and fish;
- Cause physical injury to delicate eye and gill membranes by abrasion;
- Restrict food availability to fish and, in so doing, affect growth rates;
- Restrict normal movements and migrations of fish; and,
- Inhibit egg development (Alabaster and Lloyd 1984).

Temperature

In Canadian environments, wide seasonal variations in temperatures affect physical and chemical interactions among chemicals, thereby modifying toxicity and the resistance of organisms to stress. Temperature plays a major role in influencing aquatic life and the physical and chemical parameters of the aquatic environment. Changes in temperature also influence the solubility and reaction equilibria of many chemicals (Mullins 1977). Increases in temperature decrease the solubility of dissolved gases (H₂, N₂, CO₂ and O₂) in water. Within a range of 0-30°C, for example, oxygen solubility decreases by approximately 50%. Viscosity, surface tension, compressibility, specific heat, ionization constants, and latent heat of vaporization all decrease as the temperature increases (Houston 1982). Increases in temperature result in increases in thermal conductivity, vapour pressure, the solubility of salts, and the rate of chemical oxidation of substances (Westman 1985). Heating of surface waters also creates a thermal discontinuity within a stable water body and divides the water into thermal strata, each with its own physical, biological and chemical characteristics.

Temperature changes affect the movement, respiratory and metabolic rates, behaviour, and reproduction of most aquatic organisms. Aquatic biota differ in their tolerance to temperature changes according to factors such as species, age, acclimation temperature, dissolved oxygen, exposure to toxic substances and season (Alabaster and Lloyd 1984; Rand and Petrocelli 1985). Temperature increases also increase respiration rates and rates of metabolism and excretion. Thus, an organism requires more oxygen in an environment that actually contains less oxygen than at lower temperatures. In poikilotherms, the rates of metabolism and excretion can be expected to double for every 10°C increase in temperature (Connell and Miller 1984). The discharge of warm water may also have more subtle effects, such as giving false temperature cues to aquatic organisms and causing inappropriate behaviour for the time of year (e.g., migration and spawning; Duffus 1980).

Temperature is an important factor in determining the toxic effects of pollutants, such as ammonia (i.e., ammonia toxicity increasing at higher temperatures). There is no easily defined pattern for predicting the effects of temperature on the toxicity of pollutants to aquatic organisms. For example, Spear and Pierce (1979) reported on the complexity of the relationship between temperature and copper toxicity. There is also evidence that temperature affects the solubility and volatility of many chemicals in water (Connell and Miller 1984).

Dissolved Oxygen

The oxygen dissolved in surface waters is largely derived from the atmosphere and from the photosynthetic activity of algae and higher order aquatic plants. In the surface waters of productive lakes, photosynthesis may produce supersaturation during the day, while respiration will result in oxygen depression during the night (Macan 1974). Dissolved oxygen concentrations vary daily and seasonally, depending on:

- The species of phytoplankton present;
- Light penetration;
- Nutrient availability;
- Temperature;
- Salinity;
- Water movement;
- Partial pressure of atmospheric oxygen in contact with the water;
- Thickness of the surface film; and,
- Bio-depletion rates (by aquatic organisms and oxidation and decomposition processes; Hart 1974; Mullins 1977; McNeely *et al.* 1979).

Dissolved oxygen concentrations in sediment are affected by microbial metabolism, mixing with oxygenated water, and the chemical exchanges between the sediment and water (Wetzel 1975; Golterman 1975).

Dissolved oxygen is required for aerobic respiration. At low concentrations, it may become a limiting factor for the maintenance of life. The lower lethal limit depends on the species. The sensitivity of aquatic organisms to low concentrations of dissolved oxygen differs among species, life stages (e.g., eggs, larvae, adults) and according to activity (e.g., feeding, growth, reproduction; Alabaster and Lloyd 1984). Depending on the intensity and duration of low dissolved oxygen concentrations, a change in species diversity may develop. The effects of toxicants may be magnified if aquatic organisms are under the stress of low or inadequate dissolved oxygen. Low concentrations of dissolved oxygen result in accelerated irrigation of respiratory surfaces, thus increasing the exposure of these surfaces to any toxicants present in water (Warren 1971; Sprague 1985). The increased ventilation rate may also increase the likelihood that gills become clogged with suspended material; alternatively, gill surfaces could be damaged if the material is abrasive.

Anaerobic conditions result in a reduction of the oxidation states of metal ions, which markedly affects the solubility of many metals (i.e., particularly those that usually precipitate as hydroxides; Wetzel 1975; Mullins 1977). Aquatic organisms may be affected directly from decreased dissolved oxygen concentrations. Organisms can also be affected indirectly from toxic effects that result from chemical changes resulting from decreased concentrations of dissolved oxygen in localized areas (Connell and Miller 1984).

Nutrients

Nutrients play a major role in the synthesis of living material. Some elements are needed only in trace amounts. Eutrophication refers to the addition of excess quantities of nutrients to water bodies and the effects of these nutrients on water quality and on aquatic life.

The availability of nitrogen and phosphorus to plants is governed by a complex series of biologically mediated reactions. The nitrogen cycle is one of the major bio-geochemical cycles. The principal aspects of the cycle are fixation of molecular nitrogen, ammonification of organically bound nitrogen, nitrification, and denitrification (Verschueren 1983). Molecular nitrogen undergoes a complex series of interactions in the nitrogen cycle and is eventually converted to ammonia (NH₃), nitrite ion (NO₂-), and nitrate ion (NO₃-). Both ammonia and nitrate are readily bioavailable to plants.

Some forms of nitrogen can also exert toxic properties. Factors such as pH, temperature, the presence of other pollutants, and concentrations of dissolved oxygen, calcium, and alkalinity influence the toxic effects of ammonia. The action of some mixtures of ammonia and other toxicants is usually synergistic (copper, zinc, phenol, hydrogen cyanide) although at all but low ratios it is additive with nitrate (Russo 1985).

Nitrites are rapidly oxidized to nitrate in the presence of an adequate oxygen supply, resulting in only trace levels usually being found in surface waters. The relationship between nitrite toxicity and pH indicates that beyond pH 6.4-9.0, the toxicity of total nitrite decreases as pH increases. Some anions, such as Cl^{-} , Br^{-} , SO_{2}^{4-} , PO_{3}^{4-} and NO_{3-} , moderate nitrite toxicity to varying degrees (Russo 1985).

The availability of phosphorus to biota depends on the uptake and release rates of the biota, chemical speciation (e.g., organic or inorganic bound phosphorus) and the relative abundance and residence time of the dissolved phosphorus fraction. The predominant orthophosphate forms at pH 6-8 are H_2PO_4 . (10%) and HPO_4^{2-} (90%; Reid and Wood 1976). Phosphates will readily complex with cations that are available in the water (e.g., Fe, Al, Ca), and will form insoluble complexes, chelates and salts (Stumm and Morgan 1970). The formation and dissolution of these compounds are major components of the phosphorus cycle and are a function of pH, the concentration of phosphates, metal ions and ligands, the solubility of various metal-phosphate compounds, the redox potential and biotic activities (bacteria, fungi, plankton, invertebrates; Wetzel 1975; Thurston *et al.* 1979). These associations will remove phosphate from the water column and reduce the concentration of some metals by precipitation of the metals as phosphate-containing salts (Babich and Stotzky 1983).

Nutrient enrichment and eutrophication result in many changes in aquatic populations and communities. The species composition of phytoplankton may shift to those more tolerant of nutrient-rich conditions. Under these circumstances, blue-green algae may dominate. Increases in algal productivity lead to increased decomposition of organic matter and a corresponding utilization of dissolved oxygen. Low concentrations of dissolved oxygen in the hypolimnion of lakes often occur in the summer because of these decomposition processes, and stratification affects the exchange with atmospheric oxygen (IJC 1978). Population diversity and density for fish and benthic organisms will be affected, and, if conditions persist for long periods, different biotic communities may become established.

A1.3 Environmental Fate Processes in Natural Waters

A number of processes can affect the fate and concentrations of chemical constituents in water. Some of the environmental fate processes that should be considered during the development of site-specific WQOs include:

- Sorption;
- Ion exchange;
- Formation of complexes;
- Solubility;
- Precipitation and co-precipitation;
- Volatilization;
- Oxidation-reduction;
- Hydrolysis;
- Photolysis and photo-transformation; and,
- Microbial degradation.

These processes can significantly affect the availability, toxicity, persistence and fate of COPCS in water. As with other parameters, the rate and degree to which these processes occur depend on the prevailing local environmental conditions.

Sorption

Sorption is the process whereby COPCs form associations with suspended particulates, sediments, or other materials. Adsorption can reduce the concentrations of trace metals and organic compounds in natural waters beyond that which would be expected by equilibrium solubility calculations (Pagenkopf 1978; Drever 1982). The tendency for a substance to sorb onto particulate surfaces affects its mobility and ultimate fate in waters (Verschueren 1983). Sorption tends to increase as solubility decreases.

Potential sorbents include clay minerals, inorganic and organic colloids (gels of ferric hydroxide, manganese hydroxide and silicic acid; humic colloids) and the surfaces and integuments of living and dead organisms (Ruttner 1953; Mill 1980). The extent of sorption of a compound from water onto a solid is a function of (Pagenkopf 1978; Verschueren 1983):

- Factors regulating equilibrium (e.g., temperature, pH, atmospheric pressure and ionic strength);
- Physical and chemical characteristics of the sorbent;
- The surface area of the solid; and,

• The nature and distribution of the binding sites on the surface.

There are different types of sorption, ranging from adsorption by Van der Waals forces, which exert only a weak bond between the solute and the sorbent, to chemisorption, which involves more definite chemical interaction (Pagenkopf 1978).

Ion Exchange

The process of ion exchange involves the exchange of ions adsorbed on a surface with ions in water. Ion exchange affects the mobility and fate of chemical substances in water. It exerts an important control on water chemistry at the water-sediment interface (Drever 1982).

The nature, degree and rate of ion exchange depend on the properties of the dissolved ions and those of the available complementary ions. The process of ion exchange is also regulated by time, the type of bond that develops, pH, temperature, the presence and concentration of competing ions, and the selective properties of individual sorbents (Matthess and Harvey 1982).

Clay minerals, iron hydroxides, manganese oxides and organic matter can sorb cations in water and release an equivalent amount of cations back into solution (Horowitz 1985). These processes are important in altering the composition of natural waters (Stumm and Morgan 1970). Oxides and organic matter, which frequently coat clay minerals, often have high exchange capacities (Drever 1982). Heavy metals can be released from clays depending on the prevailing conditions of the solution. The ion-exchange capacity (amount of exchangeable ions) of silt can be exceeded so that metals in water may remain in the free and soluble (and biologically available) forms (Golterman 1975; Matthess and Harvey 1982). Ion exchange also affects the fate of organic compounds in water. The pesticides paraquat and diquat, for example, may be removed from water by cation exchange with organic matter and clay minerals (Connell and Miller 1984).

Formation of Complexes

The forms of metal ions in solution are important for determining chemical, biochemical and biological effects. Each metal ion has a speciation pattern that is a function of the stability of the hydrolysis products and the tendency of the metal ion to form complexes with other ligands (Connell and Miller 1984). Chelates are the result of complexes with more than one ligand group. Reactions forming complexes often involve sequences of soluble complex ions and insoluble forms, depending on the metal, ligand concentrations, and the pH. These interactions determine metal speciation in water and contribute greatly to the overall regulation of metal ion concentration in water (Pagenkopf 1978).

The pH affects the degree of complex formation. At low pH, H^+ competes with the metal ions for the ligand, whereas at high pH, OH^- competes with the ligand for the coordinative positions on the metal ion. At both high and low pH, mixed hydrogen-metal and hydroxide-ligand complexes can occur. The tendency towards

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complex formation increases with the ionization potential of the metal and with increasing tendency for the ligand to donate electrons. Redox changes will affect metal speciation by direct changes in the oxidation state of the metal ions [e.g., Fe(II) to Fe(III)], as well as by redox changes in available and competing ligands or chelates (Connell and Miller 1984).

The behaviour of metals is greatly affected by interactions between aqueous and solid phases. Dissolved metal complexes can be removed from water on contact with the surfaces of particulate matter and deposited to sediment beds. Enrichment and remobilization of metals in sediments depend on factors such as chemical composition, salinity, pH, redox values and local hydrodynamic conditions (Connell and Miller 1984). Metal concentrations in solution that are higher than those calculated are often explained by chelation with organic molecules. Chelation may also contribute to masking the presence of metals in water (Stumm and Morgan 1970). The bioavailability of dissolved substances tends to decrease with the formation of complexes.

Solubility

The solubility of a substance represents the total amount of solute species that will remain permanently in solution under a given set of water conditions. It is an intrinsic property of a substance and helps to determine its distribution in solution (Verschueren 1983; Connell and Miller 1984). Under natural conditions, equilibrium is rarely reached and can be shifted by variations in the concentrations of competitive ions and organic substances in solution (Waite 1984). Environmental factors, such as pH, redox conditions, temperature, hardness and the presence and nature of dissolved solids and organic matter, also affect the solubility of a substance in water (Stumm and Morgan 1970; Mullins 1977).

The solubility product (Ks) refers to the product of the concentrations of the ionic species involved in dissolution. The solubility of individual substances helps to determine the activity of dissolved substances and the degree of complex formation (Pagenkopf 1978). A chemical's water solubility will affect its susceptibility to hydrolysis, photolysis, forming complexes, volatilization, oxidation, reduction, and biodegradation (Verschueren 1983).

For gases, the solubility of both electrolyte and non-electrolyte-forming gases in solution is commonly described by Henry's constant. The solubility of non-electrolyte forming gases, such as oxygen, is inversely proportional to the vapour pressure at a given temperature. The solubility of electrolyte-forming gases is also strongly dependent on temperature, usually decreasing as the temperature rises (Mackay 1980).

The soluble forms of metals are usually simple or complex ions, or un-ionized organometallic chelates or complexes. In general, an increase in temperature will result in an increase in solubility of most inorganic salts. The solubility of many organic substances can be influenced by:

- The nature of the interactions in solution between the substance and water (i.e., hydrophobicity); and,
- In the case of a solid, its melting point relative to the system temperature.

Many organic solutes tend to form colloidal particles in water (which may result in concentrations of several milligrams per litre), thereby masking the true dissolved concentration (Mackay 1980).

Precipitation and Co-precipitation

The chemical properties of minerals can be changed by precipitation reactions, which remove them from water. The extent to which a compound will precipitate can be determined from the solubility product constant. Both the rate and extent of precipitate formation will depend on the compound and the prevailing local environmental conditions (Lee and Jones 1983).

Precipitation reactions in natural waters largely involve carbonate and hydroxide salts. Other salts such as sulphates, phosphates, chlorides, and silicates can also precipitate out of solution. Ferric iron and Mn (IV) often precipitate as hydrous oxides. Many transitional metals form hydroxy complexes near pH 7.0 (Pagenkopf 1978). At higher pH values, carbonate adsorption and co-precipitation are important removal processes for Zn, Co, Cd and Pb (Pagenkopf 1978; Connell and Miller 1984).

Co-precipitation is the simultaneous precipitation of an otherwise soluble component and an insoluble salt (Pagenkopf 1978). Co-precipitation occurs as isomorphic inclusion, surface adsorption, solid-solution formation, and occlusion. Isomorphic inclusion occurs when an ion of similar dimensions and chemical properties fits into the structure of the precipitate without causing significant disruption of the crystal structure of the precipitate. Hydrous oxides and other solids have a large surface area and can adsorb large quantities of other ions. In solid-solution formation, the solute dissolves within the solid solution. With occlusion, solutes are trapped within the crystal lattice of the precipitate. Co-precipitation and replacement processes are important in removing trace metals from water in a more stable phase (e.g., copper co-precipitation with ferric hydroxides; Matthess and Harvey 1982).

Volatilization

Volatilization refers to the change of state from a solid or liquid phase to the vapour phase, and the subsequent movement by advection or diffusion (Neely and Blau 1985b). It is recognized as an important transport process for many chemicals characterized by low solubility and low polarity (Mackay *et al.* 1980). Transport of a compound from sediments or the bottom of lakes or rivers to the atmosphere depends on a series of stages and controlling rates (or resistance). These stages of diffusion may include:

• Release from sediments;

- Diffusion through the layers of the lake hypolimnion, thermocline or epilimnion;
- Diffusion to the water-air interface through the liquid surface film;
- Transfer across the water-air interface; and,
- Diffusion through the atmospheric film to the atmosphere.

Water turbulence and wind speed (NRCC 1981) also influence the rates of volatilization.

The relative volatility of organic chemicals from water can be determined based on vapour pressure and water solubility (Hamaker 1972). In order to estimate the absolute vaporization rate of low-solubility organics from water, Mackay and Leinonen (1975) elaborated on Hamaker's concept. Their work indicates that the water-air partition ratio of the organic chemical (calculated from its vapour pressure and solubility) will determine whether the liquid or vapour-phase resistance controls the rate of vapour loss. The calculations show that most organic substances of low solubility will rapidly vaporize from water at low levels of clay or organic colloids (Spencer and Farmer 1980). The principal variables that need to be considered in the calculations of volatilization rates of solutes from lakes and other water bodies are those describing:

- The phase equilibrium (i.e., Henry's law constant or fugacity capacities, refer to articles by Mackay and Paterson 1982; 1984);
- The kinetics of the system in terms of resistance, mass transfer coefficients and diffusivities; and,
- The physical and chemical properties of the solute (i.e., sorption and air/water partition properties; Mackay *et al.* 1980; Mackay 1981).

