

# Guidance for the Derivation and Application of Water Quality Objectives in British Columbia

April, 2013

Water Protection and Sustainability Branch  
Environmental Sustainability and Strategic Policy Division  
Ministry of Environment

## Executive Summary

Water quality objectives (WQOs) are science-based tools that provide an effective basis for managing the resources in aquatic ecosystems and describe conditions that should be met to protect the designated uses of freshwater, estuarine, and marine ecosystems. They are used in conjunction with other management tools, such as waste discharge authorization processes, treatment technology, and enforcement, to achieve environmental conditions that support sustainable resource use. In BC, water quality guidelines (WQG) are designed to have broad application on a provincial scale. Where the WQGs are not appropriate (either under-protective or over-protective), they may be modified as WQOs with the goal of protecting or enhancing the existing water quality. This document presents an update of the BC Ministry of Environment's *Methods for Deriving Site-Specific Water Quality Objectives in British Columbia and Yukon* (MacDonald 1997) and incorporates key aspects of the document *Principles for Preparing Water Quality Objectives in British Columbia* (BC MOE 1986). The goal of this report is to provide specific guidance on when and how to develop WQOs.

Water quality objectives are an extension of the WQGs, and, therefore, the development of WQOs is subject to the same level of scientific rigour as the WQGs. It is the policy of the BC MOE that WQOs are established following the principle of avoiding the degradation of existing water quality, upgrading existing water quality, or protecting water quality for the most sensitive designated use (drinking water, aquatic life, wildlife, agriculture, recreation, industrial supplies).

Water quality objectives can be broadly described as “site-specific” or “site-adapted”. A site-specific WQO establishes an acceptable level for a water quality variable at a site through either: a) direct adoption of the BC-approved WQG for that variable; b) establishing the upper limit of background concentrations of a variable at the site as the WQO, or c) deriving a site-specific WQO based on data collected at the site (e.g., using the resident species procedure). Site-adapted WQOs take certain characteristics of the site into consideration to modify an approved WQG for application at that site. Examples of site-adapted WQOs are those derived using the recalculation procedure or a water effect ratio.

While WQOs can be developed for any waterbody with the objective of protecting existing water quality, certain conditions must be met before initiating the development of site-adapted WQOs. In most cases where the goal is to protect existing water quality, adoption of the generic BC-approved WQG as the WQO is sufficient (section 3.4.1). If the natural background concentration of a given variable exceeds the BC-approved WQG, the background concentration procedure can be used to determine an appropriate WQO (section 3.4.2). Where the approved WQG is based on organisms not relevant to the site in question, the recalculation procedure may be used to derive site-adapted WQOs (section 3.4.4). When the approved WQGs do not account for site characteristics that could modify toxicity, the water effect ratio procedure allows for modification of generic WQGs (section 3.4.5). Finally, when the approved WQG does not adequately reflect the species composition at the site, and the water quality

conditions at the site influence the toxicity of the variable of concern, the resident species procedure can be used to develop a WQO that is unique to that site (section 3.4.6).

The procedures recommended in this document apply directly to the development of WQOs for metals and metalloids in freshwater systems; however, they are also applicable to organic substances and to marine and estuarine systems. These site-specific procedures, however, will generally not apply to substances that tend to bioaccumulate and/or biomagnify in the environment, since WQGs for these substances are usually not based on their toxicity but their potential to bioaccumulate in aquatic organisms to levels that may be harmful to consumers. General WQO development methods do not exist for these and will require special consideration on a site-specific basis. Water quality objectives are developed and approved by the BC MOE and may include support from stakeholders (e.g. industrial users, non-government organizations etc.). Once approved, WQOs constitute official BC MOE policy and must be considered in ministry decisions affecting that waterbody.

The development of WQOs is not limited to the methods described in this document. The BC MOE will continue to review new approaches for deriving WQOs, recognizing the potential for new science and unique, site-specific circumstances, and will adopt new procedures that are scientifically valid and consistent with existing policies. Examples include benthic invertebrate bio-monitoring (section 4.1), ecoregions (section 4.2), and emerging technologies such as the biotic ligand model and ecotoxigenomics (section 4.3).

Monitoring to assess attainment of WQOs is an essential component of the overall environmental adaptive management process. Each WQO report includes a water quality monitoring program to determine if the WQOs are being attained which includes: site locations; frequency of monitoring; variables to monitor; and sampling periods. The monitoring program will be largely driven by the data required to satisfy the WQOs themselves. For example, average concentrations are generally based on a minimum of 5 evenly-spaced samples collected over a 30-day period.

While the framework and procedures described in this document are intended to provide a cost-effective basis for deriving WQOs that are protective of aquatic resources in BC, there are certain limitations (section 5.0) which must be considered, including:

- The uncertainties associated with the derivation process which could influence the predictive ability of the WQOs. Environmental effects monitoring should be implemented to determine if the WQOs are effectively protecting water uses and attainment monitoring programs should be followed to ensure the WQOs are being met.
- WERs derived using the WER procedure are directly applicable to the conditions represented during toxicity testing. If the most sensitive conditions are not appropriately identified or if wastewater discharge characteristics change significantly, the WERs must be re-evaluated to ensure designated water uses are being protected.
- The WQOs for the protection of aquatic life derived using the recommended framework are toxicity-based. Site-specific consideration will need to be provided for variables of concern

which have the potential to bioaccumulate or biomagnify, as general WQO development methods do not exist for these substances.

- Compliance with WQOs in receiving water systems does not relieve wastewater dischargers from obligations associated with other environmental legislation.
- The procedures recommended in this document generally apply to single chemicals and single wastewater discharges. More sophisticated experimental designs will be required for more complicated scenarios such as mixtures of contaminants and multiple discharges.

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## Acronyms

BC MOE	British Columbia Ministry of Environment
CABIN	Canadian Aquatic Biomonitoring Network
CALA	Canadian Association for Laboratory Accreditation
CCME	Canadian Council of Ministers of the Environment
CCREM	Canadian Council of Resource and Environmental Ministers
EC <sub>10</sub>	Effects concentration (10% of test organisms)
EPD	Environmental Protection Division
IDZ	Initial dilution zone
LC <sub>50</sub>	Lethal concentration (50% of test organisms)
RCA	Reference condition approach
US EPA	United States Environmental Protection Agency
WER	Water effects ratio
WQG	Water quality guideline
WQO	Water quality objective

## **1.0 Introduction**

British Columbia (BC) has diverse hydrological resources in our glaciers, lakes, rivers, wetlands, and aquifers. This water is not evenly distributed in time or space, and the demands placed upon it are highly variable, creating both challenges and opportunities. To help ensure that our communities are safe and our aquatic ecosystems are healthy, the BC Ministry of Environment (BC MOE), as part of its mandate to protect water quality, develops water quality objectives (WQOs) for specific bodies of fresh, estuarine, and coastal marine surface waters of the Province. This report describes the role of WQOs in managing BC's water resources, discusses factors which must be considered in preparing them, and outlines acceptable approaches for their development.

### **1.1 History**

In 1982, the Auditor General released a report documenting a comprehensive audit of the BC MOE, which focussed on the Ministry's waste management program at that time (BC Office of the Auditor General 1982). With respect to water quality, the report noted that without defining acceptable limits for concentrations in specific terms, the acceptability of observed concentrations in the environment and the Ministry's operational performance could not be reliably assessed. The report suggested that a combination of Province-wide and site-specific water quality standards may be necessary and recommended that the Ministry establish procedures to report on the results of monitoring ambient concentrations against acceptable limits.

In response, the Ministry developed policies to guide the development of Province-wide water quality guidelines (WQGs) and site-specific WQOs. In the mid-1980s, several guideline and objectives documents were released, establishing the basis of the current system. As of August 2012, BC has WQGs for 40 substances and site-specific WQOs for 61 waterbodies.



## **1.2 Water Quality Objectives Defined**

Water quality objectives are science-based tools that provide an effective basis for managing aquatic ecosystems. They are prepared on a site-specific basis, with due regard for the water quality, water uses (including aquatic life), water movement, and waste discharges at a given location. Water quality objectives represent the physical, chemical, and biological characteristics of water, biota, and sediment that protect the most sensitive designated water uses at a particular site. Water quality objectives are used in conjunction with other management tools, such as waste discharge authorization processes, treatment technology, and enforcement, to achieve environmental conditions that support sustainable resource use. Once approved, the WQOs constitute official ministry policy and provide guidance for resource managers to use in protecting water uses in specific waterbodies. In general, WQOs are prepared only for those waterbodies and water quality variables that may be significantly affected by human activities, either now or in the future.

Water quality objectives are based on BC WQGs, which relate the physical, chemical, or biological characteristics of water, biota, or sediment to their effects on water use, including aquatic life. In BC, WQGs provide a consistent basis for assessing water quality conditions throughout much of the Province. The WQGs are derived for the protection of 6 major water uses, including:

- drinking water sources and food processing;
- aquatic life;
- wildlife;
- agricultural (irrigation and livestock watering);
- recreation and aesthetics; and
- industrial water supplies.

The WQGs provide basic scientific information about the effects of water quality variables on water uses and apply province-wide. They are used to assess water quality issues and concerns and to establish WQOs (BC MOE 1986, CCREM 1987).

While WQGs are intended to protect the designated uses of aquatic ecosystems, it is possible that they may be over-protective or under-protective at sites with unique conditions. For example, the most sensitive taxonomic grouping represented in the toxicological data set used to derive the generic guidelines may not be present at the site of interest. Similarly, a substance may be more or less toxic in site water (i.e., due to factors such as pH, water hardness, complexing agents, and the cumulative effects of other constituents in the water) than it is under the range of conditions that are represented in the toxicological data set. Under these circumstances, it might be necessary to modify the generic WQGs to account for conditions that occur at the site.

### **1.3 Purpose of Report**

This document is based on three key reports: *Principles for Preparing Water Quality Objectives in British Columbia* (BC MOE 1986); *Methods for Deriving Site-Specific Water Quality Objectives in British Columbia and Yukon* (MacDonald 1997); and, *Guidance on the Site-Specific Application of Water Quality Guidelines in Canada: Procedures for Deriving Numerical Water Quality Objectives* (CCME 2003). While several procedures have been created to support the development of site-specific WQOs (e.g., Niyogi and Wood 2004), with potential for new methods in the future (e.g., Van Aggelen et al. 2009), there are currently 4 approaches recommended by both the BC MOE and the Canadian Council of Ministers of the Environment (CCME):

- direct adoption of approved WQGs;
- site-specific adoption of the upper limit of background concentrations;
- derivation of site-adapted WQOs (which involves modification of the BC-approved WQGs); and,
- development of site-specific WQOs (using only site-specific data).

The procedures recommended under these approaches will likely provide environmental managers with the tools needed to derive WQOs in BC. New procedures for other approaches will be developed on an as-needed basis.

There are 3 main goals of this report:

1. To compile and update the information provided in previous guidance documents;
2. To clarify the BC MOE's expectations with respect to the development and application of WQOs in BC; and
3. To provide specific guidance on developing WQOs using the recommended approaches and procedures.

The procedures recommended in this document apply directly to the development of WQOs for metals and metalloids in freshwater systems; however, they are also applicable to organic substances and to marine and estuarine systems. These site-specific procedures, however, will generally not apply to substances that tend to bioaccumulate and/or biomagnify in the environment, since WQGs for these substances are usually not based on their toxicity but their potential to bioaccumulate in aquatic organisms to levels that may be harmful to consumers. Special consideration on a site-specific basis will be required for substances that bioaccumulate or biomagnify, as general WQO development methods do not exist for these. The BC MOE will continue to review new approaches for developing WQOs to ensure they are scientifically and technically sound, and consistent with the BC Government's commitment to protect our water resources.

## **2.0 A Framework for the Development of Water Quality Objectives**

### **2.1 Philosophical Basis for Developing Water Quality Objectives**

Two distinct strategies are commonly used in setting WQOs in BC: 1) for waterbodies with good existing water quality, the objectives are set to avoid degradation of the existing conditions; and 2) the objectives are set to protect the water quality for the designated water uses. The second approach may allow some degradation of existing water quality to accommodate waste assimilation while still protecting the designated water uses (i.e., use of the assimilative capacity), but it may also entail enhancement of water quality where it is currently poorer than that desired for the designated water uses.

Assimilative capacity is the ability of a waterbody to receive contaminants without impairing the use of the water by man, animals, and plants. The concept of using assimilative capacity in managing the water resource is controversial, because of differences in public opinion and because it is difficult to define. It is different for each contaminant, or mixture of contaminants, and a thorough understanding of the aquatic ecosystem is required. Interrelated measurements of water quantity and quality, sediments, and aquatic life must be made. The pressure to use or not use assimilative capacity can be high, especially in cases requiring costly pollution control measures to maintain water quality or where the public and stakeholders have divergent opinions.

The water uses designated for protection (see Section 1.2) are the existing and potential uses that might reasonably be made of the water in the future. The waterbody must be inherently capable of supporting these water uses. As long as the designated water uses are protected, some degradation of existing water quality may be acceptable, provided that all reasonable and preventative measures are taken to protect water quality conditions.

## 2.2 Development of Water Quality Guidelines

Before discussing the development of WQOs in depth, it is useful to have a good understanding of how WQGs are developed in BC. The development of WQGs and methods for their application to produce WQOs has a province-wide scope. Water quality guidelines are developed for the protection of designated water uses (see Section 1.2). Existing WQGs and methods from the literature and other jurisdictions are evaluated and those that are appropriate to conditions in BC are adopted or developed from this analysis. Water quality guidelines are subject to wide review prior to finalization, and are reviewed from time to time as new information becomes available. Water quality guidelines are developed or updated on a provincial priority basis.

Water quality guidelines for aquatic life are the most difficult to develop. These guidelines are based mainly on the science of ecotoxicology (i.e., integrating ecology and toxicology to determine the effect of toxicants on various life forms). This is an area of science which is continually evolving as research progresses. It should be noted that there are several sources of uncertainty and therefore it is necessary to apply uncertainty (i.e., safety) factors when developing WQGs. Sources of uncertainty include:

- laboratory to field differences;
- single to multiple contaminants (additive, synergistic, antagonistic effects);
- toxicity of metabolites;
- intra and inter-species differences (limited species to conduct tests on, which may not include the most sensitive species);
- indirect effects (e.g., foodweb dynamics);
- whole life-cycle vs. partial life-cycle (difficulty in determining the most sensitive life stage);
- delayed effects;
- other stressors (habitat loss) or contaminants in the environment that may have an unknown effect (cumulative effects); and
- impacts of climate change (species may be more vulnerable with additional stressors).

There are several fundamental principles used in developing water quality guidelines in BC.

These are:

- BC guidelines are science-based and intended for generic provincial application. They do not account for special site-specific factors where they exist, or for socio-economic factors.
- All higher components of the aquatic ecosystem (e.g., algae, macrophytes, invertebrates, amphibians, and fish) are considered if the data are available. Where data are available but limited, the development of interim guidelines is preferable to no guidelines at all.
- The approach to develop guidelines for aquatic life reflects the philosophy that all forms of aquatic life and all aquatic stages of their life cycle are to be protected during indefinite exposure. Protection of aquatic life is characterized by protection of individuals and as such, also protects populations. It should be noted however, that this approach may not protect individuals weakened to some degree through age, illness, or injury. Whether this goal can be realized is a separate issue and does not influence the guideline derivation procedure.
- For some substances both a short-term maximum (acute) and a long-term average (chronic) guideline are recommended as provincial water quality guidelines, provided sufficient toxicological data are available. Short-term maximum guidelines are set to prevent severe effects such as lethality to aquatic organisms from short-term exposures to contaminants. Long-term average guidelines are set to protect aquatic organisms from sub-lethal and lethal effects over the long-term. Both conditions should be met to protect aquatic life. For other substances which may not be acutely toxic but, due to their low water solubilities (e.g., PCBs and dioxins), ability to bioaccumulate, or mode of action (e.g., endocrine disruptors), the guideline is a single value representing a long-term, no-effect level, which should not be exceeded at any time.
- Unless otherwise specified, a guideline refers to the total concentration of a substance in an unfiltered sample. Total concentrations will apply unless it can be demonstrated that the relationship between other measures of the substance and their toxicity is

firmly established, and analytical techniques have been developed that unequivocally identify the toxic fraction of a substance in a consistent manner using routine field-verified measurements.

- BC guidelines are generally the basis for the derivation of site-specific water quality objectives, which take local circumstances into account.

The WQGs developed for BC, along with information on local conditions, provide the basis for establishing WQOs and provide benchmarks for the evaluation of water quality data. For more information on the development of WQGs in BC, see Meays (2012).

### **2.3 Guiding Principles for the Development of Water Quality Objectives**

The development of WQOs is based on a detailed water quality assessment and requires extensive knowledge of the physical, chemical, and biological characteristics of the waterbody under consideration. Once such information is acquired, WQOs are derived considering the taxonomic groups of organisms and environmental conditions that are relevant to the site. Water quality objectives specify a range of values when possible; generally short-term maximum and/or minimum (acute) values that are not to be exceeded at any time, and average (chronic) values that apply to a longer term (e.g., 30 days). Both acute and chronic WQOs may be established for the same substance to support water quality management.

Water quality objectives do not apply within the initial dilution zone (IDZ), which is the initial portion of the larger effluent mixing zone, for point source wastewater discharges. The extent of the IDZ is defined on a site-specific basis, with due regard to water uses, aquatic life (including migratory fish), and other waste discharges. Initial dilution zones are normally relatively small (e.g., up to 100 m from the point of effluent discharge, but not exceeding 25 – 50% of the width of a waterbody), and are essential to allow for the initial mixing between effluents and the receiving water. If IDZs did not exist, effluent quality would have to meet WQOs, which would be costly and impractical.

Within an IDZ, water quality may exceed WQOs and sub-lethal effects on aquatic life may occur, but effluent quality and dilution in the IDZ should be such that acutely toxic

conditions do not occur (i.e., short-term maximum WQOs should be met). Initial dilution zones should not impinge on water intakes, bathing beaches, shellfish beds, fish spawning beds, aquatic macrophyte beds serving as a rearing area for important aquatic species, or any other sensitive area requiring protection. Outside of the IDZ, water quality should be suitable for all designated water uses, and should protect aquatic life from sub-lethal effects, as a minimum.

While the WQOs are intended to protect the designated uses of the aquatic ecosystem, they may allow for changes from background conditions. However, such alterations in ambient water quality are permitted only when the BC MOE considers that some waste assimilative capacity is available and can be used without compromising use-protection. Where water quality has already been degraded, the WQOs will establish the goal to be met by corrective measures. Therefore, the WQOs provide an effective basis for water management (including setting effluent permit limits), when used in conjunction with other regulatory tools. Once the WQOs are set, periodic assessments are conducted to determine if the WQOs are being attained, and to refine the WQOs and management strategies, if necessary, to ensure that the desired water quality is maintained.

Site-specific WQOs may be derived in partnership with other levels of government, and with input from regulated interests or non-governmental organizations. Therefore, it is important to establish a set of guiding principles that enables the development of site-specific WQOs that are consistent with the BC MOE's mandate. The following guiding principles for the development of WQOs (some of which have been discussed above) are based on the philosophies established by the BC MOE (BC MOE 1986; MacDonald 1997) and the CCME (2003):

- WQOs are developed to protect the most sensitive water use at the site.
- WQOs apply to the site in question and any potentially affected waters downstream of the site, unless otherwise stated.
- The water uses to be protected include: raw water for drinking water supplies and food processing; recreation and aesthetics; aquatic life; wildlife; agriculture (including livestock water and irrigation); and, industrial uses.



- The BC-approved WQGs for the most sensitive water use should be adopted as the preliminary WQO for each water quality variable for a site.
- For the protection of aquatic life, the WQOs are developed to protect individuals of the most sensitive species and all stages of their life cycle.
- At sites which have atypical water quality characteristics or ecological receptors, the BC-approved WQGs may be modified up or down to account for site-specific factors.
- The administrative rules (see Section 2.6) specify the conditions under which the BC-approved WQGs can be modified or site-adapted.
- Indicators to evaluate attainment of WQOs at the site under consideration may include: chemical (numerical WQOs), toxicological (toxicity test results), and/or biological (aquatic ecosystem community structure, etc.) values.
- Third parties can contribute information which may be considered in deriving the WQOs for a given waterbody, given that the information meets the Ministry's standards and expectations. Any information submitted by partners will be reviewed and approved for use by the appropriate BC MOE qualified professionals (e.g., R.P. Bio., P. Ag., P. Eng.) before it is used in developing a WQO.
- WQO documents must be signed off by a MOE qualified professional before it can be submitted for approval.
- WQOs are approved at the executive level of the BC MOE and, once approved, constitute official Ministry policy and are to be considered in any relevant Ministry decisions regarding water quality for that waterbody.
- The overall information requirements and approval process is the same for all WQOs, regardless of the designated water uses to be protected and land use activities within the watershed of concern.
- Those developing WQOs for approval in BC are to follow the guidance provided in this document.

## 2.4 Types of Water Quality Objectives

Water quality objectives can be broadly described as “site-specific” or “site-adapted”. A site-specific WQO establishes an acceptable level for a water quality variable at a site through either:

- a) direct adoption of the BC-approved WQG for that variable (Section 3.4.1);
- b) establishing the upper limit of background concentrations of a variable at the site as the WQO (Section 3.4.2), or
- c) deriving a site-specific WQO based on data collected at the site (e.g., the resident species procedure, Section 3.4.6).

Site-adapted WQOs take certain characteristics of the site into consideration to modify an approved WQG, using a BC MOE-approved methodology, for application at that site. Examples of site-adapted WQOs are those derived using the recalculation procedure (Section 3.4.4) or a water effect ratio (Section 3.4.5).

There are 3 general types of WQOs developed in BC. *Provisional WQOs* are set where the information available about the local conditions (e.g., water quality, water use, aquatic life, waste discharges, etc.) and/or the WQGs for a substance are inadequate for the establishment of scientifically defensible WQOs. Provisional WQOs are deliberately conservative, and a monitoring or study program is specified that will lead to the establishment of permanent objectives.

*Permanent WQOs* are established when the information available about the local conditions and WQGs is adequate. A monitoring program is specified to assess the degree of attainment of the WQOs. Both provisional and permanent WQOs are subject to wide review before they are adopted, and permanent WQOs are reviewed from time to time and are subject to revision as new information becomes available.

*Short-term and long-term WQOs* may be used where existing water quality does not suit all desired water uses, and it is feasible to improve the water quality over time. The short-term objectives would protect water uses to a certain degree until the long-term objectives can be

achieved. The WQO document should define what is meant by short-term (e.g., 1 – 5 years) and long-term (e.g., 5 – 10 years).

## **2.5 Justifying the Development of Water Quality Objectives**

It is the policy of the BC MOE that WQOs are established following the principle of avoiding the degradation of existing water quality, upgrading existing water quality, or protecting the water quality for the most sensitive designated use (see Appendix 1). If the goal is to protect designated uses, then certain conditions must be met before an approach other than direct adoption of the approved BC WQGs is considered. These include the following:

- The natural background concentrations of a given variable exceed the BC-approved WQG.
- There are site-specific circumstances affecting the toxicity (either increasing toxicity or decreasing toxicity) of the contaminant(s) in question.
- The data set used to derive the BC-approved WQG includes taxonomic groups that do not occur or have the potential to occur within the waterbody in question.

The development of WQOs should not be driven solely by predicted or modelled concentrations of variables anticipated as a result of a particular land use impacting a particular waterbody. Predicted increases can, however, initiate an assessment to determine if there is proper justification for developing WQOs at a particular site. When there are toxicity-modifying factors (ameliorating or aggravating) present, WQOs must be based on the natural background concentrations of these factors, not levels that have been altered due to human land use (e.g., hardness).

