MINISTRY OF ENVIRONMENT AND PARKS
PROVINCE OF BRITISH COLUMBIA

WATER QUALITY CRITERIA FOR COPPER
TECHNICAL APPENDIX

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Resource Quality Section
Water Management Branch

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1. INTRODUCTION

This document discusses the effects of copper on the various water use categories which include drinking water, aquatic life, wildlife, livestock watering, irrigation, recreation and aesthetics, and industrial water supplies. Although copper is an essential micro-nutrient to life, excessive amounts can impart an unpleasant taste in drinking water and may cause liver damage in humans and other animals. Aquatic organisms are particularly sensitive to excessive levels of copper in water, and therefore a large portion of this document focuses on the toxicity of copper to aquatic life. Where applicable, or where sufficient information exists, criteria are recommended to protect water users from copper originating from anthropogenic sources. Standards, objectives, criteria, and accompanying rationales from other jurisdictions are reviewed and their suitability for British Columbia waters is considered.

Because of the extensive amount of literature on copper, a large portion of the information used in this document has been extracted from recent reviews documenting the numerous toxicological studies pertaining to this contaminant. The purpose of this document was not to re-review the extensive amount of original literature already addressed in recent publications, but instead, to focus on the most applicable information which could be used to formulate defensible criteria for British Columbia waters.
2. FORMS AND TRANSFORMATIONS IN THE ENVIRONMENT

2.1 FORMS AND TRANSFORMATIONS

In the aquatic environment copper may exist in:

(i) solution; as hydrated free cupric ion Cu$^{2+}$, as complexed cupric ion, and as simple or complexed undissociated cupric compounds¹. Cu(III) is rarely encountered naturally; Cu(I) or cuprous copper is sometimes found but in aerated water of pH 6 to 8 it is readily oxidized to cupric, Cu(II)².

(ii) suspended particulates, as precipitates (hydroxide complexes, phosphates, sulphides) or adsorbed onto other particles which may settle on the bottom¹.

The forms of copper present in any particular waterbody are dependent upon a number of variables, including bicarbonate/carbonate, phosphate and pH equilibria, hardness, alkalinity, and suspended particulate content. Other substances, such as organic complexing agents, will affect the form of copper present. In the absence of other complexing or adsorbing agents, alkalinity and pH govern copper speciation by the formation of carbonato- and hydroxo-complexes. In such cases, Cu$^{2+}$ and CuCO$_3$ are expected to be the predominant freshwater forms³.

At pH values and bicarbonate concentrations of most freshwaters, cupric copper reacts with bicarbonate and hydroxide to give malachite:

\[ 2 \text{Cu}^{2+} + \text{HCO}_3^{-} + 2\text{OH}^- \xrightarrow{\text{Cu}_2(\text{OH})_3\text{CO}_3 + \text{H}^+} \]

Malachite is quickly precipitated from solutions in which copper is present at concentrations greater than about 0.5 mg/L⁴.
At lower concentrations of copper in solutions with a pH less than 8.0 the reaction between cupric copper and hydroxide is unimportant compared with that occurring between cupric copper and bicarbonate:

$$\text{Cu}^{2+} + \text{HCO}_3^- \rightleftharpoons \text{CuCO}_3 + \text{H}^+$$

Stiff\textsuperscript{19} has shown that except in acidic waters, the stability constant of this reaction is such that the concentration of carbonate-complexed copper will exceed that of cupric copper.

On a global basis, Gibbs\textsuperscript{4} estimated that only about one percent of the copper transported in rivers was in soluble form, 85 percent was associated with crystalline material, 4.5 percent with organic material, 5.7 percent was bound to metal hydroxide coatings, and 3.5 percent was adsorbed onto suspended particulates. On the other hand, Spear and Pierce\textsuperscript{3} reported that the adsorption of copper to the surface of silt particles may constitute 20 to 80 percent of the total copper transported in rivers. These percentages can vary greatly among locales and at different times within a given locale. For example, Gibbs\textsuperscript{4} found that in the Yukon River 3.3 percent of the copper was in the dissolved state, 87.3 percent was associated with crystalline material, 3.8 percent as metallic coatings, 3.3 percent in organic material, and 2.3 percent was adsorbed on solids. At the other end of the spectrum, McDuffie \textit{et al.}\textsuperscript{5} found that in the Susquehanna River in New York State, 53 percent of the copper was transported in the dissolved state and 1, 15, and 31 percent was carried by the sand, silt, and clay, respectively.

In marine waters, the degree of inorganic complexing tends to increase with increasing salinity. The predominant forms of dissolved copper will be associated with the ligands, hydroxide, carbonate, and chloride (e.g., CuCO\textsubscript{3}, Cu(OH)\textsubscript{2}, and CuCl\textsuperscript{+}). According to Florence and Batley\textsuperscript{177}, Cu\textsuperscript{2+} is expected to be only a few percent of the dissolved copper. In marine waters, 67 percent of the total copper may be complexed with organics. Organic complexing increases with increasing pH and increasing redox potential\textsuperscript{3}. 
2.2 SAMPLE PREPARATION TECHNIQUES

There are four main methods of reporting trace metals in water:\n
(i) dissolved metals, which are those metals of an unacidified sample that pass through a 0.45-μm membrane filter.

(ii) total metals, which are those metals in an unfiltered sample that are soluble after vigorous digestion with concentrated acid (this does not necessarily include mineral-bound metals depending on the specific analytical methodology), or the sum of the concentration of metals in both dissolved and suspended fractions.

(iii) acid-extractable metals, which are those metals in solution after treatment of an unfiltered sample with hot dilute mineral acid.

(iv) residue or suspended metals, which are those metals of an unacidified sample retained by a 0.45-μm membrane filter. These metals can be estimated by calculation:

\[ M(R) = M(T) - M(D) \]

where \( M \) = Metal, \( R \) = Residue, \( T \) = Total, and \( D \) = Dissolved

The U.S. EPA recently proposed an alternative analytical technique for metals termed "acid-soluble metals". They define acid-soluble metals as that portion which passes through a 0.45-μm membrane filter after the sample is acidified to pH 1.5 to 2.0 with nitric acid. This analytical technique has been proposed by the United States Environmental Protection Agency (U.S. EPA) for their most recent criteria for copper. However, this technique, which is basically an acid-extractable technique (see Section 2.2 (iii)), has to be approved and standardized before it is used for the implementation of U.S. EPA regulatory programs.

Another technique which is presently being investigated is the use of an ion-exchange column using a strong acid or a chelating resin. The rationale for the development of this technique is based upon the expectation that the free or weakly complexed forms of copper are the major toxic species and that, by passing a water sample through a strongly acidic cation exchanger for saltwater or a chelating resin for freshwater, the free and
labile copper is retained on this column. The copper retained on this column is then measured and is expected to reflect more closely the biologically available copper than other techniques presently in use. The method for copper in freshwater is being developed by the Inland Waters Directorate\textsuperscript{15} and the marine water technique is being developed by Zorkin et al.\textsuperscript{16} through funding provided by Environment Canada. While promising, these techniques are still in the early development stages.
3. OCCURRENCE IN THE ENVIRONMENT

3.1 NATURAL SOURCES

Natural copper deposits in the form of chalcopyrite (CuFeS₂), chalcocite (Cu₂S), bornite (Cu₄FeS₄), and carbonate ores such as malachite [Cu₂(CO₃)(OH)₂] and azurite [Cu₃(CO₃)₂(OH)₂] are found in igneous, metamorphic, and sedimentary rocks and are common throughout British Columbia, except for the northeast corner of the province. Deposits of native copper also occur, but these are less common. Igneous rocks contain the highest average concentration (55 mg/kg) of copper followed by the sedimentary rocks: shale (45 mg/kg), sandstone (5 mg/kg) and limestone (4 mg/kg). Copper can be released from these rocks by weathering and oxidation, and through acid generation from bacterial attack of pyritic minerals. However, McNeely et al. report that little dissolved copper in water is of natural origin because most copper minerals are relatively insoluble under normal conditions. In terms of total copper, Bertine and Goldberg estimated that 40 to 67 percent of the annual global input to the environment is from natural weathering. For the Rhine River, Hueck estimated that only 10 percent of the total copper originated from natural sources.

3.2 ANTHROPOGENIC SOURCES

According to McNeely et al., elevated concentrations of copper in the aquatic environment are usually related to anthropogenic sources rather than natural sources. Industrial sources of copper include mining, electroplating, petroleum refining, metal works, and foundries. Copper is widely used in the manufacture of textiles, anti-fouling paints, electrical conductors, and cooking utensils. Acid mine drainage frequently contains high levels of copper. Also, smelters may release copper into the atmosphere. This airborne copper eventually will enter the aquatic environment. Copper is the active ingredient in some pesticides applied to agricultural crops to inhibit fungal growth. Also, copper salts are often applied to reservoirs to control nuisance algal growth. Other anthropogenic activities, such as road building, can accelerate the release of copper to the aquatic environment.
Copper is used extensively for plumbing fixtures and pipes. Copper, dissolved from these fittings, is the cause of the persistent green stain often found on porcelain sinks beneath a dripping faucet.

Therefore copper introduced to the aquatic environment may originate from any of a number of industrial sources, as well as from municipal outfalls. On an annual global basis it is estimated that 33 to 60 percent of the total copper entering the aquatic environment originates from anthropogenic sources and, according to Bertine and Goldberg\textsuperscript{17a}, about one-third of this amount is contributed in sewage.

Locally, at the Iona Sewage Treatment Plant which serves Vancouver, 39 composite samples taken from April, 1978 to January, 1979 indicated that total copper ranged from \(<0.04\) to \(0.41\) mg/L and dissolved copper ranged from \(<0.04\) to \(0.25\) mg/L\textsuperscript{18a}. Composite samples taken from the Annacis Sewage Treatment Plant in 1980 showed average total copper concentrations of 0.22 mg/L in the raw sewage and 0.19 mg/L in the final effluent following primary treatment\textsuperscript{18b}.

3.3 LEVELS IN WATER AND SEDIMENT

According to McNeely \textit{et al.}\textsuperscript{8,}, copper generally is present only in trace amounts in natural surface waters up to concentrations of 0.005 mg/L, and higher levels are usually associated with anthropogenic sources. Spear and Pierce\textsuperscript{3} state that dissolved copper concentrations in Canadian surface waters rarely exceed 0.005 mg/L. The Fraser River Estuary Study\textsuperscript{7} reported the median concentrations of total and dissolved copper in the Lower Fraser River were 0.005 and 0.002 mg/L, respectively. For most streams in British Columbia, the median concentration for both total and dissolved copper is 0.002 mg/L\textsuperscript{7}. Examples of total copper concentrations (50th and 90th percentiles) measured at Federal-Provincial monitoring sites for a number of rivers throughout B.C. to June, 1986, are as follows\textsuperscript{19}:
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<th>50th Percentile</th>
<th>90th Percentile</th>
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<td>Peace R. near B.C./Alta. border</td>
<td>28</td>
<td>0.003</td>
<td>0.011</td>
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<td>Quinsam R. near mouth</td>
<td>9</td>
<td>0.002</td>
<td>0.017</td>
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<td>26</td>
<td>0.003</td>
<td>0.008</td>
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<td>90</td>
<td>0.005</td>
<td>0.011</td>
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<td>114</td>
<td>0.002</td>
<td>0.003</td>
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<td>34</td>
<td>0.001</td>
<td>0.005</td>
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<td>Kootenay R. at Creston</td>
<td>55</td>
<td>0.002</td>
<td>0.003</td>
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<td>Elk R. at Phillips Bridge</td>
<td>33</td>
<td>0.002</td>
<td>0.003</td>
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<tr>
<td>Okanagan R. at Oliver</td>
<td>95</td>
<td>0.002</td>
<td>0.004</td>
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<td>Flathead R. at U.S. border</td>
<td>72</td>
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<td>0.007</td>
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<td>43</td>
<td>0.003</td>
<td>0.009</td>
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<td>Thompson R. at Spences Bridge</td>
<td>17</td>
<td>0.002</td>
<td>0.008</td>
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<td>Similkameen R. 9 km N. of U.S. border</td>
<td>97</td>
<td>0.003</td>
<td>0.007</td>
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The B.C. Ministry of Environment and Parks\(^{190}\) has recently completed a preliminary assessment of the impact of acid mine drainage on the water quality of a coastal river system. The Tsolum River near Courteney on Vancouver Island receives acid mine drainage via Pyrrhotite Creek from an abandoned open pit copper mine on Mt. Washington. Total copper concentrations as high as 12.7 mg/L and a mean of 1.82 mg/L have been measured in Pyrrhotite Creek about 3 km downstream from the minesite. Total copper concentrations measured in the Tsolum River near the confluence with Headquarters Creek which supported a salmon hatchery, were as high as 0.080 mg/L and averaged about 0.020 mg/L. The high copper concentrations in the river system, coupled with low water hardness (<20 mg/L CaCO\(_3\)), depressed pH, and the presence of other elevated trace metal concentrations are believed to be largely responsible for the extremely poor returns of spawning pink salmon to the hatchery (see Section 5.5.1(a)).
The degree of metal concentration within sediments is largely dependent on particle size. A study which investigated cross-sectional variability in the lower Fraser River showed that fine-grained sediments usually had a higher metal content than coarse-grained sediments. This result was attributed to the larger surface area available for adsorption.

Sediments are often considered reservoirs or sinks for metals which may be available for uptake by aquatic biota. Copper in interstitial water samples collected 8 to 9 cm below the sediment-water interface in Lake Superior was 2 to 8 times higher than in the water samples taken 4 cm above the interface. Another study demonstrated that a lake retained 98 percent of the total copper input. Of that amount, approximately 98 percent was incorporated into the sediments and the remainder was retained in the water column as soluble copper or as suspended sediment. Hall et al. found that the distribution and levels of copper in sediments of the Brunette River near New Westminster, British Columbia, were closely related to urban and industrial activities. Copper sediment concentrations in an industrial area had a median value of 83 mg/kg (dry weight), whereas concentrations in a residential area had a median value of 14.6 mg/kg (dry weight). Copper concentrations in sediments of the Brunette River ranged from 11 to 1765 mg/kg (dry weight).

McNeely et al. reported that the copper content of seawater normally ranges from 0.001 to 0.025 mg/L, and that higher concentrations are usually associated with anthropogenic sources. On a global basis Lewis and Cave reported that the average copper concentration for coastal waters was about 0.002 mg/L, and that concentrations were usually higher in near-shore surface waters, especially during periods of high runoff. Locally, in Juan de Fuca Strait, copper concentrations ranged from 0.0014 to 0.0038 mg/L at a depth of 150 m. In June, concentrations in Saanich Inlet ranged from 0.0087 at the surface to 0.0017 mg/L at a depth of 221 m. In August, concentrations ranged from 0.0034 mg/L at the surface to 0.001 mg/L at 190 m. Water samples collected periodically from Howe Sound between 1972 and 1981 had a median concentration of total copper of 0.003 mg/L, with a
maximum recorded value of 0.006 mg/L\textsuperscript{14}. These local samples may be influenced to some degree by anthropogenic sources but considering the available dilution, any influence is probably minor.

Spear and Pierce\textsuperscript{3} report that the levels of dissolved copper in the freshwater-saltwater mixing zone of estuaries are expected to increase since greater ionic strength causes desorption from sediment particles. Also, estuaries may be the major depositional site for particulate copper transported by rivers, but currents and tidal action may result in remobilization of these deposits\textsuperscript{3}.

The transfer of copper between bottom materials and the overlying water is a complex process, depending on numerous factors such as the redox potential (Eh), the nature and the concentration of copper, the organic and inorganic ligands present, the pH, and the particle size of the bottom sediments\textsuperscript{15,16}. Krantzberg and Stokes\textsuperscript{16} investigated the influence of benthic macroinvertebrates on copper speciation in sediments from a lake which is becoming acidified. In laboratory tests, the invertebrates stimulated the flux of copper from sediments to water with a transfer from more strongly complexed forms to adsorbed and cation exchangeable forms.

3.4 LEVELS IN BIOLOGICAL TISSUES

Algae can accumulate copper to levels which are much higher than the water. For example, the green alga Cladophora glomerata, in filtered Lake Ontario water, accumulated copper by factors ranging from 1900 to 2000. Bioconcentration factors of 1000 were obtained for western Lake Erie and 2500 for the Spokane River\textsuperscript{17}. Locally, the southern basin of Buttle Lake on Vancouver island receives a mine effluent which contains copper. In the winter (1984-1985), copper concentrations in the algae ranged from 73 to 434 µg/g (dry weight), and concentrations in the water ranged from 3 to 6 µg/L. Bioconcentration factors calculated from these concentrations ranged from 24 000 to 109 000\textsuperscript{18,3}. 
Rooted macrophytes exposed to copper concentrations of 9 and 2 µg/L accumulated 20 to 88 µg/g and 6 to 34 µg/g copper in their roots. The leaves accumulated 18 to 81 µg/g and 4 to 21 µg/g, respectively. A positive correlation existed between copper content in the sediment and the roots of Eleocharis and Nymphaea. However, there was no such relationship for the roots of Equisetum and Nuphar. Lemna valdiviana, a free-floating vascular macrophyte, accumulated 10 000 times the copper measured in the water. Murdoch and Capobianco found that among several plants surveyed submerged macrophytes accumulated more copper than emergent macrophytes.

According to Spear and Pierce, bioconcentration of copper by invertebrates can vary widely. Concentration factors ranging from 500 to 13,500 times the level measured in the water have been reported. In summer, 1981, a copper concentration of 20 µg/g (wet weight) was measured in zooplankton captured in Buttle Lake near the discharge (see above) and the copper concentration in the water averaged 11 µg/L. This gives a bioconcentration factor of about 1800.

Bioconcentration factors of about 40 to 220 were calculated for rainbow trout caught in the Buttle Lake/Campbell Lake system on Vancouver Island in 1981.

Copper in muscle and liver tissue was measured in a number of fish species from the Fraser River. The average copper concentration in the muscle tissue of several freshwater species (219 samples) was 0.36 µg/g (wet weight). The average concentration in the livers of these fish was 14.3 µg/g. Generally, these concentrations were less than those in fish from other freshwater systems in Canada. Adult sockeye salmon, recently returned from the ocean to the Fraser River, had much higher levels of copper than the freshwater fish, especially in the liver. On a wet weight basis the average concentration in the muscle tissues of the sockeye was 0.78 µg/g, whereas the average concentration in the livers was 207 µg/g. The median concentration of total copper in the lower Fraser River was
5 µg/L. This gives bioconcentration factors of about 70 and 2900 for the muscle and liver tissue of freshwater fish, and about 150 and 41 400 for the muscle and liver tissue of sockeye salmon, respectively. The reason for the difference in levels between the freshwater fish and the migrating sockeye salmon was not known but may be related in some way to the marine environment from which the sockeye had recently returned.

Young et al.\textsuperscript{205} determined that under laboratory conditions the threshold limit for the accumulation of copper by the sabellid polychaete (Eudistylia vancouveri) lies between 3 and 6 µg/L total copper in seawater. At copper concentrations above this threshold, copper accumulates mainly in the branchial crown and causes injury to the radioles (gills).
4. DRINKING WATER SUPPLY (INCLUDES FOOD PROCESSING)

4.1 EFFECTS

Copper is an essential element for human metabolism. Physiologically, copper participates in the formation of blood and the utilization of iron in hemoglobin synthesis, the production and cross-linking of elastin and collagen in major blood vessels, and is present in many enzymes necessary for oxidative metabolism.

Demayo and Taylor indicate that occurrences of copper deficiency or copper toxicity in humans are rare. Malnutrition and malabsorption are the main causes of copper deficiency which usually occurs in premature infants. Acute effects, such as vomiting or diarrhea, are related to the ingestion of milligram quantities of copper. An acute dose might occur if acidic food or drink has been in prolonged contact with copper.

Some chronic effects suspected of being related to copper toxicosis include pulmonary deposition and fibrosis, and granulomas and malignant liver tumours reported in some vineyard workers. However, further studies investigating the carcinogenicity of copper were inconclusive, and in some cases copper was found to have anticarcinogenic properties. One report of suspected copper poisoning in a 15-month old infant suggests that drinking water containing more than 0.8 mg/L may constitute a potential hazard if exposure is prolonged. On the other hand, no effects have been observed in humans on high cereal diets which contribute as much as 5.8 mg/day of copper.

