EXPERIMENTAL AND MODELING INVESTIGATION OF METAL RELEASE FROM METAL-SPIKED SEDIMENTS

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Abstract—In sediments that contain iron monosulfide, cadmium, nickel, lead, zinc, and silver(I) form insoluble metal sulfides that lower the metal ion activity in the sediment–pore water system, thereby reducing toxicity. However, metal sulfides are susceptible to oxidation by molecular oxygen resulting in metal solubilization. To better understand the sources and sinks of metal sulfides in sediments, iron monosulfide–rich freshwater sediments were spiked with cadmium, nickel, lead, zinc, or silver(I) and placed into cylindrical cores with an overlying layer of oxygen-saturated water. Measurements of the dissolved metal concentration in the overlying water were made as a function of time and the vertical profiles of acid-volatile sulfide (AVS) and simultaneously extracted metal (SEM) were measured after 150 d. A one-dimensional reactive and transport model has been employed to help elucidate processes controlling the fate of metals in sediments. The model incorporates metal-sulfide formation, metal-sulfide oxidation, and metal partitioning onto sediment organic carbon and iron oxyhydroxide to simulate the vertical transport of metals throughout the sediment core.

Keywords—Acid-volatile sulfide  Metal sulfide  Oxidation  Sediment  Transport modeling

INTRODUCTION

The toxicity of metals in sediments is influenced strongly by metal–sediment chemical interactions. In the presence of iron monosulfide (FeS(s)), dissolved concentrations of Cu²⁺, Cd²⁺, Ni²⁺, Pb²⁺, Zn²⁺, and Ag⁺ are lowered significantly by the formation of insoluble metal sulfides [1]. This is advantageous because the toxicity of metals in sediments is determined by the metal ion activity of the sediment–pore water system [2] as reflected in the pore water concentrations [2,3]. Therefore, sediments containing significant total metal concentrations are not toxic when there is sufficient FeS(s) available to form metal sulfides [3–8].

The metal sulfides formed in sediments would represent a permanent sink for metals if they were completely unreactive. However, metal sulfides are oxidized by molecular oxygen in sediments, thereby releasing potentially toxic metal ions to the pore water [9]. The susceptibility of metal sulfides toward oxidation and the amount of oxygen present, therefore, are important factors in the solubilization of metals in sulfide-rich sediments.

A numerical model previously has been developed in order to predict the fate and transport of toxic metals in sediments [5]. This model incorporates metal interactions with iron monosulfide, iron oxyhydroxide (FeOOH(s)), and particulate organic carbon (POC), as well as the various mechanisms of formation and loss of metal sulfides in sediments. The experimental data used to verify and calibrate this model consisted of data for Cd²⁺ only.

The purpose of this paper is to present the results of a series of additional experiments designed to extend the model calibration to Ni²⁺, Pb²⁺, Zn²⁺, and Ag⁺. Unlike the previous model [5], the model described here calculates metal fluxes to the overlying water. Additionally, FeS(s) solubility equilibrium is explicitly included. We expect that the results from this work will allow for a better understanding of metal cycling in systems containing sulfide-rich sediments.

Theoretical background

In sediments free of significant metal contamination, the majority of reduced sulfur is present in the form of iron sulfides [9]. These include amorphous iron monosulfide (FeS(s, amorph)), mackinawite (Fe₃S₄(s)), pyrite (FeS₂(s)), and pyrite (FeS₄(s)). Amorphous iron monosulfide is the most reactive and believed to be phase controlling the concentration of dissolved sulfide in both freshwater and marine sediments [9–11].

Iron monosulfide plays an important role in sediments because of its ability to act as a sink for potentially toxic transition metals. Addition of many divalent transition metals (e.g., Cu²⁺, Ni²⁺, Pb²⁺, Zn²⁺) to a sediment containing FeS(s) results in the formation of a metal-sulfide precipitate, MS(s), whereby iron is released to the pore water [5]

\[ M^{2+} + FeS(s) = MS(s) + Fe^{2+} \] (1)

The displacement reaction shown in Equation 1 is driven by the fact that these metal sulfides are more insoluble than FeS(s). In this manner, the bioavailability and toxicity of heavy metals is diminished in sulfide-containing sediments.

The presence of reactive sulfide in sediments is measured as acid-volatile sulfide (AVS), the amount of sulfide that is evolved from a cold 1-M hydrochloric acid extraction [9]. The extraction procedure dissolves essentially all of the iron monosulfides (amorphous FeS(s) and mackinawite), but does not
dissolve pyrite. The other metal sulfides (CdS(s), NiS(s), PbS(s), ZnS(s), Ag₂S(s)) are extracted in varying degrees depending upon their method of formation, surface area, and crystallinity [12]. Thus

\[ \text{AVS} = [\text{FeS(s)}] + \sum_{\text{MS}} \alpha_{\text{MS}}[\text{MS(s)}] \]  

(2)

where \( \alpha_{\text{MS}} \) is the fraction of MS(s) extracted by the AVS procedure and the summation includes all metal sulfides, mentioned above, that contribute to AVS.

The metal that is released from a sediment sample during the AVS extraction is called the simultaneously extracted metal (SEM) [5]. The SEM for a specific metal, M (SEM_M), is the sum of the pore water (aqueous phase) metal (\( M_aq \)), metal sorbed to solids (\( M_p \)), metal precipitates other than metal sulfides solubilized in 1 M hydrochloric acid (\( M_s \)), and the extractable portion of metal sulfides (\( \alpha_{\text{MS}} \)[MS(s)]):

\[ \text{SEM}_M = M_aq + M_p + M_s + \alpha_{\text{MS}}[\text{MS(s)}] \]  

(3)

The quantity SEM_{TOT} is defined as the sum of all the individual metals that are released during an SEM analysis, which form metal sulfides that are more insoluble than FeS(s)

\[ \text{SEM}_{TOT} = \sum_{M} \text{SEM}_M \]  

(4)

The FeS(s) is present when the AVS is greater than the SEM_{TOT}.

The displacement reaction (Eqn. 1) occurs for all metals that form sulfides more insoluble than FeS(s) [3]. As a consequence, when the AVS is greater than the SEM_{TOT}, the activity of potentially toxic metal ions in the pore water is low and no toxicity is observed [3–8]. When the AVS is less than SEM_{TOT}, the available FeS(s) is exhausted, and free metal is present in the pore water and/or adsorbed to sediment particles. Hence, the AVS and SEM_{TOT} can be used to predict whether a toxic effect is expected in metal-contaminated sediments [3,4,6–8].

The amount of AVS and SEM in a sediment layer varies temporally with the availability of dissolved oxygen [13,14]. In the oxic layer of sediments, metal sulfides are oxidized, resulting in consumption of AVS and release of metals to the pore water

\[ \text{MS(s)} + 2\text{O}_2 \rightarrow \text{M}^{2+} + \text{SO}_4^{2-} \]  

(5)

Equation 5 is written with sulfite as the end product of MS(s) oxidation for convenience, although other sulfur-containing end products are possible. By the reaction described above, the oxic layer of sediments is enriched in SEM_{TOT} relative to AVS via the oxidation of metal sulfides. Therefore, quantitative estimates of the extent of metal-sulfide oxidation in sediments are necessary to determine pore water metal concentrations and sediment toxicity.

**MATERIALS AND METHODS**

All solutions were prepared using deionized water with a resistivity of 18 MΩ·cm (Aqua Solutions Solution 2000 Water Purification System, Jasper, GA, USA). All stock solutions were stored in borosilicate glass volumetric flasks before use. All glassware were soaked in 1 M HNO₃ (Fisher Scientific, Hampton, NH, USA) and rinsed several times with deionized water before use.

**Chemical reagents**

The salts Ni(NO₃)₂·6H₂O (nickel nitrate), Zn(NO₃)₂·6H₂O (zinc nitrate), Cd(NO₃)₂·4H₂O (cadmium nitrate), Pb(NO₃)₂ (lead nitrate), and AgNO₃ (silver nitrate) all were purchased from Fisher Scientific. Solution pH was buffered using 3-(N-morpholino)propanesulfonic acid (Sigma, St. Louis, MO, USA). Concentrated HCl and NaOH were purchased from Fisher Scientific and used to adjust solution pH.

