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Lake Sediments: Sources or Sinks of Industrially Mobilized Elements?

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The once rather pessimistic outlook on the environmental impact of trace elements dispersed from Sudbury's smelters is gradually being replaced by a more optimistic view. The optimism has been prompted by several clear indications that the recent period of declining smelter emissions has resulted in both biological (Gunn and Keller 1990; Keller et al. 1992a) and chemical (Keller et al. 1992b) improvements in local lakes.

Lake sediments can become the ultimate site of deposition for many of the trace elements introduced into the environment, but sediments cannot be considered as a stable and non-reactive milieu. Potent chemical and biochemical reactions and transformations occur in the sediments, making the biogeochemical behavior of deposited trace elements highly dynamic. The relevant processes include microbially mediated decomposition of organic matter, precipitation and dissolution of minerals, sorption and desorption of trace elements on living and non-living particles, and the diffusion of dissolved constituents along concentration gradients (Fig. 14.1).

In this context, it is relevant to ask whether processes in the lake sediments influence the rate or extent of whole-lake recovery and whether the sediment environment itself exhibits either beneficial or undesirable responses. In particular, if sediments release potentially harmful chemicals back to the overlying waters, this might slow the rate of lake recovery. There are strong indications that in sulfur-rich sediments containing little or no oxygen, the precipitation of sulfide minerals can greatly limit the solubility of many trace elements (Carignan and Nriagu 1985). Although, in contrast, oxygen-rich sediments generally show undersaturation with respect to trace element solid phases (Tessier 1992), trace element dissolution may, in fact, be insignificant because oxygen-rich sediments commonly have a high content of iron and manganese oxyhydroxides, and these insoluble compounds exhibit a great capacity for trace metal sorption.

In this chapter, we present details on some of the processes controlling the solubility and hence the mobility of metals and other trace elements in lake sediments near Sudbury and discuss the consequences of lowered sulfur emission rates and in-lake sulfur reduction on sediment pH and trace element geochemistry.

Chemical Element Profiles in Lake Sediments

Facilities for smelting copper and nickel ores are everywhere known as a major source of atmospheric emissions of iron, sulfur, and the trace elements antimony, arsenic, cadmium, cobalt, copper, lead, nickel, selenium, and zinc (Nriagu and Pacyna 1988). What happens to
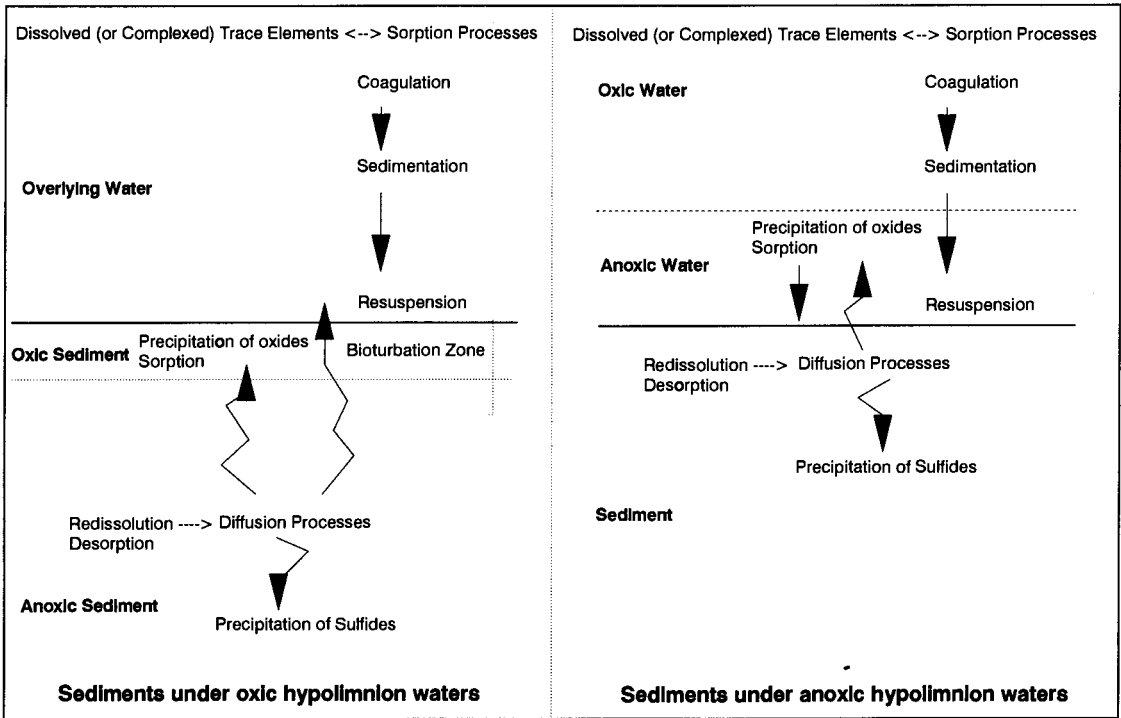
FIGURE 14.1. Schematic representation of the processes controlling the behavior of trace elements in sediments.

