BIOTURBATION AND THE OXIDATION OF SULFIDE IN SEDIMENTS

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ABSTRACT—The effects of oxygen diffusion and biodegradation of natural organic material on the development of a sulfide-free layer in an iron sulfide-containing sediment were investigated by means of mathematical models. The presence of FeS immobilizes most toxic heavy metals as insoluble sulfides. Molecular diffusion of O_2 into the sediment is sufficiently slow that it is unlikely to mobilize significant quantities of toxic metals unless they are concentrated in a very thin layer at the top of the sediment. However, modeling of bioturbation (the mixing of sediment by action of the macrobiota—worms, clams, etc.) indicates this can be a potential problem. Bioturbation constants at the upper end of the commonly accepted range (3×10^{-12} to 3×10^{-9} m^2/sec) result in the relatively rapid destruction of FeS even when organic matter is present in the sediment.

Measurements of acid-volatile sulfide (AVS) and simultaneously extractable metals (SEM) to assess the potential toxicities of sediments contaminated with heavy metals has been proposed and discussed by DiToro and his coworkers (1990, 1991, 1992), by Ankley and his collaborators (1991, 1993), by Carlson et al. (1991), and by Zhuang et al. (1994). Howard and Evans (1993) have discussed the seasonal and spatial variations in AVS in sediments from a seasonally anoxic lake.

The analytical methodology involved in determining SEM/AVS ratios has been presented in detail by Allen et al. (1993) and in a draft analytical method authored by Allen et al. (1991).

More recently, Dilks et al. (1995) reviewed the general problem of the binding of metals in sediments, including the impact of sulfides. These authors also presented a model for the interaction of sulfide simultaneously with Cd, Pb, Zn, Ni, and Cu.

Here we first briefly review the rationale for the use of SEM/AVS ratios in assessing the potential toxicity of metal-containing sediments. Then we discuss some simple models for the diffusion of dissolved oxygen into organic-containing sediments. This is followed by the development of a model for the investigation of the effects of bioturbation (churning and dispersion of sediment by the bottom macrobiota) on the distribution of sulfide in sediments. The last section deals with results and conclusions.

RATIONALE FOR USE OF SEM/AVS RATIOS IN ASSESSING SEDIMENT TOXICITY

In this section we first review the impact of the presence of excess solid FeS in the sediment on the solubility and bioavailability of a representative toxic heavy metal, cadmium. We then turn to the effect of pH on sulfide solubilities. The analysis presented here is simplified from that presented in DiToro et al. (1991) in that all thermodynamic activity coefficients are assumed to be unity; this makes the analysis easier to follow and does not result in any logical inconsistencies. This is followed by discussion of the thermodynamics of the reactions of solid metal sulfides with dissolved oxygen. Equilibrium constants and

thermodynamic data were taken from Atkins (1989) and Moeller et al. (1984). Two simple models for the diffusion of dissolved oxygen into biologically active organic-containing sediments from the overlying water column are then examined. The section closes with a number of caveats with regard to the uncritical interpretation of SEM/AVS ratios.

Effect of Excess Solid FeS on Cd Availability—In anoxic sediments there is commonly a substantial reservoir of sulfide in the form of solid FeS. This keeps the solubilities of such toxic metals as Cd, Cu, Hg, Pb, Ni, Zn, and Ag at quite low levels, since the solubility products of their sulfides are all much smaller than that of FeS. The analysis showing this for Cd is as follows. Similar calculations for the other heavy metals produce similar results.

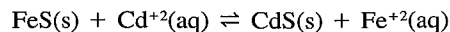The solubility products for the reactions

$$FeS(s) \rightleftharpoons Fe^{+2}(aq) + S^{-2}(aq) \quad \text{and}$$

$$CdS(s) \rightleftharpoons Cd^{+2}(aq) + S^{-2}(aq)$$
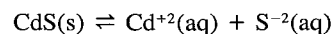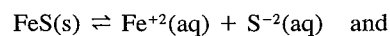
are

$$K_{FeS} = 4.2 \times 10^{-17} = [Fe^{+2}][S^{-2}] \quad \text{and}$$

$$K_{CdS} = 2 \times 10^{-28} = [Cd^{+2}][S^{-2}]$$

The equilibrium constant for the reaction

$$FeS(s) + Cd^{+2}(aq) \rightleftharpoons CdS(s) + Fe^{+2}(aq)$$

is given by

$$K = \frac{[Fe^{+2}]}{[Cd^{+2}]} = K_{FeS}/K_{CdS} = 2.1 \times 10^{11}$$

So, if solid FeS is present, the equilibrium molar concentration of dissolved cadmium can be no larger than
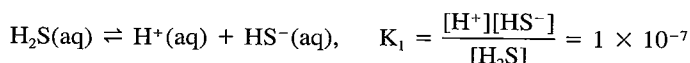
$$[Cd^{+2}] = 4.8 \times 10^{-12}[Fe^{+2}]$$

Evidently the concentrations of dissolved Cd in anoxic sediments containing FeS(s) will invariably be extremely small. If solid MnS, a relatively soluble sulfide, is present the situation is similar.

Effect of pH on the Solubilities of Metal Sulfides—In order to use the above result, we must have a method for calculating $[Fe^{+2}]$. We carry out the analysis for a generic divalent metal, M^{+2}, then examine the solubilities of CdS and FeS as they depend on the pH of the aqueous phase.
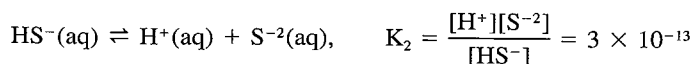
Consider the solution of a metal sulfide MS, represented by

$$MS(s) \rightleftharpoons M^{+2}(aq) + S^{-2}(aq), \qquad KMS = [M^{+2}][S^{-2}]$$
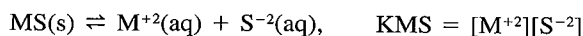
Hydrogen sulfide, H_2S, is a weak acid, with ionization reactions

$$H_2S(aq) \rightleftharpoons H^+(aq) + HS^-(aq), \qquad K_1 = \frac{[H^+][HS^-]}{[H_2S]} = 1 \times 10^{-7}$$

and

$$HS^-(aq) \rightleftharpoons H^+(aq) + S^{-2}(aq), \qquad K_2 = \frac{[H^+][S^{-2}]}{[HS^-]} = 3 \times 10^{-13}$$

Multiplying these last two equations together gives

$$K_1K_2 = \frac{[H^+]^2[S^{-2}]}{[H_2S]} = 3 \times 10^{-20}$$

Solving this for $[S^{-2}]$ gives

$$[S^{-2}] = \frac{K_1K_2[H_2S]}{[H^+]^2}$$

From the solubility product expression for MS we have

$$[M^{+2}] = \frac{K_{MS}}{[S^{-2}]} = \frac{KMS[H^+]^2}{K_1K_2[H_2S]}$$

as the expression for the concentration of M in contact with its solid sulfide MS. In aqueous solutions saturated with hydrogen sulfide at 1 atm, $[H_2S] = 0.1$ mol/l, approximately.