In a recently published article, Nolan, a general medical practitioner in Vancouver, B.C., has noted a relationship between abnormal hair copper levels and psychological disorders in humans. He suggested that these disorders which are related to the biochemical syndrome of histaminic schizophrenia and include rapid thought patterns, insomnia, depression, memory loss, and also psychotic symptoms of hallucinations, paranoia, and
obsession-compulsion may be attributed to a higher than normal ingestion of copper through diet and drinking water. Random sampling of standing home faucet water in Vancouver showed that concentrations frequently exceeded the National and Provincial drinking water standards of 1 mg/L for finished water. He suggested that the elevated levels in the tap water may be caused by contact of the Vancouver soft water supply with copper plumbing.

There are several processes within the food processing industry which can be affected by copper. For example, in food preserving industries copper causes undesirable colour reactions, forming tannates and sulphides. In the case of milk, industrial metals such as copper are catalysts for the oxidation of fatty matter and for the hydrolysis of milk constituents. Metal contamination causes oily, fatty, and fishy tastes in milk products\textsuperscript{17}.

4.2 CRITERIA FROM THE LITERATURE

Criteria, objectives, and standards to protect consumers from excessive copper in drinking water have been compiled from other jurisdictions (Table 1). A comparison of approaches used by other jurisdictions can help in developing criteria for British Columbia waters.

Copper criteria have been established by other jurisdictions primarily for aesthetic reasons, and are reasonably consistent at a maximum acceptable level of about 1.0 mg/L. Above this level, copper may cause a bitter taste, an odour, and may stain plumbing fixtures.

In a number of cases, other jurisdictions, including Health and Welfare Canada\textsuperscript{16,19} and the U.S. EPA\textsuperscript{20,21,22} failed to specify the form of copper to be measured. This may not be a serious omission because there is unlikely to be a great deal of difference between total copper and dissolved copper due to the clarity of drinking water. However, the form of copper should be specified to ensure that the intended forms are measured.
<table>
<thead>
<tr>
<th>CRITERIA STATEMENTS</th>
<th>CRITERIA VALUES</th>
<th>JURISDICTION</th>
<th>DATE</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1962 USPHS drinking water standards, recommended limit = 1.0 mg/L</td>
<td>1.0 mg/L</td>
<td>U.S. Public Health Service</td>
<td>1962</td>
<td>27</td>
</tr>
<tr>
<td>1968 U.S. surface water criteria for public water supplies permissible limit = 1.0 mg/L</td>
<td>1.0 mg/L</td>
<td>U.S. EPA</td>
<td>1971</td>
<td>28</td>
</tr>
<tr>
<td>Guideline for raw water objective level = &lt;0.01 mg/L</td>
<td>&lt;0.01 mg/L</td>
<td>Canada</td>
<td>1972</td>
<td>29</td>
</tr>
<tr>
<td>Guideline for raw water acceptable level = 1.0 mg/L</td>
<td>1.0 mg/L</td>
<td>Canada</td>
<td>1972</td>
<td>29</td>
</tr>
<tr>
<td>On basis of taste preference, copper should not exceed 1.0 mg/L in public water supplies</td>
<td>1.0 mg/L</td>
<td>U.S. EPA</td>
<td>1972</td>
<td>20</td>
</tr>
<tr>
<td>On basis of taste preference, copper should not exceed 1.0 mg/L in public water supplies</td>
<td>1.0 mg/L</td>
<td>Australia</td>
<td>1974</td>
<td>30</td>
</tr>
<tr>
<td>Max. concentration for total copper = 0.02 mg/L</td>
<td>0.02 mg/L</td>
<td>Saskatchewan</td>
<td>1975</td>
<td>24</td>
</tr>
<tr>
<td>Max. concentration for total copper = 0.02 mg/L</td>
<td>0.02 mg/L</td>
<td>U.S. EPA</td>
<td>1976</td>
<td>21</td>
</tr>
<tr>
<td>Max. concentration for total copper = 0.02 mg/L</td>
<td>0.02 mg/L</td>
<td>Alberta</td>
<td>1977</td>
<td>23</td>
</tr>
<tr>
<td>Max. acceptable concentration for copper in finished drinking water = 1.0 mg/L</td>
<td>1.0 mg/L</td>
<td>Canada</td>
<td>1978</td>
<td>18</td>
</tr>
<tr>
<td>Max. acceptable concentration for copper in finished drinking water = 1.0 mg/L</td>
<td>1.0 mg/L</td>
<td>British Columbia</td>
<td>1982</td>
<td>25</td>
</tr>
<tr>
<td>Objective concentration for copper in finished drinking water = &lt;1.0 mg/L</td>
<td>&lt;1.0 mg/L</td>
<td>Canada</td>
<td>1978</td>
<td>18</td>
</tr>
<tr>
<td>Objective concentration for copper in finished drinking water = &lt;1.0 mg/L</td>
<td>&lt;1.0 mg/L</td>
<td>British Columbia</td>
<td>1982</td>
<td>25</td>
</tr>
<tr>
<td>No increase above naturally occurring concentrations are allowed in waters subject to simple disinfection</td>
<td>no increase</td>
<td>Montana</td>
<td>1980</td>
<td>22</td>
</tr>
<tr>
<td>For organoleptic criterion (e.g. odour) the estimated level is 1 mg/L</td>
<td>1 mg/L</td>
<td>U.S. EPA</td>
<td>1980</td>
<td>22</td>
</tr>
<tr>
<td>CRITERIA STATEMENTS</td>
<td>CRITERIA VALUES</td>
<td>JURISDICTION</td>
<td>DATE</td>
<td>REFERENCE</td>
</tr>
<tr>
<td>----------------------------------------------------------------------------------</td>
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<td>-----------</td>
</tr>
<tr>
<td>Recommended objective (as total copper) for raw public water supply = 0.5 mg/L</td>
<td>0.5 mg/L</td>
<td>Canada</td>
<td>1981</td>
<td>1</td>
</tr>
<tr>
<td>Maximum acceptable limit for copper = 1.0 mg/L</td>
<td>1.0 mg/L</td>
<td>Manitoba</td>
<td>1983</td>
<td>34</td>
</tr>
<tr>
<td>Copper should not be present in a water supply in excess of 1.0 mg/L</td>
<td>1.0 mg/L</td>
<td>Ontario</td>
<td>1984</td>
<td>31</td>
</tr>
<tr>
<td>The 95th percentile and maximum allowable concentration of total copper in water direct to potable supply are 0.05 and 0.075 mg/L, respectively.</td>
<td>0.05 mg/L 0.075 mg/L</td>
<td>United Kingdom</td>
<td>1984</td>
<td>33</td>
</tr>
<tr>
<td>WHO drinking water guideline for copper = 1.0 mg/L</td>
<td>1.0 mg/L</td>
<td>World Health Organization</td>
<td>1984</td>
<td>26</td>
</tr>
<tr>
<td>For general application, the raw water copper concentration should not exceed 1.0 mg/L</td>
<td>1.0 mg/L</td>
<td>CCREM</td>
<td>1987</td>
<td>174</td>
</tr>
<tr>
<td>Proposed regulatory maximum level for copper in drinking water = 1.3 mg/L</td>
<td>1.3 mg/L</td>
<td>U.S. EPA</td>
<td>1986</td>
<td>32</td>
</tr>
</tbody>
</table>
Alberta\textsuperscript{23} and Saskatchewan\textsuperscript{24} have not established water-use categories. Instead, these provinces have established a single criterion for total copper (0.02 mg/L) which is designed to protect the most sensitive use. For copper, the most sensitive use probably applies to aquatic life; a level of 0.02 mg/L is unnecessarily stringent for water used specifically for human consumption.

The British Columbia Ministry of Health\textsuperscript{25} has adopted the Canadian Drinking Water Guidelines\textsuperscript{18} of 1.0 mg/L (maximum acceptable concentration) and <1.0 mg/L (objective concentration) for finished drinking water in British Columbia. The Inland Waters Directorate\textsuperscript{1} recommended a level of 0.5 mg/L total copper in raw public water supplies as being more appropriate. This level was based on three points:

(i) the human body obtains enough copper from a normal diet;

(ii) prolonged ingestion of larger doses of copper may produce liver damage; and

(iii) surface waters in Canada are not known to contain more than 0.5 mg/L of copper.

The Inland Waters Directorate\textsuperscript{1} also recommends that any water used in food processing should meet the drinking water criterion.

The Canadian Council of Resource and Environment Ministers (CCREM)\textsuperscript{17} has recently published new national water quality guidelines. For copper the guideline states that the concentration in raw drinking water should not exceed 1.0 mg/L. This guideline is based on the Canadian Drinking Water Guideline\textsuperscript{18} of 1.0 mg/L for copper in finished drinking water.
4.3 RECOMMENDED CRITERION

The British Columbia Ministry of Environment recommends adopting the copper objective recommended by the Inland Waters Directorate\(^1\). This criterion applies to total copper in raw drinking water.

Criterion

In raw drinking water (including food processing water), total copper should not exceed 0.5 mg/L.

4.4 RATIONALE

The rationale for this criterion is based in part upon the rationale given by the Inland Waters Directorate\(^1\) (Section 4.2), and to ensure a palatable water supply. In addition, the 0.5 mg/L total copper criterion for raw water will allow for some contamination from copper plumbing, which is bound to occur (see Section 4.1), before the British Columbia drinking water quality standard for finished water (1.0 mg/L) applies.
5. AQUATIC LIFE

5.1 EFFECTS ON ALGAE

5.1.1 FRESHWATER ALGAE

Spear and Pierce\textsuperscript{3}, the U.S. EPA\textsuperscript{2}, and Demayo and Taylor\textsuperscript{1} have recently reviewed the effects of copper on freshwater algae. In summary, Spear and Pierce\textsuperscript{3} reported that the copper concentrations which inhibited growth in freshwater algae ranged from 10 to 1600 μg/L. The range of inhibitory concentrations was mainly dependent upon experimental conditions, which included the complexing capacity of the test water, the test site location (this also relates to the complexing capacity of the water) and, to a lesser degree, the species of algae tested. For example, Gachter \textit{et al.}\textsuperscript{19} demonstrated a 50 percent reduction in photosynthesis when \textit{Chlorella} sp. was exposed to 38 μg/L copper, whereas 70 μg/L copper was required to elicit the same response when 1 μM EDTA (a metal chelator) was added to the test water.

Reduction of photosynthesis for two species of blue-green algae (\textit{Aphanizomenon} sp. and \textit{Anabaena} sp.) occurred at a copper concentration of 10 μg/L after three days exposure\textsuperscript{1}. Some recovery was noted after five days of exposure to 10 μg/L, but there were no signs of recovery after exposure to 40 μg/L. When measured as Cu\textsuperscript{2+}, concentrations as low as 1 to 2 μg/L have been shown to suppress photosynthesis in \textit{Nitzschia paelea}, but there was suspicion that the distilled water, used as the diluent, was contaminated with copper and thus influenced the results\textsuperscript{17}. Steeman-Nielson \textit{et al.}\textsuperscript{94} reported that a copper concentration of 10 μg/L reduced photosynthesis in \textit{Chlorella pyrenoidosa}.

Spear and Pierce\textsuperscript{3} reported that, in most cases, copper concentrations which inhibit growth are not significantly different from levels which inhibit photosynthesis. Inhibitory concentrations to 30 species of freshwater algae after 28 days exposure ranged from 25 to 1600 μg/L\textsuperscript{95}. Another study using filamentous algae isolated from various river sites demonstrated
that inhibitory copper concentrations ranged from 60 to 700 µg/L. Gachter et al.\textsuperscript{39} reported that growth of *Chlorella* sp. was inhibited by concentrations between 2 and 50 µg/L and Steeman-Nielsen and Kamp-Nielsen\textsuperscript{3} reported growth inhibition of the same species at a concentration of 5 µg/L. Spear and Pierce\textsuperscript{3} concluded that the growth reduction threshold for a given species of alga varies according to the experimental conditions (i.e., complexing capacity of the medium).

According to Demayo and Taylor\textsuperscript{1}, almost twice as much copper was required to inhibit respiration in algae as was needed to reduce growth and photosynthesis.

Additions of 5 and 10 µg/L copper to a lake did not reduce the total accumulation of biomass, but blue-green algae were almost totally eliminated and replaced by more tolerant green algae and diatoms\textsuperscript{30}.

The tolerance of algae to copper usually increased as the pH and temperature of the water increased, enabling algae to tolerate higher copper concentrations. However, one study\textsuperscript{107} revealed that when the tolerance (growth rate) was expressed as a function of cupric ion activity, tolerance at the different pH levels was not significantly different (i.e., the variation due to pH was minimized). Conversely, another study\textsuperscript{3} demonstrated that at least one species (*Chlorella pyrenoidosa*) was more tolerant to copper at pH 5 than at pH 8.

Mierle and Stokes\textsuperscript{35} demonstrated that water hardness, per se, did not appear to be a significant factor in influencing the toxic level of copper to *Scenedesmus*, but Ca$^{2+}$ appears to reduce bioaccumulation of copper and increase the tolerance.

Spear and Pierce\textsuperscript{3} and Demayo and Taylor\textsuperscript{1} reported that organic metabolic wastes excreted by algae and other organisms can increase the complexing capacity of water, and thus reduce the toxicity of copper to algae. It is not known if this type of complexing of copper is a significant factor in detoxifying copper in the natural environment.
In shallow waters, where the photic zone is at or near the bottom, algae may play a role in mobilizing sediment-bound copper. They immediately take up the small amount of copper released to the water by the sediment, preventing the copper in the water and sediment from reaching equilibrium and thus causing the release of more copper from the sediment\(^2\). On the other hand, one could argue that algae act as a sink since they bind the free copper released from sediments and return it to the sediments when they die.

5.1.2 COPPER AS A BIocide

Copper (in the form of copper sulphate) is often used as a biocide for controlling algae or other nuisance organisms in water used for drinking water or recreational purposes. Recent data on a group of shallow lakes in southern Minnesota, which have been treated with copper sulphate for nearly 60 years to reduce excessive algal growth, revealed the occurrence of short-term and long-term effects\(^1\). Short-term effects included:

(i) the intended temporary killing of algae,
(ii) dissolved oxygen depletion by decomposition of dead algae,
(iii) accelerated phosphorus recycling from the lake bed and recovery of the algal population within 7 and 21 days, and
(iv) occasional fish kills due to oxygen depletion or copper toxicity or both.

Long-term effects included:

(i) copper accumulation in the sediments,
(ii) tolerance adjustments of certain algal species to higher copper sulphate dosages,
(iii) shift of species from green to blue-green algae and from game fish to coarse fish,
(iv) disappearance of macrophytes, and
(v) reduction in benthic invertebrates.

Based on these results, Hanson and Stefan\(^1\) concluded that while copper sulphate treatments are popular because they kill and remove algae
almost instantaneously, immediate or cumulative side effects can be harmful to many other aquatic organisms.

Taub and Kindig\textsuperscript{169} have also studied the effects of copper sulphate treatment on aquatic ecosystems using Standardized Aquatic Microcosms (3 litre communities consisting of a chemically defined medium, 10 algal and 5 invertebrate species, plus unidentified microorganisms). At high copper concentrations, invertebrates and algae were severely damaged during almost all of the 63-day experiment; only low densities of copper-tolerant algae persisted. At lower copper concentrations, the effects were less severe and persisted for a shorter duration. Invertebrate grazers were hindered for a longer period than were the copper-tolerant algae, which resulted in blooms of these algae. Eventually, as the copper levels diminished, the grazer population increased and terminated the algal blooms.

Another investigation\textsuperscript{170} indicated that copper sulphate, applied to a lake (Figure 8 Lake, Alberta) to control algae, killed all the amphipods; chironomids and oligochaetes were only found below 12 cm of sediment. Furthermore, the sulphate concentrations in the lakewater tripled. Apparently, the sulphate-reducing bacteria in the sediments were suppressed. These bacteria are important in alkalinity production. The toxicity in the sediments lasted for 15 months after the last copper sulphate treatment. The treatment dose was not unusually high.

Effler et al.\textsuperscript{171} showed that three low-level copper sulphate applications to a lake caused only small copper increases (maximum of 5 \mu g/L) of short duration (2-5 days), but caused significant reductions in the water column bacteria. The treatment failed to induce effective algicidal action in the target phytoplankton populations of the lake. Zooplankton and submerged macrophytes were not affected and the phytoplankton and bacteria populations recovered within about one week.

Data reviewed for this document have indicated that copper concentrations which can suppress algal growth are within the range of concentrations which are harmful to other aquatic organisms. In view of the long-term
consequences of copper sulphate treatments, many states in the USA and many European countries have disallowed the use of copper sulphate to suppress algal growth\textsuperscript{170}.

Copper sulphate is also used as a molluscid to kill the intermediate snail hosts of parasitic protozoa which cause a skin irritation in humans called "swimmer's itch". Cultus Lake, B.C. has been treated intermittently with copper sulphate for this problem since the early 1950's. Following a treatment in 1978, the Department of Fisheries and Oceans and the Environmental Protection Service studied the environmental impact of the treatment and conducted a survey to determine the incidence of swimmer's itch\textsuperscript{172}. Resident fish netted in treatment areas did not contain significantly higher copper concentrations than fish sampled in non-treated control areas, even though the post-treatment water was contaminated with copper for a short time (less than 24 hours) at levels as high as 130 µg/L dissolved copper. However, a questionnaire survey of recreational users of Cultus Lake indicated no improvement in the occurrence of swimmer's itch after treatment.

A recent outbreak of swimmer's itch in a Saskatchewan lake was also treated with copper sulphate but, instead of improving the situation, the incidence of swimmer's itch increased. It was believed that the uptake of copper in the host snails resulted in the parasitic protozoa leaving the snails at an accelerated rate and thus increased the infection of humans\textsuperscript{173}.

5.1.3 MARINE ALGAE

Spear and Pierce\textsuperscript{3}, the U.S. EPA\textsuperscript{2}, and Lewis and Cave\textsuperscript{96} have recently reviewed the effects of copper on marine algae. In summary, Spear and Pierce\textsuperscript{3} noted that the copper concentrations which inhibited growth in marine algae ranged from 3 to 4500 µg/L. As was the case for freshwater algae, the range of inhibitory concentrations was primarily dependent upon the experimental conditions (i.e., the complexing capacity of the test water). For example, for the marine diatom Skeletonema costatum exposed to copper, the growth reduction threshold in water with low complexing capacity
was 10 µg/L, but in water to which phosphate was added (high complexing capacity) the threshold copper concentration was 500 µg/L\textsuperscript{15,17}. Davey et al.\textsuperscript{97} demonstrated that a copper concentration as low as 3 µg/L in artificial seawater with low complexing capacity could reduce growth in *Thallasiosira pseudonana* by 70 percent when compared to controls. Even in natural seawater, growth was reduced by 50 percent in a copper concentration of 3 µg/L.

Steele and Thursby\textsuperscript{166} demonstrated that copper concentrations of 4.6 µg/L reduced tetrasporophyte growth, and 4.7 µg/L reduced female growth in the attached red algae, *Champia parvula*. A copper concentration of 7.3 µg/L copper stopped sexual reproduction in this species. Although this species is subtropical and therefore not indigenous to B.C. marine waters, the data for *Champia parvula* should not be overlooked until information is available regarding the sensitivity to copper of red algae species found locally.

Increased temperature was found to increase the tolerance of *Skeletonema costatum* to copper. At 18°C, the inhibitory concentration was 50 µg/L and at 20-30°C the inhibitory concentration ranged from 160 to 250 µg/L\textsuperscript{15}. However, Mandelli\textsuperscript{98} demonstrated that accumulation of copper increased in the same species with increased temperature.

Reductions in photosynthesis appeared to be a less sensitive indicator of copper toxicity than cell growth according to the results of Overnell\textsuperscript{98}. Copper concentrations required to produce a 50 percent reduction of photosynthesis in 7 algal species ranged from 1200 to 6400 µg/L.