**Sediment oxidation experiments**

The purpose of these experiments was to measure changes in overlying water metal concentrations and the vertical distribution of AVS and SEM in a sediment column exposed to oxygen-saturated overlying water. Sediment was collected in 10-gal plastic containers from Van Cortlandt Pond (Riverdale, NY, USA), sieved (2-mm mesh), homogenized, and stored in sealed glass jars at 4°C. The AVS and SEM of the sediment were measured immediately after collection. Approximately 225 ml of sediment was added to 250-ml jars and the sediment was spiked at a prespecified molar ratio of metal to AVS. The metals used for the spiking were nitrate salts of nickel, cadmium, lead, zinc, and silver(I). The spiked sediment jars were stirred for 20 min and left to equilibrate for approximately two weeks in sealed glass containers at 4°C to allow for the displacement reaction (Eqn. 1) to proceed.

Cylindrical containers (Acrylite brand Plexiglas, Wasco, Cambridge, MA, USA) with a 45-mm inner diameter and 16.0 cm in length were constructed with silicon-sealed bottoms to house the sediment used in experiments. The cylinders were filled with metal-spiked sediment to a depth of 8.0 cm, followed by 6.5 cm of water containing 5.0 mM of 3-(N-morpholino)propanesulfonic acid (pH 7.0). Duplicate sediment cores were used for sediment spiked with nickel, cadmium, lead, zinc, and silver(I). The overlying water of these cores was bubbled continuously with water-saturated air without disturbing the material at the sediment-water interface. The time zero for these experiments corresponded with the start of bubbling. Samples of the overlying water (5 ml) were taken by pipette periodically over the course of 150 d. The volume of sample taken and the gradual loss of volume due to evaporation was replaced with 5.0 mM of 3-(N-morpholino)propanesulfonic acid. At the end of 150 d, the overlying water was removed by pipette, and the sediment cores were placed in a freezer. Once the cores were thoroughly frozen, a bench band saw was used to cut uniform circular slices of sediment from 5 to 10 mm in thickness. The AVS and SEM of these slices were analyzed immediately thereafter.

In addition to the metal-spiked sediment experiments, a series of sediment oxidation experiments were conducted with nonspiked sediment collected from Van Cortlandt Pond. These sediments contained appreciable amounts of zinc and, therefore, are referred to as having natural contamination. The experiments proceeded in the same fashion as the spiked sediments with the exception that triplicate cores were employed.

**Analytical methods**

Total dissolved nickel (Ni₅⁺), cadmium (Cd₂⁺), lead (Pb₄⁺), zinc (Zn₂⁺), and silver (Ag⁺) in the overlying water of sediment columns were analyzed using atomic absorption spectrophotometry in flame mode with an air-acetylene flame or in graphite furnace mode (Perkin-Elmer, Wellesley, MA, USA). Nickel, zinc, cadmium, lead, and silver atomic absorption spectrophotometry standards were supplied by Fisher Scientific. Solution pH was measured using a combination electrode (Orion Model 910600, Waltham, MA, USA) and a pH/ion meter (Orion Model SA 720). The AVS of each slice was determined
using procedures given in Allen et al. [15]. The SEM was determined using flame–atomic absorption spectrophotometry.

**Modeling approach**

A numerical one-dimensional transport and reactive sediment model has been developed previously to predict AVS and SEM vertical profiles for sediments exposed to molecular oxygen through contact with an overlying water column [5]. In the model, the sediment is segmented into thin vertical layers, and mass balance equations are solved in each layer. The model computes the vertical profiles of iron sulfide, metal sulfide, sorbed metal (to particulate organic carbon and iron oxyhydroxide), and dissolved oxygen. The sediment mass balance equation is

\[
\frac{\partial[c(z, t)]}{\partial t} = \frac{\partial}{\partial z} \left( f_\text{d} D_d(z, t) \frac{\partial[c(z, t)]}{\partial z} \right) + f_\phi \frac{\partial[c(z, t)]}{\partial \phi}
\]

where \( c(z, t) \) is the concentration of chemical per unit bulk volume of the sediment as a function of the depth \( z \), time \( t \), \( f_\text{d} \) is the fraction of the chemical that is in the particulate form, \( f_\phi \) is the fraction of the chemical in the dissolved form, \( D_d(z, t) \) is the diffusion coefficient for particulate phase mixing, \( D_d \) is the diffusion coefficient for pore water mixing, and \( \phi \) is the sediment porosity. The \( K_i \) terms represent all sinks (+) or sources (−) of the chemical that are independent of the chemical concentration.

The metal-sulfide chemical reactions that are modeled are shown in Figure 1A. The oxidation of metal sulfides by dissolved oxygen occurs in the oxic layer of the sediment. For metal not bound as metal sulfide, the pore water metal and metal sorbed to POC and iron oxyhydroxide are assumed to be at equilibrium. Metal in the pore water can diffuse upward to the overlying water column or downward to the anoxic portion of the sediment, depending on the vertical concentration gradients. If iron sulfide is present, pore water metal can displace Fe(II) in FeS(s) from iron metal sulfides MS(s) (Eqn. 1).

The iron reactions included in the model are shown in Figure 1B. Iron sulfide is oxidized by dissolved oxygen in the oxic layer to form FeOOH(s). In addition, any particulate or dissolved Fe(II) also is oxidized by dissolved oxygen. In the anoxic layer, the concentration of dissolved sulfide and Fe(II) is controlled by the solubility of FeS(s). Finally, FeS(s) is consumed by the displacement reaction with pore water metal to form metal sulfides (Eqn. 1). Further details are given in Di Toro et al. [5] and the Appendix.

**Initial conditions.** The initial conditions specify the state of the sediment at the start of model simulations. Because the available measurements, e.g., AVS, are composites of the model state variables (Eqn. 2), it is necessary to estimate the state variable initial conditions using a series of mole balance calculations (Table 1). The data used in these calculations are the experimentally measured AVS (AVS\textsuperscript{EXP}) and SEM (Σ SEM\textsuperscript{EXP}) of the sediment before spiking with a particular metal. The sediment used in these experiments contained significant concentrations of SEM\textsubscript{Pb} (4–5 μmol/g dry) and SEM\textsubscript{Zn} (10–18 μmol/g dry) before spiking.

The initial conditions at the start of the model simulations were calculated using the following approach. The amount of iron sulfide present in the sediment before addition of the metal spike is the difference between the experimentally measured AVS and the sum of the metal SEM.

\[
[\text{FeS(s)}]_{\text{EXP}} = \text{AVS}_{\text{EXP}} - \sum M \text{SEM}_{M}^{\text{EXP}}
\]

In this calculation, we assume that the molar ratio of metal to sulfide is 1.0 for Pb and Zn. The total sulfide available to form metal sulfides, TOTS(−II)\textsuperscript{EXP}, then is calculated using the following equation:

\[
\text{TOTS(−II)}_{\text{EXP}} = [\text{FeS(s)}]_{\text{EXP}} + \sum M \frac{\text{SEM}_{M}^{\text{EXP}}}{\alpha_{\text{MS}}}
\]

where SEM\textsubscript{M}\textsuperscript{EXP} is divided by \( \alpha_{\text{MS}} \) in order to correct for the extraction efficiency. It is assumed that the portion of metal sulfides that are not extractable in 1 M of HCl acid still will take part in the metal displacement and metal-sulfide oxidation reactions. Although unsatisfying, experimental data were not available to give assistance in this area.

The concentrations of PbS(s) and ZnS(s) in the sediment before spiking, [MS(s)]\textsuperscript{EXP}, then were calculated using
spiked experiments. Because ZnS(s) and PbS(s) are lost by oxidation and extract to varying degrees in the AVS measurement, the MS(s) state variable has its own oxidation rate coefficient (k_{MS}) and extraction fraction (\alpha_{MS}). However, MS(s) does not participate in the metal-displacement reaction. A final correction is required for the total available sulfide. Previous control experiments revealed that a considerable amount of AVS (~20%) is lost from sediments during the metal-spiking process. It is probable that either FeS(s) is lost via oxidation by molecular oxygen or that sulfide present in the sediment pore water is lost due to volatilization because the metal spiking is performed open to the atmosphere. Therefore, the total available sulfide was lowered by 20% to account for the loss of sulfide during the metal-spiking process.

