

Northwest Science Forum

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A Comment on the Future Environmental Status of Coeur d'Alene Lake, Idaho

Abstract

Coeur d'Alene (CDA) Lake sits some 80 km downstream of the Bunker Hill lead-zinc smelter complex in northern Idaho, a scenic region that is experiencing rapid population growth. As a result, there is some concern about future eutrophication and the relationship between that and the fate of dissolved and particulate heavy metals introduced to the lake via largely historic mining and smelting activities upstream. Based on recent research, the United States Geological Survey (USGS) has concluded that "most" of the metals in the sediments of CDA Lake are associated with iron oxides. Because such phases are soluble under anoxic conditions, concern has been expressed that depletion of oxygen from the deep waters in the future could permit the release to the lake waters of a significant fraction of the metals currently sequestered by the sediments, and this could have unwelcome environmental consequences. This suggestion has been published in the open scientific literature and it appears to have been accepted uncritically by an array of government entities and concerned parties. I argue here that the conclusion that "most" of the metals are associated with oxides is not supported by the data collected by USGS personnel, which invalidates the extrapolated concern about metal release. A more serious environmental insult would appear to be oxygen depletion *per se*, which is likely to occur if increased residential development is allowed to reverse the decline in nutrient inputs that has occurred over the past 15 years.

Introduction

Mining and smelting activities have been conducted for more than a century in the watershed of the Coeur d'Alene River in northern Idaho. As a result, the waters of Coeur d'Alene (CDA) Lake have for many years hosted lead and zinc concentrations well above natural levels. Recent work by the United States Geological Survey (USGS) has shown that, in addition to the water column, the sediments in the south-central part of the lake are relatively enriched in a number of metals including copper, cadmium, lead, and zinc (Horowitz et al., 1993). Chemical extractions of the deposits have been made in an effort to determine the

mode of occurrence of the metals, i.e. are they adsorbed onto particle surfaces or have they been precipitated in various discrete mineral phases that form as a result of post-depositional chemical reactions? (A third option is that the enrichments simply represent the deposition of metal-rich particles that have been carried to the lake by local rivers). Determination of the mode of occurrence is fundamental to any attempt to predict the potential future behaviour of the metals. For example, by determining whether or not the metals are coupled to certain oxide minerals or phases in the sediments, it might be possible to forecast the extent of release or uptake under certain water quality scenarios for Coeur d'Alene Lake.

One of the principal conclusions offered by Horowitz et al. (1993) is that "most of the enriched trace elements...are associated with an operationally defined Fe (iron) oxide phase". If true, such an association represents a pool of metals that could be released to the overlying lake water should future eutrophication cause the oxygen concentration to be fully depleted in deep waters. Taken at face value, this could have a temporary negative impact on water quality. However, the term "operationally defined" is critically important in drawing such a conclusion, because it refers to the experimental conditions used in the laboratory to distinguish the apparent metal-iron oxide association, and not actual conditions in the field. The results of such experiments are notoriously difficult to interpret, and they typically yield conclusions that are equivocal. The controversial nature of such work is not well known to scientists outside this field of research, and this can lead to misinterpretations of the original results. For example, the cautious but scientifically ambiguous term "operationally-defined iron oxide-metal associations" used by Horowitz et al. (1993) was incorrectly interpreted by the authors of the CDA Lake Management Plan (November, 1994, p. 23) who state conclusively that, "The vast majority of the [sedimentary] trace elements were associated with iron oxides...". It will be shown in this comment that the sample handling and laboratory techniques used by USGS personnel cast serious doubt on the validity of this conclusion. Without more scientifically rigorous and thorough research, the association imputed between oxides and metals must be viewed as speculation.

Critical Review of Previous Work

Background

An ordered sequence of post-depositional chemical reactions occurs naturally in lake sediments, and is driven by the decomposition of organic matter by bacteria. Assuming that the bottom water in the lake contains dissolved oxygen (the usual condition in most lakes year-round), organic matter on the lake floor will first be decomposed ("oxidized") by aerobic bacteria to produce carbon dioxide and water, amongst other metabolic products. Oxygen (O_2) is consumed during this reaction. Some of the organic matter that settles to the lake floor gets buried in the sediments, and supports continued bacterial metabolism below

the sediment-water boundary. If the consumption of oxygen by aerobes in shallow subsurface sediments exceeds the rate at which O_2 can migrate downward to replace that used, the oxygen content falls to zero at some sub-bottom depth. This usually occurs in lake sediments within the upper several centimetres. Once oxygen is depleted, different bacterial communities continue decomposing organic matter by taking advantage, in sequence, of the oxygen present in different "oxidizing agents". In preferred order, these are nitrate (NO_3^-), manganese oxides, iron oxides, and sulfate (SO_4^{2-}). Important products of the decomposition reactions in the sediments are dissolved manganese, dissolved iron, and dissolved hydrogen sulphide. Thus, with increasing depth in the pore waters in the sediments, an observer could expect to see, in order, the disappearance of oxygen, the disappearance of nitrate, the appearance of dissolved manganese, the appearance of dissolved iron, and the appearance of dissolved hydrogen sulfide.