As a starting point in the development of WQOs, the BC-approved WQGs are used as preliminary WQOs (see Section 3.2). Once this has been done, the following questions must be answered to determine if a deviation from the BC-approved WQGs in the development of WQOs is actually justified in a given situation:

***Is the upper limit of background concentrations greater than the preliminary WQO?***

If natural background concentrations of a given variable are naturally elevated and higher than the guideline level, there is justification for developing WQO using the background concentration procedure (see Section 3.4.2). The upper limits of natural background concentrations are determined using the 95<sup>th</sup> percentile of relevant data (see Section 3.1) and may be determined on a seasonal basis (e.g., clear-flow and turbid-flow periods). Natural background concentrations at a site are based on conditions prior to development affecting the waterbody in question. If development has already taken place, background conditions are determined at either an un-impacted site upstream of the development or discharge site, or at a suitable reference site from a nearby location, including other waterbodies and watersheds.

***Is the lowest available limit of quantitation greater than the preliminary WQO?***

Determining if a WQO is being met will not be possible if the lowest available method detection limit is greater than the WQO. This should not be an issue at most environmental laboratories, given the analytical capabilities currently available. If this situation does occur, there is justification to adjust the preliminary WQO to reflect this limitation. However, it should be noted in the WQO document that when a lower limit of analytical quantification is achieved, the WQO will be lowered accordingly.

***Is the preliminary WQO based on organisms not relevant to the site in question?***

If the WQG used to derive the preliminary WQO is based on a taxonomic grouping that is not present at the site, and does not have the potential to occur at the site or within influence of the site, there may be justification for developing a WQO using the recalculation procedure (see Section 3.4.4 and Appendix 4). It is important to note that removing toxicity data from the toxicological data set may necessitate the generation of additional toxicity data to meet the minimum requirement for WQG/WQO development. The WQO report writer is advised to consult with the MOE Water Quality Guidelines Science Specialist when this situation arises.

***Does the preliminary WQO account for site characteristics that could modify toxicity?***

There are a number of chemical, physical, and biological factors that can potentially influence (positively or negatively) the site-specific toxicity of contaminants (see Appendix 2). If these conditions can be demonstrated, there may be justification to develop WQOs using the WER procedure (see Section 3.3.5). It is important to note that, because BC MOE policy is to protect or improve existing water quality (including low-risk characteristics such as hardness), toxicity tests for determining WERs are ran using un-modified site water.

***Are there other circumstances present that warrant consideration of another approach?***

In some cases, there may be a need to take a different approach to assess the suitability of the preliminary WQO. The resident species procedure (see Section 3.3.6) is available for situations where both the resident species and site-specific conditions may be such that the preliminary WQO is inappropriate. Where the resident species approach is used, the minimum number of tests required for WQG development is also required. It is also possible that conditions are such that a new approach is required. In these cases it is extremely important that BC MOE staff responsible for setting WQOs ensure that the development of WQOs is justified and that all Ministry requirements are met.

If at least one of these tests is met, there may be adequate justification to develop a site-specific WQO that differs from the WQGs. Proponents should give careful consideration to these tests before initiating the process or spending resources unnecessarily (both the proponents and the Ministry's). If the development of WQOs cannot be justified, proponents will need to explore other waste management options with input from the appropriate BC MOE staff.

## **2.6 Summary of Rules for Developing Water Quality Objectives**

The derivation of WQOs is a complex process that requires detailed information on the site under investigation, the contaminants present at the site, and the 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 are provided to simplify the derivation of WQOs. The following rules outline when it is appropriate to adopt the generic WQGs directly, to modify the generic WQGs, and to develop WQOs on a site-specific basis in BC:

- i. BC-approved WQGs should be adopted as WQOs at all sites unless the generic WQG for a substance is lower than the upper limit of background (i.e., 95<sup>th</sup> percentile) at the site under investigation.
- ii. The analytical limits of quantitation for chemical substances vary depending on the extraction and quantitation techniques used, the medium sampled, and the laboratory considered. For the purposes of WQOs derivation, the analytical limits of quantitation that are typically achieved at the National Water Quality Laboratory (Burlington, Ontario) and/or relevant CALA-certified laboratories in BC should be used to evaluate the applicability of a preliminary WQO.
- iii. BC-approved 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 BC-approved WQG and that the site under investigation has atypical levels of that factor. For example, the generic WQG for copper accounts for water hardness (Singleton 1987). However, this guideline does not account for the potential influence of high levels of dissolved organic matter (DOM) on copper toxicity. Therefore, it may be appropriate to evaluate the applicability of the generic copper guidelines at sites with high levels of DOM and, if necessary, modify it to reflect site-specific water quality characteristics.
- iv. BC-approved 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 BC-approved WQG are not representative of the species that occur at the site under investigation.
- v. BC-approved WQGs must be available for each of the designated water uses at the site before selecting a preliminary WQO, unless it can be demonstrated that the available guidelines include the most sensitive water uses (protection of aquatic life is generally the most sensitive water use).

- vi. If BC-approved WQGs are not available for one or more water uses at the site, WQGs may be derived using the approved protocols for guideline development in BC. This is the role of the MOE's Water Quality Guideline Science Specialist, who is to be contacted in such an event.
- 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 additional toxicological and/or environmental fate data needed to support the derivation of the WQG may be necessary (BC MOE regional staff, in consultation with the provincial Water Quality Guidelines Science Specialist, will determine what additional data are required). 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, the data necessary to determine these levels should be collected. If the site in question has been altered by anthropogenic factors, an appropriate reference site should be designated and used to determine appropriate background levels.
- 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 an appropriate representative of the BC MOE.
- x. The preliminary WQO 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 (e.g., McPhail and Lindsey 1970; Scott and Crossman 1973; Hart 1973; McPhail

2007). Information on the distribution of freshwater fish is also available on the BC Ministry of Environment's Fisheries Inventory Data Queries website (<http://a100.gov.bc.ca/pub/fidq/main.do>). 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 valid;

- 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 any valid 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;
- d. If a member of an order of amphibians occurs or could occur at a site (e.g., Pacific tree frog from the family Hylidae), then the toxicity data on any of the amphibian species within that order (e.g., western toad from the family Bufonidae, bullfrog from the family Ranidae, etc.) must be included in the site-specific toxicological data set;
- e. If a member of a phylum or subphylum of freshwater invertebrates occurs or could occur at a site (e.g., *Daphnia* from the subphylum Crustacea), then the toxicity data on any of the invertebrate species within that phylum or subphylum (e.g., class Ostracoda, subclass Copepoda, 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 in the waterbody in question, 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 known 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 BC WQGs (Meays 2012). 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 assurance/quality control (QA/QC) procedures, including acceptable control and reference toxicant tests. For additional information on bioassay procedures, see Environment Canada's Biological Methods Publications List ([http://www.etc-cte.ec.gc.ca/organization/bmd/bmd\\_publist\\_e.html#2.2](http://www.etc-cte.ec.gc.ca/organization/bmd/bmd_publist_e.html#2.2)).
- xiii. The preliminary WQO 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. In these cases, detailed science-based rationale must be provided to the appropriate BC MOE representative for approval prior to pursuing this option.
- xiv. The water effects ratio (WER) procedure provides a direct means of modifying preliminary WQOs to account for site-specific water quality characteristics. Using this procedure, WERs for each priority substance at the site are calculated and used to modify the preliminary WQO. If a WER is developed for more than one variable at a site, additional toxicity tests must be conducted to show that the combination of all variables at their proposed new site-specific WQO levels is acceptable.

## **2.7 Compliance with Water Quality Objectives**

In BC, WQOs are enabled under various pieces of legislation including the *Environmental Management Act*, the *Forest and Range Practices Act*, and the *Drinking Water Protection Act*.

In certain cases, WQOs are used to address specific legislative requirements (e.g., *Water Act*, *Municipal Sewage Regulation*, *Private Managed Forest Land Council Regulation*). However, compliance with WQOs is often not directly enforceable. Discharge limits specified in permits, approvals, and orders issued by the BC MOE may be based on WQOs and so waste dischargers may have to abide by WQOs indirectly. More importantly, however, WQOs provide a means to increase environmental awareness and promote and enhance shared environmental stewardship. When the minimum requirements to protect a water resource have been defined and formalized as WQOs, all stakeholders with an interest in that waterbody have results-based goals to help guide resource management decisions.

Assessing whether WQOs are being met can be difficult because of the temporal and spatial variability of water quality, and the occurrence of isolated high values that may be due to analytical or sampling error, natural events, or waste discharges. Several principles should be observed to reduce the difficulty of assessing whether objectives are being met:

1. The natural variability and extremes of water quality should be considered when establishing WQOs.
2. Both upstream control sites and downstream test sites should be monitored simultaneously when possible to account for natural influences on water quality.
3. Waste discharges should be monitored at the same time as receiving water to determine their influence on water quality.

Coordinated monitoring of effluents and receiving water will aid in assessing cause-effect relationships and the significance of water quality values that do not meet the objectives. A monitoring program to assess whether objectives are being met (i.e., WQO attainment) will be specified whenever WQOs are established (further details are provided in Section 3.6).

To aid in this assessment, the WQOs should specify the following:

- the statistical values (e.g., maximum, minimum, 90<sup>th</sup> percentile, median, geometric mean, etc.) that are to be met by the WQO;

- the exact form of the substance to be measured (e.g., dissolved, total, etc.), including the analytical methods to be used and detection limits where appropriate;
- the geographic locations, times of the year, and depths (if applicable) for which the WQOs apply; and
- the type of samples (e.g., grab or composite), the minimum number of samples, and the sampling period.

### **3.0 Deriving Water Quality Objectives in British Columbia**

There are 4 general approaches that can be taken in developing site-specific WQOs:

- adoption of approved WQGs;
- adoption of the upper limit of background concentrations;
- derivation of site-adapted WQOs (which involves the modification of BC-approved WQGs, and
- Development of site-specific WQOs (e.g., using site-specific data).

This chapter provides specific guidance on the application of the recommended procedures for deriving WQOs under these approaches. The BC MOE will continue to review new approaches for WQO development, recognizing the potential for new science and unique, site-specific circumstances, and will adopt new procedures that are scientifically valid and consistent with existing policies. An overview of the process for deriving WQOs in BC is illustrated in Figure 1.

#### **3.1 Preliminary Steps**

Development of numerical WQOs in BC requires a water quality assessment involving a number of steps (see Appendix 3). The first step in this process involves identification of the designated uses of the water resources (see Section 1.2). Next, a list of potential contaminants is prepared using information on the existing and proposed human activities in the basin. Identifying the variables of concern at a given site is achieved through appropriate baseline monitoring, review of existing information, or a combination of both. Screening the data on wastewater and receiving water quality using the BC-approved WQGs will also help determine any potential contaminants. However, it may be necessary to utilize more sophisticated methods to identify the contaminants that represent significant hazards to aquatic organisms when complex mixtures of contaminants are present in wastewaters or receiving waters. A thorough understanding of the hydrology of the waterbody in question is required to project when contaminant concentrations and loadings will be the greatest. Once the contaminants are identified, the available BC- approved WQGs for each substance and each water use are

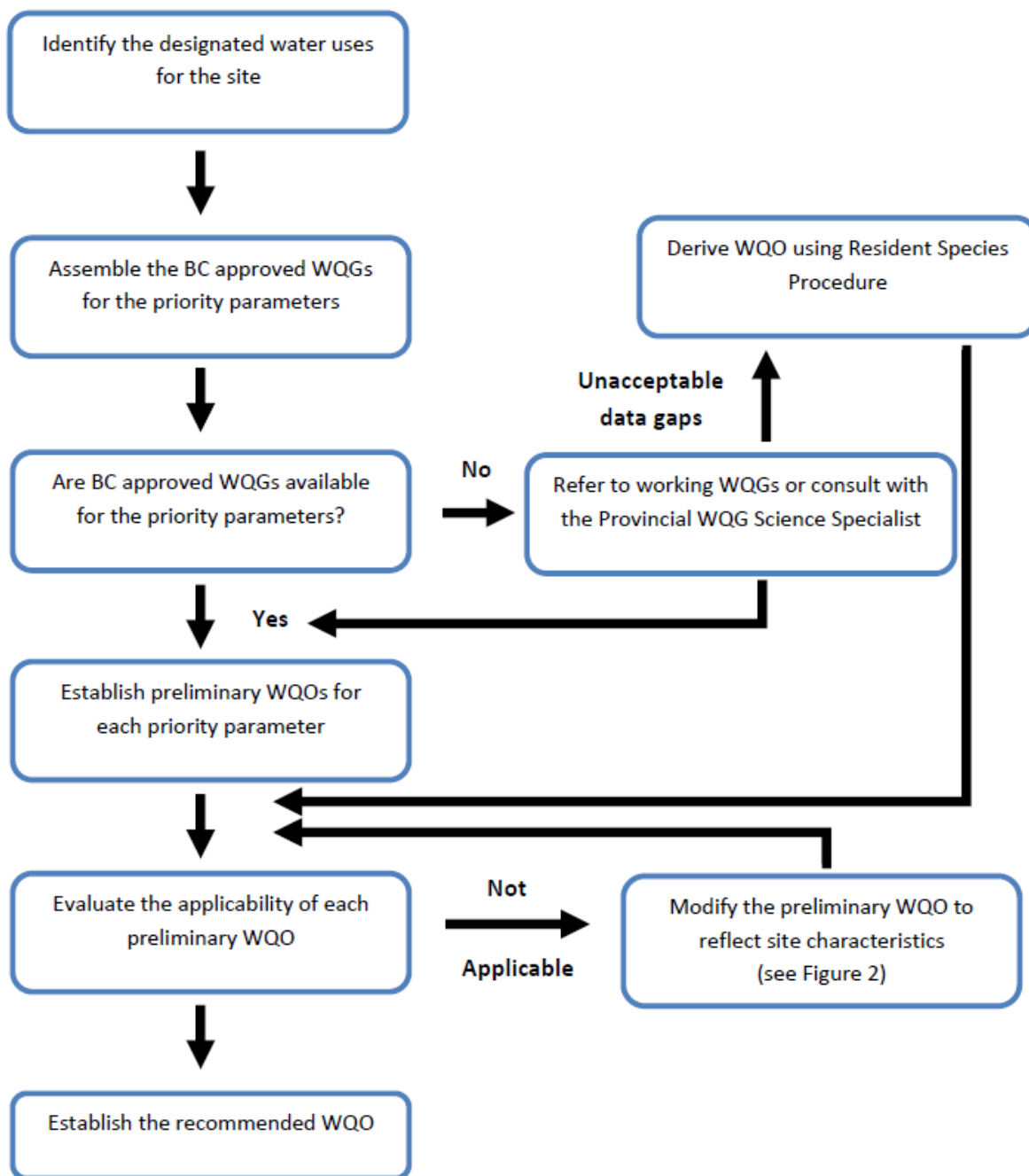


Figure 1. An overview of the process of deriving numerical water quality objectives in BC.

compiled, including any modifying factors required 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 (see Section 3.2).

To develop WQOs for a waterbody, knowledge of the following is required:

- BC-approved WQGs and their application. Guidelines provide, as much as possible, information on short-term (acute) and long-term (chronic) effects, persistence, accumulation in biota or sediment, antagonistic or synergistic effects with other substances, and environmental fate of substances.
- The existing and potential water quality of the waterbody.
- The temporal and spatial variability of water quality variables.
- The existing and potential aquatic life in the waterbody, including species, geographic distribution of species, life history or stage use (e.g., spawning, rearing, migration), the presence of rare or endangered species, and the importance of the aquatic life to man.
- The flow or circulation pattern of the waterbody, and its relation to the quality of water, sediments and aquatic life.
- The existing and potential loadings of contaminants from point and diffuse sources, and their relation to water movement and quality, including the behaviour of the contaminants in the local water.
- The existing and potential uses of the water.

The above points form the basis of the water quality assessment required to derive the preliminary WQOs (see details provided in Appendix 3). The water quality assessment can be based on existing data, new data generated specifically for the project, or a combination of both. It will establish the levels of water quality variables, including any ameliorating or confounding factors (e.g., hardness), which need to be considered when setting the preliminary WQOs. It is important to recognize any additional variables required to determine guideline levels for certain variables (e.g., pH and temperature for ammonia), and the amount of sampling required to determine certain levels (e.g., 5 weekly samples within 30 days for the calculation of average concentrations). A general format for the water quality assessment is

provided in Appendix 3. Additional guidance for designing a water quality monitoring program is provided in Cavanagh et al. (1998).

### **3.2 Determining Background Levels**

Once the water quality assessment has been completed, natural background levels for each variable can be determined. In this application, the term “background” refers to concentrations of substances not significantly altered by human land use. This can be pre-operational background (i.e., pristine conditions) which can be used as a benchmark to measure future changes against, or post-operational background, in which case upstream or other suitable reference sites will be required to determine if a particular land use activity is affecting water quality at the site in question. The data used to determine background levels should include measurements from “worse case scenarios”, such as low flow and high flow periods, when variable concentrations are likely to be elevated. To be consistent with other BC MOE policies and procedures (e.g., Contaminated Sites Regulation), the 95<sup>th</sup> percentile of available data is used to determine the upper limit of background concentrations. In some cases, it may be appropriate to examine background levels on a seasonal basis; for example, turbidity may be measured according to the clear and turbid-flow portions of the hydrograph (see Caux et al. 1997). Regional Environmental Impact Biologists in the BC MOE use their professional judgement to determine the appropriateness of the data used to calculate background levels.

It is important to be clear as to what background represents in a particular situation. If background refers to pristine, pre-operational conditions, a numerical value should be specified in the WQO technical report for each variable. If background refers to post-operational conditions, then a suitable reference site upstream of the test site should be identified and characterized in addition to the test site.

### **3.3 Establishing Preliminary Water Quality Objectives**

In most cases, the BC-approved WQGs provide an appropriate starting point for establishing site-specific WQOs. The first step is to assemble the WQGs for each of the designated water uses within the waterbody under consideration. If the WQGs are expressed

in terms of factors that influence toxicity, then the appropriate value(s) for the site should be determined. For example, the BC WQGs for manganese (average concentration), for the protection of freshwater aquatic life, are 0.7, 0.8, 1.0, 1.3, and 1.9 mg/L at a water hardness of 25, 50, 100, 150, and 300 mg/L, respectively. If the site under investigation has an average water hardness of 25 mg/L, then the lowest of these values, 0.7 mg/L, would be applicable and would be identified as the WQG for the protection of aquatic life. The WQGs for other substances and water uses would also be assembled at this stage of the process.

The next step is to establish a preliminary WQO. In general, the lowest of the WQGs for the designated uses of water at the site (i.e., the most sensitive) are adopted as the preliminary WQO for each priority contaminant. In doing so, you are selecting a level that will protect all designated uses of the water. For example, a site downstream of a molybdenum mine provides water for a variety of purposes including source drinking water, fish habitat, irrigation and livestock watering. The BC-approved WQGs for each of these water uses are 0.25, 2.0, and 0.05 mg/L, respectively. In this example, the recommended WQGs for irrigation and livestock watering, which is the lowest of the 3 WQGs, would be adopted as the preliminary WQO.

Once the preliminary WQO has been selected for each priority substance, its applicability to the site under consideration must be evaluated. This process is outlined in Figure 3. At least 4 factors must be considered in the evaluation of the preliminary WQO, including:

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



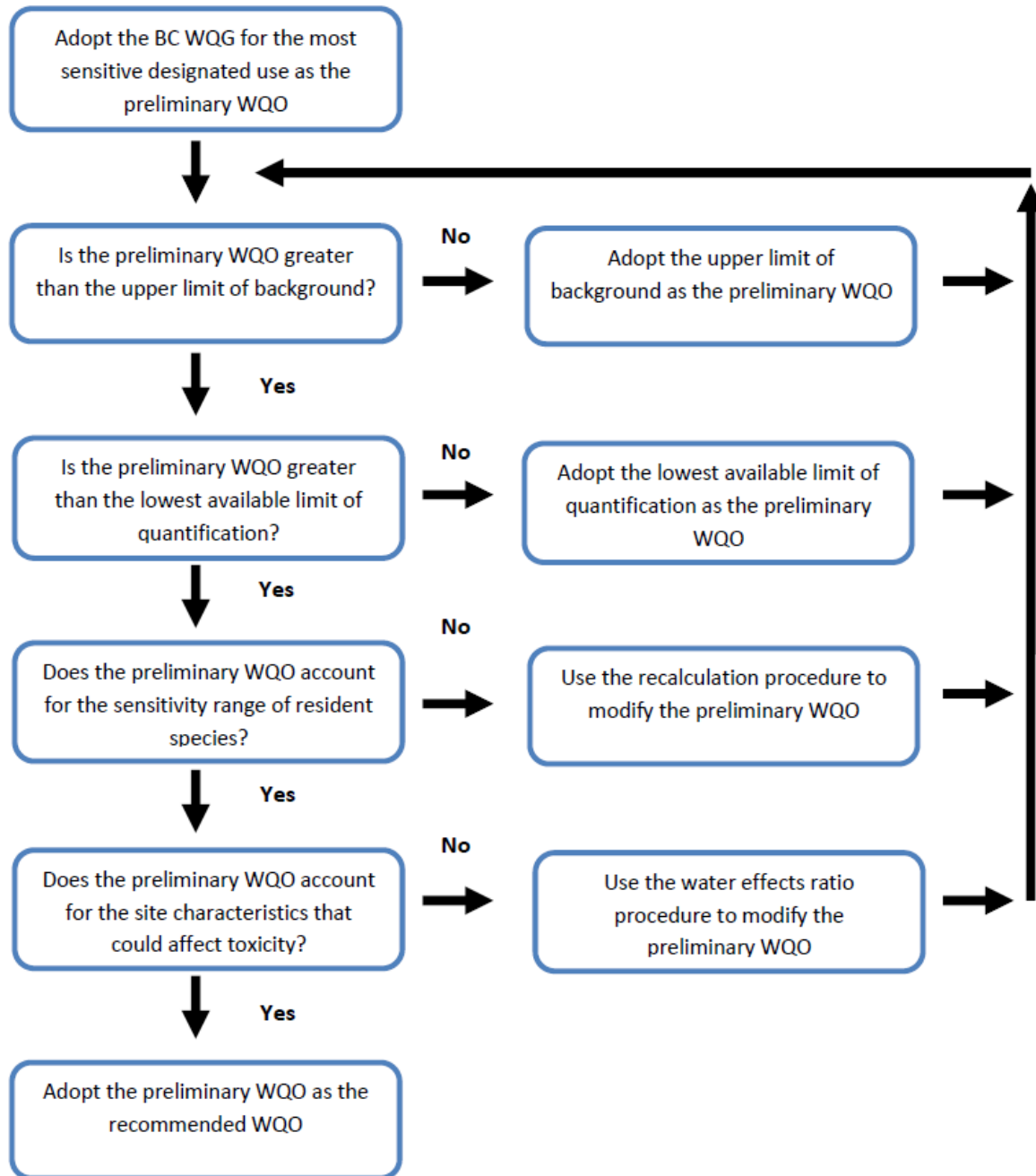


Figure 2. The recommended process for evaluating and modifying preliminary water quality objectives in BC.

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 preliminary WQO. 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. However, if historical data are not available, it may be possible to collect the necessary information at appropriate reference sites. In river systems, reference sites are generally established immediately upstream of known contaminant sources. However, a nearby stream system, that drains an area with similar geological 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. Similar methods (considering current and tides) would also be appropriate for selecting reference sites in lacustrine, estuarine, and marine systems.

Determination of natural background concentrations of water quality variables is complicated due to the inherent variability in water quality conditions. Water quality conditions in surface waters may vary both spatially (i.e., depth, cross-sectional, longitudinal, etc.) and temporally (i.e., daily, seasonal, annual). Therefore, sampling programs to establish baseline or background conditions must be designed to characterize this variability and the site-specific WQOs must 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.). For these variables, background levels may be expressed as a regression equation with confidence intervals (Valiela and Whitfield 1988).

