Canadian Sediment Quality Guidelines for the Protection of Aquatic Life

COPPER

Copper (Cu) is an essential trace element that can be toxic to aquatic biota at elevated concentrations. Copper enters aquatic systems through aerial deposition or surface runoff. Because of its affinity for particulate matter, mainly fractions of iron, manganese oxides, and organic matter, Cu tends to accumulate in sediments (Campbell and Tessier 1996). Because a variety of organisms live in, or are in contact with, bed sediments, sediments act as an important route of exposure to aquatic organisms. Canadian interim sediment quality guidelines (ISQGs) and probable effect levels (PELs) for Cu can be used to evaluate the degree to which adverse biological effects are likely to occur as a result of exposure to Cu in sediments.

Canadian ISQGs and PELs for Cu were developed using a modification of the National Status and Trends Program approach as described in CCME (1995) (Table 1). The ISQGs and PELs refer to total concentrations of Cu in surficial sediments (i.e., top 5 cm), as quantified by digestion with a strong acid (e.g., aqua regia, nitric acid, or hydrochloric acid) followed by determination by a standard analytical protocol.

The majority of the data used to derive ISQGs and PELs for Cu are from studies on field-collected sediments that measured concentrations of Cu, along with concentrations of other chemicals, and associated biological effects, as compiled in the Biological Effects Database for Sediments (BEDS) (Environment Canada 1998). The Cu data sets for freshwater and marine sediments are large, with the freshwater data set containing 116 effect entries and 370 no-effect entries and the marine data set containing 105 effect entries and 335 no-effect entries (Figures 1 and 2). The BEDS represents a wide range of concentrations, types of sediment, and mixtures of chemicals. Evaluation of the percentage of effect entries for Cu that are below the ISQGs, between the ISQGs and the PELs, and above the PELs (Figures 1 and 2) indicates that these values define three ranges of chemical concentrations: those that are rarely, occasionally, and frequently associated with adverse biological effects, respectively (Environment Canada 1998).

Toxicity

Adverse biological effects for Cu in the BEDS include decreased benthic invertebrate diversity, reduced abundance, increased mortality, and behavioural changes, among others (Environment Canada 1998, Appendixes IIa and IIb). For example, snails, a relatively sensitive gastropod, were less abundant at locations in the Niagara River, Ontario, where the mean concentration in sediments was 52.2 $mg \cdot kg^{-1}$, compared to sites with concentrations of 26.0 $mg \cdot kg^{-1}$ Cu, which is less than the ISQG (Jaagumagi 1988). In marine sediments, Ferraro et al. (1991) reported that the abundance of echinoderms (e.g., starfish and sea urchins) at Palos Verdes, California, was low in sediments where the mean concentration was 109 $mg \cdot kg^{-1}$, whereas abundance was high in sediments with 18.0 $mg \cdot kg^{-1}$ Cu, which is below the marine ISQG.

Spiked-sediment toxicity tests for Cu report the onset of toxicity to benthic organisms at higher concentrations than those observed in field studies. This is likely a result of the shorter exposure times used in laboratory studies, as well as exposure to Cu only as opposed to chemical mixtures containing Cu (Environment Canada 1998). For example, 14-d LC_{50}s were 380 $mg \cdot kg^{-1}$ for *Hyalella azteca*, a freshwater amphipod, which is approximately double the freshwater PEL, while 10-d LC_{50}s for *Chironomus tentans*, a midge, were approximately six times the freshwater PEL (i.e., 1110 $mg \cdot kg^{-1}$) (Milani et al. 1996). Similarly, 48-d LC_{25}s for *Protothaca staminea*, a marine clam, occurred at a concentration of 38.2 $mg \cdot kg^{-1}$, which is twice the marine ISQG (Phelps et al. 1985).

In sublethal spiked-sediment toxicity tests, growth of a freshwater amphipod, *H. azteca*, and a midge, *C. tentans*, was significantly reduced at concentrations of 89.8 $mg \cdot kg^{-1}$ and 496 $mg \cdot kg^{-1}$, respectively (Milani et al. 1996). Other freshwater spiked-sediment toxicity tests did not demonstrate adverse effects at concentrations of Cu that were known to occur in aquatic environments (Environment Canada 1998). Sublethal effects of Cu to marine organisms in spiked-sediment toxicity tests include delayed predator avoidance response (i.e., burial) in the clams *P. staminea* and *Mya arenaria*. Although

Table 1. Interim sediment quality guidelines (ISQGs) and probable effect levels (PELs) for copper ($mg \cdot kg^{-1}$ dw).