There are some complications in this basic picture, however. Dissolved manganese and iron both react with oxygen to form their respective oxides. The upward migration of the dissolved elements through the pore waters from the depths at which they are released to solution will support precipitation of manganese and iron oxide phases near the sediment-bottom water interface where dissolved O_2 is present. Over time, as sedimentation continues, these oxides get buried, only to be redissolved and again migrate upwards to repeat the cycle. This "diagenetic cycling" phenomenon causes the oxides to accumulate just below the sediment-water interface, in the so-called "aerobic zone". In much of Coeur d'Alene Lake this zone appears to be <1 to ~3 cm thick, based on available data.

Manganese and iron oxides effectively adsorb a wide range of dissolved metals from solution. The trace metals, zinc and lead, for example, can be adsorbed onto such phases near the sediment surface, and released to solution upon burial and dissolution of the oxides. This will support upward migration of the dissolved trace metals, and possible release to the overlying lake water, although this will be countered by readsorption onto freshly-precipitating manganese and iron oxides in the aerobic zone. Thus, metals such as zinc and lead tend to cycle, at least partly, with the major oxide phases during diagenesis

In the natural aging cycle of lakes, progressive infilling leads gradually to increases in dissolved nutrients which support the growth of plankton. Human activities, such as the input of sewage or runoff from agricultural areas, can greatly accelerate this natural process. Such "artificial" inputs can increase the plankton growth to the point where the enhanced settling of dead organic matter to the lake floor leads to oxygen depletion in the deep waters. One consequence of this is clear: the oxide phases in the surface sediments will dissolve progressively when the aerobic zone disappears, potentially releasing dissolved metals directly to the lake water. It is for this reason that the USGS thought it important to determine the proportions of zinc and lead that are associated with oxides in Coeur d'Alene Lake sediments. In the following section, the approach used by USGS scientists to make such determinations is critically assessed.

Chemical Extraction Studies

It is very difficult to determine with any degree of confidence the proportions of trace metals associated with various components in aquatic sediments. Most investigators who attempt such studies use the sequential extraction scheme developed about seventeen years ago by Andre Tessier and his colleagues (Tessier et al., 1979). In the application of the method, a sediment sample is subjected to a progressive five-step chemical attack in which the sample is exposed to increasingly stronger chemical compounds. The amounts of the trace metals of interest removed at each step are determined by chemical analysis of the extract solutions. Five fractions among which a given trace metal may be partitioned are defined by the approach of Tessier et al (1979):

1. Exchangeable fraction: includes metal ions loosely sorbed on particle surfaces, extracted using $MgCl_2$ or sodium acetate solutions at room temperature and at neutral pH.

2. Carbonate fraction: includes metals associated with carbonate phases, and thus susceptible to release under acid conditions. This fraction is extracted by exposing the residue from step 1 to a weak acetic acid-sodium acetate solution at room temperature.

3. Iron- and manganese-oxide-bound fraction: includes metals strongly adsorbed by oxides. The residue from step 2 is attacked with hydroxylamine

hydrochloride in acetic acid at 96 °C. This is a chemically reducing solution which is designed to mimic the anoxic (oxygen-free) conditions seen in natural sediments below the aerobic zone.

4. Organic-matter-bound fraction: includes trace metals bound to organic matter. The residue from step 3 is exposed to a multi-reagent solution containing HNO_3 and H_2O_2 .

5. Residual fraction: the residue from step 4 is fully dissolved in a very strong acid mixture.

One of the major concerns associated with application of the sequential extraction technique is the degree to which the method simulates natural processes. For example, the strong reagents and fast reactions inherent to the approach differ drastically from the weak reagents and slow kinetics typically found in nature. The specificity of the individual reactions is also controversial. The amount of metal extracted at each step is a complex function of the extraction reagent type and concentration, the sequence of application, temperature, exposure time, extent of readsorption, and the solid to solution ratio. Thus, the extracts are termed "operationally defined" (Tessier, et al., 1989), which means that the fractions to some degree reflect the experimental conditions employed, rather than true geochemical partitioning. Nevertheless, partial extractions can be used pragmatically in sediment geochemistry studies if they are applied with discrimination and care. The scientific danger lies in the uncritical use of such techniques and in over-interpretation of the results.