At a pH of 6, $[H^+] = 10^{-6}$ M, and at an $[H_2S]$ of 0.01 M the solubility of Fe^{+2} is given by

$$[Fe^{+2}] = \frac{4.2 \times 10^{-17} \times (10^{-6})}{3 \times 10^{-20} \times 0.01} = 1.4 \times 10^{-7} \text{ M}$$

In similar fashion, the dissolved Cd(II) concentration under these conditions is

$$[Cd^{+2}] = 6.7 \times 10^{-19} \text{ M}$$

which is vanishingly small.

In 1 M $[H^+]$, the conditions of the AVS/SEM protocol, one finds that the $[Fe^{+2}]$ is sufficiently large that all of the FeS must have dissolved. The $[Cd^{+2}]$ is given by

$$[Cd^{+2}] = \frac{2 \times 10^{-28} \times (1)^2}{3 \times 10^{-20} \times 0.01} = 6.7 \times 10^{-7} \text{ M} = 0.075 \text{ mg/l}$$

This indicates that if the initial total sediment Cd concentration was appreciable, the treatment provided by the AVS/SEM protocol may not dissolve all the solid CdS. If the final $[H_2S]$ is 0.001, the aqueous cadmium concentration is increased to 7.5 mg/l. Even more of the HgS and CuS initially present are likely to remain undissolved under the AVS/SEM protocol. Allen et al. (1993) have found experimentally that CuS and pyrite are not dissolved under the conditions of the AVS analysis. Such undissolved metal sulfides contribute to neither the AVS nor the SEM measurements. As long as the sediments remain anoxic, these sulfides are not dissolved by the acid treatment and can be regarded as bound and inert. The more soluble sulfides, such as FeS and MnS, however, are dissolved, yielding both M^{+2} and H_2S.
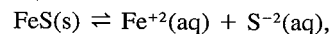
TABLE 1. Solubility products for heavy metal sulfides

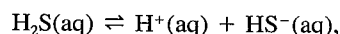| Metal sulfide	$K_{MS} = [M^{+2}][S^{-2}]$
CdS	2×10^{-28}
CuS	6×10^{-36}
FeS	4.2×10^{-17}
HgS	4×10^{-53}
NiS	3×10^{-19}
PbS	1×10^{-28}
ZnS	2×10^{-24}

The solubility products of the heavy metals and most of the transition metals (with the exception of Mn) are substantially less than that of FeS (Table 1, or Table 2 in DiToro et al., 1992). Therefore, if acid treatment yields a total molar concentration of dissolved M^{+2} (less Fe^{+2} and Mn^{+2}) that is less than the molar concentration of H_2S calculated for the solution from the quantity of H_2S recovered by acid treatment and sparging, one has more than enough sulfide present to bind all of these metals (except for iron and manganese) as insoluble sulfides. This is the rationale behind the use of SEM/AVS ratios in sediment toxicity estimation. If there is more than enough sulfide to bind the environmentally significant metals, they will remain immobile and nontoxic. This is verified by the findings reported by DiToro et al. (1990, 1991, 1992), Ankley et al. (1991, 1993), Carlson et al. (1991), and Zhuang et al. (1994).

However, some sediments for which the SEM/AVS ratios are greater than unity also are observed to be nontoxic. (DiToro et al., 1992; Ankley et al., 1993). This is because toxic metals may be immobilized by other mechanisms than conversion to insoluble sulfides. Adsorption on clays, on hydrous Fe and Mn oxides, and on naturally occurring organic material may contribute to the immobilization of toxic metals (Dilks et al., 1995).
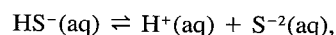
An alternative approach to the impact of pH on the solubilities of toxic metals in sediments containing excess solid FeS is as follows. The reactions of interest are

$$FeS(s) \rightleftharpoons Fe^{+2}(aq) + S^{-2}(aq),$$

$$K_{FeS} = [Fe^{+2}][S^{-2}] = 4.2 \times 10^{-17}$$

$$H_2S(aq) \rightleftharpoons H^+(aq) + HS^-(aq),$$

$$K_1 = \frac{[H^+][HS^-]}{[H_2S]} = 1.0 \times 10^{-7}$$

$$HS^-(aq) \rightleftharpoons H^+(aq) + S^{-2}(aq),$$

$$K_2 = \frac{[H^+][S^{-2}]}{[HS^-]} = 3 \times 10^{-13}$$

It is assumed that solid FeS is present and the pH of the water in the sediment is known. From the stoichiometry of the reactions we have

$$[Fe^{+2}] = [H_2S] + [HS^-] + [S^{-2}]$$

From the equilibrium equations for H_2S we obtain

$$[HS^-] = [H^+][S^{-2}]/K_2 \quad \text{and}$$

$$[H_2S] = [H^+][HS^-]/K_1 = [H^+]^2[S^{-2}]/K_1K_2$$

Substitution into the stoichiometry relationship gives

TABLE 2. Heavy metal concentrations (mg/1) in equilibrium with FeS at various pH values.

| Metal sulfide | KMS | pH | | | | |
		5	6	7	8	9
CdS	2×10^{-28}	2.0×10^{-10}	2.0×10^{-11}	2.0×10^{-12}	2.0×10^{-13}	2.0×10^{-14}
PbS	1×10^{-28}	1.8×10^{-10}	1.8×10^{-11}	1.8×10^{-12}	1.8×10^{-13}	1.8×10^{-14}
CuS	6×10^{-36}	3.4×10^{-18}	3.4×10^{-19}	3.4×10^{-20}	3.4×10^{-21}	3.4×10^{-22}
Ag_2S	7×10^{-50}	8.7×10^{-14}	2.7×10^{-14}	8.7×10^{-15}	2.7×10^{-14}	8.7×10^{-16}

$$[Fe^{+2}] = [S^{-2}] \cdot \{ 1 + [H^+]/K_2 + [H^+]^2/K_1K_2 \}$$

Substitution of this result into the solubility product expression then gives

$$K_{FeS} = [S^{-2}] \cdot \{ 1 + [H^+]/K_2 + [H^+]^2/K_1K_2 \}$$

from which

$$[S^{-2}] = \left[\frac{KFeS}{1 + [H^+]/K_2 + [H^+]^2/K_1K_2} \right]^{1/2}$$

The aqueous molar concentration of a toxic metal ion M^{+2} is then given by

$$[M^{+2}] = K_{MS}/[S^{-2}]$$

Some illustrative results are given in Table 2. Evidently as long as solid FeS is present in the sediments these toxic heavy metals will be immobilized.