Once the available data are compiled, they must be examined for outliers. For the purpose of assessing preliminary WQOs, the term background refers to the upper limit of background levels. This is the maximum level we would expect to measure a particular variable

at any time under natural conditions. It is important to be confident that the data being used to estimate background levels are actually real. Therefore, any outliers need to be further examined to determine if, in fact, they are true values and not the result of sampling or data management errors. When the validity of the data has been confirmed, the upper limit of background is determined by calculating the 95<sup>th</sup> percentile value. It is important to remember that background levels, in some cases, may need to be calculated on a seasonal basis depending on clear and turbid-flow periods.

### **3.4 Setting Water Quality Objective Levels**

At most sites, the BC-approved WQGs can be adopted directly as WQOs. Infrequently, the WQGs may require modification before they can be adapted 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. 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 the toxicity to aquatic life; or the waterbody may contain only a warm-water 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. In each of these situations, the development of site-adapted WQOs would be appropriate (e.g., water effects ratio procedure or recalculation procedure) to account for the sensitivities of resident species and/or the effect of site water characteristics on contaminant toxicity. The conditions justifying the development of WQOs, however, must be clearly demonstrated at the start of the process.

In rare cases, it may be necessary to develop WQOs on a site-specific basis, utilizing only site-specific data, particularly when a high level of accuracy in the resultant WQOs is required; for example, when insufficient toxicological data are available to develop generic WQGs for a particular substance. Alternatively, there may not be sufficient information available on the physical, chemical, and biological characteristics of the receiving water system to modify the BC-approved WQGs to consider site conditions. In each of these cases, additional information would be required in order to develop WQOs.

In BC, WQOs are usually based on the direct adoption of the BC-approved WQGs (Section 3.3.1) or the natural background levels (Section 3.3.2) at a particular site. If neither of these approaches is appropriate, WQGs can be adapted to the site using either the recalculation procedure (Section 3.3.4) or the water effect ratio procedure (Section 3.3.5). If conditions require a site-specific WQO, the resident species procedure can be employed (Section 3.3.6). Any variations in the procedures outlined here or application of new methods must be approved by the BC MOE prior to the development of WQOs.

#### **3.4.1 Adoption of Generic Water Quality Guidelines**

In BC, WQGs are developed to provide a high level of protection for designated water uses. For example, 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. In addition, WQGs are developed to be broadly applicable to surface water in BC; therefore, the BC-approved WQGs are likely to be appropriate for establishing WQOs at most sites in BC. If the preliminary WQO (i.e., the BC-approved WQG) is greater than the upper limit of background concentrations, then the preliminary WQO should be further evaluated to determine its applicability to the site under consideration (see Figure 2) and if all conditions are met, the preliminary WQO can be recommended as the WQO.

A thorough understanding of a specific WQG and its application is required before it can be proposed as a WQO. Several WQGs are dependent on other conditions at the site (e.g., pH, temperature, hardness) or are based on increases above background conditions (e.g., turbidity). The levels of any dependent variables should be established in the water quality assessment. If background is based on pre-operational conditions, numerical values for each WQO can be defined in the technical report. Numerical WQOs can also be defined for post-operational background conditions if the range of values is below the BC-approved WQGs for that variable. This may not be possible if the water quality assessment shows that the levels of water quality variables fluctuate considerably, in which case it may be necessary to calculate the appropriate WQO level for each sampling event. Whenever possible, however, a defined numerical WQO

should be established to ensure a clear understanding of the conditions required to protect the designated water uses at the site.

If the preliminary WQO is lower than the upper limit of background concentrations, 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 preliminary WQO (Section 3.3).

There are several circumstances under which the preliminary WQOs (i.e., the generic WQGs) would not be directly adopted as the WQO (see Figure 2). Specifically, modification of the generic WQG would be justified if the toxicity of a substance could be influenced by the unique conditions at the site. The toxicity of some metals is reduced by site-specific levels of hardness, pH, and dissolved organic carbon. For example, organic carbon in waters has the ability to bind some fractions of metals. Therefore, 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 and other factors such as UV radiation may also be important in evaluating the toxicity of metals and other substances that sorb to organic carbon (e.g., Brooks et al. 2007a; 2007b). Biogeochemistry and other factors which can change the bioavailability or speciation of substances must be considered (i.e. changes in pH, temperature and oxygen) when developing WQOs (see Appendix 2). It is also important to recognize that these modifying factors may change over time and this should be accounted for in the final WQO. Conversely, site-specific conditions may not be consistent with those under which the generic WQGs were derived (e.g., adequate dissolved oxygen in the lab vs. low dissolved oxygen levels at the site) resulting in an increase in toxicity of that substance. The applicability of the generic WQG to the site should be questioned in situations where such conditions occur.

The sensitivity of resident species is also an important consideration in the assessment of the preliminary WQO. Typically, BC 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 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. Once these factors have been considered, it can be determined if a modification of the BC-approved WQGs is required.

The following sections outline the procedures for developing site-adapted WQOs in BC. Further guidance is provided in Appendices 4 and 5.

### **3.4.2 Background Concentration Procedure**

Determination of the most appropriate method for establishing background concentrations requires consideration of a number of factors related to the waterbody 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 waterbodies, 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 periods (e.g., in areas affected by mining or urban development). In such cases, it may be necessary to identify nearby reference areas with similar geological, topographical, physiographical, and climatological features to define background levels of naturally occurring substances.

When the preliminary WQO is lower than the natural background concentration of the contaminant under consideration, it will be necessary to revise the preliminary WQO upward using the background concentration procedure. In this approach, the upper limits of natural background concentrations of a contaminant in water are determined (i.e. 95<sup>th</sup> percentile concentration) 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 should not be degraded, and as long as there is no change from background concentrations, there should be no harmful effects or danger to the aquatic ecosystem. This approach has been used most commonly to define WQOs for waterbodies in

Canada with good existing water quality, including several river systems (e.g., Dunn 1989; MacDonald and Smith 1990) and Burrard Inlet (Nijman and Swain 1989).

The background concentration approach is directly applicable to the development of site-specific WQOs for pristine waters within BC. In addition, 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 WQOs 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).

### **3.4.3 Analytical Limit of Quantification**

Monitoring to assess attainment of the preliminary WQOs is challenging when the preliminary WQO is lower than the best available analytical limit of quantification (i.e., the method detection limit or reportable detection limit) for that substance. The analytical limits of quantification that are typically achieved at Environment Canada's National Laboratory for Environmental Testing (Burlington, Ontario) can be used as the benchmarks for comparison to the preliminary WQOs. Alternatively, the analytical limits of quantification that are typically achieved by accredited laboratories in BC could be used if they are lower than those of the National Water Quality Laboratory. The analytical limits of quantification that are achieved in laboratory analyses must be below the level defined by the preliminary WQO, preferably by a factor of two or more (CCME 2003). If the preliminary WQO is lower than the analytical limit of quantification that is routinely achieved using the best available methods, it will be difficult to reliably evaluate the appropriateness of the preliminary WQO. In this case, analytical laboratories should be asked to refine the available methods to improve detection limits. A provisional WQO could be set at the achievable analytical level until the improved detection limit can be established.

### 3.4.4 Recalculation Procedure

Modification of the generic WQGs is justifiable at sites with atypical assemblages of aquatic organisms (i.e., the species that occur, or that potentially occur, at the site include only a portion of those represented in the complete toxicological data set). At these types of sites, the recalculation procedure may be used to derive site-adapted WQOs. Aquatic species that occur at the site include those taxonomic groups (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.

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. Guidance on proper biological data collection methods is provided in the BC MOE's *Freshwater Biological Sampling Manual* (Cavanagh et al. 1997) and *The Canadian Aquatic Biomonitoring Network Field Manual* (BC MOE 2009). When the biological survey at the site is complete, toxicological data on the taxonomic groups or life stages that are not expected to occur at the site should be eliminated from the toxicological data set used to derive the WQG for the variable of concern. This reduced data set is then examined to determine if the minimum data set requirements for deriving WQGs are met (see Meays 2012). If sufficient data are available, a site-adapted WQO can be calculated using the procedure outlined in the formal protocol for developing WQGs. If the minimum data requirements are not met, additional biological testing may be conducted to



obtain the necessary information. These tests would be performed on resident species or appropriate surrogate species in laboratory water.

Using this procedure, data on taxonomic groups that do not occur at the site under consideration are eliminated from the data set that was assembled to formulate the generic WQG. A site-adapted WQO is then calculated using the same method 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 provincial WQGs are met (Meays 2012). Otherwise, additional toxicity testing on resident species or appropriate indicator organisms 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 BC. When used in conjunction with the protocol for the derivation of WQGs for the protection of aquatic life (Meays 2012), the recalculation procedure provides a practical means of modifying the generic WQGs to reflect the sensitivities of the taxonomic groups 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 or taxonomic group represented in the complete toxicological database does not occur, or does not have the potential to 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 surrogate species. Therefore, it should be possible to derive the site-adapted WQOs for many substances.

Some 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. More specific guidance on applying the recalculation procedure is provided in Appendix 4.

### **3.4.5 Water Effect Ratio Procedure**

The water effect ratio (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 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 factors (such as suspended particulate matter) at a site can also affect the bioavailability of the substance under consideration. Water effect ratios are expected to appropriately take into account the synergistic, antagonistic, and additive effect of other constituents of the site water; therefore, consideration of the factors that could influence the toxicity and/or bioavailability of a substance at a site are likely to improve the applicability of the resultant WQO. The WER is used to account for natural conditions which may be influencing the toxicity of a substance on a site-specific basis; it is not to be based on levels of ameliorating factors that have been elevated by effluent discharges or human land use activities (e.g., where hardness levels have become artificially elevated due to mining activities). The following discussion provides an overview of the WER procedure. A full description of the proper methods for developing WERs is provided in US EPA (1994).

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. Indicator species can be resident species or acceptable non-resident species that are used as surrogates

for resident species. Typically, rainbow trout (*Onchorynchus mykiss*), fathead minnows (*Pimephales promelas*), the cladoceran *Ceriodaphnia dubia*, and the alga *Selenastrum capricornutum* are used to assess the influence of site water quality conditions on the toxicity of contaminants because they are easy to culture, widely available, and consistently generate reliable data (Willingham 1988; MacDonald et al. 1989). Moreover, they are representative of species that are typically found in BC. 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, the generic WQG would be divided by a factor of 2 to obtain the site-adapted value. Conversely, if a substance is half as toxic in site water as it is in laboratory water, the generic WQG would be multiplied by a factor of 2.

Toxicity data on at least 1 fish and 1 invertebrate species are required to calculate the geometric mean WER, which is then used to modify the generic WQG (US EPA 1994). The results of these bioassays are used to calculate a WER for each test as follows:

$$\text{WER} = \text{Site Water EC}_{10} \div \text{Laboratory Water EC}_{10}$$

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 is calculated. The geometric mean, rather than the arithmetic mean, is calculated because the distribution of the WERs is unknown (i.e., the WERs are not necessarily normally distributed). The final WER is then used to modify the generic guidelines, as follows:

$$\text{WQO} = \text{Preliminary WQO} \times \text{WER}$$

If the two ratios are not similar, then it is necessary to conduct additional paired indicator species bioassays, using laboratory and site water, to confirm or refute the results of the initial tests. If WERs are being determined for more than one contaminant at a site, one or more additional toxicity tests must be conducted at the end to demonstrate that the combination of all contaminants at their proposed new site-specific concentrations is

acceptable (USEPA 1994). It is important to recognize that WERs are determined on a site-specific basis and apply only to the site for which they are developed.

The WER procedure is likely to be directly applicable to the derivation of site-adapted WQOs in BC, particularly for contaminants 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 2002a; 2002b; DOE 1996; 2007a; 2007b; 2007c; 2007d; 2008). These methods provide a reliable basis for determining WERs for priority substances allowing for the modification of the generic WQGs for the protection of aquatic life. This type of information can also be used to derive WQOs on a site-specific basis, provided that the minimum data requirements identified in the WQG protocol (Meays 2012) have been met.

By explicitly considering the toxicity of a substance in the site water, the WER 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). Toxicity tests, in general, range from 96-hour acute tests to 28-day (or greater) chronic tests. 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). More specific guidance on applying the WER procedure is provided in Appendix 5.

### **3.4.6 Resident Species Procedure**

The derivation of site-specific WQOs is justified if the toxicological data used to derive the WQG does not adequately reflect the species composition at the site, and the water quality conditions at the site influence the toxicity of the variable of concern. The resident species procedure accounts for both of these factors. As the name implies, species found at the site in question are used in new, additional toxicity tests using site water to develop a WQO that is unique to that site.

This procedure involves the generation of a complete data set on the toxicity of the substance under consideration using site water and resident species. In accordance with the BC protocol for deriving water quality guidelines (Meays 2012), at least 6 species of aquatic organisms that are resident at the site must be represented in this data set, including 3 fish species, 2 invertebrate species, and 1 algae or aquatic vascular plant species. The site-specific toxicity data generated are used directly to establish the final WQOs for the substance at the site. In applying the resident species procedure, the BC protocol for developing WQGs (Meays 2012) must be followed.

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. Water quality objectives 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 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.

Due to the costs associated with the implementation of this procedure, the resident species procedure is likely to have only limited application in BC. Nevertheless, the procedure provides a consistent and reliable basis for deriving site-specific 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.

### **3.5 Approval Process**

Communication is an essential element in the WQO development process. BC MOE staff will discuss the need to develop WQOs with proponents and stakeholders to determine if it is warranted, especially where this requires the modification of generic WQGs. If any work (e.g., toxicity tests) required to support the development of WQOs is to be conducted by project proponents, it should be reviewed with BC MOE qualified professionals; this will reduce the risk of doing work incorrectly.

Water quality assessments and objectives are prepared by BC MOE regional operations staff. While proponents can contribute to this work, the BC MOE is responsible for producing the final report and approving the WQOs as Ministry policy. Draft reports are reviewed by BC MOE Headquarters staff to ensure provincial consistency, and the final drafts are then provided to stakeholders (e.g., other ministries and jurisdictions, First Nations, non-government organizations, industry, the public) for comments and input.

Once the report is finalized, it is signed off by the appropriate MOE Regional Operations office (e.g., Regional Manager, Environmental Protection Division) and forwarded to Headquarters for approval by the appropriate BC MOE executive (e.g., Assistant Deputy Minister, Environmental Sustainability Division and/or Environmental Protection Division). Once approved, WQOs constitute official BC MOE policy and are to be considered in any BC MOE decisions regarding the water quality of that waterbody.

### **3.6 Monitoring for Attainment of Water Quality Objectives**

Monitoring to assess attainment of the WQOs is an essential component of the overall environmental adaptive management process. Attainment monitoring is generally conducted within a year of establishing the WQOs to confirm that they are correct. Monitoring can then be conducted on a regular basis and within a time frame that makes sense in terms of available resources, activities within the watershed, and provincial reporting. Over time, regular attainment monitoring will help identify any trends in water quality and help guide resource management decisions. If results show changes in water quality over time (either improving or declining), it may be necessary to revise the WQOs to reflect the level of protection needed for a waterbody. Finally, attainment monitoring results are valuable for reporting on conditions within individual watersheds, and contribute to provincial reporting on water quality.

Each WQO report must include a proposed water quality monitoring program to determine if the WQOs are being attained in the future. The water quality monitoring program should include:

- site locations;
- frequency of monitoring;
- variables to monitor, and;
- the sampling period.

Monitoring sites should be located where the WQOs are likely to be exceeded. The frequency of sampling will be determined, to a large degree, from the quality and quantity of data required to satisfy the WQOs themselves. Allowances must be made for the type of statistic required (e.g., maximum, mean, median, 90<sup>th</sup> percentile) which in itself defines the minimum frequency (e.g., mean of 5 weekly samples collected in a 30-day period). The time of year the sampling occurs in is determined by:

- the time of year the WQO applies to (e.g., recreation season), and;
- the time(s) during the year when the WQO is likely to be exceeded.

The monitoring program should include all variables for which WQOs have been developed, and any variables which the WQOs are dependent on (e.g., pH, temperature, etc.).

A quality assurance component is required for the monitoring program and should include submission of blanks, replicates, and standard reference materials.

For average WQOs, it is important to recognize that the WQO may be attained even though individual sampling results exceed the WQO value within the 30-day sampling period (Figure 4).

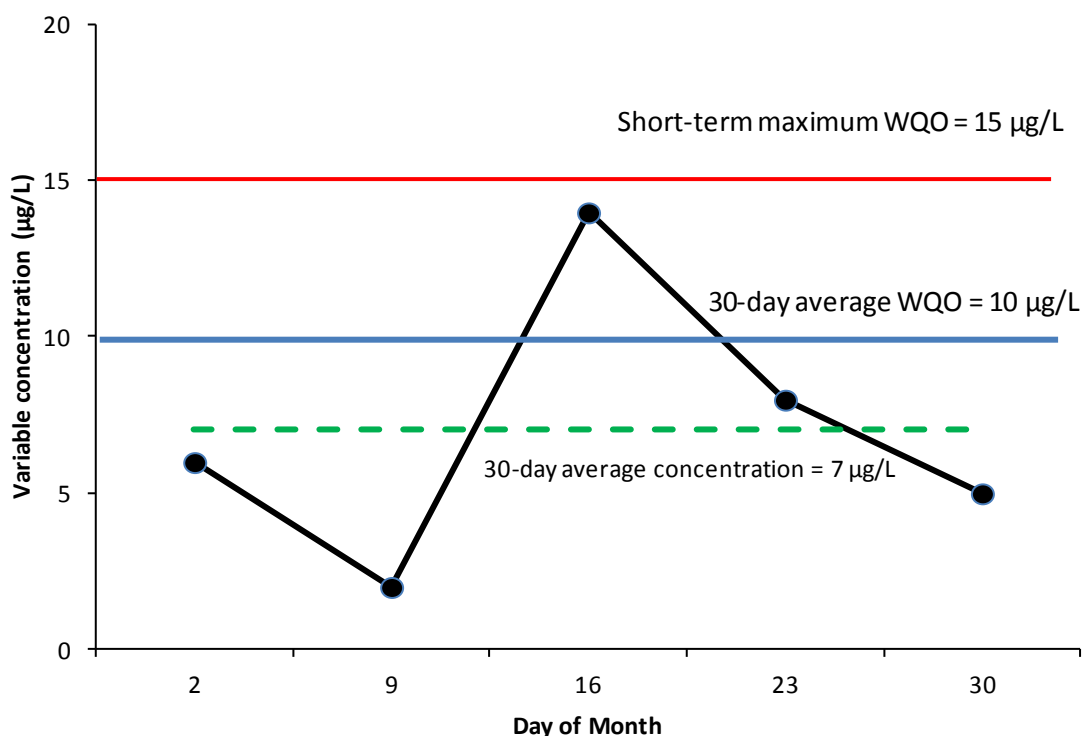


Figure 3. A generic example of the application of water quality objectives where the red line represents the short-term maximum water quality objective (15 µg/L) and the blue line represents the long-term average water quality objective (10 µg/L). The black line represents the monitoring results over a 30-day period. Note that an individual measured concentration exceeds the average objective, but the average concentration over the 30-day period calculated from the results (represented with the green dashed line) is below the average WQO value.



## **4.0 Future Directions**

### **4.1 Biomonitoring**

British Columbia, like many other jurisdictions, has traditionally addressed point-source discharges of contamination to aquatic ecosystems with a focus on water chemistry. This approach provides a fairly simple result to be measured against set guidelines for various water uses to determine the suitability of the water for that use. In recent years, there has been more emphasis on the management of non-point source discharges which can be difficult to assess in terms of the sources and cumulative impacts. While monitoring of chemical variables is an important component of water quality management, it provides only a snapshot in time which is dependent on a number of conditions at the time of sampling. A more complete environmental assessment of a given waterbody requires consideration of the biological components of the ecosystem in addition to the chemical and physical components.

Biomonitoring methods use living organisms to provide insight into environmental conditions. Several different biotic groups have been used in biomonitoring, but one of the most useful groups are the benthic (bottom-dwelling) invertebrates, which include mayflies, freshwater shrimps, stoneflies, caddis flies and worms.

Benthic invertebrates are ideal for use in bioassessment for a number of reasons:

- they are sedentary, and thus constantly exposed to the effects of pollution;
- they are reasonably long-lived (1-3 years in north-temperate waters) so the effects of environmental stressors can be time-integrated; and
- they occur in high diversity, so many different species can potentially react to many different types of impacts.

In BC, and across Canada, the biological monitoring of freshwater ecosystems is being coordinated through Environment Canada's CABIN (Canadian Aquatic Biomonitoring Network) program. The key to assessing the condition of waterways through CABIN is the use of the Reference Condition Approach (RCA). Reference sites are established based on minimal impacts by human use, and provide users with a baseline for assessing potentially impaired sites. The reference sites represent as many different geographic regions and stream sizes as

possible and are used to establish the type of community of organisms expected to occur in the range of natural habitat types present in regions covered by the CABIN network. Once the reference condition has been established, sites suspected of being impaired are sampled. Differences between the organisms found at the reference sites and the test-site indicate the extent, if any, of impairment at the site.

Biomonitoring provides a direct and effective measure of the integrity of a waterbody through the status of its living systems. The value in biomonitoring is that it integrates all conditions and impacts over the recent past and can improve our understanding of the cumulative effects of the range of stressors present. These stressors may be chemical (contaminants in water or sediment) and/or physical (habitat disturbance) in nature. In an aquatic environment, water quality refers to the quality of the entire aquatic ecosystem: the water, the bottom sediments, and the organisms. It therefore makes sense to include the products of the system (i.e., the living organisms) to assess the impacts of land and water uses associated with the waterbody. Biological assessments provide reasonable outcome-based performance measures that allow managers to adjust operational plans before impacts occur. Therefore, the inclusion of biological WQOs (e.g., RCA scores) will increase the validity and effectiveness of the final WQOs for a waterbody.

#### **4.2 Ecoregional Approach to Water Quality Objectives**

The development of WQOs requires a certain amount of resources and establishing WQOs for a number of individual waterbodies may be challenging. To address this problem, the Vancouver Island Region of the BC MOE's Environmental Protection Division has implemented an ecoregion approach to develop WQOs which apply broadly over a large geographic area. Ecoregions are land areas with similar climate, geology, and hydrology. The ecoregion approach for WQOs assumes that fundamental baseline water quality is similar in all streams and lakes throughout each ecoregion. Water quality objectives are developed for representative lakes and streams for each ecoregion and then applied to the remaining lake and streams watersheds within that ecoregion. Over time, priority watersheds within each ecoregion are monitored to verify that validity of the WQOs and to determine if the WQOs are

being met for individual watersheds. This is an approach that warrants further consideration for application on a provincial basis. A complete description of the Vancouver Island ecoregion approach is provided in Deniseger et al. (2009).

#### **4.3 Emerging Technologies**

Science is continuously evolving providing resource managers with improved tools and approaches to protect aquatic resources. The biotic ligand model (BLM) is one such tool that has received significant interest in recent years. The BLM is an approach that evaluates the manner in which water chemistry affects the speciation and biological availability of metals in aquatic systems. A key component of BLMs is the site of action of toxicity on an organism, known as the biotic ligand (e.g., gill tissue). The BLM is used to predict the degree of metal binding at the site of action, with the level of accumulation of the metal related to a toxicological response. The BLM takes into account the characteristics of the site water to predict the response of an organism, which reflects the current understanding of both the chemistry of the ambient water and the physiology of the organism (Paquin et al. 2002). Biotic ligand models are metal and organism-specific, and the level of development varies for each. One limitation is that BLMs have largely been based on acute toxicity and the need for chronic toxicity-based BLMs has been recognized (Niyogi and Wood 2004). Further review of the BLM approach is provided in Paquin et al. (2002), Niyogi and Wood (2004) and Van Genderen et al. (2007).

The field of ecotoxicogenomics (the application of omic profiling methods to problems in environmental toxicology and ecotoxicology) is showing great potential for use in environmental assessment and monitoring (Bundy et al. 2009), and presents important opportunities to improve our understanding of the molecular mechanisms underlying toxic responses to environmental contaminants (Snape et al. 2004). Some of the likely uses include (i) as a screening tool for chemicals that might cause adverse chronic effects; and (ii) as a tool to determine the mode of action of a toxicant, at the metabolic level, as part of a comprehensive

risk assessment (Bundy et al. 2009). There are several key questions that ecotoxicogenomics can be used to address, including:

- Which genes are turned on, and what do they do?
- Is there variation in gene expression in response to environmental change, and is this variation adaptive?
- What are the ecosystem-, community-, and population-level consequences of the molecular transformations performed by these genes (Snape et al. 2004)?

