



Canadian Sediment Quality Guidelines for the Protection of Aquatic Life

MERCURY

Mercury (Hg) is a nonessential trace element that can be toxic to aquatic biota at elevated concentrations. Under Schedule I of the Canadian Environmental Protection Act (CEPA 1985), Hg is considered a toxic substance. Mercury exists in the environment in a wide variety of inorganic and organic forms. Three stable valence states of mercury exist: elemental or metallic Hg (Hg^0), the mercurous ion (Hg_2^{2+}), and the mercuric ion (Hg^{2+}) (Andren and Nriagu 1979). The exact chemical identity of organic Hg is not always known, with the exception of the association of the methylmercury cation (CH_3Hg^+) with simple anions, such as chloride, or large molecules, such as proteins (WHO 1990). Mercury also readily chelates with organic matter (humic and fulvic acids) forming stable complexes (Suzuki et al. 1991). The high affinity of Hg for organic ligands on particles and colloids means that Hg is easily transported to bed sediments from the water column (Stordal et al. 1996). Because a variety of organisms live in, or are in contact with, bed sediments, sediments can act as an important route of exposure to aquatic organisms. Canadian interim sediment quality guidelines (ISQGs) and probable effect levels (PELs) for Hg can be used to evaluate the degree to which adverse biological effects are likely to occur in aquatic biota as a result of exposure to Hg in sediments.

Canadian ISQGs and PELs for Hg 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 Hg 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 Hg are primarily from studies on field-collected sediments that measured concentrations of Hg, along with concentrations of other chemicals, and associated biological effects. Data are compiled in the Biological Effects Database for Sediments (BEDS) (Environment Canada 1997). The Hg data sets for freshwater and marine sediments are large, with the freshwater data set containing 85 effect entries and 280 no-effect entries and the marine data set containing 66 effect entries and 265 no-effect entries (Figures 1 and 2). The BEDS represents a wide range of concentrations of Hg, types of sediment, and mixtures of chemicals. Evaluation of the percentage of effect entries for Hg 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 concentrations: those that are rarely, occasionally, and frequently associated with adverse biological effects, respectively (Environment Canada 1997).

Toxicity

Adverse biological effects for Hg in the BEDS include lethality, reduced fertilization, and impaired development of early life stages of benthic organisms. For example, decreased abundance of Gastropoda and Chironomidae has been reported at sites in Toronto Harbour, Ontario, where mean concentrations of Hg were $0.987 \text{ mg}\cdot\text{kg}^{-1}$ and $1.09 \text{ mg}\cdot\text{kg}^{-1}$, respectively, which exceed the freshwater ISQG by over fivefold (Jaagumagi 1988; Jaagumagi et al. 1989). By comparison, in the same harbour, a relatively high abundance of gastropods and chironomids was observed at sites with mean concentrations of $0.013 \text{ mg}\cdot\text{kg}^{-1}$ and $0.009 \text{ mg}\cdot\text{kg}^{-1}$, respectively, which are much lower than the freshwater ISQG of $0.17 \text{ mg}\cdot\text{kg}^{-1}$.

In Atlantic marine sediments from Maryland, a mean concentration of $0.180 \text{ mg}\cdot\text{kg}^{-1}$ Hg, which is above the marine ISQG, was associated with significant mortality of an amphipod, *Leptocheirus plumulosus* (McGee et al. 1993). In comparison, much lower mortality was observed in sediments with a mean concentration of $0.050 \text{ mg}\cdot\text{kg}^{-1}$ (McGee et al. 1993), which is below the marine ISQG.

Spiked-sediment toxicity tests for Hg 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 and exposure to Hg only as opposed to chemical mixtures containing Hg (Environment Canada 1997). For example,

