



## Canadian Sediment Quality Guidelines for the Protection of Aquatic Life

## ARSENIC

Arsenic (As) is a metalloid that is considered nonessential to living organisms. It is stable in four oxidation states (+5, +3, 0, and -3) that can exist simultaneously in aquatic systems in a variety of inorganic and organic forms. The dominant form of inorganic As in oxygenated freshwater and marine systems is arsenate ( $\text{As}^{5+}$ ;  $\text{AsO}_4^{3-}$ ). Other forms of As that may also be present are arsenite ( $\text{As}^{3+}$ ;  $\text{AsO}_3^{3-}$ ) and organic species, such as monomethylarsonic acid, dimethylarsinic acid, and arsenobetaine, a trimethylarsonic compound (Ferguson and Gavis 1972; Cullen and Reimer 1989; Shiomi 1994). Elemental As ( $\text{As}^0$ ) rarely occurs, and the reduced species,  $\text{As}^{3-}$ , only exists under extremely low reducing conditions (Ferguson and Gavis 1972).

The global decrease in As production since the 1980s is attributed to an increased awareness of the environmental consequences of the use of products containing As. However, As still enters the aquatic environment from natural and anthropogenic sources through aerial deposition or runoff. The strong affinity of As for aquatic particles, particularly iron and manganese oxides, results in its deposition in bed sediments in association with these materials. Sediments, therefore, act as an important route of exposure for aquatic organisms to As. Canadian interim sediment quality guidelines (ISQGs) and probable effect levels (PELs) for As can be used to evaluate the degree to which adverse biological effects are likely to occur as a result of exposure to As in sediments.

Canadian ISQGs and PELs for As 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 As 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 As are from studies on field-collected sediments that measured concentrations of As, along with concentrations of other chemicals, and associated biological effects. Biological effects associated with concentrations of As in sediments are compiled in the Biological Effects Database for Sediments (BEDS) (Environment Canada 1998). The As data sets for freshwater and marine sediments are large, with the freshwater data set containing 53 effect

entries and 189 no-effect entries and the marine data set containing 39 effect entries and 172 no-effect entries (Figures 1 and 2). The BEDS represents a wide range of concentrations of As, types of sediment, and mixtures of chemicals. Evaluation of the percentage of effect entries for As that are below the ISQGs, between the ISQGs and the PELs, and above the PELs for As (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

In general, the toxicity of As to aquatic organisms decreases in the following order: arsenite ( $\text{As}^{3+}$ ) > arsenate ( $\text{As}^{5+}$ ) > monomethylarsonic acid > dimethylarsinic acid > arsenobetaine (Hindmarsh and McCurdy 1986; Shiomi 1994). Marine organisms tend to have higher concentrations of As than freshwater organisms (Maeda et al. 1990; Environment Canada 1998); however, Francesconi and Edmonds (1993) observed that higher concentrations of As in marine organisms are not a biological risk because the bioaccumulation of As to higher trophic levels is from a relatively nontoxic organic form, such as arsenobetaine.

Adverse biological effects for As in the BEDS include decreased benthic invertebrate abundance, increased mortality, and behavioural changes (Environment Canada 1998, Appendixes IIa and IIb). For example, in Toronto Harbour, Ontario, the abundance of chironomids was low at locations where the mean concentration of As in sediments was  $6.87 \text{ mg}\cdot\text{kg}^{-1}$ , which is above the freshwater ISQG of  $5.9 \text{ mg}\cdot\text{kg}^{-1}$ , compared to sites with lower concentrations of As at  $1.2 \text{ mg}\cdot\text{kg}^{-1}$  (Jaagumagi 1988; Jaagumagi et al. 1989). Concentrations in sediments that are associated with adverse biological