Oxidation-Reduction

Oxidation and reduction processes are often referred to as those associated with the loss and gain of electrons, respectively. Oxidative or reducing capacity can be described by the redox potential (Eh), that is a numerical index of the intensity of oxidizing or reducing conditions within a system (Hem 1985). The chemical forms of many pollutants are modified by their oxidation-reduction properties and by the oxidizing and reducing characteristics of the environment in which they are found (Connell and Miller 1984). For example, the biogeochemical cycling of iron and, to a lesser degree, manganese is influenced by the spatial and temporal variations of the redox conditions of the water body (Wetzel 1975).

Photosynthesis and bacterial degradation of organic matter largely determine redox conditions in rivers and lakes. In photosynthesis, carbon dioxide is converted to organic matter and oxygen. If molecular oxygen is available, the products of bacterial respiration and decomposition are essentially the reverse of those of photosynthesis. During respiration, carbon is released as CO₂. In the absence of molecular oxygen,

decomposition of organic matter proceeds by a series of reactions that yield successively less energy. Some of the more important reactions are:

- Denitrification; in which bacteria oxidize organic carbon to CO₂ using the oxygen from the nitrate ion;
- Deamination of amino acids. Under aerobic conditions, amino acids will decompose to nitrogen free compounds and ammonia. The unionized ammonia then combines with H+ to form ammonium and causes a net increase in pH;
- Reduction of Mn(IV) and Fe(III) oxides to form the more soluble Mn(II) and Fe(II). The reduction of oxides will result in the release of phosphates and heavy metals adsorbed to the oxides;
- Sulphate reduction, in which bacteria oxidize organic matter to CO₂ using the oxygen from sulphate (SO₄²⁻). The by-product, hydrogen sulphide (H₂S), is toxic to most biota; and,
- Fermentation reactions that occur at various pE values (measure of redox intensity) and depends on the particular organic compound affected.

There may be substantial differences in redox environment throughout a specific body of water. In lakes, redox conditions result from the balance between the decomposition of organic matter and the concentration of dissolved oxygen. The total amount of organic matter falling into the hypolimnion during stratification will determine whether these waters will become anaerobic. In an oligotrophic lake, the supply of nutrients is low and so is photosynthetic production; the water is oxygenated at all depths and the pE remains high. In eutrophic lakes, where productivity is high, the hypolimnion may become anaerobic (Drever 1982). During overturn of this type of eutrophic lake, hydrogen sulphide and other compounds, such as heavy metals, may be mixed into the epilimnion. For example, the solubility of metals that normally precipitate as hydroxides may increase, and phosphorus may be released from sediments due to the dissolution of ferric hydroxide and oxides onto which the phosphorus is adsorbed (Connell and Miller 1984).

Hydrolysis

Hydrolysis occurs when an organic compound or metal salt reacts with water and results in the net exchange of a functional group for a hydroxyl group (Connell and Miller 1984). The importance of hydrolysis is that the reaction introduces a hydroxyl group into the parent molecule. For organic compounds, the resulting product is usually more vulnerable to further breakdown by biodegradation and photolysis. In addition, the hydroxyl group makes the compound more water-soluble and, therefore, reduces the potential for bioconcentration (Neely and Blau 1985a).

Soluble hydrolysis products are important in aquatic environments where metal ions are present. The low cation concentrations and the relatively wide range of pH within which hydroxo and oxo complexes may exist

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can significantly alter the chemical behaviour of these metals (Eichenberger and Chen 1982). The chemical species and oxidation states of hydrolytic products can control many aspects of chemical behaviour, such as:

- Adsorption of soluble species on particulates;
- Likelihood of the metal species to coagulate colloid particles and to form precipitates;
- Solubility of the controlling solid phase;
- Extent to which the ions can be complexed in solution; and,
- Oxidation or reduction of the metal species (Stumm and Morgan 1970; Eichenberger and Chen 1982).

Hydrolysis data are important in assessing the risks from organic chemicals having hydrolyzable functional groups (i.e., carboxylic acid, phosphoric acid and sulphonic acid, esters, amides, alkyl halides, carbamates, epoxides and phosphoric esters). In addition, such data are used to estimate kinetic rates for various compounds (including structure-activity relationships data) and to predict the half-lives of organic chemicals in aquatic systems (Connell and Miller 1984).

Photolysis and Phototransformation

Photochemical transformations induced by sunlight can occur by one or more processes, depending on the structure of the chemical and the presence of other substances (USEPA 1979). Sufficient radiation energy must be absorbed to overcome the bond energies and allow dissociation for these changes to occur. Photochemical changes occur by two principal mechanisms:

- Direct absorption (direct photolysis) of light by the substance followed by reaction; or,
- Electron or energy transfer (indirect photolysis) through an intermediate (photosensitizer; Moore and Ramamoorthy 1984).

The direct absorption of sunlight can result in cleavage of bonds, dimerization, oxidation, hydrolysis, or rearrangement (Zepp 1980). In an effort to predict photolysis rates as a function of the time of day, season, location and water depth, equations have been developed using solar irradiance, quantum yield, and the absorption spectra of pollutants (Zepp and Baughman 1978). If pollutant concentrations are low, the rate of direct photolysis of chemicals (Kp) in water can be represented by a simple first-order expression (i.e., the rate is directly proportional to pollutant concentration and the first-order rate constant depends on light intensity). The rate of photochemical oxidation by indirect photolysis can be represented by a second-order expression (Connell and Miller 1984).

The colour and clarity of the water body influence the rates of direct and indirect photolysis. Suspended sediment influences photolysis in water by: contributing to light attenuation; scattering light, which in turn diffuses down-welling radiation; affecting partitioning processes; and removing pollutants from underwater light by sorption to sediment settling downward. Vertical mixing in lakes also affects the amount of light received by a pollutant (Zepp 1980).

Colour, clarity, and concentrations of natural sensitizers and singlet oxygen will affect indirect photolysis (NRCC 1981). The assessment of indirect photolysis is complicated by the fact that many photochemical processes may be involved and that the molecular structures of the photosensitizers that mediate indirect photolysis have not been identified. In a photosensitized reaction, light absorbed by a sensitizer molecule (e.g., humic matter) in water results in an excited state that can transfer its energy efficiently to another compound in water via a series of complex and competitive processes under certain conditions. The exact nature of the pathways of these processes remains to be determined (Zepp 1980). The photochemical decomposition of pesticides, for example, may proceed by means of a series of photolytic reactions, including photo-oxidation, photonucleophilic hydrolysis, and reductive dechlorination. These reactions will be influenced by factors such as the presence of natural photosynthesizers, pH and dissolved oxygen (Connell and Miller 1984).

Microbial Degradation

The biodegradation of pollutants by microorganisms (e.g., bacteria, fungi, protozoa, and algae) is an important removal and transformation process in water and sediments. Information concerning biodegradation processes is critical to evaluating persistence, particularly for organic compounds likely to be solubilized or dispersed in or on water. The reactions associated with these processes include oxidation, reduction, hydrolysis and, occasionally, rearrangements. These reactions are a function of the molecular structure and concentration of the substance, size, type and growth rate of microbial assemblages, nutrients available and environmental characteristics such as temperature, pH, ionic strength, and oxidation-reduction conditions. The nature, dynamics, viability and metabolic status of the microorganism populations complicate them.

In most large bodies of water, the water column is stratified into several layers, each with different temperature, availability of light, nutrient content, and oxygen concentration. In general, the upper portion of the water column is considered aerobic, while the deeper region may be anaerobic. The sediment may also be stratified into oxidized and reduced layers. Each layer may be expected to contain different types of microbial populations with distinct metabolic activities (Neely and Blau 1985b). Bacterial population density within the sediment may be several orders of magnitude higher than that found in the water column (Neely and Blau 1985a). To degrade the variety of naturally occurring and synthetic organic compounds, biodegradation involves the actions of many diverse microbial populations, with separate but complementary capabilities (Neely and Blau 1985a).

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The action of microorganisms on natural and synthetic compounds may bring about one or more of the following processes: mineralization; detoxification; co-metabolism; and, activation. Mineralization involves the conversion of an organic compound into inorganic products. Detoxification refers to the conversion of a toxic substance into relatively innocuous metabolites. Co-metabolism involves microbial metabolism of a compound that the microorganism(s) cannot use as a nutrient. Activation is the conversion of a non-toxic compound into one that is toxic (Alexander 1980). Partial degradation by microbiota may result in a:

- Less toxic compound;
- Compound more toxic than the parent compound;
- Toxic compound, whereas the original molecule was nontoxic at environmental concentrations;
- More persistent compound than the parent compound; or,
- Compound subject to biomagnification or to changes different from those of the parent compound (Alexander 1980).

Microbial activity may also enhance the release of metals from sediments by formation of compounds capable of complexing metal ions. A major concern of microbial activity relates to the conversion of inorganic metal compounds to organometallic molecules as a result of enzyme-catalyzed oxidative and reductive processes. The formation of methyl compounds of, for example, arsenic, lead, mercury, selenium and tin provides one means of the release of highly toxic substances to the environment (Golterman *et al.* 1983).

Synthetic organic molecules are not necessarily amenable to microbial degradation. If the microbial enzymes necessary for metabolism are absent or the substance is protected in some way by the physical and chemical properties of the environment, the compound will persist. Persistence may range from several months to years (Alexander 1980).

A1.4 Mechanisms of Toxicity

Substances may interact with the cells of aquatic organisms in many ways. The actions of toxic substances may increase or decrease the passage of substances into the cell for energy production or maintenance of the osmotic and electrical balance of the cell. The substances may also react with enzymes or the metabolites of enzymatic reactions (Warren 1971; Connell and Miller 1984). For example, the toxic mechanisms for metal ions generally fall into three categories (Connell and Miller 1984):

- Blocking the essential biological functional groups of biomolecules (e.g., proteins and enzymes);
- Displacing essential metal ions in biomolecules; and,
- Modifying the active conformation of biomolecules.

Some studies suggest that chlorinated hydrocarbons act by dissolving the fatty membrane surrounding nerve fibres and interfering with the transport of ions in or out of the fibre. For organophosphates, the site of toxic action is the synaptic gap of nerves. Organophosphates and carbamate pesticides de-activate the enzyme acetylcholinesterase (AChE), which normally breaks down acetylcholine once it has carried the impulse across the synaptic gap. Interference with the breakdown process results in an accumulation of acetylcholine and a series of extraneous nerve impulses (tremors, convulsions, paralysis) (Mullins 1977). Other pesticides (e.g., organochlorine insecticides) often induce increased activity of hepatic enzyme systems at extremely low levels of exposure. This activity may influence other metabolic processes and cause synergistic or antagonistic effects through stimulation of enzyme systems responsible for metabolizing pesticides.

Narcosis is the minimum level of toxicity exerted by any chemical, and is a non-specific reversible disturbance of the membrane, assuming that death does not occur. It can occur in all organisms, including bacteria and plants. Organic chemical molecules present in the body of the organism cause narcosis, although the mechanism of action and the specific receptor sites are not clear. There are two theories concerning narcosis: the critical volume theory and that of protein binding. The critical volume theory is that changes in the lipid component of cell membranes result from increased volumes due to the dissolved toxicant. The protein binding theory states that toxicants bind to receptor sites of specific dimensions in the hydrophobic regions of proteins. Many organic chemicals can be metabolized by organisms, resulting in lower narcotic activity than would be otherwise predicted.

Various characteristics of water and of organisms may change the toxicity of water pollutants to aquatic organisms. Both abiotic and biotic characteristics act as modifying factors. Abiotic factors include the physical and chemical characteristics of the water. The biotic factors consist of the features that relate to the organism, such as species, life stage, size, nutritional status, general health and degree of acclimation to natural environmental conditions or to the pollutant (Sprague 1985). Several major modifying factors (e.g., temperature, pH, and dissolved oxygen) are discussed in sections above.

Appendix 2 Development of Water Quality Objectives Using the Recalculation Procedure: A Case Study for Zinc in the South McQuesten River Basin, Yukon

The South McQuesten and North McQuesten rivers are major tributaries to the Stewart River. From its headwaters near Keno City in west central Yukon, the South McQuesten River flows some 150 km to its confluence with the Stewart River, which eventually discharges into the Yukon River. The major tributaries to the South McQuesten River include Christal Creek, Flat Creek, Haldane Creek, and Galena Creek.

There is a long history of mineral exploration and mine development in the McQuesten River watershed. Silver-lead-zinc mineralization was first discovered in the vicinity of Galena Creek in 1906. Since that time, many small silver deposits have been mined. In addition, a number of larger mining operations have been established in the area. Collectively, these historic mining activities have resulted in a diversity of pits, adits, tailings piles, and wasterock dumps throughout the basin. The available water quality data indicate that surface run-off from abandoned mine sites and/or discharges of leachate from abandoned tailings piles are releasing contaminants into surface waters within the South McQuesten River basin, including Christal Creek, Flat Creek, Galena Creek, and the South McQuesten River mainstem. In particular, the levels of zinc in receiving water systems represent a potential concern for the fish and aquatic organisms that utilize or potentially utilize habitats within the watershed.

In 1997, a proposal to re-open a mine in the watershed was submitted to regulatory agencies. The associated mining operations would involve both underground and open pit mining at a number of locations in the vicinity of Keno City. As protection of fish and aquatic life is a primary water management goal in the watershed, regulatory agencies and mining interests faced the challenge of developing WQOs that will support this important water use in the South McQuesten River and tributaries.

The Canadian WQGs (CCREM 1987; CCME 1999) provide essential information for defining the water quality conditions needed to protect aquatic organisms in the South McQuesten River watershed. However, it was recognized that a portion of the toxicological data that was assembled to support derivation of the Canadian WQGs for zinc (Nagpal 1997) were not directly relevant for assessing zinc toxicity in a northern river basin. For this reason, the recalculation procedure was used to develop site-adapted WQOs for zinc in the South McQuesten River and associated tributaries.

A2.1 Derivation of Preliminary Water Quality Objectives for Zinc

Derivation of site-adapted WQOs is an iterative process that requires both substance-specific and site-specific data. The first step in this process is to identify the use protection goals for the site (Figure A2.1). In the South McQuesten River Basin, protection of fish and other aquatic organisms has been identified as a primary water management goal. In addition, the system is used to a limited extent to provide raw water for drinking water supplies. As wildlife are an integral element of the ecosystem, it is important to protect the ungulates, waterfowl, fur-bearers, and other wildlife species that utilize the river as a drinking water source. Therefore, protection of these three water uses has been identified as a high priority management goal for the South McQuesten River Basin.

The second step in the objectives development process involves selection of a preliminary WQO (PeWQO) from the available Canadian WQGs. The recommended WQGs for zinc for the protection of freshwater aquatic life vary depending on the ambient water hardness in the receiving water system. In the South McQuesten River Basin, water hardness varies considerably between sites and during different flow periods (Table A2.1).

Using the available information on stream hydrology, it is apparent that the low flow period encompasses the months between November through April. The high flow period generally occurs during May and June, while the moderate flow period includes the months between July through October.

Comparison of the Canadian WQGs for zinc that apply to the three major water uses in the South McQuesten River system indicates that protection of fish and aquatic life is the most sensitive water use (CCREM 1987; Nagpal 1997; CCME 1999). For this reason, the WQGs for the protection of fish and aquatic life were used to establish the PeWQOs for zinc within the study area. Specifically, the concentrations of zinc in each receiving water system that would be predicted to protect aquatic life were calculated using the equation (Nagpal 1997; CCME 1999):

WQG (Φ g/L) = 7 + 0.755 • (hardness - 90)

Application of this equation makes it possible to determine the concentrations of zinc in each stream reach and at each flow stage that would likely be protective of freshwater aquatic life (i.e., the preliminary WQOs; Table A2.2).

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A2.2 Evaluation of the Preliminary Water Quality Objectives

The second step in the WQOs development process involves evaluation of the applicability of the PeWQO to the site under investigation. This evaluation necessitates consideration of background concentrations, analytical limits of quantification, the factors that could affect the bioavailability and/or toxicity of the substance, and the relevance of the complete toxicological data set to the site.

It is difficult to establish background concentrations of zinc in the South McQuesten River system for several reasons. First, exploration and mining activities have occurred throughout the upper river basin; therefore, it is difficult to identify suitable upstream locations that have not been influenced by these activities. Second, exploration and mining have been prevalent within the river basin for nearly a century; therefore, pre-development water quality data are not available. Finally, it is difficult to identify suitable reference areas in the vicinity of the study area because mining activities are so prevalent within this region of Yukon. Nonetheless, it could be argued that the concentrations of total zinc measured in the South McQuesten River upstream of Christal Creek would be close to background levels.