While several challenges must be addressed before this technology can be broadly applied (Ankley et al. 2006; Van Aggelen et al. 2009), the potential use of ecotoxicogenomics in future WQO (and WQG) development is encouraging.

## 5.0 Summary

In BC, WQGs are designed to have broad application on a provincial scale. Where the guidelines are not appropriate (either under-protective or over-protective), they can be modified as WQOs with the goal of protecting or enhancing the existing water quality. The framework for developing numerical WQOs presented here for application in BC includes three general approaches: adoption of generic water quality guidelines; modification of generic water quality guidelines to consider site-specific factors (i.e., site-adapted WQOs); and derivation of site-specific WQOs. This document presents an update of the BC MOE's *Methods for Deriving Site-Specific Water Quality Objectives in British Columbia and Yukon* (MacDonald 1997) and incorporates key aspects of the document *Principles for Preparing Water Quality Objectives in British Columbia* (BC MOE 1986).

In this update, emphasis is placed on certain aspects of the WQO development process including:

- Validation and verification that the development of WQOs is actually warranted;
- Communication between BC MOE representatives and development project proponents and stakeholders to ensure appropriate background studies are done and that water quality assessments and objectives are being developed correctly and according to BC MOE policies and procedures; and
- Proper application of the methods used to modify the generic WQGs.

Once approved, WQOs become part of a growing network of standards that can be used to help assess and report on provincial water quality. Each Water Quality Assessment and Objectives report includes a recommended monitoring program to determine if the WQOs are being attained. Regular attainment monitoring should be part of the regional water quality monitoring plan with the frequency of monitoring required determined by the specifics of the WQO report. In addition to reporting on water quality, regular attainment monitoring will show if any refinements to the approved WQOs are required over time.

The framework and procedures described in this document are intended to provide a cost-effective basis for deriving WQOs that are protective of aquatic resources in BC.

Nonetheless, these tools have certain limitations which must be considered during the implementation process, including:

- The WQOs developed using the recommended framework and procedures represent levels or concentrations that are predicted to protect the designated uses of receiving water systems. However, there are a number of uncertainties in the derivation process which could influence the predictive ability of the WQOs. For this reason, environmental effects monitoring programs (e.g., biomonitoring) should be implemented to determine if the WQOs are effectively protecting water uses. The results of such monitoring programs should be used to adjust the WQOs, if necessary. Monitoring programs to assess the level of attainment with the WQOs are also required.
- The WERs derived using the WER procedure are directly applicable to the conditions represented during toxicity testing. If water sampling occurs when the WERs are likely to be the lowest or if such conditions are simulated, then the resultant WQOs will be protective of aquatic life under a wide range of conditions. However, if the most sensitive conditions are not appropriately identified, then sensitive aquatic organisms could be at risk during certain portions of the year. Therefore, the results of subsequent monitoring activities (e.g., environmental effects monitoring) should be used to determine if the WQOs are adequately protecting designated water uses. Importantly, the WERs must be re-evaluated if the characteristics of wastewater discharges change significantly.
- The WQOs for the protection of aquatic life derived using the recommended framework and procedures are toxicity-based. These WQOs do not consider the potential for bioaccumulation or biomagnification, nor the associated effects of bioaccumulation or biomagnification on consumers of aquatic organisms (i.e., humans and wildlife). For this reason, bioaccumulation- and biomagnification-based WQOs will require special consideration on a site-specific basis as general WQO development methods for these substances do not exist.

- Compliance with the WQOs in receiving water systems does not relieve wastewater dischargers from obligations associated with other environmental legislation (e.g., *Environmental Management Act, Fisheries Act, Canadian Environmental Protection Act*).
- The procedures recommended in this document generally apply to single chemicals and single wastewater discharges. While these procedures can be applied to more complicated scenarios (e.g., mixtures of contaminants), more sophisticated experimental designs will be required to address such situations. In addition, the BCMOE will need to investigate or implement techniques for allocating the available assimilative capacity of receiving water systems to various user groups, while still accommodating the needs of future generations.

## References

- Alabaster, J.S. and Lloyd, R. 1984. Water quality criteria for freshwater fish. 2nd edition. Food and Agriculture Organization of the United Nations. 361 pp.
- Alexander, M. 1980. Biodegradation of toxic chemicals in water and soil. In Dynamics, Exposure and Hazard Assessment of Toxic Chemicals. R. Haque (ed.). Ann Arbor Science Publ., Inc., Ann Arbor, Michigan. pp. 179-190.
- Ankley, G.T., Daston, G.P., Degitz, S.J., Denslow, N.D., Hoke, R.A., Kennedy, S.W., Miracle, A.L., Perkins, E.J., Snape, J., Tillitt, D.E., Tyler, C.R., and Versteeg, D. Toxicogenomics in regulatory ecotoxicology. Environ. Sci. Technol., 40(13): 4055-4065.
- ASTM (American Society for Testing and Materials). 2004. Standard guide for conducting *Daphnia magna* life-cycle toxicity tests. E 1193-97. In: Annual Book of ASTM Standards. Volume 11.06. West Conshohoken, Pennsylvania.
- ASTM (American Society for Testing and Materials). 2007a. Standard guide for conducting acute toxicity tests with fishes, macroinvertebrates, and amphibians. E 729-96. In: Annual Book of ASTM Standards. Volume 11.06. West Conshohoken, Pennsylvania.
- ASTM (American Society for Testing and Materials). 2007b. Standard guide for conducting static toxicity tests with microalgae. E 1218-04e1. In: Annual Book of ASTM Standards. Volume 11.06. West Conshohoken, Pennsylvania.
- Babich, H. and Stotzky, G. 1983. Influence of chemical speciation on the toxicity of heavy metals to the microbiota. In Aquatic Toxicology. J.O. Nriagu (ed.). John Wiley & Sons, Inc., New York. pp. 1-46.
- BC DLFWR (British Columbia Department of Lands, Forests, and Water Resources). 1974. Report on pollution control objectives for the chemical and petroleum industries of British Columbia. Water Resources Services, Victoria, BC.
- BC MOE (British Columbia Ministry of Environment). 1975a. Report on pollution control objectives for municipal type waste discharges in British Columbia. Water Management Branch, Victoria, BC.
- BC MOE (British Columbia Ministry of Environment). 1975b. Report on pollution control objectives for food processing, agriculturally oriented, and other miscellaneous industries of British Columbia. Water Management Branch, Victoria, BC.
- BC MOE (British Columbia Ministry of Environment). 1977. Pollution control objectives for the forest industry of British Columbia. Pollution Control Board, Victoria, BC.
- BC MOE (British Columbia Ministry of Environment). 1979. Pollution control objectives for the mining, smelting, and related industries of British Columbia. Pollution Control Board, Victoria, BC.



- BC MOE (British Columbia Ministry of Environment). 1986. Principles for preparing water quality objectives in British Columbia. Resource Quality Section. Water Management Branch. Victoria, BC. Available at:  
<http://www.env.gov.bc.ca/wat/wq/BCguidelines/principles.html>
- BC MOE (British Columbia Ministry of Environment). 1996. Developing water quality objectives – a user’s guide. Water Quality Branch, Victoria, BC. Available at:  
[http://www.env.gov.bc.ca/wat/wq/BCguidelines/wq\\_ob\\_user\\_guide/usersguide.html](http://www.env.gov.bc.ca/wat/wq/BCguidelines/wq_ob_user_guide/usersguide.html)
- BC MOE (British Columbia Ministry of Environment). 2003. British Columbia field sampling manual. Water, Air and Climate Change Branch. Victoria, BC. Available at:  
[http://www.env.gov.bc.ca/epd/wamr/labsys/field\\_man\\_pdfs/fld\\_man\\_03.pdf](http://www.env.gov.bc.ca/epd/wamr/labsys/field_man_pdfs/fld_man_03.pdf)
- BC MOE (British Columbia Ministry of Environment). 2009. The Canadian aquatic biomonitoring network field manual. BC Ministry of Environment, Science & Information Branch. Available at:  
[http://www.ilmb.gov.bc.ca/risc/pubs/aquatic/cabin/CABIN\\_field\\_manual.pdf](http://www.ilmb.gov.bc.ca/risc/pubs/aquatic/cabin/CABIN_field_manual.pdf)
- British Columbia Office of the Auditor General. 1982. Report of the Auditor General for the year ended 31 March 1981. Province of British Columbia, Office of the Auditor General. Available online at: <http://www.bcauditor.com/pubs/1981/annual/report-auditor-general-1981>
- Borgmann, U. 1983. Metal speciation and toxicity of free metal ions to aquatic biota. In Aquatic Toxicology. J.O. Nriagu (ed.). John Wiley & Sons, New York. pp. 47-72.
- Bowen, H.J.M. 1979. Environmental Chemistry of the Elements. Academic Press Inc., New York. p. 14.
- Brooks, M.L., Meyer, J.S., and McKnight, D.M. 2007a. Photooxidation of wetland and riverine dissolved organic matter: altered copper complexation and organic composition. *Hydrobiologia*, 579: 95-113.
- Brooks, M.L., Meyer, J.S., and Boese, C.J. 2007b. Toxicity of copper to larval *Pimephales promelas* in the presence of photodegraded natural dissolved organic matter. *Canadian Journal of Fisheries and Aquatic Sciences*, 64: 391-401.
- Bundy, J.G., Davey, M.P., and Viant, M.R. 2009. Environmental metabolomics: a critical review and future perspectives. *Metabolomics*, 5: 3-21.
- CCME (Canadian Council of Ministers of the Environment). 2003. 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.
- CCREM (Canadian Council of Resource and Environment Ministers). 1987. Canadian water quality guidelines. Task Force on Water Quality Guidelines. Ottawa, Ontario.

- Cavanagh, N., Nordin, R.N., and Warrington, P.D. 1997. Freshwater biological sampling manual. BC Ministry of Environment, Lands and Parks, Water Management Branch. Available at:  
<http://ilmbwww.gov.bc.ca/risc/pubs/aquatic/freshwaterbio/assets/freshwaterbio.pdf>
- Cavanagh, N., Nordin, R.N., Pommen, L.W., and Swain, L.G. 1998. Guidelines for designing and implementing a water quality monitoring program in British Columbia. BC Ministry of Environment, Lands and Parks, Water Management Branch. Available at:  
<http://ilmbwww.gov.bc.ca/risc/pubs/aquatic/design/index.htm>
- Connell, D.W. and Miller, G.J. 1984. Chemistry and ecotoxicology of pollution. John Wiley & Sons, New York. 444 pp.
- Deniseger, J., Epps, D., Barlak, R., and Swain, L. 2009. Use of the ecoregion approach to setting water quality objective in the Vancouver Island Region, British Columbia Ministry of Environment. Available online at: <http://www.env.gov.bc.ca/wat/wq/objectives/eco-vanc-island/ecoregion-report.pdf>.
- DOE (Environment Canada). 1996. Biological test method: Acute lethality test using *Daphnia* spp. Report EPS 1/RM/11. Environmental Protection, Conservation and Protection. Ottawa, Ontario.
- DOE (Environment Canada). 1997a. Biological test method: Test for survival and growth in sediment using the freshwater amphipod *Hyalella azteca*. Report EPS 1/RM/33. Environmental Protection, Conservation and Protection. Ottawa, Ontario.
- DOE (Environment Canada). 1997b. Biological test method: Test for survival and growth in sediment using larvae of freshwater midges (*Chironomus tentans* or *Chironomus riparius*). Report EPS 1/RM/32. Environmental Protection, Conservation and Protection. Ottawa, Ontario.
- DOE (Environment Canada). 2000a. Biological test method: Acute lethality test using threespine stickleback. Report EPS 1/RM/11. Environmental Protection, Conservation and Protection. Ottawa, Ontario.
- DOE (Environment Canada). 2000b. Reference method for determining acute lethality of effluents to *Daphnia magna*. Report EPS 1/RM/14. Environmental Protection, Conservation and Protection. Ottawa, Ontario.
- DOE (Environment Canada). 2007a. Biological test method: Acute lethality test using rainbow trout. Report EPS 1/RM/9. Environmental Protection, Conservation and Protection. Ottawa, Ontario.
- DOE (Environment Canada). 2007b. Reference method for determining acute lethality of effluents to rainbow trout. Report EPS 1/RM/13. Environmental Protection, Conservation and Protection. Ottawa, Ontario.

- DOE (Environment Canada). 2007c. Biological test method: Test of reproduction and survival using the cladoceran, *Ceriodaphnia dubia*. Report EPS 1/RM/21. Environmental Protection, Conservation and Protection. Ottawa, Ontario.
- DOE (Environment Canada). 2007d. Biological test method: Growth inhibition test using the freshwater alga (*Selenastrum capricornutum*). Report EPS 1/RM/25. Environmental Protection, Conservation and Protection. Ottawa, Ontario.
- DOE (Environment Canada). 2008. Biological test method: Test of larval growth and survival using fathead minnows. Report EPS 1/RM/22. Environmental Protection, Conservation and Protection. Ottawa, Ontario.
- Drever, J.I. 1982. The Geochemistry of Natural Waters. Prentice-Hall, Englewood Cliffs, New Jersey. 388 pp.
- Duffus, J.H. 1980. Environmental toxicology. Edward Arnold (Publishers) Ltd., London. pp. 105-107.
- Dunn, G.W. 1989. An approach used to establish site-specific water quality indicators on interprovincial streams. Proceedings of the CCME Workshop on the Development of Water Quality Objectives. Canadian Council of Ministers of the Environment. Ottawa, Canada.
- Eichenberger, B.A. and Chen, K.Y. 1982. Origin and nature of selected inorganic constituents in natural waters. *In* Water Analysis. Vol. 1. Inorganic Species. Part I. R.A. Minear and L.H. Keith (eds.). Academic Press, Inc., New York. pp. 1-54.
- ENSR (ENSR Consulting and Engineering). 1995. Development of site-specific water quality criteria for copper in the Upper Clark Fork River. Phase I and II Program Testing Results Final Report. Fort Collins, Colorado.
- ENSR (ENSR Consulting and Engineering). 1996. Development of site-specific water quality criteria for copper in the Upper Clark Fork River. Phase III WER Program, Testing Results Final Report. Fort Collins, Colorado.
- Faust, S.D. and Aly, D.M. 1981. Chemistry of natural waters. Ann Arbor Sci. Publ. Inc., Ann Arbor, Michigan. 400 pp.
- Golterman, H.L. 1975. Physiological limnology. An approach to the physiology of lake ecosystems. Elsevier Scientific Publ. Co., Amsterdam, The Netherlands. 489 pp.
- Golterman, H.L., Sly, P.G. and Thomas, R.L. 1983. Study of the relationship between water quality and sediment transport. United Nations Educational, Scientific and Cultural Organization, Paris, France. 231 pp.
- Hamaker, J.W. 1972. *In* Organic chemicals in the soil environment. C.A.I. Goring and J.W. Hamaker (eds.). Marcel Dekker, New York. pp. 341-397. (Cited in Spencer and Farmer 1980).

- Hart, B.T. 1974. A compilation of Australian water quality criteria. Australian Water Resources Council, Department of the Environment and Conservation, Canberra, Australia. Tech. Pap. No. 7. Res. Proj. No. 71/36. 187 pp.
- Hart, J. L. 1973. Pacific fishes of Canada. Bulletin 180. Fisheries Research Board of Canada. Ottawa, Ontario. 740 pp.
- Hem, J.D. 1985. Study and Interpretation of the Chemical characteristics of natural water. 3rd edition. Water Supply Paper 2254. U.S. Geological Survey, Alexandria, Virginia. 263 pp.
- Horne, R.A. 1978. The chemistry of our environment. John Wiley & Sons, New York. pp. 235-301.
- Horowitz, A.J. 1985. A primer on trace metal-sediment chemistry. U.S. Geological Survey Water Supply Paper 2277. U.S. Geological Survey, Alexandria, Virginia. 67 pp.
- Houston, A.H. 1982. Thermal effects upon fishes. Associate Committee on Scientific Criteria for Environmental Quality. National Research Council of Canada. Ottawa, Ontario. NRCC No. 18566.
- Hynes, H.B.N. 1970. The Ecology of running waters. University of Toronto Press, Toronto, Ontario. 555 pp.
- Ingersoll, C. G., Brumbaugh, W. G., Farag, A. M., La Point T. W., and Woodward, D. F. 1992. Milltown Endangerment Assessment Project: Effects of metal-contaminated sediment, water, and diet on aquatic organisms. National Fisheries Contaminant Research Center. US Fish and Wildlife Service. Columbia, Missouri.
- IJC. 1978. Annual Report to the International Joint Commission by the Great Lakes Research Advisory Board, Windsor, Ontario. 64 pp.
- Kranck, K. 1980. Sedimentation processes in the sea. *In* The Hand book of Environmental Chemistry. Vol. 2. Part A. Reactions and Processes. O. Hutzinger (ed.). Springer-verlag, Berlin/Heidelberg, Germany. pp. 62-75.
- Laxen, D.P.H. 1983. The chemistry of metal pollutants in water. *In* Pollution: Causes, Effects and Controls. 1983. R.M. Harrison (ed.). R. Soc. Chem., Burlington House, London. pp. 104-123.
- Leckie, J. O. and Davis, J. A. 1979. Aqueous environmental chemistry of copper. *In* Copper in the Environment. Part 1: Ecological Cycling. J.O. Nriagu (Ed.). Wiley and Sons. Toronto, Ontario. pp. 89-121.
- Lee, G.F. and Jones, R.A. 1983. Translation of laboratory results to field conditions: the role of aquatic chemistry in assessing toxicity. *In* Aquatic Toxicology and Hazard Assessment. 6th Symp., ASTM Spec. Tech. Publ. 802. W.E. Bishop, R.D. Cardwell and B.B. Heidolph (eds.). American Society for Testing and Materials, Philadelphia, Pennsylvania. pp. 328-349.

- Leland, H.V. and Kuwabara, J.S. 1985. Trace metals. *In* Fundamentals of Aquatic Toxicology. Methods and Applications. G.M. Rand and S.R. Petrocelli (eds.). McGraw-Hill International Book Co., New York. pp. 374-415.
- Macan, T.T. 1974. Freshwater ecology. Longman Group Ltd., London. 343 pp.
- MacDonald, D.D. 1997. Methods for deriving site-specific water quality objectives in British Columbia and Yukon. British Columbia Ministry of Environment.
- MacDonald, D.D., Fidler, L.E., and Valiela, D. 1987. Site-specific water quality criteria for fish and aquatic life in the Canadian portion of the Flathead River basin: Nitrate, nitrite, and ammonia. Water Quality Branch, Environment Canada, Vancouver, BC.
- MacDonald, D.D., Willingham, W.T., Parrish, L.P., Rodriguez, G.J., Lazorchak, J. M., and Love J.W. 1989. Using in situ bioassays as a basis for the development of water quality objectives: A case study of the Arkansas River. Presented at the 1989 Workshop on the Derivation and Use of Water Quality Objectives. Halifax, Nova Scotia.
- MacDonald, D.D. and Smith, S.L. 1990. A strategy approach to the development and implementation of environmental quality objectives in the territorial portion of the Slave River Basin. Report prepared for the Water Resources Division, Indian and Northern Affairs Canada. Yellowknife, Northwest Territories.
- Mackay, D. 1980. Solubility, partition coefficients, volatility, and evaporation rates. *In* The Handbook of Environmental chemistry. Vol. 2. Part A. Reactions and Processes. O. Hutzinger (ed.). Springer-verlag, Berlin/Heidelberg, Germany. 307 pp.
- Mackay, D. 1981. Environmental and laboratory rates of volatilization of toxic chemicals from water. *In* Hazard Assessment of Chemicals. Current Developments. Vol.1. J. Saxena and F. Fisher (eds.). Academic Press, New York. pp. 303-322.
- Mackay, D. and Leinonen, P.J. 1975. Rate of evaporation of low solubility contaminants from water bodies to atmosphere. *Environ. Sci. Technol.* 9:1178-1180.
- Mackay, D., Shiu, W.Y., and Sutherland, R.J. 1980. Estimating volatilization and water column diffusion rates of hydrophobic contaminants. *In* Dynamics, Exposure and Hazard Assessment of Toxic Chemicals. R. Hague (ed.). Ann Arbor Science Publ., Inc., Ann Arbor, Michigan. pp. 127-142.
- Mackay, D. and Paterson, S. 1982. Fugacity revisited. The fugacity approach to environmental transport. *Environ. Sci. Technol.* 16: 654A-660A.
- Mackay, D. and Paterson, S. 1984. Spatial concentration distributions. *Environ. Sci. Technol.* 17: 207A-214A.
- Matthess, G. and Harvey, J.C. 1982. The properties of groundwater. John Wiley & Sons, Inc., New York. 406 pp.

- McNeely, R.N., Neimanis, P., and Dwyer, L. 1979. Water quality sourcebook. A guide to water quality parameters. Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa.
- McPhail, J.D. 2007. The freshwater fishes of British Columbia. University of Alberta Press, Edmonton, AB.
- McPhail, J.D. and Lindsey, C.C. 1970. Freshwater fishes of northwestern Canada and Alaska. Fisheries Research Board of Canada. Bulletin 173.
- Meays, C.L. 2012. Derivation of water quality criteria to protect aquatic life in British Columbia. British Columbia Ministry of Environment, Science & Information Branch, Victoria, BC. Available at: <http://www.env.gov.bc.ca/wat/wq/pdf/wq-derivation.pdf>.
- Mill, T. 1980. Data needed to predict the environmental fate of organic chemicals. *In* Dynamics, Exposure and Hazard Assessment of Toxic Chemicals. R. Hague (ed.). Ann Arbor Science Publ., Inc., Ann Arbor; Michigan. pp. 297-322.
- Moore, J.W. and Ramamoorthy, S. 1984. Organic chemicals in natural waters. Applied Monitoring and Impact Assessment. Springer-Verlag, New York Inc., New York. p. 11.
- Mullins, T. 1977. The chemistry of water pollution. *In* Environmental Chemistry. J.O. Bockris (ed.). Plenum Press, New York. pp. 331-400.
- Nagpal, N.K. 1997. Water quality guidelines for zinc. Prepared for the CCME Task Force on Environmental Quality Guidelines. British Columbia Ministry of Environment, Lands and Parks, Victoria, BC. Available at: <http://www.env.gov.bc.ca/wat/wq/BCguidelines/zinc/zinctech.pdf>
- Neely, W.B. and Blau, G.E. 1985a. Environmental Exposure from Chemicals. Vol.I. Chemical Rubber Co. Press. Boca Raton, Florida.
- Neely, W.B. and Blau, G.E. 1985b. Environmental Exposure from Chemicals. Vol.II. Chemical Rubber Co. Press. Boca Raton, Florida.
- Nijman, R. and Swain, L.G. 1989. Coquitlam-Pitt River area, Burrard Inlet: Water quality assessment and objectives. Water Management Branch. BC Ministry of Environment. Victoria, British Columbia.
- Niyogi, S. and Wood, C.S. 2004. Biotic ligand model, a flexible tool for developing site-specific water quality guidelines for metals. Environmental Science and Technology, 38, No. 23, 6177-6192.
- NRCC (National Research Council of Canada). 1981. A Screen for the relative persistence of lipophilic organic chemicals in aquatic ecosystems - An analysis of the role of a simple computer model in screening. Associate Committee on Scientific Criteria for Environmental Quality, NRCC, Ottawa. NRCC No. 18570. 304 pp.