Thermodynamics of Sulfide Oxidation—What happens, however, if the sediments should become oxic? For this we examine the thermodynamics of the reaction

$$CdS(s) + 2O_2(g) \rightarrow Cd^{+2}(aq) + SO_4^{-2}(aq)$$

ΔG_0 −156.5   0   −77.61   −744.53 kJ/mol
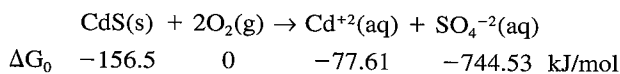
The standard Gibbs free energies of formation of the reactants and products are as indicated, from which the standard Gibbs free energy change of the reaction is −665.6 kJ/mol, demonstrating that thermodynamically this is an extremely spontaneous reaction.

One obtains similar results for other heavy metal sulfides (Table 3). Oxidation of the solid metal sulfide to the aqueous metal sulfate by O2 is very spontaneous thermodynamically. This is consistent with the fact that sulfide ores are readily converted

TABLE 3. Standard free energies of reaction for the oxidation of some heavy metal sulfides, MS(s) + 2 $O_2(g)$ → $MSO_4(aq)$.

Metal Sulfide	ΔG_o(kJ/mol)
CdS	−665.6
CuS	−625.4
FeS	−723.0
HgS	−532.4
NiS	−710.6
PbS	−670.3
ZnS	−690.3

to oxides, carbonates, etc., on exposure to the atmosphere (i.e., weathering) (Carpenter and Hayes, 1976; US EPA, 1976; Archer et al., 1988; Klusman and Edwards, 1977). The conclusion is that metals are immobilized as sulfides only as long as they are in anoxic environments. This is in agreement with the results reported by Zhuang et al. (1994); aeration of sediments containing cadmium for one month results in a large decrease in AVS and a substantial increase in dissolved metals. This increase is moderated by the adsorption of some of the released metals by the hydrous oxides of iron and/or manganese that are formed; however, 200–400% increases were observed, indicating that the binding capacities of sediments for metals decreases substantially on aeration.

Diffusion of Oxygen into Biologically Active Sediment Layers—One of the mechanisms by which oxygen can be transported into sediments is by simple molecular diffusion. Here we examine the contribution of molecular oxygen diffusion. It is assumed that the sediment contains organic material that consumes oxygen during biodegradation.

Let us consider a planar layer of sediment of large thickness containing organic material or other biological oxygen demand and aerobic and/or facultative microorganisms. Let $C(x,t)$ be the dissolved oxygen concentration in the sediment at a depth below its surface x at time t. Then, if we assume oxygen uptake to be first order in $[O_2]$,

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - kC \tag{1}$$

where D = diffusivity of oxygen in the sediment, m^2/sec, and k = first-order rate constant for oxygen uptake, sec^{-1}. Also, C_o = dissolved oxygen (DO) concentration at $x = 0$, kg/m^3, equal to the DO concentration of the overlying water. In the steady state, this equation becomes

$$0 = D\frac{d^2 C}{dx^2} - kC \tag{2}$$

the desired solution to which is

$$C(x) = C_o * \exp[-(D/k)^{1/2}x] \tag{3}$$

Evidently, the characteristic length associated with the system is

$$L_{diff} = (D/k)^{-1/2} \tag{4}$$

If we estimate $D = 10^{-10}$ m^2/sec and $k = 1$ $day^{-1} = 1.16 \times 10^{-5}$ sec^{-1}, then L = 3 mm, and we can expect a sulfide-free layer on the top of the sediments of the order of a cm in thickness.

If oxygen consumption is zero order, then equation (2) becomes

$$0 = D\frac{d^2C}{dx^2} - k' \tag{5}$$

where k' is the rate of oxygen consumption (kg/m³ sec). The general solution to this equation is

$$C(x) = (k'/2D)x^2 + c_1x + c_2 \tag{6}$$

One boundary condition is that

$$C(0) = c_2 = C_o, \tag{7}$$

where C_o is equal to the sediment porosity times the DO concentration in the overlying water column.

A second constraint is obtained by the requirement that the flux of oxygen into the sediment at the top ($x = 0$) must be equal to the total rate of oxygen consumption in the oxic layer of sediment, of as yet unknown thickness L. This yields

$$D\frac{dC(0)}{dx} = -Lk' = Dc_1 \tag{8}$$

so

$$c_1 = -Lk'/D \tag{9}$$

Then

$$C(x) = (k'/2D)x^2 - (k'L/D)x + Co \tag{10}$$

Since L is the thickness of the sulfide-free layer we must have $C(L) = 0$, which gives after rearrangement

$$L = (2DCo/k')^{1/2} \quad \text{and} \tag{11}$$

$$C(x) = (k'/2D)x^2 - (2k'Co/D)^{1/2}x + Co \tag{12}$$

If we assume that $k' = 1$ mg/1 day, Co = 8 mg/l, and D = 2×10^{-10} m²/sec, we find that the oxic layer is about 0.52 cm in thickness.

In either case, no sulfides will be present in this thin oxic layer. Therefore, toxic metals cannot be immobilized as sulfides here, although they may possibly be immobilized in adsorbed form or as hydrous oxides or carbonates, etc. They may be expected to diffuse to regions of lower concentrations both up to the overlying water and down to the anoxic sediments, where they will be tied up as solid sulfides.

If the sediment is exposed to oxygen for a sufficiently long time, the biodegradable organics in the upper layers may be destroyed, in which case one can expect substantially thicker sulfide-free layers than are calculated above. This point was explored by investigating numerical and approximate solutions to equations (13) and (14).