Data on the background concentrations of zinc in the South McQuesten River upstream of Christal Creek are generally lower than the preliminary WQOs. While the single measurement of total zinc at high flow (33 :g/L) exceeds the preliminary WQOs, it is likely that typical background concentrations of dissolved zinc during high flow would be lower than the PeWQOs. The average concentrations of total zinc measured during moderate (14.3 :g/L) and low flow periods (17 :g/L) are also lower than the PeWQOs. Therefore, it is not unreasonable to conclude that the preliminary WQO are applicable for the various stream reaches and flow periods.

Subsequently, the preliminary WQOs for dissolved zinc were evaluated relative to analytical limits of quantification. Using standard Inductively Coupled Plasma (ICP) technology, analytical detection limits of 5 :g/L are routinely achieved for zinc. Much lower detection limits (i.e., 0.5 :g/L) can be achieved using ICP-MS technology. Therefore, it is possible to monitor for attainment of the preliminary WQOs using existing and readily available analytical methods.

A recent review of the available toxicological data on zinc provides a basis for identifying the factors that have the potential to influence the toxicity of zinc (Nagpal 1997; CCME 1999). The results of this review indicated that several environmental factors have the potential to modify zinc toxicity, including water hardness, calcium, magnesium, salinity, pH, temperature, and the presence of other metals. Of these, water hardness (including concentrations of calcium and magnesium) was found to be the most important factor, with toxicity decreasing with increasing water hardness. Zinc was also found to be most toxic at near neutral pH (i.e., pH 7) and at elevated water temperatures. While there was variability in the results, the presence of other metals generally increased the toxicity of zinc to aquatic organisms. Of these factors, only water hardness is considered in the derivation of WQGs for zinc. Insufficient information was located to adjust the guidelines based on the concentrations of other metals, pH, or water temperature. For this reason, there was no basis for adjusting the PeWQOs for zinc in the South McQuesten River.

The toxicological data set for zinc that was utilized to derive the generic WQGs contains information on a wide variety of freshwater organisms (Table A2.3). Many of these species do not occur or do not have the potential to occur in the South McQuesten River. For this reason, it is appropriate to refine the toxicological data set and recalculate the preliminary WQOs using the appropriate protocol (i.e., CCME 1991; 1999). The steps involved in applying the recalculation procedure are described below.

A2.3 Application of the Recalculation Procedure in the South McQuesten River Basin

Application of the recalculation procedure requires information of the types of aquatic organisms that occur in the water body under investigation. The results of biological monitoring programs provides a basis for describing the macroinvertebrate and fish communities that occur or are expected to occur in the South McQuesten River system. These biomonitoring data show that the South McQuesten River contains the following families of fish and classes/orders of macroinvertebrates:

Fish	Invertebrates
Salmonidae (salmon and trout)	Oligochaeta (aquatic worms)
Esocidae (pike)	Cladocera (water fleas)
Petromyzontidae (lampreys)	Copepoda (copepods)
Gadidae (cod)	Ostracoda (ostracods)
Catostomidae (suckers)	Arachnida (water mites)
Cyprinidae (minnows)	Plecoptera (stoneflies)
	Ephemeroptera (mayflies)
	Tricoptera (caddisflies)
	Diptera (flies)
	Gastropoda (snails)
	Pelecypoda (bivalves)

Examination of the available literature indicates that many of these groups of fish and invertebrates are reflected in the toxicological data set. Excluding the fish families that do not occur in the vicinity of the

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proposed mine site, the LOEL is 0.005 mg/L of zinc (Table A2.4). Exposure to this concentration of zinc for 18 days resulted in 60% mortality to brown trout yolk-sac fry (Sayer *et al.* 1989). The LOEL for freshwater invertebrates in the focussed toxicological data set is 0.015 mg/L. Exposure to this concentration of zinc resulted in a 57% decrease in the abundance of benthic macroinvertebrates within four days (Clements *et al.* 1988). These LOELs are the same as those identified in the overall toxicological data set, which indicates that the aquatic organisms that occur in the watercourses nearby the proposed mine site are as sensitive to zinc as those represented in the data set used to derive the generic WQGs. Therefore, application of the recalculation procedure does not support refinement of the preliminary WQOs that were established from the generic WQGs for fish and aquatic life.

The WQOs derived using the recommended procedures may be established as the final WQOs for the South McQuesten River and tributaries. Attainment of the WQO would result in water quality conditions that would support aquatic life and the other, less stringent, water uses (i.e., wildlife and raw water for drinking water supply).

Appendix 3 Development of Water Quality Objectives using the Water Effect Ratio (WER) Procedure: A Case Study for Copper in the Upper Clark Fork River, Montana

The Clark Fork River is the largest tributary of the Columbia River in the northwestern United States. The Clark Fork River flows from its headwaters in the vicinity of Butte, Montana to Lake Pend Oreille in northeastern Idaho. From the lake, the Pend Oreille River flows some 180 km to its confluence with the Columbia River near Trail, British Columbia.

The headwaters of the Clark Fork River lie in a mineral-rich portion of the Rocky Mountains. Between 1880 and 1972, more than 400 million metric tonnes of sulfide ore deposits were extracted and smelted in the watershed. While most of the mining and smelting facilities were concentrated in the vicinity of Anaconda and Butte, more than 230 km of the Upper Clark Fork River have been contaminated by historic mining activities (i.e., from Butte to the Milltown Reservoir, which is located near Missoula, Montana). Mining wastes are no longer released into the river system; nonetheless, roughly 15 million m³ of tailings and heavy metal sludge have been incorporated into the riverbed, floodplain, and reservoir sediments (Ingersoll *et al.* 1992). As a result, the Upper Clark Fork River contains elevated levels of arsenic, copper, cadmium, lead, manganese, and zinc, which have the potential to compromise the designated uses of water in the basin.

The water effect ratio (WER) procedure was used to develop site-adapted WQOs for copper in the Upper Clark Fork River. Implementation of this procedure involved conducting water column toxicity tests to derive water effect ratios for several stream reaches in the Upper Clark Fork River. The information used in this case study was drawn from several reports that were produced by ENSR Consulting and Engineering to support the derivation of site-specific WQO for copper (ENSR 1995; 1996). Rather than reproducing this information directly, it was utilized to develop a case study that illustrated the procedures that were recommended in this document.

A3.1 Derivation of a Preliminary WQO for Copper in the Upper Clark Fork River

Identification of use protection goals is the first step in the WQOs development process. The available information indicates that the Clark Fork River currently supports a variety of water uses. In 1985, for example, the Clark Fork River and its tributaries supported a three million dollar recreational fishery, which targeted primarily on coldwater fish species such as brown trout, rainbow trout, west slope cutthroat trout and bull trout (Ingersoll *et al.* 1992). In addition to coldwater fish assemblages, the downstream reaches of this river also support healthy and diverse communities of aquatic invertebrates and plants. This river system is used directly as a raw drinking water supply for several communities in western Montana and as a source of water for irrigation and livestock watering. Protection and enhancement of these water uses has been identified as a high priority goal for the Upper Clark Fork River.

The second step in the WQOs development process involves the selection of a PeWQO from the available generic WQC and guidelines. The WQGs applicable to copper, for the designated water uses in the Upper Clark Fork River are (CCREM 1987; Nagpal *et al.* 1995; CCME 1999):

Designated Water Use	Water Quality Guideline
Raw Water for Drinking Water Supply	1 mg \cong L ⁻¹
Fish and Aquatic Life	0.002 mg \cong L ⁻¹ (at hardness of #120 mg \cong L ⁻¹)
Irrigation	0.2 mg \cong L ⁻¹ (sensitive crops)
Livestock Watering	0.5 mg \cong L ⁻¹ (sheep)
Recreation and Aesthetics	None

The WQGs for copper are dependant on water hardness (CCREM 1987; CCME 1999). The water hardness in the Clark Fork River varies seasonally, with the lowest levels observed in late spring (roughly 120 mg/L as CaCO₃). At this water hardness, the Canadian and British Columbia WQGs are 0.002 mg/L and 0.005 mg/L, respectively.

Stakeholders have indicated that it is desirable to protect and maintain each of the designated uses of water in the Upper Clark Fork River. For this reason, the WQG for the most sensitive use was adopted as the PeWQO (i.e., the WQG for the protection of fish and aquatic life of 0.002 mg \cong L⁻¹ or 2 :g \cong L⁻¹ of copper).

Next, the PeWQO was evaluated to assess its applicability to the Upper Clark Fork River. As a first step, the PeWQO was compared to background levels of copper in the Upper Clark Fork River. Because mining has occurred virtually continuously for the last century in the river basin, it was not possible to determine historic

background levels of copper in the Upper Clark Fork River. Because mining occurred in the headwaters of the system, it was not possible to select an upstream site to establish background levels of metals. For these reasons, a nearby reference station was established in an area with similar minerology to estimate background levels of copper. Data collected at this site indicate that background levels of dissolved copper are typically $< 1.2 : g \cong L^{-1}$. Since the PeWQO of copper is greater than background levels, no adjustment of the PeWQO is necessary. Likewise, it was not necessary to adjust the PeWQO to account for analytical limits of quantification (i.e., detection limits of $< 1 : g \cong L^{-1}$ are typically achieved for copper using ICP technology).

In some cases, it may be warranted to adjust the PeWQO to account for atypical species assemblages that are present at the site under consideration. For example, the PeWQO may need to be adjusted if it is based on effects to coldwater fish species and the water body under consideration supports wamrwater fish species only. Concurrent examination of the biological inventory data for the site and the toxicological data set for copper revealed that the Upper Clark Fork River contains representatives of the most sensitive families of fish to copper. Therefore, implementation of the recalculation procedure to consider the data on resident species only would not change the PeWQO. Therefore, the PeWQO was not adjusted based on this evaluation.

There is some data in the scientific literature that indicates that the bioavailability of copper can be influenced by a number of water quality characteristics, including the presence of humic acids, phosphates, sulphides, and fine particulates in the water column (Leckie and Davis 1979; Stiff 1971). The results of environmental monitoring indicated that elevated levels of several of these variables occur, at least seasonally, in the Upper Clark Fork River (ENSR 1995; 1996). For this reason, the WER procedure was implemented at this site to determine if adjustment of the PeWQO was warranted.

A3.2 Determination of Water Effect Ratios

Implementation of the indicator species procedure necessitates side-by-side toxicity testing in site water and in laboratory dilution water. The toxicity testing program developed for the Upper Clark Fork River investigation consisted of five bioassays for rapidly assessing the acute and chronic toxicity of copper to sensitive vertebrate and invertebrate species, including:

- *Ceriodaphnia dubia*, 48-hour survival, static;
- Ceriodaphnia dubia, 3-brood survival and reproduction, static renewal;
- Fathead minnow (Pimephales promelas), 96-hour survival, static;
- Fathead minnow, 7-day survival and growth, static renewal; and,
- Rainbow trout (Oncorhynchus mykiss), 96-hour survival, static.

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For each toxicity test, paired bioassays were conducted in water collected directly from the site and in laboratory water that was reconstituted to match the hardness and alkalinity of the site water. Water was collected at two sites on the Upper Clark Fork River (i.e., downstream of Warm Springs Pond and at Deer Lodge) to determine if spatial differences in water quality would influence the toxicity of copper. At each site, water samples were collected during four low flow periods and one high flow period to determine if seasonal differences in the characteristics of site water were likely to influence the toxicity of copper to the indicator species that were tested.

The results of the toxicity testing program indicated that copper was generally less toxic in site water than it was in standard laboratory dilution water. For each site, sampling date, and toxicity test, the effective concentration of copper in site water was divided by the effective concentration of copper in laboratory water to determine a water effect ratio (WER; Table A3.1). Overall, the WERs obtained in the study ranged from 1.56 to > 25.6 for total copper and 1.04 to 10.6 for dissolved copper. These results were used to calculate the Final WERs for total and dissolved copper for each sampling period at each site (*see Table A3.2 and Table A3.3*).

Examination of the WERs obtained in this study provides a number of insights for establishing WQOs. First, the WERs determined for each site and sampling period, using the results of five distinct toxicity tests, were generally similar (i.e., within a factor of three). The chronic toxicity test with *Ceriodaphnia dubia* and the acute toxicity test with rainbow trout generally yielded the lowest WERs.

Temporal patterns in the WERs were difficult to interpret from the data that were generated. In some of the toxicity tests, the highest WERs were observed during the high flow period in the spring. For other tests, the WERs calculated for the high flow period were among the lowest. Due to the lack of distinct temporal patterns of toxicity, the WERs for the five sampling periods were averaged for each sampling site and toxicity test. The two lowest average WERs were used to calculate the Final WER for each site. The Final WERs for total and dissolved copper in the Upper Clark Fork River downstream of Warm Springs Pond were 2.70 and 2.20, respectively. Slightly lower WERs were determined for the Upper Clark Fork River at Deer Lodge (i.e., 2.23 for total copper and 1.83 for dissolved copper).

The WERs developed in this study were used to modify the PeWQO that was formulated previously. The following equation was used to develop the final water quality objectives (FWQOs) for the Upper Clark Fork River:

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Using this equation, the FWQO for total and dissolved copper in the Upper Clark Fork River downstream of Warm Springs Pond were 5.4 and 4.4 : $g\cong L^{-1}$, respectively. At Deer Lodge, the FWQOs for total and dissolved copper were 4.5 and 3.7 : $g\cong L^{-1}$, respectively.

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Appendices Tables and Figures

Table A2.1 Summary of water hardness data for the South McQuesten River and tributaries

	Water Hardness (mg/L)									
Location	High Flow	Moderate Flow	Low Flow							
South McQuesten River upstream of Christal Creek	90	130	170							
Christal Creek at Hanson Road	165	270	415							
South McQuesten River downstream of Christal Creek	100	125	200							
Flat River upstream of South McQeston River	165	290	320							
South McQuesten River downstream of Flat Creek South McQuesten River 9 km downstream of Flat	110	170	220							
Creek	105	135	210							

Table A2. 2 Preliminary water quality objectives for dissolved zinc in the South McQuesten River and tributaries.

	W	WQOs for Zinc (µg/L)								
Location	High Flow	Moderate Flow	Low Flow							
South McQuesten River upstream of Christal Creek	7	37.2	67.4							
Christal Creek at Hanson Road South McQuesten River downstream of Christal	63.6	142.9	252.4							
Creek	14.5	33.4	90							
Flat River upstream of South McQeston River	63.5	158	180.7							
South McQuesten River downstream of Flat Creek South McQuesten River 9 km downstream of Flat	22.1	67.4	98.2							
Creek	18.3	41	97.6							

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
											Rehwoldt <i>et</i>
Anguilla rostrata	<20 cm	S, M, 2	ZnNO3	7.8	6.5	17.0	-	53	14.6	TLm-96 hr	al.
(American eel)	<20 cm	S, M, 2	ZnNO3	7.8	6.5	17.0	-	53	20	TLm-48 hr	1971
	<20 cm	S, M, 2	ZnNO3	7.8	6.5	17.0	-	53	21.6	TLm-24 hr	
Catostomus	~17.7 g	F,M,1	ZnCl2	-	-	12.1	-	-	2.2	LC50-96 hr	Duncan &
commersoni	~17.7 g	F,M,1	ZnCl2	-	-	12.1	-	-	2.48	LC50-72 hr	Klaverkamp
(white sucker	~17.7 g	F,M,1	ZnCl2	-	-	12.1	-	-	2.96	LC50-48 hr	1983
- unfed)	~17.7 g	F,M,1	ZnCl2	-	-	12.1	-	-	5.58	LC50-24 hr	
	~17.7 g	F,M,1	ZnCl2	-	-	12.1	-	-	13.3	LC50-12 hr	
Clarias lazera	subadult	S,N,2	ZnSO4	6.7	90%	15.3	-	20-22	40	LC50-96 hr	Hilmy <i>et al</i> .
	subadult	S,N,2	ZnSO4	6.7	90%	15.3	-	20-22	46	LC50-72 hr	1987
	subadult	S,N,2	ZnSO4	6.7	90%	15.3	-	20-22	52	LC50-48 hr	
	subadult	S,N,2	ZnSO4	6.7	90%	15.3	-	20-22	58	LC50-24 hr	
	subadult	S,N,2	ZnSO4	6.7	90%	9.3	-	20-22	52	LC50-96 hr	
	subadult	S,N,2	ZnSO4	6.7	90%	9.3	-	20-22	58	LC50-72 hr	
	subadult	S,N,2	ZnSO4	6.7	90%	9.3	-	20-22	60	LC50-48 hr	
	subadult	S,N,2	ZnSO4	6.7	90%	9.3	-	20-22	68	LC50-24 hr	
	subadult	S,N,2	ZnSO4	6.7	90%	18.5	-	20-22	38	LC50-96 hr	
	subadult	S,N,2	ZnSO4	6.7	90%	18.5	-	20-22	43	LC50-72 hr	
	subadult	S,N,2	ZnSO4	6.7	90%	18.5	-	20-22	52	LC50-48 hr	
	subadult	S,N,2	ZnSO4	6.7	90%	18.5	-	20-22	56	LC50-24 hr	
	subadult	S,N,2	ZnSO4	6.7	90%	25.0	-	20-22	26	LC50-96 hr	