these elements after they fall into or are carried into lakes in the Sudbury area?

It is apparent from many investigations that significant quantities of trace elements have been deposited in the sediments of Sudbury area lakes, and sulfur, copper, and nickel enrichment can still be detected more than 60 km away (Semkin and Kramer 1976; Nriagu et al. 1982). Enrichment factors, defined as the ratio of total element concentration in the surficial layer to the average concentration in the deeper or precolonial layers, are generally lower in the acidic than the non-acidic lakes near Sudbury, reflecting the higher solubility of trace elements at lower pH (Carignan and Nriagu 1985; Tessier 1992). Figure 14.2 shows total concentrations of several elements as a function of depth below the sediment surface observed in McFarlane Lake, a mesotrophic near-neutral lake in Sudbury, during the early 1980s (Nriagu et al. 1982; Nriagu 1983; Nriagu and Coker 1983; Nriagu and Wong 1983). More recent studies (Dillon and Smith 1984;

Nriagu and Rao 1987) show a sharp decline in the metal content of the most recently deposited sediment in Clearwater, Silver, and McFarlane lakes.

The decline in metal levels in the upper layer (i.e., the most recent sediments) could be a reflection of lowered smelter emission rates (Nriagu and Rao 1987). However, the fine-scale distribution patterns of trace elements in the surface sediments must be interpreted with caution because trace elements levels may be influenced by chemical transformations and element remobilization that occurred after deposition (Carignan and Nriagu 1985; Carignan and Tessier 1985; Belzile and Tessier 1990). The degree of oxidation or reduction of the sediment surface and the position of the sulfate-reducing zone seem to be particularly important factors. The location of the sulfate-reducing zone within the sediment profile controls the location of metal sulfide precipitation, and in sulfur-enriched lakes, such precipitates are undoubtedly important. In Sudbury