After the sediment was spiked with a particular metal (Ni, Pb, Zn, Cd, or Ag(I)), the total metal present in the sediment was calculated by accounting for the metal present in the sediment upon its collection and the metal added, where M_{spike} is the concentration of the metal of interest due to the metal spike (Table 1, Eqn. 4). Subsequently, the initial concentrations of metal sulfide, [MS(s)]_0, total dissolved metal, M_{TOT}, and [FeS(s)]_0 were calculated (Table 1, Eqns. 5–8). The values of these initial conditions vary depending upon whether the entire available sulfide has been used to form metal sulfides. Because the sediment is well mixed at the start of the experiment, the sediment pore water is lost due to volatilization because the metal spiking is performed open to the atmosphere. Therefore, the total available sulfide was lowered by 20% to account for the loss of sulfide during the metal-spiking process.

**Common parameter calibration.** The experiments described above yielded vertical profiles for AVS and SEM at the termination of the experiment, as well as overlying water metal concentrations as a function of time. These results were used to calibrate the sediment metal flux model. Model parameters that are common to all of the data sets (Table 3) were determined by calibration before the metal-specific parameters. Model parameters related to the cycling of iron also are common to all data sets; however, they were calibrated using only the nickel-spiked data set as discussed later (see Nickel-spiked data set section).

**Metal displacement.** For the model simulations, it was assumed that the metal-displacement reaction (Eqn. 1) occurs rapidly for all metals considered in this study [5]. The value for the metal-displacement rate constant, k_{disp} was adjusted such that sorbed metal was not present when FeS(s) was avail-

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**Table 1. Equations used for calculating model initial conditions**

<table>
<thead>
<tr>
<th>Equation</th>
<th>Description</th>
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<tbody>
<tr>
<td>1.</td>
<td>([\text{FeS(s)}]<em>{\text{EXP}} = \text{AVS}</em>{\text{EXP}} - \sum_{\text{MS}} \text{SEM}_{\text{MS}})</td>
</tr>
<tr>
<td>2.</td>
<td>(\text{TOTS}(-\text{II})<em>{\text{EXP}} = [\text{FeS(s)}]</em>{\text{EXP}} + \sum_{\text{MS}} \text{SEM}_{\text{MS}})</td>
</tr>
<tr>
<td>3.</td>
<td>([\text{MS}(s)]<em>{\text{EXP}} = \frac{\text{SEM}</em>{\text{MS}}}{\alpha_{\text{MS}}})</td>
</tr>
<tr>
<td>4.</td>
<td>(\text{TOTM} = \frac{\text{SEM}<em>{\text{MS}}}{\alpha</em>{\text{MS}}} + M_{\text{spike}})</td>
</tr>
<tr>
<td>5.</td>
<td>(\text{TOTS}(-\text{II}) = \text{TOTS}(-\text{II})<em>{\text{EXP}} + \sum</em>{\text{MS}} [\text{MS}(s)]_{\text{EXP}})</td>
</tr>
<tr>
<td>6.</td>
<td>([\text{MS}(s)]<em>0 = \sum</em>{\text{MS}} [\text{MS}(s)]_{\text{EXP}})</td>
</tr>
</tbody>
</table>

For TOTM > TOTS(-II):

7a. \([\text{MS}(s)]_0 = \text{TOTS}(-\text{II})\)
7b. \(M_{T,0} = \text{TOTM} - [\text{MS}(s)]_0\)
7c. \([\text{FeS(s)}]_0 = 0\)

For TOTM < TOTS(-II):

8a. \([\text{MS}(s)]_0 = \text{TOTS}(-\text{II})\)
8b. \(M_{T,0} = 0\)
8c. \([\text{FeS(s)}]_0 = \text{TOTS}(-\text{II}) - [\text{MS}(s)]_0\)

\(^a\) FeS(s) = iron monosulfide; AVS = acid-volatile sulfide; SEM = simultaneously extracted metal; \(\alpha_{\text{MS}}\) = metal-sulfide extraction fraction; MS(s) = metal sulfide; TOTM = total metal concentration; \(M_{\text{spike}}\) = metal spike concentration; \(M_{T,0}\) = initial dissolved metal concentration. The EXP superscript is used to denote quantities measured experimentally.

\(^b\) The summation is applied only to the metal sulfides that are more insoluble than the metal that was used to spike the sediment. See text for further explanation.

\([\text{MS}(s)]_{\text{EXP}} = \frac{\text{SEM}_{\text{MS}}}{\alpha_{\text{MS}}}\)  \(\tag{9}\)

Because significant amounts of Pb and Zn were present in these sediments upon collection, their effect upon the amount of sulfide available to form metal sulfides with the spiked metal need to be included. For spiked metals that form metal sulfides that are more insoluble than PbS(s) and ZnS(s) (e.g., Cd), the spiked metal replaces Zn and Pb according to Equation 10

\(\text{M}^{2+} + \text{ZnS(s)} \rightarrow \text{MS(s)} + \text{Zn}^{2+}\) \(\tag{10}\)

In this case, the total available sulfide, TOTS(-II) is equal to TOTS(-II)_{EXP}. For metals that form metal sulfides that are more soluble than ZnS(s) and PbS(s) (e.g., Ni), the replacement reaction does not occur, and the available sulfide is equal to the difference between TOTS(-II)_{EXP} and the sum all of the more insoluble metal sulfides

\(\text{TOTS}(-\text{II}) = \text{TOTS}(-\text{II})_{\text{EXP}} - \sum_{\text{MS}} [\text{MS}(s)]_{\text{EXP}}\)  \(\tag{11}\)

In this way, the presence of ZnS(s) and PbS(s) in the sediment decreases the amount of available sulfide for metals, such as Ni.

The model contains one metal sulfide state variable, MS(s), which corresponds only to the spiked-metal employed in each experiment. However, it also was necessary to model the effects of the other metal sulfides present (i.e., ZnS(s), PbS(s)) because they contribute to the experimentally measured AVS. Therefore, a second metal-sulfide phase, MS(s), was added as a state variable in the model that represents the sum of the metal sulfides that are more insoluble than the spiked metal. This state variable was necessary for only the nickel- and zinc-
Because biota were not present in these experiments, particulate mixing processes: Particle mixing (bioturbation) and diffusion. AVS profiles necessitates changing water.

Dissolution of sulfide. The amount of AVS in the anoxic portion of sediment cores increased over the course of all experiments. To illustrate this, results from a preliminary set of sediment core experiments are shown in Figure 3. Six identical sediment cores were constructed where sediment was spiked with Ag(I). Each core was analyzed for AVS at various depths at different time intervals. The AVS in the anoxic portion of the sediment (depths lower than 3.5 cm) increased by approximately 60 \( \mu \text{mol/g} \) after 120 d. Presumably, sulfide was produced in the anoxic portion of the sediment core by microbial oxidation of particulate organic carbon with sulfate as the electron acceptor.