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - kC \cdot S(BOD) \tag{13}$$

$$\frac{BOD}{t} = -kC \cdot S(BOD) \tag{14}$$

where BOD = sediment BOD concentration, kg O_2/m^3 of sediment and the function S(BOD) is defined as a unit step function,

$$S(BOD) = \begin{cases} 1, & BOD > 0 \\ 0, & BOD \leq 0 \end{cases}$$

It is assumed that BOD removal is first order in oxygen and zero order in BOD. For $k = 1$ day⁻¹, D = 10^{-10} m²/sec, initial BOD concentration = 1000 mg/kg of sediment, the rate of growth of the BOD-free layer was extremely slow, of the order of a few cm per decade. These results are in excellent agreement with an independent approximate treatment that assumes steady states for oxygen in the BOD-free and BOD-containing layers. Therefore we conclude that combined molecular diffusion of oxygen and oxidative depletion of BOD in the sediments can be neglected in considering the reoxygenation of sediments unless the sediments are extremely poor in BOD. Only the thin oxic boundary layers discussed above are likely to result from diffusion of oxygen.

Howard and Evans (1993) observed significant spatial-temporal variability in sediment AVS concentrations in three lakes. Dilks et al. (1995) note the marked differences in the behavior of oxic surface sediments and anoxic deeper sediments with respect to metal binding. In the surface (oxic) layer, binding primarily is to organic matter and hydrous Fe and Mn oxides. An oxygen transport process of some sort is well-known experimentally which appears to be substantially more efficient than the simple molecular diffusion of oxygen into the sediments.

Given our estimates for the thickness of the oxic layer and information on the concentrations of heavy metals, one can estimate the flux of heavy metals into the overlying water column to ascertain the extent of the risk generated. This risk is likely to be quite small if only diffusion is operative, but the experimental results indicate this may well not be the case.

DEVELOPMENT OF A MODEL FOR BIOTURBATION EFFECTS ON SULFIDE-CONTAINING SEDIMENTS

Here we present a simple model for the oxidation of sulfide in sediment undergoing bioturbation and containing iron and organic material. Mass transport of all species in the sediment is assumed to take place by bioturbation. Bioturbation is defined by Thibodeaux (1996) as the mixing of surface and near-surface sediments by the activities of benthic organisms such as worms, molluscs, crustaceans, etc. This may involve crawling or plowing through the sediments, burrowing into them, and ingestion and excretion of sediments. The geometry of the system is represented in Fig. 1. These bioturbation processes are assumed to be effective down to a specified depth below the surface of the sediment, below which mass transport of any sort can be neglected. Thibodeaux (1996) reports this as being of the order of 17 to 40 cm. Oxygen is assumed to be present at a constant concentration in the water overlying the sediment. In this model, no replenishment of the sediment is assumed during the course of a simulation. For information on sediment deposition rates see Thibodeaux (1996) or Stumm and Morgan (1996).

The objective is to gain insight into the conditions that one can expect in sediments containing sulfur species, and how these conditions can be expected to evolve with time. Specifically, we wish to know the rate at which the thickness of the oxic layer below the water column-sediment boundary increases with time.

The sulfide-metal-oxygen-carbonate system is quite complex. It quickly became apparent that including detailed treatments of all the chemical processes occurring and all of the aqueous species present in a model in which bioturbation is to be represented by distributed dispersion was computationally beyond our means. We therefore relied on information in Stumm and Morgan's book (1996) to simplify the system as much as possible without excluding any of the essential processes.

Analysis—The following species are assumed to be present in the sediment:

FeS—The only form of sulfidic sulfur assumed to be present.

It is assumed that the concentrations of such dissolved species as H_2S and HS^- are sufficiently low that these can be neglected in the calculations.

$FeCO_3$—It is assumed that $FeCO_3$ is present when sulfide is oxidized to sulfate and there is insufficient oxygen to oxidize Fe(II) to Fe(III). $FeCO_3$ is generally less soluble than $Fe(OH)_2$ under ambient conditions in sediments (Stumm and Morgan, 1996), and CO_2 is available from biodegrading organic matter.

Fe_2O_3—The extremely low aqueous solubility of hydrous ferric oxide under oxidizing conditions make it the obvious choice for the Fe(III) species (Stumm and Morgan, 1996).
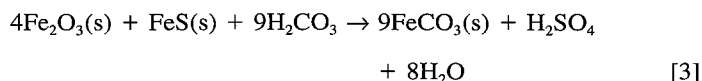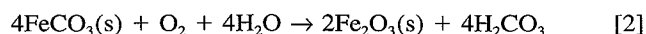
CH_2—This formula is simply a generic representation of bio-degradable organic matter.

H_2SO_4—Represents all forms of S(VI). Sulfate is assumed to be soluble and can be lost by diffusion to the overlying water column or by biomediated reduction to sulfide in the absence of oxygen and Fe(III).
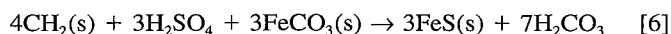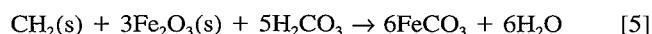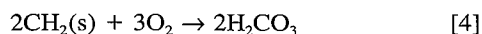
O_2—Dissolved oxygen can be transported into the sediment by bioturbation, which is assumed to be the only significant mode of transport.

H_2O and H_2CO_3 are presumed to be present in excess at all times.