As reported for freshwater algae, organic metabolic wastes excreted by algae and other organisms can increase the complexing capacity of seawater and thus reduce the toxicity of copper to algae. For example, Erickson\textsuperscript{16} demonstrated that the 72 h EC50 of the marine alga *Thalassiosira pseudonana* was increased from 5 µg/L in fresh seawater to 30 µg/L in aged seawater owing to the increased amount of metabolic end-products which complexed copper in the aged samples.
Locally, in Saanich Inlet, Vancouver Island, a series of experiments were performed on the toxicity of copper to marine aquatic life using large volume (68 m³) semi-transparent polyethylene enclosures moored in the inlet. This Controlled Ecosystem Pollution Experiment (CEPEX) program was designed to investigate the effects of copper on the resident aquatic community which was captured when deploying the enclosures. Aspects of copper toxicity to algae studied during the CEPEX program included the effects of copper on:

(i) the dominance and diversity of algae;¹⁹⁵
(ii) phytoplankton standing crop and diversity;¹⁹⁶
(iii) silicic acid uptake by a marine phytoplankton population;¹⁹⁷
(iv) phytoplankton nitrogen metabolism and nitrogen budgets.¹⁹⁸

In summary, copper concentrations in the range of about 5 to 10 μg/L were found to affect the various aspects studied. Generally, populations of copper-sensitive algae declined after introducing the copper (as CuSO₄) and were soon replaced by copper-tolerant algae such as microflagellates. The copper-sensitive components of the original ecosystem were made available by surviving heterotrophic bacteria thus providing a source of plant nutrients for the establishment of succeeding phytoplankton regimes.¹⁹⁹

5.2 EFFECTS ON AQUATIC MACROPHYTES

According to Spear and Pierce³, rooted vascular plants are considered to be relatively tolerant of copper concentrations in water and sediments, although only a small amount of information is available. Hydrilla sp., a freshwater species, showed no adverse effects when exposed to 250 μg/L for four days.⁷ In another study, Nuphar variegatum and Potamogeton sp. found in Indian Lake, Massachusetts were not visibly affected after being exposed to 116 μg/L copper.¹²

Free-floating macrophytes may be more sensitive to copper than rooted macrophytes. Growth of duckweed (Lemna valdiviana), a free-floating vascular plant, was inhibited by 50 percent at 100 μg/L.⁸ This plant also
accumulated three times the level of copper found in the control and 10 000 times the concentration in the culture solution. At concentrations greater than 100 μg/L of copper, the copper entered the cell rapidly causing a severe reduction in growth and eventually death.

No information was available for marine macrophytes.

5.3 EFFECTS ON INVERTEBRATES

5.3.1 FRESHWATER INVERTEBRATES

(a) Acute Toxicity

According to Spear and Pierce³, little information exists on the tolerance of freshwater invertebrates to copper. Short-term lethal levels (24 to 96 h LC50's) for several species ranged from 13 to 8300 μg/L copper. Studies indicate that acute toxicity often varies with the water chemistry, the water temperature, the species, and the life stage.

In general, adults are usually more tolerant to copper than larvae. The most sensitive species and life stage listed by Spear and Pierce³ for short-term lethality was pre-adult Physa heterostropha (pond snail) with an LC50 of 13 μg/L. The LC50 for adults was 69 μg/L. The exposure time in both cases was less than 96 hours. More recent data¹⁵ reviewed by the U.S. EPA² have indicated that, in terms of acute toxicity, Daphnia magna is the most sensitive freshwater aquatic organism tested to date with an LC50 of 6.5 μg/L in water with a hardness of 250 mg/L CaCO₃. The exposure period was not reported.

The water chemistry, such as the complexing capacity, pH, alkalinity, and hardness, can affect the short-term lethality of copper. For example, in terms of complexing capacity, the addition of an organic chelator increased the 96 h LC50 for pre-adult pond snails (Physa sp.) from 16 to 34 μg/L copper in water hardness of 20 mg/L CaCO₃, and from 13 to 53 μg/L in water hardness of 100 mg/L CaCO₃.¹⁵ Furthermore, Lind et al.⁵¹ demonstrated
that toxicity of copper to *Daphnia pulicaria* decreased with increased total organic carbon content in a variety of surface waters. LC 50's varied up to 30-fold depending on the total organic carbon content, and this variability was attributed to the complexing capacity of organics. On the other hand, the presence of other contaminants such as zinc may enhance the toxicity of copper as noted in Section 5.5.3.

Regarding alkalinity, Howard et al.\(^5\) compared the toxicity to *Physa* sp. exposed to cupric carbonate suspended in Cultus Lake water (alkalinity of 130 mg/L CaCO\(_3\)) and Seymour Mountain water (alkalinity of 10 mg/L CaCO\(_3\)). The results indicated that *Physa* sp. was more sensitive in Seymour Mountain water, presumably because of greater solubility and greater dissociation of cupric carbonate at lower alkalinity.

Spear and Pierce\(^3\) suggested that the tolerance of freshwater invertebrates to copper may increase with water hardness. They based this on a study which demonstrated that the 96 h LC50 for *Physa* sp. was increased from about 30 to 110 μg/L copper when water hardness was increased from about 25 to 160 mg/L CaCO\(_3\). Also, the U.S. EPA\(^2\) proposed a hardness relationship to develop the national freshwater aquatic life criterion based on a number of studies which showed increased tolerance of invertebrates (as well as fish) to copper in water with increased hardness (discussed more fully in Section 5.6). On the other hand, Demayo and Taylor\(^1\) stated that hardness did not appear to have much effect on copper toxicity to invertebrates, but that there were few data that could be directly compared. They did report examples, however, that showed the tolerance of invertebrates to copper to increase with increased water hardness. The 96 h LC50 for *Philodina rotifera* was increased from 700 to 1100 μg/L copper when hardness was increased from 25 to 81 mg/L CaCO\(_3\)\(^5\). Similarly, the 48 h LC50 for *Tubifex tubifex* (oligochaete) was increased from 210 to 890 μg/L when water hardness was increased from 34.2 to 261 mg/L CaCO\(_3\)\(^5\).

Since pH, hardness, and alkalinity are interrelated (i.e., a change in one causes the others to vary), the influence of each of these three characteristics is not easily discernible. For invertebrates, no informa-
tion was available which discusses the influence of each of these characteristics alone. However, some data were available for freshwater fish and a discussion of this topic is presented in Section 5.5.1(a).

Temperature changes also have been shown to affect the toxicity of copper. Miles *et al.* demonstrated that the sensitivity of four invertebrate species to copper increased with increasing temperature. The 24 h LC50's (in µg/L copper) were as follows:

<table>
<thead>
<tr>
<th>Temp</th>
<th>Species</th>
<th>Daphnia pulex</th>
<th>Daphnia magna</th>
<th>Philodina acuticornis</th>
<th>Nitocris sp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>10°C</td>
<td>70</td>
<td>90</td>
<td>430</td>
<td>3200</td>
<td></td>
</tr>
<tr>
<td>15°C</td>
<td>30</td>
<td>50</td>
<td>300</td>
<td>1800</td>
<td></td>
</tr>
<tr>
<td>20°C</td>
<td>20</td>
<td>10</td>
<td>210</td>
<td>560</td>
<td></td>
</tr>
</tbody>
</table>

Similarly, Cairns *et al.* reported 48 h LC50's of 90, 70, 40, and 7 µg/L copper at water temperatures of 5, 10, 15, and 25°C, respectively. It is not clear from these studies whether the increased toxicity with increased temperature was caused by a shift in the chemical equilibria, or if temperature is an additional stressor (i.e., an additive effect).

(b) Chronic Toxicity and Sublethal Effects

Exposure of invertebrates to chronic levels of copper has produced a number of sublethal effects which may affect their ability to survive in nature. According to Spear and Pierce, incipient lethal levels (the concentration beyond which the organism can no longer live for an indefinite period of time) for several species of freshwater invertebrates in soft water (<50 mg/L CaCO₃) ranged from 7 to 14 µg/L copper.

Sublethal levels of copper have been shown to affect behaviour, reproduction and growth. These effects are demonstrated by the following examples.
In terms of behaviour, the snail (*Taphius glabratu*) appeared normal on exposure to 5 µg/L copper, but showed signs of distress after 24 hours when exposed to 50 and 100 µg/L.

Hatching success of *Daphnia magna* was reduced by 16 and 50 percent on exposure to 22 and 35 µg/L copper, respectively, in soft water (45 mg/L CaCO₃ hardness). Studies on the asexual budding of *Hydra* exposed to copper demonstrated that this primitive invertebrate was able to counteract the stress on its reproductive system up to a level of 5 µg/L copper. On exposure to 10 µg/L, asexual budding of *Hydra* was reduced. The level of no-effect was set between 2.5 and 5 µg/L.

Long-term growth studies on *Campeloma decisum* (mollusc), and *Gammarus pseudolimnaeus* (crustacean) in soft water (hardness of 45 mg/L CaCO₃) indicated that they did not grow at concentrations exceeding 8 µg/L, and the percent survival was reduced at concentrations as low as 2 µg/L.

5.3.2 MARINE INVERTEBRATES

According to Spear and Pierce, marine invertebrates are least tolerant to copper during development stages involving calcification. Also, as for freshwater invertebrates, larval stages are generally more sensitive to copper than adults.

(a) Acute Toxicity

The U.S. EPA reported that the Pacific oyster (*Crassostrea gigas*) and blue mussel (*Mytilus edulis*) are the most sensitive animal species tested with LC₅₀ values of 5.3 and 5.8 µg/L copper for the embryos, respectively. Adult Pacific oysters are more tolerant than pre-adult forms with an LC₅₀ of 560 µg/L. Spear and Pierce reported that concentrations of 6 to 10 µg/L are acutely toxic to early life stages of copepods.
Comparison of the acute toxicity of copper to marine planktonic copepod (Acartia clausi) populations from polluted and non-polluted areas indicated that pollution-adapted copepods were more tolerant to copper than those which had not been pre-exposed\(^\text{29}\). The 48 h LC50's for the populations from the polluted and non-polluted areas were 82 and 34 µg/L copper, respectively.

Carmel et al.\(^\text{21}\) separated juvenile prawns (P. indicus) into 3 different size groups and exposed them to copper in water of different salinities. They found that the toxicity was dependent upon both the salinity and the size of the prawns. At low salinity (15 ppt) the larger prawns were more sensitive (120 h LC50 of 300 µg/L) and at high salinity (30 ppt) the smaller prawns were more sensitive (120 h LC50 of 430 µg/L).

(b) Chronic Toxicity and Sublethal Effects

Spear and Pierce\(^\text{3}\) reported that, during chronic exposures concentrations as low as 10 µg/L were lethal to pelecypods (oysters, clams and mussels). Incipient lethal levels for a gastropod (whelk) and a crustacean (lobster) were found to be 200 and 56 µg/L copper, respectively. Pesch et al.\(^\text{20}\) reported an incipient LC50 value of 9.3 µg/L copper for the bay scallop Argopecten irradians. At a concentration of 5 µg/L, 10 percent of the scallops died after 42 days of exposure.

Copper has been shown to cause sublethal effects on behaviour, development, growth, metabolism, fecundity (egg production rate), feeding, respiratory rates, and longevity.

Regarding behaviour, Stephenson and Taylor\(^\text{59}\) noted that the burrowing activity of the clam (Venerupis decussata) was inhibited after 65 days in a copper concentration of about 10 µg/L. After 25 days, the EC50 was estimated to be about 100 µg/L. Normal burrowing activity resumed in the absence of copper. Phelps et al.\(^\text{88}\) conducted a long-term bioassay using littleneck clams (Protothaca staminca) and found an increase in burrowing times when sediment copper concentrations were 4.4 µg/g. Mortalities of 5
and 25 percent occurred at 12.4 and 30.1 μg/g, respectively. Also, barnacle larvae (B. balanoides) failed to attach to a substrate after a 12-hour exposure to 10 μg/L copper⁶⁰.

Mandelli⁶¹ showed that oysters (Crassostrea virginica) failed to spawn on exposure to 22 and 42 μg/L, but spawning activity was not affected at 4 μg/L.

Regarding growth and development, a nominal concentration of 3 μg/L copper inhibited the pre-calcification metamorphosis stage of barnacles (B. balanoides)⁶⁰. According to Coglianese and Martin⁶², the Pacific oyster (C. gigas), British Columbia’s only commercial species, was unaffected by a copper concentration less than 5 μg/L. Levels above this caused abnormal development in the embryo. For the sea urchin (Paracentrotus lividus), exoskelton growth of the late larval stage was inhibited by 10 and 20 μg/L copper⁶³. Pesch et al.⁶⁴ found that 5 μg/L ionic copper inhibited scallop (Argopecten irradians) growth by 43 percent after 42 days in a flowing water exposure system.

Invertebrate metabolism appeared to tolerate higher copper levels than the other characteristics discussed. For example, copper concentrations of 300, 500 and 1000 μg/L significantly reduced oxygen consumption of the mussel (Mytilus edulis), whereas a level of 200 μg/L only slightly reduced oxygen consumption as compared to controls⁶⁵. Oxygen consumption of the mud snail (Nassarius obsoletus) was reduced by 50 percent after exposure to 250 μg/L for 72 hours⁶⁶.

Laboratory experiments were performed to determine the sublethal levels of copper which affect feeding, respiratory rates, fecundity, and longevity of the marine planktonic copepod Acartia clausi, collected from polluted and non-polluted areas²⁶⁷. Copper concentrations in the range of 1 to 10 μg/L affected all activities tested in copepods from the non-polluted source. The pollution-adapted population was more resistant to sublethal copper stress. While respiration and longevity were affected at concentrations
similar to those from the non-polluted area, ingestion rate was not affected at 1 μg/L. Fecundity was higher than that in copepods from the non-polluted area in copper concentrations up to 10 μg/L.

Several studies on the chronic toxicity of copper to marine zooplankton communities were performed during the CEPEx program described in Section 5.1.3. These studies included the effects of copper on:

(i) the dynamics of micro-zooplankton populations\(^2\)\(^{0}\);
(ii) the dynamics of macro-zooplankton populations\(^2\)\(^{0}\);
(iii) ingestion, filtration, and fecal pellet production rates of copepods and on feeding rates of euphausids and ctenophores\(^2\)\(^{0}\);
(iv) feeding, fecundity (egg production rate), respiration, and excretion\(^2\)\(^{0}\).

In summary, sublethal stress on fecundity and feeding occurred in the range of 1 to 10 μg/L copper after 5 to 10 days. Similar results were noted in duplicate experiments performed in Loch Ewe, Scotland\(^2\)\(^{1}\). Respiratton and excretion rates proved to be poor indicators of sublethal stress to copper. CEPEx enclosures treated with 10 and 50 μg/L both showed changes in community structure of the micro- and macro-zooplankton taxa after 28 days as compared to controls but grazing by carnivorous "jellies" (ctenophores and medusae) complicated the results. The authors were unsure if the changes were due to the direct toxic action of copper, or if the changes resulted from modifications to other trophic levels of the contained population.

As noted in Section 3.4, the sabellid polychaete (Eudistyliya vancouveri) was shown to accumulate copper under laboratory conditions where concentrations in the seawater exceeded between 3 to 6 μg/L. Above this threshold concentration copper accumulated mainly in the branchial crown and eventually caused necrosis (cell death) in the radioles (gills)\(^2\)\(^{0}\),\(^{2}\)\(^{0}\).
5.4 EFFECTS ON AMPHIBIANS

Birge and Black\textsuperscript{76} demonstrated that exposure of the embryo-larval stage of some amphibians (southern gray treefrog, \textit{Hyla chrysoscelis} and the northern leopard frog, \textit{Rana pipiens}) to copper levels of 5 to 10 \( \mu \text{g/L} \) in water with a hardness of 100 \( \text{mg/L} \) (\textit{CaCO}_3) produced appreciable frequencies of mortality. Based on the toxicity of copper to developmental stages of fish and amphibians, Birge and Black\textsuperscript{76} recommended that practical limits for copper probably should be established within ranges of 2 to 5 \( \mu \text{g/L} \) in soft or medium hard water, and 5 to 8 \( \mu \text{g/L} \) in hard water.

5.5 EFFECTS ON FISH

5.5.1 FRESHWATER FISH

(a) Acute Toxicity

According to Spear and Pierce\textsuperscript{3}, the short-term lethal tolerance of freshwater fish to copper is mainly dependent upon the hardness of the water. The actual mechanism of how increasing water hardness increases the tolerance of fish to soluble copper is not clear. One hypothesis suggested by Spear and Pierce\textsuperscript{3} is that calcium-magnesium hardness may act intrinsically upon cell-membrane permeability at the gills.

A search of the literature indicated that small steelhead (\textit{Salmo gairdneri}) fry (1 to 6 g) were the most sensitive fish species tested to date\textsuperscript{68}. LC50 values were calculated for 96 and 168 h exposure periods to copper in soft water (10 \( \text{mg/L} \) \textit{CaCO}_3) at pH 4.7, 5.7, and 7.0. Fish were acclimated to test pH for eight days prior to testing. The 96 h LC50's for copper at the three pH levels were 66.0, 4.2, and 2.8 \( \mu \text{g/L} \), respectively. The 168 h LC50's were similar to the 96 h values. Interestingly, the fish were most tolerant at the lowest pH. This anomaly is discussed further, later in this section. Chinook salmon (\textit{Oncorhynchus tshawytscha}) fry were also found to have a low tolerance to copper, with a 96 h LC50 of 10 \( \mu \text{g/L} \) when tested in soft water (13 \( \text{mg/L} \) \textit{CaCO}_3) at pH 7.2\textsuperscript{18,2}.
Based on the acute toxicity/hardness relationship, Spear and Pierce\(^9\) have developed formulae for predicting the toxicity (LC50's) of copper to certain taxonomic groups of fishes. For example, the LC50's for coho and chinook salmon range from 10 \(\mu\)g/L in soft water to 125 \(\mu\)g/L in hard water according to the equation:

\[
\text{LC50 (mg/L Cu)} = 0.0014 H^{0.79} (\text{mg/L CaCO}_3) \text{ where H represents water hardness. The development of this formula incorporated exposure periods which ranged from 48 hours to 21 days. Similar equations have been developed for the order Perciformes (perch-like fishes), the order Cypriniformes (minnow-like fishes), and other salmonid species\(^9\).}
\]

Other factors which have been shown to affect the acute lethality of copper to fish include temperature, pH, alkalinity, sodium, fish size, and the complexing capacity of the water.

In a study by Chakoumakos et al\(^6\), the toxicity of copper to cutthroat trout (Salmo clarki) under different conditions of alkalinity and hardness was examined. The study found that the acute toxicity (96 h LC50) of copper was inversely correlated with water hardness and alkalinity. When the alkalinity was constant, hardness determined the LC50, and when hardness was constant, alkalinity determined the LC50. When alkalinity and hardness were constant, the copper concentration determined the LC50. Chapman and McCrady\(^12\) tested the lethal response of chinook fry (1.35 g) to copper in water at four different hardnesses. The 96 h LC50's for these tests were 10, 25, 90, and 125 \(\mu\)g/L copper in water hardnesses of 13, 46, 182, and 359 mg/L CaCO\(_3\), respectively.

The relationship between temperature and copper toxicity is not completely understood\(^1\). Some studies have shown that this relationship depends on exposure time and concentration of copper. When exposed to acutely lethal concentrations of copper, survival times for juvenile rainbow trout (Salmo gairdneri) were increased or decreased at a temperature of 6°C versus 15°C, depending on the copper concentration and exposure time. Other
studies indicated a reduced survival time for a number of species with increased temperature, or no alteration in the LC50's at different temperatures.

Demayo and Taylor concluded that copper is generally precipitated as malachite at alkaline pH (see Section 2.1) and survival time of fish is longer, but there are few studies documenting the effects of pH alone on the toxicity of copper because of the interrelationship of pH, alkalinity, and hardness. One study by Miller and Mackay demonstrated that at pH 5.4 copper was the major factor which caused mortality, whereas at pH 5.2, in the absence of copper, no mortality occurred. However, between pH 4.7 and 3.5 the tolerance of fish to copper increased, and was attributed to mucous secretions by the gills stimulated by the low pH. The mucous was thought to chelate the copper and reduce the toxic action of copper. Similarly, Cisinano et al showed that steelhead trout fry exposed to copper in soft water (10 mg/L CaCO₃) at pH 4.7, 5.7, and 7.0 for 96 and 168 hours were more tolerant to copper at the lowest pH. The 96 h LC50's for the three pH's tested were 66.0, 4.2, and 2.8 µg/L, respectively. The 168 h LC50's were similar to the 96 h LC50's. The authors suggested that the hydrogen ions at low pH interfered with metal uptake by the fish. On the other hand, Shaw and Brown demonstrated that the 96 h LC50's for rainbow trout exposed to copper at pH 6.5 and 7.5 at constant alkalinity were not significantly different. They proposed that CuCO₃, the predominant species of copper at pH 7.5 (see Section 2.1), may have contributed to the toxic action.

Spear and Pierce suggested that increased sodium content of water may increase the tolerance of fish to copper by modifying cell membrane permeability. A study using zebra fish (Brachydanio rerio), a tropical species, demonstrated that the 96 h LC50 was increased from a calculated level of 15 µg/L (using the formula for Cypriniformes) to 150 µg/L when the sodium content was increased from 13 to 62 mg/L, Na⁺.