- O'Donnel, J.R., Kaplan, B.M., and Allen, H.E. 1985. Bioavailability of trace metals in natural waters. *In* Aquatic Toxicology and Hazard Assessment. 7th Symp. ASTM Spec. Tech. Publ. 854. R.D. Cardwell, R. Purdy and R.C. Bahner (eds.). American Society for Testing and Materials, Philadelphia, Pennsylvania. pp. 485-500.
- Pagenkopf, G.K. 1978. Introduction to natural water chemistry. Marcel Dekker, Inc., New York. 272 pp.
- Paquin, P.R., Gorsuch, J.W., Apte, S., Batley, G.E., Bowles, K.C., Campbell, P.G.C., Delos, C.G., Di Toro, D.M., Dwyer, R.L., Glavez, F., Gensemer, R.W., Goss, G.G., Hogstrand, C., Janssen, C.R., McGeer, J.C., Naddy, R.B., Playle, R.C., Santore, R.C., Schneider, U., Stubblefield, W.A., Wood, C.M., and Wu, K.B. 2002. The biotic ligand model: a historical overview. *Comp. Biochem. Physiol., Part C*, 133: 3-35.
- Rand, G.M. and Petrocelli, S.R. 1985. Introduction. *In* Fundamentals of Aquatic Toxicology. Methods and Applications. G.M. Rand and S.R. Petrocelli (eds.). McGraw-Hill International Book Co., New York. pp. 1-28.
- Reid, G.K. and Wood, R.D. 1976. Ecology of inland waters and estuaries. D. van Nostrand Co., New York. 485 pp.
- Russo, R.C. 1985. Ammonia, nitrite, and nitrate. *In* Fundamentals of Aquatic Toxicology. Methods and Applications. G.M. Rand and S.R. Petrocelli (eds.). McGraw-Hill International Book Co., New York. pp. 455-471.
- Ruttner, T. 1953. Fundamentals of limnology. University of Toronto Press, Toronto, Ontario. 295 pp.
- Scott, W.B. and Crossman, E.J. 1973. Freshwater fishes of Canada. Bulletin 184. Fisheries Research Board of Canada. Ottawa, Ontario.
- Singleton, H.J. 1987. Water quality criteria for copper. Resource Quality Section. Water Management Branch. BC Ministry of Environment. Victoria, BC.
- Snape, J.R., Maund, S.J., Pickford, D.B., Hutchinson, T.H. Ecotoxicogenomics: the challenge of integrating genomics into aquatic and terrestrial ecotoxicology. *Aquat. Toxicol.*, 67: 143-154.
- Spear, P.A. and Pierce, R.C. 1979. Copper in the aquatic environment: chemistry, distribution, and toxicology. National Research Council of Canada. Ottawa, Ontario.
- Spencer, W.F. and Farmer, W.J. 1980. Assessment of the vapor behavior of toxic organic chemicals. *In* Dynamics, Exposure and Hazard Assessment of Toxic Chemicals. R. Hague (ed.). Ann Arbor Science Publ., Inc., Ann Arbor, Michigan. pp. 143-161.
- Sprague, J.B. 1985. Factors that modify toxicity. *In* Fundamentals of Aquatic Toxicology. Methods and Applications. G.M. Rand and S.R. Petrocelli (eds.). McGraw-Hill International Book Co., New York. pp. 124-163.

- Stiff, M. J. 1971. The chemical states of copper in polluted fresh water and a scheme of analysis to differentiate them. *Water Research* 5: 585-599.
- Stumm, W. and Morgan, J.J. 1970. *Aquatic chemistry. An introduction emphasizing chemical equilibria in natural waters.* John Wiley & Sons, New York. 583 pp.
- Thurston, R.V., Russo, R.C., and Emerson, K. 1979. *Aqueous Ammonia Equilibrium - Tabulation of Percent Un-Ionized Ammonia.* EPA Ecol. Res. Ser. U.S. Environmental Protection Agency, Duluth, Minnesota. EPA-600/3-79-091. p. iii. (Cited in Russo 1985.)
- USEPA (U.S. Environmental Protection Agency). 1979. *Water-related environmental fate of 129 priority pollutants. Vol. I. Introduction and Technical Background, Metals and Inorganics, Pesticides and PCBs.* Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, D.C. EPA-440/4-79-029a. pp. 2-1-2-16.
- USEPA (United States Environmental Protection Agency). 1983. *Water quality standards handbook.* Office of Water Regulations and Standards. Washington, DC.
- USEPA (U.S. Environmental Protection Agency). 1992. *Interim guidance on interpretation and implementation of aquatic life criteria and metals.* Office of Science and Technology. Health and Ecological Criteria Division. Washington, DC. (As cited in ENSR 1996).
- USEPA (United States Environmental Protection Agency). 1994. *Interim guidance on determination and use of water-effect ratios for metals.* EPA 823-B-94-001. Office of Water. Office of Science and Technology. Washington, District of Columbia.
- USEPA (United States Environmental Protection Agency). 2002a. *Methods for measuring the acute toxicity of effluents to freshwater and marine organisms.* 5<sup>th</sup> Ed. EPA-821-R-02-012. U.S. Environmental Protection Agency, Washington, DC.
- USEPA (United States Environmental Protection Agency). 2002b. *Short-term methods for estimating chronic toxicity of effluents and receiving waters to freshwater organisms.* 4<sup>th</sup> Ed. EPA-821-R-02-013. U.S. Environmental Protection Agency, Washington, DC.
- Valiela, D. and Whitfield, P.H. 1988. *Designing site-specific water quality objectives and monitoring.* *Water Pollution Research Journal of Canada*, 23(4): 510-518.
- Van Aggelen, G., Ankley, G.T., Baldwin, W.S., Bearden, D.W., Benson, W.H., Chipman, K.J., Collette, T.W., Craft, J.A., Denslow, N.D., Embry, M.R., Falciani, F., George, S.G., Helbing, C.C., Hoekstra, P.F., Iguchi, T., Kagami, Y., Katsiadaki, I., Kille, P., Liu, L., Lord, P.G., McIntyre, T., O'Neill, A., Osachoff, H., Perkins, E.J., Santos, E.M., Skirrow, R.C., Snape, J.R., Tyler, C.R., Versteeg, D., Viant, M.R., Volz, D.C., Williams, T.D., and Yu, L. 2009. *Integrating Omic Technologies into Aquatic Ecological Risk Assessment and Environmental Monitoring: Hurdles, Achievements and Future Outlook.* *Environmental Health Perspectives*, 118: 1-5.



- Van Genderen, E., Gensemer, R., Smith, C., Santore, R., and Ryan, A. 2007. Evaluation of the biotic ligand model relative to other site-specific criteria derivation methods for copper in surface waters with elevated hardness. *Aquat. Toxicol.*, 84: 279-291.
- Verschueren, K. 1983. Handbook of environmental data on organic chemicals. van Nostrand Reinhold Co., New York. pp. 1-135.
- Waite, T.D. 1984. Principles of water quality. Academic Press, Inc. Orlando, Florida. 101 pp.
- Warren, C.E. 1971. Biology and water pollution control. W.B. Saunders Co., Philadelphia, Pennsylvania. 434 pp.
- Westman, W.E. 1985. Ecology, Impact Assessment, and Environmental Planning. John Wiley & Sons, New York. 532 pp.
- Wetzel, R.G. 1975. Limnology. W.B. Saunders Co., Philadelphia, Pennsylvania. 743 pp.
- Willingham, T. W. 1988. Using in situ bioassays as a basis for the development of site-specific water quality criteria. *In* D. D. MacDonald (ed.). Proceedings of the Canada-British Columbia Workshop on Water Quality Guidelines and Objectives: Focus on the Fraser. Water Quality Branch, Environment Canada, Vancouver, BC.
- Zepp, R.G. 1980. Assessing the photochemistry of organic pollutants in aquatic environment. *In* Dynamics, Exposure and Hazard Assessment of Toxic Chemicals. R. Hague (ed.). Ann Arbor Science Publ., Inc., Ann Arbor, Michigan. pp. 69-110.
- Zepp, R.G. and Baughman, G.L. 1978. Prediction of photochemical transformation of pollutants in the aquatic environment. *In* Aquatic Pollutants: Transformation and Biological Effects. O. Hutzinger, I.H. van Lelyveld and B.C.J. Zoeteman (eds.). Proc. of the 2nd Int. Symp. on Aquatic Pollutants, Noordwijkerhout, Amsterdam, September 26-28, 1977. Pergamon of Canada Ltd., Toronto, Ontario. pp. 237-274.

## Glossary

**Actual downstream water:** Water collected from a location downstream and outside the initial dilution zone where wastewater is fully mixed with the receiving water.

**Acute:** Having a sudden onset, lasting a short time, of a stimulus severe enough to induce a response rapidly. Can be used to define either the exposure or the response to an exposure (effect).

**Ambient:** Refers to conditions in the receiving environment.

**Assimilation:** The incorporation of absorbed substances into cellular material.

**Assimilative capacity:** The ability of a waterbody to receive contaminants without impairing the use of water by humans, plants, and animals.

**Background concentration:** The concentration of substances in water not significantly altered by human land use or activities. The background concentration is determined by calculating the 95<sup>th</sup> percentile of acceptable background data.

**Background concentration procedure:** Refers to procedures where WQOs are based on background (ambient or natural) concentrations of a contaminant in water.

**Bioaccumulation:** A process by which chemical substances are accumulated by aquatic organisms from water directly or through consumption of food containing chemicals.

**Bioassay:** Test used to evaluate the potency of a chemical by comparing its effect on a living organism with the effect of a control, which is conducted under identical conditions.

**Bioavailable:** The fraction of total chemical in the surrounding environment (i.e., water, sediment, suspended particles, and food) which can be taken up by organisms.

**Bioconcentration:** A process by which there is a net accumulation of a chemical directly from water into aquatic organisms resulting from simultaneous uptake and elimination.

**Biological monitoring:** Direct measurement of changes in the biological status of a habitat based on evaluations of the number and distribution of individuals or species.

**Biomagnification:** Result of the bioconcentration and bioaccumulation processes, indicating that tissue concentrations of chemicals increase as the chemical passes up through two or more trophic levels.

**Biomass:** The living weight of a plant or animal population, usually expressed on a unit area basis.

**Biota:** The sum total of the living organisms of any designated area.

**Chronic:** Involving a stimulus that lingers for a long time - several weeks to years, depending upon reproductive cycle of the aquatic species. Can be used to define either the exposure or the response to an exposure (effect).

**Chronic test:** A comparative study in which organisms that are subjected to different treatments are observed for a long period or a substantial portion of their life span.

**Clear-flow period:** The portion of the annual hydrograph when suspended solids concentrations are less than 25 mg/L.

**Community:** An assemblage of organisms characterized by a distinctive combination of species occupying a common environment and interacting with one another.

**Concentration:** The quantifiable amount of chemical in the surrounding water, food, or sediment.

**Control:** A treatment in a toxicity test that duplicates all the conditions of the exposure treatment but contains no test material.

**Cumulative:** Brought about, or increased in strength, by successive additions at different times or in different ways.

**Designated Water Use:** Water uses that are protected at a specific location, including drinking water, aquatic life and wildlife, agriculture (irrigation and livestock watering), recreation aesthetics, and industrial water use.

**Detection limit:** The smallest concentration of a substance that can be reported as present with specified degree of certainty by an analytical procedure.

**Dilution capacity:** Ratio of water in the receiving environment to which effluents are discharged.

**EC<sub>x</sub>:** The concentration of a material in water that is estimated to be effective in producing some sublethal response in X% of the test organisms (typically EC<sub>10</sub> or EC<sub>20</sub>). It is usually expressed as a time-dependent value.

**Effluent:** Liquid waste material which may be discharged to the environment.

**Exposure:** The amount of physical or chemical agent that reaches a target or receptor.

**Fate:** Disposition of a material in various environmental compartments (*e.g.*, soil, sediment, water, air, biota) as a result of transport, transformation and degradation.

**Hardness:** The concentration of all metallic cations, except those of the alkali metals, present in water. In general, it is a measure of the concentration of calcium and magnesium ions in water and is frequently expressed as mg/L calcium carbonate equivalent.

**Hydrograph:** A chart that measures the amount of water flowing past a specified point as a function of time.

**Indicator Species:** Acceptable nonresident species used as surrogates for resident species in toxicity tests. In a receiving environment, it refers to an acceptable resident species used as a surrogate for valuable resident species for conducting tests of various nature.

**Initial dilution zone (IDZ):** Initial portion of a larger effluent mixing zone adjacent to a wastewater discharge. According to the *Fisheries Act* effluent entering the IDZ must not be acutely toxic. Extent of IDZ is defined on a site-specific basis and should not impinge on such areas as water intakes, bathing beaches, shellfish beds, fish spawning and rearing areas, areas of sensitive vegetation, or other environmentally sensitive areas.

**LC<sub>x</sub>:** The concentration of material in water that is estimated to be effective in producing some sublethal response in X% of the test organisms (typically LC<sub>50</sub>). It is usually expressed as a time-dependent value.

**Long-term water quality objective:** Long-term WQOs may be used where existing water quality does not suit all desired water uses, and it is feasible to improve the water quality over time.

**Most sensitive water uses:** The designated water use(s) requiring the most conservative limits for protection.

**Natural background concentration:** The concentration of a substance in an environmental medium in a geographic area, not including any contribution from human-made sources.

**Permanent water quality objective:** WQOs established when information available about local conditions and WQC or WQGs is adequate. Although labeled as permanent, they are subject to review and revision as new information becomes available. The term permanent describes the adequacy of data supporting the WQO rather than the longevity of the WQO.

**Preliminary water quality objective:** First estimates of WQOs that are usually based on WQC/WQGs for the most sensitive aquatic species, but have not considered other factors such as natural background concentrations of the substance, sensitivity of resident species, and other physical and chemical characteristics that affect toxicity of a substance.

**Provisional water quality objective:** Deliberately conservative WQOs set where the information available about the local conditions (e.g., water quality, water use, aquatic life, waste discharges, etc.) and/or the WQC or WQGs for a substance are inadequate for the establishment of scientifically defensible objectives.

**Range-finding test:** Important preliminary test to be conducted for determining WERs. The purpose of test is to determine the chemical concentration range likely to cause a response in a test organism. Such information is necessary for designing definitive toxicity test that determine effective concentrations of toxicant in site water.

**Raw water:** Surface or ground water that is available as a source of drinking water but has not received any treatment.

**Recalculation procedure:** A procedure by which WQOs are adapted from WQC or WQGs by accounting for statistically significant differences between the sensitivity range of species of aquatic organisms represented in the complete toxicological data set and that of the species that occur (or historically occurred) at the site under consideration.

**Resident species procedure:** A procedure by which WQOs are derived directly from data that consider both the sensitivity of species that occur at a particular site and the influence of site water characteristics on the toxicity of a particular substance.

**Short-term objectives:** Interim water quality objectives established to protect water uses to a certain degree until the long term objectives can be achieved.

**Simulated downstream water:** A mixture of upstream water and wastewater at a known ratio.

**Tolerance:** The ability of an organism to withstand adverse or other environmental conditions for an indefinitely long exposure without dying.

**Toxicant:** An agent or material capable of producing an adverse response (effect) in biological system, seriously injuring structure or function or producing death.

**Toxicity:** The inherent potential or capacity of a material to cause adverse effects in a living organism.

**Toxicity test:** The means by which the toxicity of a chemical or other test material is determined. It is used to measure the degree of response produced by exposure to a specific level or concentration of stimulus.

**Turbid-flow period:** The portion of the annual hydrograph when suspended solids concentrations are greater than 25 mg/L.

**Uncertainty (safety) factor:** A number used to provide an extra margin of safety beyond the known or estimated sensitivities of aquatic organisms.

**Variable:** A measurable or quantifiable characteristic or feature.

**Water effect ratio procedure:** Refers to the procedure by which WQOs are adapted from WQC or WQGs, through the use of WERs, by accounting for unique physical and/or chemical characteristics of water affecting the bioavailability of contaminants at the site under consideration.

**Water effects ratio (WER):** Ratio of the toxicity of a particular substance in water from the site to its toxicity in laboratory water. It is used directly to convert generic WQGs or WQC to site-adapted WQO.

**Water quality:** A term used to describe the chemical, physical and biological characteristics of water, usually in respect to its suitability for a particular purpose.

**Water quality guideline:** A maximum and/or minimum value for a physical chemical, or biological characteristic of water, biota or sediment which must not be exceeded to prevent specified detrimental effects from occurring to a water use under specified environmental conditions.

**Water quality objective:** A numerical concentration or narrative statement which has been established to support and protect the designated uses of water at a specified site. It may be a WQC/WQGs adapted to protect the most sensitive designated water use at a specified location with an adequate degree of safety, taking local circumstances into account.

**Working water quality guidelines:** Water quality guidelines that have not yet been formally approved by the BCMOE. These guidelines are obtained from various Canadian (primarily the CCME) and North American jurisdictions. The working guidelines provide benchmarks for those substances that have not yet been fully assessed and endorsed by the BCMOE. They are reviewed by the BCMOE on a priority basis for their formal approval and use in BC.

**Xenobiotic:** A foreign chemical or material not produced in nature and not normally considered a constitutive component of a specified biological system. This term is usually applied to manufactured chemicals.

## **Appendix 1**

### **Policy Statements Regarding Water Quality Guidelines and Objectives**

**Policy: 6.10.03.02** (Original signed by G. R. Armstrong, Deputy Minister, August, 1991.)

#### **It is the Policy of the Ministry:**

That reports on ambient water quality criteria and objectives, previously approved and signed by the Deputy Minister, be approved and signed by the Assistant Deputy Minister, Programs.

That reports on ambient water quality criteria and objectives approved by the Assistant Deputy Minister, Programs, constitute official ministry policy on these aspects of water quality, and that they will be considered in any decisions affecting water quality made within the Ministry of Environment.

#### **Reasons for Policy:**

- To enable signing and approval of the reports by the Assistant Deputy Minister, Programs, instead of the Deputy Minister without incurring any loss in the status, force or effect of the reports as statements of ministry policy.

**Policy: 6.10.03.03** (Original signed by B.E. Marr, Deputy Minister, March 1985)

#### **It is the Policy of the Ministry:**

That water quality criteria, applicable province-wide, be developed for use in producing site-specific water quality objectives appropriate for designated water use classes.

That water quality objectives be established for specific bodies of fresh and estuarine surface waters and coastal marine waters of the province, as a part of the ministry's mandate to manage water quality.

That water quality objectives be set following the principle of avoiding the degradation of existing water quality, upgrading existing water quality or protecting the water quality for a designated water use.

That water quality objectives be based on water quality criteria or similar information, and on water quality assessments. Assessments will take into account the characteristics of the

ambient water, the sediments, aquatic life, the stream flow regime, the water movement and contaminant loadings from point and diffuse sources on a site specific basis.

That monitoring be proposed which will allow the ministry to determine whether the objectives are being met and whether modifications are needed to make the objectives more or less restrictive.

That a long-term program of ambient water quality monitoring be established in selected important waterways of British Columbia to determine existing water quality and to monitor trends in water quality. This trend monitoring network would complement programs now in existence for administering waste management and fish management concerns. Selection of waterways will depend on their significance from a provincial, inter-provincial or international point of view.

That the Resource Quality Section of the Water Management Branch take the lead role in developing province-wide water quality criteria and site specific water quality objectives, and in proposing a long-term monitoring program. This will be done in consultation with regions, other sections of the Water Management Branch, Waste Management, Fish Management and Wildlife Management Branches and appropriate health agencies. Advice will also be sought, as required, from relevant federal and regional agencies.

That the responsibility for objectives monitoring and long-term monitoring be shared among the Waste Management, Fish Management and Water Management Programs. Water Management will generally be responsible for that monitoring which is not directly related to Waste Management or Fish Management, and which is not within the jurisdiction of the Ministry of Health.

#### **Reasons for Policy:**

- To determine the quality of water in important waterways and to detect changes therein which may be significant to the management of the water resource.
- To ensure that the quality of the aquatic resource is maintained.
- To guide the issuance of permits, licences and orders related to water quantity and quality.
- To assist decision makers in planning for future developments which could affect the aquatic resource.



## **Appendix 2 (Adopted from CCME 2003)**

### **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 variables 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.

#### **A2.1 Differences Between Waterbodies**

Differences in the nature of rivers, reservoirs and lakes are 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.

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). 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 is 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, seasonal 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 with high concentrations 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, thermal environment, 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.

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 contaminants. 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.

## **A2.2 Water Quality Characteristics**

The water quality characteristics of receiving water systems are 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.

### **pH**

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 variables 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), 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 un-ionized ammonia ( $\text{NH}_3$ ) and the ammonium ion ( $\text{NH}_4^+$ ) in receiving waters. Because the un-ionized ammonia form is much more toxic than the ammonium ion, total ammonia tends to be more toxic at elevated pH levels (i.e., low pH favours 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 procedure 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 waterbody. 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 ( $\text{CaCO}_3$ ), and is used as an indication of water type, buffering capacity, and productivity of a waterbody (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 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 WQGs 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 generally ameliorates the toxicity of nitrite in freshwater systems. There are some organisms (e.g., glochidia of freshwater mussels, amphibians) which are sensitive to increased levels of chloride.

## Metals

The development of WQOs for metals is complex because their toxicity is affected by a number of site-specific 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 potential, temperature, hardness, CO<sub>2</sub> 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<sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, 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  $\text{Cd}_2^+$ ,  $\text{Cu}_2^+$ ,  $\text{Pb}_2^+$ , and  $\text{Zn}_2^+$  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 metal values includes dissolved metals and that fraction of solid metals that can easily become soluble in ambient conditions (USEPA 2002a; 2002b). 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 metal values allow 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 adsorptive properties of colloids and particles can change with different physical and chemical conditions.

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

- clogging the filtering apparatus of some immature stages of insects (e.g., caddisfly larvae) and fish;
- causing physical injury to delicate eye and gill membranes by abrasion;
- restricting food availability to fish and, in so doing, affect growth rates;
- restricting normal movements and migrations of fish; and,
- inhibiting 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 variables 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 ( $H_2$ ,  $N_2$ ,  $CO_2$  and  $O_2$ ) 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 ( $\text{NH}_3$ ), nitrite ion ( $\text{NO}_2^-$ ), and nitrate ion ( $\text{NO}_3^-$ ). 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  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{SO}_4^{4-}$ ,  $\text{PO}_3^{4-}$  and  $\text{NO}_3^-$ , 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  $\text{H}_2\text{PO}_4^-$  (10%) and  $\text{HPO}_4^{2-}$  (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 results 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.

### **A2.3 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 contaminants in water. As with other variables, the rate and degree to which these processes occur depend on the prevailing local environmental conditions.

## **Sorption**

Sorption is the process whereby contaminants 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:

- 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 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 (Verschuere 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 ( $K_s$ ) 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 (Verschuere 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 CO<sub>2</sub>. 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 CO<sub>2</sub> 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<sup>+</sup> 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  $\text{CO}_2$  using the oxygen from sulphate ( $\text{SO}_4^{2-}$ ). The by-product, hydrogen sulphide ( $\text{H}_2\text{S}$ ), 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 precipitates 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 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 ( $K_p$ ) 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 in water, light absorbed by a sensitizer molecule (e.g., humic matter) 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).

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).

#### **A2.4 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 3**

### **A General Format for Making Water Quality Assessments**

The water quality assessment is an integral part of the water quality objectives development process. The information gathered at this stage will help inform the development of the final WQOs. The following sections provide guidance on the minimum requirements for water quality assessments used in the development of WQOs in BC and are based largely on information presented in the document *Developing Water Quality Objectives – A User’s Guide* (BC MOE 1996).

#### **A3.1 Hydrology, Limnology and/or Oceanography**

Include, as appropriate, a description of the water body with major tributaries and other important features of the area, such as stream and river flows (including Water Survey of Canada gauging stations), lake characteristics and water retention times, and/or marine currents and tidal action. Especially important are seven-day low flows (mean annual and 1-in-10 year) and their timing so that you can make worst-case calculations in chapters that follow. For lakes, include bathymetric maps (can be obtained from Ministry of Environment’s online *Fisheries Inventories Data Queries*) and present any profile information in time/depth diagrams. Other pertinent information may include factors such as precipitation quantities and climate normals (available online from Environment Canada).