The model represents organic carbon in three classes: Labile carbon (\( G_1 \)), refractory carbon (\( G_2 \)), and inert carbon (\( G_3 \)).

\[
\begin{align*}
D_e & = 1.0 \times 10^{-8} \text{ m/d} \\
K_{G_1} & = 3.5 \times 10^{-1} \text{ d} \cdot \text{m}^{-1} \\
K_{G_2} & = 1.8 \times 10^{-2} \text{ d} \cdot \text{m}^{-1} \\
K_{G_3} & = 3.5 \times 10^{-2} \text{ d} \cdot \text{m}^{-1} \\
K_{M,S} & = 1.8 \times 10^{-5} \text{ d} \cdot \text{m}^{-1} \\
K_{AVS} & = 3.1 \text{ L/mg O}_2 \cdot \text{d} \\
K_{G_1,AVS} & = 0.1 \text{ mg O}_2/\text{L} \\
K_{G_2,AVS} & = 1 \times 10^{8} \text{ L/mmol} \cdot \text{d} \\
K_{G_3,AVS} & = 1 \times 10^{8} \text{ L/mmol}^{3} \cdot \text{d} \\
K_{FeS} & = 1 \times 10^{-3} \text{ mg O}_2/L \\
K_{FeS,disp} & = 2.5 \times 10^{-4} \text{ mmol/L}^2 \\
T_{TOTFe} & = 160 \text{ \mu mol Fe/g} \\
K_{Fe,S} & = 1 \times 10^{1} \text{ L/kg solids} \\
K_{Fe,O_2} & = 5 \times 10^{-2} \text{ L/mg O}_2 \cdot \text{d} \\
POC_{G_1} & = 0.40 \text{ mg C/g solids} \\
POC_{G_2} & = 4.0 \text{ mg C/g solids} \\
POC_{G_3} & = 12.0 \text{ mg C/g solids} \\
\sigma_{FeS} & = 0.01 \text{ L/mmol} \cdot \text{d} \\
\sigma_{sat} & = 0.8 \\
\phi & = 0.9 \text{ L/L bulk} \\
\rho & = 2.5 \text{ kg solids/L solids} \\
\Delta & = 0.001 \text{ m} \\
l & = 85 \text{ Number of segments} \\
H & = 0.065 \text{ m} \\
O_2 & = 10.0 \text{ mg O}_2/L \\
Temp. & = 25.0 \text{ degrees C} \\
\end{align*}
\]

The model assumes a smaller rate constant resulted in the simultaneous presence of sorbed metal and FeS(s).

Dispersions coefficients. The original model considered two mixing processes: Particle mixing (bioturbation) and diffusion. Because biota were not present in these experiments, particle phase mixing was set to a small value (\( D_e = 10^{-8} \text{ m}^2/\text{d} \)) so that its effect upon metal transport was negligible. The dispersion coefficient, \( D_e \) was adjusted separately for each metal. Although this parameter should not be metal specific, i.e., it should be a constant for all the experiments, a successful calibration was not possible without varying its value. In addition, the values of \( D_e \) that were required for calibration were, on average, one order of magnitude larger than typical molecular diffusion coefficients. The large dispersion coefficients were attributed to gas production within the sediment. Over the course of experiments, gas bubbles began to appear in the anoxic portion of the sediment, leading to significant expansion of the sediment core (0–10 mm). We suspect that passage of these bubbles through the sediment column to the surface produced the enhanced pore water mixing required in the model calibration [16].

An example of the differences in the extent of pore water mixing can be seen by comparing the vertical distribution of AVS in the two duplicate cores from the silver-spiked experiment (Fig. 2). Because Ag_2S(s) is not acid-extractable (\( \alpha_{Ag_S} = 0 \)), AVS is comprised only of FeS(s). The depth over which the AVS is consumed entirely is determined only by the rate at which oxygen is transferred by pore water mixing because the rate of FeS(s) oxidation is rapid by comparison [17]. The different depths of the oxidation front indicate a difference in the value for \( D_e \). Fitting the model to these AVS profiles necessitates changing \( D_e \) because the rate of oxidation is limited entirely by the supply of oxygen from the overlying water.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Fig2.png}
\caption{Experimentally determined and model-simulated vertical profiles for the silver-spiked sediment data set. Symbols represent experimentally measured acid-volatile sulfide (AVS). Lines represent model-calculated AVS. For the silver spiked experiments, the experimentally measured AVS is iron sulfide. The (A) data set, represented by open symbols, was fit using \( D_e = 1.5 \times 10^{-3} \text{ m}/\text{d} \). The (B) data set represented by closed symbols was fit using \( D_e = 9.0 \times 10^{-4} \text{ m}/\text{d} \).}
\end{figure}

Production of sulfide. The amount of AVS in the anoxic part of the sediment core is determined only by the supply of oxygen from the overlying water.
the sediment-water interface: $d = 3.5$ cm; $h = 4.5$ cm; $\Delta = 5.5$ cm; $d = 6.5$ cm.

Fig. 3. Experimentally measured acid-volatile sulfide (AVS) as a function of time for a silver-spiked sediment oxidation experiment. Data symbols represent measured quantities of AVS at various depths below the sediment-water interface: $\Diamond = 3.5$ cm; $\times = 4.5$ cm; $\bigtriangleup = 5.5$ cm; $\square = 6.5$ cm.

[18,19]. Therefore, it is necessary to estimate the quantity of labile ($G_1$) carbon at the start of the experiment. Unfortunately, it is not possible to measure the concentration of reactive carbon in a sediment against the large background of $G_3$ unre- active carbon. The concentrations of $POC_{G_1}$ and $POC_{G_2}$ were kept at a ratio of 1:10, consistent with other estimates of the relative concentrations of $G_1$, $G_2$, and $G_3$ carbon in sediments [18] and calibrated according to the amount of production that was needed to reproduce the AVS profile in the anoxic zone of the sediment. In all cases, these values were $POC_{G_2} = 0.40$ mg C/g and $POC_{G_1} = 4.0$ mg C/g sediment, respectively.

**Metal-specific parameter calibration.** The metal-specific parameters included the dispersion coefficient ($D_m$), the metal-sulfide oxidation rate constant ($k_\text{MS}$), the metal-sulfide extraction fraction ($\sigma_\text{ms}$), the partition coefficient for sorption onto POC ($K_{\text{POC}}$), the POC sorption capacity ($\sigma_\text{oc}$), the partition coefficient for sorption onto iron oxyhydroxide ($K_{\text{FeOx}}$), and the iron oxyhydroxide sorption capacity ($\sigma_\text{fe}$).

**Sorption to POC and iron oxyhydroxide.** Metal sorption to POC and iron oxyhydroxide is pH-dependent [1]. However, the prediction of the pH in pore water is well known to be difficult [20]. For this model it was assumed that the pH was constant in the pore water for the duration of the experiment. This is a reasonable assumption because the overlying water was well buffered and the buffer is expected to diffuse into the pore water.

The model uses Langmuir adsorption isotherms to calculate partitioning of metals to POC and iron oxyhydroxide [5]. The model parameters related to metal sorption are of primary importance because they determine the relative concentrations of metal in the sediment and pore water. Values for $K_{\text{POC}}$ and $\sigma_\text{oc}$ for metal sorption onto sediment organic carbon are available for some of the metals used in this study [21]. For these metals, the values used in the final model calibration were kept to within a factor of 10 to the experimentally determined values while maintaining an adequate fit to the experimental data.

When values for these parameters were not available in the literature, they were treated as fitting parameters. Adsorption constants and sorption site densities from Dzombak and Morel [22] were available for all of the metals investigated in this study. These adsorption constants were modified to partition coefficients for use in the model (see Appendix). Values for $K_{\text{FeOx}}$ used in the final model calibration were modified to partition coefficients for use in the model (see Appendix). Values for $K_{\text{FeOx}}$ used in the final model calibration were within a factor of 10 of the modified values from Dzombak and Morel [22]. The value of $\sigma_\text{fe}$ was set at 0.2 mol/mol for all metals [22]; it was not adjusted during the calibration.

**RESULTS AND DISCUSSION**

The results from the five metal-spiked experiments and the naturally contaminated sediment oxidation experiments are shown in Figures 4 and 5. All metal-specific parameters employed in the final calibration are listed in Table 4. For all experiments, AVS was lost at the top of the sediment core after 150 d of exposure to an oxygen-saturated water column. In general, the depth at which all of the AVS was lost and the amount of AVS in the lower part of the sediment core differed across the experiments.

The SEM vertical profiles also were vastly different across the experiments. For example, SEM was greater at the top of the sediment core relative to the bottom for the nickel-spiked and lead-spiked experiments. In the zinc-spiked experiment, however, the exact opposite was observed. The experimental data for metal in the overlying water also was quite puzzling. In the nickel-spiked and zinc-spiked data sets, the overlying water metal concentrations initially increased rapidly, reached a maximum value, and then decreased slowly (Figs. 4C and 5F). In the remainder of the data sets, the overlying water metal concentrations slowly increased and then reached a plateau (Figs. 4F, 4I, and 5I).

