# **Copper Water Quality Guideline for the Protection of Marine and Estuarine Aquatic Life** (Reformatted Guideline from 1987)

Ministry of Environment and Climate Change Strategy Water Protection & Sustainability Branch





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#### **EXECUTIVE SUMMARY**

The B.C. Ministry of Environment and Climate Change Strategy (ENV) develops province-wide ambient Water Quality Guidelines (WQGs) for substances or physical attributes that are important for managing both the fresh and marine surface waters of B.C. WQGs do not have direct legal standing but are used to provide a basis for the evaluation of data on water, sediment, and biota for water quality and environmental impact assessments.

The approach to develop WQGs for aquatic life is based on the guiding principle that guideline values are protective of all forms of aquatic life and all aquatic life stages over indefinite exposure (ENV, 2012). For some substances both a long-term chronic (30-day average) and a short-term acute (maximum) guideline are recommended as provincial WQGs, provided sufficient toxicological data are available. To meet a WQG, both of its components (i.e., chronic long-term and acute short-term) must be met. However, an exceedance of the WQGs does not imply that unacceptable risks are present, but that the potential for adverse effects may be increased and additional investigation and monitoring may be warranted.

This WQG for the protection of marine and aquatic life was derived in 1987 by the B.C. Ministry of Environment. Although the format has been updated, all of the technical information remains unchanged. For updated information on industrial and economic importance of Cu and the analysis of Cu in environmental samples please see <u>Copper Water Quality Guideline for the Protection of Freshwater Aquatic Life-Technical Report</u><sup>1</sup>.

Both chronic and acute WQGs for the protection of marine and aquatic life were derived in 1987 for total Cu. The chronic WQG is 2  $\mu$ g/L total Cu and the acute WQG is 3  $\mu$ g/L total Cu. If natural background levels of total Cu exceed the chronic or acute WQGs, then any decisions to increase Cu above background conditions should be based on site-specific conditions.

<sup>&</sup>lt;sup>1</sup> Available at: <u>https://www2.gov.bc.ca/assets/gov/environment/air-land-water/water/waterquality/water-quality-guidelines/approved-wqgs/copper/bc\_copper\_wqg\_aquatic\_life\_technical\_report.pdf</u>

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#### 1. INTRODUCTION

The B.C. Ministry of Environment and Climate Change Strategy (ENV) develops province-wide ambient Water Quality Guidelines (WQGs) for substances or physical attributes that are important for managing both the fresh and marine surface waters of B.C. WQGs do not have direct legal standing but are used to provide a basis for the evaluation of data on water, sediment, and biota for water quality and environmental impact assessments.

The approach to develop WQGs for aquatic life is based on the guiding principle that guideline values are protective of all forms of aquatic life and all aquatic life stages over indefinite exposure (ENV, 2012). For some substances both a long-term chronic (30-day average) and a short-term acute (maximum) guideline are recommended as provincial WQGs, provided sufficient toxicological data are available. To meet a WQG, both of its components (i.e., chronic long-term and acute short-term) must be met. However, an exceedance of the WQGs does not imply that unacceptable risks are present, but that the potential for adverse effects may be increased and additional investigation and monitoring may be warranted.

The WQG for the protection of marine and aquatic life was derived in 1987 by the B.C. Ministry of Environment. Although the format has been updated, all of the technical information remains unchanged. For updated information on industrial and economic importance of Cu and the analysis of Cu in environmental samples please see the <u>Copper Water Quality Guideline for the Protection of Freshwater Aquatic Life-Technical Report<sup>1</sup> (ENV, 2019).</u>

#### 2. PHYSICAL AND CHEMICAL PROPERTIES OF COPPER IN MARINE WATER

In marine waters, the degree of inorganic complexing tends to increase with increasing salinity. The predominant forms of dissolved Cu will be associated with the ligands, hydroxide, carbonate, and chloride (e.g., CuCO<sub>3</sub>, Cu(OH)<sub>2</sub>, and CuCl<sup>+</sup>) (Spear and Pierce, 1979). According to Florence and Batley (1980), Cu<sup>2+</sup> is expected to be only a few percent of the dissolved Cu. In marine waters, 67 percent of the total Cu may be complexed with organics. Organic complexing increases with increasing pH and increasing redox potential (Spear and Pierce, 1979).