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
	subadult	S,N,2	ZnSO4	6.7	90%	25.0	_	20-22	33	LC50-72 hr	
	subadult	S,N,2	ZnSO4	6.7	90%	25.0	-	20-22	37	LC50-48 hr	
	subadult	S,N,2	ZnSO4	6.7	90%	25.0	-	20-22	41	LC50-24 hr	
Cyprinus carpio	<20 cm.	S, M, 2	ZnNO3	7.8	6.5	17.0	-	53	7.8	TLm-96 hr	Rehwoldt <i>et</i> al.
(carp)	<20 cm.	S, M, 2	ZnNO3	7.8	6.5	17.0	-	53	9.3	TLm-48 hr	1971
	<20 cm.	S, M, 2	ZnNO3	7.8	6.5	17.0	-	53	14.3	TLm-24 hr	
Fundulus	<20 cm.	S, M, 2	ZnNO3	7.8	6.5	17.0	-	53	19.1	TLm-96 hr	Rehwoldt <i>et al.</i>
diaphanus	<20 cm.	S, M, 2	ZnNO3	7.8	6.5	17.0	-	53	20.7	TLm-48 hr	1971
(banded kilifish)	<20 cm.	S, M, 2	ZnNO3	7.8	6.5	17.0	-	53	22.6	TLm-24 hr	
Jordanella floridae (flagfish)	juvenile (4 - 5 wks)	F,M,1	ZnSO4	7.1- 7.8	8.3	25.0	42	44	1.5	LC50-96 hr	Spehar 1976
Labeo rohita	juvenile	NA	-	-	-	-	-	-	65	LC50-96 hr	Bengeri and
(cypriniform fw fish)	adult	NA	-	-	-	-	-	-	77	LC50-96 hr	Patil 1986
Lebistes	adult male	S,M,2	ZnSO4	8.3	5.8	22.0	85	118	240	LC25-96 hr	Sehgel & Saxena
reticulatus	(~70 mg)	S,M,2	ZnSO4	8.3	5.8	22.0	85	118	300	LC50-96 hr	1986
(unfed)	. –,	S,M,2	ZnSO4	8.3	5.8	22.0	85	118	375	LC75-96 hr	
		S,M,2	ZnSO4	8.3	5.8	22.0	85	118	212	LC25-96 hr	
		S,M,2	ZnSO4	8.3	5.8	22.0	85	118	278	LC50-96 hr	
		S,M,2	ZnSO4	8.3	5.8	22.0	85	118	325	LC75-96 hr	

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
Lepomis gibbosus	<20 cm	S,M,2	ZnNO3	7.8	6.5	17.0		53	20	TLm-96 hr	Rehwoldt <i>et</i> al.
(pumpkinseed)	<20 cm <20 cm	S,M,2 S, M, 2	ZnNO3 ZnNO3	7.8 7.8	6.5 6.5	17.0 17.0	-	53 53	21.8 25.2	TLm-48 hr TLm-24 hr	at. 1971
Lepomis macrochirus	49 mm	F,M,1	ZnSO4	6.8- 7.5	6.6-9.5	22.0	23.2-32.8	21.2-59.2	3.2	LC50-96 hr	Thompson <i>et al.</i> 1980
(bluegill)	adult adult	F,M,1 F,M,1	-	7.5 7.5	-	15.0 15.0	18 300	20 360	5.4 40.9	LC50-96 hr LC50-96 hr	Pickering & Henderson 1966 Pickering & Henderson 1966
<i>Morone saxatilis</i> (striped bass)	larvae	NA	-	-	-	-	-	-	0.100-0.119	LC50-96 hr	EPA 1980 & 1987
	fry	NA	-	-	-	-	-	-	0.430- 1.180	LC50-96 hr	
	adult	NA	-	-	-	-	-	-	6.7	LC50-96 hr	EPA 1980 & 1987
<i>Oncorhyncus</i> <i>clarki</i> (cutthroat trout)	-	NA	-	-	-	-	-	-	0.061- 0.600	LC50-96 hr	EPA 1980; Mayer & Ellersieck1986

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
Oncorhyncus mykiss	fry	NA	-	-	-	-	-	-	0.090- 0.093	LC50-96 hr	EPA 1980 & 1987
(rainbow trout)	parr	NA	-	-	-	-	-	30	0.24- 0.83	LC50-96 hr	EPA 1980
	parr	NA	-	-	-	-	-	500	4.7	LC50-96 hr	
	parr	NA	-	-	-	-	-	350	1.19- 4.52	LC50-96 hr	
	fry	NA	-	-	-	-	-	-	0.689	LC50-96 hr	
	0.6 g	F,M,1	-	-	-	-	-	-	0.169	LC50-96 hr	Buhl & Hamilton 1990
	juvenile	F,M,1	-	6.8	-	12.0	25	26	0.43	LC50-96 hr	Sinely <i>et al.</i> 1974
	juvenile	F,M,1	-	7.6	-	15.0	43	47	0.52	LC50-96 hr	Holocombe and
	juvenile	F,M,1	-	7.2	-	16.0	170	179	2.96	LC50-96 hr	Andrew 1978
	juvenile	F,M,1	-	7.8	-	15.5	-	504	4.8	LC50-96 hr	Solbe 1974
Pimephales	24 hr	S,M,2	ZnSO4	7-7.5	>5	25.0	225-245	280-300	0.33	LC50-96 hr	Schubauer-
promelas	24 hr	S,M,2	ZnSO4	8-8.5	>5	25.0	225-245	280-300	0.5	LC50-96 hr	Berigan 1993
(fathead minnow)	24 hr	S,M,2	ZnSO4	6-6.5	>5	25.0	225-245	280-300	0.78	LC50-96 hr	
	larvae	F,M,1	-	-	-	-	-	-	0.6	LC50-96 hr	Spear 1981
	adult	F,M,1	-	7.5	-	15.0	18	20	0.87	LC50-96 hr	Pickering and
	adult	F,M,1	-	7.5	-	15.0	300	360	33.4	LC50-96 hr	Henderson

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
											1966
	adult	F,M,1	-	8	-	25.0	57	50	4.7-6.1	LC50-96 hr	Mount 1966
	adult	F,M,1	-	8.6	-	25.0	-	100	6.4	LC50-96 hr	
	adult	F,M,1	-	8	-	25.0	162	200	8.2-21.0	LC50-96 hr	
	adult	F,M,1	-	6.2	-	25.0	-	166	7.6	LC50-96 hr	Rachlin & Perlmutter 1968
	immature 2-3 g	F,M,1	ZnSO4	7.7	6.7	23.0	162	203	9.2	TLm-96 hr	Spehar 1976
	immature 2-3 g	F,M,1	ZnSO4	7.7	6.7	23.0	162	203	12.5	TLm-96 hr	
Poecilia reticulata	5 days	F,M,1	ZnSO4	7.16	7.86	25.1	33.5	Salinity=30	1.74	LC50-96 hr	Pierson 1981
(guppy - fed)	mature male	S,M,2	ZnSO4	7.16	7.86	25.1	33.5	Salinity=30	5.05	LC50-96 hr	
	mature female	S,M,2	ZnSO4	7.16	7.86	25.1	33.5	Salinity=30	6.4	LC50-96 hr	
Roccus americanus	<20 cm	S,M,2	ZnNO3	7.8	6.5	17.0	-	53	10.2	TLm-48 hr	Rehwoldt <i>et</i> al.
(white perch)	<20 cm	S,M,2	ZnNO3	7.8	6.5	17.0	-	53	13.6	TLm-24 hr	1971
	<20 cm	S,M,2	ZnNO3	7.8	6.5	17.0	-	53	14.3	TLm-96 hr	
Roccus saxatilis	<20 cm	S,M,2	ZnNO3	7.8	6.5	17.0	-	53	6.7	TLm-96 hr	Rehwoldt <i>et</i> al.
(striped bass)	<20 cm	S,M,2	ZnNO3	7.8	6.5	17.0	-	53	10	TLm-48 hr	1971
	<20 cm	S,M,2	ZnNO3	7.8	6.5	17.0	-	53	11.2	TLm-24 hr	

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
Oncorhynchus mykiss	small (1-6 g)	F,M,1	ZnCl2	7	>90%	15.0- 16.0	-0.2	9.2	0.066	LC50-96 hr	Cusimano & Brakke 1986
(steelhead trout)	small (1-6 g)	F,M,1	ZnCl2	5.7	>90%	15.0- 16.0	1.7	9.2	0.097	LC50-96 hr	
	small (1-6 g)	F,M,1	ZnCl2	4.7	>90%	15.0- 16.0	11	9.2	0.671	LC50-96 hr	
	juvenile	F,N,2	ZnSO4	-	-	15.0	-	soft water	0.43	LC50-96 hr	Sinley et al.
	juvenile	F,N,2	ZnSO4	-	-	15.0	-	hard water	7.21	LC50-96 hr	1974
	eyed eggs	F,N,2	ZnSO4	-	-	11.0	-	soft water	2.72	LC50-96 hr	
	Eggs: 5 d post- fertilization	S,M,2	ZnSO4	7.8	99.8% sat.	8.6	-	87.8	24	LC50-48 hr	Shazili and Pascoe 1986
	Eggs: 10 d post-fertiliz.	S,M,2	ZnSO4	7.8	99.80% sat.	8.6	-	87.8	<1.0 (extrapolated)	LC50-48 hr	
	Eggs: 15 d post-fertiliz.	S,M,2	ZnSO4	7.8	99.8% sat.	8.6	-	87.8	9.1	LC50-48 hr	
	Eggs: 22 d post-fertiliz.	S,M,2	ZnSO4	7.8	99.8% sat.	8.6	-	87.8	7	LC50-48 hr	
	Eggs: 29 d post-fertiliz.	S,M,2	ZnSO4	7.8	99.8% sat.	8.6	-	87.8	4.3	LC50-48 hr	
	Eggs: 36 d post-fertiliz.	S,M,2	ZnSO4	7.8	99.8% sat.	8.6	-	87.8	9.2	LC50-48 hr	
Oncorhynchus mykiss	Alevins: 2 d post-hatch	S,M,2	ZnSO4	7.8	99.8% sat.	8.6	-	87.8	3.2	LC50-48 hr	Shazili and Pascoe 1986
(steelhead trout)	Alevins: 7 d post-hatch	S,M,2	ZnSO4	7.8	99.8% sat.	8.6	-	87.8	3.4	LC50-48 hr	

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
Salmo trutta (brown trout)	yearlings (8-10 g)	F,M,1	ZnSO4	9.11	10.1- 10.3	15.0	103	204	0.46	LC50-96 hr	Everall <i>et al.</i> 1989
	yearlings (8-10 g)	F,M,1	ZnSO4	7.03	10.1- 10.3	15.0	103	204	0.64	LC50-96 hr	
	yearlings (8-10 g)	F,M,1	ZnSO4	7.89	10.1- 10.3	15.0	103	204	1	LC50-96 hr	Everall <i>et al.</i> 1989
	yearlings (8-10 g)	F,M,1	ZnSO4	4.1	10.1- 10.3	15.0	103	204	2.02	LC50-96 hr	
	yearlings (8-10 g)	F,M,1	ZnSO4	5.89	10.1- 10.3	15.0	103	204	2.69	LC50-96 hr	
	yearlings (8-10 g)	F,M,1	ZnSO4	5.02	10.1- 10.3	15.0	103	204	3.2	LC50-96 hr	
	yearlings (8-10 g)	F,M,1	ZnSO4	8.03	10.1- 10.3	15.0	62	10	<0.14	LC50-96 hr	
	yearlings (8-10 g)	F,M,1	ZnSO4	9.06	10.1- 10.3	15.0	62	10	0.22	LC50-96 hr	
	yearlings (8-10 g)	F,M,1	ZnSO4	7.07	10.1- 10.3	15.0	62	10	0.6	LC50-96 hr	
	yearlings (8-10 g)	F,M,1	ZnSO4	3.98	10.1- 10.3	15.0	62	10	1.07	LC50-96 hr	
	yearlings (8-10 g)	F,M,1	ZnSO4	6.01	10.1- 10.3	15.0	62	10	1.41	LC50-96 hr	
	yearlings (8-10 g)	F,M,1	ZnSO4	5.06	10.1- 10.3	15.0	62	10	2.31	LC50-96 hr	

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO3)	Conc. (mg/L)	Effect	Reference
Salvelinus fontinalis (brook trout)	juvenile	F,M,1	ZnSO4	-	-	15.0	-	soft water	2	LC50-96 hr	Holcombe et al. 1979
<i>Tilapia zilli</i> (bolti)	subadult	S,N,2	ZnSO4	6.7	90% sat.	25.0	-	20-22	13	LC50-96 hr	Hilmy <i>et al.</i> 1987
	subadult	S,N,2	ZnSO4	6.7	90% sat.	25.0	-	20-22	16	LC50-72 hr	
	subadult	S,N,2	ZnSO4	6.7	90% sat.	25.0	-	20-22	18	LC50-48 hr	
	subadult	S,N,2	ZnSO4	6.7	90% sat.	25.0	-	20-22	22	LC50-24 hr	
	subadult	S,N,2	ZnSO4	6.7	90% sat.	18.5	-	20-22	21	LC50-96 hr	
	subadult	S,N,2	ZnSO4	6.7	90% sat.	18.5	-	20-22	24	LC50-72 hr	
	subadult	S,N,2	ZnSO4	6.7	90% sat.	18.5	-	20-22	29	LC50-48 hr	
	subadult	S,N,2	ZnSO4	6.7	90% sat.	18.5	-	20-22	33	LC50-24 hr	
	subadult	S,N,2	ZnSO4	6.7	90% sat.	15.3	-	20-22	27	LC50-96 hr	
	subadult	S,N,2	ZnSO4	6.7	90% sat.	15.3	-	20-22	32	LC50-72 hr	
	subadult	S,N,2	ZnSO4	6.7	90% sat.	15.3	-	20-22	34	LC50-48 hr	
	subadult	S,N,2	ZnSO4	6.7	90% sat.	15.3	-	20-22	38	LC50-24 hr	

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
	subadult	S,N,2	ZnSO4	6.7	90% sat.	9.3	-	20-22	33	LC50-96 hr	
	subadult	S,N,2	ZnSO4	6.7	90% sat.	9.3	-	20-22	40	LC50-72 hr	
	subadult	S,N,2	ZnSO4	6.7	90% sat.	9.3	-	20-22	45	LC50-48 hr	
	subadult	S,N,2	ZnSO4	6.7	90% sat.	9.3	-	20-22	49	LC50-24 hr	
Oncorhyncus mykiss (steelhead)	adult male	F,M,1	ZnCl2	7.45	10.4	10.3	55	83	1.755	LC50-96 hr	Chapman & Stevens 1978
	swim-up alevins	F,M,1	ZnCl2	7.1	10.2	11.6- 12.8	22	23	0.093	LC50-96 hr	Chapman 1978b
	5-8 month parr	F,M,1	ZnCl2	7.3	10.2	11.6- 12.8	22	23	0.136	LC50-96 hr	
	smolts	F,M,1	ZnCl2	7.1	10.2	11.6- 12.8	22	23	>0.651	LC50-96 hr	
	newly hatched alevins	F,M,1	ZnCl2	7.1	10.2	11.6- 12.8	22	23	0.815	LC50-96 hr	
<i>Oncorhynchus nerka</i> (sockeye salmon)	immature	F,M,1	_	_	_	_	_	_	0.75	LC50-96 hr	Chapman 1978a
Oncorhyncus tshawytscha	juvenile	F,M,1	ZnSO4	7.1- 7.2	85% sat	12-Nov	18-19	20-21	0.04	LC10-96 hr	Finlayson & Verrue 1982

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
(chinook salmon)	juvenile	F,M,1	ZnSO4	7.1- 7.2	85% sat	12-Nov	18-19	20-21	0.084	LC50-96 hr	
	smolts	F,M,1	_	_	_	_	_	_	0.446	LC50-96 hr	EPA 1987
	swim-up alecins	F,M,1	_	7.3- 7.5	10.2	11.6- 12.8	22	23	0.097	LC50-96 hr	Chapman 1978b
	5-8 month parr	F,M,1	_	7.1	10.2	11.6- 12.8	22	23	0.463	LC50-96 hr	
	newly hatched alevins	F,M,1	_	7.3- 7.5	10.2	11.6- 12.8	22	23	>0.661	LC50-96 hr	Chapman 1978b
	smolts	F,M,1	_	7.1	10.2	11.6- 12.8	22	23	0.701	LC50-96 hr	
Salmo salar (Atlantic salmon)	immature immature	D		_	_	_		14 20	0.42 0.6	LC50-96 hr LC50-96 hr	EPA 1980
Oncorhynchus kisutch	adult male	F,M,1	ZnCl2	7.4	9.8	13.7	20	25	0.905	LC50-96 hr	Chapman & Stevens 1978
(coho salmon)	_	F,M,1	_	_	_	_	3.8	5	0.28	LC50-96 hr	McLeay 1976
	0.5-0.9 g	F,M,1	_	_	_	-	3.8	5	0.82- 1.81	LC50-96 hr	
Ptychocheilus oregonesis	juvenile ~6.6g	F,M,1	ZnCl2	7.1- 7.5	>8.6	12	22	23	3.498	96-h LC50	Andros & Garon 1980
(Northern	juvenile ~5.1g	F,M,1	ZnCl2	7.1-	>8.6	12	22	23	3.693	96-h LC50	

