Canadian Sediment Quality Guidelines for the Protection of Aquatic Life

CADMIUM

Cadmium (Cd) is a nonessential trace element that can be toxic to aquatic biota at elevated concentrations. A recent assessment of Cd under the Canadian Environmental Protection Act (CEPA) indicated that dissolved and soluble forms of inorganic Cd are entering the Canadian environment in quantities or concentrations, or under conditions, that are having, or may have, a harmful effect on the environment (Government of Canada 1994). Cadmium enters aquatic systems through aerial deposition or runoff and accumulates in bed sediments by association with particulate matter, such as organic matter and iron and manganese hydroxides, or by precipitating out of solution with carbonate or sulphide (Landrum and Robbins 1990; Burton 1992). Sediments, therefore, act as an important route of exposure for aquatic organisms. Canadian interim sediment quality guidelines (ISQGs) and probable effect levels (PELs) for Cd can be used to evaluate the degree to which adverse biological effects are likely to occur as a result of exposure to Cd in sediments.

Canadian ISQGs and PELs for Cd 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 Cd 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 with determination by a standard analytical protocol.

The majority of the data used to derive ISQGs and PELs for Cd are from studies on field-collected sediments that measured concentrations of Cd, along with concentrations of other chemicals, and associated biological effects, as compiled in the Biological Effects Database for Sediments (BEDS) (Environment Canada 1997). The Cd data sets for freshwater and marine sediments are large, with the freshwater data set containing 86 effect entries and 363 no-effect entries and the marine data set containing 107 effect entries and 326 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 Cd 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 1997).

Toxicity

Adverse biological effects for Cd in the BEDS include decreased benthic invertebrate abundance, increased mortality, and behavioural changes, among others (Environment Canada 1997, Appendixes IIa and IIb). For example, the relatively sensitive taxa Ephemeroptera, Plecoptera, and Tricoptera were less abundant in Penetang Harbour (Lake Huron, Ontario), where the mean concentration of Cd was 0.77 $mg\cdot kg^{-1}$, which is above the freshwater ISQG, compared to sites with concentrations of 0.38 $mg\cdot kg^{-1}$ Cd (Jaagumagi 1988). Similarly, increased mortality, decreased reburial, and increased emergence were observed in *Lepidactylus dytiscus*, an amphipod (Hall et al. 1992). In the lab, the test organisms were exposed for a 10- and 20-d period to estuarine sediments (Chesapeake Bay, U.S.A.) that contained a mean concentration of Cd of 1.6 $mg\cdot kg^{-1}$, which is above the marine ISQG (Hall et al. 1992). In this study, sediments containing <0.2 $mg\cdot kg^{-1}$ Cd, which is below the marine ISQG, did not induce adverse biological effects in this species.

Spiked-sediment toxicity tests for Cd 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 of these laboratory studies, as well as exposure to Cd only, as opposed to chemical mixtures containing Cd (Environment Canada 1997). For example, 10-d LC_{50}s for *Rhepoxynius abronius*, a marine amphipod, ranged from 6.9 to 11.5 $mg\cdot kg^{-1}$ (Swartz et al. 1985; Mearns et al. 1986; Ott 1986; Robinson et al. 1988), which is close to the marine PEL of 4.2 $mg\cdot kg^{-1}$.

Further, Di Toro et al. (1990) demonstrated a protective effect of high concentrations of acid volatile sulphide (AVS). In this study, it was shown that the 10-d LC_{50}s for *Rhepoxynius hudsoni* and *Ampelisca abdita* were