FIGURE 14.2. Concentration profiles of arsenic, selenium, nickel, copper, and sulfur in sediments of McFarlane Lake showing the surface enrichment attributed to emissions from smelters (from Nriagu et al. 1982; Nriagu 1983; Nriagu and Coker 1983; Nriagu and Wong 1983).
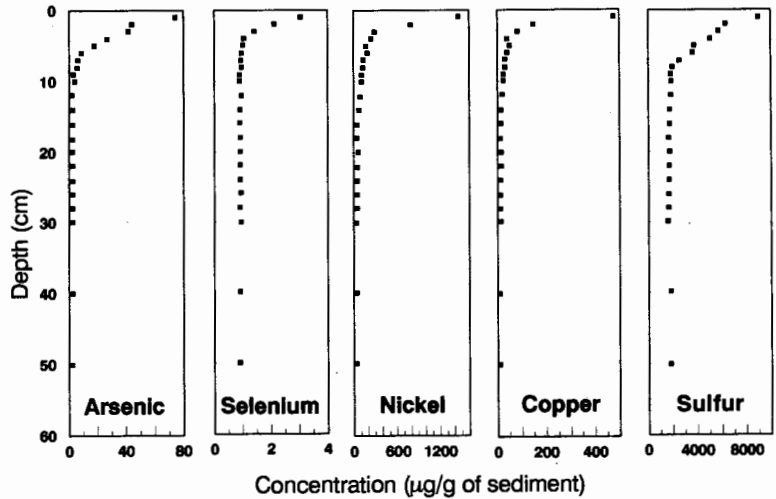
area lakes, the zone of maximum sulfur concentration may sometimes occur immediately beneath the sediment surface, but it has frequently been found below the 5-cm depth (Fig. 14.3) (Morris, *unpublished data*). Lowered trace element concentrations could also result from dilution effects associated with the sediment surface. Potential diluting materials are freshly sedimented organic material, especially in productive lakes, and iron and manganese oxyhydroxides, particularly in unproductive lakes. In unproductive lakes, with little organic matter settling to the bottom, organic decomposition may consume so little oxygen
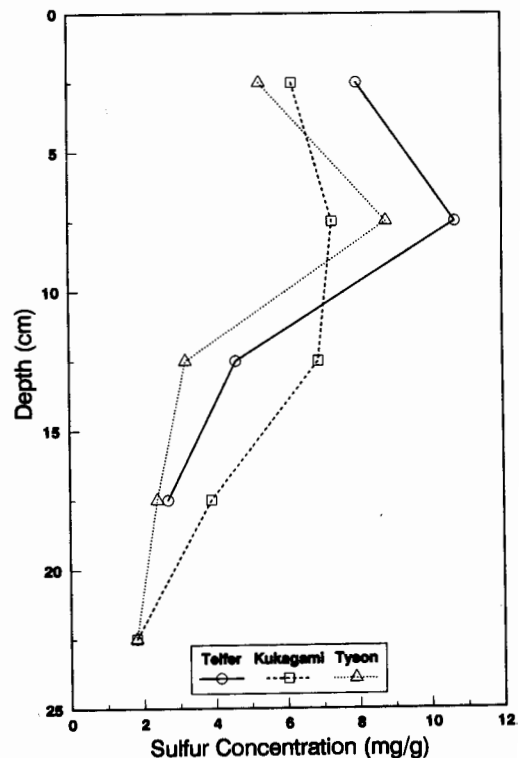
FIGURE 14.3. Depth-distributions of total sulfur in three lakes near Sudbury (from Morris, *unpublished data*).

that the sediment surface remains oxidized. These circumstances allow high concentrations of iron and manganese oxyhydroxides to persist at the sediment surface.

Processes That Transport Elements to Sediments

In lakes near Sudbury, as elsewhere, total concentrations of dissolved trace elements are usually relatively low in the water column; this is because there are effective processes transporting incoming trace elements to the lake bottom. What are these processes and how do they function?

The sedimentation of biogenic particulates is an important mechanism by which trace elements are removed from the water column (Sigg 1985; Sigg et al. 1987). Various planktonic organisms take up trace elements from the water by physiological processes. More important, chemical complexation may bind trace elements to dead plankton, to particles of decaying plant material, to fecal pellets of planktonic animals and protozoans, and to humic particles, and all these tend to sink to the lake bottom and thus remove trace elements from the water column. Another important mechanism moving trace elements from solution to the sediments involves the more or less continuous scavenging by iron and manganese oxyhydroxides. Iron and manganese are very abundant in most soils. Because these two metals tend to precipitate rapidly in the presence of oxygen, they typically enter lakes dissolved in anoxic groundwater seepages or directly as oxyhydroxides. Once in the lake, dissolved forms usually encounter dissolved oxygen and a near-neutral pH, and insoluble oxyhydroxides begin to form (Stumm and Morgan 1981). Because precipitated iron and manganese oxyhydroxides readily adsorb or form complexes with many dissolved ions, trace elements are firstly scavenged from the water column and then are carried to the bottom when the precipitates sink (Belzile and Tessier 1990; Tessier 1992).