Interpretation of the experimental data for the vertical profiles of AVS and SEM and the temporal profile for overlying water metal concentration was facilitated when examined in conjunction with the modeling results. As we shall see, the values for the metal-specific parameters have a large effect upon the transport of metal throughout the sediment column.

**Nickel-spiked data set**

Figure 4A to C shows vertical profiles of AVS and $SEM_{Ni}$ and the temporal profile for overlying water Ni concentration. The duplicate A and B cores showed similar results. The AVS was zero to a depth of approximately 30 mm and a constant level of AVS (50 $\mu$mol/g) at depths greater than 45 mm (Fig. 4A). Below 45 mm, $SEM_{Ni}$ increased with decreasing depth (Fig. 4B). At depths greater than 45 mm, $SEM_{Ni}$ was a value constant (40 $\mu$mol/g). After a sharp initial increase in the overlying water Ni concentration over the first 15 d, Ni$_{\text{g}}$ gradually decreased over the duration of the experiment (Fig. 4C).

After calibration, the model reproduced the vertical profile of AVS. Diffusion of molecular oxygen into the sediment from the overlying water resulted in the oxidation of NiS(s) in the upper portion of the core. A relatively rapid NiS(s) oxidation rate constant ($k_{\text{NiS}} = 0.1$ L/mg O$_2$ – d) was necessary in the final calibration so that all of the AVS was oxidized to a depth of 30 mm. Model sensitivity analyses revealed that this depth was dependent upon the magnitudes of $k_{\text{MS}}$ and $D_m$. In addition, $k_{\text{FeOx}}$ also controlled the slope of the AVS oxidative front. Large values for $k_{\text{MS}}$ resulted in shallow slopes for the oxidative front because reaction progress became limited by oxygen transport from the overlying water.
Although the experimental data show a larger amount of SEM$_{Ni}$ in the oxic portion relative to the anoxic portion of the sediment column, the model simulations indicated that Ni was cycled from the top to bottom of the sediment core. Nickel present in the sediment pore water diffused into the anoxic portion of the core where FeS(s) was being produced continually. This process provides a mechanism for NiS(s) reformulation via the metal-displacement reaction (Eqn. 1). Because only 20% of the NiS(s) is extracted in the AVS procedure ($\alpha_{NiS} = 0.2$), this cycling effect is not apparent from the AVS and SEM$_{Ni}$ experimental data. Model simulations showed that SEM$_{Ni}$ in the oxic portion of the core was a direct measurement of Ni present in the pore water or adsorbed to POC and FeOOH(s). In the anoxic portion of the core, SEM$_{Ni}$ largely was comprised of the extractable fraction of NiS(s).

The sharp initial increase in the overlying water Ni concentration indicated a large flux of Ni from the sediment to the overlying water at the start of the experiment. Due the presence of Zn and Pb in the sediment upon its collection, initial condition calculations indicated that there was more Ni added than available sulfide (TOTNi $>$ TOTS[–II]) resulting in dissolved Ni present in the sediment pore water at the start of the experiment ($N_{i,0}  \neq 0$; Table 2). Because the overlying water at the start of the experiment did not contain Ni, a large concentration gradient was established across the sediment-water interface. The reversal of the Ni flux, as indicated by

---

**Fig. 4.** Experimental and model-predicted vertical profiles of (A, D, G) acid-volatile sulfide (AVS); (B, E, H) simultaneously extracted metal (SEM); and (C, F, I) temporal profile of overlying water metal concentration for the metal-spiked sediment experiments. Each row represents results from a different metal-spike (nickel, cadmium, or lead) as indicated in the upper right corner of each plot. Closed circles (●) represent A-sediment oxidation replicate; open circles (○) represent B replicate. Dashed (---) lines represent the initial AVS and SEM, respectively.
Fig. 5. Experimental and model-predicted vertical profiles of (A, D, G) acid-volatile sulfide (AVS); (B, E, H) simultaneously extracted metal (SEM); and (C, F, I) temporal profile of overlying water metal concentration for the metal-spiked sediment experiments. Each row represents results from a different metal spike (silver, zinc, or naturally contaminated [nc] zinc) as indicated in the upper right corner of each plot. In (A–F), closed circles (●) represent A-sediment oxidation replicate and open circles (○) represent B replicate; in (G–I), circles (●) represent data averaged over three sediment core replicates. Dashed lines (—) represent the initial AVS and SEM, respectively.

Table 4. List of metal-specific calibrated parameter values

<table>
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<tr>
<th></th>
<th>Ni</th>
<th>Cd</th>
<th>Pb</th>
<th>Zn</th>
<th>Ag</th>
<th>Units</th>
<th>Reference</th>
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<tr>
<td>(D_d)</td>
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<td>(1.7 \times 10^{-3})</td>
<td>(1.0 \times 10^{-3})</td>
<td>(2.3 \times 10^{-3})</td>
<td>(1.0 \times 10^{-3})</td>
<td>m²/d</td>
<td></td>
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<tr>
<td>(\alpha_{\text{SEM}})</td>
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<td>0.8</td>
<td>0.8</td>
<td>0.6</td>
<td>0.0</td>
<td>dimensionless</td>
<td></td>
</tr>
<tr>
<td>(k_{\text{SEM}})</td>
<td>0.1</td>
<td>0.008</td>
<td>0.03</td>
<td>0.01</td>
<td>1.0 \times 10^{-4}</td>
<td>L/mg O₂ – d</td>
<td></td>
</tr>
<tr>
<td>(K_{\text{SEM}})</td>
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<td>(4.0 \times 10^{6})</td>
<td>(4.0 \times 10^{6})</td>
<td>(1.0 \times 10^{2})</td>
<td>(3.0 \times 10^{6})</td>
<td>L/kg OC</td>
<td>[21]</td>
</tr>
<tr>
<td>(K_{\text{OC}})</td>
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<td>(4.8 \times 10^{7})</td>
<td>(1.9 \times 10^{7})</td>
<td>(1.0 \times 10^{7})</td>
<td>(1.0 \times 10^{4})</td>
<td>mmol/kg OC</td>
<td>[21]</td>
</tr>
<tr>
<td>(\sigma_{\text{OC}})</td>
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<td>(5.0 \times 10^{7})</td>
<td>(4.0 \times 10^{7})</td>
<td>(1.0 \times 10^{7})</td>
<td>(4.5 \times 10^{-2})</td>
<td>L/mmol Fe</td>
<td>[22]</td>
</tr>
<tr>
<td>(K_{\text{Fe}})</td>
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<td>((2.5 \times 10^{7}))</td>
<td>((4.0 \times 10^{7}))</td>
<td>((2.0 \times 10^{7}))</td>
<td>((1.0 \times 10^{-5}))</td>
<td>mmol/mmol Fe</td>
<td>[22]</td>
</tr>
</tbody>
</table>

*Values in parentheses are reported in the literature. A dash (—) indicates that values were not available.
the decrease in overlying water Ni after 15 d, resulted from Ni adsorption onto FeOOH(s) within the oxic portion of the sediment. As Fe(II) was oxidized rapidly to FeOOH(s) by diffusion of oxygen into the sediment, sites for metal sorption onto FeOOH(s) were being supplied in the upper part of the sediment core. Sorption of Ni onto FeOOH(s) lowered the pore water concentration and reversed the concentration gradient and the flux.

Iron system

Due to the importance of FeOOH(s) on Ni fluxes across the sediment-water interface, the nickel data set was used to calibrate the iron system. The parameters resulting from this calibration were used for the other data sets. Parameters related to the transport and transformation of iron include the initial concentration of oxidizable Fe(II), TOTFe₀, the oxidation rate of FeS(s), \( k_{\text{FeS}} \), the oxidation rate constant of dissolved and sorbed Fe(II), \( k_{\text{Fe,DO}_2} \), and the partition coefficient between the aqueous and solid phases of Fe(II), \( K_{\text{IIFe,Fe}} \).

