Canadian Sediment Quality Guidelines for the Protection of Aquatic Life

LEAD

Lead (Pb) is a nonessential trace element that is toxic to biota at elevated concentrations. Lead is rarely found in its elemental state (Pb^0) in nature, but more commonly occurs in its monovalent (Pb^{1+}), divalent (Pb^{2+}), and tetravalent (Pb^{4+}) states, with divalent Pb being the most common. Lead can also form organometallic compounds, such as tetraethyllead, which was the largest single source of Pb to the atmosphere prior to 1990, when it was used as an antiknock additive in gasoline (Lavallée and Fedoruk 1989). Lead entering aquatic systems through aerial deposition or runoff is deposited in bed sediments in association with particulate matter, such as iron and manganese oxides, or is precipitated out of solution with carbonate or sulphide (Eisler 1988; Prosi 1989). Sediments, therefore, act as an important route of exposure to Pb for aquatic organisms. Lead is listed as a toxic substance in Schedule I of the Canadian Environmental Protection Act (CEPA). Under CEPA, a substance is considered toxic if it is entering the Canadian environment in quantities or concentrations, or under conditions, that are having or may have a harmful effect in the environment. Canadian interim sediment quality guidelines (ISQGs) and probable effect levels (PELs) can be used to evaluate the degree to which adverse biological effects are likely to occur as a result of exposure to Pb in sediments.

Canadian ISQGs and PELs for Pb were developed using a modification of the National Status and Trends Program approach as described in CCME (1995) (Table 1). The ISQGs refer to total concentrations of Pb 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 Pb are from studies on field-collected sediments that measured concentrations of Pb, along with concentrations of other chemicals, and associated biological effects. Biological effects associated with concentrations of Pb in sediments are compiled in the Biological Effects Database for Sediments (BEDS) (Environment Canada 1998). The Pb data sets for freshwater and marine sediments are large, with the freshwater data set containing 83 effect entries and 357 no-effect entries and the marine data set containing 95 effect entries and 307 no-effect entries (Figures 1 and 2). Both data sets represent a wide range of concentrations of Pb, types of sediment, and mixtures of chemicals. Evaluation of the percentage of effect entries for Pb 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 Pb in the BEDS include increased mortality, decreased benthic invertebrate abundance and diversity, and abnormal development (Environment Canada 1998, Appendixes IIa and IIb). For example, in Toronto Harbour, Ontario, Jaagumagi et al. (1989) observed a high abundance of amphipods at sites where the mean concentration of Pb in the sediment was 10.8 $mg \cdot kg^{-1}$, which is below the freshwater ISQG. In contrast, a low abundance of amphipods was observed at sites where the mean concentration of Pb was 398 $mg \cdot kg^{-1}$, which is higher than the freshwater PEL. In marine sediments, McGreer (1982) observed that *Macoma balthica*, an estuarine bivalve, was absent from sites in the Fraser River estuary, British Columbia, when concentrations of Pb were 81.7 $mg \cdot kg^{-1}$, whereas these organisms were present at sites with 14 $mg \cdot kg^{-1}$ of Pb, which is lower than the marine ISQG.

Spiked-sediment toxicity tests for Pb report the onset of toxicity to benthic organisms at concentrations higher 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 Pb only as opposed to chemical mixtures containing Pb (Environment Canada 1998). For example, Bird et al. (1995) reported 100% mortality when *Chironomus tentans* was exposed for 14 d to freshwater sediment spiked with 31 900 $mg \cdot kg^{-1}$ Pb, which is approximately 350 times the freshwater PEL and 900 times the freshwater ISQG.

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

	Freshwater	Marine/estuarine
ISQG	35.0	30.2
PEL	91.3	112

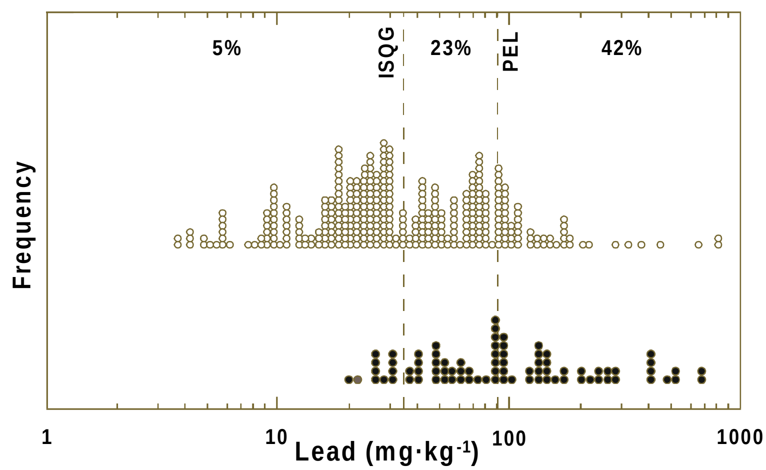

Figure 1. Distribution of concentrations of lead in freshwater sediments that are associated with adverse biological effects (●) and no adverse biological effects (○). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and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