#### **A3.2 Water Uses**

It is desirable to obtain public input into the perceived water uses which should be protected for a water body. Sub-divide water uses into categories such as contact recreation (contact local Ministry of Health office), licensed water withdrawals (available from the Water Stewardship Division of the Ministry of Environment) and use by aquatic life. The most important uses are those that will be affected by waste discharges, or uses that will affect streamflow and hence the dilution of a waste discharge further downstream. Additional information needed for important water uses includes:

**Drinking water:**

- type of water treatment provided (e.g., chlorination, filtration, sedimentation, etc.)
- timing of use (e.g., year-round, seasonal)
- number of connections

**Aquatic life and wildlife:**

- species and life stages present or potentially present
- geographic distribution of species and life stages
- seasonal distribution of species and life stages (e.g., spawning, rearing, migration)
- presence of rare or endangered species
- areas used by shellfish

**Recreation:**

- type of recreation (e.g., water contact versus non-water contact activities)
- area and timing of use (i.e., the recreation season)

**Irrigation:**

- timing of use (i.e., the irrigation season)
- type of crops
- type of soils and soil chemistry
- water application rates (i.e., depth per year, short-term versus long-term irrigation)

**Livestock watering:**

- timing of use (e.g., year-round, seasonal)
- type and numbers of animals

**Industrial:**

- timing of use
- type of industry and process (i.e., determine what the water is used for)

Note the locations of licensed water withdrawals on a map, and tabulate information related to the type of withdrawal, licence number and associated volumes for each type of withdrawal (see table below). Also note any constraints which may exist to some use (such as

climate, no soil available on which to grow crops, a domestic licence not used for drinking water but for livestock watering, etc.).

Table X. Summary of current water licences for \_\_\_\_\_.

Type of withdrawal	Total number of licences	Licensed volume	Licence numbers
Domestic			
Irrigation			
Industrial			

### A3.3 Permitted Discharges

In BC, the MOE regulates the discharge of industrial wastes under the *Environmental Management Act* through the use of permits, authorizations and regulations. These are usually associated with discharges to soil or water and will have the potential to impact water quality. Information on permitted discharges is available from the Environmental Protection Division of the BC MOE. Each permit and authorization should be described in terms of the operation or process, and the permit requirements. Monitoring data for the discharge can be summarized in a table as shown below. These data should be discussed in terms of loadings, dilution available in the IDZ and with complete mixing, and in the case of discharges to ground, the distance to surface waters. A discussion should also be included of substances which may have an environmental impact due to the nature of the discharge, but for which no data are available.

Table Y. Summary of effluent discharged from \_\_\_\_\_ (PE\_\_\_\_\_).

Variable	No. of values	Maximum	Minimum	Median	Mean	Standard Deviation
BOD <sub>5</sub>						
Suspended solids						
Fluoride						

The following points should also be considered for inclusion in this section and apply to present and future waste discharges, projected over the planning period (next 5 to 20 years):

- A map showing the location of discharges (scale of 1:100,000 to 1:250,000, with larger inset maps as required).
- A summary of the present effluent monitoring data including flows, concentrations, and loadings.
- A description of effluent dispersion in terms of initial dilution, dilution after complete mixing, time and distance to achieve complete mixing, and effluent plume behaviour.

It may also be useful to project the future waste loadings for existing and future waste discharges. Population projections can be used to project future municipal waste loads. Industrial waste load projections require specific information about expanded or new operations, and existing waste loads or waste loads from similar operations elsewhere may provide a basis for projections. The effects on receiving waters can be assessed in two ways:

1. by calculating the impact of various effluent loads at different river flows, or dilutions in the case of lakes and marine waters, for initial dilution and complete mixing cases; and
2. by summarizing observed water quality impacts under specific conditions. This analysis would pinpoint important contaminants and their effect on receiving waters.

#### **A3.3.1 Impacts from Discharges**

Include in the discussion any critical single or periodic receiving water measurements showing the possible impact on water quality of a particular discharge. Place these types of tables within the text (see example below) since they are short, do not disturb the flow of the text when reading the assessment, and allow the data to be easily examined simultaneously with the explanation.

Table Z. Fecal coliform concentrations (CFU/100 mL) for sites near PE12345

Date	200 m u/s Hwy. 97	100 m u/s PE 146	400 m d/s PE 146	1.6 km d/s PE 146	8 km d/s PE 146	16 km d/s PE 146	20 km d/s PE 146
April 22 1987	10	20	100	8	14	20	60
Sep. 16 1987	130	13	564	540	540	920	350
Nov. 13 1991	6	17	7	16	12	120	250

When a large number of discharges occur to a large area, summarize the information based on tributaries and/or river reach as shown in the following table.

Reach: Tete Jaune Cache to Nechako River				
Permitee	Permit Number	Report section	Discharge Type	Permitted volume (m <sup>3</sup> /d)
Village of McBride	PE 402	4.2.1	Municipal	750
Northwood Upper Fraser	PE 2655	4.2.2	Municipal	273
Reach: Nechako River Confluence to Hope				
Quesnel River Pulp Company	PE 5803	4.3.12	Industrial	28,000
Cariboo Pulp and Paper	PE 1152	4.3.13	Industrial	118,200
City of Williams Lake	PE 255	4.3.14	Municipal	6,820

#### A3.4 Non-Point Sources

Non-point or *diffuse* sources refer to activities which can contribute contaminants to a water body in a diffuse manner, but which do not result in a discharge through a pipe which is under permit. Examples of these types of discharges are storm water from a city, or agricultural runoff. Precipitation chemistry information (obtained from Environment Canada) might appropriately be placed in this chapter. For non-point source discharges, provide information for factors such as the areas of forestry activities, agricultural land use, numbers of homes using

septic tanks and tile fields, soil sensitivity (to generate surface runoff or leaching to ground water), and numbers and locations of livestock grazing.

#### **A3.4.1 Impacts From Intensive Agricultural Operations**

Presented below is an example table estimating increases in concentrations in a water body due to livestock grazing. These estimates are based upon literature values (e.g., Bangay 1976) for the amount of nitrogen (N) and phosphorus (P) generated by types and sizes of different livestock, and on the:

- number of livestock units in an area;
- length of time in that area; and
- number of weeks over which the accumulated wastes might be released.

Assumptions which we might make and which should be stated as such in the Technical Report include:

- all the wastes generated over the period reach the water body;
- all the wastes accumulated over a certain time period are transported to the water body; and
- flows in the water body are consistent throughout the release period.

Table X. Summary of estimated phosphorus and nitrogen concentrations (mg/L) resulting under different grazing scenarios.

	Release Period					
	One week		Two Weeks		Three weeks	
	P	N	P	N	P	N
Reach						
Upper Fraser River	0.58	4.95	0.29	2.48	0.15	1.24
Middle Fraser River	1.11	9.50	0.55	4.80	0.28	2.40



### A3.4.2 Impacts From Stormwater Discharges

You may often be able to estimate loadings from storm water discharges using existing studies undertaken in BC, extrapolating actual loadings to the area of interest. Below is an example presenting the final results for this type of information for an assessment report. Calculations should be based on worst-case loadings which reflect maximum quantities of contaminants after a period of dry weather when these have accumulated.

Table X. Summary of estimated increases in water quality variable loadings to two sites in the Fraser River from stormwater runoff.

	Est. increases in loading (kg/d)		Est. increases in concentration (mg/L)	
	Prince George	Quesnel	Prince George	Quesnel
Aluminum	15.7	2.40	0.0017	0.0003
Cadmium	2.13	0.32	0.0002	0.0001
Zinc	3.38	0.52	0.0004	0.0001
Suspended Solids	578.1	88.9	0.06	0.009
Total Nitrogen	40.95	6.30	0.004	0.0007
Total Phosphorus	5.15	0.79	0.0005	0.0001

### A3.5 Ambient Water Quality

Ambient water quality data should be summarized in tables at the end of the text. The sources for data will vary from Region to Region, but in general may include Ministry data files, the Ministry EMS data base, data from federal government Departments such as Environment Canada (and their Water Quality Monitoring and Surveillance Program) or Fisheries and Oceans Canada, universities, and volunteer monitoring programs. Below is an example of a common data summary.

Table Y. Summary of ambient water quality data for Site E\_\_\_\_\_ for the period of \_\_\_\_\_.

<b>Variable (mg/L or as noted)</b>	<b>No. of values</b>	<b>Maximum</b>	<b>Minimum</b>	<b>Median</b>	<b>Mean</b>	<b>Standard deviation</b>
Alkalinity						
pH (pH units)						
Dissolved oxygen						
Temperature (°C)						
Turbidity (NTU)						
Suspended solids						
Sulphate						
Copper (total)						

In assessing water quality you should:

- identify and detail data and/or information gaps;
- examine the range of values obtained at each station relative to applicable water quality guidelines (refer to the appropriate technical document to ensure the WQG is being applied correctly);
- document the number and extent that each variable exceeds the criteria;
- allow for the effect (within expected conditions for the water body itself) of ancillary variables such as pH, temperature, conductivity, and hardness which can affect the toxicity of some substances;
- consider the dilution capacity of downstream waterbodies which may have more sensitive designated water uses than upstream waterbodies;
- examine loadings and potential increases or decreases in the water quality variables in the water body from natural sources, such as tributary streams;
- examine loadings and potential increases or decreases in the water quality variables in the water body from anthropogenic sources;
- discuss ameliorating factors which may necessitate that criteria considered should be relaxed or made more stringent (e.g., complexing, hardness);
- ultimately, propose WQOs for a reach of the water body where anthropogenic sources are (or may be) responsible for changes in a variable that threatens water uses. You should seek public input at this point.

### A3.6 Proposing Water Quality Objectives

It is recommended that key variables (e.g., those that exceed WQGs or need WQOs) be displayed in graphs or tables within the text. This will allow important spatial and temporal aspects of their distribution to be displayed.

If the WQO applies to an area which includes a permitted point-source discharge (e.g., an outfall), include a statement in the text which defines the IDZ where the WQO does not apply. The layout for the first objective proposed and the definition of the IDZ would be similar to:

The proposed WQO for induced suspended solids concentrations to protect aquatic life are that **for background concentrations of less than 100 mg/L, suspended solids could increase by as much as 10 mg/L, while for background concentrations greater than 100 mg/L, suspended solids concentrations could increase by up to 10%.** These WQOs apply along the Given River, from Point 1 to Point 2, except in the IDZ of effluent discharges.

#### A3.6.1 Common Water Quality Objectives

In most instances, the proposed WQOs are the same as the BC-approved WQG for a variable of concern in relation to the water uses designated for protection (i.e., designated water uses). Approved WQGs are documented in technical reports for each variable and are available online at [http://www.env.gov.bc.ca/wat/wq/wq\\_guidelines.html](http://www.env.gov.bc.ca/wat/wq/wq_guidelines.html). The technical reports should be referred to for proper application of the WQG. For variables without approved WQGs, refer to *A Compendium of Working Water Quality Guidelines for British Columbia* available at <http://www.env.gov.bc.ca/wat/wq/BCguidelines/working.html>.

### **A3.6.2 Proposing Water Quality Objectives for Atypical Situations**

There are times when the BC-approved WQGs cannot be used directly as WQOs for various reasons. These are discussed in the following sections.

#### ***Naturally Elevated Concentrations***

An example would be a certain metal in a water body that occurs at levels that are naturally higher level than the WQG. In such situations, we usually decide that, as long as there is no change from background concentrations (defined as the 95<sup>th</sup> percentile of appropriate data), no harmful effects should take place. We define the term “no change” as a difference of not greater than 20% going from upstream to downstream from a discharge or series of discharges. We rationalize the 20% increase (this percentage can be reduced in situations where replicate sampling has been carried out with the monitoring program) as not being an increase since:

- the precision for measurement of low concentration metals in replicate samples is not usually better than 20% in ideal situations in a laboratory
- natural variability is often greater than 20%

This approach has been used in many published water quality assessments in BC. Another approach which has been used when there were enough data, is to base the WQO on the historical background levels, allowing little or no change from one or more of the historical statistics.

#### ***Characteristics with no Published Criteria***

In other situations, there may be a need to develop WQOs for variables for which there are no published guidelines. For example, data from uncontaminated areas (background) could be compared to those from more populated or contaminated areas. Then literature values could be used to determine what concentrations may cause an adverse effect, providing a

number which is protective of a given waterbody. Sediment quality objectives for Burrard Inlet (Nijman and Swain, 1989) were developed on this basis.

### ***Challenging Existing Criteria***

In very rare situations, you may find that the approved or working WQGs are over restrictive for a given situation. In these cases, refers to Sections 3 and 4 of this report for specific guidance. For all situations, apply sound logic, and convey this logic to the reader of the Technical Report.

### **A3.7 Proposed Water Quality Monitoring Program**

Every WQO technical report should include a water quality monitoring program that will allow you to check for attainment of the WQOs in the future. Points to consider the development of a water quality monitoring program are discussed in Section 3.6 of the main report.

## Appendix 4

### Development of Water Quality Objectives Using the Recalculation Procedure

The following is a hypothetical example designed to illustrate the application of the recalculation procedure. This example follows the process outlined in Figure 2 of the main document. For the purpose of this example, only a maximum WQO is developed. Determining the appropriate chronic preliminary WQO (30-day average) would follow the same approach.

A major development is being planned for a relatively pristine watershed. There is sufficient water quality data to establish background conditions for the stream in question. The stream has considerable fish (Salmonidae and Cottidae) and invertebrate (Oligochaeta, Ostracoda, Plecoptera, Ephemeroptera, Trichoptera, Diptera, and Gastropoda) populations. There are also good wildlife populations in the watershed and the stream has some withdrawals for drinking water purposes in the lower reaches. Therefore, designated water uses for the waterbody are aquatic life, wildlife, and source drinking water.

#### ***Step 1: Adopt the generic WQGs for the most sensitive uses as the preliminary WQO:***

Based on information from similar situations elsewhere, there are three variables of concern associated with the type of development proposed: X, Y, and Z. The table below lists the BC-approved WQGs for each variable. Based on the information provided, aquatic life is the most sensitive water use, therefore WQOs will be developed to protect the water quality for that use. The aquatic life WQGs listed below are now adopted as the preliminary WQOs.

Variable	Aquatic Life		Drinking Water	Wildlife
	Maximum	30-day Average	Maximum	Maximum
X	20 µg/L	5 µg/L	300 µg/L	900 µg/L
Y	100 µg/L	10 µg/L	450 µg/L	800 µg/L
Z	200 µg/L	20 µg/L	1,000 µg/L	1,500 µg/L

**Step 2: Determine the upper limit of background:**

A review of the available water quality data for this stream shows 95<sup>th</sup> percentile values for X, Y, and Z as 8 µg/L, 48 µg/L, and 66 µg/L, respectively. Because each of these values are below the preliminary maximum WQOs, there is no need to modify the preliminary maximum WQOs using the background concentration procedure.

**Step 3: Determine the lowest level of quantitation:**

For each of variables X, Y, and Z, the method detection limit (MDL) is 0.5 µg/L. Because the MDL for each is below the preliminary WQO, there is no need to modify the preliminary WQO using the analytical limit of quantitation procedure.

**Step 4: Determine if the toxicity data used to derive the WQG is representative of the site:**

The aquatic species represented in the toxicity data sets used to derive the approved WQG for each variable are provided in the table below:

<b>X</b>	<b>EC<sub>50</sub></b>	<b>Y</b>	<b>EC<sub>50</sub></b>	<b>Z</b>	<b>EC<sub>50</sub></b>
<i>Oncorhynchus mykiss</i> (rainbow trout)	76 µg/L	<i>O. mykiss</i>	200 µg/L	<i>O. mykiss</i>	425 µg/L
<i>O. clarki</i> (cutthroat trout)	104 µg/L	<i>O. clarki</i>	256 µg/L	<i>O. clarki</i>	590 µg/L
<i>O. kisutch</i> (coho salmon)	98 µg/L	<i>O. kisutch</i>	306 µg/L	<i>O. kisutch</i>	480 µg/L
<i>Salmo trutta</i> (brown trout)	80 µg/L	<i>Catostomus commersoni</i> (white sucker)	429 µg/L	<i>Lepomis macrochirus</i> (bluegill)	680 µg/L
<i>Pimephales promelas</i> (fathead minnow)	40 µg/L	<i>H. azteca</i>	480 µg/L	<i>H. azteca</i>	760 µg/L
<i>Hyalella azteca</i> (amphipod)	112 µg/L	<i>D. magna</i>	390 µg/L	<i>D. magna</i>	630 µg/L
<i>Daphnia magna</i> (water flea)	200 µg/L	<i>Biomphalaria glabrata</i> (freshwater snail)	560 µg/L	<i>Epeorus latifolium</i> (mayfly)	400 µg/L
<i>Selenastrum capricornutum</i> (green alga)	150 µg/L	<i>S. capricornutum</i>	860 µg/L	<i>Lemna minor</i> (aquatic macrophyte)	1,220 µg/L

Each guideline has satisfied the minimum requirements for the number of studies required to derive the WQG (i.e., 3 fish, 2 invertebrates, 1 plant). For variables Y and Z, the most sensitive species were rainbow trout and mayflies, respectively, and the final WQGs (maximum concentration at any time) was derived based on toxicity test results for these species after applying a safety factor of 0.5. For variable X however, the most sensitive species was *P. promelas*, a species belonging to a family (Cyprinidae) not found in the waterbody being considered, and is not known to be found in any of the adjacent drainages. Therefore, there is justification for modifying the generic BC-approved WQG using the recalculation procedure. All of the other taxonomical groups listed are represented in this stream, and so only *P. promelas* is removed from the data set. The data set still meets the minimum requirements with 4 fish species. Now brown trout are the most sensitive species and, after the application of a safety factor of 0.5, the preliminary WQO is 40 µg/L.

***Step 5: Re-evaluate the new preliminary WQO***

The new preliminary WQO for X is greater than the upper limit of background concentrations (Step 2), greater than the lowest available limit of quantitation (Step 3), and now accounts for the sensitivity range of resident species for the site in question.

***Step 6: Determine if there are site characteristics that could affect toxicity***

The toxicity of variable X is not influenced by any ameliorating such as pH, temperature, or hardness, so there is no need to modify the new preliminary WQO any further using the water effects ratio procedure.

***Step 7: Adopt the preliminary WQOs as the recommended WQOs***

After considering all of the steps for evaluating preliminary WQOs, the recommended WQOs for this example are:

- Variable X: 40 µg/L (maximum concentration at any time)
- Variable Y: 100 µg/L (maximum concentration at any time)
- Variable Z: 200 µg/L (maximum concentration at any time)



***Final notes:***

This example has demonstrated the procedures for modifying a generic acute WQG using the recalculation procedure. It is also possible a chronic preliminary WQO could require modification and in these cases, the procedures outline here would also be followed.

The recalculation procedure will not always result in a less stringent WQO. In cases where the minimum requirement of studies (i.e., 3 fish, 2 invertebrates, 1 plant) are not satisfied, additional toxicity tests with relevant species would be required to complete the data set. In these instances, it is possible that the additional data may result in a WQO that is lower than the generic WQG.

## **Appendix 5**

### **Development of Water Quality Objectives**

#### **Using the Water Effect Ratio (WER) Procedure**

A variety of physical and chemical characteristics of water have been shown to alter the bioavailability and toxicity of chemicals in freshwater ecosystems. While some of these factors have been considered in the derivation of generic water quality guidelines (WQG), atypical water quality characteristics (e.g., hardness, pH, temperature, total organic carbon, etc.) have the potential to render such WQGs over-protective or under-protective of aquatic life at certain sites. In these situations, it is appropriate to modify the generic WQGs to account for differences in the toxicity of a substance caused by the physical or chemical characteristics of site water. Information on the factors that can influence the toxicity of water-borne substances is provided in Appendix 2.

The water effect ratio (WER) procedure has been used as the primary basis for modifying generic WQGs for the protection of aquatic life. General guidance for deriving site-specific WQOs using this procedure is available in USEPA (1994). To determine a WER, side-by-side toxicity tests are performed to measure the toxicity of the substance in site water and laboratory water. The WER is calculated by dividing the effective concentration of the substance (e.g.,  $LC_{50}$ ) in site water by the effective concentration of the substance in laboratory water. By conducting such paired toxicity tests (both acute and chronic) with several indicator species (e.g., rainbow trout, fathead minnows, and water fleas) at key locations and under various environmental conditions (e.g., high flow, low flow, etc.), it is possible to determine WER(s) that are appropriate for modifying the generic WQGs. Using this procedure, the site-adapted WQO can be calculated by multiplying the generic WQG by the appropriate WER. The applicability of this approach to the site under consideration can be enhanced by conducting the toxicity tests with resident species of aquatic organisms found at the site in question.

The waterbodies in BC have a broad range of water quality characteristics; therefore, many locations could have conditions that differ substantially from those represented in the

toxicological database that was used to derive the generic WQGs. Such real differences in water quality could influence the bioavailability and toxicity of water-borne contaminants, potentially necessitating the derivation of site-adapted or site-specific WQOs at a number of sites. To accommodate for this possibility, the procedures for developing WERs must be straightforward and flexible. This is consistent with the role of WQOs in the overall water management process in BC. That is, ambient WQGs and WQOs are intended to provide environmental managers with tools to support better decisions regarding the multiple use of aquatic resources, including permitting of wastewater discharges.

The detailed guidance that has been developed by USEPA (1994) provides a comprehensive basis for implementing the WER procedure for modifying the generic WQGs. Because it is part of USEPA's formal process for establishing effluent quality standards and ambient water quality standards (which are legally enforceable), the documented procedures must be highly regimented and anticipate a broad range of potential scenarios and difficulties. As such, the USEPA guidance tends to be very complicated, difficult to understand, and expensive to implement, which limits its applicability in BC. Nonetheless, this guidance provides an excellent technical basis for recommending the following simplified procedures that respond more directly to the interests and needs of stakeholders in BC.

#### **A5.1 Study Plan Design for Deriving Water Effects Ratios**

Implementation of the WER procedure requires significant time and resources. For this reason, the benefits and costs of using the procedure to develop site-specific WQOs should be weighed carefully. Some of the factors that should be considered in such an evaluation include:

- **The reliability of existing water chemistry data.** That is, the measurements of the substance of concern could be erroneously high due to sample contamination during collection, handling, storage, preparation or analysis. Re-evaluation of ambient water quality could eliminate the need to adjust the WQGs;
- **The potential for reducing discharges of the contaminant.** In some cases, it may be possible to reduce the contaminant emissions from a wastewater source relatively easily and inexpensively, which could eliminate the need to adjust the WQGs;

- **The potential for bioaccumulation of the contaminant.** For certain substances, the bioaccumulation-based WQGs (i.e., for the protection of human health and/or wildlife from adverse effects associated with the accumulation of toxic substances in aquatic organisms) will be as low or lower than the WQGs that are derived based on acute effects to aquatic organisms. Therefore, determination of the WER would not influence the final WQOs that are established for the site, thereby eliminating the need for site-adjusted WQOs; and,
- **The applicability of the recalculation procedure.** In many cases, the recalculation procedure will provide a scientifically-defensible and cost-effective basis for adjusting the WQGs to account for atypical assemblages of aquatic organisms. Such adjustments may eliminate the need to further modify the WQO.

While the results of this type of evaluation will often indicate that alternate measures should be pursued preferentially, implementation of the WER procedure may still be warranted under certain circumstances. In these cases, a study plan for determining WERs at the site must be developed and submitted to BC MOE staff for review. The study plan should include, at minimum, the following elements:

- Detailed description of the waterbodies under investigation (tributary network, seasonal flow regime, water uses, land uses, etc.);
- Listing of the existing WQGs and WQOs;
- Rationale for modifying the preliminary WQO to account for site characteristics;
- Summary of the available information on ambient water quality, effluent quality, streamflows, effluent volumes, biota and any known conditions relevant to the site (e.g., winter stress syndrome, history of fish kills, etc.);
- Description of the overall experimental design;
- Sampling plan for receiving waters and wastewaters;
- Description of the procedures that will be used for collecting, handling, and storing receiving water and wastewater samples;

- Description of the analytical methods that will be used to determine the characteristics of receiving water and wastewater samples (including measurements of all physical and chemical variables);
- Listing of the toxicity tests that will be used in the study (i.e., specific protocols should be identified) and an appropriate rationale for their selection;
- Description of standard operating procedures for toxicity testing and laboratory operations;
- Description of quality assurance/quality control (QA/QC) procedures that will be used and the criteria that will be employed to assess the resultant data; and,
- Description of the procedures that will be used to evaluate, interpret, and report the resultant data.