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

	Freshwater	Marine/estuarine
ISQG	0.6	0.7
PEL	3.5	4.2

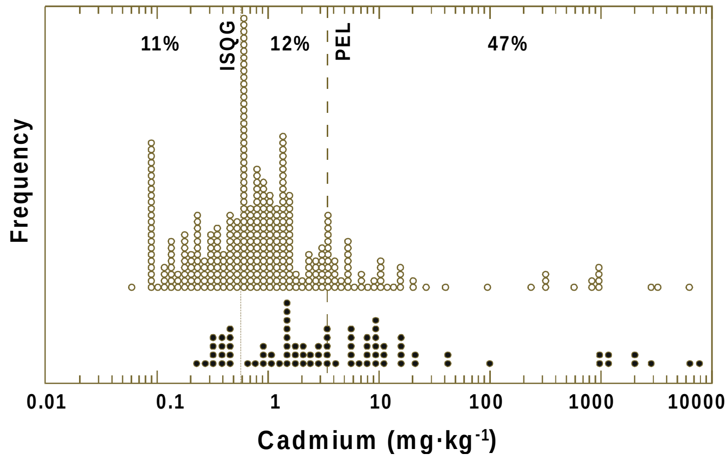

Figure 1. Distribution of Cd concentrations in freshwater sediments that are associated with adverse biological effects (●) and no adverse biological effects (○). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above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

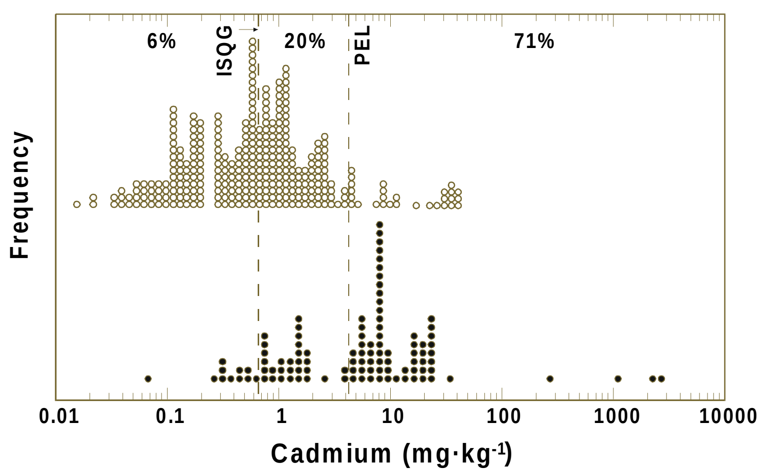

Figure 2. Distribution of Cd concentrations in marine and estuarine sediments that are associated with adverse biological effects (●) and no adverse biological effects (○). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL,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

approximately 50 and 500 times higher, respectively, than the marine PEL.

Sublethal effects of Cd to marine organisms in spiked-sediment toxicity tests include effects on emergence and reburial of *R. abronius* at concentrations ranging from 6.5 to 16.2 $mg \cdot kg^{-1}$, which is just above the marine PEL (Swartz et al. 1985; Mearns et al. 1986). Sediment avoidance was also observed when *Rhepoxynius* spp. and *Eohaustorius sencillus* were exposed to similar concentrations (Oakden et al. 1984a, 1984b). In contrast, the times and rates of burrowing for three species of polychaete worms and the feeding behaviour of one of those species (i.e., *Glycera dibranciata*), were unaffected after 28-d exposure to concentrations of Cd that were 10 times the marine PEL (Olla et al. 1988).

In freshwater spiked-sediment toxicity tests, reproduction of the burrowing oligochaete worm *Tubifex tubifex* was adversely affected when the concentration of Cd (i.e., 12 $mg \cdot kg^{-1}$) was greater than the freshwater PEL and the total organic carbon (TOC) content was 1%. At similar concentrations of Cd, but with a TOC content of 12%, no adverse effects were observed (Day et al. 1994). These results suggest that organic matter may modify the toxicity of Cd to freshwater benthic organisms. Other freshwater spiked-sediment toxicity tests did not demonstrate adverse effects of Cd at concentrations known to occur in aquatic environments (Environment Canada 1997).

Results of both marine and freshwater spiked-sediment toxicity tests indicate that concentrations of Cd 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. Furthermore, these studies provide additional evidence that toxic levels of Cd in sediments are similar to the PELs, confirming that adverse effects are more likely to be observed when concentrations of Cd exceed the PELs. The ISQGs and PELs for Cd are therefore expected to be valuable tools for assessing the ecotoxicological relevance of concentrations of Cd in sediments.