Sulfur may accumulate in the sediments because more dissolved sulfur ions, such as sulfate, diffuse into the sediment than diffuse out. This occurs because anaerobic layers in the sediment harbor species of bacteria that can break down or oxidize organic matter by reducing sulfate and other sulfur ions to hydrogen sulfide (Stumm and Morgan 1981). Some of the hydrogen sulfide generated may return from the sediment to the lake water by diffusing upward or in rising bubbles, but because hydrogen sulfide is highly reactive, much of the sulfur will be fixed in solids through the formation of highly insoluble sulfides (Stumm and Morgan 1981). In acidic Clearwater Lake (pH 4.8), concentration profiles of dissolved copper, nickel, and zinc near the sediment–water interface suggest that these metals were also diffusing into the sediments along a concentration gradient and then precipitating (Fig. 14.4). These findings contradict other field studies (Sigg et al. 1987) that have emphasized the removal of trace elements from the water column through binding to sinking particles, and it may be that the diffusion of trace metals into sediments is only significant in very acidic lakes.

Chemical Transformations within the Sediments

What circumstances or processes influence the mobility and distribution of trace elements after they have become part of the sediments? Here, more detailed focus must be put on factors that control the stability of iron and manganese oxyhydroxides and the formation of metal sulfides.

Importance of Iron Oxyhydroxides

At or near their surface, typical lake sediments become anoxic, reducing environments because of oxygen consumption during the microbial decomposition of organic matter. In circumstances in which stronger oxidants such as dissolved oxygen, nitrate, or manganese oxides have already been depleted, the iron in

FIGURE 14.4. Depth-distributions of dissolved zinc, copper, nickel, and pH values in porewaters and overlying waters at a littoral station of Clearwater Lake. *Horizontal line* represents the sediment–water interface (from Carignan and Nriagu 1985).
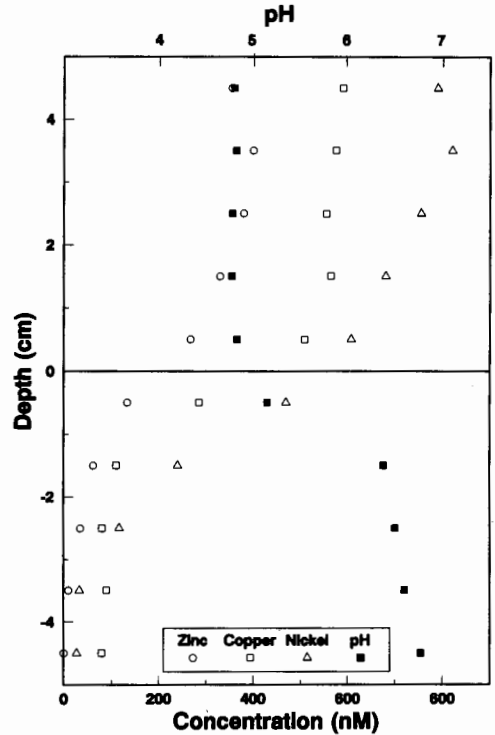
oxyhydroxides converts from the ferric oxidation state Fe(III) to the ferrous state Fe(II), and the former iron oxyhydroxides dissolve. Consequently, trace elements complexed with iron oxyhydroxides are released into solution and are then immediately free to move away by diffusion.

Arsenic provides an excellent example of the close coupling between a trace element's chemical behavior and that of iron (Belzile and Tessier 1990). In Figure 14.5, each profile of dissolved iron and dissolved arsenic shows a peak located a few centimeters below the sediment–water interface; both elements were released to solution by the reductive dissolution of buried iron oxyhydroxides. In summer or winter lake stagnation periods, oxygen depletion at the sediment surface and the consequent upward migration of the oxidation-reduction transition zone into the water column can also lead to seasonal episodes of iron and trace element dissolution (see Fig. 14.1). Because the peaks in the concentration of dissolved iron Fe(II) and dis-

solved arsenic are situated below the sediment surface (Fig. 14.5), two sink propagating mechanisms are implied. Above the peaks, oxygen was apparently diffusing downward from the lake water, oxidizing upward diffusing Fe(II), and enriching the surficial sediments in iron oxyhydroxides. Simultaneously, upward diffusing arsenic was being removed from solution in this zone by iron oxyhydroxide sorption (Belzile and Tessier 1990). Below the peaks, downward diffusing dissolved Fe(II) and arsenic were probably precipitated by reactions involving hydrogen sulfide. Sufficient hydrogen sulfide can be generated because Sudbury's lakes are sulfur-enriched.