The amount of dissolved iron in sediments is determined by many chemical factors, including the solubility of various iron precipitates, sorption to sediment particles, and reduction potentials [23]. To simplify matters, an empirical partition coefficient was used to compute the dissolved and particulate iron fractions [5]. The pore water iron concentration in sediments typically is between 5 and 25 mg/L [11]. The iron partition coefficient was calibrated so as to supply dissolved iron within this range of values (Table 3).

Oxidation rates of FeS(s) are known [17]. The oxidation rate of dissolved and precipitated Fe(II) to Fe(III) and subsequent conversion to iron oxyhydroxide are known to be relatively fast at pH 7.0 [17]. The value of \( k_{\text{Fe,DO}_2} \) was set equal to 0.1 L/mg O₂ d, so that Fe(II) oxidation was limited by the diffusion of oxygen to the oxidation front.

The initial concentration of reactive Fe(II) (TOTFe₀) was determined by calibration of the SEMNi vertical profile in the oxic portion of the sediment. It is assumed that sorption to iron oxyhydroxide is more important than sorption to sediment organic carbon based on the temporal behavior of the flux to the overlying water. The reversal of the direction of the flux, first from the sediment to the overlying water, and then from the overlying water into the sediment, is occurring in the presence of a constant amount of sediment organic carbon, which is not possible if sorption to organic carbon were the primary partitioning phase.

Figure 6 shows the model simulations of the iron system for the nickel-spiked experiment. As time elapses, Fe(II) is oxidized (Fig. 6A) to iron oxyhydroxide that is deposited at the surface of the sediment core (Fig. 6B). Pore water mixing supplies the oxic layer with Fe(II), which then is oxidized. In this manner, iron is cycled from the anoxic to the oxic layer of the sediment, contributing additional sorption sites for metals. Note that the vertical profile for SEMNi to a depth of 40 mm (Fig. 4B) closely mirrors the simulated iron oxyhydroxide profile shown in Figure 6B.

Cadmium-spiked data set

Duplicate A and B cores for the AVS and SEMCd vertical profiles, and for the overlying water Cd concentration, are presented in Figure 4D to F. After 150 d, most of the AVS was lost from the top 40 mm of the sediment core. However, there was some AVS present at depths just below the sediment-water interface. The SEMCd data from the two duplicate cores, although scattered, suggest some accumulation of Cd at a depth near about 20 mm. The overlying water temporal profile shows a gradual release of Cd from the sediment over the first 20 d, followed by a plateau in CdT from 20 to 150 d.

Unlike the nickel-spiked data set, the AVS is not consumed completely in the oxic portion of the sediment core at the end of the experiment. Because FeS(s) is oxidized very rapidly, the AVS measured within the first 40 mm of the core was due only to CdS(s). Diffusion of oxygen into the sediment, therefore, resulted in loss of AVS via CdS(s) oxidation. However, CdS(s) was present in the upper part of the sediment core in the presence of molecular oxygen. These two features of the AVS vertical profile were reproduced using a relatively small value of the oxidation rate constant (\( k_{\text{cad}} = 0.008 \text{ L/mg O}_2 d \)).
The model SEMCd predicted accumulation of SEMCd at the oxic–anoxic interface (z = 30 mm). As CdS(s) was oxidized in the oxic portion of the sediment core, the liberated Cd diffused downward to the anoxic portion of the core where FeS(s) was being produced via sulfate reduction. Similar to the nickel-spiked experiment, this provides a mechanism for CdS(s) reformation via the metal-displacement reaction (Eqn. 1). However, this modeling result is different from that of the nickel-spiked experiment where NiS(s) was formed throughout the entire anoxic portion of the sediment core. This difference in the extent and location of metal cycling is related to the predicted pore water concentrations of Ni and Cd. Because the predicted Cd pore water concentrations were relatively low, vertical fluxes of Cd were small and CdS(s) was reformed only at the oxic–anoxic interface.

The model was unable to reproduce the rapid release of Cd to the overlying water due to the relatively slow oxidation rate of CdS(s) used in the final calibration to reproduce the AVS profile. However, the model does predict correctly the eventual plateau in overlying water Cd. The modeling simulations indicated that Cd released to the sediment pore water during CdS(s) oxidation mostly was trapped within the anoxic portion of the core by reformation of CdS(s).

**Lead-spiked data set**

Figure 4G to I shows the modeling and experimental results for duplicate A and B cores for the AVS and SEM Pb vertical profiles, and for the temporal overlying water Pb concentration. After 150 d, AVS was lost to a depth of about 40 mm and there was no AVS to a depth of about 15 mm. The SEMb data from the A core suggests a slight depletion of Pb in the oxic portion of the sediment, whereas the data from the B core suggest accumulation of Pb. The overlying water temporal profile shows a rapid release of Pb from the sediment over the first 20 d, followed by a plateau in Pb over the remainder of the experiment.

The AVS vertical profile is reproduced adequately by the model, correctly simulating the loss of all AVS to a depth of 15 mm. Diffusion of oxygen into sediment core resulted in the oxidation of PbS(s). The depth at which all of the AVS was lost and the steep slope of the oxidative front are indicative of the relatively large value of the oxidation rate constant used in the final calibration (kOx = 0.03 L/mg O2 · d). In the anoxic portion of the sediment core, the increase in AVS after 150 d was due to formation of FeS(s).

After PbS(s) was oxidized, the model predicted that the Pb released to the pore water was trapped in the oxic layer of the sediment core via adsorption to FeOOH(s). The experimental data for Core B supports this prediction, although the model underpredicted the magnitude of SEMb. The modeling simulations do not predict any cycling of Pb from the oxic to the anoxic portion of the sediment core. Because Pb sorption to FeOOH(s) is very strong, Pb released by PbS(s) oxidation did not result in a large flux of Pb to the overlying water.

**Silver-spiked data set**

The silver-spiked sediment experiments yielded two cores with widely different vertical profiles of AVS (Fig. 5A). The vertical profiles show a loss of AVS to approximately 30 mm and the AVS present in the anoxic portion of the core after 150 d was approximately 40 μmol/g. Throughout most of the sediment column, the SEMAg was below our instrument detection limits (Fig. 5B). A small amount of SEMAg (1 – 6 μmol/g) was found within the first 10 mm. The concentration of Ag(I) in the overlying water (Fig. 5C) was below our instrument limit of detection (~5 μg/L).

From the SEMAg vertical profile, it is clear that Ag2S(s) is not dissolved in the AVS extraction (αAg2S is equal to zero). Therefore, the measured AVS mostly is due to FeS(s). The model simulation, using values for kOx and kOAg, determined via calibration of a previous data set [5] slightly overpredict the production of FeS(s). The loss of AVS to about 30 mm indicates that the FeS(s) produced by organic matter diagenesis was oxidized readily via diffusion of molecular oxygen from the overlying water.

In the final model calibration, the simulated overlying water Ag(I) was assumed to be below or near our instrument detection limit. This sets an upper limit of 1 × 10^-5 L/mg O2 · d on kAgS, the oxidation rate of Ag2S(s). However, the slight release of Ag(I) suggested by the nonzero SEMAg within the first 10 mm suggests that the rate constant may be slightly larger.

**Zinc-spiked data set**

The model calibration for zinc is more constrained than the other metals because the calibration for the metal-spiked and naturally contaminated sediment data sets were performed concurrently. This produces a common set of parameters for zinc while staying within the confines of published and experimental data.

The experimental data for the A and B cores for the zinc-spiked sediment experiment are shown in Figure 5D to F. The vertical profile shows an oxidative loss of AVS to a depth of about 40 mm. The vertical SEMZn profile shows an accumulation in the anoxic portion of the sediment relative to the oxic portion. The overlying water Zn increased over the first 10 d followed by a gradual decrease over the next 150 d.