The relationship between fish size and copper toxicity varies with the life stage, fish weight, and the copper concentration. For example, Hedtke
et al.\textsuperscript{71} showed the 96 h LC50's for 56-, 130- and 151-day old juvenile coho salmon were 50, 166, and 212 µg/L, respectively. Conversely, Anderson and Spear\textsuperscript{72} showed that the 96 h LC50's for large (176 grams) and small (3.9 grams) rainbow trout were similar and, at higher concentrations (400 µg/L) the smaller fish survived twice as long (38 hours) as compared to the larger fish.

The complexing capacity of the water, which can determine the amount of labile copper that may be present, can play a significant role in the acute toxicity of copper to fish. Andrew\textsuperscript{73} demonstrated that the 96 h LC50 of total copper for fathead minnows (\textit{Pimephales promelas}) in lake water with low complexing capacity was 4 times lower (more toxic) (96 h LC50 of 200 µg/L) than in lake water with high complexing capacity. However, when expressed in terms of the specific activity of cupric ion, Cu\textsuperscript{2+}, the 96 h LC50's were similar. Andrew\textsuperscript{73} concluded that the toxicity of copper is directly related to the ionic activity of Cu\textsuperscript{2+}.

Substances shown to complex copper include phosphates, humic acid, suspended particulate matter, and organic chelators such as glycine, EDTA and NTA. In general, as the concentrations of these substances increased, the toxicity of copper decreased. For example, Andrew\textsuperscript{73} demonstrated that the 48 h LC50 for blunt nose minnows (\textit{Pimephales notatus}) in the absence of phosphate was 5600 µg/L copper. In the presence of 7.7 mg/L P (as Na\textsubscript{2}HPO\textsubscript{4}) and 17.4 mg/L P (as Na\textsubscript{3}P\textsubscript{2}O\textsubscript{7}), the LC50's were increased to 20 000 and 11 000 µg/L copper, respectively. In the presence of increasing suspended humic material, Brown \textit{et al.}\textsuperscript{74} showed the tolerance of rainbow trout to copper (measured as total copper) to increase. However, when samples were micro-filtered (0.45 µm) prior to analysis (i.e., measured as soluble copper), the toxicity increased with increasing levels of suspended material. Spear and Pierce\textsuperscript{3} suggested that some of the adsorbed copper may have been toxic. Techniques used to measure complexing capacity and an example of its use for assessing the toxicity of copper to fish on a site-specific basis (Babine Lake) are discussed in Section 5.6.3.
Another factor which may influence the tolerance of fish to copper is pre-acclimation to sublethal concentrations of copper. In a review of the literature, Alderdice and McLean\textsuperscript{18} noted that previous exposure of fish to sublethal concentrations of heavy metals increased the tolerance to or decreased mortality resulting from exposure to otherwise lethal concentrations. Naive fish - those not previously exposed, such as fish migrating from a feeder stream into a contaminated stream, or fish introduced to a metal-contaminated stream from a hatchery - may be less tolerant than pre-exposed fish when subjected to a sudden increase in heavy metal concentration. Exposure of fish to sublethal concentrations of heavy metal induces the formation of metallothionein in the liver which binds the metal and is thought to buffer the interference of metals with cellular metabolic processes\textsuperscript{18}. Metallothionein synthesis in fish is discussed further in Section 5.5.1(b) and its application for assessing water quality and developing site-specific criteria is outlined in Section 5.6.4.

A recent preliminary investigation by the B.C. Ministry of Environment and Parks\textsuperscript{190} into the impact of acid mine drainage on a coastal river system (see Section 3.3) concluded that copper concentrations in the river were toxic to salmonids. The 168 h LC50's for steelhead, rainbow trout and pink salmon ranged from 37 to 72 µg/L copper using the river water. Concentrations of copper in the river frequently exceeded 37 µg/L. As pointed out in Section 3.3, a combination of the high copper concentrations, low water hardness, depressed pH, and the presence of other metals at elevated concentrations were believed to be responsible for the extremely poor pink salmon returns to a hatchery on the river system.

(b) Chronic Toxicity and Sublethal Effects

Studies have shown that mortality to fish can continue during chronic exposure to copper. For example, at a water hardness of 30 mg/L CaCO\textsubscript{3}, the 11 month LC50 for fathead minnows was 18.6 µg/L copper\textsuperscript{23}. This concentration was 0.25 of the 96 h LC50. Based on a review of time-mortality curves for a number of species, Spear and Pierce\textsuperscript{3} suggested that 48 and 96 h LC50's may be used cautiously to estimate the incipient lethal levels of copper.
Sublethal effects of copper to fish have been extensively studied and include effects on reproduction, behaviour, growth, osmoregulation, blood chemistry, olfaction, respiration and metabolism, enzyme activity, teratogenesis, and resistance to disease. Demayo and Taylor¹, Spear and Pierce³, and the U.S. EPA² have conducted extensive literature reviews on these topics in recent years. The concentrations of copper which produce various effects have been summarized in a graphical presentation by Spear and Pierce³ (reproduced in Figure 1).

Some more recent studies by Birge and Black⁷⁶ (not included in Figure 1) showed that copper concentrations between 1 and 5 μg/L (hardness of 100 mg/L CaCO₃) caused teratogenesis in rainbow trout. The most serious teratogenic effects were skeletal deformities in the developing embryos.

Brook trout (Salvelinus fontinalis) also proved to be particularly sensitive during early development. Based on the hatching success, survival, and growth of brook trout eggs, Sauter et al.⁷⁷ estimated that the MATC (Maximum Acceptable Toxicant Concentration) for brook trout in soft water (hardness of 37.5 mg/L CaCO₃) was between 3 and 5 μg/L copper.

There is some indication that chronic levels of copper lower the resistance to disease in fish. Eels (Anguilla anguilla) continuously exposed to 30-60 μg/L copper for 2-4 months died from bacterial infections, whereas control eels not exposed to copper remained healthy⁷⁸.

Regarding behaviour, several laboratory and field tests have been performed to determine the concentrations of copper which can cause avoidance and attraction in fish. Laboratory studies demonstrated that Atlantic salmon (Salmo salar) avoided copper concentrations as low as 4 to 5 μg/L¹². Goldfish (Carassius auratus) showed attraction to copper levels of 11 to 17 μg/L, but the attraction response decreased as the copper concentration increased⁷⁹. Spear and Pierce³ advised that caution should be exercised when applying avoidance thresholds to the natural environment because the movements of fish in laboratory tests are somewhat restricted.
THE RANGES OF THRESHOLD COPPER CONCENTRATIONS\(^{(a)}\)
KNOWN TO PRODUCE VARIOUS EFFECTS IN FRESHWATER FISH

\(2300 \mu g/l\)

\(40 \mu g/l\)

\(30 \mu g/l\)

\(20 \mu g/l\)

\(10 \mu g/l\)

\(5 \mu g/l\)

\(1\)

\(10\)

\(100\)

\(1000\)

\(10000\)

CONCENTRATION OF Cu (\(\mu g/l\))

(a) Concentrations pertain to waters that are relatively free of agents which may complex or adsorb dissolved copper.

(from Spear and Pierce\(^3\))
Also, natural waters often have higher complexing capacities which may increase the avoidance threshold concentration.

Growth of rainbow trout was inhibited by a copper concentration as low as 10 μg/L in soft water (hardness of 20 mg/L CaCO₃) at pH 6⁷⁰⁰. Spear and Pierce⁸ noted that exposure of fish to copper for short durations usually did not have long-term effects on the size of fish, but chronic exposure usually prevented test fish from attaining the size of control fish.

Based on the activity of the enzyme, plasma glutamic oxaloacetic transaminase (PGOT), and on other physiological changes in the blood, a "no effect" level of 11 μg/L copper was calculated for the brown bullhead (Ictalurus nebulosus)⁹⁰⁰.

Copper concentrations known to inhibit spawning in freshwater fish range from 10.6 to 18.4 μg/L for fathead minnows (hardness of 31 mg/L CaCO₃)⁷⁰⁰ and from 17.4 to 32.5 μg/L for brook trout (hardness of 45 mg/L CaCO₃)⁸¹⁰.

Copper is reported to affect osmoregulation in fish by interfering with the control of water intake or excretion through the gills⁹². Laboratory exposure of Babine Lake juvenile sockeye salmon (Oncorhynchus nerka) to 30 μg/L copper for 144 hours in freshwater followed by 24 and 48 hours exposures to saline water demonstrated that the fish were unable to regulate plasma sodium levels. However, because of the complexing capacity of Babine Lake water, a concentration of 105 to 154 μg/L copper was calculated as the threshold range which might interfere with the osmoregulatory capabilities of these fish⁹³. Similarly, juvenile coho salmon, exposed to 20 μg/L copper in freshwater for 6 days and transferred to copper-free saltwater, were unable to survive the transition⁹⁰⁰. Spear and Pierce⁸ concluded that a hazardous situation may exist for anadromous fish exposed to copper contamination before migrating to the ocean.

Based on studies investigating the loss of olfactory response of carp (Cyprinus carpio) to sugar and salt and of rainbow trout to L-serine, after
exposure to copper, Spear and Pierce[^3] estimated that the threshold concentration of copper required to inhibit chemosensory abilities in fish was between 30 and 40 μg/L.

Waiwood and Beamish[^4] demonstrated that 40 μg/L copper (pH 7.75 and hardness of 100 mg/L CaCO₃) increased the metabolic rate of rainbow trout by 5 to 25 percent over control fish.

Fish exposed to sublethal concentrations of copper can accumulate the copper in the body tissues, especially the liver. According to McCarter *et al.*[^5], fish, on exposure to copper and other trace metals, produce a low molecular weight protein in the liver called metallothionein. Metallothionein was thought by some researchers to bind the copper, and thus to act as a protective mechanism which prevents spillover to high molecular weight proteins involved in key biochemical processes. However, recent research by Roch *et al.*[^6] showed that copper is bound to high molecular weight proteins simultaneously with being bound to metallothionein. They suggested that the synthesis of metallothionein tends to buffer the interference of metals with cellular metabolic processes, but does not remove the interference completely. Another interesting aspect of Roch and McCarter's research[^7] is that increased copper in food ingested by fish failed to stimulate production of copperthionein, nor did it reduce the tolerance of fish to stress. Dissolved copper in water, on the other hand, affected both these conditions, and therefore the primary site of attack of copper would appear to be through the gills.

5.5.2 MARINE FISH

(a) Acute Toxicity

According to Spear and Pierce[^8], there is a paucity of information regarding the toxicity of copper to marine fish. For adults, 96 h LC50's usually range from about 1400 to 3000 μg/L.
The early life stages of marine fish are generally more sensitive than adults to copper. The lowest (most toxic) LC50's for embryo's of the summer flounder (Paralichthys dentatus) and winter flounder (Pseudopleuronectes americanus) were 11.9 and 52.7 µg/L, respectively\(^9\). The exposure periods were not reported. Studies generally indicated that increasing pH\(^8\) and salinity\(^8\) reduced the sensitivity of fish to copper. None of the above studies were performed on species indigenous to British Columbia coastal waters.

Rice and Harrison\(^2\) exposed Pacific herring (Clupea harengus pallasii) embryos and larvae to copper in a flow-through bioassay system. Significant embryo mortalities occurred at a copper concentration of 35 µg/L. Herring larvae continuously exposed to copper showed significant mortality at 300 µg/L.

Toxicity data for anadromous salmonid species are included in the section on freshwater fish (Section 5.5.1) because most tests were performed using young fish exposed to copper in freshwater.

(b) Chronic Toxicity and Sublethal Effects

Blaxter\(^9\) demonstrated that exposure of herring (Clupea harengus) gametes to 30 µg/L copper reduced fertilization by 50 percent. Continuous exposure of fertilized herring eggs to 30 µg/L did not affect hatching success, but teratogenic affects were apparent in 70 percent of the larvae. Rice and Harrison\(^2\) showed that herring embryos exposed to 36-h pulses of 100 µg/L copper during late development stages showed increased tolerance when exposed to copper after the response period. However, embryos exposed to pulsed copper during the early developmental stages grew significantly less.

Regarding behaviour, Blaxter\(^9\) also demonstrated that copper concentrations of 90 and 130 µg/L inhibited normal vertical migration patterns of herring in response to light.
Histological observations of winter flounder gills revealed cellular damage following exposure of the fish to 180 μg/L for 28 days.

A study\textsuperscript{92} investigating the effects of copper on the growth of juvenile chum salmon (Oncorhynchus keta) in seawater was performed using the CEPEX enclosures described in Section 5.1.3. These enclosures were enlarged to 1700 m\textsuperscript{3} so that the water column and associated plankton captured during deployment of the enclosures would support fish growth. A copper concentration of 2.5 μg/L caused no observable effect on the growth and survival of the fish after 45 days when compared to controls. However, because of the difference of fish growth among some of the test enclosures, their was suspicion that copper may have altered the spectrum of prey items available to fish. In another study 50 percent of plaice (Pleuronectes platessa) larvae, which are not indigenous to B.C. coastal waters, stopped feeding after exposure to 3 μg/L copper for 13 days, 55 days after hatching\textsuperscript{91}.

Steele\textsuperscript{93} studied the locomotor behaviour of sea catfish (Arius felix) in a 16-choice circular tank before and after 72 hours of exposure to sublethal concentrations of Cu\textsuperscript{2+}. Changes in locomotor activity and orientation depended on the concentration of Cu\textsuperscript{2+}. Test fish exposed to 5, 10 and 50 μg/L Cu\textsuperscript{2+} demonstrated hypoactivity immediately after exposure, whereas 100 and 200 μg/L elicited hyperactivity. Turning behaviour (orientation) was significantly increased in test fish exposed to concentrations between 10 and 200 μg/L. Although 10 and 50 μg/L elicited hypoactivity, fish exposed to these concentrations displayed shifts in orientation not significantly different from those produced at higher concentrations.

5.5.3 MULTIPLE TOXICITY

In addition to factors such as hardness, pH, alkalinity, and complexing capacity of a waterbody discussed in previous Sections, the simultaneous presence of other contaminants can modify the toxicity of copper to fish. Table 2 contains a summary of the effects of other pollutants on the toxicity of copper. Depending on the pollutant, the toxicity of the mixture can
<table>
<thead>
<tr>
<th>POLLUTANTS</th>
<th>SPECIES</th>
<th>HARDNESS mg/L CaCO₃</th>
<th>EFFECT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu, Zn</td>
<td>rainbow trout</td>
<td>15-21-320</td>
<td>additive (low Cu concentrations)</td>
</tr>
<tr>
<td>Cu, NH₃</td>
<td></td>
<td>--</td>
<td>synergistic (high Cu concentration)</td>
</tr>
<tr>
<td>Cu, Zn</td>
<td>guppies</td>
<td>--</td>
<td>additive</td>
</tr>
<tr>
<td>Cu, Ni</td>
<td>guppies</td>
<td>--</td>
<td>synergistic</td>
</tr>
<tr>
<td>Cu, Ni, dieldrin and</td>
<td>guppies</td>
<td>--</td>
<td>additive</td>
</tr>
<tr>
<td>potassium pentachlorophenate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu, Zn</td>
<td>guppies</td>
<td>--</td>
<td>synergistic (2.5 times)</td>
</tr>
<tr>
<td>Cu, Ni</td>
<td>guppies</td>
<td>--</td>
<td>additive</td>
</tr>
<tr>
<td>Cu, Zn, Ni</td>
<td>rainbow trout</td>
<td>soft</td>
<td>additive</td>
</tr>
<tr>
<td>Cu, phenol</td>
<td>rainbow trout</td>
<td>--</td>
<td>additive</td>
</tr>
<tr>
<td>Cu, Zn, phenol</td>
<td>rainbow trout</td>
<td>--</td>
<td>additive (at acutely toxic Cu levels)</td>
</tr>
<tr>
<td>Cu, Zn, Ni</td>
<td>rainbow trout</td>
<td>--</td>
<td>additive</td>
</tr>
<tr>
<td>Cu, Zn</td>
<td>atlantic salmon</td>
<td>20</td>
<td>additive (at incipient lethal Cu level)</td>
</tr>
<tr>
<td>Cu, Mn</td>
<td>marine diatom</td>
<td>--</td>
<td>decreased Cu toxicity</td>
</tr>
<tr>
<td>Cu, Zn, Cd</td>
<td>fathead minnow</td>
<td>--</td>
<td>less than additive</td>
</tr>
<tr>
<td>Cu, humic substances</td>
<td>rainbow trout</td>
<td>--</td>
<td>decreased Cu toxicity</td>
</tr>
<tr>
<td>Cu, suspended organic solids</td>
<td>rainbow trout</td>
<td>--</td>
<td>decreased Cu toxicity</td>
</tr>
<tr>
<td>Cu, domestic sewage</td>
<td>rainbow trout</td>
<td>--</td>
<td>decreased Cu toxicity</td>
</tr>
<tr>
<td>Cu, humic acids</td>
<td>atlantic salmon</td>
<td>14</td>
<td>decreased Cu toxicity</td>
</tr>
<tr>
<td>Cu, lignosulphonate</td>
<td>atlantic salmon</td>
<td>14</td>
<td>decreased Cu toxicity</td>
</tr>
<tr>
<td>Cu, Zn, NTA</td>
<td>brook trout</td>
<td>14</td>
<td>decreased Cu toxicity</td>
</tr>
<tr>
<td>Cu, Zn, EDTA</td>
<td>brook trout</td>
<td>14</td>
<td>decreased Cu toxicity</td>
</tr>
<tr>
<td>Cu, spent sulphite liquor</td>
<td>atlantic salmon</td>
<td>8-10</td>
<td>decreased Cu toxicity</td>
</tr>
<tr>
<td>Cu, low dissolved oxygen</td>
<td>atlantic salmon</td>
<td>--</td>
<td>increased Cu toxicity</td>
</tr>
</tbody>
</table>

* compiled from reference 1.
be increased or decreased compared to the toxicity of copper alone. For pollutants that increased the toxicity of the mixture, the toxicity of the pollutants was additive, except for high concentrations of copper and zinc which had a synergistic (multiplicative) effect. Many organic wastes caused a decrease in the toxicity of the mixture, due presumably to the formation of copper complexes.

Based on a comprehensive review of the literature, the European Inland Fisheries Advisory Commission\textsuperscript{167} and Alabaster and Lloyd\textsuperscript{152} concluded that multiple toxicity, due to commonly occurring toxicants in sewage and industrial wastes, is believed only to occur at or near lethal levels of the individual toxicants.

5.6 CRITERIA FROM THE LITERATURE

5.6.1 CRITERIA FROM OTHER JURISDICTIONS

Criteria, objectives, and standards to protect aquatic life from copper have been compiled from a number of jurisdictions and tabulated in Tables 3 and 4. Criteria to protect freshwater aquatic life generally range between 2 and 20 μg/L. A similar range of levels has been used to protect marine life. Criteria developed by some jurisdictions for freshwater aquatic life vary with water hardness. These criteria are presented in a graph (Figure 2) together with copper toxicity data (acute and chronic) so that the degree of protection offered by each jurisdiction can be assessed.

Criteria to protect aquatic life from copper have varied over the years, depending on a number of factors such as the laboratory capabilities, the acquisition of new information, and the principles followed by a particular jurisdiction.