The above hypotheses were confirmed when Teflon sheets inserted into the sediments collected iron oxyhydroxide precipitates near the sediment surface, and iron sulfide precipitates a few centimeters deeper (Belzile et al. 1989). The decline in dissolved arsenic below its peak may have resulted
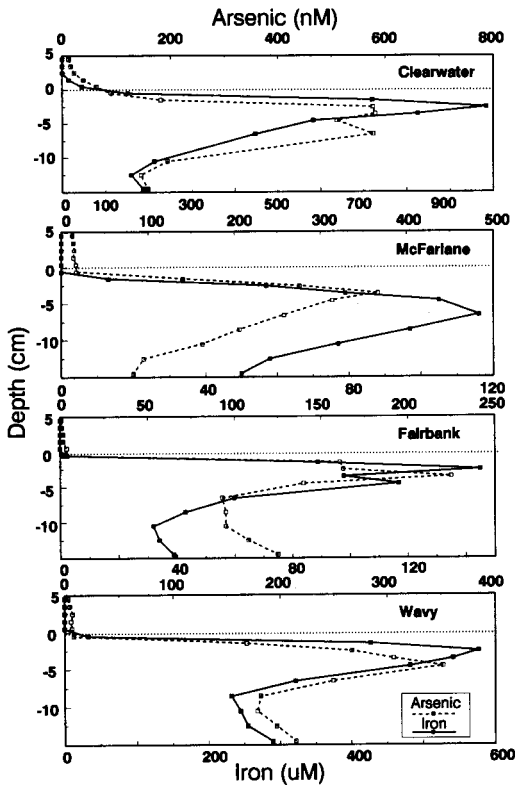
FIGURE 14.5. Depth-distributions of total dissolved arsenic and iron in porewaters and overlying waters of four lakes near Sudbury. *Horizontal dotted lines* represent the sediment–water interface (from Belzile and Tessier 1990).

from precipitation of arsenic sulfides (As_2S_3 or FeAsS) and arsenic adsorption onto iron sulfide; these reactions have been reported frequently elsewhere (Aggett and O'Brien 1985; Belzile and Lebel 1986; Edenborn et al. 1986; Belzile 1988).

If the sediment's surface is sufficiently reduced, dissolved ferrous iron and trace elements may be released directly into the overlying anoxic lake water, and the sediment may become a source rather than a sink for dissolved trace elements. This is shown for arsenic in Figure 14.5 at a site in Clearwater Lake. Two factors tend to minimize the significance of such releases. First, oxygenated lake water will usually occur at some level higher in the water column. Here, oxygen will limit the upward diffusion of ferrous iron by again precipitating iron oxyhydroxides (see Fig. 14.1), which will bind with trace elements returning them again toward the lake bottom. Second, in sulfur-enriched Sudbury lakes, the hydrogen sulfide available near the surface of anoxic

sediments may be sufficient to react with most of the dissolving arsenic, ferrous iron, and trace metal ions and may render them insoluble before they have time to diffuse appreciably into the lake water.

Precipitation of Sulfides— Saturation Indices

Porewater profiles of dissolved copper, nickel, and zinc in Clearwater Lake showed distinct losses in metal solubility that were associated with the transition to anoxia at 2 cm below the sediment–water interface (see Fig. 14.4). This correlation with anoxia suggested that the low dissolved metal concentrations may have resulted from precipitation of copper, nickel, and zinc sulfides. Saturation index calculations (Box 14.1) for the zone observed to be low in dissolved metals indeed showed that saturation of the porewaters was to be expected with respect to zinc sulfide and nickel

Box 14.1.