The zinc-spiked data set, the model simulations correctly predict the loss of all AVS within the first 15 mm by employing a relatively large rate constant for ZnS(s) oxidation. However, the model underpredicted the amount of AVS in the anoxic portion of the sediment core. It was not possible to obtain an adequate model fit for both AVS and SEMZn in the lower part of the core because they are both dependent upon the value of αZnS. In the final calibration, αZnS was equal to 0.60. Increasing the value of αZnS to obtain an adequate fit to the AVS experimental data resulted in overprediction of SEMZn. The inability of the model to fit simultaneously the AVS and SEMZn data may be related to the assumption that the FeS(s) displacement reaction (Eqn. 2) is fast. Slow kinetics for Zn replacement of Fe(II) in FeS(s) would result in more AVS in the anoxic portion of the sediment core and a better fit to the

As Fe(II) was oxidized to FeOOH(s), new sorption sites were created for Pb in the oxic portion of the core. Because sorption to iron oxyhydroxide was very strong, Pb released by PbS(s) oxidation did not result in a large flux of Pb to the overlying water.
data. An adequate fit to SEM\textsubscript{Zn} then would be obtained by lowering the value of $\alpha_{Zn}$. As with the nickel-spiked experiment, Zn was cycled from the top of the sediment core to the bottom over the course of 150 d. Along with the Zn present initially in the pore water, Zn released by ZnS(s) oxidation diffused to the anoxic portion of the sediment core and reformed ZnS(s). Because the magnitude of $K_{an}$ and $K_{doc}$ for Zn were relatively low, adsorption of Zn onto POC and FeOOH(s) were relatively weak and the concentration of Zn in the pore water was high. Thus, the flux of Zn to the lower portion of the sediment was large enough that all of the FeS(s) was converted to ZnS(s).

The behavior of the Zn concentration in the overlying water was similar to that found for the nickel-spiked data set. The initial condition calculations for the zinc-spiked experiment indicated that there was more Zn added than available sulfide (TOTZn > TOTS(−II)), resulting in Zn present in the sediment pore water at the start of the experiment ($Zn_{(w)} \neq 0$; Table 2). Because the sediment pore water contained a high initial Zn concentration, the initial flux of Zn to the overlying water was due to the concentration gradient established across the sediment-water interface. The reversal of the Zn flux, as indicated by the decrease in overlying water Zn, resulted from production of additional sorption sites via Fe(II) oxidation to FeOOH(s).

Naturally contaminated data set

The results for the naturally contaminated sediment experiment averaged over three replicate cores are shown in Figure 5G to I. As noted earlier, the sediment collected for use in this study contained high levels of zinc. As a result, we chose to monitor overlying water zinc as a function of time and the vertical profiles of SEM\textsubscript{Zn} at the end of the experiment. The vertical profiles show oxidative loss of AVS to a depth of about 15 mm and a relatively constant amount of SEM\textsubscript{Zn} throughout the column. The overlying water Zn rapidly increased to approximately 20 $\mu$M over the first 20 d, followed by a plateau in the overlying water Zn over the remainder of the experiment.

The model reproduced the major features of both the spiked (Fig. 5D–G) and naturally contaminated (Fig. 5H–I) data sets, including the three-order-of-magnitude difference in overlying water concentrations. The model calibration of these two data sets used the same metal-specific parameters with the exception of dispersive mixing coefficient. The value of $D_z$ employed in the final calibration ($D_z = 2.0 \times 10^{-4}$ m$^2$/d) was lower than for the others ($D_z = 1.0–3.5 \times 10^{-4}$ m$^2$/d). The naturally contaminated sediment experiment was performed at a later date than the spiked experiments and with sediment collected at a different time of year and at a different location from Van Cortlandt Pond. This may have caused different rates of gas production that would result in less pore water mixing for this set of experiments.

Modeling assessment

The model employed here was a modified and expanded version of a previously described model [5] that has been updated to include fluxes to an overlying water column and to simulate FeS(s) precipitation and dissolution. The modeling framework, however, does not include potentially important process such as metal sorption to other phases (e.g., manganese (hydr)oxides) or the effects of other metal-solubility controlling phases (e.g., pyrite). Despite these shortcomings, we view the modeling effort here as a success because model simulations clearly aided in the interpretation of the experimentally observed vertical profiles of AVS and SEM and temporal profiles of overlying water metal concentration. A key example of this was the observed change over time in the direction of metal flux to the overlying water for the nickel- and zinc-spiked sediment experiments. This was an unexpected experimental result where the model proved especially useful.

The modeling effort described here is a necessary step in the progression toward a more complete and mechanistically based model. Manganese cycling, metal sorption onto manganese (hydr)oxides, and the potential for incorporation of metals into pyrite need to be considered. Additionally, a model framework with a solution technique for inclusion of full metal-speciation calculations is a logical extension of the approach described in this work.

In light of this work, additional experimental measurements are required to aid in modeling efforts. Measurements of sediment-dissolved iron, sulfide, carbonate, and sulfate were not made in this study. However, vertical profiles of their concentrations are necessary to set model state parameters within appropriate ranges. Measurements of pH throughout the sediment column also are necessary to assure that vertical pH gradients do not develop over time.

Finally, additional experimental work is required to quantify important model-fitted parameters and assess the validity of key assumptions. Rate coefficients for metal-sulfide oxidation reactions and parameters for metal sorption onto various sediment solid phases are necessary to reduce the number of fitting parameters and produce a more general metal mobilization model. The assumption that the fraction of metal sulfides that do not extract in 1 M of HCl still take part in displacement and oxidation reactions has yet to be addressed. If the metal-sulfide fraction not extractable in acid is not susceptible to oxidation, there would be less potential for metal release because the reactive metal-sulfide pool would be decreased. In effect, this oxidation-resistant fraction would represent a permanent sink for metals in sediments.

CONCLUSION

A sediment-metal flux model has been calibrated using temporal profiles of overlying water metal concentration and vertical profiles of AVS and SEM for Cd, Ni, Pb, Zn, and Ag(I). The experimental data for overlying water metal concentration showed two distinct behaviors, depending upon the metal used for the sediment spike. For the nickel- and zinc-spiked experiments, we observed a large initial flux of metal to the overlying water, followed by a slow but gradual decrease in the overlying water metal concentration. This temporal behavior was related to the amount of metal present in the pore water at the start of the experiment. Because the total metal present in the sediment at the start of the experiment exceeded the sulfide available to form metal sulfides, there was a significant concentration of metal in the pore water, resulting in a large concentration gradient across the sediment-water interface and a large initial flux to the overlying water. Model simulations showed that creation of additional metal sorption sites by Fe(II) oxidation to iron oxyhydroxide lowered the pore water metal concentration and reversed the direction of the metal flux. For the cadmium-spiked, lead-spiked, and naturally contaminated zinc experiments, we observed a small initial flux to the overlying water, followed by a plateau in the overlying water metal concentration. Model results indicated that
release of metal to the overlying water resulted from metal-sulfide oxidation.

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REFERENCES


APPENDIX 1

Modeling of iron sulfide

Amorphous iron sulfide is assumed to be the controlling phase for sulfide solubility [7]. Due to an uncertain second acidity constant for H2S (hydrogen sulfide), the solubility of FeS(amorph) is written in terms of HS− (bisulfide ion) [24]

FeS(amorph) + H+ ⇌ Fe2+ + HS−  (12)

Assuming activity corrections are negligible, we can write the corresponding mass action law in terms of concentrations of Fe2+, HS−, and H+, respectively,

*Krams = [Fe2+] [HS−] /[H+]  (13)

Note that the solubility of sulfide is pH-dependent.

Because the model assumes a fixed pH (7.0) and employs one state variable to represent dissolved sulfide, a modified form of Equation 13 is necessary to describe FeS(amorph) equilibrium. To accomplish this, we define total dissolved sulfide, ST, as the sum of the concentrations of H2S and HS−. At any pH, the fraction of ST present as HS− is calculated in the usual way

[HS−] = ST *Krams / [H+]  (14)

where Krams is the acid dissociation constant for H2S(aq). Thus, Equation 13 can be written in terms of ST instead of [HS−]

*Krams ST = [Fe2+] [S−]/[H+]  (15)

We define a conditional solubility product constant, K′rams, that is independent of pH and written in terms of only model state variables

Krams′ = [Fe2+] ST  (16)

By rearranging Equation 14, we obtain an expression for Krams′ in terms of [H+], Krams, and *Krams*

Krams′ = *Krams [H+] / [H+]  (17)

Taking *Krams equal to 10−2.9 [10] and Krams equal to 10−7.0, Krams′ is equal to 2.5 × 10−10 mol/L2 at pH 7.0.