Following its review, the study plan should be revised in accordance with the reviewers' comments and distributed to everyone who will be involved with the implementation of each element of the study.

## **A5.2 Developing a Sampling Plan for Wastewaters and Receiving Waters**

Development of a focussed sampling plan to support the derivation of site-adapted WQOs requires detailed information on the site under consideration, as described above. Such a sampling plan should:

- Identify the boundaries of the study area;
- Identify the stream reaches and other waterbodies for which WQOs will be derived;
- Identify the sampling sites within each stream reach and waterbody that will be sampled to collect dilution water;
- Identify the sampling sites for each wastewater stream that will be sampled to collect dilution water;
- Identify the dates or hydrological conditions when water and wastewater samples will be collected; and,

- Specify the procedures that will be used to sample water and wastewater on each date and at each site.

Identification of the boundaries of the study area and the stream reaches of concern within the study area is an important step in the overall WQOs development process. Ideally, entire drainage basins will be considered during the development of WQOs. However, practical considerations related to the availability of resources and variability in water quality conditions may preclude this option at many locations. The factors that should be considered in designating stream reaches within the study area include the number and location of wastewater discharges, water quality characteristics, hydrological characteristics, habitat use by sensitive species, and the location of physical features (e.g., impassable falls, dams, tributaries, etc.). Obviously, the level of effort and costs increase with the number of stream reaches that are considered for the derivation of WQOs.

Identification of sampling sites for receiving waters and wastewaters within the study area is dependent on the overall experimental design for the project. The desired source of dilution water is one important consideration in this process. WERs can be determined using dilution water from several sources, including upstream water, actual downstream water, or simulated downstream water (USEPA 1994). Upstream water is generally used when the factors that could mitigate or increase the toxicity of priority contaminants are present primarily in the receiving water. Actual downstream water (*i.e.*, collected from a location outside of the IDZ where the wastewater is fully mixed with the receiving water) or simulated downstream water (*i.e.*, a mixture of upstream water and wastewater at a known ratio) is used as dilution water when wastewaters contribute substances that could mitigate or increase contaminant toxicity (e.g., total organic carbon, lime, etc.).

The sampling strategy should be designed to facilitate determination of WERs at the locations and under the conditions that the contaminant is likely to be the most toxic. If information is available to identify these locations and conditions with some certainty, then it should be possible to streamline the sampling program appropriately. If, for example, the presence of humic acids is identified as the primary factor that could mitigate copper toxicity, then it should be possible to determine where and when the concentrations of humic acids are

likely to be the lowest in receiving waters. WERs, determined for those locations and time periods, would likely result in the derivation of WQOs that would likely be protective at other sites and at other times. If some component of the wastewater is identified as the factor that is likely to mitigate toxicity (e.g., total organic carbon), then it should be possible to determine when the concentrations of that factor in receiving water are likely to be the lowest (*i.e.*, during extreme streamflows or low wastewater discharge volumes). The WQOs that are derived using the WERs for these conditions are likely to be protective under a variety of other conditions as well. One approach for determining the seasonal variability in WERs would be to conduct quarterly sampling to cover a range of flow conditions, water quality characteristics, and species sensitivities.

While simulated downstream water may seem like the most unnatural of the three types of dilution water, it offers some important advantages (USEPA 1994). Because the effluent and upstream water are combined in the laboratory, it is possible to simulate conditions at the edge of the IDZ, after complete mixing, at different points in the stream, and under different streamflow conditions. Therefore, it is possible to simulate the conditions under which the contaminant is likely to be the most toxic and determine the corresponding WER. In addition, it is possible to simulate conditions that could occur at different times of the year and determine the WERs needed to establish seasonal WQOs. Therefore, simulated downstream water should be used preferentially to determine WERs at sites that are affected by wastewater discharges. In contrast, upstream water should be used as dilution water at sites that are not yet affected by wastewater discharges.

The sampling plan should provide guidance regarding the collection of water and wastewater samples for use in biological testing. Decisions regarding the collection of grab or composite samples should be based on the objectives of the test, on the variability of water quality and flow conditions in the receiving water system, and on the variability of water quality and discharge volume of the wastewater, if applicable. Grab samples are easy to collect and provide an indicator of conditions at a specific time. However, such samples may not be representative of conditions over a longer period of time, possibly necessitating additional testing under different conditions. Composite samples are collected over a longer period time

(usually 24 hours) and are, therefore, likely to reflect short-term variability in water or wastewater quality and be more representative. Therefore, composite sampling should be used preferentially to collect water and wastewater samples for determining WERs.

### **A5.3 Recommended Procedures for Collecting, Handling, and Storing Water and Wastewater Samples**

Standard methods for collecting, handling, and storing water and wastewater samples for use in biological testing have been developed by various organizations. For example, USEPA has developed detailed guidance for sampling and handling effluent and receiving waters for use in toxicity testing (USEPA 2002a; 2002b). Environment Canada developed specific procedures for sampling effluents, leachates, and receiving waters for use in toxicity testing with various aquatic organisms (DOE 2007c; 2007d; 2008). The American Society for Testing and Materials has also published standard methods for conducting a variety of toxicity tests, which include guidance on the collection, handling, and storage of receiving water and wastewater (ASTM 2004; 2007a; 2007b). The BC Ministry of Environment has also recommended methods for sampling freshwater and effluents (Cavanagh et al. 1997; BC MOE 2003). These guidance documents should be consulted for detailed information related to sample collection, handling and storage procedures.

The following general guidance is provided to assist practitioners in the development of sampling plans that support the determination of WERs:

- All sampling activities should be conducted at the pre-determined sampling sites that are identified in the sampling plan, as practicable;
- Composite sampling should be used preferentially to collect wastewater samples for toxicity testing (provided that proper sample handling procedures are used); grab sampling is generally acceptable for collecting receiving waters;
- Composite water and wastewater samples should be collected over a 24-hr period (USEPA 2002a; 2002b);



- For static renewal tests, receiving water and wastewater samples should be collected prior to each renewal period, as practicable (DOE 2008);
- Samples should be collected in glass or teflon containers (of appropriate volume) to minimize the sorption of chemicals. Polyethylene or polypropylene containers are less desirable, but may be used for sample transport and storage (DOE 2007c);
- All containers must be thoroughly cleaned and rinsed with uncontaminated water prior to shipment to the site. Prior to sample collection, containers should be rinsed with the water sample to be collected (DOE 2007d), taking care that the rinse water does not inadvertently contaminate the final water sample;
- Aeration during the collection of water and wastewater samples should be minimized to reduce the loss of volatile chemicals (*i.e.*, containers should be completely filled to minimize air space and the sample should be collected so that the water flows smoothly and does not bubble; USEPA 2002b);
- Upon collection, each sample container must be filled, sealed, and labelled. Labelling should include at least sample type, source, date, time and duration of collection, sample preservation method and name of sampler (DOE 2007c; 2007d; 2008);
- The elapsed time between the collection of samples and the initiation of the toxicity test should not exceed 36 hours (DOE 2007c; 2007d; 2008). It is important to maintain effective communications with the test laboratory to assure that the sampling and toxicity testing schedules are coordinated;
- Composite samples should be chilled during and following collection (USEPA 2002b);
- Water and wastewater samples should be chilled and maintained at 4 °C during collection and storage (USEPA 2002a); and,
- Samples collected for off-site toxicity testing (*i.e.*, when testing is not conducted at a mobile laboratory) should be chilled to 4 °C, shipped on ice to the laboratory, transferred to a refrigeration unit, and stored at 4 °C prior to use (USEPA 2002b). Samples must not freeze during transport (DOE 2007c).

#### A5.4 Recommended Observations and Measurements

The results of aquatic toxicity tests can be strongly influenced by the physical and chemical conditions to which the test organisms are exposed. For this reason, it is necessary to carefully control conditions during toxicity testing to assure compliance with test protocols and, hence, the validity of the toxicity tests. In addition, it is necessary to monitor conditions during the bioassay to support interpretation of the resultant toxicity data. The following information should be collected during WER studies:

- The site water (*i.e.*, upstream water, downstream water after mixing, or simulated downstream water) and laboratory water used in the study should be fully characterized prior to toxicity testing, including conventional variables (e.g., hardness, pH, DO, water temperature, alkalinity, conductivity, suspended solids, and total organic carbon during collection and at start of test,), total and dissolved metals, and appropriate organic contaminants (DOE 2007c; ASTM 2007a);
- Temperature, pH, and DO must be measured in the chemistry controls of each treatment group for both site water and laboratory water. The measurements must be performed on the same schedule for both of the side-by-side tests, at the intervals specified in the protocol for the specific toxicity test (USEPA 1994);
- In the range-finding test, it is not necessary to measure the concentrations of the toxicant under consideration in any of the treatment groups (*i.e.*, nominal concentrations are acceptable);
- In the definitive toxicity test, the concentrations of the toxicant should be measured in all test solutions at the midpoint of the test (for static tests) or the midpoint of each renewal period (for static renewal tests). Alternatively, toxicant concentrations may be measured at the beginning and end of the test or each renewal period. At minimum, the concentrations of the toxicant must be measured in all treatments in which some but not all of the test organisms were adversely affected, the highest treatment that did not adversely affect any test organism, and the lowest treatment that adversely affected all of the test organisms;

- For metals, both total and dissolved concentrations must be measured in all test solutions (USEPA 1994);
- The response data for all of the concentrations in the dilution series should be reported to facilitate more detailed evaluation of the toxicity data; and,
- Appropriate quality assurance/quality control measures (e.g., replicates, sample splits, matrix spikes, etc.) must be performed to support all analytical results (USEPA 1983).

#### **A5.5 Selection of Toxicity Tests**

Application of the WER procedure necessitates the design and implementation of an aquatic toxicity testing program using site water and standard laboratory water. One of the challenges associated with the development of site-specific WQOs is the selection of toxicity tests that are appropriate for determining WERs under the unique conditions that occur at each site. To assist practitioners in this field, the USEPA (1994) established criteria for selecting appropriate toxicity tests for determining WERs. These criteria were reviewed and evaluated to identify selection criteria that could be cost-effectively applied in BC, as follows:

- At least 2 distinct toxicity tests should be conducted to facilitate the determination of WERs, including one acute bioassay and one short-term chronic bioassay. A third toxicity test (preferably a short-term chronic test) should be conducted if the results of the range-finding tests suggest that the two primary tests are likely to produce substantially different WERs (i.e., more than a factor of 3; USEPA 1994);
- The test species used to determine WERs should be in different orders and should include at least one vertebrate and one invertebrate;
- The toxicity tests should be conducted on sensitive life stages of sensitive species of aquatic organisms and measure sensitive endpoints for that life stage;
- The test organism should be sensitive to the substance or substances that are being tested;

- The test organism should be readily available throughout the duration of the testing period;
- Standard protocols for conducting the toxicity test should be available from recognized sources (e.g., Environment Canada, USEPA, ASTM);
- The duration of the toxicity test should be appropriate for the species and life stage that is tested and for the endpoint that is being measured; and,
- Static renewal or flow-through tests must be used when exposure durations exceed 48 hours.

The recommended toxicity tests for determining WERs fall into two general categories, depending on the duration of the bioassay relative to the life span of the test organism. Acute toxicity tests are conducted over a short period of time in relation to the organism's life span, generally lasting minutes, hours, or a few days. By comparison, chronic bioassays span a significant portion of the organism's life span (often more than 10%) and are particularly appropriate for evaluating substances that are persistent in the aquatic environment (DOE 2007c).

Aquatic toxicity tests are further categorized based on the type of system that is used to expose the test organism to the chemical substance under consideration. Static toxicity tests utilize the simplest test system, as the organism is exposed to the same test solution for the duration of the test (that is, the test solution is not replaced or renewed). In static renewal tests, the test solutions are renewed periodically during the test, usually at the beginning of each 24-hour period of testing (DOE 2007c). The most complicated test system is employed in flow-through toxicity tests. In this type of bioassay, the test organism is exposed to fresh test solution throughout the duration of the tests by continuously pumping the solution directly to testing chambers via a diluter system (USEPA 2002b). The advantages and limitations of the various types of toxicity test are listed in Table A5.1 (USEPA 2002a).

Toxicity data for WQG or WQO development are classified as primary, secondary, or unacceptable, with preference for primary data. Flow-through experiments are preferred for primary studies, however static renewal tests may also be acceptable. Static tests are acceptable for secondary

studies. Toxicity data that do not meet the conditions of primary or secondary data are classified as unacceptable (Meays 2012).

Table A5.1. Advantages and limitations of static and flow-through toxicity tests.

Static Test	
Advantages	Limitations
<ul style="list-style-type: none"> <li>• Simple and inexpensive</li> <li>• Very cost effective</li> <li>• Relatively low resource requirements (space, manpower, equipment); staff can perform many sequential tests on samples collected over time</li> <li>• Small volume (1 – 20 L) of effluent required</li> <li>• Provides some measure of toxicity (i.e., aging of the effluent in a non-renewable static test)</li> </ul>	<ul style="list-style-type: none"> <li>• Results do not reflect temporal changes in effluent toxicity</li> <li>• DO depletion may result from high COD, BOD, or metabolic wastes</li> <li>• Possible loss of toxicants through volatilization and/or adsorption to the exposure vessels</li> <li>• Generally less sensitive than flow-through test because the toxic substances may degrade or be absorbed reducing the apparent toxicity. There is less chance of detecting slugs of toxic wastes or other temporal variations in waste properties</li> </ul>
Flow-through Test	
Advantages	Limitations
<ul style="list-style-type: none"> <li>• Provide a more representative evaluation of effluent toxicity, especially if toxicity varies with time</li> <li>• DO concentrations are more easily maintained in the test chambers</li> <li>• Higher loading rates (i.e., biomass) may be used</li> <li>• The possibility of loss of toxicant due to volatilization, adsorption, degradation, and uptake is reduced</li> </ul>	<ul style="list-style-type: none"> <li>• Large volumes of effluent and dilution water are required</li> <li>• Test equipment is more complex and expensive, and requires more maintenance and attention</li> <li>• More space is required to conduct tests</li> <li>• Does not measure the effect of aging of the waste on toxicity</li> <li>• Because of resources required, it may be very difficult to perform multiple or overlapping sequential tests</li> </ul>

Based on the review of the available literature, the following tests are likely to be the most appropriate for determining WERs using the water effect ratio procedure:

- 48-hour acute toxicity test using water fleas, including *Daphnia magna*, *Daphnia pulex*, or *Ceriodaphnia dubia* (static test; EC<sub>50</sub> or LC<sub>50</sub> as preferred endpoints);
- 7-day short-term chronic toxicity test using the water fleas, *Ceriodaphnia dubia* (static renewal test; IC<sub>50</sub> for survival and reproduction as preferred endpoints);
- 96-hour acute toxicity test using the amphipod, *Gammarus* sp. (static renewal test; EC<sub>50</sub> or LC<sub>50</sub> as preferred endpoints);
- 48-hour acute toxicity test using fathead minnows (*Pimephales promelas*; static test; LC<sub>50</sub> as preferred endpoint);
- 96-hour acute toxicity test using fathead minnows (*Pimephales promelas*; static renewal test; LC<sub>50</sub> as preferred endpoint);
- 7-day short-term chronic toxicity test using larval fathead minnows (*Pimephales promelas*; static renewal test; IC<sub>50</sub> for survival and growth as preferred endpoints); and,
- 96-hour acute toxicity test using a salmonid within the genus *Oncorhynchus* or *Salmo* (static renewal test; EC<sub>50</sub> or LC<sub>50</sub> as preferred endpoints).

Any combination of these tests may be used to support the derivation of WERs, provided that the selection criteria listed above are met. A listing of the available toxicity tests for determining WERs for various metals and metalloids in freshwater systems is presented in Table A5.2 (USEPA 1994). Similarly, the available tests for determining WERs for metals and metalloids in saltwater systems are listed in Table A5.3 (USEPA 1994). Among the species commonly tested, rainbow trout and *C. dubia* generally provide the lowest WERs; therefore, at least one of these species should be tested whenever possible. Comparable recommendations for selecting toxicity tests for determining WERs for organic contaminants were not located in the literature.

Table A5.2. Available toxicity tests for determining water effect ratios (WERs) for metals and metalloids in freshwater systems. Ce: *Ceriodaphnia* species; Da: *Daphnia* species; Si: *Simocephalus* species; On: *Oncorhynchus* species; Sa: *Salmo* species; PP: *Pimephales promelas*.

Metal	Primary Tests	Secondary Tests
Aluminum	7-d IC <sub>25</sub> on survival and/or reproduction for <i>Ceriodaphnia</i> sp.	48-hr EC <sub>50</sub> for Daphnid (Ce, Da or Si)
Arsenic (III)	48-hr EC <sub>50</sub> for Daphnid (Ce, Da or Si); 96-hr EC <sub>50</sub> for <i>Gammarus</i> sp.	7-d IC <sub>25</sub> on survival and/or reproduction for <i>Ceriodaphnia</i> sp.; 7-d IC <sub>25</sub> on survival and growth for minnow (PP) larvae
Cadmium	48-hr EC <sub>50</sub> for Daphnid (Ce, Da or Si); 96-hr EC <sub>50</sub> for Salmonid (On or Sa); 48-hr EC <sub>50</sub> for minnow (PP) larvae	7-d IC <sub>25</sub> on survival and/or reproduction for <i>Ceriodaphnia</i> sp.; 7-d IC <sub>25</sub> on survival and growth for minnow (PP) larvae
Chromium (III)	96-hr EC <sub>50</sub> for <i>Gammarus</i> sp.; 96-hr for Salmonid (On or Sa); 48-hr EC <sub>50</sub> for Daphnid (Ce, Da or Si)	7-d IC <sub>25</sub> on survival and growth for minnow (PP) larvae; 7-d IC <sub>25</sub> on survival and/or reproduction for <i>Ceriodaphnia</i> sp.
Chromium (VI)	48-hr EC <sub>50</sub> for Daphnid (Ce, Da or Si); 96-hr EC <sub>50</sub> for <i>Gammarus</i> sp.	7-d IC <sub>25</sub> on survival and/or reproduction for <i>Ceriodaphnia</i> sp.; 96-hr EC <sub>50</sub> for <i>Gammarus</i> sp.
Copper	48-hr EC <sub>50</sub> for Daphnid (Ce, Da or Si); 48-hr LC <sub>50</sub> for minnow (PP) larvae 96-hr EC <sub>50</sub> for <i>Gammarus</i> sp.	7-d IC <sub>25</sub> on survival and/or reproduction for <i>Ceriodaphnia</i> sp.; 48-hr LC50 for minnow (PP) larvae
Lead	48-hr EC <sub>50</sub> for Daphnid (Ce, Da or Si); 96-hr EC <sub>50</sub> for <i>Gammarus</i> sp.	7-d IC <sub>25</sub> on survival and/or reproduction for <i>Ceriodaphnia</i> sp.
Mercury	48-hr EC <sub>50</sub> for Daphnid (Ce, Da or Si); 96-hr EC <sub>50</sub> for <i>Gammarus</i> sp.	None identified
Nickel	48-hr EC <sub>50</sub> for Daphnid (Ce, Da or Si); 96-hr LC <sub>50</sub> for minnow (PP) larvae	7-d IC <sub>25</sub> on survival and/or reproduction for <i>Ceriodaphnia</i> sp.; 7-d IC <sub>25</sub> on survival and growth for minnow (PP) larvae
Selenium	None identified	None identified
Silver	48-hr EC <sub>50</sub> for Daphnid (Ce, Da or Si); 7-d IC <sub>25</sub> on survival and growth for minnow (PP) larvae	7-d IC <sub>25</sub> on survival and/or reproduction for <i>Ceriodaphnia</i> sp.; 7-d IC <sub>25</sub> on survival and growth for minnow
Zinc	48-hr EC <sub>50</sub> for Daphnid (Ce, Da or Si); 7-d IC <sub>25</sub> on survival and growth for minnow (PP) larvae	7-d IC <sub>25</sub> on survival and/or reproduction for <i>Ceriodaphnia</i> sp.; 7-d IC <sub>25</sub> on survival and growth for minnow (PP) larvae

Table A5.3. Available toxicity tests for determining water effect ratios (WERs) for metals and metalloids in marine systems. Cr: *Crassostrea* species; Mu: *Mulinia* species; My: *Mytilus* species; Me: *Mercenaria* species; Mys: *Mysidopsis* species; Ho: *Holmesimysis* species; AR: *Arbacia* species; SP: *Strongylocentrotus purpuratus*

Metal	Primary Tests	Secondary Tests
Arsenic (III)	7-d IC <sub>25</sub> on survival, growth and/or reproduction for mysid (Mys or Ho); 48-hr EC <sub>50</sub> on mortality and development for sea urchin larvae (AR or SP)	7-d IC <sub>25</sub> on survival and/or reproduction for <i>Ceriodaphnia</i> sp.; 7-d IC <sub>25</sub> on survival and growth for minnow (PP) larvae
Cadmium	7-d IC <sub>25</sub> on survival, growth and/or reproduction for mysid (Mys or Ho); 48-hr EC <sub>50</sub> on mortality and development for sea urchin larvae (AR or SP)	96-hr EC <sub>50</sub> for mysid (Mys or Ho); 48-hr EC <sub>50</sub> for <i>Acartia</i> species or marine crustacean larvae
Chromium (VI)	7-d IC <sub>25</sub> on survival, growth and/or reproduction for mysid (Mys or Ho); 20-d IC <sub>25</sub> on survival and growth of the polychaete <i>Neanthes</i> species	96-hr EC <sub>50</sub> for mysid (Mys or Ho); 96-hr LC <sub>50</sub> for the juvenile or adult polychaete <i>Nereis</i> species or marine crustacean larvae
Copper	7-d IC <sub>25</sub> on survival and development for the mollusc <i>Mulinia</i> species; 48-hr EC <sub>50</sub> on mortality and development for sea urchin larvae (AR or SP)	48-hr EC <sub>50</sub> for mortality and development for mollusc larvae (Cr, Mu, My or Me); 48-hr EC <sub>50</sub> on mortality and development for sea urchin larvae (AR or SP)
Lead	7-d IC <sub>25</sub> on survival, growth and/or reproduction for mysid (Mys or Ho)	48-hr EC <sub>50</sub> for mortality and development for mollusc larvae (Cr, Mu, My or Me); 7-d IC <sub>25</sub> on survival, growth and/or reproduction for mysid (Mys or Ho)
Mercury	None identified	96-hr EC <sub>50</sub> for mysid (Mys or Ho); 48-hr EC <sub>50</sub> for mortality and development for mollusc larvae (Cr, Mu, My or Me)
Nickel	7-d IC <sub>25</sub> on survival, growth and/or reproduction for mysid (Mys or Ho); 7-d IC <sub>25</sub> on survival and development for the mollusc, <i>Mulinia</i> species	96-hr EC <sub>50</sub> for mysid (Mys or Ho); 48-hr EC <sub>50</sub> for mortality and development for mollusc larvae (Cr, Mu, My or Me)
Selenium	7-d IC <sub>25</sub> on survival, growth and/or reproduction for mysid (Mys or Ho)	48-hr EC <sub>50</sub> for <i>Acartia</i> species or marine crustacean larvae; 7-d IC <sub>25</sub> on survival, growth and/or reproduction for mysid (Mys or Ho)



Table A5.3 cont. Available toxicity tests for determining water effect ratios (WERs) for metals and metalloids in marine systems. Cr: *Crassostrea* species; Mu: *Mulinia* species; My: *Mytilus* species; Me: *Mercenaria* species; Mys: *Mysidopsis* species; Ho: *Holmesimysis* species; AR: *Arbacia* species; SP: *Strongylocentrotus purpuratus*

Metal	Primary Tests	Secondary Tests
Silver	7-d IC <sub>25</sub> on survival, growth and/or reproduction for mysid (Mys or Ho); 7-d IC <sub>25</sub> on survival and development for the mollusc, <i>Mulinia</i> species	48-hr EC <sub>50</sub> for mortality and development for mollusc larvae (Cr, Mu, My or Me); 48-hr EC <sub>50</sub> for <i>Acartia</i> species or marine crustacean larvae
Zinc	7-d IC <sub>25</sub> on survival, growth and/or reproduction for mysid (Mys or Ho); 7-d IC <sub>25</sub> on survival and development for the mollusc, <i>Mulinia</i> species	48-hr EC <sub>50</sub> for mortality and development for mollusc larvae (Cr, Mu, My or Me); 96-hr EC <sub>50</sub> for mysid (Mys or Ho)

Considerably less guidance is available for applying the resident species procedure for deriving site-specific WQOs. Nonetheless, standard methods are available for conducting toxicity tests with many fish, invertebrate, amphibian and algal species that occur in BC waters, including:

- coho salmon (*Oncorhynchus kisutch*; ASTM 2007a);
- rainbow trout (*Oncorhynchus mykiss*; DOE 2007a; 2007b);
- brook trout (*Salvelinus fontinalis*; ASTM 2007a);
- fathead minnow (*Pimephales promelas*; DOE 2008);
- threespine stickleback (*Gasterosteus aculeatus*; DOE 2000a);
- channel catfish (*Ictalurus punctatus*; ASTM 2007a);
- bluegill sunfish (*Lepomis macrochirus*; ASTM 2007a);
- green sunfish (*Lepomis cyanellus*; ASTM 2007a);
- water fleas (*Daphnia magna*, *Daphnia pulex*, *Daphnia pulicaria*, *Ceriodaphnia dubia*; DOE 1996; 2000b; 2007c; ASTM 2007a);
- amphipods (*Gammarus lacustris*, *Gammarus fasciatus*, *Gammarus pseudolimnaeus*; ASTM 2007a; *Hyaella azteca*; DOE 1997a);

- crayfish (*Oronectes* sp., *Cambarus* sp., *Procambarus* sp., *Pacifastacus leniusculus*; ASTM 2007a);
- stoneflies (*Pteronarcys* sp.; ASTM 2007a);
- mayflies (*Baetis* sp., *Ephemerella* sp., *Hexagenia limbata*, *Hexagenia bilineata*; ASTM 2007a);
- midges (*Chironomus* sp.; ASTM 2007a; DOE 1997b);
- snails (*Physa integra*, *Physa heterostrophia*, *Amnicola limosa*; ASTM 2007a);
- planaria (*Dugesia tigrina*; ASTM 2007a);
- frog (*Rana* sp.; ASTM 2007a);
- toad (*Bufo* sp.; ASTM 2007a); and,
- green alga (*Selenastrum capricornutum*; DOE 2007d; ASTM 2007a).