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

	Freshwater	Marine/estuarine
ISQG	5.9	7.24
PEL	17.0	41.6

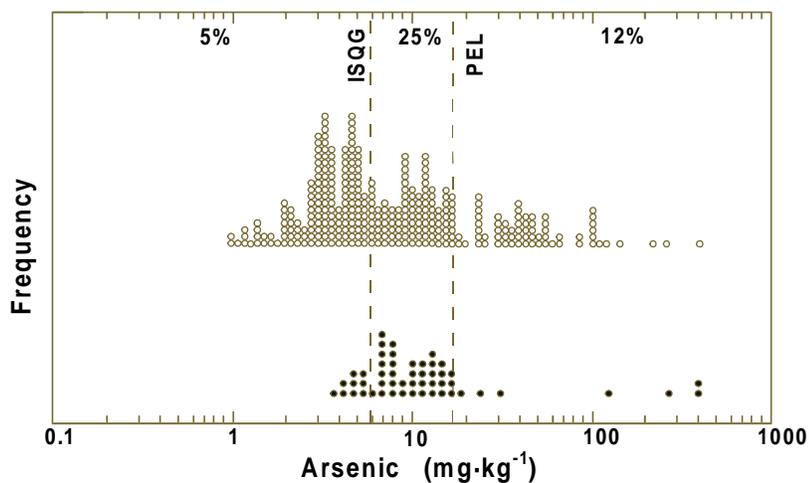


Figure 1. Distribution of As concentrations in freshwater sediments that are associated with adverse biological effects (●) and no adverse biological effects (○). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL, and above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

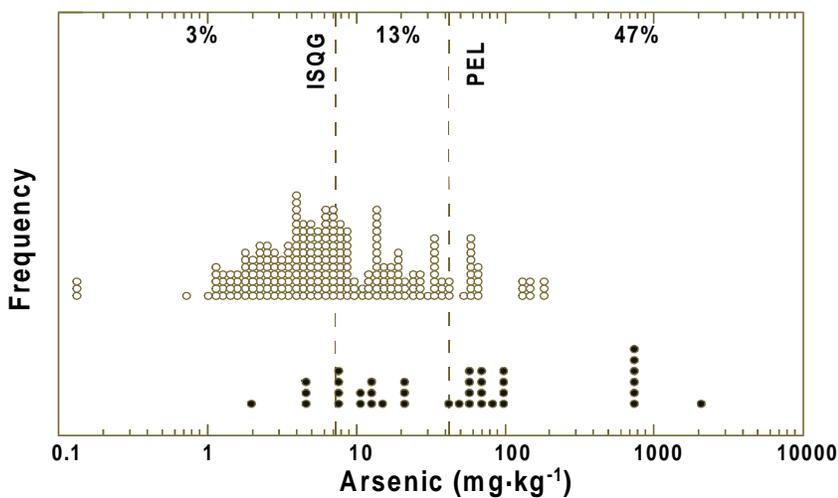


Figure 2. Distribution of As concentrations in marine and estuarine sediments that are associated with adverse biological effects (●) and no adverse biological effects (○). Percentages indicate proportions of concentrations associated with effects in ranges below the ISQG, between the ISQG and the PEL,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

effects in freshwater invertebrates are consistently above the freshwater PEL (Environment Canada 1998). In the Curtis Creek estuary (Baltimore, Maryland), increased mortality was observed in juvenile *Leptocheirus plumulosus*, an amphipod, at  $8.17 \text{ mg}\cdot\text{kg}^{-1}$ , which is above the marine ISQG; however, at  $3.4 \text{ mg}\cdot\text{kg}^{-1}$ , which is below the marine ISQG, no effect was observed on the amphipods (McGee et al. 1993).

Spiked-sediment toxicity tests can provide quantifiable relationships between responses of test organisms and concentrations of chemicals in sediments under controlled laboratory conditions. Currently, results from such tests are not available for As in either marine or freshwater sediments.

Results from these and other studies (Environment Canada 1998) indicate that effects are more likely to be observed when concentrations of As exceed the ISQGs, confirming that these guidelines represent concentrations below which adverse biological effects will rarely occur. The ISQGs and PELs for As are therefore expected to be valuable tools for assessing the ecotoxicological relevance of concentrations of As in sediments.