Saturation index (SI) is defined as log (IAP/Ksp), where Ksp is the solubility-product constant. The ion activity product (IAP) is equal to the product of the specific activity (a) of the different ions forming a precipitate or solid. A simplified way of calculating the IAP for iron sulfide (FeS) would be

$$IAP\ FeS = (a_{Fe}2+)\ (a_S2-)$$

But because of the very weak second dissociation constant of H_2S, the HS^- ion is more relevant to this calculation than the S^{2-} ion considered above. A better way of calculating the IAP would therefore be

$$IAP\ FeS = (aFe^{2+})\ (a_{HS}-/a_H+)$$

Negative values of IAP indicate undersaturation and no precipitation. The precipitate should be forming if the IAP value is either zero, indicating saturation, or greater than zero, indicating supersaturation.

sulfide and indicated oversaturation with respect to copper sulfide (Carignan and Nriagu 1985; Carignan and Tessier 1985). It was concluded, therefore, that sediments more than 2 cm below the sediment–water interface are a sink for trace metals in Sudbury area lakes. These sediments would only cease to be a sink in the event that they ceased to be anaerobic. Such a situation occurred when Lake Laurentian was drained and reflooded in 1982. Subsequent increases in the concentrations of metals in water and macrophyte tissues were observed (Keller 1984).

Similar patterns of trace element insolubility have also been found with arsenic and iron, and they occurred in lakes representing a range of pH levels (Fig. 14.5). Saturation index calculations and analysis of black deposits on Teflon collectors (Belzile et al. 1989) indicate that dissolved iron concentrations can also be controlled in anoxic porewaters by precipitation of a sulfide such as iron sulfide. Finally, an increase in pH has been observed in Sudbury area sediments at the levels of intense sulfate

reduction (see Fig. 14.4), especially where the sediment surface is anoxic and high in porosity (Fig. 14.6). This phenomenon is consistent with the hypothesis that the reduction of iron oxyhydroxides, the reduction of sulfates to sulfides, the precipitation of iron sulfide, and the generation of alkalinity occur concurrently.

$$4Fe(OH)_3(s) + 4SO_42- + 9CH_2O \rightarrow$$
$$4FeS(s) + CO_2 + 8HCO_3- + 11H_2O \quad (1)$$
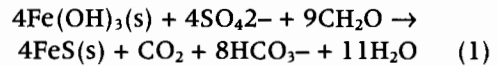
Metal Sorption on Oxide Surfaces—The Influence of pH

In contrast with anoxic porewaters, where precipitation of sulfides seems to control the concentrations and solubilities of dissolved trace element, oxic porewaters and overlying waters do not show saturation with known solid phases of trace elements. More specifically, arsenic (Belzile and Tessier 1990), cadmium, copper, lead, nickel, and zinc (Tessier et al., 1994) should not form any oxide, hydroxide, or carbonate precipitates either within or above oxic lake sediments, because the relevant saturation indices have negative values. Because iron and sometimes manganese oxyhydroxides do precipitate in and above oxic sediments and because these compounds have the ability to adsorb trace elements, the evidence for adsorption should be examined in more detail. According to the surface complexation theory for low-density adsorption (Tessier et al., 1994), the propensity of any trace metal to adsorb onto iron oxyhydroxide can be represented by an apparent equilibrium constant (K_M), which can be determined by

$$K_M = \frac{N_{Fe}\ {}^\bullet K_M}{[H^+]^{m+1}} = \frac{\{Fe-O-M\}}{\{Fe-Ox\}[M^{z+}]} \quad (2)$$

