Water Quality

Water Quality Criteria for Copper

Overview Report

Prepared pursuant to Section 2(e) of the
Environment Management Act, 1981

Original signed by T. R. Johnson
Deputy Minister
Environment and Parks
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Summary

This report is one in a series which establishes water quality criteria for British Columbia. The report sets criteria for copper to protect a number of uses. These include drinking water, freshwater and marine aquatic life, wildlife, livestock watering, irrigation, and recreation. For aquatic life, the criteria are expressed in terms of a maximum and a 30-day average concentration to address the short-term and long-term effects of copper separately. These criteria vary according to the hardness of the water. For other water uses, the criteria are set only as maximum concentrations. Actual values are summarized in the Tables.

The criteria are consistent with the Canadian Water Quality Guidelines published by the CCREM in March, 1987, except for drinking water and aquatic life.

For drinking water, our receiving water criterion is lower than the CCREM guideline in order to allow for internal contributions from copper piping systems.

For freshwater aquatic life, the CCREM offers only maximum values more restrictive than ours. The criteria in this report are more flexible and suitable to provincial background conditions. We also recommend that copper not be used as a pesticide in waters where fisheries are an important resource. The CCREM did not set criteria for marine and estuarine aquatic life.

The two major uses of the criteria are:

1. as a guideline for assessments of water quality conditions
2. as one of the factors considered in setting water quality objectives for a specific body of water

If a form of copper other than total copper is to be used for an objective, then this form (e.g., dissolved, extractable, etc.) will need to be determined by site-specific studies.

Tables

Table 1: Summary of Water Quality Criteria for Copper

Water Use	**30-day Average µg/L Total Copper**	**Maximum µg/L Total Copper**
Raw Drinking Water Supply	—	500 µg/L
Fresh Water Aquatic Life (when average water hardness as $CaCO_3$ is less than or equal to 50 mg/L)	less than or equal to 2 µg/L	(0.094(hardness)+2) µg/L (hardness as mg/L $CaCO_3$)
Fresh Water Aquatic Life (when average water hardness as $CaCO_3$ is greater than 50 mg/L)	less than or equal to 0.04 (mean hardness) µg/L	(0.094(hardness)+2) µg/L (hardness as mg/L $CaCO_3$)
Wildlife	None proposed	300 µg/L
Livestock Water Supply	None proposed	300 µg/L
Irrigation Water Supply	None proposed	200 µg/L
Recreation and Aesthetics	None proposed	1000 µg/L
Marine and Estuarine Aquatic Life	less than or equal to 2 µg/L	3 µg/L

1. the average is calculated from at least 5 weekly samples taken in a period of 30 days.
2. when detailed knowledge on the bioavailable forms of copper is available, the form of copper in the criteria for aquatic life can be modified, as justified by the data
3. if natural background levels exceed the criteria for aquatic life, the increase in total copper above natural levels to be allowed, if any, should be based on site-specific data.

Preface

THE MINISTRY OF ENVIRONMENT, LANDS AND PARKS (now called Ministry of Water, Land and Air Protection) develops province-wide ambient water quality guidelines for variables that are important in the surface waters of British Columbia. This work has the following goals:

1. to provide guidelines for the evaluation of data on water, sediment, and biota
2. to provide guidelines for the establishment of site-specific ambient water quality objectives

Ambient water quality objectives for specific waterbodies will be based on the guidelines and also consider present and future uses, waste discharges, hydrology/limnology/oceanography, and existing background water quality. The process for establishing water quality objectives is more fully outlined in *Principles for Preparing Water Quality Objectives in British Columbia*, copies of which are available from Water Quality Section of the Water Management Branch.

Neither guidelines nor objectives which are derived from them, have any legal standing. The objectives, however, can be used to calculate allowable limits or levels for contaminants in waste discharges. These limits are set out in waste management permits and thus have legal standing. The objectives are not usually incorporated as conditions of the permit.

The definition adopted for a guideline is:

> ***A maximum and/or a minimum value for a physical, chemical or biological characteristic of water, sediment or biota, which should not be exceeded to prevent specified detrimental effects from occurring to a water use, including aquatic life, under specified environmental conditions.***

The guidelines are province-wide in application, are use-specific, and are developed for some or all of the following specific water uses:

- Raw drinking, public water supply and food processing
- Aquatic life and wildlife
- Agriculture (livestock watering and irrigation)
- Recreation and aesthetics
- Industrial (water supplies)

The guidelines are set after considering the scientific literature, guidelines from other jurisdictions, and general conditions in British Columbia. The scientific literature gives information on the effects of toxicants on various life forms. This information is not always conclusive because it is usually based on laboratory work which, at best, only approximates actual field conditions. To compensate for this uncertainty, guidelines have built-in safety factors which are conservative but reflect natural background conditions in the province.