	Freshwater	Marine/estuarine
ISQG	35.7	18.7
PEL	197	108

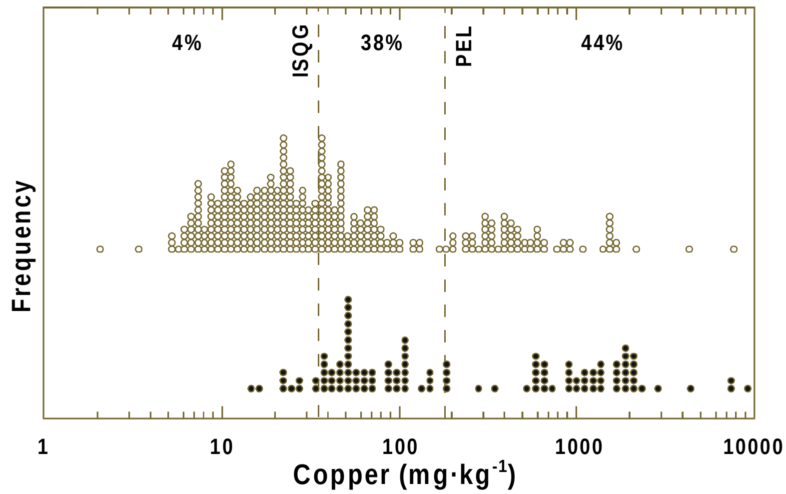

Figure 1. Distribution of Cu concentrations in freshwater sediments that are associated with adverse biological effects (●) and no adverse biological effects (○). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above the PEL.

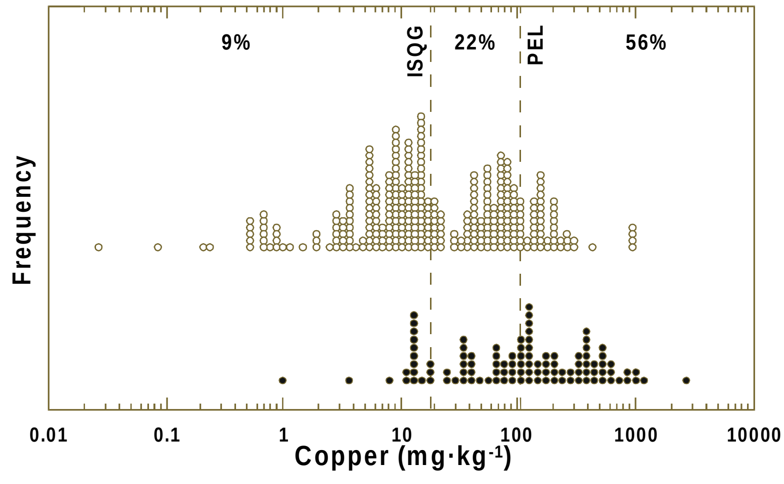

Figure 2. Distribution of Cu concentrations in marine and estuarine sediments that are associated with adverse biological effects (●) and no adverse biological effects (○). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above the PEL.

burial time increased for *P. staminea* at a concentration of 4.4 $mg \cdot kg^{-1}$ Cu, which is below the marine ISQG, statistically significant differences in reburial times were measured at concentrations between 13.6 and 23.4 $mg \cdot kg^{-1}$ (Phelps et al. 1985).

The toxicity of Cu in sediments can be mitigated by various sediment fractions (Environment Canada 1998). For example, Malueg et al. (1986) observed higher LC_{50}s for *Daphnia magna* when peat (i.e., organic matter) was added to the system. Similarly, Austen et al. (1994) observed a higher abundance of nematodes in sediment having high organic matter content when compared to sediments low in organic matter, with similar dosages of Cu. These results suggest that organic matter may decrease the toxicity of Cu to freshwater and marine benthic organisms.

Results of both marine and freshwater spiked-sediment toxicity tests indicate that concentrations of Cu that are associated with adverse effects are consistently above the ISQGs, confirming that these guidelines represent concentrations below which adverse biological effects will rarely occur. Further, these studies provide additional evidence that toxic levels of Cu in sediments are similar to the PELs, confirming that adverse effects are more likely to be observed when concentrations of Cu exceed the PELs. The ISQGs and PELs for Cu are therefore expected to be valuable tools for assessing the ecotoxicological relevance of concentrations of Cu in sediments.