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
squawfish)				7.5							
Gasterosteus	-	NA	65ZnCl2	-	-	-	-	282	0.5-1.0	gill damage	Perwak et al.
aculeatus (stickleback)	-	NA	65ZnCl2	-	-	-	-	282	1	increased oxygen uptake	1980
<i>Jordanella floridae</i> (flagfish)	all fish	F,M,1	ZnSO4	7.1- 7.8	8.3	25	42	44	>0.047	Fish contain higher amounts of Zn than control- 30 d	Spehar 1976
	females	F,M,1	ZnSO4	7.1- 7.8	8.3	25	42	44	0.085	significantly lower growth- 30 days	
	larvae	F,M,1	ZnSO4	7.1- 7.8	8.3	25	42	44	0.139	zero survival in 30 days	
	life-cycle	NA	-	-	-	-	-	-	26-51	MATC	U.S. EPA (1987)
Leiopotherapon unicolor	60-80 g	S,N,2	ZnSO4	-	>90% sat.	25	-	-	10	sig. increase in ventilation rate	Gehrke 1988
(spangled perch)	60-80 g	S,N,2	ZnSO4	-	>90% sat.	25	-	-	20	development of a	
										significant bryocardia	
Lepomis macrochirus	-	F,M,1	-	-	-	-	-	-	0.076- 0.235	reproductive inhibition	Sparks <i>et al.</i> 1972
(bluegill)	-	F,M,1	-	-	-	-	-	-	0.1	55 ⁻	Ellgaard <i>et al.</i> 1978
	fry	NA	-	-	-	-	-	-	0.235	lethal in 3 days	EPA 1980 & 1987

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
Noemacheilus		F,M,1	-	-	-	-	-	-	1.9-2.0	LC50-25 days	Solbe & Flook
<i>barbatulus</i> (stone loach)	6.5-11 cm	F,M,1	ZnSO4	~7.5	~91% sat.	11.8- 13.9	-	291-297	~2.0	LC50-7 days	1975
Oncorhyncus clarki	-	F,M,1	-	-	-	-	-	-	0.36	none dead in 14 days	Nehring & Goettl 1974
(cutthroat trout)	-	F,M,1	-	-	-	-	-	-	0.67	LC50-14 days	1974
(cutthroat trout) Oncorhyncus nykiss	5 months 3.0 g wet	F,M,1	ZnCl2	6.6	10	12.6	25	33	0.17	LC50-120 hr	Anadu <i>et al.</i> 1989
(rainbow trout)	immatures	NA	-	-	-	-	-	-	0.0056	avoidance, 10-20 min. test	EPA 1980 & 1987
	life cycle	NA	-	-	-	-	-	-	0.140- 0.547	MATC	EPA 1980 & 1987
	immatures	NA	-	-	-	-	-	-	0.047 (4*)	94% avoidance, 40-min. test	EPA 1987
	immatures	NA	-	-	-	-	-	-	0.352	hyperglycemia-9 days	
	larvae +alevins	F,M,1	-	-	-	-	-	-	0.01 (2*)	LC54-28 days	Affleck 1952
	early life-stage	F,M,1	-	-	-	-	-	-	0.070- 0.140	LC50-25 days	Sinely <i>et al.</i> 1974
	juveniles	F,M,1	-	-	-	-	-	-	0.081	hyperglycemia-24 hr	Wagner 1980

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
	juveniles	F,M,1	_	-	-	-	-	-	0.210- 1.120	Increased blood glucose in 7-63 days	Watson & McKeown 1976
	adults	F,M,1	-	-	-	-	-	360	1.12	reduced growth -85 days	
(rainbow trout)	juveniles	F,M,1	-	-	-	-	-	-	0.69	increased respiration- 24 hr	Sellers <i>et al.</i> 1975
	larvae and alevins	F,M,1	-	-	-	-	-	-	0.40- 2.80	LC50-120 hr	Edwards & Brown 1967
	juveniles	F,M,1	-	-	-	-	-	-	0.41	LC50-14 days	Nehring & Goettl 1974
	juveniles	F,M,1	-	-	-	-	-	-	0.31	LC20-14 days	000ttl 1971
Pimephales promelas	life cycle	NA	-	-	-	-	-	-	0.078- 0.145	MATC	EPA 1980 & 1987
(fathead minow)	adult	NA	-	-	-	-	-	-	0.18	65-83% reduction in	
	juveniles	NA	-	-	-	-	-	-	0.125	fecundity in 10 months reduced growth -7 days	EPA 1987
	larvae	F,M,1	-	-	-	-	-	-	0.152- 0.294	LC84 - 8 weeks	Benoit & Holcombe 1978
	adults	F,M,1	-	-	-	-	-	-	0.48	reduced growth - 30 days	Broderius & Smith 1979

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
	adults	F,M,1	-	-	-	-	-	-	0.8	LC50 - 30 days	Bengtsson 1974
	embryo-larvae	NA	-	-	-	-	-	-	0.5-1.4	50% developmental malformations -96 hr	Dawson <i>et al.</i> 1988
	embryo-larvae	NA	-	-	-	-	-	-	3.6	LC50 - 6 days	
	10 month life cycle	F,M,1	ZnSO4	7.7	6.7	15-25	162	203	0.18	# eggs/female= 17% of control	Brungs 1969
	10 month life cycle	F,M,1	ZnSO4	7.7	6.7	15-25	162	203	0.32	eggs rarely spawned	
Pimephales promelas	10 month life cycle	F,M,1	ZnSO4	7.7	6.7	15-25	162	203	0.66	eggs rarely spawned	Brungs 1969
(fathead minow)	10 month life cycle	F,M,1	ZnSO4	7.7	6.7	15-25	162	203	1.3	30-49% survival of fry- 20days	
	10 month life cycle	F,M,1	ZnSO4	7.7	6.7	15-25	162	203	2.8	no hatching success	
Poecilia reticulatus	-	NA	-	-	-	-	-	80	1.15	growth inhibition	Perwak <i>et al.</i> 1980
(guppy)	age 5 days	F,M,1	ZnSO4	7.16	7.86	25	33.5	42.4	1.45	167.5-h LC50	Pierson 1981
		F,M,1	ZnSO4	7.16	7.86	25	33.5	42.4	0.607	reproduction inhibited	
Oncorhychus mykiss	-	NA	ZnSO4	-	-	-	-	13-15	0.0056	threshold avoidance level -20 min.	Perwak <i>et al.</i> 1980
(rainbow trout)	1-6 g	F,M,1	ZnCl2	7	>90% sat.	15-16	11	-	0.066	LC50-168 hr	Cusimano & Brakke 1986

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
	1-6 g	F,M,1	ZnCl2	5.7	>90% sat.	15-16	1.7	-	0.097	LC50-168 hr	
	1-6 g	F,M,1	ZnCl2	4.7	>90% sat.	15-16	-0.2	-	0.501	LC50-168 hr	
	juv. 4.5-7.5 g	F,M,1	ZnCl2	6.97- 7.05	9.3	15	10.8	31.3	0.11	LC50- 96 h to120 h	Bradley & Sprauge 1985
	juv. 4.5-7.5 g	F,M,1	ZnCl2	6.97- 7.05	9.3	15	8.1	30.2	0.17	LC50- 96-120 hr	
	juv. 4.5-7.5 g	F,M,1	ZnCl2	6.97- 7.05	9.3	15	23.8	31.2	0.19	LC50- 96-120 hr	
	juv. 4.5-7.5 g	F,M,1	ZnCl2	6.97- 7.05	9.3	15	8.6	387	4.46	LC50- 96-120 hr	
(rainbow trout)	juv. 4.5-7.5 g	F,M,1	ZnCl2	6.97- 7.05	9.3	15	24.3	389	5.16	LC50- 96-120 hr	Bradley & Sprauge 1985
	juv. 4.5-7.5 g	F,M,1	ZnCl2	5.46- 5.59	9.3	15	<1.0	31.4	0.088	LC50- 96-120 hr	
	juv. 4.5-7.5 g	F,M,1	ZnCl2	5.46- 5.59	9.3	15	<1.0	394	9.95	LC50- 96-120 hr	
	juv. 4.5-7.5 g	F,M,1	ZnCl2	5.46- 5.59	9.3	15	<1.0	389	11.1	LC50- 96-120 hr	
	juv. 4.5-7.5 g	F,M,1	ZnCl2	8.97- 9.01	9.3	15	23.7	30.9	4.53	LC50- 96-120 hr	
	juv. 4.5-7.5 g	F,M,1	ZnCl2	8.97- 9.01	9.3	15	32.9	373	>87.90	LC50- 96-120 hr	
	2g fingerlings										

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
<i>Oncorhychus</i> <i>mykiss</i> (rainbow trout)	through sexual maturity-2 yrs old	F,N,2	ZnSO4	7.81	6.8	16.2	238	333	Š0.320	0.0% mortality -21 months	Sinley <i>et al.</i> 1974
	same as above	F,N,2	ZnSO4	7.81	6.8	16.2	238	333	0.64	6.4% mortality -21 months	
	same as above	F,N,2	ZnSO4	7.81	6.8	16.2	238	333	1.055	10.0% mortality -21 months	
	same as above	F,N,2	ZnSO4	7.81	6.8	16.2	238	333	2.2	23.0% mortality - 21 months	
	eyed eggs continuing until sexual maturity	F,N,2	ZnSO4	6.8	6.8	12.7	25	26	0.011- 0.547	no sig. change in egg mortality	
Salmo trutta (brown trout)	yolk-sac fry	F,M,1	-	4.5	-	-	-	soft water	0.0049 - 0.0196	60-95% died in18 d; ~40% with noncalcified vertebrae center	Sayer <i>et al.</i> 1989
<i>Salvelinus fontinalis</i> (brook trout)	3rd generation eggs	F,M,1	ZnSO4	7.0- 7.7	9.8	5.0-15.0	41.8	45.4	0.266	fragility sig. increased (p=0.05)	Holcombe <i>et</i> al. 1979
	2nd generation embryos	F,M,1	ZnSO4	7.0- 7.7	9.8	5.0-15.0	41.8	45.4	1.36	Hatchability sig. reduced (p=0.05)	

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
	"fresh" embryos	F,M,1	-	7.2- 7.9	11.6	9	41.3	45.9	1.368	Survival sig. reduced (p=0.05)	
	adults	F,M,1	-	-	-	-	-	-	0.63	LC17-14 days	Nehring & Goettl 1974
	adults	F,M,1	-	-	-	-	-	-	0.96	LC50-14 days	
<i>Oncorhynchus kisutch</i> (coho salmon)	juvenile	F,M,1	_	_	_	_	_	_	0.5-10.7	decreased white blood cells in 24 h	McLeay 1975
Oncorhynchus nerka	adult-smolt	F,M,1	ZnCl2	7.2	9	_	_	35	0.03- 0.112	no adverse effects-18 months	Chapman 1978a
(sockeye salmon)	embryo-smolt	F,M,1	ZnCl2	7.2	9	_	_	35	0.242	no adverse effects-18 months	
	immatures	NA	_	-	_	_	_	_	0.447	115-h LC50	U.S. EPA 1980
Oncorhynchus tshawytscha (chinook salmon)	newly hatched alevins	F,M,1	ZnCl2	7.3- 7.5	10.2	~12	_	23	>0.661 0.364- 0.661	200-h LC50 200-h LC10	Chapman 1978b
(chinook salmon)	swim-up alevins	F,M,1	ZnCl2	7.1	10.2	~12	_	23	0.097 0.068	200-h LC50 200-h LC10	
	5-8 mon. parr	F,M,1	ZnCl2	7.3- 7.5	10.2	~12	_	23	0.395 0.268	200-h LC50 200-h LC10	
	smolts	F,M,1	ZnCl2	7.1	10.2	~12	_	23	0.364 0.170	200-h LC50 200-h LC10	Chapman 1978b

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
Oncorhynchus mykiss (steelhead)	newly hatched alevins	F,M,1	ZnCl2	7.1	10.2	~12	_	23	0.555 0.256	186-h LC50 186-h LC10	
	swim-up alevins	F,M,1	ZnCl2	7.1	10.2	~12	_	23	0.093 0.054	200-h LC50 200-h LC10	
	5-8 mon. parr	F,M,1	ZnCl2	7.3- 7.5	10.2	~12	_	23	0.120 0.061	200-h LC50 200-h LC10	
	smolts	F,M,1	ZnCl2	7.1	10.2	~12	_	23	0.278 0.084	200-h LC50 200-h LC10	Chapman 1978b
	embryo	F,M,1	ZnCl2	6.9- 7.1	>8.7	12	25	25	0.819	86% mortality in 72 d (9.6% in control)	Cairns et al.
	embryo	F,M,1	ZnCl2	6.9- 7.1	>8.7	12	25	25	0.444	18% mortality in 72 d	1982
	embryo	F,M,1	ZnCl2	6.9- 7.1	>8.7	12	25	25	0.262	8% mortality in 72 d	
Salmo salar	parr	_	_	_	_	_	_	_	0.05	50% avoidance - 4h	U.S. EPA 1987
(Atlantic salmon)	parr	_	_	_	_	_	_	_	0.1	avoidance within 20 min.	Spear 1981
	immature	-	_	_	_	_	_	_	0.1-0.5	21-d LC50	U.S. EPA 1980
Ptychochelilus oregonensis	6.58 g	F,M,1	ZnCL2	7.1- 7.5	>8.6	12	20	30	3.65	168-h LC50	Andros & Garton 1980
						107	,				

Species	Life Stag	e	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
(northern quawfish)	0.51 g		F,M,1	ZnCL2	7.1- 7.5	>8.6	12	20	30	2.95	168-h LC50	
Ancylus fluviatilis	juvenile mm	<2	S,M,2	ZnSO4	-	-	10	-	-	0.08	LC50-100 days	Willis 1988
(gastropoda)	juvenile mm	<2	S,M,2	ZnSO4	-	-	10	-	-	0.09	LC50-90 days	
	juvenile mm	<2	S,M,2	ZnSO4	-	-	10	-	-	0.18	LC50-80 days	
	juvenile mm	<2	S,M,2	ZnSO4	-	-	10	-	-	0.19	LC50-70 days	
	juvenile mm	<2	S,M,2	ZnSO4	-	-	10	-	-	0.2	LC50-60 days	
	juvenile mm	<2	S,M,2	ZnSO4	-	-	10	-	-	0.26	LC50-50 days	
	juvenile mm	<2	S,M,2	ZnSO4	-	-	10	-	-	0.36	LC50-40 days	
	juvenile mm	<2	S,M,2	ZnSO4	-	-	10	-	-	0.54	LC50-30 days	
	juvenile > 3 mm		S,M,2	ZnSO4	-	-	10	-	-	0.13	LC50-100 days	
	juvenile > 3 mm		S,M,2	ZnSO4	-	-	10	-	-	0.13	LC50-90 days	
	juvenile > 3 mm		S,M,2	ZnSO4	-	-	10	-	-	0.24	LC50-80 days	

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
(gastropoda)	juvenile > 3 mm	S,M,2	ZnSO4	-	-	10	-	-	0.33	LC50-70 days	
	juvenile > 3 mm	S,M,2	ZnSO4	-	-	10	-	-	0.6	LC50-60 days	
	juvenile > 3 mm	S,M,2	ZnSO4	-	-	10	-	-	0.86	LC50-50 days	
	juvenile > 3 mm	S,M,2	ZnSO4	-	-	10	-	-	1.34	LC50-40 days	
	juvenile > 3 mm	S,M,2	ZnSO4	-	-	10	-	-	1.22	LC50-30 days	
	adult	S,M,2	ZnSO4	-	-	10	-	-	0.1	no adverse effect on reproduction- 100 days	
	adult	S,M,2	ZnSO4	-	-	10	-	-	0.18	reproduction reduced- 100 d	
<i>Biomphalaria</i> glabrata (FW snail	embryo)	NA	-	-	-	-	-	-	0.5	survival reduced 50% by day 33	Munzinger & Guarducci 1988
<i>Chironomus</i> <i>riparius</i> (diptera, chironomidae)	larvae	S,M,2	-	7.3- 7.7	-	20	-	-	0.1	Significant delay in development for all instar	Timmermans et al. 1992
<i>Corbicula sp.</i> (Asiatic clam)	adult 13-16 mm	F,M,1	ZnSO4	8.31	-	25.11	49.5	70.7	0.034	30-d EC50 (growth) *sig. diff. enzyme activity-10 d	Farris <i>et al.</i> 1989

