Response to Comment on "Phase Associations and Mobilization of Iron and Trace Elements in Coeur d'Alene Lake, Idaho"

SIR: We thank the Editor for the opportunity to respond to concerns voiced by Horowitz, Elrick, and Cook (*1*) regarding our March 1998 research communication (*2*). These concerns appear to center around three issues: acknowledgment of the scope of their efforts (*3–5*), reservations expressed by ourselves and others (*6*) as to their sample processing methods, and discrepancies between our respective data sets as to the phase associations of iron and trace elements in Coeur d'Alene Lake (CDA). On the basis of their observations, Horowitz et al. (*3–5*) conclude that sulfides form a small fraction of CDA Lake bed sediments and that those sulfides present are of detrital rather than authigenic origin.

In the early 1990s Horowitz and colleagues extensively sampled bed sediments throughout CDA Lake. The results of these efforts are detailed in peer-reviewed publications and government documents (*3–5,7*). Our recent communications on CDA Lake sediment biogeochemistry (*2, 8*) note the scope of these efforts. While the problem of heavy metal contamination in the Coeur d'Alene Basin has been recognized for more than half a century (*8*), it is the research of Horowitz et al. (*3–5, 7*) which brought to light the full extent of contamination within the lake itself.

We still maintain concern over the issue of how sample processing can affect the outcome of sediment analyses. Horowitz et al. (*3–5, 7*) determined that a majority of metals were bound in oxide phases. This finding may be explained by the handling practices to which their surface and deeper sediments were exposed: aerobic handling in the field, aerobic handling in the lab, and aerobic extraction. Minerals containing reduced constituents such as ferrous iron or sulfide, particularly freshly formed amorphous sulfides that are common in such environments, are easily oxidized when oxygenated (*10*). Horowitz et al. (*3*) found that the majority of the metals were contained in relatively small particles, a size most susceptible to rapid oxidation. Horowitz et al. also reported an oxide rind on many of their larger particles (*3*), an observation suggesting postremoval oxidation. Anoxic sediments when processed using standard anaerobic techniques will generally not show these features. Further, it seems to be circular reasoning to examine sediments under oxygenated conditions, observe that the materials are of an oxide nature, and then support the handling procedures on the basis of finding only oxidized materials.

Sulfur speciation and relative abundance were not performed on the core materials described in (*2*). Such analyses will be essential to elucidate the details of iron and sulfur cycling in this environment. However, we have both published and preliminary data which suggests that authigenic sulfidogenesis is occurring in CDA Lake sediments. First, numbers of cultivable sulfate reducing bacteria (SRB) approach 10^6 cells/g wet weight sediment, even in the top 10 cm of CDA Lake sediments (*8*). Second, when additional deep sediment cores from CDAL were analyzed by our methods, the mean percentages ($\pm$SD) of Pb, Zn, and As associated with the perchloric acid-extractable fraction were

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TABLE 1. Acid-Volatile Sulfide and Simultaneously Extracted Metals in Lake Coeur d'Alene Sediments

	CDA delta	CDA Lake	St. Joe delta
AVS (μmol/g dry wt)			
mean	2.31	1.35	0.45
std dev	1.47	0.59	0.84
range	0.63–5.59	0.40–2.41	bdl–2.40[a]
N	34	34	34
SEM (units)			
mean	5.58	9.53	1.87
SEM:AVS ratio	2.4	7.1	5.8

[a] bdl = below detection limit.

51% (*13*), 66% (*10*), and 41% (*10*), respectively. Finally, in July 1998 we assayed three deep sediment cores for acid volatile sulfide (AVS) and simultaneously extractable metals (SEM). One core was obtained from the CDA River delta, one from CDA Lake proper, and one from the pristine St. Joe River delta at the southern-most end of the lake. Cores were transported and processed anaerobically as described (*2, 8*), and AVS and SEM were assayed at 4 cm depth intervals using standard protocols (*11, 12*). The mean concentrations of AVS in CDA delta and CDA Lake (Table 1) are markedly higher than those reported for other oligotrophic freshwater lakes and are as high or higher than values reported for estuarine sediments (*13*). Since fine-grained, amorphous sulfides are expected to be the most readily oxidized, it is unlikely that these materials have been transported into the lake. It is more probable that they are of authigenic origin. Significantly, the relatively high SEM values and SEM:AVS ratios indicate that despite elevated AVS concentrations there is still a large fraction of metals in CDA sediments that is potentially bioavailable.