The site-specific water quality objectives are, in most cases, the same as guidelines. However, in some cases, such as when natural background levels exceed the guidelines, the objectives could be less stringent than the guidelines. In relatively rare instances, for example if the resource is unusually valuable or of special provincial significance, the safety factor could be increased by using objectives which are more stringent than the guidelines. Another approach in such special cases is to develop site-specific guidelines by carrying out toxicity experiments in the field. This approach is costly and time-consuming and therefore seldom used.

Guidelines are subject to review and revision as new information becomes available, or as other circumstances dictate.

The guidelines apply to the ambient raw water source before it is diverted or treated for domestic use.

The Ministry of Health regulates the quality of water for domestic use after it is treated and delivered by a water purveyor.

Guidelines relating to public health at bathing beaches are the same as those used by the Ministry of Health which regulates the recreation and aesthetic use.

Recommended Guidelines

These criteria are based on a detailed analysis given in a technical document. The criteria are consistent with the Canadian Water Quality Guidelines (CCREM Guidelines) issued by the Canadian Council of Resource and Environment Ministers (1987), except as noted.

1. RAW DRINKING WATER (INCLUDES FOOD PROCESSING WATER)

In raw drinking water with or without treatment, total copper should not exceed 500 µg/L.

This value is lower than that recommended by the CCREM (1.0 mg/L) for raw drinking water to allow for some internal contribution from distribution systems (i.e., copper plumbing) before the BC Ministry of Health drinking water quality standard (1.0 mg/L) for finished water applies.

2. AQUATIC LIFE

For aquatic life, the criteria are expressed in terms of total copper. This provides the most general application and the safest in the absence of detailed site-specific information. However, when detailed knowledge on the bioavailable forms of copper in a waterbody is available, the form of copper in the criteria can be modified, as justified by the data (see Application of Criteria).

2.1 Freshwater Aquatic Life

30-Day Average Copper Criteria

(a) The 30-day average concentration of total copper (based on a minimum of 5 approximately weekly samples) should not exceed 2 µg/L when average water hardness over the same period (expressed as mg/L CaCO3) is less than 50 mg/L. When average water hardness is greater than 50 mg/L the 30-day average concentration should not exceed the numerical value (in µg/L) given by the formula:

0.04(average hardness)

where water hardness is reported as mg/L $CaCO_3$.

Examples based on this formula (rounded to the nearest µg/L) are as follows:

Average Water Hardness in mg/L $CaCO_3$	**30-Day Average Total Copper Criterion in µg/L**
less than or equal to 50	2
75	3
100	4
125	5

150	6
175	7
greater than 200	8
greater than 250	10

Maximum Copper Criteria

(b) The maximum concentration of total copper should not exceed at any time the numerical value (in µg/L) given by the formula:

0.094(hardness)+2

where water hardness is reported as mg/L **$CaCO_3$.**

Examples based on this formula (rounded to the nearest µg/L) are as follows:

Water Hardness in mg/L $CaCO_3$	Maximum Total Copper Criteria in µg/L
0	2
10	3
20	4
50	7
75	9
100	11
125	14
150	16
175	18
200	21

250	26

High Natural Background Copper Criteria

(c) If natural background levels exceed (a) or (b) above, then the increase in total copper above background to be allowed, if any, should be based on site-specific conditions.

The CCREM guidelines also vary with water hardness but specify only a more restrictive maximum value rather than the maximum and 30-day average proposed here. The B. C. criteria will be more flexible and suitable to provincial background conditions.

2.2 Marine and Estuarine Aquatic Life

(a) The 30-day average concentration of total copper (based on a minimum of 5 approximately weekly samples) should not exceed 2 µg/L ***(b) The maximum concentration of total copper should not exceed 3 µg/L at any time*** ***(c) If natural background levels of total copper exceed (a) or (b) above, then the increase in total copper above background to be allowed, if any, should be based on site-specific conditions.***

There are no CCREM Guidelines for copper for marine and estuarine aquatic life.

3. WILDLIFE

The maximum concentration of total copper in waters frequented by wildlife should not exceed 300 µg/L.

There are no CCREM Guidelines for the specific protection of wildlife.

4. LIVESTOCK

The maximum concentration of total copper in livestock drinking water should not exceed 300 µg/L.

The CCREM has recommended separate guidelines for cattle, swine and poultry, and sheep based on the different sensitivities of these groups of animals to copper. The single value recommended here is designed to protect all livestock because it is based on the toxicity of copper to sheep which are the most sensitive animals to copper. While this single value may be overprotective for less sensitive species, it does not restrict an area to the raising of only the more tolerant species.

5. IRRIGATION

In irrigation waters, the maximum total copper concentration should not exceed 200 µg/L.