## 3. COPPER LEVELS IN MARINE WATER

NcNeely et al. (1979) reported that the Cu content of seawater normally ranges from 1 to 25  $\mu$ g/L, and that higher concentrations are usually associated with anthropogenic sources. On a global basis Lewis and Cave (Lewis and Cave, 1979) reported that the average Cu concentration for coastal waters was about 2  $\mu$ g/L, and that concentrations were usually higher in near-shore surface waters, especially during periods of high runoff. Locally, in Juan de Fuca Strait, Cu concentrations ranged from 1.4 to 3.8  $\mu$ g/L at a depth of 150 m. In June, concentrations ranged from 3.4  $\mu$ g/L at the surface to 1.7  $\mu$ g/L at a depth of 221 m. In August, concentrations ranged from 3.4  $\mu$ g/L at the surface to 1  $\mu$ g/L at 190 m (Lewis and Cave, 1979) Water samples collected periodically from Howe Sound between 1972 and 1981 had a median concentration of total copper of 3  $\mu$ g/L, with a maximum recorded value of 6  $\mu$ g/L (Squamish Estuary Air and Water Quality Work Group, 1981). 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 (1979) report that the levels of dissolved Cu 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 Cu transported by rivers, but currents and tidal action may result in remobilization of these deposits (Spear and Pierce, 1979).

<sup>&</sup>lt;sup>1</sup>Available at: <u>https://www2.gov.bc.ca/assets/gov/environment/air-land-water/water/waterquality/water-quality-guidelines/approved-wqgs/copper/bc\_copper\_wqg\_aquatic\_life\_technical\_report.pdf\_</u>

#### 4. EFFECTS

#### 4.1. Marine Algae

Spear and Pierce (1979), the U.S. EPA (USEPA, 1985), and Lewis and Cave (1979) have recently reviewed the effects of Cu on marine algae. In summary, Spear and Pierce (1979) noted that the Cu concentrations which inhibited growth in marine algae ranged from 3 to 4,500 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 Cu, 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 Cu concentration was 500 µg/L (Steemann-Nielsen and Wium-Andersen, 1970; Jensen et al., 1976). Davey et al. (1973) demonstrated that a Cu 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 Cu concentration of 3 µg/L.

Steele and Thursby (1983) demonstrated that Cu concentrations of 4.6  $\mu$ g/L reduced tetrasporophyte growth, and 4.7  $\mu$ g/L reduced female growth in the attached red algae, *Champia parvula*. A Cu concentration of 7.3  $\mu$ g/L Cu stopped sexual reproduction in this species. Although this species is sub-tropical 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 Cu of red algae species found locally.

Increased temperature was found to increase the tolerance of *Skeletonema costatum* to Cu. At 18°C, the inhibitory concentration was 50  $\mu$ g/L and at 20-30°C the inhibitory concentration ranged from 160 to 250  $\mu$ g/L (Guillard and Ryther, 1962). However, Mandelli (1969) demonstrated that accumulation of Cu increased in the same species with increased temperature.

Reductions in photosynthesis appeared to be a less sensitive indicator of Cu toxicity than cell growth according to the results of Overnell (1976). Copper concentrations required to produce a 50 percent reduction of photosynthesis in seven algal species ranged from 1,200 to 6,400  $\mu$ g/L.

Organic metabolic wastes excreted by algae and other organisms can increase the complexing capacity of seawater and thus reduce the toxicity of Cu to algae. For example, Erickson (1972) demonstrated that the 72-h EC<sub>50</sub> of the marine alga *Thalassiosira pseudonana* was increased from 5  $\mu$ g/L in fresh seawater to 30  $\mu$ g/L in aged seawater owing to the increased amount of metabolic waste products which complexed Cu in the aged samples.

Locally, in Saanich Inlet, Vancouver Island, a series of experiments were performed on the toxicity of Cu to marine aquatic life using large volume (68 m<sup>3</sup>) semi-transparent polyethylene enclosures moored in the Inlet. This Controlled Ecosystem Pollution Experiment (CEPEX) program was designed to investigate the effects of Cu on the resident aquatic community which was captured when deploying the enclosures. Aspects of Cu toxicity to algae studied during the CEPEX program included the effects of Cu on:

- (i) the dominance and diversity of algae (Thomas and Seibert, 1977);
- (ii) phytoplankton standing crop and diversity (Thomas et al., 1977);
- (iii) silicic acid uptake by a marine phytoplankton population (Goering et al., 1977);
- (iv) phytoplankton nitrogen metabolism and nitrogen budgets (Harrison et al., 1977).

In summary, Cu concentrations in the range of about 5 to 10  $\mu$ g/L were found to affect the various aspects studied. Generally, populations of Cu-sensitive algae declined after introducing the Cu (as CuSO<sub>4</sub>)

and were soon replaced by Cu-tolerant algae such as microflagellates. The Cu-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 (Vaccaro et al., 1977).