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
	adult 13-16 mm	F,M,1	ZnSO4	8.06	-	25.11	49.8	72.3	1.1	LC50-30 days *sig. growth inhibition - 20	
	15 10 1111									days	
(Asiatic clam)	juvenile & adult	F,M,1	-	~8.2	-	20.6- 25.5	38.6-59.2	66.0-88.8	>0.020	sig. reduced shell & weight growth- 30d	Farris <i>et al.</i> 1989
	juvenile & adult	F,M,1	-	~8.2	-	20.6- 25.5	38.6-59.2	66.0-88.8	1	~30% mortality -30 days	
Daphnia magna (water flea)	12 € 12 hr	S,N,2	ZnCl2	7.74	near sat.	-	-	45.3	0.07	3-wk EC16 (reproduction)	Biesinger & Christensen
	12 € 12 hr	S,N,2	ZnCl2	7.74	near sat.	-	-	45.3	0.102	3-wk EC50 (reproduction)	1972
	newborns	S,M,2	ZnSO4	8.2 -9.5	-	-	100-119	130-160	0.1	significant reduction in longevity	Winner 1981
<i>Epeorus latifolium</i> (mayfly)	Larvae	F,M,1	ZnSO4	7.9- 8.0	-	15.5	-	83 µg/L	0.1-0.3	growth inhibition- 2 weeks; all dead before emergence	Hatakeyama 1989
	Larvae	F,M,1	ZnSO4	7.9	-	15.5	-	83 µg/L	fed algae	no decrease in	
				-8.0					with 940	growth rate	
	Larvae	F,M,1	ZnSO4	7.9	-	15.5	-	83 μg/L	µg/g fed	Wk 1: growth rate	
				-8.0					algae with	55% of control;	

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
									1380 μg/g	Wk 2: restoration of	
									μg/g	normal growth rate	
	Larvae	F,M,1	ZnSO4	7.9	-	15.5	-	83 μg/L	fed algae	growth and	
				-8.0					with >	emergence	
									2000 μg/g	significantly affected	
<i>Ephydatia</i> <i>fluviatilis</i> (freshwater sponge)	-	F,N,2	ZnCl2	7.0	-	25	-	30 mg/L Ca, 30 mg/L Mg	0.0065	reduced growth rate	Francis & Harrison 1988
(freshwater sponge)	-	F,N,2	ZnCl2	7.0	-	25	-	30 mg/L Ca, 30 mg/L Mg	>0.032 (4*)	tissue deterioration & death (3-wk post- exposure)	Francis & Harrison 1988
Erpobdella octulata (leech)	juveniles <4 mg wet hatched	S,M,2	ZnSO4	-	-	10	-	15	0.06	LC50-70 days	Willis 1989
	adults >15 mg wet	S,M,2	ZnSO4	-	-	10	-	15	0.1	LC50-70 days	
	juveniles	S,M,2	ZnSO4	-	-	10	-	15	0.222	LC50-60 days	Willis 1989
	adults	S,M,2	ZnSO4	-	-	10	-	15	0.32	inhibited reproduction- 60 d	
	juveniles	S,M,2	ZnSO4	-	-	10	-	15	0.34	LC50-50 days	
	juveniles adults	S,M,2 S,M,2	ZnSO4 ZnSO4	-	-	10 10	-	15 15	0.39 0.6	LC50-40 days LC50-60 days	

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
	adults	S,M,2	ZnSO4	-	-	10	-	15	1.9	LC50-50 days	
	adults	S,M,2	ZnSO4	-	-	10	-	15	4.8	LC50-40 days	
Hyalella azteca	0-1 week	S,N,2	-	7.9	-	25	90	130	0.0056	75% survival- 6 wks	Borgmann <i>et al</i> .
(amphipod)				-8.6					(control)	63% survival- 10 wks	1993
	0-1 week	S,N,2	-	7.9	-	25	90	130	0.042	72% survival- 6 wks	
				-8.6						51% survival- 10 wks	
	0-1 week	S,N,2	-	7.9	-	25	90	130	0.108	68% survival- 6 wks	
				-8.6						35% survival- 10 wks (sig. diff. from control)	
Insect community	30 d of coloni- zation on trays in Clinch River	F,M,1	-	8.93	8.9	22.4	59	85	0.015 (2*)	macroinvertebrate abundance reduced by 57% within 4 days	Clements <i>et al.</i> 1988
<i>Moina macrocopa</i> (crustacean)	newborn <24 hr	S,N,2	ZnSO4	6.5	-	24-27	-	-	0.01(1*)	LT50 (time at which 50% of animals died)- 9.8 days	Wong 1993
1	newborn <24 hr	S,N,2	ZnSO4	6.5	-	24-27	-	-	0.02 (3*)	LT50- 10.00 days	
	newborn <24 hr	S,N,2	ZnSO4	6.5	-	24-27	-	-	0.1	LT50- 7.33 days	

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
	newborn <24 hr	S,N,2	ZnSO4	6.5	-	24-27	-	-	0.25	LT50- 7.67 days	
	newborn <24 hr	S,N,2	ZnSO4	6.5	-	24-27	-	-	0.5	LT50- 4.25 days	Wong 1993
	newborn <24 hr	S,N,2	ZnSO4	6.5	-	24-27	-	-	0.7	LT50- 4.50 days	
	newborn <24 hr	S,N,2	ZnSO4	6.5	-	24-27	-	-	0.5	significant reduction in survivorship	
	newborn <24 hr	S,N,2	ZnSO4	6.5	-	24-27	-	-	>0.700	average lifespan reduced by more than 50%	
<i>Orconectes virilis</i> (Crayfish)	adult	S,M,2	ZnSO4	7.1	8	18	15	26	84	LC50-2 weeks	Mirenda 1986
Physa heterotropha (Pond snail)	adults 12-15 mm	S,N,2	ZnSO4	7.3	-	70°F	-	20	4.9	TLm-120 hr	Wurtz 1962
Tanytarsus	embryogenesis;	S,M,2	ZnCl2	7.5	8.7	22	43.9	46.8	0.0368	LC50-10 days	Anderson <i>et al</i> .
<i>dissimilis</i> (chironomidae): insect	hatching & larval development	S,M,2	ZnCl2	7.5	8.7	22	43.9	46.8	0.08 -0.100	10% larval survival	1980
Cladocera: Holopedium gibberum		S,M,2	65Zn		7.1				0.015	sig. reduced population	Marshall <i>et al.</i> 1983

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
Total clacedora		S,M,2	65Zn		7.1				0.015	total population unaffected	
Copepoda: Calanoid nauplii		S,M,2	65Zn		7.1				0.015	sig. reduced population	
Cyclopoid naupli		S,M,2	65Zn		7.1				0.015	sig. reduced population insig. reduced population	
Total copepoda									0.015	population	
Rotifers:											
Keratella cochlea	aris	S,M,2	65Zn		7.1				0.015	sig. increae in population	
Gastropus stylife	r	S,M,2	65Zn		7.1				0.015	sig. reduced population	
Polyarthra vulga		S,M,2	65Zn		7.1				0.015	sig. reduced population	
Conochilis unicon	rnis	S,M,2	65Zn		7.1				0.015	sig. reduced population	
Collotheca mutab	bilis	S,M,2	65Zn		7.1				0.015	sig. reduced population insig. reduct. in	
Total rotifers									0.015	population	
Euglena gracilis		S,N,2	Zn2+	-	-	21-28	-	-	0.0075	significant decrease in mean population size	Mills 1976
						27-day,			10.0		
Azolla filiculoide. (water fern)	³⁵ 25 g wet	S,N,2	ZnSO4	-	-	22- night	-	-	10.0- 13.0	Growth rate= 44% of control in 7 d	Sela <i>et al.</i> 1989

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
	25 g wet	S,N,2	ZnSO4	-	-	27-day, 22- night	-	-	12.6	Acetylene reduction (1.9% of control in 5 d)	
Azolla pinnata (macrophyte)	-	S,N,2	ZnSO4	7	-	25	-	-	0.948	EC50-96 hr (growth)	Guar <i>et al.</i> 1994
<i>Cladophora</i> glomerata (green alga)	growths of similar size, age and condition were selected.	F,M,1, river simulation velocity - after 3 hr exposure to {Zn}, Cladophon recovered in Chu 10 medium fo 1 week, ar was then	ZnSO4 ra or	_	-	-	-	-	0.4	First toxic signs, 2 of 4 samples showed cytoplasmic abnormalities	Mchardy & George 1990
	same as above	observed. same as above	ZnSO4	-	-	-	-	-	1	3 samples had damaged filaments	
	same as above	same as above	ZnSO4	-	-	-	-	-	1.75	all 4 samples displayed evidence of toxicity	

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
(green alga)	same as above	same as above	ZnSO4	-	-	-	-	-	4	99% of their filaments completely colourless and dead	
<i>Eichhornia</i> <i>crassipes</i> (water hyacinth)	mature plants	S,N,2	ZnSO4	-	-	28-30	-	-	9	30% weight reduction	Delgado <i>et al.</i> 1993
<i>Euglena gracilis</i> (algae)	-	S,N,2	ZnCl2	-	-	25	-	-	50 µM	strong inhibition of O ₂ evolution- 10 days	DeFilippis & Ziegler 1993
Lemna trisulca	-	S,M,2	-	7.8- 8.3	-	28	-	-	>0.195 - 0.293	decrease in multiplication rate	Huebert & Shay 1992
(submerged aquatic macrophyte)	-	S,M,2	-	7.8- 8.3	-	28	-	-	0.325	EC50 (final yield)	
inder oprig to j	-	S,M,2	-	7.8- 8.3	-	28	-	-	0.915	EC50 (multiplication rate)	
<i>Lemna minor</i> (aqua. macrophyte)	-	S,N,2,	-	-	-	25-28	-	-	10; 0.23	IC50 (10 mg/L); growth at 93% of control	Dirilgen and Inel 1994a, b
Scenedesmus quadricauda	-	S,M,2	ZnSO4	8	-	constant	-	-	0.25	EC50-4 hr (photosynthesis)	Starodub <i>et al.</i> 1987

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
	-	S,M,2	ZnSO4	4.5	-	20	-	-	0.1	Growth rate- 15 days= 0.100 (sig. different from control)	
(green algae)	-	S,M,2	ZnSO4	6.5	-	20	-	_	0.1	Growth rate- 15 days= 0.101	
	-	S,M,2	ZnSO4	8.5	-	20	-	-	0.1	Growth rate- 15 days= 0.122	
	-	S,M,2	ZnSO4	4.5	-	20	-	-	0.225	Growth rate- 15 days 0.040 (sig. different from control)	
	-	S,M,2	ZnSO4	6.5	-	20	-	-	0.225	Growth rate- 15days= 0.042 (sig. different from control)	
	-	S,M,2	ZnSO4	8.5	-	20	-	-	0.225	Growth rate- 15 days= 0.131	
		S,N,2	ZnSO4	4.5		20			0.5	Growth rate- 15 days= 0.000 (sig. different from control)	
	-	S,N,2	ZnSO4	6.5	-	20	-	-	0.5	Growth rate- 15 days= 0.026 (sig. different from control)	

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
Scenedesmus quadricauda		S,N,2	ZnSO4	8.5		20			0.5	Growth rate- 15 days= 0.109 (sig. different from control)	Starodub <i>et al.</i> 1987
	-	-	-	-	-	-	-	-	0.002	first deleterious effect	Matulova 1978
Selanastrum capricornutum	-	NA	-	_	-	-	-	-	0.03 (2*)	Some growth inhibition- 7 d	EPA 1980
(green alga)	-	NA	-	-	-	-	-	-	0.040- 0.068 (3*)	95% growth inhibition- 14 d	
	-	NA	-	-	-	-	-	-	0.1	100% growth inhibition- 7 d	
	-	S,M,2, AAPBT medium	ZnCl2	6.8- 7.2	-	24	8.2	14.9	0.03 (2*)	Initiation of growth rate inhibition	Bartlett <i>et al.</i> 1974
	-	as above	ZnCl2	6.8- 7.2	-	24	8.2	14.9	0.12	Complete inhibition of growth rate	
S. capricornutum	-	as above	ZnCl2	6.8- 7.2	-	24	8.2	14.9	0.12	Complete inhibition of growth rate	Bartlett <i>et al.</i> 1974
	-	as above	ZnCl2	6.8- 7.2	-	24	8.2	14.9	0.12	algicidal	
	-	S,N,2	ZnSO4	6.0- 6.3	-	24	-	-	0.0041	7-d EC50	Chiaudani & Vighi, 1978

Table A2. 3 A summary of the available data on the toxicity of zinc to aquatic organisms (from Nagpal 1997).

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
<i>Spirodela polyrhiza</i> (macrophyte)	-	S,N,2	ZnSO4	7	-	25	-	-	0.935	EC50-96 hr (growth)	Guar <i>et al.</i> 1994
Plankton community (Lake Michigan)	submerged carboys	S,N,2	-	-	-	-	-	-	0.015	Signific. reduction in chlorophyll <u>a</u> , primary productivity, DO, zooplankton diversity & populations, and community similarity	Marshall <i>et al.</i> 1983
KEY EC = Effective Coo IC = Inhibition Coo LC = Lethal Concr MATC = Maximum LT = Median Age TLm = Lethal Three	ncentration netration n Acceptable Tole of Death		entration								

S = Static Test Method

F = Flowthrough Test Method

M = Measured

Table A2. 3 A summary of the available data on the toxicity of zinc to aquatic organisms (from Nagpal 1997).

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
N = Nominal											
NA = Not											
Available											
1 = Primary											
2 = Secondary											

Note: This table was prepared from information obtained from the AQUIRE database. References for these tables were unable to be retrieved.

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
Catostomus	~17.7 g	F,M,1	ZnCl2	_	-	12.1	_	-	2.2	LC50-96 hr	Duncan &
commersoni	~17.7 g	F,M,1	ZnCl2	-	-	12.1	-	-	2.48	LC50-72 hr	Klaverkamp
(white sucker	~17.7 g	F,M,1	ZnCl2	-	-	12.1	-	-	2.96	LC50-48 hr	1983
- unfed)	~17.7 g	F,M,1	ZnCl2	-	-	12.1	-	-	5.58	LC50-24 hr	
	~17.7 g	F,M,1	ZnCl2	-	-	12.1	-	-	13.3	LC50-12 hr	
Cyprinus carpio	<20 cm.	S, M, 2	ZnNO3	7.8	6.5	17.0	-	53	7.8	TLm-96 hr	Rehwoldt <i>et</i> al.
(carp)	<20 cm.	S, M, 2	ZnNO3	7.8	6.5	17.0	-	53	9.3	TLm-48 hr	1971
	<20 cm.	S, M, 2	ZnNO3	7.8	6.5	17.0	-	53	14.3	TLm-24 hr	
<i>Oncorhyncus</i> <i>clarki</i> (cutthroat trout)	-	NA	-	-	-	-	-	-	0.061- 0.600	LC50-96 hr	EPA 1980; Mayer & Ellersieck1986
Oncorhyncus mykiss	fry	NA	-	-	-	-	-	-	0.090- 0.093	LC50-96 hr	EPA 1980 & 1987
(rainbow trout)	parr	NA	-	-	-	-	-	30	0.24- 0.83	LC50-96 hr	EPA 1980
	parr	NA	-	-	-	-	-	500	4.7	LC50-96 hr	
	parr	NA	-	-	-	-	-	350	1.19- 4.52	LC50-96 hr	
	fry	NA	-	-	-	-	-	-	0.689	LC50-96 hr	
	0.6 g	F,M,1	-	-	-	-	-	-	0.169	LC50-96 hr	Buhl & Hamilton

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
											1990
	juvenile	F,M,1	-	6.8	-	12.0	25	26	0.43	LC50-96 hr	Sinely <i>et al.</i> 1974
	juvenile	F,M,1	-	7.6	-	15.0	43	47	0.52	LC50-96 hr	Holocombe and
	juvenile juvenile	F,M,1 F,M,1	-	7.2 7.8	-	16.0 15.5	170	179 504	2.96 4.8	LC50-96 hr LC50-96 hr	Andrew 1978 Solbe 1974
Oncorhynchus mykiss	small (1-6 g)	F,M,1	ZnCl2	7	>90%	15.0- 16.0	-0.2	9.2	0.066	LC50-96 hr	Cusimano & Brakke 1986
(steelhead trout)	small (1-6 g)	F,M,1	ZnCl2	5.7	>90%	15.0- 16.0	1.7	9.2	0.097	LC50-96 hr	
	small (1-6 g)	F,M,1	ZnCl2	4.7	>90%	15.0- 16.0	11	9.2	0.671	LC50-96 hr	
	juvenile	F,N,2	ZnSO4	-	-	15.0	-	soft water	0.43	LC50-96 hr	Sinley et al.
	juvenile	F,N,2	ZnSO4	-	-	15.0	-	hard water	7.21	LC50-96 hr	1974
	eyed eggs	F,N,2	ZnSO4	-	-	11.0	-	soft water	2.72	LC50-96 hr	
	Eggs: 5 d post-fertiliza	S,M,2 ation	ZnSO4	7.8	99.80% sat.	8.6	-	87.8	24	LC50-48 hr	Shazili and Pascoe 1986
	Eggs: 10 d post- fertiliz.	S,M,2	ZnSO4	7.8	99.80% sat.	8.6	-	87.8	<1.0 (extrapolated)	LC50-48 hr	
	Eggs: 15 d post- fertiliz.	S,M,2	ZnSO4	7.8	99.8% sat.	8.6	-	87.8	9.1	LC50-48 hr	