Concentrations

Concentrations of Cd in marine and freshwater sediments vary substantially across Canada (Environment Canada 1997). 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 0.32 $mg \cdot kg^{-1}$ and 0.63 $mg \cdot kg^{-1}$, respectively (P.W.B. Friske 1996, GSC, Ottawa, pers. com.). A comparison of the background concentrations in the combined lake and stream NGR database (n = 78 735) to the freshwater ISQG and PEL reveals that the ISQG and the PEL for Cd fall at the 82nd and 98.25th percentiles, respectively (R.G. Garrett 1997, GSC, Ottawa, pers. com.). This demonstrates that background concentrations of Cd across most of Canada are lower than the freshwater ISQG of 0.6 $mg \cdot kg^{-1}$. In marine systems, mean background concentrations of Cd, estimated from deep layers of sediment cores (>10 cm) from a variety of published sources, ranged from 0.16 $mg \cdot kg^{-1}$ to 4.24 $mg \cdot kg^{-1}$ (i.e., well below the marine ISQG to just above the marine PEL) (Environment Canada 1997).

Concentrations of Cd in surficial sediments located close to point sources of contamination frequently exceed estimates of background concentrations (Environment Canada 1997). For example, concentrations in sediments as high as 19.8 $mg \cdot kg^{-1}$ have been measured in marine harbours receiving various industrial inputs and as high as 235 $mg \cdot kg^{-1}$ in freshwater lakes near mining and smelting operations (Environment Canada 1997).

Additional Considerations

Regardless of the origin of Cd 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 incidence of adverse biological effects in response to Cd exposure is site-specific. Site-specific factors that influence bioavailability include the sensitivity of individual species, the 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 and sulphide levels) factors (Environment Canada 1997).

Benthic organisms are exposed to particulate and dissolved Cd in interstitial and overlying waters and to sediment-bound Cd through surface contact and sediment ingestion. However, the dissolved forms of Cd are believed to be the most readily bioavailable (Loring and Prosi 1986). Cadmium associated with sediment fractions that exhibit cation-exchange capacity or that are easily reduced is generally more bioavailable than that associated with other fractions (Environment Canada 1997). Cadmium associated with other sediment phases, such as inorganic solid phases, organic matter, and oxides of iron and manganese, may become bioavailable as a result of changes in ambient environmental conditions that affect the distribution of Cd between dissolved and particulate phases (e.g., sediment turbation, decrease in pH, and increase in redox potential). In contrast, Cd 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 Cd is ingested, its bioavailabilty depends on various factors, including enzyme activity and gut pH (Environment Canada 1997).

Recently, the role of AVS in modifying Cd bioavailability in anoxic sediments has received substantial attention. A model has been proposed to predict the absence of cationic trace metal bioavailability (and hence toxicity) when the molar ratio of simultaneously extractable metals (SEM), including Cd, to AVS in sediments is <1 (or when the difference is <0) due to complexation of metals with available sulphide (Di Toro et al. 1990; MacDonald and Salazar 1995). Although laboratory studies provide evidence for a lack of bioavailability of Cd when the SEM/AVS ratio in sediment is <1, several limitations exist in the model's applicability to predicting the bioavailability of Cd in the field (Hare et al. 1994; Leonard et al. 1995; Environment Canada 1997). However, the role of AVS and other factors that modify the bioavailability of Cd should be considered, along with the recommended ISQGs and PELs, in site-specific assessments of Cd in sediments.

Currently, the degree to which Cd will be bioavailable at particular sites cannot be predicted conclusively from the physicochemical characteristics of the sediments or the attributes of endemic organisms (Environment Canada 1997). Nonetheless, the incidence of adverse biological effects associated with exposure to Cd increases as concentrations of Cd increase in a range of sediment types (Figures 1 and 2). Therefore, the recommended Canadian ISQGs and PELs for Cd will be useful in assessing the ecotoxicological significance of Cd in sediments.

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