It is likely that these standard tests could be adapted for use with numerous other species that are closely related to the species listed above. However, additional quality assurance data should be collected to assure the validity of the toxicity test when non-standard species are used.

#### **A5.6 Recommended Protocols for Conducting Toxicity Tests**

Standard methods have been developed for each of the toxicity tests that are recommended for determining WERs using the water effect ratio procedure. The methods that have been developed by Environment Canada (DOE 1996; 2000a; 2000b; 2007a; 2007b; 2007c; 2007d; 2008), and the US Environmental Protection Agency (USEPA 2002a; 2002b) generally provide direct and accessible information on:

- The hazards that may be associated with the use of the toxicity test;
- The apparatus needed to perform the toxicity test, including facilities, dilution systems, and test chambers;
- The requirements for dilution water, including appropriate sources, treatment, and characterization;

- Handling of the test materials, including preparation of stock solutions and test concentrations;
- Test organisms, including species, age, source, care and handling, feeding, disease treatment, holding acclimation, and quality;
- Test procedures, including experimental design, test duration, and required observations and measurements;
- Analytical methodology;
- Criteria for assessing test acceptability; and,
- Calculation of results.

While such protocols provide detailed guidance for implementing toxicity tests, some additional guidance is required to adapt the procedures to WER determinations. The specific modifications that are required to implement the water effect ratio procedures are identified in the following sections.

#### **A5.6.1 Range-finding Tests**

A range-finding test should be conducted for all of the toxicity tests that will be used to determine WERs. The purpose of the range-finding test is to determine the range of chemical concentrations that are likely to cause a response in the test organism. This information is important for designing definitive toxicity tests that determine effective concentrations of the toxicant precisely in site water. Considerations for conducting range-finding tests include:

- For each species, life stage, and endpoint, the information in the toxicological data set should be used to estimate the effective concentration of the toxicant;
- Range-finding tests should be conducted using the type of site water that will be used in the definitive toxicity test (*i.e.*, upstream water, actual downstream water, or simulated downstream water);
- Range-finding tests should include appropriate negative control treatments (solvent only) to assure the validity of each test;
- Range-finding tests must be initiated within 36 hours of collecting the site water;

- Range-finding tests should be conducted for 8 to 96 hours using the same life stages of the same species that will be used in the definitive toxicity tests;
- The concentrations tested in the range-finding tests should increase from roughly a factor of 10 below the value indicated in the toxicological data set for the appropriate endpoint, life stage, and species. The concentrations in the dilution series should increase by a factor of 3.2 to 10 from the lowest concentration tested. Generally, six to eight concentrations should be tested to span the possible range of effective concentrations of the toxicant. For example, if the lowest 96-hr LC<sub>50</sub> of copper to *Daphnia magna* in the toxicological data set was reported to be 6.5 µg/L, then the dilution series for the range-finding test might include concentrations ranging from 0.6 to 201 µg/L (e.g., 0.0, 0.6, 1.9, 6.1, 19.7, 62.9, and 201 µg/L);
- All of the dose-response data generated during the toxicity test should be reported; and,
- Appropriate statistical procedures (e.g., Probit analysis) should be applied to the results of the range-finding test to determine median effective concentrations of the toxicant in site water (based on nominal toxicant concentrations).

#### **A5.6.2 Definitive Toxicity Tests**

The results of the definitive toxicity tests will be used to determine the WERs for modifying the generic WQGs. Therefore, it is desirable to generate highly reliable data in the definitive toxicity tests to reduce the degree of uncertainty associated with the WERs. Some of the considerations for conducting the definitive toxicity tests include:

- Definitive toxicity tests must be conducted using site water and appropriate laboratory dilution water;
- Definitive toxicity tests must be conducted using the same type of site water that was used in the range-finding test;

- Definitive toxicity tests conducted in site water and in laboratory water must include appropriate positive (reference toxicant) and negative (solvent only) control treatments to assure the validity of each test;
- Definitive toxicity tests must be initiated within 3 – 5 days of collecting the site water;
- The results of the range-finding test should be used to identify an appropriate dilution series for the toxicity tests that are conducted using site water. The concentrations in the dilution series should increase by a factor of 1.3 to 2.0 from the lowest concentration tested (a factor of 1.4 is recommended). Generally, eight to nine concentrations should be tested to span the possible range of effective concentrations of the toxicant;
- The information in the toxicological database should be used to identify an appropriate dilution series for the toxicity tests that are conducted using laboratory water. The concentrations in the dilution series should increase by a factor of 1.1 to 1.5 from the lowest concentration tested (a factor of 1.4 is recommended). Generally, six to seven concentrations should be tested to span the possible range of effective concentrations of the toxicant; and,
- Appropriate statistical procedures (e.g., Probit analysis) should be applied to the results of the definitive toxicity tests to determine median effective concentrations of the toxicant in site water and in laboratory water (based on measured concentrations of the toxicant).

### **A5.6.3 Laboratory Dilution Water**

Determination of WERs requires information on the toxicity of priority substances in both site water and in laboratory water. Therefore, selection and preparation of dilution water is a critical element of the overall WQOs development process. Some of the considerations for selecting and preparing laboratory dilution water for conducting toxicity tests include:

- Laboratory dilution water should be available in adequate supply, acceptable to the test organisms, be of uniform quality, and not unnecessarily affect the results of the test. The laboratory dilution water must be a ground water, surface water, dechlorinated tap water, diluted mineral water, or reconstituted water that has been demonstrated to be acceptable to aquatic organisms;
- Laboratory dilution water must satisfy the requirements identified in the protocol for the toxicity tests that will be used in the study. At minimum, test organisms should survive through acclimation and testing without showing signs of stress, such as discolouration, unusual behaviour, or death;
- The characteristics of the laboratory dilution water should be similar to those of the site water in terms of water hardness, alkalinity, and pH;
- The concentrations of total organic carbon and total suspended solids must be less than 5 mg/L in laboratory dilution water;
- The results of the toxicity tests conducted in laboratory dilution water should be comparable to those conducted at other laboratories (i.e., similar to the data represented in the toxicological database).

#### **A5.6.4 Site Dilution Water**

Determination of WERs requires side-by-side toxicity testing of priority substances in site water and in laboratory water. Some of the considerations for selecting and preparing site dilution water include:

- Two types of site water may be used in toxicity tests: upstream water and actual downstream water;
- Upstream water represents the least complicated source of dilution water because plumes, mixing zones, and effluent variability do not have to be taken into account. This approach is particularly relevant for deriving WQOs for waterbodies that are not yet influenced by wastewater discharges. However, this approach does not consider the

effects of wastewater quality on the toxicity of the substance or substances under investigation;

- Actual downstream water ought to provide the most relevant source of dilution water for determining WERs for waterbodies that are influenced by wastewater discharges. However, the application of this approach is limited by uncertainties regarding the size of the mixing zone, the extent of mixing at specific locations, and temporal variability in receiving water quality downstream of wastewater discharges (i.e. due to differences in effluent quality, effluent volume, and streamflows). While it may be possible to identify the most appropriate locations and time periods for obtaining dilution water from this source, logistical considerations may restrict sampling activities (e.g., due to ice cover or access problems);
- Dilution water for the toxicity tests conducted using site water should be obtained at times when the WERs are likely to be the lowest (i.e. when the factors that are likely to mitigate toxicity are at the lowest levels).

#### **A5.6.5 Test Organisms**

A wide variety of aquatic organisms may be used to determine WERs. Some of the factors that should be considered in the selection and handling of test organisms include:

- The test organisms should be obtained, cultured, held, acclimated, fed, and handled in accordance with the guidance provided in the protocol for the specific toxicity test that is to be used in the study;
- Test organisms must be acclimated to the laboratory dilution water for at least 48 hours prior to the initiation of toxicity tests;
- The organisms used in a pair of side-by-side tests must be drawn from the same population and tested under identical conditions;
- Test organisms must be assigned to treatment groups in a random or impartial basis;
- The test organisms must be added to the test chambers for the side-by-side tests at the same time; and,

- The test organisms must be observed at the intervals specified in the toxicity test protocol and relevant observations must be appropriately recorded.

#### **A5.6.6 Spiking Procedures**

To determine WERs, toxicity tests must be conducted in both site water and laboratory water that have been spiked with a range of chemical concentrations. Some of the considerations for spiking laboratory and site water include:

- A stock solution should be prepared using a highly soluble form of the toxicant. For metals, it is generally acceptable to use nitrate, chloride, and sulphate salts;
- Reagent or better grade chemicals must be used to prepare stock solutions for spiking water samples;
- The same stock solution must be used to add the toxicant to all of the tests that are conducted at the same time;
- For the toxicity tests conducted using site dilution water, the test solutions should be prepared using one of the four spiking procedures recommended by USEPA (1994). The preferred method involves the following steps:
  1. prepare a large volume of simulated downstream water by mixing the effluent and the upstream water at the desired ratio;
  2. divide the mixture into two portions;
  3. prepare a large volume of the highest test concentration of the toxicant using one portion of the simulated downstream water;
  4. perform serial dilutions using the well-mixed spiked and unspiked samples of the simulated downstream water (*i.e.*, using a graduated cylinder); and,
  5. allow the samples to equilibrate for a period of 1 to 3 hours.
- For the toxicity tests conducted using laboratory dilution water, the test solutions should be prepared using one of the two spiking procedures recommended by USEPA (1994). The preferred method involves the following steps:



1. prepare a large volume of the highest test concentration of the toxicant in the laboratory dilution water;
  2. perform serial dilutions using the well-mixed spiked and unspiked samples of the laboratory dilution water (*i.e.*, using a graduated cylinder); and,
  3. allow the samples to equilibrate for a period of 1 to 3 hours.
- For each treatment group, sufficient identical replicates must be prepared to support both biological testing and chemical analyses (*i.e.*, chemistry only controls).

The foregoing guidance on spiking procedures applies directly to metals and metalloids. Significantly less information was located on spiking procedures for organic substances. While many of the recommended procedures will be appropriate for use with organic chemicals, modifications will be required for volatile organics. For example, it may be necessary to renew test solutions more frequently or conduct flow-through toxicity tests to determine WERs for certain substances. Such deviations from the recommended procedures should be highlighted in the study plan and discussed with regulatory authorities prior to implementation.

#### **A5.6.7 Conducting Toxicity Tests**

A variety of toxicity testing protocols are available which provide detailed guidance for conducting toxicity tests with freshwater organisms. However, some additional guidance is required for applying these toxicity tests to the WQO development process, as follows (USEPA 1994):

- The recommendations in the toxicity test protocols concerning temperature, loading, feeding, dissolved oxygen, aeration disturbance, and controls must be followed; and,
- There must be no differences between the side-by-side tests conducted using site water and laboratory water, other than the composition of the dilution water and the concentrations of the substances tested.

#### **A5.6.8 Recommended Quality Assurance and Quality Control Measures**

Determination of WERs requires high quality information on the toxicity of chemicals of concern in site water and in laboratory water. For this reason, it is necessary to evaluate the acceptability of the toxicity tests that were conducted before the results are used to derive site-specific WQOs. In general, acute and short-term chronic toxicity tests should be considered unacceptable if:

- All test chambers (e.g., water baths) were not identical;
- Treatments were not randomly assigned to individual test chamber locations;
- A required negative control treatment (i.e. solvent only) was not included in the test;
- The test was conducted with organisms that were treated for disease within 10 days of the initiation of the test;
- The test organisms were not appropriately acclimated to the dilution water prior to the test;
- Individual test organisms were not randomly or impartially assigned to test chambers;
- More than 10% of the organisms in the control treatment(s) showed signs of disease or stress (in some tests, higher control mortality is acceptable);
- Dissolved oxygen and temperature were not measured at appropriate intervals during the test;
- Dissolved oxygen and temperature were not maintained within acceptable limits during some portion of the test;
- Toxicant concentration (dissolved and total) is not measured at the beginning and end of the test;
- No treatment other than the control treatment killed or affected less than 37% of the test organisms exposed to it;
- No treatment killed or affected more than 63% of the test organisms exposed to it; and,
- The sensitivities of the test organisms were not evaluated within the seven days immediately preceding the toxicity tests. Recommended reference toxicants for evaluating the sensitivity of each test organism include sodium dodecylsulfate, sodium

pentachlorophenate, cadmium chloride, phenol, copper chloride, copper sulphate and zinc sulphate (instructions for the use of reference toxicants and expected LC<sub>50</sub> values are generally provided with the samples) (ASTM 2007a).

#### **A5.6.9 Recommended Procedures for Calculating Water Effect Ratios**

The results of the toxicity tests conducted using site water and laboratory water provide an effective basis for determining how ambient water quality conditions are likely to influence the toxicity of priority substances in freshwater ecosystems. Calculation of WERs using the results of toxicity tests requires several steps, including:

- Compile all of the physical, chemical and biological data collected during the toxicity tests;
- Evaluate the acceptability of the toxicity tests and chemistry data using the quality assurance criteria that were identified in the study plan;
- For each toxicant and water type, report all of the dose-response data collected during the toxicity test;
- For each toxicant and each water type (*i.e.*, site water a, site water b, etc.), calculate median effective concentrations (*e.g.*, LC<sub>50</sub>, EC<sub>50</sub>, or IC<sub>50</sub>) and 95% confidence limits using the average measured concentrations in the test chambers during the test. Probit analysis should be used preferentially to determine median effective concentrations; however, several other procedures can also be used (*e.g.*, Logit analysis, Spearman-Kärber, trimmed Spearman-Kärber, Inhibition concentration method, etc.; West, Inc. and Gulley 1996);
- If the laboratory water toxicity tests were conducted at a different water hardness than the site water toxicity tests, the laboratory water effective concentrations should be adjusted to account for the differences in water hardness. The simplest adjustment procedure involves multiplying the measured effective concentration for the test by the ratio of the predicted toxic concentration in the site water and the predicted toxic concentration in the laboratory water. These values can be determined using the

toxicity vs. hardness relationships that are reported in the open literature and the WQG documents.

- For each test endpoint, calculate WERs for each toxicant and water type by dividing the median effective concentration of the substance in site water by the median effective concentration of the substance in laboratory water. For metals, WERs should be calculated for both total and dissolved concentrations;
- Compare the WERs that were calculated for the various test endpoints. If the WERs for the two toxicity tests agree within a factor of three, no additional testing is required to revise the WQOs. Lack of agreement between the WERs for the same chemical and water type necessitates additional toxicity testing to generate at least one additional WER;
- Calculate final WERs for each chemical and water type by determining the geometric mean of the comparable WERs obtained from the various toxicity tests. When more than two WERs have been determined (i.e. when the first two WERs were not comparable), the final WER should be calculated as the geometric mean of the two lowest WERs. For metals, final WERs should be determined for both total and dissolved concentrations.

The procedures recommended in this document for calculating the final WER are less complicated than those that have been applied in the United States (see USEPA 1994). The recommended simplification of the procedures is intended to make the procedure more accessible and understandable to potential practitioners. In addition, the modifications reflect the mechanics of the WQG derivation process in Canada, in which a safety factor is applied to the lowest observed effect level. This conservative approach provides room for flexibility in the derivation of the site-specific WQOs, while still providing a margin of safety for protecting designated water uses.

## **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, BC.

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 m<sup>3</sup> 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 WERs 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 to support the derivation of a 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 recommended in this document.

### **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 \$3M

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 preliminary WQO from the available generic WQGs. The WQGs applicable to copper, for the designated water uses in the Upper Clark Fork River are (Singleton 1987):

- Raw water for drinking water supply: 500 µg/L
- Fish and aquatic life: 13 µg/L (at hardness of  $\leq 120$  mg/L)
- Irrigation: 200 µg/L
- Livestock watering 300 µg/L
- Recreation and aesthetics: 1,000 µg/L

The WQGs for copper are dependent 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  $\text{CaCO}_3$ ). At this water hardness, the Canadian and BC 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 preliminary WQO (i.e. the WQG for the protection of fish and aquatic life of 13 µg/L of copper).

Next, the preliminary WQO was evaluated to assess its applicability to the Upper Clark Fork River. As a first step, the preliminary WQO 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 mineralogy to estimate background levels of copper. Data collected at this site indicate that background levels of dissolved copper are typically  $<1.2 \mu\text{g/L}$ . Since the preliminary WQO of copper is greater than background levels, no adjustment of the preliminary WQO is necessary. Likewise, it was not necessary to adjust the preliminary WQO to account for analytical limits of quantitation (i.e. detection limits of  $< 1 \mu\text{g/L}$  are typically achieved for copper using ICP technology).

In some cases, it may be warranted to adjust the preliminary WQO to account for atypical species assemblages that are present at the site under consideration. For example, the preliminary WQO may need to be adjusted if it is based on effects to coldwater fish species and the water body under consideration supports warm-water 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 preliminary WQO. Therefore, the preliminary WQO 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 preliminary WQO was warranted.

### **Determination of Water Effect Ratios**

Implementation of the WER 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.

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 WER (see Table A5.4 for an example). Overall, the WERs obtained in the study ranged from 1.42 to 11.0 for total copper and 1.04 to >5.82 for dissolved copper.

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 3). 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 5



sampling periods were averaged for each toxicity test at each site. The geometric mean of the two lowest average WERs was calculated to determine the final WER at each site for both total and dissolved copper (Tables A5.5 and A5.6, respectively). 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 (2.23 for total copper and 1.83 for dissolved copper).

Table A5.4. Example of water effects ratios for the Upper Clark Fork River (downstream of Warm Springs Pond) using the results of toxicity tests for rainbow trout.

<b>Sampling Date</b>	<b>LC<sub>50</sub> in Site Water (µg/L)</b>	<b>LC<sub>50</sub> in Lab Water (µg/L)</b>	<b>Water Effect Ratio Site LC<sub>50</sub>/Lab LC<sub>50</sub></b>
Low flow – winter	385	111	3.47
Low flow – early spring	335	102	3.28
High flow – late spring	255	81.0	3.15
Low flow – fall	245	80.8	3.03
Low flow – late fall	296	137	2.16
Mean WER			3.02

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

$$\text{WQO} = \text{Preliminary WQO} \times \text{WER}$$

Using this equation, the WQO for total and dissolved copper in the Upper Clark Fork River downstream of Warm Springs Pond were 35 and 29 µg/L, respectively. At Deer Lodge, the WQOs for total and dissolved copper were 29 and 24 µg/L, respectively.

Table A5.5. Calculated water effects ratios for total copper in the Upper Clark Fork River.

		Water Effect Ratio					
Sampling Site	Sampling Date	Rainbow trout	Fathead minnow	Fathead minnow	<i>C. dubia</i>	<i>C. dubia</i>	Final WER
		Acute Test	Acute test	Chronic test	Acute test	Chronic test	
UCFR d/s from Warm Springs Pond	Low flow - winter	3.47	7.98	4.16	ND	2.02	
	Low flow – early spring	3.28	11.00	3.04	6.12	>7.84	
	High flow – late spring	3.15	3.49	3.64	4.11	3.003	
	Low fall - fall	3.03	3.12	1.42	1.56	1.92	
	Low flow – late fall	2.16	7.60	3.76	2.65	2.67	
	Mean WER	3.02	6.64	3.20	3.61	2.41	<b>2.70</b>
UCFR at Deer Lodge	Low flow - winter	2.38	6.36	2.59	2.76	1.59	
	Low flow – early spring	2.41	4.44	3.36	2.10	3.20	
	High flow – late spring	2.55	4.77	1.64	8.79	1.78	
	Low fall - fall	1.89	5.44	1.89	1.91	2.35	
	Low flow – late fall	2.02	7.75	3.33	1.86	2.18	
	Mean WER	2.25	5.75	2.56	3.48	2.22	<b>2.23</b>

ND = not determined

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

Table A5.6. Calculated water effects 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>	<i>C. dubia</i>	Final WER
		Acute Test	Acute test	Chronic test	Acute test	Chronic test	
UCFR d/s from Warm Springs Pond	Low flow - winter	2.56	5.11	3.43	ND	1.38	
	Low flow – early spring	2.25	4.58	2.39	4.24	>5.82	
	High flow – late spring	2.98	3.14	3.64	3.91	2.26	
	Low fall - fall	2.77	1.94	1.32	1.52	1.83	
	Low flow – late fall	2.07	2.27	3.18	2.92	2.21	
	Mean WER	2.53	3.41	2.79	3.15	1.92	<b>2.20</b>
UCFR at Deer Lodge	Low flow - winter	1.78	3.71	1.60	1.76	1.04	
	Low flow – early spring	1.72	2.86	2.31	1.50	2.74	
	High flow – late spring	2.06	3.46	1.53	3.07	1.64	
	Low fall - fall	1.61	3.52	1.76	1.65	2.54	
	Low flow – late fall	1.70	2.02	3.33	1.48	1.91	
	Mean WER	1.77	3.11	2.11	1.89	1.97	<b>1.83</b>

ND = not determined

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