where {Fe-O-M} is the equilibrium concentration of the adsorbed trace metal, {Fe-Ox} is the concentration of the iron fixed in iron oxyhydroxides, [M^{z+}] is the equilibrium concentration of the trace metal ion remaining free in solution, and N_{Fe} is the number of adsorbing sites per mole of iron oxyhydroxides.
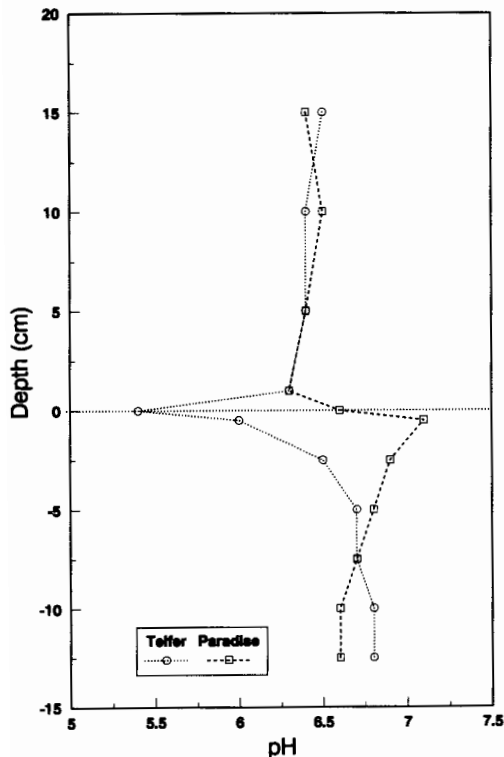
FIGURE 14.6. Profiles of pH values measured at the sediment interface of two lakes located at approximately 50 km from Sudbury. Paradise Lake showed a negative redox potential at 2.5 cm in the sediments that had also a low bulk density (high water content) and a high excess of sulfur. Telfer Lake showed a positive redox potential value at 2.5 cm, and sediments had a high bulk density and a smaller excess of sulfur than Paradise Lake. *Horizontal dotted line* represents the sediment–water interface (from Morris, *unpublished data*).

The concentration of both iron oxyhydroxides {Fe-Ox} and adsorbed trace metal {Fe-O-M} can be determined by analyzing partial chemical extracts from samples of oxic sediments or by inserting Teflon collectors in oxic sediments and subsequently dissolving and analyzing the iron oxyhydroxide-trace metal complexes that deposit on them. The concentrations of the dissolved free metal ions $[M^{z+}]$ is calculated from the total dissolved trace metal and the inorganic ligands concentrations in the overlying waters, using porewater peepers (Carignan 1984).

On theoretical grounds, the adsorption of trace metals by iron oxyhydroxides should increase with ambient pH (Equation 2). To test this prediction in the natural environment, the apparent equilibrium constant for the adsorption of zinc on iron oxyhydroxides (K_{Zn}) was determined for oxic sediments from 41 lakes spread over an area of 350,000 km² in Ontario and Quebec. When these K_{Zn} values are regressed on lake pH (Fig. 14.7), the expected trend is observed, and differences in pH

explained about 90% ($r^2 = .89$) of the variation in K_{Zn} (Tessier et al. 1989). In the same geographic area, similar linear regression models having slopes close to 1 were also obtained for the adsorption of cadmium ($r^2 = .80$; $n = 26$), copper ($r^2 = .75$; $n = 39$), lead ($r^2 = .81$; $n = 7$), and nickel ($r^2 = .87$; $n = 29$) (Tessier 1992).

Substantial reductions in sulfur emissions from Sudbury area smelters have allowed lake pH values to increase, and sulfate reduction has increased sediment pH in many local lakes. Trace metal solubilities should therefore be decreasing in most Sudbury area lakes because sorption to iron oxyhydroxides has undoubtedly been increasing. In the past 20 years, the pH of Clearwater Lake has increased from 4.3 (Dillon et al. 1986) to 5.0 (Belzile, *unpublished data*). Assuming a constant ratio of adsorbed metal to iron oxyhydroxides, Equation 2 indicates that the solubility of zinc has declined by more than seven times during the past two decades, and the situation should be similar for other trace metals.