Due to the lack of information regarding chronic toxicity or sublethal effects of contaminants, early criteria were often determined by multiplying the acute toxicity (96 h LC50) by an application factor. The application
### TABLE 3
COPPER CRITERIA FOR FRESHWATER AQUATIC LIFE

<table>
<thead>
<tr>
<th>CRITERIA STATEMENTS</th>
<th>CRITERIA VALUES</th>
<th>JURISDICTION</th>
<th>DATE</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Once a 96 hour LC50 has been determined using the receiving water in question and the most sensitive important species in the locality as the test organism, a concentration of copper safe to aquatic life in that water can be estimated by multiplying the 96 hour LC50 by an application factor of 0.1.</td>
<td></td>
<td>U.S. EPA</td>
<td>1972</td>
<td>20</td>
</tr>
<tr>
<td>In soft water (&lt;50 mg/L CaCO₃) the copper criterion should be 0.13 of the incipient LC50</td>
<td></td>
<td>Canada</td>
<td>1972</td>
<td>29</td>
</tr>
<tr>
<td>In medium-hard water (60-120 mg/L CaCO₃) the copper criterion should be 0.08 of the incipient LC50</td>
<td></td>
<td>Canada</td>
<td>1972</td>
<td>29</td>
</tr>
<tr>
<td>In hard water (&gt;120 mg/L CaCO₃) the copper criterion should be 0.03 of the incipient LC50</td>
<td></td>
<td>Canada</td>
<td>1972</td>
<td>29</td>
</tr>
<tr>
<td>Max. concentration for total copper = 20 μg/L</td>
<td>20 μg/L</td>
<td>Sask.</td>
<td>1975</td>
<td>24</td>
</tr>
<tr>
<td>For protection of freshwater aquatic life 0.1 times 96 h LC50 for non-aerated bioassay of a sensitive aquatic resident species</td>
<td></td>
<td>U.S. EPA</td>
<td>1976</td>
<td>21</td>
</tr>
<tr>
<td>The criteria should be based on the 50th and 95th percentile concentrations of soluble copper and they should be 0.05 and 0.2 of the threshold LC50, respectively. For example, for water hardnesses of 10, 50, 100 and 300 mg/L (as CaCO₃) the approximate maximum annual 50th percentile concentrations of soluble copper are 1.0, 6.0, 10.0 and 28.0 μg/L, respectively, and the 95th percentile concentrations are 5.0, 22.0, 40.0 and 112.0 μg/L, respectively.</td>
<td>1.0 to 112.0 μg/L</td>
<td>EIFAC</td>
<td>1976</td>
<td>102</td>
</tr>
</tbody>
</table>
TABLE 3 (Continued)
COPPER CRITERIA FOR FRESHWATER AQUATIC LIFE

<table>
<thead>
<tr>
<th>CRITERIA STATEMENTS</th>
<th>CRITERIA VALUES</th>
<th>JURISDICTION</th>
<th>DATE</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max. concentration for copper = 20 μg/L</td>
<td>20 μg/L</td>
<td>Alberta</td>
<td>1977</td>
<td>23</td>
</tr>
<tr>
<td>The application factor (0.1 times the 96 h LC50) given by the U.S. EPA (1976)</td>
<td></td>
<td>American</td>
<td>1979</td>
<td>99</td>
</tr>
<tr>
<td>should be replaced with a specific concentration</td>
<td></td>
<td>Fisheries Society</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Concentrations of copper in an unfiltered sample should not exceed 5 μg/L to</td>
<td>5 μg/L</td>
<td>International</td>
<td>1980</td>
<td>103</td>
</tr>
<tr>
<td>protect aquatic life</td>
<td></td>
<td>Joint Commission</td>
<td></td>
<td></td>
</tr>
<tr>
<td>For protection of freshwater aquatic life the maximum 24-hour average for total</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>recoverable copper = 5.6 μg/L or the maximum at any time should not exceed the</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>numerical value given by ( e^{(0.94[ln,(hardness)])-1.23} ) e.g., at hardness = 100,</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>criterion = 22 μg/L</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recommended objective (as total copper) for protection of aquatic life = 2 μg/L</td>
<td>2 μg/L</td>
<td>Canada</td>
<td>1981</td>
<td>1</td>
</tr>
<tr>
<td>The criteria should be based on the 50th and 95th percentile concentrations of</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>soluble copper and they should be 0.05 and 0.2 of the threshold LC50, respectively.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>For example, for water hardmesses of 10, 50, 100 and 300 mg/L (as CaCO₃), the</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>approximate maximum annual 50th percentile concentrations of soluble copper are 1.0,</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.0, 10.0 and 28.0 μg/L, respectively, and the 95th percentile concentrations are</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.0, 22.0, 40.0 and 112.0 μg/L, respectively</td>
<td>1.0 to 112.0 μg/L</td>
<td>Alabaster and Lloyd</td>
<td>1982</td>
<td>152</td>
</tr>
</tbody>
</table>
### Table 3 (Continued)

**Copper Criteria for Freshwater Aquatic Life**

<table>
<thead>
<tr>
<th>Criteria Statements</th>
<th>Criteria Values</th>
<th>Jurisdiction</th>
<th>Date</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>In each 30 consecutive days: (a) the average concentration (in μg/L) of active copper should not exceed the numerical value given by $e^{0.905[\ln(\text{hardness})]-1.785}$; (b) the maximum concentration should not exceed the numerical value given by $e^{0.905[\ln(\text{hardness})]-1.413}$; and (c) the concentration may be between (a) and (b) for up to 96 hours. e.g., at hardness = 100, the criterion average = 11 μg/L</td>
<td>U.S. EPA (draft)</td>
<td>1983</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>Maximum acceptable concentration to protect freshwater aquatic life is 5.6 μg/L total copper</td>
<td>5.6 μg/L</td>
<td>Manitoba</td>
<td>1983</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Quebec</td>
<td>In prep.</td>
<td>185</td>
</tr>
<tr>
<td>The dissolved copper concentration for salmonid hatcheries should not exceed 2, 5, 11, 22 and 64 μg/L for water hardneses (as CaCO$_3$)of 10, 25, 50, 100, and 300 mg/L, respectively</td>
<td>2 to 64 μg/L</td>
<td>Canada Dept. of Fisheries and Oceans</td>
<td>1983</td>
<td>100</td>
</tr>
<tr>
<td>For coastal hatcheries where successful migration and salt water adaptation immediately upon release are critical, the maximum acceptable dissolved copper concentration is 5 μg/L</td>
<td>5 μg/L</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Concentrations of copper in an unfiltered sample should not exceed 5 μg/L to protect aquatic life</td>
<td>5 μg/L</td>
<td>Ontario</td>
<td>1984</td>
<td>31</td>
</tr>
<tr>
<td>For water hardness of 10, 50, 100, and 300 mg/L (as CaCO$_3$) the recommended average concentrations of dissolved copper are 1, 6, 10, and 28 μg/L, respectively, and the mandatory 95th percentile concentrations are 5, 22, 40, and 112 μg/L, respectively</td>
<td>1.0 to 112 μg/L</td>
<td>United Kingdom</td>
<td>1984</td>
<td>33</td>
</tr>
</tbody>
</table>
TABLE 3 (Continued)

COPPER CRITERIA FOR FRESHWATER AQUATIC LIFE

<table>
<thead>
<tr>
<th>CRITERIA STATEMENTS</th>
<th>CRITERIA VALUES</th>
<th>JURISDICTION</th>
<th>DATE</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freshwater aquatic organisms and their uses should not be affected unacceptably if the 4-day average concentration of copper (in μg/L) does not exceed the numerical value given by $e^{(0.8545[\ln(\text{hardness})]-1.465)}$ more than once every 3 years on the average, and if the 1-hour average concentration (in μg/L) does not exceed the numerical value given by $e^{(0.9422[\ln(\text{hardness})]-1.464)}$ more than once every 3 years on the average. For example, at water hardnesses of 50, 100 and 200 mg/L (as CaCO₃), the 4-day average concentrations are 6.5, 11.8, and 21.4 μg/L, and the 1-hour average concentrations are 9.2, 17.7 and 34.0 μg/L, respectively. The criteria should be applied in terms of total recoverable copper until an EPA approved analytical technique for acid soluble copper is developed.</td>
<td>U.S. EPA</td>
<td>1985</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>For water hardness ranges of 0-120, 120-180, and &gt;180 mg/L (as CaCO₃), the proposed maximum total recoverable copper concentrations are 2.3, and 4 μg/L, respectively</td>
<td>2.0 to 4.0 μg/L</td>
<td>CCREM</td>
<td>1987</td>
<td>174</td>
</tr>
<tr>
<td>CRITERIA STATEMENTS</td>
<td>CRITERIA VALUES</td>
<td>JURISDICTION</td>
<td>DATE</td>
<td>REFERENCE</td>
</tr>
<tr>
<td>-----------------------------------------------------------------------------------</td>
<td>-----------------</td>
<td>--------------</td>
<td>------</td>
<td>-----------</td>
</tr>
<tr>
<td>Levels less than 10 μg/L present minimal risk to the marine environment</td>
<td>10 μg/L</td>
<td>U.S. EPA</td>
<td>1972</td>
<td>20</td>
</tr>
<tr>
<td>Concentrations above 50 μg/L constitute a hazard to marine life</td>
<td>50 μg/L</td>
<td>U.S. EPA</td>
<td>1972</td>
<td>20</td>
</tr>
<tr>
<td>For protection of marine life 0.1 times 96 h LC50 for non-aerated bioassay of a sensitive aquatic resident species</td>
<td></td>
<td>U.S. EPA</td>
<td>1976</td>
<td>21</td>
</tr>
<tr>
<td>The application factor (0.1 times the 96 h LC50) given by the U.S. EPA (1976) should be replaced with specific concentration</td>
<td></td>
<td>American Fisheries Society</td>
<td>1979</td>
<td>99</td>
</tr>
<tr>
<td>To protect marine aquatic life the maximum 24-hour average for total recoverable copper = 4.0 μg/L and the maximum at any time = 23 μg/L</td>
<td>4.0 to 23 μg/L</td>
<td>U.S. EPA</td>
<td>1980</td>
<td>22</td>
</tr>
<tr>
<td>To protect saltwater aquatic life and its uses, in each 30 consecutive days: (a) the average concentration of active copper should not exceed 2.0 μg/L; (b) the maximum concentration should not exceed 3.2 μg/L; and (c) the concentration may be between 2.0 and 3.2 μg/L for up to 96 hours</td>
<td>2.0 to 3.2 μg/L</td>
<td>U.S. EPA (draft)</td>
<td>1983</td>
<td></td>
</tr>
<tr>
<td>Recommended average concentration of dissolved copper to protect marine life is 5 μg/L</td>
<td>5 μg/L</td>
<td>United Kingdom</td>
<td>1984</td>
<td>33</td>
</tr>
<tr>
<td>Saltwater aquatic organisms and their uses should not be affected unacceptably if the 1-hour average concentration of copper does not exceed 2.9 μg/L more than once every 3 years on the average. The criteria should be applied in terms of total recoverable copper until an EPA-approved analytical technique for acid-soluble copper is developed.</td>
<td>2.9 μg/L</td>
<td>U.S. EPA</td>
<td>1985</td>
<td>2</td>
</tr>
</tbody>
</table>
FIGURE 2

RELATIONSHIP BETWEEN COPPER TOXICITY DATA (ACUTE AND CHRONIC) AND WATER HARDNESS FOR FRESHWATER ORGANISMS, AS COMPARED TO CRITERIA FROM VARIOUS JURISDICTIONS

United Kingdom, EIFAC, and Alabaster and Lloyd
(Approx. maximum annual 95th percentile criterion)

Canada Dept. Fisheries and Oceans Salmonid Hatchery Criterion (Maximum)

U.S. EPA (1-hour average criterion)

U.S. EPA (4-day average criterion)

B.C. (Maximum criterion)

EIFAC, and Alabaster and Lloyd (Approx. maximum annual 50th percentile criterion), and the United Kingdom (average criterion)

B.C. (30-day average criterion)

CCREM (Proposed maximum criterion)

* Obtained from various literature sources
factors most commonly used were 0.1 and 0.01, depending on whether the contaminant was considered persistent or non-persistent. If the contaminant could accumulate and persist in the environment and in the tissues of organisms, then the lower value (0.01) was often used to calculate the criterion to protect aquatic life from long-term harmful effects. If the contaminant was non-persistent, then 0.1 was often used. Former Canadian criteria used a variation of this technique whereby the application factor was adjusted according to the hardness of the water (see Table 3). As more data regarding the chronic and sublethal effects of copper became available, there was a trend to specify criteria in terms of absolute concentrations. The specification of copper criteria as absolute concentrations was recommended by the American Fisheries Society (Table 3).

The relationship between water hardness and the acute toxicity of copper in freshwater is well documented. Some jurisdictions such as the U.S. EPA and the Canada Department of Fisheries and Oceans have developed formulae for freshwater copper criteria so that the hardness of a particular waterbody is considered (see Table 3). Similarly, the European Inland Fisheries Advisory Commission (EIFAC), Alabaster and Lloyd, and the United Kingdom have specified approximate maximum annual 50th and 95th percentile copper concentrations for rainbow trout which vary with water hardness.

Between 1980 and 1985, the U.S. EPA has considered averaging periods of 24 hours, 30 days, and 4 days for criteria to address chronic effects; a maximum instantaneous, a 4-day maximum in a 30-day period, and a one-hour average concentration were considered to address acute effects (Table 3). The most recent (1985) U.S. EPA approach bases the criterion for acute effects on a one-hour average concentration and the chronic effects on a 4-day average concentration. These averaging periods replace the 1983 draft criteria which recommended a maximum concentration over 96 hours of cumulative events for acute effects and a 30-day average for chronic effects. The main reasons for these changes were, in the case of chronic toxicity, that a shorter averaging period (4 days instead of 30 days) would limit the
duration and magnitude of excursions above the chronic criterion concentration. Recent evidence\textsuperscript{186,187} has shown that fluctuating concentrations of copper (near the lethal threshold) are more toxic than a continuous concentration even though the average is the same. On the other hand, Buckley et al.\textsuperscript{188}, Alderdice and McLean\textsuperscript{184}, and Dixon and Sprague\textsuperscript{193} demonstrated that salmonids pre-exposed to sublethal levels of copper increased their tolerance to acute exposures (see Section 5.5.1(a)). This increased tolerance was attributed to the synthesis of metallothionein or other hepatoproteins (see Sections 5.5.1(a) and 5.5.1(b)). For acute toxicity, the change from a 96-hour maximum concentration to a one-hour average concentration was considered appropriate by the U.S. EPA because high concentrations of some materials can cause death in one to three hours.

The U.S. EPA criteria were derived using a somewhat complex statistical procedure developed by Stephan et al.,\textsuperscript{101} and are intended to protect at least 95% of a group of diverse genera. If a sensitive species is economically, recreationally or socially important, then the criterion is based on toxicity data for that sensitive species. The U.S. EPA criterion to protect aquatic life from acute toxicity is based upon the "Final Acute Value" (a Genus Mean Acute Value derived using statistical procedures based on 96 h LC50's). In the case of an important sensitive species, the criterion is based upon the "Species Mean Acute Value" which becomes the "Final Acute Value". The "Final Acute Value" is divided by a safety factor of two to determine the "Criterion Maximum Concentration", which is the criterion level (specified as a 1-hour average) designed to protect aquatic life from acute effects.

The U.S. EPA 4-day average criterion level, which is designed to protect organisms from the chronic effects of copper, is derived by dividing the "Final Acute Value" by the geometric mean of the acute-chronic ratios (inverse of the application factor) for sensitive organisms. This value has been called the "Criterion Continuous Concentration" by the U.S. EPA.
The U.S. EPA acute and chronic freshwater criteria are both expressed as regression equations and are based on the relationship of toxicity to water hardness. These equations \( e^{0.9422 \ln(\text{hardness}) - 1.464} = \) Criterion Maximum Concentration and \( e^{0.8545 \ln(\text{hardness}) - 1.465} = \) Criterion Continuous Concentration, expressed in \( \mu g/L \) copper, are presented graphically with toxicity data in Figure 2, together with criteria from other jurisdictions.

Examples of acute (1-hour average) and chronic (4-day average) criterion levels for copper using the U.S. EPA formulae for various water hardnesses are as follows:

<table>
<thead>
<tr>
<th>Hardness (mg/L CaCO₃)</th>
<th>4-day Average Criterion (μg/L)</th>
<th>1-hour Average Criterion (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.8</td>
<td>2.0</td>
</tr>
<tr>
<td>20</td>
<td>3.0</td>
<td>3.9</td>
</tr>
<tr>
<td>50</td>
<td>6.5</td>
<td>9.2</td>
</tr>
<tr>
<td>100</td>
<td>11.8</td>
<td>17.7</td>
</tr>
<tr>
<td>150</td>
<td>16.7</td>
<td>25.9</td>
</tr>
<tr>
<td>200</td>
<td>21.4</td>
<td>34.0</td>
</tr>
<tr>
<td>250</td>
<td>25.9</td>
<td>42.0</td>
</tr>
</tbody>
</table>

While there is plenty of evidence to support the water hardness/acute toxicity relationship, there is less evidence to suggest that a similar relationship holds for long-term sublethal toxicity, especially to the degree permitted by the U.S. EPA 4-day average criterion. Even though the U.S. EPA\(^2\) has recommended a 4-day average criterion which varies significantly with water hardness, it admits that "the available data concerning the effect of hardness on the chronic toxicity of copper is somewhat inconclusive".

The Inland Waters Directorate\(^1\), on the other hand, has chosen to disregard the water hardness/toxicity relationship by establishing a single low criterion level which would apply to all situations encountered. Although
this agency considers that hardness is not a significant factor in sublethal
toxicity, it mentions that, after a comprehensive review of the literature,
the maximum acceptable toxicant concentration lies between 3 and 5 \( \mu g/L \) in
soft water and between 5 and 8 \( \mu g/L \) in hard water. This statement appears
to be taken from Birge and Black\(^7\) who undertook long-term studies on the
toxicity of copper to embryo-larval stages of fish and amphibians. They
concluded from these studies, and from other toxicological data reviewed in
the literature, that practical limits for copper probably should be estab-
lished within ranges of 2 to 5 \( \mu g/L \) in soft or medium hard water and 5 to
8 \( \mu g/L \) in hard water. The Canadian Council of Resource and Environment
Ministers (CCREM)\(^{17} \) has recently developed new water quality guidelines.
These guidelines recommend maximum total copper concentrations of 2 \( \mu g/L \) in
soft to medium hard water (0-120 mg/L as CaCO\(_3\)), 3 \( \mu g/L \) in hard water
(120-180 mg/L), and 4 \( \mu g/L \) in very hard water (>180 mg/L). These values are
far more conservative than the calculated range of values recommended by the
U.S. EPA\(^2 \), the Canadian Department of Fisheries and Oceans\(^{18} \), Alabaster and
Lloyd\(^{19} \), the European Inland Fisheries Advisory Commission\(^{20} \), or the
United Kingdom\(^3 \).

The water hardness/toxicity relationship does not apply to marine
aquatic life because of the high constant hardness of marine water. Thus,
the U.S. EPA\(^2 \) and the United Kingdom\(^3 \), the only agencies which have set any
copper criteria for marine aquatic life, have recommended single values of
2.9 \( \mu g/L \) (total copper) as a 1-hour average and 5 \( \mu g/L \) average, (dissolved
copper), respectively, for marine situations (see Table 4).

The U.S. EPA marine criterion was based on the acute toxicity of copper
to embryos of the blue mussel and Pacific oyster which were the most sensi-
tive marine species tested to date with 96 h LC50's of 5.8 and 5.3 \( \mu g/L \)
copper, respectively. According to the U.S. EPA\(^2 \), the only marine chronic
value available (77 \( \mu g/L \) copper reduced spawning success of the mysid,
*Mysidopsis bahia*) was unacceptable for use in determining a chronic
criterion because of the tolerance of this species to copper, and because
lower acute values were available for other organisms. Therefore, for
marine waters, the "Criterion Maximum Concentration" of 2.9 μg/L copper (calculated according to the method outlined earlier in this Section) was considered appropriate for use as the "Final Chronic Value". It was considered likely, by the U.S. EPA, that a concentration that would not cause acute lethality to early life stages of sensitive species would not cause chronic toxicity either. Hence, a single criterion of 2.9 μg/L copper (expressed as a 1-hour average) was used to protect marine organisms from both acute and chronic effects of copper.

The U.S. EPA\textsuperscript{2} has introduced a new concept to its most recent aquatic life criteria. It permits the criteria to be exceeded an average of once every three years. The reasoning behind this concept is based on the U.S. EPA's best scientific judgement that three years is the average amount of time it would take an unstressed system to recover from a pollution event\textsuperscript{101}.

5.6.2 FORMS OF COPPER FOR CRITERIA

On reviewing criteria from other jurisdictions, there appears to be some discrepancy regarding which form of copper should be measured. Some jurisdictions failed to specify the intended form of copper. The Canada Department of Fisheries and Oceans\textsuperscript{100}, the European Inland Fisheries Advisory Commission (EIFAC)\textsuperscript{102}, the United Kingdom\textsuperscript{33}, and Alabaster and Lloyd\textsuperscript{152} have specified soluble copper as the target form, whereas the International Joint Commission\textsuperscript{102} for the Great Lakes and most other Canadian jurisdictions have chosen to be more stringent and have specified total copper. The U.S. EPA\textsuperscript{2}, on the other hand, has recently proposed switching from total copper to "acid-soluble copper" as the target form in fresh and marine waters. Acid-soluble copper is operationally defined as the copper that passes through a 0.45-μm membrane filter after the sample is acidified to pH 1.5 to 2.0 with nitric acid. The time allowed between acidification of the water sample and filtration can vary anywhere from 10 minutes to 24 hours. The U.S. EPA\textsuperscript{2} claims that this variation will probably not affect the results substantially. The rationale for this choice is to
capture the hydroxo- and carbonato-copper complexes and weakly adsorbed copper which may be biologically available. However, at this time, no U.S. EPA approved method for measuring acid-soluble copper is available to implement the criteria through the regulatory programs of the U.S. EPA. Until the method is approved, the U.S. EPA recommends that the criteria be applied in terms of total recoverable copper.