The CCREM has recommended separate guidelines for copper in irrigation water depending on the crop and soil types. The single criterion recommended here is the same as the lowest value recommended by the CCREM. This single low value was recommended so that crop rotation, from tolerant to sensitive species, could be practiced freely without fear of toxic conditions in the irrigation water.

6. RECREATION AND AESTHETICS

In water used for recreational activities, total copper should not exceed a maximum of 1000 µg/L.

There are no CCREM Guidelines for copper in water used for recreational activities.

Application of Guidelines for Aquatic Life

1. FORMS OF COPPER AND PROBLEMS IN APPLYING CRITERIA

The criteria recommended here have the following two applications: assessing existing water quality data and setting water quality objectives. The application will determine how the criteria should be used. In either case there are advantages and disadvantages to using any one of the sample preparation techniques that are presently available and that can be performed on a routine, province-wide basis. The advantages and disadvantages of these techniques are reviewed below.

1.1 Total Copper

The advantage of total copper is that all the copper that may potentially be toxic is included in the measurement (i.e., if the total copper concentration measured in a waterbody is within the criteria limits, then it can be concluded with confidence that no copper problems exist). Another advantage of total copper is that, for comparative purposes, there is sometimes a considerable amount of historical background data available. Furthermore, total copper is a relatively inexpensive measurement and can be easily monitored on a routine basis.

The main disadvantage of using total copper to assess water quality is that a large fraction of the total copper may be in forms that are biologically unavailable (e.g., organically complexed or sorbed by particulates). Therefore total copper may overestimate toxicity, especially in a turbid waterbody with high complexing capacity.

1.2 Dissolved Copper

The main advantage of dissolved copper is that most of the bioavailable copper is likely to be in the dissolved fraction. The measurement excludes particulate copper which is less likely to be biologically available. Another advantage of dissolved copper is that, for comparative purposes, there is sometimes a considerable amount of historical background data available. Furthermore, dissolved copper is a relatively inexpensive measurement and can easily be monitored on a routine basis.

The disadvantages of using dissolved copper to assess water quality are that it may overestimate or underestimate the bioavailable copper, depending on the waterbody. Soluble copper may be weakly adsorbed onto particulates which may be retained in the non-filterable fraction of a sample. Also, cupric ions (Cu^{2}+) can sorb onto the filter and sample container. In either case the measurement of dissolved copper may underestimate the bioavailable copper. On the other hand, a portion of the dissolved copper may be complexed with soluble organic ligands rendering it biologically unavailable. This would lead to the bioavailable copper being overestimated. Therefore caution should be exercised in predicting toxicity on the basis of dissolved copper measurements.

Dissolved copper is an operationally defined measurement (i.e., that which can pass through a 0.45-µm filter). Therefore the species of copper included in the measurement are not known; only relative comparisons can be made between various sites and between different times at the same or different locations, which adds an additional degree of uncertainty to the assessment.

1.3 Extractable Copper

The advantage of extractable copper is that it includes weakly sorbed copper in the particulate fraction which may be biologically available; also included is the dissolved copper fraction which is likely to contain most of the bioavailable copper.

The disadvantage of extractable copper is that, like dissolved copper, it can include copper complexed with soluble organic ligands so the bioavailable copper may be overestimated. Also, extractable copper, like dissolved copper, is an operationally defined measurement and therefore is subject to the same uncertainties. Furthermore, the results of different methods of analyzing extractable copper are not readily comparable. Another disadvantage of extractable copper is that the analytical technique is not restrictive enough (i.e., no standard time period between sample collection and analysis) to ensure reproducible results. Recent evidence indicates that reproducibility may be acceptable if this time period is restricted to 7 days. Caution should be exercised when comparing historical levels of extractable metals because no time restriction on sample storage was specified in the past. Furthermore, there are a number of different extractable procedures in the literature, sufficiently different that the results are not comparable to each other. A measurement for extractable copper will likely be between total and dissolved copper for a particular waterbody. In eutrophic waters, extractable copper is likely to be closer to total copper values than to dissolved copper values, whereas in oligotrophic waters, extractable, dissolved, and total copper values are likely to be similar.

2. ASSESSMENT OF EXISTING WATER QUALITY DATA

Because extractable or total copper can only overestimate bioavailable copper, it can be concluded with confidence that no harm to aquatic life will occur if total or extractable copper levels in a waterbody are below the recommended criteria levels. Dissolved copper, on the other hand, can underestimate or overestimate the bioavailable copper; therefore caution should be exercised when assessing water quality in terms of dissolved copper, to which the criteria would normally not apply.