### 4.2. Marine Invertebrates

According to Spear and Pierce (1979), marine invertebrates are the least tolerant to Cu during development stages involving calcification. Also, as with freshwater invertebrates, larval stages are generally more sensitive to Cu than adults.

#### 4.2.1. Acute Toxicity

The U.S. EPA (USEPA, 1985) reported that the Pacific oyster (*Crassostrea gigas*) and blue mussel (*Mytilus edulis*) are the most sensitive animal species tested with  $LC_{50}$  values of 5.3 and 5.8 µg/L Cu for the embryos, respectively. Adult Pacific oysters are more tolerant than pre-adult forms with an  $LC_{50}$  of 560 µg/L. Spear and Pierce (1979) reported that concentrations of 6 to 10 µg/L are acutely toxic to early life stages of copepods.

Comparison of the acute toxicity of Cu to marine planktonic copepod (*Acartia clausi*) populations from polluted and non-polluted areas indicated that pollution-adapted copepods were more tolerant to Cu than those which had not been pre-exposed (Moraitou-Apostolopoulou and Verriopoulos, 1979). The 48-h  $LC_{50}$ s for the populations from the polluted and non-polluted areas were 82 and 34 µg/L Cu, respectively.

Carmel et al. (1983) separated juvenile prawns (*F. indicus*) into three different size groups and exposed them to Cu 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  $LC_{50}$  of 300 µg/L) and at high salinity (30 ppt) the smaller prawns were more sensitive (120-h  $LC_{50}$  of 430 µg/L).

#### 4.2.2. Chronic Toxicity and Sublethal Effects

Spear and Pierce (1979) reported that, during chronic exposures, concentrations as low as 10  $\mu$ g/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  $\mu$ g/L Cu, respectively. Pesch et al. (1979) reported an incipient LC<sub>50</sub> value of 9.3  $\mu$ g/L Cu for the bay scallop *Argopecten irradians*. At a concentration of 5  $\mu$ g/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 (1975) noted that the burrowing activity of the clam (*Venerupsis decussata*) was inhibited after 65 days in a Cu concentration of about 10  $\mu$ g/L. After 25 days, the EC<sub>50</sub> was estimated to be about 100  $\mu$ g/L. Normal burrowing activity resumed in the absence of Cu. Phelps et al., (1985) conducted a long-term bioassay using littleneck clams (*Protothaca staminca*) and found an increase in burrowing times when sediment Cu concentrations were 4.4  $\mu$ g/g. Mortalities of 5 and 25 percent occurred at 12.4 and 30.1  $\mu$ g/g, respectively. Also, barnacle larvae (*B. balanoides*) failed to attach to a substrate after a 12-hour exposure to 70  $\mu$ g/L Cu (Pyefinch, and Mott, 1948).

Mandelli (1975) showed that oysters (*Crassostrea virginica*) failed to spawn after exposure to 22 and 42  $\mu$ g/L, but spawning activity was not affected at 4  $\mu$ g/L.

Regarding growth and development, a nominal concentration of 3  $\mu$ g/L Cu inhibited the pre-calcification metamorphosis stage of barnacles (*B. balanoides*) (Pyefinch and Mott, 1948). According to Coglianese

and Martin (1981), the Pacific oyster (*C. gigas*), B.C.'s only commercial species, was unaffected by a Cu concentration less than 5  $\mu$ g/L. Levels above this caused abnormal development in the embryo. For the sea urchin (*Paracentrotus lividus*), exoskeleton growth of the late larval stage was inhibited by 10 and 20  $\mu$ g/L Cu (Bougis, 1965). Pesch et al. (1979) found that 5  $\mu$ g/L ionic Cu inhibited scallop (*Argopecten irradians*) growth by 43 percent after 42 days in a flowing water exposure system.

Invertebrate metabolism appeared to tolerate higher Cu levels than the other characteristics discussed. For example, Cu concentrations of 300, 500 and 1,000  $\mu$ g/L significantly reduced oxygen consumption of the mussel (*Mytilus edulis*), whereas a level of 200  $\mu$ g/L only slightly reduced oxygen consumption as compared to controls (Scott and Major, 1972). Oxygen consumption of the mud snail (*Nassarius obsoletus*) was reduced by 50 percent after exposure to 250  $\mu$ g/L for 72 hours (MacInnes and Thurberg, 1973).