Horowitz et al. (*1*) express doubt that lake bottom waters having sulfate values of $1.0–6.6$ mg L^{-1} can support significant biotic sulfidogenesis. These low values may themselves be evidence that CDA Lake sediments act as a sulfate sink. Furthermore, it has been suggested that the rate and extent of sediment sulfidogenesis may not be easily predicted from estimates of aqueous sulfate. In studying an oligotrophic lake in northern Wisconsin, Urban et al. (*14*) observe sediment sulfate reduction rates far higher than can be accounted for by sulfate diffusion from overlying waters. They conclude that sulfur oxidation occurs—even in anaerobic sediments. The mechanism(s) underlying this phenomenon likely involve both abiotic and biotic processes including bacterial sulfur disproportionation (*15*) in the presence of Fe and Mn oxides. Our lab is currently engaged in a project aimed at characterizing the Lake CDA sediment microflora. Of 12 anaerobic enrichment cultures initiated with sediments taken from various depths at two sites in the CDA delta, all 12 demonstrated the ability to disproportionate elemental sulfur within 14 days and thiosulfate within 28 days (*16*). Such organisms could be expected to generate sulfate from organic or elemental sulfur, with sulfate subsequently being reduced to sulfide by resident SRB.

How might we account for the discrepancy between data presented in refs *2* and *3–5, 7*? Flotation or density measurements can be very useful methods for defining mineral fractions within well crystallized materials, such as those contained in materials of geological origin (igneous, metamorphic, or sedimentary rocks). Unfortunately, authigenic materials within lake or river sediments may not be conducive to such measurements for a number of reasons.

First, meta-stable phases are the rule rather than the exception in active surface environments (*17*, *18*) resulting in hydrated phases that are often poorly crystalline and very fine grained. As a result of their hydrated and porous structure, the density of such phases is much lower than predicted based on well crystallized, large grained materials of similar chemical composition. Furthermore, iron monosulfides are precursors to the development of pyrite (e.g., ref *19*) under many environments and will again usually be expressed as small, fined grained amorphous materials that have a lower density than expected for well crystallized pyrite. Finally, an additional source of error in density measurements arises from the possibility of heterogeneous nucleation within soil and sediment environments. Heterogeneous rather than homogeneous precipitation is likely because of the diminished nucleation energy (*18*) and is commonly observed in freshwater systems (*20*). Surface coatings of hydrous iron oxides, sulfides, or carbonates may occur on the aluminosilicate matrix that dominates the solids of the CDAL sediments. The contribution of the aluminosilicate core in the heterogeneous materials could result in misleading density measurements when compared to pure mineral phases. The findings by Horowitz et al. (*3*) of predominantly light fraction material in these sediments does not therefore necessarily contradict the observation that a large proportion of metal is associated with an operationally defined sulfide fraction.

In conclusion, Horowitz et al. (*3*−*5*, *7*) have made important contributions toward documenting the extent of iron and trace element enrichment in Coeur d'Alene Lake. We nevertheless contend that the handling of anaerobic sediments can have significant impact on the outcome of chemical and densitometric analyses. We also believe that to the extent that CDA Lake sediments have undergone diagenetic transformations, densitometric analyses can be misleading. Finally, the repeated observation of large amounts of perchloric acid extractable metals, the magnitude of AVS in CDA Lake sediments, and the extraordinary numbers of cultivable sulfate reducers in this environment all support the hyopthesis that biotic sulfur cycling is a significant process in CDA Lake sediments. This hypothesis may help explain the observation that although these sediments are highly enriched in Pb, Zn, As, and other metal(loid)s, the overlying waters continue to comply with Federal drinking water standards (*21*).

Acknowledgments

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