The following processes are assumed to be stoichiometric and very rapid on the time scale of bioturbation:

$$FeS(s) + 2O_2 + H_2CO_3 \rightarrow FeCO_3(s) + H_2SO_4 \quad [1]$$

$$4FeCO_3(s) + O_2 + 4H_2O \rightarrow 2Fe_2O_3(s) + 4H_2CO_3 \quad [2]$$

$$4Fe_2O_3(s) + FeS(s) + 9H_2CO_3 \rightarrow 9FeCO_3(s) + H_2SO_4$$
$$+ 8H_2O \quad [3]$$

The following reactions, presumably biomediated, are assumed to occur at finite rates.

$$2CH_2(s) + 3O_2 \rightarrow 2H_2CO_3 \quad [4]$$

$$CH_2(s) + 3Fe_2O_3(s) + 5H_2CO_3 \rightarrow 6FeCO_3 + 6H_2O \quad [5]$$

$$4CH_2(s) + 3H_2SO_4 + 3FeCO_3(s) \rightarrow 3FeS(s) + 7H_2CO_3 \quad [6]$$

The rates R_i of reactions [4], [5], and [6] are assumed to be governed by Monod-type kinetics, as shown below.

$$R_4 = k_4 \frac{[CH_2]}{[CH_2]_4 + [CH_2]} \cdot \frac{[O_2]}{[O_2]_4 + [O_2]} = -\left(\frac{1}{3}\right)\frac{d[O_2]}{dt}$$

$$= -\left(\frac{1}{2}\right)\frac{d[CH_2]}{dt} \quad (15)$$

$$R_5 = k_5 \frac{[CH_2]}{[CH_2]_5 + [CH_2]} \cdot \frac{[Fe_2O_3]}{[Fe_2O_3]_5 + [Fe_2O_3]} = -\frac{d[CH_2]}{dt} \quad (16)$$

$$R_6 = k_6 \frac{[CH_2]}{[CH_2]_6 + [CH_2]} \cdot \frac{[FeCO_3]}{[FeCO_3]_6 + [FeCO_3]}$$

$$\cdot \frac{[H_2SO_4]}{[H_2SO_4]_6 + [H_2SO_4]} \quad (17)$$

Here, the brackets indicate concentrations in moles per m^3 of water for dissolved components, and in moles per m^3 of bulk sediment for solids.

Let v = sediment porosity; x = distance into sediment from the sediment-water interface, m; D_{bio} = bioturbation constant, m^2/sec; $[M](i)$ = concentration of species M in volume element i at time t, moles/m^3 of water (dissolved solutes) or moles/m^3 of sediment (solids); Δx = thickness of one volume element of sedi-

water column

bioturbating sediment

region of active bioturbation
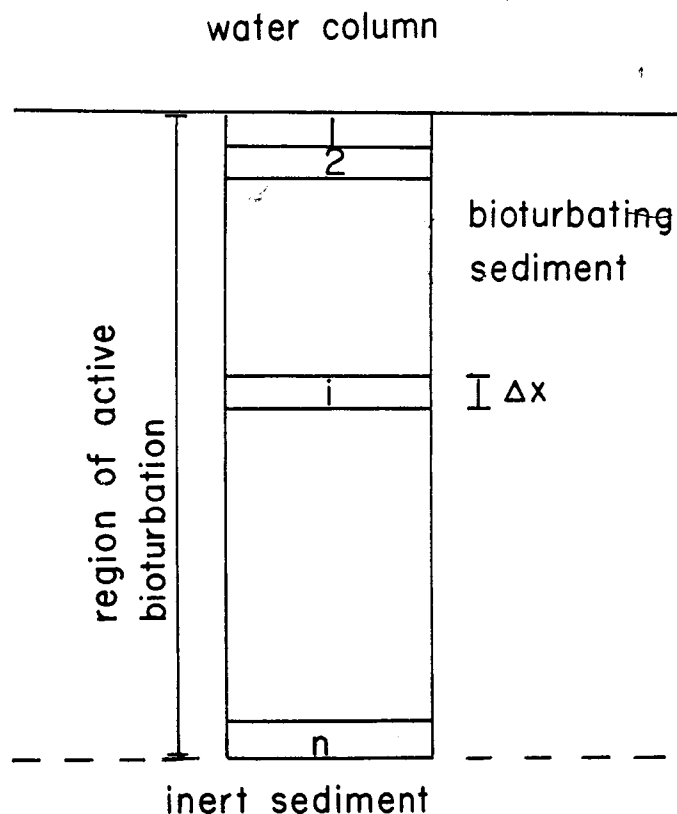
$\downarrow \Delta x$

inert sediment

FIG. 1. Sediment and overlying water column. L = thickness of the layer in which bioturbation is significant. x = thickness of one of the volume elements into which the sediment layer is partitioned for mathematical analysis.

ment, m; and n = number of volume elements into which the sediment domain is partitioned.

The rate equations for the concentrations of the various species M involve three types of contributions. First, material is moved between volume elements by bioturbation, which is represented here by a dispersion-like term, following one of Thibodeaux's (1996) approaches.

$$\left[\frac{\partial[M]_i}{\partial t}\right]_{bioturb} = D_{bio}\{[M]_{i+1} - 2[M]_i + [M]_{i-1}\}/(\Delta x)^2 \quad (18)$$

At the bottom of the domain of interest, below the range of bioturbation, we assume a no-flow boundary condition, which gives

$$\left[\frac{\partial[M]_n}{\partial t}\right]_{bioturb} = D_{bio}\{-[M]_n + [M]_{n-1}\}/(\Delta x)^2 \quad (19)$$

At the top of the domain of interest, at the water-sediment interface, we assume a no-flow boundary condition for the solids, which gives for them

$$\left[\frac{\partial[M]_1}{\partial t}\right]_{bioturb} = D_{bio}\{[M]_2 - [M]_1\}/(\Delta x)^2 \quad (20)$$

For dissolved solutes (oxygen and sulfate), the boundary condition at the top of the domain of interest is

$$\left[\frac{\partial[M]_1}{\partial t}\right]_{bioturb} = D_{bio}\{[M]_2 - 3[M]_1 + 2[M]_0\}/(\Delta x)^2 \quad (21)$$

where $[M]_0$ is the concentration of M in the overlying water

TABLE 4. Default values of the model parameters.

Thickness of sediment layer in bioturbation	30 cm
Sediment porosity	0.65
O_2 concentration in overlying water column	8 mg/l
Initial O_2 concentration in pore water	0 mg/l
Initial H_2SO_4 concentration in pore water	0 mg/l
Sediment density	1.58 gm/cm³
Initial CH_2 concentration in bulk sediment	1000 mg/kg
Initial FeS concentration in bulk sediment	100 mg/kg
Initial $FeCO_3$ concentration in bulk sediment	0 mg/kg
Initial Fe_2O_3 concentration in bulk sediment	0 mg/kg
k_4	6 mg O_2/kg day
$[CH_2]^4$, Monod parameter	10 mg/kg
$[O_2]^4$, Monod parameter	1 mg/l
k_5	0.2 mg CH_2/kg day
$[CH_2]^5$, Monod parameter	10 mg/kg
$[Fe_2O_3]^5$, Monod parameter	5 mg/kg
k_6	0.2 mg CH_2/kg day
$[CH_2]^6$, Monod parameter	10 mg/kg
$[H_2SO_4]^6$, Monod parameter	1 mg/l
$[FeCO_3]^6$, Monod parameter	1 mg/l
Bioturbation constant (all species in sediment)	3×10^{-9} m²/sec
Number of volume elements	50
Δt	2160 sec

column (assumed constant). Dissolved solutes may be transferred by bioturbation between the overlying water column and the top of the sediment.