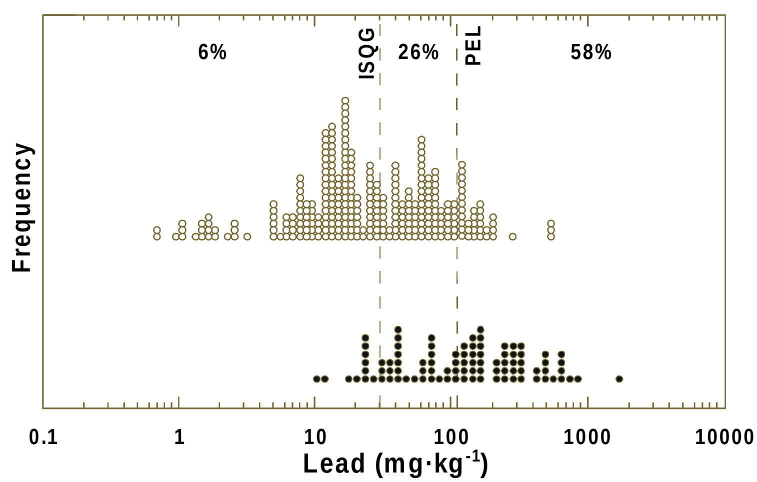

Figure 2. Distribution of concentrations of lead in marine and estuarine sediments that are associated with adverse biological effects (●) and no adverse biological effects (○). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the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

In a sublethal spiked-sediment toxicity test, using field sediments containing a mixture of Pb and other trace metals, mobility was significantly reduced in the freshwater midge *Daphnia magna* after 24-h exposure to 13 400 mg·kg^{-1} Pb and 48-h exposure to 7000 mg·kg^{-1} Pb (Dave 1992a, 1992b).

Organic Pb compounds are synthesized primarily as a result of human activities (Prosi 1989). Although organic Pb compounds are generally more toxic than inorganic Pb, their distribution in the environment is usually limited (Neves et al. 1990; Bunce 1994). The level of toxicity of organic forms of Pb is proportional to the degree of alkylation, such that the tetraalkylleads are the most toxic (Thayer 1984). In addition, natural sources of tetraalkyllead are formed by methylation of organic Pb and, to a lesser extent, inorganic Pb (Thayer 1984). The mode of natural methylation, whether it be abiotic or biotic, is still in dispute.

Although limited in number, spiked-sediment toxicity test results for freshwater and marine sediments indicate that toxic levels of Pb are consistently above the ISQGs, confirming that these guidelines adequately represent concentrations below which adverse biological effects will rarely occur. Further, these studies provide additional evidence that toxic levels of Pb in sediments are similar to or greater than the PELs (Environment Canada 1998). The ISQGs and PELs for Pb are therefore expected to be valuable tools for assessing the ecotoxicological relevance of concentrations of Pb in sediments.

Concentrations

Concentrations of Pb in freshwater and marine sediments vary substantially across Canada (Environment Canada 1998). Mean background concentrations of Pb in Canadian lake and stream sediments represented in the Geological Survey of Canada's (GSC) National Geochemical Reconnaissance (NGR) program database (Friske and Hornbrook 1991) are 6 mg·kg^{-1} and 12.7 mg·kg^{-1}, respectively (R.G. Garrett 1997, GSC, Ottawa, pers. com.). When compared to background concentrations in the combined lake and stream NGR database (n = 154 886), the freshwater ISQG and PEL for Pb falls at the 97.0th and 99.54th percentiles, respectively (R.G. Garrett 1997, GSC, Ottawa, pers. com.). This demonstrates that background concentrations of Pb across most of Canada are lower than the ISQG of 35.0 mg·kg^{-1}. In marine systems, the mean concentration of Pb, estimated from deep layers of sediment cores (>10 cm) from a variety of published sources, ranged from 7 to 23.4 mg·kg^{-1}, which are also below the marine ISQG (Environment Canada 1998).

Concentrations of Pb in surficial sediments close to point sources of contamination frequently exceed estimates of background concentrations (Environment Canada 1998). For example, mean concentrations as high as 3000 mg·kg^{-1} have been measured in freshwater sediments of lakes and rivers near manufacturing plants and as high as 15 400 mg·kg^{-1} in marine harbours receiving various industrial and sewage inputs (Bailey 1988; Goyette and Boyd 1989; Léger 1993; Bird et al. 1995).

Additional Considerations

Regardless of the origin of Pb 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 exposure to Pb 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 chemical speciation), biological (e.g., feeding behavior and uptake rates), and geochemical (e.g., phosphorous, organic matter, and metal oxides) factors that affect the bioavailability of Pb (Environment Canada 1998).

Benthic organisms are exposed to particulate and dissolved Pb in interstitial and overlying waters, as well as to sediment-bound Pb through surface contact and ingestion of sediments. Lead 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 1998). Furthermore, changes in ambient environmental conditions (e.g., sediment turbation, decrease in pH, and increase in redox potential) can increase the bioavailability of Pb associated with inorganic solid phases, oxides of iron and manganese, and organic matter. Relative to other trace metals (i.e., copper, zinc, cadmium, and nickel) and other sediment phases, Pb has the greatest affinity for oxides (Tessier 1992). Lead that is bound within the crystalline lattices of clay and other minerals that are associated with the acid-extractable or residual sediment fractions is generally considered to be the least bioavailable. Once Pb is ingested, its availability depends on various factors, including enzyme activity and gut pH (Environment Canada 1998).

The availability of Pb in sediments can also be mitigated by sulphides (Environment Canada 1998). Recently, models have been proposed that consider the role of acid volatile sulphide (AVS) in modifying the bioavailability of simultaneously extractable metals (SEM) in anoxic sediments (Di Toro et al. 1992; Casas and Crecelius 1994). Acid volatile sulphide, such as iron 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. These models predict 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 (Hare et al 1994; Ankley et al. 1996; Environment Canada 1998). However, the role of AVS and other factors that modify the bioavailability of Pb should be considered, along with the recommended ISQGs and PELs in site-specific assessments of Pb in sediments.

Currently, the degree to which Pb 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 1998). Nonetheless, the incidence of adverse biological effects associated with exposure to Pb increases as concentrations of Pb increase in a range of sediment types (Figures 1 and 2). Therefore, the recommended Canadian ISQGs and PELs for Pb will be useful in assessing the ecotoxicological significance of Pb in sediments.

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