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

	Freshwater	Marine/estuarine
ISQG	0.17	0.13
PEL	0.486	0.70

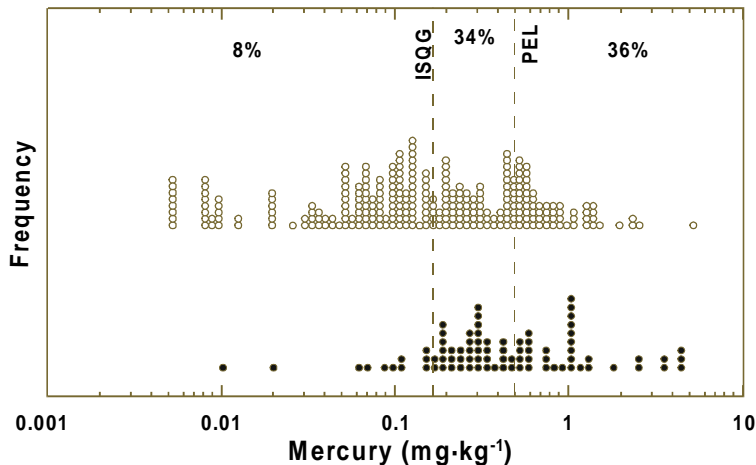


Figure 1. Distribution of Hg concentrations in freshwater sediments that are associated with adverse biological effects (●) and no adverse biological effects (○). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above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

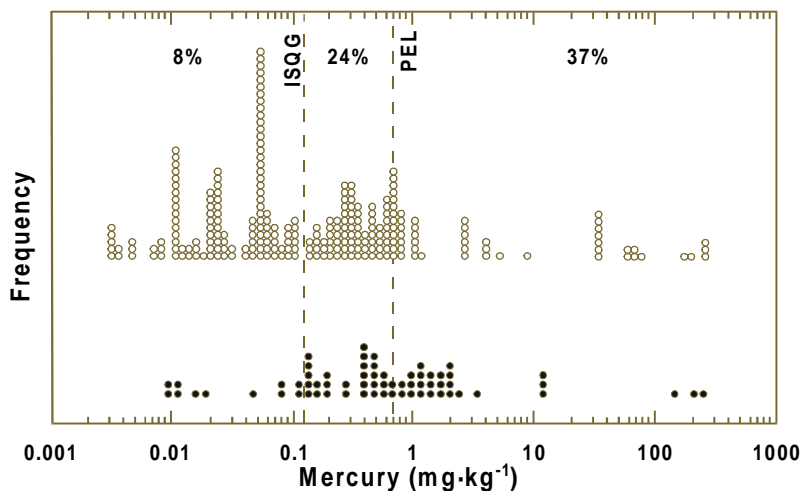


Figure 2. Distribution of Hg concentrations in marine and estuarine sediments that are associated with adverse biological effects (●) and no adverse biological effects (○). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL,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

a 10-d LC₅₀ of 15.2 mg·kg⁻¹ was calculated for a freshwater amphipod, *Hyalella azteca*, which is more than 100 times the marine ISQG (Swartz et al. 1988).

Although limited in quantity, the available toxicological data indicate that concentrations of Hg in sediments associated with adverse effects are consistently above the ISQGs, confirming that the ISQGs represent concentrations below which adverse biological effects will rarely occur. Further, these studies provide additional evidence that toxic levels of Hg in sediments are similar to, or greater than, the PELs, confirming that adverse effects are more likely to be observed when concentrations of Hg exceed the PELs. The ISQGs and PELs for Hg are therefore expected to be valuable tools for assessing the ecotoxicological relevance of concentrations of Hg in sediments.

Concentrations

Concentrations of Hg in freshwater and marine sediments vary considerably across Canada, with the highest concentrations being reported in industrial areas and harbours (Environment Canada 1997). At present, few studies have measured concentrations of methylmercury in Canadian sediments, however, the fraction of methylmercury in sediments is generally only 0.01–10% of the total mercury (Langston 1982; Bernhard and George 1986). Therefore, the data summarized below refer to total concentrations of Hg in sediments.

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 0.074 mg·kg⁻¹ and 0.075 mg·kg⁻¹, respectively (P.W.B. Friske 1996, GSC, Ottawa, pers. com.). The highest concentrations of Hg have been measured in New Brunswick, Ontario, and British Columbia, where concentrations are influenced by the type of bedrock and local geochemical deposits (Environment Canada 1997). When compared with the background concentrations in the combined lake and stream NGR database (n = 131 658), the freshwater ISQG and PEL for Hg fall at the 94th and 99.55th percentiles, respectively (R.G. Garrett 1997, GSC, Ottawa, pers. com.). This demonstrates that background concentrations of Hg across most of Canada are lower than the freshwater ISQG of 0.17 mg·kg⁻¹.