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
	Eggs: 22 d post- fertiliz.	S,M,2	ZnSO4	7.8	99.8% sat.	8.6	-	87.8	7	LC50-48 hr	
	Eggs: 29 d post- fertiliz.	S,M,2	ZnSO4	7.8	99.8% sat.	8.6	-	87.8	4.3	LC50-48 hr	
	Eggs: 36 d post- fertiliz.	S,M,2	ZnSO4	7.8	99.8% sat.	8.6	-	87.8	9.2	LC50-48 hr	
	Alevins: 2 d post- hatch	S,M,2	ZnSO4	7.8	99.8% sat.	8.6	-	87.8	3.2	LC50-48 hr	Shazili and Pascoe 1986
	Alevins: 7 d post- hatch	S,M,2	ZnSO4	7.8	99.8% sat.	8.6	-	87.8	3.4	LC50-48 hr	
Salmo trutta (brown trout)	yearlings (8-10 g)	F,M,1	ZnSO4	9.11	10.1- 10.3	15.0	103	204	0.46	LC50-96 hr	Everall <i>et al.</i> 1989
(brown trout)	yearlings (8-10 g)	F,M,1	ZnSO4	7.03	10.1- 10.3	15.0	103	204	0.64	LC50-96 hr	Everall <i>et al</i> . 1989
	yearlings (8-10 g)	F,M,1	ZnSO4	7.89	10.1- 10.3	15.0	103	204	1	LC50-96 hr	
	yearlings (8-10 g)	F,M,1	ZnSO4	4.1	10.1- 10.3	15.0	103	204	2.02	LC50-96 hr	
	yearlings (8-10 g)	F,M,1	ZnSO4	5.89	10.1- 10.3	15.0	103	204	2.69	LC50-96 hr	
	yearlings (8-10 g)	F,M,1	ZnSO4	5.02	10.1- 10.3	15.0	103	204	3.2	LC50-96 hr	

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
	yearlings (8-10 g)	F,M,1	ZnSO4	8.03	10.1- 10.3	15.0	62	10	<0.14	LC50-96 hr	
	yearlings (8-10 g)	F,M,1	ZnSO4	9.06	10.1- 10.3	15.0	62	10	0.22	LC50-96 hr	
	yearlings (8-10 g)	F,M,1	ZnSO4	7.07	10.1- 10.3	15.0	62	10	0.6	LC50-96 hr	
	yearlings (8-10 g)	F,M,1	ZnSO4	3.98	10.1- 10.3	15.0	62	10	1.07	LC50-96 hr	
	yearlings (8-10 g)	F,M,1	ZnSO4	6.01	10.1- 10.3	15.0	62	10	1.41	LC50-96 hr	
	yearlings (8-10 g)	F,M,1	ZnSO4	5.06	10.1- 10.3	15.0	62	10	2.31	LC50-96 hr	
Salvelinus fontinalis (brook trout)	juvenile	F,M,1	ZnSO4	-	-	15.0	-	soft water	2	LC50-96 hr	Holcombe <i>et</i> <i>al.</i> 1979
<i>Oncorhyncus mykiss</i> (steelhead)	adult male	F,M,1	ZnCl2	7.45	10.4	10.3	55	83	1.755	LC50-96 hr	Chapman & Stevens 1978
(steelhead)	swim-up alevins	F,M,1	ZnCl2	7.1	10.2	11.6- 12.8	22	23	0.093	LC50-96 hr	Chapman 1978b
	5-8 month parr	F,M,1	ZnCl2	7.3	10.2	11.6- 12.8	22	23	0.136	LC50-96 hr	
	smolts	F,M,1	ZnCl2	7.1	10.2	11.6- 12.8	22	23	>0.651	LC50-96 hr	

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
	newly hatched alevins	F,M,1	ZnCl2	7.1	10.2	11.6- 12.8	22	23	0.815	LC50-96 hr	
<i>Oncorhynchus nerka</i> (sockeye salmon)	immature	F,M,1	_	_	_	_	_	_	0.75	LC50-96 hr	Chapman 1978a
Oncorhyncus tshawytscha	juvenile	F,M,1	ZnSO4	7.1- 7.2	85% sat	12-Nov	18-19	20-21	0.04	LC10-96 hr	Finlayson & Verrue 1982
(chinook salmon)	juvenile	F,M,1	ZnSO4	7.1- 7.2	85% sat	12-Nov	18-19	20-21	0.084	LC50-96 hr	
	smolts	F,M,1	_	_	_	_	_	_	0.446	LC50-96 hr	EPA 1987
	swim-up alecins	F,M,1	_	7.3- 7.5	10.2	11.6- 12.8	22	23	0.097	LC50-96 hr	Chapman 1978b
	5-8 month parr	F,M,1	_	7.1	10.2	11.6- 12.8	22	23	0.463	LC50-96 hr	
	newly hatched alevins	F,M,1	_	7.3- 7.5	10.2	11.6- 12.8	22	23	>0.661	LC50-96 hr	Chapman 1978b
	smolts	F,M,1	_	7.1	10.2	11.6- 12.8	22	23	0.701	LC50-96 hr	
Salmo salar (Atlantic salmon)	immature immature	D	_	_	_	_	_	14 20	0.42 0.6	LC50-96 hr LC50-96 hr	EPA 1980

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
Oncorhynchus kisutch	adult male	F,M,1	ZnCl2	7.4	9.8	13.7	20	25	0.905	LC50-96 hr	Chapman & Stevens 1978
(coho salmon)	_	F,M,1	-	-	_	_	3.8	5	0.28	LC50-96 hr	McLeay 1976
	0.5-0.9 g	F,M,1	_	_	_	_	3.8	5	0.82- 1.81	LC50-96 hr	
Gasterosteus	-	NA	65ZnCl2	-	-	-	-	282	0.5-1.0	gill damage	Perwak <i>et al.</i> 1980
aculeatus (stickleback)	-	NA	65ZnCl2	-	-	-	-	282	1	increased oxygen uptake	1980
Oncorhyncus clarki	-	F,M,1	-	-	-	-	-	-	0.36	none dead in 14 days	Nehring & Goettl 1974
(cutthroat trout)	-	F,M,1	-	-	-	-	-	-	0.67	LC50-14 days	1974
Oncorhyncus mykiss	5 months 3.0 g wet	F,M,1	ZnCl2	6.6	10	12.6	25	33	0.17	LC50-120 hr	Anadu <i>et al.</i> 1989
(rainbow trout)	immatures	NA	-	-	-	-	-	-	0.0056	avoidance, 10-20 min. test	EPA 1980 & 1987
	life cycle	NA	-	-	-	-	-	-	0.140- 0.547	MATC	EPA 1980 & 1987
	immatures	NA	-	-	-	-	-	-	0.047 (4*)	94% avoidance, 40-min. test	EPA 1987
	immatures	NA	-	-	-	-	-	-	0.352	hyperglycemia-9 days	
	larvae+ alevins	F,M,1	-	-	-	-	-	-	0.01 (2*)	LC54-28 days	Affleck 1952

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
(rainbow trout)	early life- stage	F,M,1	-	-	-	-	-	-	0.070- 0.140	LC50-25 days	Sinely <i>et al.</i> 1974
	juveniles	F,M,1	-	-	-	-	-	-	0.081	hyperglycemia-24 hr	Wagner 1980
	juveniles	F,M,1	-	-	-	-	-	-	0.210- 1.120	Increased blood glucose in 7-63 days	Watson & McKeown 1976
	adults	F,M,1	-	-	-	-	-	360	1.12	reduced growth -85 days	
	juveniles	F,M,1	-	-	-	-	-	-	0.69	increased respiration- 24 hr	Sellers <i>et al.</i> 1975
	larvae and alevins	F,M,1	-	-	-	-	-	-	0.40- 2.80	LC50-120 hr	Edwards & Brown 1967
	juveniles	F,M,1	-	-	-	-	-	-	0.41	LC50-14 days	Nehring & Goettl 1974
	juveniles	F,M,1	-	-	-	-	-	-	0.31	LC20-14 days	
Oncorhychus mykiss	-	NA	ZnSO4	-	-	-	-	13-15	0.0056	threshold avoidance level -20 min.	Perwak <i>et al.</i> 1980
(rainbow trout)	1-6 g	F,M,1	ZnCl2	7	>90% sat.	15-16	11	-	0.066	LC50-168 hr	Cusimano & Brakke 1986
	1-6 g	F,M,1	ZnCl2	5.7	>90% sat.	15-16	1.7	-	0.097	LC50-168 hr	
	1-6 g	F,M,1	ZnCl2	4.7	>90% sat.	15-16	-0.2	-	0.501	LC50-168 hr	
	juv. 4.5- 7.5 g	F,M,1	ZnCl2	6.97- 7.05	9.3	15	10.8	31.3	0.11	LC50- 96 h to120 h	Bradley & Sprauge 1985

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
	juv. 4.5- 7.5 g	F,M,1	ZnCl2	6.97- 7.05	9.3	15	8.1	30.2	0.17	LC50- 96-120 hr	
Oncorhychus mykiss	juv. 4.5- 7.5 g	F,M,1	ZnCl2	6.97- 7.05	9.3	15	23.8	31.2	0.19	LC50- 96-120 hr	Bradley & Sprauge 1985
(rainbow trout)	juv. 4.5- 7.5 g	F,M,1	ZnCl2	6.97- 7.05	9.3	15	8.6	387	4.46	LC50- 96-120 hr	
	juv. 4.5- 7.5 g	F,M,1	ZnCl2	6.97- 7.05	9.3	15	24.3	389	5.16	LC50- 96-120 hr	
	juv. 4.5- 7.5 g	F,M,1	ZnCl2	5.46- 5.59	9.3	15	<1.0	31.4	0.088	LC50- 96-120 hr	
	juv. 4.5- 7.5 g	F,M,1	ZnCl2	5.46- 5.59	9.3	15	<1.0	394	9.95	LC50- 96-120 hr	
	juv. 4.5- 7.5 g	F,M,1	ZnCl2	5.46- 5.59	9.3	15	<1.0	389	11.1	LC50- 96-120 hr	
	juv. 4.5- 7.5 g	F,M,1	ZnCl2	8.97- 9.01	9.3	15	23.7	30.9	4.53	LC50- 96-120 hr	
	juv. 4.5- 7.5 g	F,M,1	ZnCl2	8.97- 9.01	9.3	15	32.9	373	>87.90	LC50- 96-120 hr	
	2 g fingerlings through sexual maturity-2 yrs old	F,N,2	ZnSO4	7.81	6.8	16.2	238	333	0.32	0.0% mortality -21 months	Sinley <i>et al.</i> 1974
	same as above	F,N,2	ZnSO4	7.81	6.8	16.2	238	333	0.64	6.4% mortality -21 months	

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
	same as above	F,N,2	ZnSO4	7.81	6.8	16.2	238	333	1.055	10.0% mortality -21 months	
	same as above	F,N,2	ZnSO4	7.81	6.8	16.2	238	333	2.2	23.0% mortality - 21 months	
Oncorhychus mykiss (rainbow trout)	eyed eggs continuing until sexual maturity	F,N,2	ZnSO4	6.8	6.8	12.7	25	26	0.011- 0.547	no sig. change in egg mortality	Sinley <i>et al.</i> 1974
Salmo trutta (brown trout)	yolk-sac fry	F,M,1	-	4.5	-	-	-	soft water	0.0049 - 0.0196	60-95% died in18 d; ~40% with noncalcified vertebrae center	Sayer <i>et al.</i> 1989
<i>Salvelinus fontinalis</i> (brook trout)	3rd generation eggs	F,M,1	ZnSO4	7.0- 7.7	9.8	5.0-15.0	41.8	45.4	0.266	fragility sig. increased (p=0.05)	Holcombe et al. 1979
	2nd generation embryos	F,M,1	ZnSO4	7.0- 7.7	9.8	5.0-15.0	41.8	45.4	1.36	Hatchability sig. reduced (p=0.05)	
	"fresh" embryos	F,M,1	-	7.2- 7.9	11.6	9	41.3	45.9	1.368	Survival sig. reduced (p=0.05)	
	adults	F,M,1	-	-	-	-	-	-	0.63	LC17-14 days	Nehring & Goettl 1974
	adults	F,M,1	-	-	-	-	-	-	0.96	LC50-14 days	

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
<i>Oncorhynchus kisutch</i> (coho salmon)	juvenile	F,M,1	_	_	_	_	_	_	0.5-10.7	decreased white blood cells in 24 h	McLeay 1975
Oncorhynchus nerka	adult- smolt	F,M,1	ZnCl2	7.2	9	_	_	35	0.03- 0.112	no adverse effects-18 months	Chapman 1978a
Oncorhynchus nerka	embryo- smolt	F,M,1	ZnCl2	7.2	9	_	_	35	0.242	no adverse effects-18 months	Chapman 1978a
(sockeye salmon)	immatures	NA	_	_	_	_	_	_	0.447	115-h LC50	U.S. EPA 1980
Oncorhynchus tshawytscha	newly hatched alevins	F,M,1	ZnCl2	7.3- 7.5	10.2	~12	_	23	>0.661 0.364- 0.661	200-h LC50 200-h LC10	Chapman 1978b
(chinook salmon)	swim-up alevins	F,M,1	ZnCl2	7.1	10.2	~12	_	23	0.097 0.068	200-h LC50 200-h LC10	
	5-8 mon. parr	F,M,1	ZnCl2	7.3- 7.5	10.2	~12	_	23	0.395 0.268	200-h LC50 200-h LC10	
	smolts	F,M,1	ZnCl2	7.1	10.2	~12	_	23	0.364 0.170	200-h LC50 200-h LC10	Chapman 1978b
Oncorhynchus mykiss	newly hatched alevins	F,M,1	ZnCl2	7.1	10.2	~12	_	23	0.555 0.256	186-h LC50 186-h LC10	
(steelhead)	swim-up alevins	F,M,1	ZnCl2	7.1	10.2	~12	_	23	0.093 0.054	200-h LC50 200-h LC10	

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
	5-8 mon. parr	F,M,1	ZnCl2	7.3- 7.5	10.2	~12	_	23	0.120 0.061	200-h LC50 200-h LC10	
	smolts	F,M,1	ZnCl2	7.1	10.2	~12	_	23	0.278 0.084	200-h LC50 200-h LC10	Chapman 1978b
	embryo	F,M,1	ZnCl2	6.9- 7.1	>8.7	12	25	25	0.819	86% mortality in 72 d (9.6% in control)	Cairns et al.
	embryo	F,M,1	ZnCl2	6.9- 7.1	>8.7	12	25	25	0.444	18% mortality in 72 d	1982
	embryo	F,M,1	ZnCl2	6.9- 7.1	>8.7	12	25	25	0.262	8% mortality in 72 d	
Salmo salar	parr	_	_	_	_	_	_	_	0.05	50% avoidance - 4h	U.S. EPA 1987
(Atlantic salmon)	parr	_	_	_	_	_	_	_	0.1	avoidance within 20 min.	Spear 1981
	immature	_	-	_	_	_	-	_	0.1-0.5	21-d LC50	U.S. EPA 1980
Ancylus fluviatilis	juvenile <2 mm	S,M,2	ZnSO4	-	-	10	-	-	0.08	LC50-100 days	Willis 1988
(gastropoda)	juvenile <2 mm	S,M,2	ZnSO4	-	-	10	-	-	0.09	LC50-90 days	
j	juvenile <2 mm	S,M,2	ZnSO4	-	-	10	-	-	0.18	LC50-80 days	
	juvenile <2 mm	S,M,2	ZnSO4	-	-	10	-	-	0.19	LC50-70 days	

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
	juvenile <2 mm	S,M,2	ZnSO4	-	-	10	-	_	0.2	LC50-60 days	
	juvenile <2 mm	S,M,2	ZnSO4	-	-	10	-	-	0.26	LC50-50 days	
	juvenile <2 mm	S,M,2	ZnSO4	-	-	10	-	-	0.36	LC50-40 days	
	juvenile <2 mm	S,M,2	ZnSO4	-	-	10	-	-	0.54	LC50-30 days	
	juvenile > 3 mm	S,M,2	ZnSO4	-	-	10	-	-	0.13	LC50-100 days	
	juvenile > 3 mm	S,M,2	ZnSO4	-	-	10	-	-	0.13	LC50-90 days	
	juvenile > 3 mm	S,M,2	ZnSO4	-	-	10	-	-	0.24	LC50-80 days	
(gastropoda)	juvenile > 3 mm	S,M,2	ZnSO4	-	-	10	-	-	0.33	LC50-70 days	Willis 1988
	juvenile > 3 mm	S,M,2	ZnSO4	-	-	10	-	-	0.6	LC50-60 days	
	juvenile > 3 mm	S,M,2	ZnSO4	-	-	10	-	-	0.86	LC50-50 days	
	juvenile > 3 mm	S,M,2	ZnSO4	-	-	10	-	-	1.34	LC50-40 days	
	juvenile > 3 mm	S,M,2	ZnSO4	-	-	10	-	-	1.22	LC50-30 days	