It is very important in partial extraction work to ensure that the integrity of the samples is not compromised by improper collection and handling. For example, exposure of anoxic sediments to the atmosphere can induce perturbations in the natural partitioning of metals. To avoid introducing such artifacts, anoxic sediments should be kept in an anaerobic atmosphere throughout the entire manipulation and extraction procedure.

The approach used by Horowitz et al. (1993) to determine trace metal partitioning in CDA Lake sediments suffers in three areas. First, Tessier et al. devised their scheme for use on oxic, surface sediments, *not* for application to anoxic sub-surface deposits. Second, no effort was made to keep the samples isolated from contact with the atmosphere. Third, application of the partial extraction technique did not follow carefully established

protocols. Near-surface sediments (upper 2 cm) were collected with an Ekman Dredge sampler, and subsampled in air. This may not have chemically biased the samples if the deposits were fully oxidized, but Horowitz et al. (1993, p. 409) note that "many of the samples obtained from the main body of Lake CDA had very thin (of the order of a few millimetres) surface veneers of reddish, fine-grained material...". Iron oxides invariably contribute such a reddish coloration. The absence of this hue just below the surface implies that anoxic conditions are established at very shallow depths. The sediment samples were subsequently kept cool on ice, shipped to Atlanta, and kept cool until processed and analysed sometime later. The processing included stirring (in air) with a glass rod (to homogenize the sample), sieving to remove large material such as wood chips, and freeze-drying. Considering that there is roughly 10,000 times more oxygen in the atmosphere than in lake bottom waters (largely because oxygen is poorly soluble in water), anoxic sediments can be rapidly oxidized when exposed to air, particularly when they are wet. Thus the handling of the samples could have altered their composition, for example by permitting oxidation of metal sulphide minerals. Such effects would bias subsequent extractions and lead to an overestimation of the content of oxide-hosted metals. Even if anoxic sediments remained unoxidized after the many handling steps, the extractions would still produce misleading results. This is because a number of sulfide minerals that are stable under anoxic conditions will be dissolved progressively in steps 2 and 3 of the Tessier et al. method. In order to reduce such uncertainties, a much more rigorous sample handling procedure would be required.

The manner in which chemical extraction techniques were used and interpreted by Horowitz et al. (1993) is problematic. Rather than conduct the five-step procedure designed by Tessier et al. (1979), only two steps were used. In the first, dried unground sample aliquots were exposed to hydroxylamine-hydrochloride in hydrochloric acid (HCl) at 50 °C for thirty minutes. This is similar to the solution used in Step 3 above, and it would have extracted, operationally, exchangeable metals,

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carbonate-hosted metals, some fraction of the metal inventory hosted by Mn and Fe oxides, and metal monosulfides, which readily dissolve in HCl. Tessier et al. (1989, p. 1516) note that hydroxylamine hydrochloride is reasonably selective in dissolving Fe and Mn from their oxyhydroxide forms, and releasing associated trace metals, *provided that carbonates have been previously removed* (italics added). Since the latter condition was not satisfied, and it is not known whether or not sulfides were present, it is misleading to make the statement, "Most of the lead (~95%) cadmium (~90%), Zn (~80%) arsenic (~75%) and copper (~55%) appear to be associated with an operationally-defined iron oxide phase..." (Horowitz et al., 1993, p. 418). Distinguishing between carbonate, sulphide and oxide hosts is important, because carbonate and sulphide phases will not dissolve under anoxic conditions, but oxides will.

A Point for Reflection

Determining the hosts for metals in contaminated sediments is a difficult scientific problem. In the case of Coeur d'Alene Lake, I suggest that it remains an open question. Even if iron oxides do turn out to be a significant host for metals on the floor of the lake, the postulated release of dissolved metals from the sediments to the overlying water under anoxic conditions remains hypothetical. In my view, the main threat to the future health of the waters and biota of the lake is the development of seasonal anoxia associated with eutrophication. To ensure that this scenario does not develop as a consequence of ongoing development pressures, continuing and perhaps more stringent constraints on inputs of phosphorus will be needed. Control of nutrient fluxes should be the primary focus of current management action in order to ensure that oxygen levels necessary for a healthy lake are maintained.

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