Other models for bioturbation described by Thibodeaux (1996) could have been used, but the above approach has the advantages of mathematical simplicity and availability of constants, which should be adequate for our purposes here.

The second group of contributions to the rates of change of the various concentrations involves the chemical reactions that are assumed to be essentially instantaneous on the time scale of the runs. Reactions [1]–[3] are treated as follows for each volume element. After a time increment Δt has been made and bioturbation has changed the concentrations in the various volume elements, reaction [1] is allowed to go to stoichiometric completion in each volume element, thereby completely using up whichever is the limiting reagent, FeS or O_2, in that volume element. Then reaction [2] is allowed to do likewise. Lastly, reaction [3] is allowed to go to completion, again using up the limiting reagent. It is assumed that H_2O and H_2CO_3 are always present in excess.

The stage is now set for calculation of the third group of contributions to the rates of change of the concentrations of the various species. Examination of reactions [4]–[6] and equations (15)–(17) for the rates of these reactions permits us to write

$$\left[\frac{\partial[O_2]}{\partial t}\right]_{slow\ react} = -3R_4/\nu \qquad (22)$$

$$\left[\frac{\partial[H_2SO_4]}{\partial t}\right]_{slow\ react} = -3R_6/\nu \qquad (23)$$

$$\left[\frac{\partial[CH_2]}{\partial t}\right]_{slow\ react} = -2R_4 - R_5 - 4R_6 \qquad (24)$$

$$\left[\frac{\partial[FeS]}{\partial t}\right]_{slow\ react} = 3R_6 \qquad (25)$$

$$\left[\frac{\partial[FeCO_3]}{\partial t}\right]_{slow\ react} = 6R_5 - 3R_6 \qquad (26)$$

$$\left[\frac{\partial[Fe_2O_3]}{\partial t}\right]_{slow\ react} = -3R_5 \qquad (27)$$

In summary, to advance one time increment Δt, one first uses equations (21)–(24) to represent the contributions from bioturbation. Fast reactions are then allowed to react to completion in the light of the limiting reagents in each volume element. Lastly, the contributions from the slow reactions are modeled by equations (22)–(27), together with equations (15)–(17). (Note that the subscripts i have been omitted from these equations for convenience here. These variables are in fact subscripted for each volume element.)

The model then permits one to observe the evolution with time of a domain of sediment initially containing FeS and organic matter CH_2 as oxygen migrates into the sediment from above and is consumed by reactions with FeS, $FeCO_3$ (produced as a product of the oxidation of FeS), and CH_2. Sulfate and Fe_2O_3, produced in the course of these reactions, can react as electron acceptors with organic matter, and Fe_2O_3 is assumed to react rapidly with FeS.

RESULTS AND DISCUSSION

The principal objective of this modeling effort was to explore the extent to which one can expect FeS to remain in the upper layers of sediments containing organic material and undergoing bioturbation. The sulfides of the toxic heavy metals Pb, Hg, Cu, and Cd have extremely small solubility products (Table 1). In the presence of solid FeS (and MnS), the solubilities of these toxic metal sulfides are extremely low, and one would expect their movement into the overlying water column to be
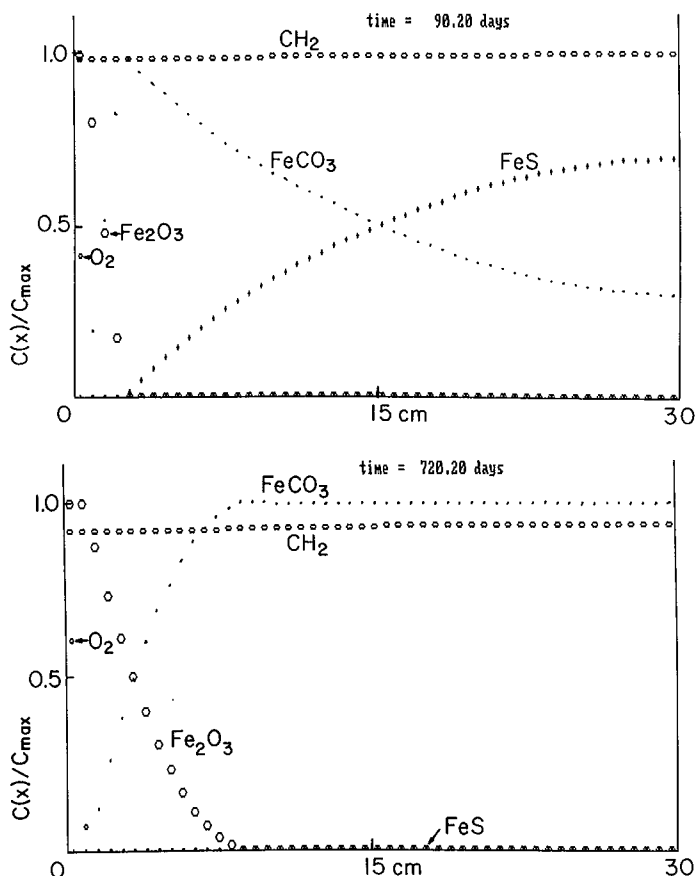
FIG. 2. Normalized plots of concentrations of dissolved O_2, CH_2, FeS, $FeCO_3$, and Fe_2O_3 as functions of distance from the water-sediment interface. $D_{bio} = 3 \times 10^{-9}$ m²/sec; elapsed time = either 90 days (a) or 720 days (b). Other parameters as in Table 4.

FIG. 3. Normalized plots of concentrations of dissolved O_2, CH_2, FeS, $FeCO_3$, and Fe_2O_3 as functions of distance from the water-sediment interface. $D_{bio} = 1 \times 10^{-9}$ m²/sec; elapsed time = 720 days. Other parameters as in Table 4.

blocked. This is the basis for the Simultaneously Extractable Metals/Acid Volatile Sulfides approach to the characterization of sediments containing toxic metals. Unfortunately, as already noted, the oxidations of the heavy metal sulfides to much more soluble sulfates are thermodynamically spontaneous processes in the presence of even quite low concentrations of O_2, as indicated by the standard free energy changes given in Table 3. A recent bench study (Morgan et al., 1992) showed that aerated PbS and CdS precipitates are significantly oxidized by a period of aeration of the order of a month.