FIGURE 14.7. Relationship between the apparent equilibrium constant for the adsorption of zinc on natural iron oxyhydroxides (expressed here as the log of the ratio of adsorbed zinc to iron oxyhydroxides and dissolved zinc) and pH obtained for 41 lakes (from Tessier et al. 1989).

$$Log\ K\ (Zn) = 1.21\ pH - 2.83$$
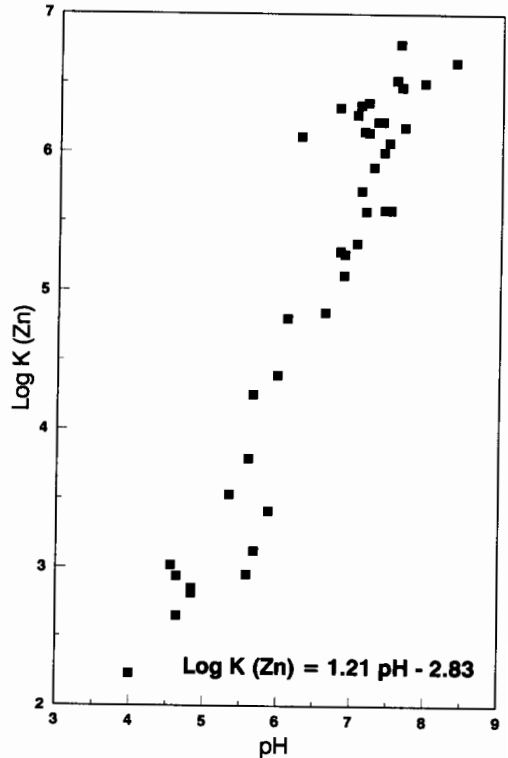
Management Implications

In some cases, the natural recovery of lake systems is not possible in a short period of time, and remedial measures (NRC 1992; Rhodes and Wiley 1993) have to be taken to mitigate the effects of acidification and contamination. One approach that has been commonly used involves the addition of a base (such as $CaCO_3$), resulting in increased pH and acid-neutralizing capacity and reduced trace elements concentrations. However, hydrologic inputs of acidic water from precipitation, stream inflow, and groundwater can cause re-acidification and an eventual deterioration in water and sediment quality (Driscoll et al. 1989). The coverage of contaminated sediments or their removal by dredging represents other approaches for which the feasibility and the cost have to be considered (Box 14.2). The dredging option requires subsequent treatment and/or disposal to reduce or eliminate the toxicity of contaminants.

Box 14.2. Ore Grade Sediments

Kelly Lake is located in the immediate vicinity of the Inco smelter. There are dumps of tailings nearby, and for many years, it has received mining and smelter effluents. Also, the lake received high atmospheric inputs of metals and trace elements, resulting in significant sediment accumulation of metals such as copper (5200 $\mu g\cdot g^{-1}$) and nickel (10,560 $\mu g\cdot g^{-1}$) but there are also significant amounts of noble metals such as platinum (1.8 $\mu g\cdot g^{-1}$), palladium (0.2 $\mu g\cdot g^{-1}$), gold (0.3 $\mu g\cdot g^{-1}$), and iridium (0.03 $\mu g\cdot g^{-1}$) in the lake sediments (Crocket and Teruta 1976). Most of the early processing methods were largely ineffective at extracting the noble metals. Considering the high value of noble metals, it might now be economically feasible to dredge and process Kelly Lake sediments to extract those metals. The challenge is to find an environmentally sound means of disposal of the extracted sediments.

Summary

Knowledge of the sedimentary processes controlling the behavior of trace elements is now good but still remains incomplete. Sediments remain a complex environment, and the contrasting behavior of some trace elements may indicate that opposite mechanisms (sedimentation/resuspension; diffusion to/from sediments; precipitation/dissolution; sorption/desorption; complexation/decomplexation) may often, in fact, operate concurrently. It is nevertheless clear that reductions of sulfur emissions greatly improved surface water quality and, consequently, sediment quality. The continuous pH increase contributes to decrease the solubility (and mobility) of trace elements through sorption processes on surficial oxic sediments. Precipitation of trace elements as sulfides that probably occur in anoxic sediments may ultimately constitute a major sink for toxic trace elements.

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