An Inland Waters Directorate task force\textsuperscript{105} assessed the various analytical techniques for metals in freshwater and sediments, and the advantages and disadvantages of using the various techniques for setting water quality objectives. The task force concluded that, theoretically, the best method was to measure the free ion (Cu\textsuperscript{2+}) concentration in the water. This conclusion has been supported by other researchers involved with the toxicity of copper. The cupric ion concentration shows a strong correlation with toxicity to algae\textsuperscript{106,107}, invertebrates\textsuperscript{73}, and fish\textsuperscript{73,74}, whereas total or dissolved copper rarely correlates well with toxicity. The often poor correlation of total or dissolved copper with toxicity has been attributed to the varying complexing capacities of different test waters. However, the concentration of the cupric ion, which is the major toxic form of copper, is always in equilibrium with complexing substances in water, and therefore provides a measurement which correlates well with the actual toxicity. At present no method exists which can measure the cupric ion concentration on a routine basis at levels which are usually encountered in the aquatic environment. According to Spear and Pierce\textsuperscript{3}, the cupric ion electrode is not accurate at concentrations less than 5 μg/L. When detection capabilities are improved, specification of the free ion concentration will likely be the direction taken for future copper criteria.

In addition to recommending the measurement of the cupric ion concentration, the task force\textsuperscript{105} also recommended that the total copper concentration in the water and in the medium and fine (≤149 μm) fraction of the bottom sediment should be measured. Furthermore, the task force\textsuperscript{105} recommended that the weights of these fractions should be measured. These measurements for total copper in the water and sediment presumably represent
the maximum potential amount of copper which can be biologically available\textsuperscript{105}.

Due to the inability to measure the cupric ion on a routine basis, the task force\textsuperscript{105} recommended that the next best alternative was to measure dissolved copper. However, as pointed out earlier in this section, dissolved copper often correlates poorly with toxicity.

Another analytical technique reviewed by the task force\textsuperscript{105} for use in water quality objectives was "extractable" copper which is defined as the dissolved copper plus copper extracted from suspended sediment by dilute mineral acid. According to the review, extractable copper has been considered by some researchers to be a better approximation of the biologically available copper than total or dissolved copper because it includes weakly sorbed copper which could easily be desorbed from particulate matter and eventually enter into biological processes. However, the use of this method was phased out because the results were often not reproducible due to varying sample storage times.

A recent study using samples of turbid Fraser River water revealed that extractable metal levels for copper, lead, zinc, nickel, and cobalt were nearly constant during the first week of storage, but levels increased significantly after about 10 days of storage\textsuperscript{108}. Exceptions were iron and manganese which decreased in concentration during the first week of storage. Michnowsky et al.\textsuperscript{108} concluded that, "in the case of water samples containing suspended sediment, the extractable metal method, as presently defined, is not restrictive enough to ensure reproducible results." However, it would seem that if a 7-day limit were imposed on the sample storage time, then the reproducibility of the extractable metal technique could be improved. Caution should be exercised when comparing historical levels of extractable metals because no time restriction on sample storage was specified in the past.
As pointed out in Section 2, the use of an ion-exchange column using a chelating resin for freshwater or a strong acid for saltwater are presently being investigated as techniques for measuring the free and weakly complexed forms of copper. These techniques may serve as useful tools for assessing water quality or for setting criteria if the measurements prove to correlate well with toxicity.

5.6.3 MEASUREMENT OF COMPLEXING CAPACITY

Another technique which has been used to estimate the biological availability of trace metals is the measurement of the complexing capacity of a particular waterbody. Various methods have been used to measure the complexing capacity of natural waters. The following discussion is based on a 1981 publication by Hart\textsuperscript{109} in which the theoretical basis of complexing capacity and the different methods used to measure it are reviewed and assessed.

In summary, to calculate the amount of metal complexed at a particular trace metal concentration, it is necessary to know the value of the conditional formation constant for the reaction. Methods used to measure the complexing capacity and the conditional formation constant involve titration of the natural water by addition of known amounts of metal ion and, after a suitable equilibration time, measurement of the unreacted metal ion or a related quantity. According to Hart\textsuperscript{109}, methods used to determine complexing capacity should ideally include the following characteristics:

(a) selectivity for the metal ion added.
(b) a capacity to measure the metal, or a related quantity, at very low concentrations.
(c) a capacity to provide information on both metal-binding ligand concentration and conditional formation constants.
(d) no requirement to add other reagents that may disturb the natural equilibrium.
(e) application over a wide range of pH values.
(f) a short time requirement
The complexing capacity of a solution is obtained indirectly by adding copper ions to the solution and measuring the remaining free copper ions by a number of methods.

Of the common methods in use, only the selective ion electrode technique is a direct measurement of free copper ions (Cu$^{2+}$). However, as pointed out earlier in this Section, the detection capability of this technique (> 5 μg/L) is not sensitive enough to measure the low levels which are usually encountered in the aquatic environment. Furthermore, the selective ion electrode is subject to varying degrees of interference from other ions in the sample$^{176}$.

With other methods, the concentration of Cu$^{2+}$ must be calculated. For example, anodic stripping voltammetry (ASV) measures the "labile" copper concentration, and the free cupric ion concentration is then obtained by correction for the copper-inorganic species and any labile copper-organic species. Amperometric titration employing ASV is the most commonly used technique to measure complexing capacity and satisfies several of the characteristics listed above. The ASV technique is sensitive, allows the determination of total ligand concentration, is reasonably rapid and applicable over a wide pH range, and stability constants may also be estimated with reasonable accuracy. A shortcoming of the technique is that ASV determines the electro-active forms of copper which include Cu2+, CuOH+, CuCO3$, and CuOAc+, if acetate is used as a buffer. The free ion concentration can be obtained provided the concentration of each of the other electro-active species can be corrected for. Other copper complexes in the sample also may affect the results by contributing to the stripping current and hence overestimate the free copper ion concentration.

Techniques other than the selective ion electrode or the amperometric titration technique employing ASV, which have been used to estimate complexing capacity include the following:

(a) Ion exchange which involves adding Cu and measuring equilibrium between solution and ion exchange resin.
(b) Biological techniques which involve measuring the suppression of phytoplankton photosynthesis or the growth suppression of bacteria.
(c) Dialysis technique which involves the addition of Cu and the separation of uncomplexed and complexed Cu by dialysis.
(d) High Performance Liquid Chromatography (HPLC).

Concentrations of copper species also have been calculated from equilibrium chemical models. These models predict how specified amounts of metals and ligands are partitioned by competing reactions in solution and solid phases\textsuperscript{152}. Results from these models are subject to variation depending on the information fed into the data base. Factors such as thermodynamic data, activity coefficient calculations, redox assumptions, temperature corrections, alkalinity corrections, and the number of complexes used may affect the results. According to Harrison\textsuperscript{122}, as more experiments are performed and the data generated are incorporated into the model, predictive capabilities will improve.

A practical application of the measurement of complexing capacity has been to determine if copper-bearing wastes entering Babine Lake (an important, sockeye salmon-rearing lake in British Columbia) were harmful to young sockeye salmon\textsuperscript{110}. The copper complexing capacity of Babine Lake was reported to be in excess of 100 \(\mu\)g/L (Cu\textsuperscript{2+}) which, when combined with the levels of copper present in the lake (4 to 44 \(\mu\)g/L), indicated that copper levels were not a threat to the fish. The technique used to determine the complexing capacity of Babine Lake was based on the method described by Chauet \textit{et al.}\textsuperscript{189}. It involves the measurement of labile copper by differential pulse anodic stripping voltammetry after a number of ionic copper spikes have been allowed to equilibrate with the complexing materials in a water sample.

5.6.4 HEPATIC METALLOTHIONEIN ANALYSIS IN FISH

Another technique which has been investigated as a tool to assess water quality and to develop site-specific criteria for copper, cadmium, and zinc
involves the measurement of metallothionein in the livers of fish. As pointed out in Section 5.5.1(b), metallothionein is a low molecular weight metal-binding protein found in the liver. Studies\textsuperscript{158,159} have demonstrated that the concentration of hepatic metallothionein in rainbow trout increases in proportion to the concentration of metals in the water. Roch et al.\textsuperscript{160} demonstrated that by making a series of measurements at different sublethal concentrations of the metals copper, zinc, and cadmium mixed in ratios typical of the test site, it is possible to describe a regression equation relating the concentration of metal in the water to the concentration of hepatic metallothionein, with confidence limits. By drawing the 95 percent confidence lines either side of the regression line, the concentration beyond which a significant increase of hepatic metallothionein will occur can be determined. An example of this technique is shown in Figure 3 using data for Buttle Lake on Vancouver Island. The relative proportions of zinc, copper, and cadmium, as they typically occurred in Buttle Lake in 1982, were 400:20:1. Using zinc as the predictor and the appropriate proportions of the three metals, this technique has been used to propose site-specific criteria for zinc (40 μg/L), copper (2 μg/L), and cadmium (<0.5 μg/L) to protect rainbow trout in Buttle Lake\textsuperscript{160}. This technique has an advantage over the use of application factors for estimating no-effect levels because it relates a metal level directly to a measurable biochemical response in fish. Furthermore, assumptions concerning the additive, synergistic, or antagonistic effects of metals are not necessary because the metallothionein technique measures these combined effects directly. This is a new concept and has not been fully accepted by the scientific community.

5.6.5 MULTIPLE TOXICITY

Concern has often been expressed regarding the greater toxicity of aqueous mixtures of contaminants to aquatic organisms than the toxicity of a single contaminant acting alone. Much of the information available on the toxicity of substances to aquatic organisms relates to materials tested singly. However, it is uncommon to find a situation where only a single contaminant is present. Instead, several harmful substances usually are
Figure 3

Determination of Safe Levels of Heavy Metals for Rainbow Trout in Bute Lake using Zinc as the Predictor

(Zn:Cu:Zn = 400:20:1)

(from Roch et al.)
present together in a waterbody receiving effluent. The International Joint Commission\textsuperscript{111}, the European Inland Fisheries Advisory Commission\textsuperscript{167}, and Alabaster and Lloyd\textsuperscript{152} have reviewed the environmental significance of aqueous mixtures of metals. Although synergistic (more than additive) or antagonistic (less than additive) effects have been shown for some mixtures of toxicants, it is generally agreed that, for most metal mixtures and other commonly-occurring constituents of sewage and industrial wastes, an additive model is adequate to describe the joint effect of toxicants in the mixture.

The International Joint Commission\textsuperscript{111} has outlined an approach to deal with mixtures of metals in the Great Lakes using an additive model as follows:

The sum of the ratios of each metal concentration (Mi) to its respective objective concentration (Oi) should not exceed 1.0, i.e.,

$$\sum \frac{M_i}{O_i} \leq 1.0$$

While the Commission points out that this criterion is scientifically indefensible, its application to surveillance data analysis may serve as an early warning signal of harmful effects to aquatic life. Also, it is unlikely that adequate information required to formulate a scientifically defensible criterion will be available in the foreseeable future.

A practical application of the additive model was demonstrated by Alderdice and McLean\textsuperscript{187} to determine if copper and zinc entering the Campbell River system on Vancouver Island were toxic to three species of salmonids. They concluded that while Campbell River water appeared to be non-toxic to pre-exposed fish populations hatched and raised in the river, the water would have been toxic to naive juvenile rainbow trout (See Section 5.5.1(a)) for most of the study period (February, 1980 to September, 1981), according to the additive model.
The EIFAC\textsuperscript{167}, the United Kingdom\textsuperscript{175}, and Alabaster and Lloyd\textsuperscript{152} agree with the concentration addition concept for metal mixtures; however, they concluded that because concentrations lower than the EIFAC recommended values for single metals do not appear to contribute to the toxicity of a mixture of metals, there is no need to adjust these recommended values downward in such situations.

5.7 \textbf{RECOMMENDED CRITERIA}

Criteria to protect aquatic life from the harmful effects of copper in fresh, estuarine, and coastal marine waters of British Columbia are modified from criteria developed by other jurisdictions, and take into account appropriate toxicological data to tailor the criteria for aquatic life found in B.C. waters. These criteria are designed to protect aquatic life from short-term acute effects and long-term sublethal effects of anthropogenically introduced copper.

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, Section 5.7.4).

5.7.1 \textbf{FRESHWATER AQUATIC LIFE}

(a) The 30-day average concentration of total copper (based on a minimum of 5 approximately weekly samples) should not exceed 2 \(\mu g/L\) when average water hardness over the same period (expressed as mg/L CaCO\(_3\)) is \(\leq 50\) mg/L. When average water hardness is greater than 50 mg/L the 30-day average concentration should not exceed the numerical value (in \(\mu g/L\)) given by the formula \([0.04(\text{average hardness})]\) where water hardness is reported as mg/L CaCO\(_3\). Examples based on this formula are as follows:
### (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 CaCO₃. Examples based on this formula (rounded to the nearest µg/L) are as follows:

<table>
<thead>
<tr>
<th>Water Hardness (mg/L CaCO₃)</th>
<th>Maximum Total Copper Criteria (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>20</td>
<td>4</td>
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</tr>
<tr>
<td>200</td>
<td>21</td>
</tr>
<tr>
<td>250</td>
<td>26</td>
</tr>
</tbody>
</table>

### (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.

#### 5.7.2 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; and
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(b) The maximum concentration of total copper should not exceed 3 μg/L at any time; or

(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.

5.7.3 APPLICATION OF CRITERIA

5.7.3.1 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.

(a) 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.
(b) 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-$\mu$m 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.

(c) 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 (Section 5.6.2). 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 dissolved copper values, whereas in oligotrophic waters, extractable, dissolved, and total copper values are likely to be similar.

5.7.3.2 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 (discussed in Section 5.6.3), analysis for metallothionein in fish liver (discussed in Section 5.6.4), 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.

5.7.3.3 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 in Section 5.7.4.2) 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 under-
estimate the bioavailable copper (discussed in Section 5.7.4.1 (b)), 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 social-economic problems, the necessary studies should be
performed to determine if increased copper levels would be detrimental.

5.7.3.4 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:

(i) 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 rela-
tive frame of reference for assessing change. The control site should
be sampled at virtually the same time as the test site.

(ii) 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 iden-
tify 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 water-
bodies 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.

5.7.3.5 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 from copper algicide treatment (Section
5.1.2), 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 algicidies.

When used as a molluscidicide for the treatment of swimmer's itch, copper sulphate appears to be ineffective, considering the results of the studies presented in Section 5.1.2. 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.

5.7.4 RATIONALE

The criteria recommended in this document for the protection of marine, estuarine, and freshwater aquatic life in British Columbia have been based, in part, on recent criteria developed by the Inland Waters Directorate¹, the U.S. EPA², the International Joint Commission¹¹, and from recommendations by Birge and Black⁶. Certain modifications have been made to tailor the criteria to B.C. waters and to provide a more appropriate level of protection for aquatic life. The criteria specified here are designed to address the short-term and long-term toxicity of copper acting alone and in combination with other metals.

The criteria are expressed in terms of total copper. This provides the most general application and is the safest in the absence of detailed site-specific information. However, when detailed knowledge on the forms and bioavailability of copper in a waterbody is available, the form of copper in the criteria can be modified, as justified by the data.
5.7.4.1 Freshwater Aquatic Life

(a) 30-day Average Criterion

The 30-day average criterion level recommended in this document is designed to protect aquatic life from long-term sublethal effects of copper. This criterion has been modified slightly from levels considered safe to sensitive aquatic life by Birge and Black\textsuperscript{76}, and is less stringent than the maximum level of 2 µg/L recommended by the Inland Waters Directorate\textsuperscript{1}.

The U.S. EPA's\textsuperscript{2} 4-day average criterion, the Canada Department of Fisheries and Oceans\textsuperscript{100} salmonid hatchery criteria, the United Kingdom's average criteria, and criteria for rainbow trout developed by Alabaster and Lloyd\textsuperscript{152} all vary considerably with water hardness. These criteria are unlikely to provide adequate protection to aquatic life in view of the copper levels which have been shown to cause chronic or sublethal effects at various water hardnesses. Figure 2 shows the toxicity data as related to water hardness from numerous studies and the relationship between the criteria from several jurisdictions and these toxicity values. Clearly, the criteria from these other jurisdictions are considerably higher than copper levels shown to produce chronic or sublethal effects to aquatic life. These criteria levels could result in toxicological consequences which are unacceptable.

Based on their results, which are among the lowest harmful effect levels reported in the literature, Birge and Black\textsuperscript{76} concluded that practical limits for copper probably should be within ranges of 2 to 5 µg/L in soft or medium hard water and from 5 to 8 µg/L in hard water to protect sensitive aquatic life. Similarly, after a comprehensive review of the literature, the Inland Waters Directorate\textsuperscript{1} also stated that, in terms of sublethal toxicity, the maximum acceptable toxicant concentration in soft water lies between 3 and 5 µg/L and in hard water between 5 and 8 µg/L. Nevertheless, the Inland Waters Directorate\textsuperscript{1} chose to be conservative and specified a single criterion (2 µg/L total copper) which would apply to all
circumstances encountered, regardless of the water hardness. This single low level can be somewhat overrestrictive for many waterbodies in British Columbia.

The range of limits recommended by Birge and Black\textsuperscript{76} appears to be more practical than the single criterion recommended by the Inland Waters Directorate\textsuperscript{1}, considering that levels encountered in natural waterbodies in British Columbia often exceed the national criterion. In addition, the limits recommended by Birge and Black\textsuperscript{76} provide a little more flexibility than the national criterion in dealing with the large variations in water hardness which occur throughout British Columbia; hardness varies from the soft water which is characteristic of coastal streams to the hard water which is typical of inland waterbodies.

For the above reasons, the recommendations by Birge and Black\textsuperscript{76} and other data reported in the literature were used to formulate a 30-day average criterion for copper which varies slightly with hardness. Since Birge and Black\textsuperscript{76} considered 37 mg/L CaCO\textsubscript{3} as soft water and 187 mg/L as hard water, the range of permissible levels for British Columbia were increased by increments of 1 μg/L copper for every 25 mg/L CaCO\textsubscript{3} above 50, according to the formula \[0.04 \times \text{average water hardness}.\] Below an average water hardness of 50 mg/L, a criterion of 2 μg/L is recommended. The incremental increases with water hardness are somewhat arbitrary choices, but they fit the recommendations of Birge and Black\textsuperscript{76}, and are below most levels reported in the literature to cause chronic or sublethal effects to aquatic life as shown in Figure 2. Also, the formula provides absolute values for comparing and assessing data and prevents varying interpretations of what might be considered hard or soft water.

Furthermore, the 30-day average criterion recommended here is similar to the national guidelines recommended by the Canadian Council of Resource and Environment Ministers\textsuperscript{17"} (see Table 3). Although some levels reported in the literature are below the 30-day average criterion recommended here, they were not considered in the formulation of the criterion because:
(i) they are below levels commonly found in the natural environment in which aquatic life is known to thrive, or

(ii) other tests performed on the same or closely related species at the same (or similar) water hardnesses showed considerably less toxicity.

(b) Maximum Criterion

The maximum concentration of copper permitted at any time is designed to protect freshwater aquatic life from short-term lethal concentrations of copper. This criterion addresses the relationship between acute toxicity and water hardness according to the formula \([0.094(\text{water hardness}) + 2]\), where water hardness is expressed as mg/L CaCO₃ and the copper criterion is given as µg/L. The relationship between acute toxicity and water hardness has been well documented in the literature. The U.S. EPA has developed a 1-hour average criterion which varies with water hardness and which is supposed to protect most aquatic life from acutely toxic levels. This criterion was considered by us to be underprotective to aquatic life in view of certain copper levels which have been reported in the literature to be acutely toxic. Figure 2 shows acute toxicity data as related to water hardness from numerous studies and the relationship between the U.S. EPA 1-hour average criterion and the toxicity values. Clearly, the U.S. EPA criterion is considerably higher than copper levels shown to be acutely toxic, especially at water hardnesses greater than about 40 mg/L (as CaCO₃). Below a water hardness of 10 mg/L (as CaCO₃) the U.S. EPA 1-hour average criterion may be overprotective. Thus, the U.S. EPA criterion maximum concentration was not adopted here. Instead, we judged the U.S. EPA chronic criterion (shown in Figure 2) to be more appropriate as a maximum criterion for the protection of freshwater aquatic life from the acute effects of copper. The logarithmic relationship used by the U.S. EPA for its chronic criterion was changed to a linear relationship with an ordinate intercept (water hardness of 0 mg/L CaCO₃) of 2 µg/L copper because:

(i) the logarithmic relationship between acute toxicity and hardness was not clear where data from numerous species were graphed; and
(11) the maximum criterion should not be less than the 30-day average criterion at any given hardness.