In freshwater sediments that are considered contaminated, concentrations as high as 15 mg·kg⁻¹ and 25 mg·kg⁻¹ have been reported for lakes and rivers, respectively, with concentrations in sediments of the Great Lakes as high as 15.03 mg·kg⁻¹ (Environment Canada 1997).

For coastal areas of Canada, reported background concentrations of Hg range from 0.010 mg·kg⁻¹ to 0.521 mg·kg⁻¹ and are highest in the Atlantic region. Concentrations of Hg in surficial sediments located close to point sources of contamination frequently exceed estimates of background concentrations. For example, concentrations as high as 22.9 mg·kg⁻¹ have been measured in marine sediments receiving various industrial inputs (Environment Canada 1997).

Additional Considerations

Regardless of the origin of Hg in sediments, aquatic organisms may be adversely affected by exposure to elevated levels. As is evident in Figures 1 and 2, the occurrence of adverse biological effects cannot be precisely predicted from concentration data alone, particularly in the concentration ranges between the ISQGs and PELs. The likelihood of adverse biological effects occurring in response to exposure to Hg at a particular site depends on the sensitivity of individual species and the endpoints examined. Further, the behaviour of Hg in sediments and the bioavailability of Hg to aquatic organisms is dependent on a number of physicochemical factors, including pH, redox potential, and temperature (Environment Canada 1997). These factors also affect the rate of mercury methylation and demethylation, which are critical processes that influence the fate and distribution of Hg in aquatic systems. In addition, the geochemical composition of sediments (e.g., particle size, organic matter content, and metal oxide and sulphide contents) and biological factors (e.g., feeding behaviour and uptake rates) will affect the bioavailability of Hg (Environment Canada 1997).

Mercury in sediment is generally found in association with organic matter or sulphides (D'Itri 1990; Suzuki et al. 1991). In anoxic sediments, Hg readily binds with available sulphides to form mercuric sulphide (HgS), a relatively stable compound that remains unreactive under anoxic conditions and adsorbs to, or co-precipitates with, acid volatile sulphide and pyrite. Mercury bound to sulphur is largely unavailable for uptake by organisms (Langston 1982). In oxic sediments, HgS can oxidize to sulphate, which is more soluble, rendering the mercuric ion available for biological uptake or binding with dissolved organics (e.g., humic and fulvic acids) (Environment Canada 1997).

Several genera of aerobic and anaerobic microorganisms are able to methylate Hg²⁺ and demethylate methylmercury (Zhang and Planas 1994). The methylation of Hg²⁺ is an important process because methylmercury is more bioavailable than inorganic species and is therefore more readily taken up by aquatic organisms (Riisgard and

Hansen 1990; Saouter et al. 1991). Although the fraction of methylmercury in sediments is small, the majority of Hg that accumulates in aquatic biota is in the methylated form (Langston 1982; Bernhard and George 1986). Ultimately, the net methylation of Hg in sediments is dictated by the availability of the mercuric ion for methylation and the activity of microorganisms.

Differences in the extent of uptake of inorganic and methylmercury species and their accumulation in biological tissues can be attributed to a variety of factors, including differences in excretion pathways, biological half-lives, and the capacity to cross membrane barriers (Saouter et al. 1991; Suzuki et al. 1991; Mason et al. 1995). Methylmercury has the capacity to biomagnify in the food web, which renders higher trophic level organisms, such as piscivorous fish and birds, especially susceptible to the accumulation of methylmercury and its potentially toxic effects.

The bioavailability and toxicity of inorganic and organic species of Hg at particular sites cannot be predicted conclusively from the physicochemical characteristics of sediments or the attributes of endemic aquatic organisms. Nonetheless, the incidence of adverse biological effects associated with exposure to Hg in sediments increases concurrently with concentrations of total Hg in a range of sediment types (Figures 1 and 2). Therefore, the recommended Canadian ISQGs and PELs for Hg will be useful in assessing the ecotoxicological significance of Hg in sediments.

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Canadian Council of Ministers of the Environment. 1999. Canadian sediment quality guidelines for the protection of aquatic life: Mercury. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

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Excerpt from Publication No. 1299; ISBN 1-896997-34-1

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