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
	adult	S,M,2	ZnSO4	-	-	10	-	-	0.1	no adverse effect on reproduction- 100 days	
	adult	S,M,2	ZnSO4	-	-	10	-	-	0.18	reproduction reduced- 100 d	
Biomphalaria glabrata (FW snail)	embryo)	NA	-	-	-	-	-	-	0.5	survival reduced 50% by day 33	Munzinger & Guarducci 1988
<i>Chironomus</i> <i>riparius</i> (diptera, chironomidae)	larvae	S,M,2	-	7.3- 7.7	-	20	-	-	0.1	Significant delay in development for all instar	Timmermans et al. 1992
<i>Corbicula sp.</i> (Asiatic clam)	adult 13-16 mm	F,M,1	ZnSO4	8.31	-	25.11	49.5	70.7	0.034	30-d EC50 (growth) *sig. diff. enzyme activity-10 d	Farris <i>et al.</i> 1989
	adult 13-16 mm	F,M,1	ZnSO4	8.06	-	25.11	49.8	72.3	1.1	LC50-30 days *sig.	
	15 10 1111									growth inhibition - 20 days	
(Asiatic clam)	juvenile & adult	F,M,1	-	~8.2	-	20.6- 25.5	38.6-59.2	66.0-88.8	>0.020	sig. reduced shell & weight growth- 30d	Farris <i>et al.</i> 1989
	juvenile & adult	F,M,1	-	~8.2	-	20.6- 25.5	38.6-59.2	66.0-88.8	1	~30% mortality -30 days	

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (⁰C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
Daphnia magna (water flea)	12 € 12 hr	S,N,2	ZnCl2	7.74	near sat.	-	-	45.3	0.07	3-wk EC16 (reproduction)	Biesinger & Christensen
	12 € 12 hr	S,N,2	ZnCl2	7.74	near sat.	-	-	45.3	0.102	3-wk EC50 (reproduction)	1972
	newborns	S,M,2	ZnSO4	8.2 -9.5	-	-	100-119	130-160	0.1	significant reduction in longevity	Winner 1981
<i>Epeorus latifolium</i> (mayfly)	Larvae	F,M,1	ZnSO4	7.9- 8.0	-	15.5	-	83 μg/L	0.1-0.3	growth inhibition- 2 weeks; all dead before emergence	Hatakeyama 1989
	Larvae	F,M,1	ZnSO4	7.9	-	15.5	-	83 µg/L	fed algae	no decrease in	
				-8.0					with 940	growth rate	
	Larvae	F,M,1	ZnSO4	7.9 -8.0	-	15.5	-	83 µg/L	μg/g fed algae with	Wk 1: growth rate 55% of control;	
									1380 μg/g	Wk 2: restoration of normal growth rate	
	Larvae	F,M,1	ZnSO4	7.9	-	15.5	-	83 µg/L	fed algae	growth and	
				-8.0					with >	emergence	
									2000 μg/g	significantly affected	

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
Insect community	30 d of coloni- zation on trays in Clinch River	F,M,1	-	8.93	8.9	22.4	59	85	0.015 (2*)	macroinvertebrate abundance reduced by 57% within 4 days	Clements <i>et</i> <i>al.</i> 1988
<i>Moina macrocladoceran</i> (crustacean)	newborn <24 hr	S,N,2	ZnSO4	6.5	-	24-27	-	-	0.01(1*)	LT50 (time at which 50% of animals died)- 9.8 days	Wong 1993
	newborn <24 hr	S,N,2	ZnSO4	6.5	-	24-27	-	-	0.02 (3*)	LT50- 10.00 days	
	newborn <24 hr	S,N,2	ZnSO4	6.5	-	24-27	-	-	0.1	LT50- 7.33 days	
	newborn <24 hr	S,N,2	ZnSO4	6.5	-	24-27	-	-	0.25	LT50- 7.67 days	
	newborn <24 hr	S,N,2	ZnSO4	6.5	-	24-27	-	-	0.5	LT50- 4.25 days	Wong 1993
	newborn <24 hr	S,N,2	ZnSO4	6.5	-	24-27	-	-	0.7	LT50- 4.50 days	Wong 1993
	newborn <24 hr	S,N,2	ZnSO4	6.5	-	24-27	-	-	0.5	significant reduction in survivorship	
	newborn <24 hr	S,N,2	ZnSO4	6.5	-	24-27	-	-	>0.700	average lifespan reduced by more than 50%	
Physa heterotropha	adults	S,N,2	ZnSO4	7.3	-	70°F	-	20	4.9	TLm-120 hr	Wurtz 1962

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
(Pond snail)	12-15 mm										
Cladocera: Holopedium gibberum		S,M,2	65Zn		7.1				0.015	sig. reduced population	Marshall <i>et al.</i> 1983
Total clacedora		S,M,2	65Zn		7.1				0.015	total population unaffected	
Copepoda: Calanoid nauplii		S,M,2	65Zn		7.1				0.015	sig. reduced population	
Cyclopoid nauplii Total copepoda		S,M,2	65Zn		7.1				0.015 0.015	sig. reduced population insig. reduct. in population	
Azolla filiculoides	25 g wet	S,N,2	ZnSO4	-	-	27-day,	-	-	10	Growth rate= 44%	Sela <i>et al.</i> 1989
(water fern)						22- night			-13.0	of control in 7 d	
	25 g wet	S,N,2	ZnSO4	-	-	27-day, 22- night	-	-	12.6	Acetylene reduction (1.9% of control in 5 d)	
Azolla pinnata (macrophyte)	-	S,N,2	ZnSO4	7	-	25	-	-	0.948	EC50-96 hr (growth)	Guar <i>et al.</i> 1994
Cladophora glomerata	growths of similar size,	F,M,1, river sim	ZnSO4 nulation	-	-	-	-	-	0.4	First toxic signs, 2 of 4 samples	Mchardy & George 1990

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
	age and condition were selected.	velocity - 3 hr expo to {Zn}, 0 recovered 10 mediu 1 week, a then obse	sure Cladophora 1 in Chu m for nd was							showed cytoplasmic abnormalities	
(green alga)	same as above	same as above	ZnSO4	-	-	-	-	-	1	3 samples had damaged filaments	Mchardy & George 1990
	same as above	same as above	ZnSO4	-	-	-	-	-	1.75	all 4 samples displayed evidence of toxicity	
	same as above	same as above	ZnSO4	-	-	-	-	-	4	2 of 4 samples had 99% of their filaments completely colourless and dead	
<i>Eichhornia</i> <i>crassipes</i> (water hyacinth)	mature plants	S,N,2	ZnSO4	-	-	28-30	-	-	9	30% weight reduction	Delgado <i>et al.</i> 1993
Euglena gracilis (algae)	-	S,N,2	ZnCl2	-	-	25	-	-	50 μΜ	strong inhibition of O ₂ evolution- 10 days	DeFilippis & Ziegler 1993

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
Lemna trisulca	-	S,M,2	-	7.8- 8.3	-	28	-	-	>0.195 - 0.293	decrease in multiplication rate	Huebert & Shay 1992
(submerged aquatic macrophyte)	-	S,M,2	-	7.8- 8.3	-	28	-	-	0.325	EC50 (final yield)	
niterophyte)	-	S,M,2	-	7.8- 8.3	-	28	-	-	0.915	EC50 (multiplication rate)	
<i>Lemna minor</i> (aqua. macrophyte)	-	S,N,2,	-	-	-	25-28	-	-	10; 0.23	IC50 (10 mg/L); growth at 93% of control	Dirilgen and Inel 1994a, b
Scenedesmus quadricauda	-	S,M,2	ZnSO4	8	-	constant	-	-	0.25	EC50-4 hr (photosynthesis)	Starodub <i>et al.</i> 1987
(green algae)	-	S,M,2	ZnSO4	4.5	-	20	-	-	0.1	Growth rate- 15 days= 0.100 (sig. different from control)	
	-	S,M,2	ZnSO4	6.5	-	20	-	-	0.1	Growth rate- 15 days= 0.101	
	-	S,M,2	ZnSO4	8.5	-	20	-	-	0.1	Growth rate- 15 days= 0.122	
	-	S,M,2	ZnSO4	4.5	-	20	-	-	0.225	Growth rate- 15 days 0.040 (sig. different from control)	

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
	-	S,M,2	ZnSO4	6.5	-	20	-	-	0.225	Growth rate- 15days= 0.042 (sig. different from control)	
	-	S,M,2	ZnSO4	8.5	-	20	-	-	0.225	Growth rate- 15 days= 0.131	
		S,N,2	ZnSO4	4.5		20			0.5	Growth rate- 15 days= 0.000 (sig. different from control)	
	-	S,N,2	ZnSO4	6.5	-	20	-	-	0.5	Growth rate- 15 days= 0.026	
(green algae)		S,N,2	ZnSO4	8.5		20			0.5	Growth rate- 15 days= 0.109 (sig. different from control)	Starodub <i>et al.</i> 1987
	-	-	-	-	-	-	-	-	0.002	first deleterious effect	Matulova 1978
Selanastrum capricornutum	-	NA	-	-	-	-	-	-	0.03 (2*)	Some growth inhibition- 7 d	EPA 1980
(green alga)	-	NA	-	-	-	-	-	-	0.040- 0.068 (3*)	95% growth inhibition- 14 d	

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
	-	NA	_	-	-	-	-	-	0.1	100% growth inhibition- 7 d	
	-	S,M,2, AAPBT medium	ZnCl2	6.8- 7.2	-	24	8.2	14.9	0.03 (2*)	Initiation of growth rate inhibition	Bartlett <i>et al.</i> 1974
	-	as above	ZnCl2	6.8- 7.2	-	24	8.2	14.9	0.12	Complete inhibition of growth rate	
	-	as above	ZnCl2	6.8- 7.2	-	24	8.2	14.9	0.12	Complete inhibition of growth rate	Bartlett <i>et al.</i> 1974
	-	as above	ZnCl2	6.8- 7.2	-	24	8.2	14.9	0.12	algicidal	
	-	S,N,2	ZnSO4	6.0- 6.3	-	24	-	-	0.0041	7-d EC50	Chiaudani & Vighi, 1978
<i>Spirodela polyrhiza</i> (macrophyte)	-	S,N,2	ZnSO4	7	-	25	-	-	0.935	EC50-96 hr (growth)	Guar <i>et al.</i> 1994

Species	Life Stage	Data type	Chemical	рН	D.O. (mg/L)	Temp. (°C)	Alkalinity (mg/L)	Hardness (mg/L as CaCO ₃)	Conc. (mg/L)	Effect	Reference
Plankton community (Lake Michigan)	submerged carboys	S,N,2	-	-	-	-	-	-	0.015	Signific. reduction in chlorophyll <u>a</u> , primary productivity, DO, zooplankton diversity & populations, and community similarity	Marshall <i>et al.</i> 1983

KEY

EC = Effective Concnetration

IC = Inhibition Concentration

LC = Lethal Concnetration

MATC = Maximun Acceptable Tolerance Concentration

LT = Median Age of Death

TLm = Lethal Thresold (50% survival)

- S = Static Test Method
- F = Flowthrough Test Method
- M = Measured
- N = Nominal

NA = Not

- Available
- 1 = Primary
- 2 = Secondary

Note: This table was prepared from information obtained from the AQUIRE database. References for these tables were unable to be retrieved.

 Table A3.1
 Calculation of Water Effect Ratios for the Upper Clark Fork River downstream of Warm Springs Pond using the results of acute toxicity tests with rainbow trout

Sampling Date	LC ₅₀ in Site Water	LC ₅₀ in Lab Water	Water Effect Ratio LC _{50 Site} / LC _{50 Lab}
Low Flow - Winter	385 μg/L	111 µg/L	3.47
Low Flow - Early Spring	335 µg/L	102 µg/L	3.28
High Flow - Late Spring	255 μg/L	81.0 µg/L	3.15
Low Flow - Fall	245 μg/L	80.8 µg/L	3.03
Low Flow - Late Fall	296 µg/L	137 µg/L	2.16
Mean WER			3.02

Table A3. 2 Calculated Water Effect Ratios for Total Copper in the Upper Clark Fork River

				Water Effect Ratio			
Sampling Site	Sampling Date	Rainbow Trout Acute Test	Fathead Minnow Acute Test	Fathead Minnow Chronic Test	<i>C. dubia</i> Acute Test	<i>C. dubia</i> Chronic Test	Final WER
UCFR D/S Warm	Low Flow - Winter	3.47	7.98	4.16	ND	2.02	2.65
Springs Pond	Low Flow - Early Spring	3.28	11.00	3.04	6.12	> 7.84	3.16
	High Flow - Late Spring	3.15	3.49	3.64	4.11	3.03	3.09
	Low Flow - Fall	3.03	3.12	1.42	1.56	1.92	1.49
	Low Flow - Late Fall	2.16	7.60	3.76	2.65	2.67	2.39
	Mean WER	3.02	6.64	3.20	3.61	2.41	2.70
UCFR at Deer							
Lodge	Low Flow - Winter	2.38	6.36	2.59	2.76	1.59	1.95
	Low Flow - Early Spring	2.41	4.44	3.36	2.10	3.20	2.10
	High Flow - Late Spring	2.55	4.77	1.64	8.79	1.78	1.78
	Low Flow - Fall	1.89	5.44	1.89	1.91	2.35	1.89
	Low Flow - Late Fall	2.02	7.75	3.33	1.86	2.18	1.94
	Mean WER	2.25	5.75	2.56	3.48	2.22	2.23

ND = not determined.

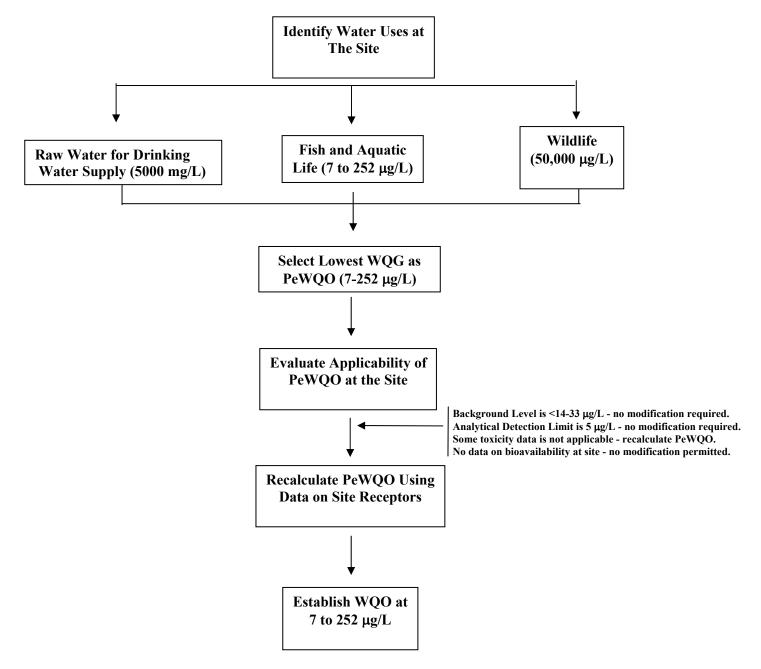
Note: The final WER was calculated as the geometric mean of the two lowest mean WERs.

Table A3.3 Calculated Water Effect Ratios for Dissolved Copper in the Upper Clark Fork River

				Water Effect Ratio			_
Sampling Site	Sampling Date	Rainbow Trout	Fathead Minnow	Fathead Minnow	<i>C. dubia</i> Acute	C. dubia	Final
		Acute Test	Acute Test	Chronic Test	Test	Chronic Test	WER
UCFR D/S Warm	Low Flow - Winter	2.56	5.11	3.43	ND	1.38	1.88
Springs Pond	Low Flow - Early Spring	2.25	4.58	2.39	4.24	> 5.82	2.32
	High Flow - Late Spring	2.98	3.14	3.64	3.91	2.26	2.60
	Low Flow - Fall	2.77	1.94	1.32	1.52	1.83	1.42
	Low Flow - Late Fall	2.07	2.27	3.18	2.92	2.21	2.14
	Mean WER	2.53	3.41	2.79	3.15	1.92	2.20
UCFR @ Deer Lodge	Low Flow - Winter	1.78	3.71	1.60	1.76	1.04	1.29
	Low Flow - Early Spring	1.72	2.86	2.31	1.50	2.74	1.61
	High Flow - Late Spring	2.06	3.46	1.53	3.07	1.64	1.58
	Low Flow - Fall	1.61	3.52	1.76	1.65	2.54	1.63
	Low Flow - Late Fall	1.70	2.02	3.33	1.48	1.91	1.59
	Mean WER	1.77	3.11	2.11	1.89	1.97	1.83

ND = not determined.

Figure A2-1. Development of Site Specific Water Quality Remediation Objectives for Zinc in the South McQuesten River.



Canadian Water Quality Guidelines for the Protection of Aquatic Life

Reference listing:

Canadian Council of Ministers of the Environment. 2003. Canadian water quality guidelines for the protection of aquatic life: Guidance on the Site-Specific Application of Water Quality Guidelines in Canada: Procedures for Deriving Numerical Water Quality Objectives. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

For further scientific information, contact:

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