One study showed that 6.5 μg/L copper was acutely toxic to Daphnia magna at water hardness of 250 mg/L (as CaCO₃), which is less than the recommended maximum or chronic criterion at this water hardness. This value was not considered in the formulation of the criteria because it is contradicted by other similar tests. The U.S. EPA also rejected this result in formulating its 1-hour average criterion because the result was considered an outlier.

5.7.4.2 Marine and Estuarine Aquatic Life

The criteria for the protection of marine aquatic life in B.C. coastal and estuarine waters are stated in terms of a maximum concentration and a 30-day average concentration of copper. These criteria are designed to address both the acute lethal effects and the long-term sublethal effects of copper.

Regarding acute toxicity, the criteria reflect recent toxicological data which demonstrated the lowest (most toxic) 96 h LC50 values of 5.3 and 5.8 μg/L copper for embryos of the Pacific oyster and the blue mussel, respectively. Based on these results, a criterion maximum concentration of 3 μg/L copper should provide adequate protection against the short-term lethal effects of copper provided the 30-day average criterion (2 μg/L) is not exceeded. This maximum criterion is close to the 1-hour average criterion (2.9 μg/L) recommended recently by the U.S. EPA.

The lowest level reported to cause long-term sublethal effects was 3 μg/L copper which inhibited growth and development in barnacle larvae, and levels above 5 μg/L which caused abnormal development in Pacific oyster embryos. Copper levels between 4 and 5 μg/L affect growth and sexual development in the red algae, Chlamia parvula. In view of these harmful-effect levels, a 30-day average criterion of 2 μg/L should provide adequate protection to sensitive marine life without being overrestrictive.
It should also be noted that because of the high hardness of marine and estuarine water, the hardness/toxicity relationship does not apply as in the case for freshwater.

5.7.4.3 High Natural Background Levels (Applies to marine, estuarine, and freshwater)

When natural copper levels exceed the recommended criteria in a waterbody, it would be unrealistic to apply the average or maximum criteria levels. Instead, an alternative criterion has been recommended for these situations which requires some knowledge of conditions in the water. The amount of increase over background permitted, if any, would depend on the site-specific circumstances such as the complexing capacity in the waterbody, hepatic metallothionein analyses in fish, the forms of copper present, or other measurements which can give some indication of the bioavailability of copper in that particular location.

If an increase over background is considered appropriate for a particular waterbody then, to be practical, the permitted increase should be greater than the normal background variation. This would take into account the natural heterogeneity of the copper concentration in the water.

5.7.4.4 Averaging Periods

In the past, a single maximum criterion value, often based on a somewhat arbitrary application factor, could have been overrestrictive for many situations. The goal of the Ministry is to provide a balance between acceptable levels of protection against acute and chronic effects (without being overrestrictive) and reasonable monitoring requirements. Therefore various averaging periods, considered by the U.S. EPA over the past five years, were reviewed (Section 5.6.1). The most recent U.S. EPA concept (one-hour average and a 4-day average) was rejected as being impractical. The U.S. EPA criteria would require very frequent monitoring to obtain average values over such short averaging periods. Such frequent monitoring
would be extremely expensive, and therefore impractical. Instead, the recommended criteria are expressed in terms of a maximum concentration and a 30-day average concentration. This approach is similar to that which was rejected by the U.S. EPA on the basis of duration and magnitude of fluctuating concentrations (see Section 5.6.1). However, the U.S. EPA criteria were considered underprotective, so this concern of fluctuating concentrations (approaching nearly lethal limits) has been addressed by adopting lower criteria than those recommended by the U.S. EPA. Furthermore, the acute criterion specified here as a maximum concentration, is more restrictive than the U.S. EPA's one-hour average acute criterion. This is because, by definition, a maximum concentration places an upper limit on a concentration permitted at any time, whereas an average does not. Therefore the recommended criteria, expressed in terms of a maximum concentration and a 30-day average concentration, will prevent excessive fluctuations over the 30-day average concentration, while still addressing both the acute and chronic effects of copper.

The new U.S. EPA concept of permitting the criteria for aquatic life to be exceeded an average of once every three years (see Section 5.6.2) was not adopted. Conceivably, this concept could result in a situation whereby a waterbody is condemned to a perpetual state of recovery, and it would defeat the entire purpose of criteria.

5.7.4.5 Monitoring Strategy

In view of the dependence of copper toxicity on the complexing capacity of a waterbody, and the realization that there is no single analytical technique that can be performed on a routine, province-wide basis to measure only the bioavailable copper, we recommend a site-specific approach to protect aquatic life from anthropogenically generated copper. This approach involves the use of water quality criteria which are backed by other assessment techniques (chemical and biological studies). It is to be used in situations where measurements suggest that a copper problem may exist or in situations where the criteria may be overprotective due to high complexing
capacity. Total copper is specified for the criteria, unless other forms can be selected on a site-specific basis, in consideration of the nature of the waterbody. Until analytical techniques are available which can measure the biologically active forms of copper (Cu$^{2+}$ and perhaps CuOH$^+$ and Cu(OH)$_2$) at sufficiently low concentrations, site-specific assessments are the only way meaningful and defensible criteria and objectives can be developed for a particular location.

5.7.4.6 Copper Mixed with Other Metals

In view of the discussion on multiple toxicity (Section 5.6.5), no separate criterion based on the concentration-addition model has been recommended for metal mixtures. This decision is based on the conclusions of the EIFAC$^{167}$, Gardiner and Mance$^{175}$, and Alabaster and Lloyd$^{152}$. They concluded that because concentrations lower than the EIFAC recommended values for individual toxicants, commonly occurring in sewage and industrial wastes, do not appear to contribute to the toxicity of mixtures of toxicants, there is no need to adjust these values downward in such situations.

The copper criteria recommended by the EIFAC$^{152}$, and Alabaster and Lloyd$^{152}$ are stated in terms of maximum annual 50th and 95th percentiles and are related to water hardness (see Table 3). This concept is somewhat analogous to the 30-day average and maximum criteria recommended for B.C. waters.

The EIFAC$^{167}$, Gardiner and Mance$^{175}$, and Alabaster and Lloyd$^{152}$ consider their criteria for individual toxicants to be below the threshold for multiple toxicity. Also, the copper criteria recommended for B.C. waters are considerably lower than those recommended by those jurisdictions. The criteria recommended here should therefore provide sufficient protection for copper mixed with other commonly occurring constituents of sewage and industrial wastes.
If multiple toxicity in a waterbody with high fisheries value is suspected for some reason, then bioassays could be used to assess the situation. If the suspected toxicants are the metals copper, zinc, and cadmium, then determination of no-effect levels by hepatic metallothionein analyses in fish (outlined in Section 5.6.4) may provide useful information for assessing the situation.
6. WILDLIFE

6.1 EFFECTS

According to Demayo and Taylor\(^1\), there is little evidence in the literature to show conclusively that copper is harmful to wildlife.

Connors et al.\(^{112}\) examined the low hatching success of common tern eggs as a consequence of heavy metal contamination near Hamilton, Ontario. Conclusive evidence of heavy metals as the causative factor could not be shown.

A survey by Ranta et al.\(^{113}\) showed that copper levels in the primary feathers of black and mallard ducks decreased with distance away from the Sudbury area.

Since the toxic effects of copper on livestock are, in all likelihood, similar for wildlife, refer to the discussion on the toxic effects of copper to livestock in Section 7.1.

6.2 CRITERIA FROM THE LITERATURE

Criteria specifically designed for the protection of wildlife have not been developed by other jurisdictions. Instead, wildlife has been grouped with the aquatic life category (see Table 3). In the practical sense, waters available for use by wildlife will usually be inhabited by aquatic life, and therefore the criteria for the more sensitive aquatic life would apply. However, for the rare circumstance where aquatic life is either absent or is not considered an important resource, the aquatic life criteria would be overrestrictive for wildlife protection. Therefore this water use has been addressed separately so that the appropriate level of protection can be used.
6.3 **RECOMMENDED CRITERION**

The criterion to protect wildlife from water-borne copper is the same as that specified for livestock and is based on the safe daily dietary intake level for sheep, which are the most sensitive animals to copper.

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

6.4 **RATIONALE**

The criterion for the protection of wildlife is the same as that specified for livestock watering. The basis for the use of the livestock criterion for the wildlife category is the likelihood that the safe concentration of copper for both groups of animals is similar. The rationale for the livestock watering criterion is presented in Section 7.4.

In the practical sense, wildlife will almost always be protected incidentally by the aquatic life criteria because, in the case of multi-use waters, the criteria for the most sensitive designated water use will apply.
7. LIVESTOCK WATERING

7.1 EFFECTS

7.1.1 EFFECTS OF COPPER ALONE

Copper is a component of a number of enzymes and therefore an essential element for animal metabolism. Excessive copper, beyond the dietary requirement, accumulates in the tissues and can lead to liver, kidney, spleen, and nervous system disorders, and eventually death.

On review of the available literature, Demayo and Taylor\textsuperscript{1} concluded that ruminants (e.g., sheep and cattle) are more sensitive than non-ruminants (e.g., swine) or poultry. The chronic toxic levels of copper in the diet of ruminants are in the range of 20 to 30 µg/g, and those for non-ruminants are over 250 µg/g.

Ingestion of a diet containing 20 to 100 µg/g copper chloride killed sheep within 24 to 48 hours\textsuperscript{12}. Ingestion of a diet containing 45 µg/g of copper starting at 10 months of age killed Finnsheep rams after 307 days on the diet\textsuperscript{11}. Nubian goats receiving daily doses of copper sulphate of 8 to 32 µg per gram Cu of body weight died after 54 to 144 days\textsuperscript{11,5}. Underwood\textsuperscript{11,6} reported that a diet containing 80 µg/g of copper produced toxic effects in young sheep. Copper poisoning has been shown to occur in sheep grazing on plants containing up to 60 µg/g, grown on cupriferous soils in Australia. A recent joint publication\textsuperscript{11,9} by Agriculture Canada and the B.C. Ministry of Agriculture reported that pastures fertilized with manure from chickens fed high dietary levels of copper have accumulated sufficiently high copper levels to be toxic to sheep. Pastures fertilized with manure from hogs fed high dietary levels of copper could also be hazardous for sheep. To prevent copper deficiency in sheep, a dietary level of 5 to 10 µg/g was recommended\textsuperscript{11,9}. The National Research Council\textsuperscript{11,2} has stated a safe intake level of about 9 mg/d for sheep.
Calves were reported to be almost as sensitive to copper poisoning as sheep\textsuperscript{117}. Soil ingestion may also have been a factor in the copper poisoning of these animals\textsuperscript{118}.

Swine fed a diet containing 125 µg/g of copper showed no significant differences from controls in terms of plasma copper concentration, growth rate, and live weight\textsuperscript{120}. A diet containing 250 µg/g of copper significantly reduced the average daily weight gain of swine\textsuperscript{121}.

According to Demayo and Taylor\textsuperscript{1}, poultry appeared to show a greater tolerance than swine to copper. Studies\textsuperscript{122,123} demonstrated that a dietary copper concentration of 350 µg/g only slightly reduced weight gain in chicks, and turkeys tolerated a dietary concentration of copper sulphate containing 676 µg/g Cu. A diet containing 500 µg/g of copper slowed the growth of male broiler chicks, but gizzard erosion was noted at a dietary copper level of 250 µg/g\textsuperscript{123}. Toxic signs have occurred in ducklings fed a diet containing 200 µg/g copper, but only when they were subjected to stress\textsuperscript{119}. In terms of daily dietary copper/body weight ratio, mallard ducks tolerated 29 µg/g of body weight and chickens tolerated 60 µg/g\textsuperscript{124}. According to Demayo and Taylor\textsuperscript{1}, the minimum lethal dose of copper in chickens, pigeons, and ducks ranged from 300 to 1500 µg/g of body weight, depending on the copper form and the condition and species of the fowl.

7.1.2 EFFECTS OF COPPER MIXED WITH OTHER METALS

The presence of molybdenum in a diet appears to affect copper poisoning in ruminants. When copper levels are high, excessive molybdenum (5 to 10 µg/g) induces copper deficiency and insufficient molybdenum induces copper toxicity\textsuperscript{1}. According to Gupta\textsuperscript{126}, chronic copper poisoning can occur in sheep on a diet containing copper at concentrations of 10 to 15 µg/g and very low levels of molybdenum (0.1 to 0.2 µg/g) and sulphate. Conversely, the National Academy of Sciences\textsuperscript{124} reported that a diet containing a low molybdenum concentration (0.5 µg/g) and a copper concentration of 8 to 10 µg/g, caused blood disorders in sheep. When the diet was molybdenum-
free, the toxic level of copper increased to 30 μg/g or more. The toxic symptoms occurred only when the liver accumulated copper to a level of about 150 μg/g (wet weight). In terms of copper deficiency in ruminants, molybdenum is suspected of impairing the utilization of dietary copper, even at molybdenum concentrations below 5 μg/g. Agriculture Canada and the B.C. Ministry of Agriculture recommend minimum, adequate, and ideal copper/molybdenum ratios for cattle feed of 3.0, 4.3, and 6.0, respectively.

Zinc and iron ameliorate the toxicity of high copper levels ingested by swine and sheep, and a deficiency of these metals intensifies copper toxicosis. Similarly, Bremner et al. demonstrated that copper in the liver of sheep was reduced by 40 percent when they were fed a diet containing 200 to 420 μg/g of zinc.

Cadmium has been shown to affect the absorption of copper by ruminants. Goats fed a diet containing 75 μg/g of cadmium for up to 19 months had a 60 percent reduction of copper in the liver. The reduction of copper in the liver of their kids was over 90 percent, which resulted in a short life expectancy. In chickens, a cadmium-supplemented diet (200 μg/g) reduced copper in the muscles, bones, and feathers, and accumulated it in the liver and kidneys.

Underwood reported that calcium carbonate and ferrous sulphide in the diet of sheep impaired copper absorption in the intestine, presumably by increasing the pH which favours the formation of insoluble copper sulphide.

Copper appears to ameliorate selenium toxicity in animals by causing the accumulation of an apparently harmless compound in the tissues. For example, ponies were protected from fatal doses of selenium (6 to 8 μg/g of body weight) by single oral doses of copper of 20 to 40 μg/g of body weight. Similarly, selenium-induced growth reduction and mortality in ducks was reduced by diets containing 1000 μg/g of copper. According to Agriculture Canada and the B.C. Ministry of Agriculture, copper and selenium deficiency frequently occur concurrently in B.C. cattle.
Copper also reduced the toxic effects of silver. A diet containing 10 to 25 μg/g of copper inhibited the growth reduction, increased mortality, reduced hemoglobin levels and reduced aortic elastin in chicks caused by 10 to 200 μg/g of silver in the diet. Hill et al. also showed that symptoms of copper deficiency were emphasized in the presence of silver.

Mercury reduced growth and increased mortality in chicks fed a copper supplemented diet. In copper-deficient chicks, mercury failed to produce either of these effects.

7.2 CRITERIA FROM THE LITERATURE

Copper criteria from other jurisdictions, specifically designed for the protection of livestock, generally range between 400 and 5000 μg/L (see Table 5). Some jurisdictions (Alberta and Saskatchewan) have not established water-use categories. Instead, these provinces have established a single criterion for total copper (20 μg/L) designed to protect the most sensitive use. For copper, the most sensitive use would apply to aquatic life, and therefore a level of 20 μg/L is overrestrictive for water used for consumption by livestock.

The criteria developed by the Inland Waters Directorate are specified in two parts. One criterion is for ruminants and another one is for all other forms of livestock, including non-ruminants and poultry. These criteria are based upon maximum safe dietary intake levels reported by Neathery and Miller (see Table 5). For ruminants, they use safe dietary intake copper levels of 20 (sheep) and 100 μg/g (cattle), and the daily water requirements of 4 to 15 L/d for sheep and 26 to 110 L/d for cattle, as reported by the National Academy of Sciences. Hence, using the maximum water requirement for sheep (15 L/d) and the safe dietary level (20 μg/g) a copper criterion in water of 1000 μg/L (rounded off) was calculated. Similarly, for non-ruminants the maximum safe dietary intake level of 150 μg/g (for pigs) was used to calculate a criterion of 5000 μg/L.
TABLE 5
COPPER CRITERIA FOR LIVESTOCK WATERING

<table>
<thead>
<tr>
<th>CRITERIA STATEMENTS</th>
<th>CRITERIA VALUES</th>
<th>JURISDICTION</th>
<th>DATE</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recommended upper limit of 500 µg/L for livestock drinking water</td>
<td>500 µg/L</td>
<td>U.S. EPA</td>
<td>1972</td>
<td>20</td>
</tr>
<tr>
<td>The derived working level for copper in livestock drinking water will range from 500 to 2000 µg/L depending upon the dietary intake of copper</td>
<td>500 to 2000 µg/L</td>
<td>Australia</td>
<td>1974</td>
<td>30</td>
</tr>
<tr>
<td>Recommended copper concentration of 500 µg/L in drinking water for livestock and poultry</td>
<td>500 µg/L</td>
<td>National Academy of Sciences</td>
<td>1974</td>
<td>136</td>
</tr>
<tr>
<td>Maximum concentration of copper = 20 µg/L</td>
<td>20 µg/L</td>
<td>Saskatchewan</td>
<td>1975</td>
<td>24</td>
</tr>
<tr>
<td>For sheep, the estimated maximum safe dietary concentration ranges from just above 5 µg/g (when molybdenum levels are low) to perhaps 20 µg/g</td>
<td>5 to 20 µg/g</td>
<td>Alberta</td>
<td>1977</td>
<td>23</td>
</tr>
<tr>
<td>For cattle, the estimated maximum safe dietary concentration is 100 µg/g</td>
<td>100 µg/g</td>
<td>Neathery and Miller</td>
<td>1977</td>
<td>134, 135</td>
</tr>
<tr>
<td>For swine, the estimated safe dietary concentration ranges from 150 to 400 µg/g</td>
<td>150 to 400 µg/g</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>For chicks, the estimated maximum safe dietary concentration is 250 µg/g</td>
<td>250 µg/g</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>For turkeys, the estimated maximum safe dietary concentration is 500 µg/g</td>
<td>500 µg/g</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recommended objective of 1000 µg/L (as total copper) if sheep and cattle present and 5000 µg/L for all other cases</td>
<td>1000 to 5000 µg/L</td>
<td>Canada</td>
<td>1981</td>
<td>1</td>
</tr>
</tbody>
</table>
### TABLE 5 (Continued)

**COPPER CRITERIA FOR LIVESTOCK WATERING**

<table>
<thead>
<tr>
<th>CRITERIA STATEMENTS</th>
<th>CRITERIA VALUES</th>
<th>JURISDICTION</th>
<th>DATE</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum acceptable concentration of 1000 µg/L as total copper</td>
<td>1000 µg/L</td>
<td>Manitoba</td>
<td>1983</td>
<td>34</td>
</tr>
<tr>
<td>Copper in water used for livestock should not exceed 500 µg/L</td>
<td>500 µg/L</td>
<td>Ontario</td>
<td>1984</td>
<td>31</td>
</tr>
<tr>
<td>Recommended average concentration of 200 µg/L total copper in water for livestock.</td>
<td>200 µg/L</td>
<td>United Kingdom</td>
<td>1984</td>
<td>33</td>
</tr>
<tr>
<td>The copper concentration in livestock drinking water should not exceed 1.0 mg/L</td>
<td>1000 µg/L</td>
<td>CCREM</td>
<td>1987</td>
<td>174</td>
</tr>
<tr>
<td>for cattle and 5.0 mg/L for swine and poultry. For sheep a maximum of 0.5 mg/L is recommended. However, these levels should be revised downward, especially for sheep, if levels of copper are high in forage plants and in soil, or if copper is regularly given to livestock as a dietary supplement</td>
<td>5000 µg/L</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>500 µg/L</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
In developing water quality criteria for Australia, Hart\(^3\) points out that the safe level of copper in livestock drinking water will depend upon the dietary intake of copper. Considering this factor and the aggravated of copper toxicity by molybdenum deficiencies, Hart\(^3\) derived a working level for copper in livestock drinking water of 500 to 2000 \(\mu\)g/L.

The National Research Council\(^{162}\) recommends a safe dietary intake level of about 9 mg/d for sheep.