Laboratory experiments were performed to determine the sublethal levels of Cu which affect feeding, respiratory rates, fecundity, and longevity of the marine planktonic copepod *Acartia clausi*, collected from polluted and non-polluted areas (Moraitou-Apostolopoulou and Verriopoulos, 1979). Copper concentrations in the range of 1 to 10  $\mu$ g/L affected all activities tested in copepods from the non-polluted source. The pollution-adapted population was more resistant to sublethal Cu stress. While respiration and longevity were affected at concentrations similar to those from the non-polluted area, ingestion rate was not affected at 1  $\mu$ g/L. Fecundity was higher than that in copepods from the non-polluted area in Cu concentrations up to 10  $\mu$ g/L.

Several studies on the chronic toxicity of Cu to marine zooplankton communities were performed during the CEPEX program described in Section 2.3.1. These studies included the effects of Cu on:

- (i) the dynamics of micro-zooplankton populations (Beers et al., 1977);
- (ii) the dynamics of macro-zooplankton populations (Gibson and Grice, 1977);
- (iii) ingestion, filtration, and fecal pellet production rates of copepods and on feeding rates of euphausids and ctenophores (Reeve et al., 1977a); and
- (iv) feeding, fecundity (egg production rate), respiration, and excretion (Reeve et al., 1977b).

In summary, sublethal stress on fecundity and feeding occurred in the range of 1 to 10  $\mu$ g/L Cu after 5 to 10 days. Similar results were noted in duplicate experiments performed in Loch Ewe, Scotland (Gamble et al., 1973). Respiration and excretion rates proved to be poor indicators of sublethal stress to Cu. CEPEX enclosures treated with 10 and 50  $\mu$ g/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 Cu, or if the changes resulted from modifications to other trophic levels of the contained population.

The sabellid polychaete (*Eudistylia vancouveri*) was shown to accumulate Cu under laboratory conditions where concentrations in the seawater exceeded between 3 to 6  $\mu$ g/L (Young et al., 1979). Above this threshold concentration Cu accumulated mainly in the branchial crown and eventually caused necrosis (cell death) in the radioles (gills) (Young et al., 1979; Young et al., 1981).

#### 4.3. Marine Fish

#### 4.3.1. Acute Toxicity

According to Spear and Pierce (1979), there is a paucity of information regarding the toxicity of Cu to marine fish. For adults, 96-h  $LC_{50}$ s usually range from about 1,400 to 3,000  $\mu$ g/L.

The early life stages of marine fish are generally more sensitive than adults to Cu. The lowest (most toxic)  $LC_{50}s$  for embryos of the summer flounder (*Paralichthys dentatus*) and winter flounder (*Pseudopleuronectes americanus*) were 11.9 and 52.7 µg/L, respectively (Cardin, 1982). The exposure periods were not reported. Studies generally indicated that increasing pH (Syazuki, 1964) and salinity (Birdsong and Avault, 1971) reduced the sensitivity of fish to Cu. None of the above studies were performed on species indigenous to British Columbia coastal waters.

Rice and Harrison (1978) exposed Pacific herring (*Clupea harengus pallasi*) embryos and larvae to Cu in a flow-through bioassay system. Significant embryo mortalities occurred at a Cu concentration of 35  $\mu$ g/L. Herring larvae continuously exposed to Cu showed significant mortality at 300  $\mu$ g/L.

#### 4.3.2. Chronic Toxicity and Sublethal Effects

Blaxter (1977) demonstrated that exposure of herring (*Clupea harengus*) gametes to 30  $\mu$ g/L Cu reduced fertilization by 50 percent. Continuous exposure of fertilized herring eggs to 30  $\mu$ g/L did not affect hatching success, but teratogenic affects were apparent in 70 percent of the larvae. Rice and Harrison (1978) showed that herring embryos exposed to 36-h pulses of 100  $\mu$ g/L Cu during late development stages showed increased tolerance when exposed to Cu after the response period. However, embryos exposed to pulsed Cu during the early developmental stages grew significantly less.

Regarding behaviour, Blaxter (1977) also demonstrated that Cu concentrations of 90 and 130  $\mu$ g/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  $\mu$ g/L for 28 days.

A study (Koeller and Parsons, 1977) investigating the effects of Cu on the growth of juvenile chum salmon (*Oncorhynchus keta*) in seawater was performed using the CEPEX enclosures described in Section 2.3.1. These enclosures were enlarged to 1,700 m<sup>3</sup> so that the water column and associated plankton captured during deployment of the enclosures would support fish growth. A Cu concentration of 2.5  $\mu$ g/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, there was suspicion that Cu 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  $\mu$ g/L Cu for 13 days, 55 days after hatching (Blaxter, 1977).