## Concentrations

Concentrations of As in freshwater and marine sediments vary substantially across Canada (Environment Canada 1998). Mean background concentrations of As 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  $2.5 \text{ mg}\cdot\text{kg}^{-1}$  and  $10.7 \text{ mg}\cdot\text{kg}^{-1}$ , respectively (R.G. Garrett 1997, GSC, Ottawa, pers. com.). When compared to background concentrations of As in the combined lake and stream NGR database ( $n = 128\,465$ ), the freshwater ISQG and PEL for As fall at the 81.9th and 94.7th percentiles, respectively (R.G. Garrett, 1997, GSC, Ottawa, pers. com.). This demonstrates that background concentrations of As across most of Canada are lower than the ISQG of  $5.9 \text{ mg}\cdot\text{kg}^{-1}$ . In marine sediments, mean background concentrations of As, estimated from deep layers of sediment cores ( $>10 \text{ cm}$ ) from a variety of published sources, ranged from  $5$  to  $10 \text{ mg}\cdot\text{kg}^{-1}$  (Environment Canada 1998), which is within the range of the marine ISQG of  $7.24 \text{ mg}\cdot\text{kg}^{-1}$ .

Concentrations of As in surficial sediments located close to point sources of contamination frequently exceed estimates of background concentrations (Environment Canada 1998). Anthropogenic inputs of As to sediments have resulted in a wide range of concentrations in surficial sediments. For example, in the Great Lakes region,

concentrations range from  $4$  to  $35 \text{ mg}\cdot\text{kg}^{-1}$ . Similarly, in marine sediments from Halifax Harbour, Nova Scotia, concentrations as high as  $64 \text{ mg}\cdot\text{kg}^{-1}$  have been reported (Environment Canada 1998).

## Additional Considerations

Regardless of the origin of As 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 As at a particular site depends on the sensitivity of individual species and endpoints examined, as well as a variety of physicochemical (e.g., pH and redox potential), geochemical (e.g., particle size, phosphorus concentrations, and metal oxides), and biological (e.g., feeding behaviour and uptake rates) factors that affect the bioavailability of As (Environment Canada 1998).

Benthic organisms are exposed to both particulate and dissolved forms of As in interstitial and overlying waters, as well as to sediment-bound As through surface contact and ingestion of sediment. Inorganic As is the predominant form of As in the sediment, water column, and interstitial water. In sediments, the fate and persistence of As are intricately connected with that of iron oxides and are influenced by redox conditions, pH, and microbial activity in the sediments (Pierce and Moore 1982; Thanabalasingam and Pickering 1986; Singh et al. 1988; DeVitre et al. 1991; Korte and Fernando 1991). Generally, As is associated with those fractions of the sediment (such as iron oxides) that are not considered readily bioavailable. However, As can be released as a result of changes to ambient environmental conditions (e.g., sediment turbation, decrease in pH, and increase in redox potential). In contrast, As 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 As is ingested, its bioavailability depends on various factors, including enzyme activity and gut pH (Environment Canada 1998).

Microorganisms in the sediments can transform inorganic As into an organic form, which can ultimately accumulate in aquatic organisms (Francesconi and Edmonds 1993; Le et al. 1994; Bright et al. 1996). Therefore, microorganisms may provide the critical biochemical link in the cycling of As in aquatic systems, since the methylated forms found in interstitial waters are by-products of microbial action (Reimer 1989; Bright et al. 1996).

Currently, the degree to which As will be bioavailable at particular sites cannot be predicted conclusively from the physicochemical characteristics of the sediments or attributes of endemic organisms. Further research should be directed at investigating factors that influence the bioavailability of As (e.g., physical, chemical, and biological factors). This information should be considered, along with the recommended ISQGs and PELs, in site-specific assessments of As in sediments. Nonetheless, an extensive review of available toxicological data indicates that the incidence of adverse biological effects associated with exposure to As increases as concentrations increase in a range of sediment types (Figures 1 and 2). Therefore, the recommended Canadian ISQGs and PELs for As will be useful in assessing the ecotoxicological significance of As in sediments.