7.3 RECOMMENDED CRITERION

The criterion to protect livestock from copper in water is based on the safe dietary intake level of 9 mg/d for sheep, recommended by the National Research Council\(^{162}\). As sheep are the most sensitive livestock to copper, the criterion will provide sufficient protection for all other species of livestock.

The maximum concentration of total copper in livestock drinking water should not exceed 300 \(\mu\)g/L.

7.4 RATIONALE

The criterion recommended in this document for the protection of livestock has been developed from information obtained from the National Research Council\(^{112}\), the National Academy of Sciences\(^{136}\), the Inland Waters Directorate\(^1\), and a joint publication of Agriculture Canada and the B.C. Ministry of Agriculture\(^{119}\).

The criterion level for ruminants (1000 \(\mu\)g/L) developed by the Inland Waters Directorate\(^1\) was not considered to be restrictive enough to protect sheep adequately from waterborne copper in addition to copper uptake from food sources, or when copper toxicity is aggravated by molybdenum deficiencies. In deriving the criterion for ruminants, the Inland Waters Directorate used the upper safe dietary level for sheep (20 \(\mu\)g/g) instead of
the lower limit (just above 5 μg/g) estimated by Neathery and Miller[19]. The upper safe limit appears dangerously close to levels shown to cause poisoning in sheep[12]. However, the lower limit (5 μg/g) may be questionable in terms of copper deficiency because the recommended dietary level for sheep is 5 to 10 μg/g[10].

We recommend a level based on the safe copper intake level of 9 mg/d for sheep as stated by the National Research Council[16]. Assuming a dry food intake for sheep of about 1 kg/d[1], and an average copper concentration in grass[12] and hay[11] in British Columbia of 5 mg/kg, the average copper intake in food would be 5 mg/d. This would permit a daily uptake of 4 mg (9 mg - 5 mg) of copper from the water. According to the National Academy of Sciences[16], the daily water requirement for sheep ranges from 4 to 15 litres. Therefore, assuming maximum water intake, the maximum acceptable concentration of copper in water should be about 300 μg/L (rounded off) for sheep. Thus, a maximum of 300 μg/L is recommended for water used by livestock. This level will allow for copper uptake from dietary sources other than drinking water.

Although this level is overprotective for other species of livestock it does not restrict an area to only the more tolerant species. In other words, the raising of sheep remains a viable option without the risk of toxic conditions.

In practice, levels of this magnitude are unlikely to be encountered, and for the majority of cases the criteria for the protection of aquatic life will apply to waters being used by livestock.
8. IRRIGATION

8.1 EFFECTS

Copper is essential to plant life but, according to the U.S. EPA\(^2\), concentrations of 100 to 1000 \(\mu g/L\) in nutrient solutions have been found toxic to a large number of plants.

The effects of copper on plants have recently been reviewed by the Inland Waters Directorate\(^1\). One of the aspects reviewed was the availability of copper in the soil to plants. According to Murphy\(^3\), Cu\(^+\) and Cu\(^2+\) are the forms of copper which can be absorbed by plants. The availability of copper to plants is dependent upon a number of factors including the soil type, its composition and texture, the microbial activity of the soil, pH, oxidation - reduction potential, moisture, rainfall, and the plant species. In general, copper is less available to plants in soils with a high organic content or high pH due to complexing with the humic materials\(^1\). Delas\(^12\) reported that the normal copper concentration in uncontaminated soils from a number of countries ranged from 20 to 50 \(\mu g/g\). The average copper concentration in British Columbia soils ranged from 10 to 30 \(\mu g/g\)\(^13\).

Levels as high as 2190 \(\mu g/g\) have been reported in the surface layer of soil on a farm near a nickel-cobalt smelter\(^14\). Copper also tends to accumulate in orchard soils as a result of treatment with copper fungicides\(^14\). According to Delas\(^12\), copper tends to stay on the soil surface where it is strongly complexed with organic material and not available for rapid uptake by plants.

Demayo and Taylor\(^1\) noted that copper does not appear to accumulate in plant tissues to the same degree as other elements. The normal range of copper in plant tissues has been reported to be from 1 to 50 \(\mu g/g\) (dry weight)\(^12\). In British Columbia, copper levels in a number of vegetables ranged from 1 to 15 \(\mu g/g\)\(^12\). In general, grasses appear to have lower average concentrations (5 \(\mu g/g\)) than legumes (15 \(\mu g/g\)). A review of several
studies by Demayo and Taylor\(^1\) indicated that fertilization with copper-contaminated sewage wastes can increase the soil copper content considerably, but accumulation of copper in the plants was relatively small. In a number of cases, copper-supplemented soil either increased or did not change the plant yield. Conversely, Webber\(^{1,2}\) demonstrated that copper-supplemented sewage applied to a field at a rate of 20 µg/g of soil reduced the yield of red beets by 19 percent and the yield of celery by 13 percent.

The addition of copper to forest soils is reported to reduce the decomposition of organic matter by affecting biological and biochemical activity\(^1\)\(^3\). Mathur and Rayment\(^4\) noted some reduction in the nitrogen mineralization rate at a copper concentration of about 50 µg/g in the soil which corresponded to three times the background concentration.

Regarding the acute toxicity of copper, Berry\(^1\)\(^5\) reported that the 5-day lethal threshold for lettuce seedlings grown in solution was 1000 µg/L. A concentration of 1300 µg/L eventually killed the plants.

Regarding the chronic toxicity of copper to plants, Davis and Beckett\(^1\)\(^6\) reported that the critical concentrations of copper in plant tissue ranged from 14 to 25 µg/g (dry weight) for a variety of plants.

In nutrient solutions supplemented with copper, the critical concentrations ranged from 300 µg/L for rape to 17 700 for barley\(^1\)\(^7\). Nutrient solutions containing copper at a concentration of 1000 µg/L reduced root growth of tomatoes and lettuce\(^1\)\(^8\), and a concentration of 2000 µg/L caused blanching in oats\(^1\)\(^7\). Delas\(^1\)\(^9\) reported that the minimum toxic concentration of copper in soil solutions was about 1000 µg/L.

Wallace and Romney\(^1\)\(^9\) reported that copper in conjunction with nickel or nickel and zinc in soil resulted in synergistic effects on bush beans.

Delas\(^1\)\(^9\) noted that copper became toxic to sensitive plants at levels of 25 to 50 µg/g of soil. In soil solutions, the minimum toxic level was about 1000 µg/L. The toxicity of copper was greater at pH values below 6 to
7 and in humid climates. A low soil exchange capacity also increased copper toxicity.

8.2 CRITERIA FROM THE LITERATURE

Criteria to protect crops from the harmful effects of copper in irrigation waters have been compiled from other jurisdictions (Table 6). Criteria levels are very consistent for the various jurisdictions and range from 200 μg/L for long-term use on all soils, or on sensitive crops, to 5000 μg/L for short-term use on fine textured soils. The similarity of the criteria from the various jurisdictions indicates a common source or method from which the criteria have been derived. Both the U.S. EPA and the Inland Waters Directorate\(^1\) have derived their criteria on the basis of the accumulation of copper in the soil because a large portion of the available data specifies the toxicity of copper to plants in terms of soil copper concentrations. For example, Chaney\(^{156}\) assumed that 1 m\(^3\) of water is used to irrigate 1 m\(^2\) of land per year. If the copper concentration of the irrigation water is 200 μg/L, the soil depth 15 cm, and soil density 1.7 kg/dm\(^3\) then 0.8 μg/g of copper will be added to the soil each year. Since the toxicity threshold of soil copper to sensitive plants (e.g. vegetables) occurs at about 25 to 50 μg/g when soil conditions are favourable for the uptake of copper by plants, then 30 years would be necessary before soil copper concentrations reached minimum toxic levels if background copper levels were negligible. Based on these determinations, Demayo and Taylor\(^1\) concluded that a maximum copper level of 200 μg/L in irrigation water would provide an ample safety factor even if background soil copper levels were not negligible.

8.3 RECOMMENDED CRITERION

A criterion to protect vegetation from the harmful effects of anthropogenically induced copper in irrigation waters has been adapted from criteria recently developed by the Inland Waters Directorate\(^1\) as follows:

In irrigation waters, the maximum total copper concentration should not exceed 200 μg/L.
<table>
<thead>
<tr>
<th>CRITERIA STATEMENTS</th>
<th>CRITERIA VALUES</th>
<th>JURISDICTION</th>
<th>DATE</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recommended maximum for irrigation waters is 200 µg/L for continuous use on all soils</td>
<td>200 µg/L</td>
<td>U.S. EPA</td>
<td>1972</td>
<td>20</td>
</tr>
<tr>
<td>Recommended maximum for irrigation waters is 5000 µg/L for short-term use on fine-textured soils</td>
<td>5000 µg/L</td>
<td>U.S. EPA</td>
<td>1972</td>
<td>20</td>
</tr>
<tr>
<td>The derived working level for copper in irrigation waters is 200 µg/L for continuous use on all soils</td>
<td>200 µg/L</td>
<td>Australia</td>
<td>1974</td>
<td>30</td>
</tr>
<tr>
<td>The recommended objective for total copper in irrigation waters is:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) 200 µg/L for continuous use on all soils or intermittent use for copper sensitive plants, e.g. vegetables</td>
<td>200 to 5000 µg/L</td>
<td>Canada</td>
<td>1981</td>
<td>1</td>
</tr>
<tr>
<td>(b) 1000 µg/L for less sensitive plants, e.g. cereals</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(c) 5000 µg/L for short-term use</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Where irrigation is the only source of water, the maximum acceptable concentration of total copper is 200 µg/L</td>
<td>200 µg/L</td>
<td>Manitoba</td>
<td>1983</td>
<td>34</td>
</tr>
<tr>
<td>Where irrigation is used as a supplemental source of water, the maximum acceptable concentration of total copper is 5000 µg/L</td>
<td>5000 µg/L</td>
<td>Manitoba</td>
<td>1983</td>
<td>34</td>
</tr>
<tr>
<td>Maximum concentration of copper in irrigation waters used continuously on all soil = 200 µg/L</td>
<td>200 µg/L</td>
<td>Ontario</td>
<td>1984</td>
<td>31</td>
</tr>
<tr>
<td>CRITERIA STATEMENTS</td>
<td>CRITERIA VALUES</td>
<td>JURISDICTION</td>
<td>DATE</td>
<td>REFERENCE</td>
</tr>
<tr>
<td>-----------------------------------------------------------------------------------</td>
<td>----------------</td>
<td>----------------</td>
<td>-------</td>
<td>-----------</td>
</tr>
<tr>
<td>Maximum concentration of copper used up to 20 years on fine textured soils of pH 6.0 to 8.5 is 5000 µg/L</td>
<td>5000 µg/L</td>
<td>Ontario</td>
<td>1984</td>
<td>31</td>
</tr>
<tr>
<td>Recommended average concentration of 500 µg/L total copper in irrigation water.</td>
<td>500 µg/L</td>
<td>United Kingdom</td>
<td>1984</td>
<td>33</td>
</tr>
<tr>
<td>The total copper concentration in irrigation water should not exceed 200 µg/L for continuous use on all soils. For irrigation of crops that have a low sensitivity to copper, such as cereals, a maximum copper concentration in irrigation water of 1000 µg/L is recommended. The concentration of copper may be increased to 5000 µg/L for use on neutral to alkaline soils for up to 20 years.</td>
<td>200 µg/L</td>
<td>CCREM</td>
<td>1987</td>
<td>174</td>
</tr>
</tbody>
</table>
8.4 RATIONALE

The rationale for the choice of the criterion is based on calculations by Chaney\(^{18}\) (Section 8.2) of soil copper accumulation through irrigation practices and upon the threshold toxicity of soil copper to sensitive plants.

The criteria specified by the Inland Waters Directorate\(^1\) were derived by Chaney's method\(^{19}\) and are reported to provide a good safety margin - especially in view that Chaney's calculations were based on irrigation practices for very arid areas such as California. The time for toxic conditions to develop (30 years) is underestimated for most agricultural regions in B.C., except perhaps for Okanagan fruit crops where application rates of 100 cm/year may occur in particularly arid years. In other regions of B.C., application rates of 10 to 40 cm/year are more typical\(^{17}\). Hence, at a copper concentration of 200 μg/L in irrigation water, copper-sensitive crops could be grown safely in most regions of B.C. for at least a century. Furthermore, since Chaney's calculations do not take into account the perpetual extraction of copper from the soil by plants which, when harvested, redistribute the copper through the food web, it is unlikely that copper will ever reach toxic levels in the soils, even in arid regions.

As noted in Table 6, the Inland Waters Directorate\(^1\) recommended separate criteria for copper in irrigation water depending upon the irrigation frequency, the soil type, and the sensitivity of the crop to copper. To simplify this approach and to remove qualitative judgements of soil type and irrigation frequency, a single criterion of 200 μg/L is recommended regardless of these factors. This single criterion will protect copper-sensitive plants on all soils, regardless of the irrigation frequency so that crop rotation can be practised freely, and not restricted to certain
copper-tolerant crops because of elevated soil copper accumulation from earlier applications.

On a practical basis, levels of this magnitude are unlikely to be encountered and, for the majority of cases, the criteria for the protection of aquatic life will apply to waters being used for irrigation purposes.
9. RECREATION AND AESTHETICS

9.1 EFFECTS

The concerns for copper in water used for recreational purposes are basically the same as those for drinking water, described in Section 4.1. Users that may be affected by copper-contaminated recreational waters include campers (using the water for drinking) and those involved in water contact recreation such as swimmers. Therefore, both taste and toxicity are of concern for these users.

9.2 CRITERIA FROM THE LITERATURE

Since the concerns for copper in water used for recreational purposes are the same as those for drinking water, other jurisdictions, such as the Inland Waters Directorate, have used the drinking water criterion to protect recreational water users. However, the copper criterion recommended for raw drinking water in B. C. (0.5 mg/L) is lower than that (1.0 mg/L) recommended by the B.C. Ministry of Health\textsuperscript{25} for finished drinking water to allow for internal contributions from the distribution system (see Section 4.4). Distribution systems do not need to be considered when setting a copper criterion for waters used solely for recreational activities (i.e., swimming, camping, etc.).

9.3 RECOMMENDED CRITERION

The finished drinking water criterion recommended by the B.C. Ministry of Health is adopted as the criterion to protect waterbodies used for recreational activities as follows:

In water used for recreational activities, total copper should not exceed a maximum of 1.0 mg/L.
9.4 RATIONALE

The rationale for this criterion is based primarily on organoleptic (taste) considerations to ensure that waters used for recreational activities remain palatable. Above a concentration of 1.0 mg/L, copper may impart an undesirable taste to water. The criterion recommended for raw drinking water (Section 4.3) was not adopted here because internal contamination from water distribution systems (i.e., copper plumbing) are not a concern in waterbodies used for recreational activities.

In practice, most waterbodies which are used for recreational activities will be protected by the criteria for aquatic life because, in the case of multi-use waters, the criteria for the most sensitive designated use will apply.
10. INDUSTRIAL WATER SUPPLIES

10.1 EFFECTS

Requirements for industrial water vary widely according to the multitude of purposes it is used for. Even within a single industry, there may be several different water quality requirements for individual processes. Industries are usually capable of treating the raw water so that it is suitable for their needs.1

One example where copper in water supplies is especially undesirable is the wool industry. Copper is readily absorbed on wool and during the bleaching process, copper catalyzes the reaction with the bleaching agent (hydrogen peroxide) which forms holes in the material.2

10.2 CRITERIA FROM THE LITERATURE

The criteria for copper in industrial water supplies range from 0 to 5000 µg/L, depending upon the process (see Table 7).

The criteria specified by the Inland Waters Directorate1 for industry is for the food and drink processing industry. This use is included with the drinking water criterion.

Because of the wide range of water quality requirements for the various industries, a single absolute criterion will not suit the needs of all industries. Most waterbodies will be protected by the criteria for aquatic life, the most sensitive water use. These criteria are similar to the natural levels in many B.C. waterbodies, and should provide adequate protection for most industrial water uses.
<table>
<thead>
<tr>
<th>CRITERIA STATEMENTS</th>
<th>CRITERIA VALUES</th>
<th>JURISDICTION</th>
<th>DATE</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Least maximum for some industrial uses is 0 µg/L</td>
<td>0 µg/L</td>
<td>Canada</td>
<td>1972</td>
<td>29</td>
</tr>
<tr>
<td>Copper levels should not exceed 50 µg/L for intermediate or high pressure boiler feedwater</td>
<td>50 µg/L</td>
<td>U.S. EPA</td>
<td>1972</td>
<td>20</td>
</tr>
<tr>
<td>Copper levels should not exceed 10 µg/L for boiler feedwater in electrical utilities</td>
<td>10 µg/L</td>
<td>U.S. EPA</td>
<td>1972</td>
<td>20</td>
</tr>
<tr>
<td>Typical maximum requirements for the textile industry range from 0 to 5000 µg/L</td>
<td>0 to 5000 µg/L</td>
<td>U.S. EPA</td>
<td>1972</td>
<td>20</td>
</tr>
<tr>
<td>Maximum concentration of 500 µg/L for food and drink processing</td>
<td>500 µg/L</td>
<td>Canada</td>
<td>1981</td>
<td>1</td>
</tr>
<tr>
<td>Maximum total copper concentration in water used for:</td>
<td></td>
<td>CCREM</td>
<td>1987</td>
<td>174</td>
</tr>
<tr>
<td>Boiler feedwater used in steam generators is &lt;10 µg/L to &lt;100 µg/L depending on type of boiler;</td>
<td>&lt;10 µg/L to &lt;100 µg/L</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cooling Towers is &lt;80 µg/L;</td>
<td>&lt;80 µg/L</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Boiler feedwater used in power generation is &lt;10 µg/L;</td>
<td>&lt;10 µg/L</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dairy is not detectable;</td>
<td>not detectable</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Textile industry ranges from &lt;10µg/L to &lt;5000 µg/L depending on the process.</td>
<td>&lt;10 µg/L to &lt;5000 µg/L</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
11. RESEARCH AND DEVELOPMENT NEEDS

Recommendations for research and development needs pertaining to aqueous copper have recently been outlined by Spear and Pierce and are repeated here with some additions:

* Electrochemical methods for measurement of various forms of copper in water should be evaluated with respect to their applicability to both laboratory and field situations. Specifically, limits of detection, possible interferences and calibration for different water characteristics must be investigated.

* Studies should be carried out to differentiate the toxic components of both "dissolved" and "non-dissolved" fractions. In particular, the toxic potency of the "non-dissolved" fraction to filter-feeding organisms needs investigation. It is further recommended that research be directed toward the applicability of microfiltration for the separation of toxic and non-toxic forms of copper.

* Quantitative relationships between copper complexing capacity and toxic potency should be investigated and an acceptable standard technique for measuring complexing capacity should be developed and made available as a routine test at the B.C. Environmental Laboratory.

* Toxicity tests should be designed for benthic organisms under laboratory conditions simulating the unique physical-chemical characteristics of the benthic habitat, paying particular attention to adsorbed and complexed forms of copper. It is further recommended that copper associated with sediment fractions be examined with respect to bioavailability and toxicity to bottom-dwelling organisms.

* The possible cumulative toxic action of copper in freshwater and marine pelecypods and other filter-feeding organisms should be investigated.

* Toxicologic criteria should be obtained for commercially and economically important freshwater fish in Canada. It is further recommended that
toxicologic criteria for representative freshwater invertebrates and marine fish be obtained.

* Algal toxicity tests should be standardized to allow interspecific comparisons.

* Clinical profiles incorporating several hematological responses of fish should be tested in field situations to determine the applicability of monitoring natural fish populations chronically exposed to copper.

* Uptake from both food and water, organ distribution, biochemical interactions and rates of accumulation and elimination should be studied. It is further recommended that studies at the organisms level be integrated into a systematic ecosystem approach, involving in particular the study of restricted food webs.

* Research on the electrophysiology of cells and tissues to determine the effect of copper (and zinc) on cell ionic- and osmoregulatory properties regarding Na, K, Cl transport and effects on properties influenced by copper (e.g., transmembrane voltages, effects on gap junctions, ion channels, and paracellular transport).

Further discussion regarding these research and development needs are provided in "Copper in the Aquatic Environment: Chemistry, Distribution and Toxicology" by Spear and Pierce³.
12. REFERENCES CITED


170. Murphy, T.P., E.E. Prepas, P.G. Manning and T. Mayer. Draft, 1986. Long-Term Effect of Copper Sulphate Treatment on Figure Eight Lake. NRW1 Contribution Series 86.... 78 pp.