One therefore expects that oxidation of the protective matrix of FeS (and/or MnS) in a sediment will be quickly followed by oxidation of any heavy metal sulfides which may be present. The resulting sulfates, carbonates, hydrous oxides, etc., are much more soluble than the sulfides, and are much more likely to be released into the overlying water column.

The simple Euler method was used for integrating the differential equations in the model forward in time. Computations were done in TurboBASIC on a Pentium®-based microcomputer.

Default parameters used in the modeling are given in Table 4. Accurate values of many of the needed parameters are not available. Because these are almost certainly site-specific, the best one can do is to select parameter values lying in a reasonable range relative to reported values. Hoeppel and Hinchee (1994) give a range for the rate of oxygen uptake by reaction of readily
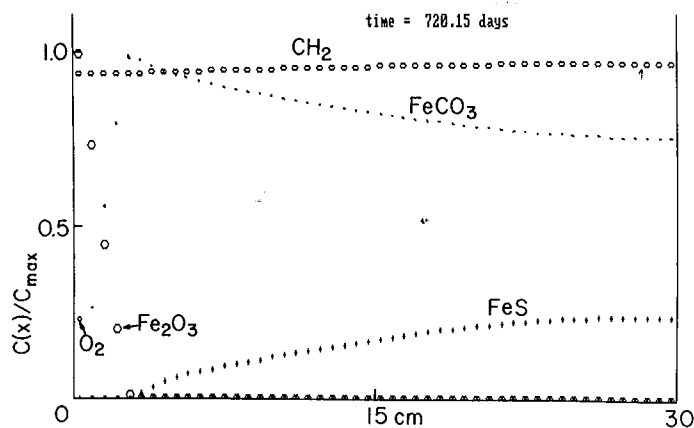
degraded organics in oxic systems of 2 to 20 mg/kg day. We selected rate constants for the biomediated reactions with the other two electron acceptors (Fe_2O_3 and sulfate) that were a good deal smaller than this, since these reactions are generally much slower than those with oxygen. Thibodeaux (1996) gives figures for bioturbation constants indicating that these range from about 3×10^{-12} to 3×10^{-9} m²/sec. We chose values of D_{bio} at the high end of this range (3×10^{-10} to 3×10^{-9} m²/sec) to err on the conservative side in assessing the impact of oxygen in mobilizing toxic metals from sulfidic sediments. The model results do not appear to be sensitive to the values of the Monod parameters, so the effects of varying these were not explored in any detail.

The effect of the bioturbation constant D_{bio} is shown in Figs. 2, 3, and 4, and in Table 5. The figures represent concentration profiles (snapshots) of the various species present after 720 days of sediment exposure to an oxic water column. Values of D_{bio} used were 3×10^{-9}, 1×10^{-9}, and 3×10^{-10} m²/sec, respectively. The layer from which heavy metals may be mobilized is that which contains no FeS. Its thicknesses after 720 days for these three runs are 9.0, 3.0, and 1.2 cm, respectively. Table 5 lists the
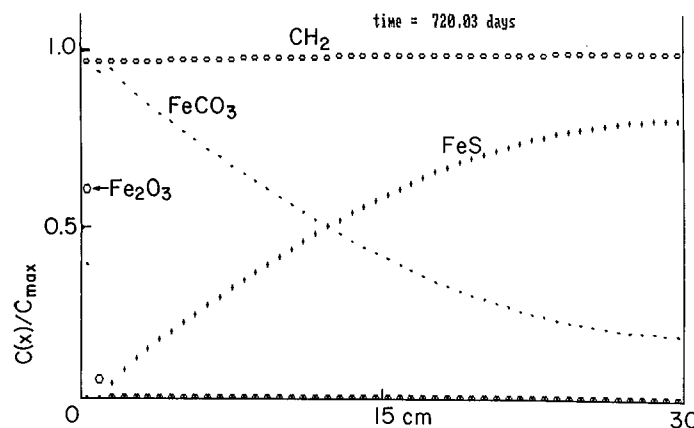
FIG. 4. Normalized plots of concentrations of dissolved O_2, CH_2, FeS, $FeCO_3$, and Fe_2O_3 as functions of distance from the water-sediment interface. $D_{bio} = 3 \times 10^{-10}$ m²/sec; elapsed time = 720 days. Other parameters as in Table 4.

TABLE 5. Effect of bioturbation constant D_{bio} on the development of a sulfide-free sediment layer. Default values of the model parameters are given in Table 4.

D_{bio} (m²/sec)	Time (days)	Sulfide-free layer thickness (cm)
3×10^{-9}	60	2.4
	180	3.6
	360	5.4
	540	6.6
	720	9.0
	845	30.0
1×10^{-9}	60	0.6
	180	1.8
	360	2.4
	540	3.0
	720	3.0
	900	3.6
	1080	3.6
	1260	3.6
	1440	4.8
3×10^{-10}	60	0.0
	180	0.0
	360	0.6
	720	1.2
	1080	1.2
	1440	1.8
	1800	1.8
	2160	1.8

TABLE 6. Effect of k_4, the rate constant for the reaction between O_2 and organic material, on development of a sulfide-free sediment layer. $D_{bio} = 3 \times 10^{-10}$ m²/sec; other parameters as in Table 4.

k_4 (mg O_2/kg day)	Time (days)	Sulfide-free layer thickness (cm)
6	60	0.0
	180	0.0
	360	0.6
	720	1.2
	1080	1.2
	1440	1.8
	1800	1.8
	2160	1.8
18	60	0.0
	180	0.0
	360	0.6
	720	1.2
	1080	1.2
	1440	1.8
	2160	1.8
54	60	0.0
	180	0.0
	360	0.6
	720	1.2
	1080	1.2
	1440	1.8
	2160	1.8

thicknesses of the sulfide-free layers as functions of time for these three runs.

By 90 days a 2.4 cm sulfide-free layer has developed for the run with the largest value of D_{bio}, as shown in Fig. 2a. By 845 days, all of the sulfide in the 30 cm bioturbation layer has been exhausted for this run; this is in agreement with the fact that the great bulk of the sulfide has been destroyed after 720 days (Fig. 2b). Note that the oxic sediment layer is only 1.2 cm thick even after 720 days. The large bioturbation constant used for this run permits sufficiently rapid mixing of the sediments and destruction of sulfides that long-term immobilization of heavy metals as sulfides would require that the overlying water be oxic only for relatively short periods of time.