## References

- Bright, D.A., M. Dodd, and K.J. Reimer. 1996. Arsenic in subarctic lakes influenced by gold mine effluent: The occurrence of organoarsenicals and hidden arsenic. *Sci. Total Environ.* 180(2):65–182.
- CCME (Canadian Council of Ministers of the Environment). 1995. Protocol for the derivation of Canadian sediment quality guidelines for the protection of aquatic life. CCME EPC-98E. Prepared by Environment Canada, Guidelines Division, Technical Secretariat of the CCME Task Group on Water Quality Guidelines, Ottawa. [Reprinted in Canadian environmental quality guidelines, Chapter 6, Canadian Council of Ministers of the Environment, 1999, Winnipeg.]
- Cullen, W.R., and K.J. Reimer. 1989. Arsenic speciation in the environment. *Chem. Rev.* 89:713–764.
- DeVitre, R., N. Belzile, and A. Tessier. 1991. Speciation and adsorption of arsenic on diagenetic iron oxyhydroxides. *Limnol. Oceanogr.* 36:1480–1485.
- Environment Canada. 1998. Canadian sediment quality guidelines for arsenic: Supporting document. Environmental Conservation Service, Ecosystem Science Directorate, Science Policy and Environmental Quality Branch, Guidelines and Standards Division, Ottawa. Draft.
- Ferguson, J.F., and J. Gavis. 1972. A review of the arsenic cycle in natural waters. *Water. Res.* 6:1259–1274.
- Francesconi, K.A., and J.S. Edmonds. 1993. Arsenic in the sea. *Oceanogr. Mar. Biol. Annu. Rev.* 31:111–151.
- Friske, P.W.B., and E.H.W. Hornbrook. 1991. Canada's National Geochemical Reconnaissance Programme. *Trans. Inst. Min. Metall.* 100:B47–B56.
- Hindmarsh, J.T., and R.F. McCurdy. 1986. Clinical and environmental aspects of arsenic toxicity. *CRC Crit. Rev. Clin. Lab. Sci.* 23(4):315–347.
- Jaagumagi, R. 1988. The in-place pollutants program. Volume V, Part B. Benthic invertebrates studies results. Ontario Ministry of the Environment, Water Resources Branch, Aquatic Biology Section, Toronto.
- Jaagumagi, R., D. Persaud, and T. Lomas. 1989. The in-place pollutants program, Volume V, Part A. A synthesis of benthic invertebrates studies. Ontario Ministry of the Environment, Water Resources Branch, Aquatic Biology Section, Toronto.
- Korte, N.E., and Q. Fernando. 1991. A review of arsenic(III) in groundwater. *Crit. Rev. Environ. Control* 21(1):1–39.
- Le, S.X.C., W.R. Cullen, and K.J. Reimer. 1994. Speciation of arsenic compounds in some marine organisms. *Environ. Sci. Technol.* 28:1598–1604.
- Maeda, S., A. Ohki, T. Tokuda, and M. Ohmine. 1990. Transformation of arsenic compounds in a freshwater food chain. *Appl. Organomet. Chem.* 4:251–254.
- McGee, B.L., C.E. Schlekot, and E. Reinhartz. 1993. Assessing sublethal levels of sediment contamination using the estuarine amphipod (*Leptocheirus plumulosus*). *Environ. Toxicol. Chem.* 12:577–587.
- Pierce, M.L., and C.B. Moore. 1982. Adsorption of arsenite and arsenate on amorphous iron hydroxide. *Water. Res.* 16:1247–1253.
- Reimer, K.J. 1989. The methylation of arsenic in marine sediments. *Appl. Organomet. Chem.* 3:475–490.
- Shiomi, K. 1994. Arsenic in marine organisms: Chemical forms and toxicological aspects. In: *Arsenic in the environment: Part II, Human health and ecosystem effects*, J.O. Nriagu, ed. John Wiley & Sons, Inc., New York.
- Singh, D.B., G. Prasad, D.C. Rupainwar, and V.N. Singh. 1988. As(III) removal from aqueous solution by adsorption. *Water Air Soil Pollut.* 42:373–386.
- Thanabalasingam, P., and W.F. Pickering. 1986. Effect of pH on interaction between As(III) or As(V) and manganese(IV) oxide. *Water Air Soil Pollut.* 29:205–216.

## Reference listing:

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

## For further scientific information, contact:

Environment Canada  
Guidelines and Standards Division  
351 St. Joseph Blvd.  
Hull, QC K1A 0H3  
Phone: (819) 953-1550  
Facsimile: (819) 953-0461  
E-mail: ceqg-rcqe@ec.gc.ca  
Internet: <http://www.ec.gc.ca>

## For additional copies, contact:

CCME Documents  
c/o Manitoba Statutory Publications  
200 Vaughan St.  
Winnipeg, MB R3C 1T5  
Phone: (204) 945-4664  
Facsimile: (204) 945-7172  
E-mail: spccme@chc.gov.mb.ca