Steele (1983) studied the locomotor behaviour of sea catfish (*Arius felis*) in a 16-choice circular tank before and after 72 hours of exposure to sub-lethal concentrations of  $Cu^{2+}$ . Changes in locomotor activity and orientation depended on the concentration of  $Cu^{2+}$ . Test fish exposed to 5, 10 and 50 µg/L  $Cu^{2+}$  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. CRITERIA FROM THE LITERATURE

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 (1985) and the United Kingdom (Mance et al., 1984), the only agencies which have set any Cu criteria for marine aquatic life, have recommended single values of 2.9  $\mu$ g/L (total Cu) as a 1-hour average and 5  $\mu$ g/L average, (dissolved Cu), respectively, for marine situations (see Table 2.1).

Criteria Statement	Criteria Values	Jurisdiction	Date	Reference
Levels less than 10 $\mu\text{g}/\text{L}$ present minimal risk to the environment	10 µg/L	U.S. EPA	1972	USEPA, 1973
Concentrations above 50 $\mu$ g/L constitute a hazard to marine life	50 μg/L	U.S. EPA	1972	USEPA, 1973
For protection of marine life 0.1 time $96$ -hLC <sub>50</sub> for non-aerated bioassay of a sensitive aquatic resident species		U.S. EPA	1976	USEPA, 1976
The application factor (0.1 times the 96-h $LC_{50}$ ) given by the U.S. EPA (1976) should be replaced with specific concentration		American Fisheries Society	1979	Windom et al., 1979
To protect marine aquatic life the maximum 24-hour average for total recoverable copper = 4.0 $\mu$ g/L and the maximum at any time= 23 $\mu$ g/L	4.0 to 23 μg/L	U.S. EPA	1980	USEPA, 1980
To protect saltwater aquatic life and its uses, in each 30 consecutive days	2.0 to 3.2 μg/L	U.S. EPA	1983	USEPA, 1980
(a) the average concentration of active copper should not exceed 2.0 $\mu\text{g/L}$				
(b) the maximum concentration should not exceed 3.2 $\mu g/L$ ; and				
(c) the concentration maybe between 2.0 $\mu g/L$ and 3.2 $\mu g/L$ for up to 96 hours.				
Recommended average concentration of dissolved copper to protect marine life is 5 µg/L	5 μg/L	United Kingdom	1984	Macne et al., 1984
Saltwater aquatic organisms and their uses should not be affected unacceptably if the 1-hour average concentration of copper does not exceed 2.9 $\mu$ g/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.	2.9 μg/L	U.S. EPA	1985	USEPA, 1985

The U.S. EPA marine criterion was based on the acute toxicity of Cu to embryos of the blue mussel and Pacific oyster which were the most sensitive marine species tested to date with 96-h LC50s of 5.8 and 5.3  $\mu$ g/L Cu, respectively. According to the U.S. EPA (1985), the only marine chronic value available (77  $\mu$ g/L Cu 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 Cu, and because lower acute values were available for other organisms. Therefore, for marine waters, the "Criterion Maximum Concentration" of 2.9  $\mu$ g/L Cu 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  $\mu$ g/L Cu (expressed as a 1-hour average) was used to protect marine organisms from both acute and chronic effects of Cu.

#### 6. RECOMMENDED CRITERIA

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

#### 6.1. Rational

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 Directorate (Demayo and Taylor, 1981), the U.S. EPA (1985), the International Joint Commission (1981), and from recommendations by Birge and Black (1979). 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 Cu acting alone and in combination with other metals.

The criteria are expressed in terms of total Cu. 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 Cu in a waterbody is available, the form of Cu in the criteria can be modified, as justified by the data.

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 Cu. These criteria are designed to address both the acute lethal effects and the long-term sublethal effects of Cu.

Regarding acute toxicity, the criteria reflect recent toxicological data which demonstrated the lowest (most toxic) 96-h  $LC_{50}$  values of 5.3 and 5.7 µg/L Cu for embryos of the Pacific oyster and the blue mussel, respectively. Based on these results, a criterion maximum concentration of 3 µg/L Cu should provide adequate protection against the short-term lethal effects of Cu 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 (1985).

The lowest level reported to cause long-term sublethal effects was 3  $\mu$ g/L Cu which inhibited growth and development in barnacle larvae, and levels above 5  $\mu$ g/L which caused abnormal development in Pacific oyster embryos. Copper levels between 4 and 5  $\mu$ g/L affect growth and sexual development in the red

algae, *Champia parvula*. In view of these harmful- effect levels, a 30-day average criterion of 2  $\mu$ g/L should provide adequate protection to sensitive marine life without being over restrictive.

#### 6.2. High Natural Background Levels (Applies to Marine, Estuarine, and Freshwater)

When natural Cu 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 Cu present, or other measurements which can give some indication of the bioavailability of Cu 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 Cu concentration in the water.

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