On the other hand, the runs having the smaller values of D_{bio} that were "snap-shotted" after 720 days (Figs. 3 and 4) show sulfide-free layers of only 3 and 1.2 cm, respectively, after 720 days. Table 5 indicates that even after quite extended periods the sulfide-free layers for these two runs are still relatively thin; 4.8 cm after about 4 years, and 1.8 cm after about 6 years, respectively. For these two systems, the rate of sulfide oxidation is slow enough that one would probably regard an SEM/AVS ratio of less than unity as a good indication that toxic heavy metals would be adequately immobilized.

The effect of the rate constant k_4 (for the reaction of CH_2 with O_2) was modeled with $D_{bio} = 3 \times 10^{-9}$ and 3×10^{-10} m²/sec. These results are shown in Tables 6 and 7. Even at an unreasonably high value of k_4 (54 mg O_2/kg day) k_4 has virtually no effect on the growth of the sulfide-free layer. This is not sur-

TABLE 7. Effect of k_4, the rate constant for the reaction between O_2 and organic material, on development of a sulfide-free sediment layer. $D_{bio} = 3 \times 10^{-9}$ m²/sec; other parameters as in Table 4.

k_4 (mg O_2/kg day)	Time (days)	Sulfide-free layer thickness (cm)
6	60	2.4
	180	3.6
	360	5.4
	540	6.6
	720	9.0
	845	30.0
18	60	1.8
	180	3.6
	360	5.4
	540	7.2
	720	9.6
	845	30.0
54	60	1.8
	180	3.0
	360	4.8
	540	6.6
	720	8.4
	845	30.0

TABLE 8. Effect of k_5, the rate constant for the reaction between organic material and Fe_2O_3, on development of a sulfide-free sediment layer. $D_{bio} = 3 \times 10^{-9}$ m²/sec; other parameters as in Table 4.

k_5 (mg O_2/kg day)	Time (days)	Sulfide-free layer thickness (cm)
0.2	60	2.4
	180	3.6
	360	5.4
	540	6.6
	720	9.0
	845	30.0
2.0·	60	1.8
	180	2.4
	720	8.4
	846	30.0
10	60	0.6
	180	1.2
	360	1.2
	540	1.8
	720	7.8
	855	30.0

TABLE 9. Effect of k_6, the rate constant for the reaction between organic matter and sulfate, on development of a sulfide-free sediment layer. $D_{bio} = 3 \times 10^{-9}$ m²/sec; other parameters as in Table 4.

k_6 (mg O_2/kg day)	Time (days)	Sulfide-free layer thickness (cm)
0.2	60	2.4
	180	3.6
	360	5.4
	540	6.6
	720	9.0
	845	30.0
2.0	60	1.2
	180	1.8
	360	3.0
	540	6.0
	720	7.8
	851	30.0
20	60	0.0
	180	0.0
	360	0.0
	540	0.0
	720	0.0
	1080	0.0
	1440	0.0
	1800	0.0

prising, since our model assumes that consumption of sulfide by O_2 is virtually instantaneous. Thus, the sediment-water boundary acts essentially as an absorbing barrier for sulfide. For these runs the rate of regeneration of sulfide from sulfate, governed by k_6, is slow.

The effect of k_5, the rate constant for the reaction of CH_2 with Fe_2O_3, is shown in Table 8. Here $D_{bio} = 3 \times 10^{-9}$ m²/sec. The effect of an increase in k_5 on the growth of the sulfide-free layer is slight, even at the unrealistically high value of k_5 of 10 mg CH_2/day. This result is not surprising, since increases in k_5 are expected to have little effect on reaction 6, in which sulfide is regenerated from sulfate.

Table 9 shows the effect of increasing the rate constant k_6, which controls the rate of reduction of sulfate to sulfide by bio-mediated reaction with organic material. At large values of k_6 (20 mg CH_2/kg day), even a very large value (3×10^{-9} m²/sec) for the bioturbation constant is insufficient to result in the formation of a sulfide-free layer in the sediment. As fast as sulfide is oxidized to sulfate at the sediment-water interface it is reduced by reaction with organic material and tied up as FeS again. The relatively large concentration of organic material assumed present in the sediment (1000 mg/kg) acts sacrificially under these conditions to maintain the sulfide level. If experimental conditions could be found under which this reaction is quite rapid, these would appear potentially to be beneficial in maintaining sulfide-containing sediments even in the presence of oxygen in the overlying water and substantial bioturbation. This might have useful field applications at contaminated sites.

Conclusions and Caveats—The AVS/SEM approach provides a valid method for ascertaining the availability of toxic metals in anoxic sediments. If, however, the sediments are disturbed (by bioturbation, scouring, river traffic, floods, etc.), one can expect these metals to be converted from the insoluble sulfides into much more soluble forms by oxidation of sulfide. This

has been observed with Cd(II) in the laboratory by Zhuang et al. (1994). In addition, at such times as the water in contact with the sediments is aerobic, diffusion of oxygen into the underlying sediments creates an aerobic layer of the order of a centimeter or so in thickness in which sulfides are oxidized and metals are mobilized.

If the overlying water is or has recently been oxic, one may expect quite different SEM/AVS ratios in the surface layer of sediment (1 cm or so in thickness) than would be found on cores taken to a depth of, say, 30 cm. The results for the cores are expected to give much higher values for the AVS and, therefore, to paint a much more optimistic picture of potential toxicity than one would observe in testing the surface layers of sediment unless the overlying water is anoxic.

At the upper end of the range of values reported by Thibo-deaux (1996) for bioturbation constants, bioturbation provides sufficient mixing of dissolved O_2 and FeS in the sediments that sulfides would be expected to be destroyed fairly quickly even in the presence of substantial concentrations of organic matter in the sediments. The model calculations indicate that sediments become sulfide-free long before they become oxic. One anticipates that toxic metals may be substantially more mobile and bioavailable in sulfide-free sediments (oxic or anoxic) than in sulfide-containing sediments. This suggests that the effects of bioturbation must be taken into consideration when interpreting SEM/AVS ratios in terms of potential heavy metal toxicity.

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