Concentrations

Concentrations of Cu in marine and freshwater sediments vary substantially across Canada (Environment Canada 1998). In the National Geochemical Reconnaissance (NGR) program database by the Geological Survey of Canada (GSC) (Friske and Hornbrook 1991), the mean background concentrations in Canadian lake and stream sediments are 31 $mg \cdot kg^{-1}$ and 32 $mg \cdot kg^{-1}$, respectively (P.W.B. Friske 1996, GSC, Ottawa, pers. com.). When compared to the background concentrations of Cu in the combined lake and stream NGR database (n = 84 089), the freshwater ISQG and PEL for Cu fall at the 74th and 98.44th percentiles, respectively (R.G. Garrett 1997, GSC, Ottawa, pers. com.). This demonstrates that background concentrations of Cu across most of Canada are lower than the ISQG of 35.7 $mg \cdot kg^{-1}$. In marine systems, mean background concentrations of Cu, estimated from deep layers of sediment cores (>10 cm) from a variety of published sources, ranged from 4.5 to 123 $mg \cdot kg^{-1}$ (i.e., below the marine ISQG to slightly greater than the marine PEL) (Environment Canada 1998).

Concentrations of Cu in surficial sediments close to point sources of contamination frequently exceed estimates of background concentrations (Environment Canada 1998). For example, mean concentrations in sediments as high as 1 581 $mg \cdot kg^{-1}$ have been measured in freshwater lakes near mining and smelting operations and as high as 440 $mg \cdot kg^{-1}$ in marine harbours receiving various industrial inputs (Environment Canada 1998).

Additional Considerations

Regardless of the origin of Cu in sediments, aquatic organisms may be adversely affected by exposure to elevated levels. The occurrence of adverse biological effects cannot be precisely predicted from concentration data alone, particularly in the concentration ranges between the ISQGs and PELs (Figures 1 and 2). The likelihood of adverse biological effects occurring in response to Cu exposure at a particular site depends on the sensitivity of individual species and endpoints examined, as well as a variety of physicochemical (e.g., pH, redox potential, and particle size), biological (e.g., feeding behaviour and uptake rates), and geochemical (e.g., organic matter, metal oxide, and sulphide) factors that affect the bioavailability of Cu (Environment Canada 1998).

Benthic organisms are exposed to particulate and dissolved Cu in interstitial and overlying waters, as well as to sediment-bound Cu through surface contact and sediment ingestion. Dissolved forms of Cu are believed to be the most readily bioavailable (Campbell and Tessier 1996). Copper associated with sediment fractions that exhibit cation-exchange capacity or with fractions that are easily reduced is generally more bioavailable (Environment Canada 1998). Furthermore, changes in ambient environmental conditions (e.g., sediment turbation, decrease in pH, and increase in redox potential) can increase the bioavailability of Cu associated with inorganic solid phases, oxides of iron and manganese, and organic matter. In contrast, Cu that is bound within the crystalline lattices of clay and some other minerals that are associated with acid-extractable or residual sediment fractions is generally considered to be the least bioavailable. Once Cu is ingested, its availability depends on various factors, including enzyme activity and gut pH (Environment Canada 1998).

Models have been proposed to predict metal uptake (and hence toxicity) in aquatic organisms from bed sediments. One model that has been proposed considers the role of acid volatile sulphide (AVS) in modifying the bioavailability of two simultaneously extractable metals (SEM), cadmium and nickel in anoxic sediments (Di Toro et al. 1992). This model is applicable to Cu and other metals that form sulphides. Acid volatile sulphide refers to the fraction of the sediment that contains a reactive pool of solid-phase sulphide that is available to bind divalent metals and thus render them unavailable for uptake by aquatic biota. The model predicts that when the molar ratio of SEM to AVS in sediments is <1, metals will not be bioavailable due to complexation with available sulphide. When the ratio is >1, bioavailability of SEM is predicted to be high. However, when the ratio is >1, the model has several limitations, as it does not take into account the importance of other binding phases that will also limit the bioavailability of a metal (Ankley et al. 1993; Hare et al. 1994; Environment Canada 1998). In addition to geochemical factors, further research should be directed at determining other factors that modify the bioavailability of Cu (e.g., physical, chemical, and biological factors). This information, along with the recommended ISQGs and PELs, should be considered in site-specific assessments of Cu in sediments.

Currently, the degree to which Cu will be bioavailable at particular sites cannot be predicted conclusively from the physicochemical characteristics of sediments or the attributes of endemic organisms (Environment Canada 1998). An extensive review of available toxicological data indicates that the incidence of adverse biological effects associated with Cu exposure increases as concentrations of Cu increase in a range of sediment types (Figures 1 and 2). Therefore, the recommended Canadian ISQGs and PELs for Cu will be useful in assessing the ecotoxicological significance of Cu in sediments.

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