The criteria recommended in this document are based predominantly on laboratory bioassays, which usually have been performed using dilution waters with low complexing capacities. The criteria are therefore likely to be overprotective for many waterbodies, especially for those in a eutrophic condition in which copper complexes may form. Therefore, based on the analyses for total, dissolved or extractable copper, it cannot be concluded with certainty that a copper problem exists in a waterbody if measurements exceed the criteria levels. If any of these measurements suggest that a copper problem exists by exceeding the criteria levels, and if copper is anthropogenically generated, then a more intensive investigation employing other techniques would have to be used to confirm that a problem exists. Other methods may include one or more assessment techniques such as measuring the complexing capacity, analysis for metallothionein in fish liver, long-term bioassays on sensitive resident species using local water, and population studies on biota (fish, benthos, algae, etc.). Because of the complexity and cost of these alternative methods, they should be reserved for waterbodies with high fisheries values, which are threatened by a controllable copper input.

3. SETTING WATER QUALITY OBJECTIVES

In setting water quality objectives for waterbodies where the copper concentration exceeds the criteria as a result of existing discharges, the form of copper stated in the objectives needs to be defined in advance. In view of the dependence of copper toxicity on the complexing capacity of a waterbody, an assessment (as outlined above) would have to be performed on a site-specific basis to determine if the biota are being harmed. From these measurements the form of copper present which correlates best with the test results can be determined.

For undeveloped waterbodies, two situations could exist. For total or extractable copper which may overestimate, but not underestimate bioavailable copper, natural background concentrations either meet the criteria or they do not. At any location, both cases may occur depending upon the time of year. When natural background concentrations equal or exceed the criteria, then any increase in total or extractable copper to be allowed should be based on site-specific data. Because dissolved copper can underestimate the bioavailable copper, the use of dissolved copper for assessment purposes is not recommended unless it is shown that it satisfactorily represents the bioavailable copper.

When natural background concentrations of total or extractable copper in undeveloped waterbodies are less than the criteria levels, then the criteria should apply in terms of total or extractable copper. However, if the levels cause an economic hardship to new development, the necessary studies should be performed to determine if increased copper levels would be detrimental.

4. CRITERIA BASED ON NATURAL BACKGROUND LEVELS

In cases where natural background levels exceed the numerical criteria, such as situations where drainage or runoff flows through mineralized areas, the term background in the context of this document can have either one of two interpretations. These are as follows:

4.1 Operational Background Levels which refer to ambient levels monitored at a control site immediately upstream or outside the influence of the area of disturbance or discharges in question. They reflect the existing control levels at any given time, which may not be the same as natural or pre-development levels, and which may change with time as upstream/upcurrent development occurs. They thus provide only a relative frame of reference for assessing change. The control site should be sampled at virtually the same time as the test site.

4.2 Pre-operational Background Levels which refer to historical background levels monitored prior to the advent of the developments in question. They provide a fixed frame of reference for assessing future change. Comparison of these levels with operational levels at the disturbed site can provide evidence of excessive levels of copper originating from the operation(s). A statistical definition of the pre-operational background level (e.g., seasonal mean, 90th percentile, etc.) will be required to apply the recommended criteria. This definition has been intentionally omitted from this document and is to be determined on a site-specific basis when setting objectives so that any permitted increase will adhere to the natural seasonal pattern in a particular waterbody.

The choice of whether to use operational or pre-operational background levels for criteria or objectives primarily depends upon the variability of background levels. Pre-operational background is preferred for waterbodies where low variability occurs. Modest monitoring of these waters can identify a fixed frame of reference which can be used to develop site-specific water quality objectives. For waterbodies where high variability occurs, operational background (control) monitoring will be required because of the difficulty in defining a fixed frame of reference. However, for some waterbodies such as transboundary waters, waters with exceptional resource values or waters where upstream control sites may be affected by future man-caused disturbances, it may be necessary to obtain a fixed frame of reference. Therefore, for some waters with high variability, extensive pre-operational monitoring may be required to define the pre-operational background levels. It may also be possible to use operational background levels as the basis for objectives initially. Then, when sufficient upstream/upcurrent data are available, one would switch to the use of a fixed frame of reference as the basis for objectives provided that significant upstream/upcurrent development has not occurred during this period.

5. COPPER AS A BIOCIDE

Copper (in the form of copper sulphate) is often used as a biocide for controlling algal problems and swimmer's itch. The short-term solution to algal problems may be compromised by long-term consequences in view of the uncertain fate of copper in the environment, the accumulation of organic matter and copper on the bottom of lakes from copper algicide treatment and studies that have demonstrated harmful effects to algae and fish at similar low copper concentrations. Therefore, where fisheries are to be protected, we recommend that alternative methods such as the source control of nutrients, appropriate placement of water intakes, aeration of bottom water and precipitation of nutrients by liming be considered instead of applying copper algicides.

When used as a molluscicide for the treatment of swimmer's itch, copper sulphate appears to be ineffective. Also, the treatment may harm more sensitive non-target organisms if the application rates are increased to effective levels. Therefore, considering the above factors, the use of copper sulphate to treat swimmer's itch is not recommended in waterbodies where fisheries are an important resource.