Equilibrium between FeS(s) and ST is modeled using a rate expression where the rate of precipitation (+) and dissolution (−) of iron sulfide is dependent on the square of the difference between [Fe2+] ST and Krams′ [25].
\[
\frac{d[FeS]}{dt} = \pm k_{\text{diss}}([Fe^{2+}]S_T - K'_s)^2
\]  
(18)

where \( k_{\text{diss}} \) is a second-order rate constant for dissolution and precipitation of FeS(s). The value of \( k_{\text{diss}} \) was assigned to be sufficiently large to force the value of \([Fe^{2+}]S_T\) to be near \( K'_s \) without introducing computational instability.

To prevent dissolution of FeS(s) in the case where it is no longer present, but to allow its production for the case of oversaturation, the rate law (Eqn. 18) is multiplied by a dampening term

\[
\frac{d[FeS]}{dt} = \pm k_{\text{diss}}([Fe^{2+}]S_T - K'_s)^2 \times \left( \frac{[FeS(s)] + X_{\text{FeS}}[1 + \text{sign}([Fe^{2+}]S_T - K'_s)]}{[FeS(s)] + X_{\text{FeS}}} \right)
\]  
(19)

where

\[
\text{sign}(x) = \begin{cases} 1 & \text{if } x \geq 0 \\ -1 & \text{if } x < 0 \end{cases}
\]  
(20)

When the difference between \([Fe^{2+}]S_T\) and \( K'_s \) is greater than zero, i.e., when the system is oversaturated, the dampening term is equal to 1 and FeS(s) will precipitate as described in Equation 18. However, when the difference between \([Fe^{2+}]S_T\) and \( K'_s \) is less than zero, i.e., when the system is undersaturated, the value of the dampening term depends upon the relative values of \( S_T \) and \( X_{\text{FeS}} \). When the value of \( S_T \) is smaller than \( X_{\text{FeS}} \), the dampening term approaches a value of zero to prevent computation of negative concentrations of FeS(s). The constant \( X_{\text{FeS}} \) (which must have the same units as \([FeS(s)]\)) is set to a small enough value that it has an effect only at very small FeS(s) concentrations. In the model calibration, \( X_{\text{FeS}} \) was assigned a value of \( 1 \times 10^{-3} \mu\text{mol/g} \) by increasing incrementally its magnitude until no negative FeS(s) concentrations were calculated. This purely is a numerical procedure and has no chemical meaning. This technique is quite effective in maintaining the equilibrium condition (Eqn. 13) with the attendant difficulties of using Equation 13 directly.

Because \( S_T \) is modeled separately from FeS(s), it also is gained and lost by the rate law described in Equation 18. An additional sink of \( S_T \) via oxidation by molecular oxygen was included in the model formulation. The second-order rate constant for loss of \( S_T \) (\( k_S \cdot n_{O_2} \)) was set to a value of \( 5 \times 10^{-2} \text{L/mg O}_2 \cdot \text{d} \); however, this reaction had minimal effect upon model simulations.

**Adsorption onto iron oxyhydroxide**

At a fixed pH, the distribution of metal between the pore water and iron oxyhydroxide is described by the following mass action law

\[
K_{\text{ads,Fe}} = \frac{M_{\text{ads,Fe}}}{[M^{2+}][\text{=}S]}
\]  
(21)

where \( M_{\text{ads,Fe}} \) is the amount of metal adsorbed onto iron oxyhydroxide (in mol/L bulk), \([M^{2+}]\) is the metal cation concentration (in mol/L water), \([\text{=}S]\) is the concentration of available surface sites (in mol/L bulk), and \( K_{\text{ads,Fe}} \) is the equilibrium constant for metal adsorption on iron oxyhydroxide (in L water/mol). A mole balance on surface sites yields the following:

\[
n_s = M_{\text{ads,Fe}} + \{\text{=}S\}
\]  
(22)

where \( n_s \) is the total number of surface sites for metal adsorption (in mol/L bulk). The value of \( n_s \) is calculated according to Equation 23

\[
\sigma_{\text{Fe}}(\text{FeOOH(s)}) = n_s
\]  
(23)

where \( \sigma_{\text{Fe}} \) is the sorption site density (in mol/mol Fe) and \( \text{FeOOH(s)} \) is the concentration of iron oxyhydroxide (in mol/L bulk). For the model calculations, it is useful to express the adsorption isotherm in terms of a partition coefficient, \( K_{\text{d,Fe}} \) (in L water/mol Fe), which is calculated using Equation 24

\[
K_{\text{d,Fe}} = \frac{K_{\text{ads,Fe}} \sigma_{\text{Fe}}}{\sigma_{\text{Fe}} + K_{\text{d,Fe}}[M^{2+}]}
\]  
(24)

By solving Equations 21 to 24 for \( M_{\text{ads,Fe}} \), we obtain the form of the Langmuir adsorption isotherm employed in the model calculations

\[
M_{\text{ads,Fe}} = \frac{K_{\text{d,Fe}} \sigma_{\text{Fe}} [M^{2+}][\text{FeOOH(s)}]}{\sigma_{\text{Fe}} + K_{\text{d,Fe}}[M^{2+}]}
\]  
(25)

Literature values for partition coefficients were required to constrain model fits to the experimental data. Equilibrium constants from Dzombak and Morel [22] for metal adsorption onto hydrous ferric oxide were transformed into partition coefficients using the following procedure. The mass action laws from for metal adsorption onto a (hydr)oxide surface are expressed as follows:

\[
K_{\text{int}} = \frac{[\text{=}FeOM}^+] [\text{H}^+]}{[\text{=}FeO}^2-][M^{2+}]
\]  
(26)

where \( K_{\text{int}} \) is the intrinsic adsorption constant, \([\text{=}FeOM}^+]\) is the concentration of metal adsorbed to the surface (in mol/L), \([\text{=}FeO}^2-\) is the concentration of neutral surface sites (in mol/L), and \([\text{H}^+]\) is the hydrogen ion concentration (in mol/L). The Type 2 (weak) sites [22] were chosen because they are more abundant and important at the high metal concentrations used in these experiments. Using a \( 2 - pK_a \) model for the (hydr)oxide surface, \([\text{=}S]\) is computed by mole balance on surface sites

\[
[\text{=}S] = ([\text{=}FeOH}_2] + [\text{=}FeO}^2-] + [\text{=}FeO}^4-)\phi
\]  
(27)

where \([\text{=}FeOH}_2]\) and \([\text{=}FeO}^2-\) represent the concentration of positively and negatively charged sites, respectively. At pH 7.0, the number of sites available for metal adsorption is approximately equal to the amount of neutrally charged sites [22]

\[
[\text{=}S] = [\text{=}FeOH}_2]\phi
\]  
(28)

In a similar way, the concentration of metal adsorbed to the surface can be expressed on a mol/L bulk basis

\[
M_{\text{ads,Fe}} = [\text{=}FeOM}^+]\phi
\]  
(29)

Using the relationships in Equations 21 to 24 and Equations 26 to 29, values for \( K_{\text{d,Fe}} \) were calculated from \( K_{\text{int}} \) according to the following:

\[
K_{\text{d,Fe}} \approx \frac{K_{\text{int}}}{[\text{H}^+]} \sigma_{\text{Fe}}
\]  
(30)

where \([\text{H}^+]\) is \( 10^{-7} \text{M} \) and \( \sigma_{\text{Fe}} \) is 0.2 mol/mol Fe for all metals [22]. The resulting values are listed in Table 3. Note that by employing intrinsic equilibrium constants we have chosen to neglect electrostatic effects on metal adsorption.