Non-Steady State Modeling of Arsenic Diagenesis in Lake Sediments

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A one-dimensional reactive transport model describing the coupled biogeochemical cycling of As, C, O, Fe, and S was used to interpret an extensive geochemical data set for dissolved As and S in pore water and sediments collected in the perennially oxygenated basin of an oligotrophic lake. Historical variations in atmospheric deposition of As and S were explicitly included as upper boundary conditions in the model calculations. The results show that the depth profile of sediment-bound As reflects both the past changes in As deposition and the diagenetic redistribution of As among the Fe(II) oxyhydroxide and Fe(II) sulfide pools. The model-predicted benthic release of dissolved As to the water column peaks 26 years after the maximum anthropogenic As input to the lake, which occurred around 1980. Two major environmental forcings of the benthic recycling of As are the organic matter degradation in the sediment and the atmospheric sulfate deposition to the lake. More oxidizing conditions associated with lower organic matter degradation rates yield a greater abundance of Fe(III) oxyhydroxides in the topmost sediment, which act as a barrier to pore water As. Variations in sulfate availability have more complex effects on benthic As mobilization, since sulfide produced by sulfate reduction may enhance both the uptake of dissolved As through the precipitation of Fe(II) sulfides and the release of dissolved As through the reductive dissolution of Fe(III) oxyhydroxides.

Introduction

The sedimentary cycle of arsenic (As), a trace metalloid that represents a worldwide public health threat (1, 2), is closely related to the cycles of other elements, in particular iron (Fe) and sulfur (S) (e.g., ref 3). Ferric iron oxyhydroxides are major sorbents of As in oxygenated aquatic environments. Reducing conditions in sediments, however, may cause the dissolution of the Fe(III) oxyhydroxides, thereby releasing As to the pore water (e.g., ref 4). Retention of As within the sediment occurs when upward migrating dissolved As is scavenged by authigenic Fe(III) oxyhydroxides (e.g., ref 5). Dissolved As may also migrate downward into more reducing zones, where it is immobilized, via either the formation of As-sulfide minerals (3) or As binding to authigenic Fe sulfide minerals (6, 7).

Reactive transport models, which simulate the interactions among the physical, geochemical, and biological processes affecting the fate and transport of As in aquatic sediments, can help delineate the time scales at which As-contaminated sediments respond to external forcings such as variations in organic matter (OM) supply, water column oxygenation, As deposition, or sulfate availability. They may also be used to assess the potential outcomes of remediation efforts. While many geochemical models have been designed to capture selected aspects of As transport (2) and reaction (e.g., refs 8 and 9) in porous media, there have been few attempts to fully integrate both types of processes (2, 10–12). Even fewer models account for the coupling of As to the cycling of the major redox-active elements, in particular, carbon, oxygen, nitrogen, sulfur, and iron (13). Furthermore, it is commonly assumed that the spatial distributions of the various forms of As are at steady state. The validity of this assumption is questionable in highly dynamic lacustrine environments.

In this paper, we develop a reactive transport model capable of predicting As release from and sequestration in lake sediments under nonsteady state conditions, and apply it to a site that has experienced variations in atmospheric deposition of As and S over the last century. Deposition of As peaked in the early 1950s as a result of the domestic use of coal (14), while sulfate deposition, mainly due to SO2 emissions from coal-fired power plants and base metal smelters in eastern North America, reached its peak value in the mid-1980s (15). The historical variations in the deposition fluxes of the two contaminants are explicitly accounted for in the model by imposing time-dependent boundary conditions at the sediment–water interface (SWI). The model is used both as a diagnostic tool to interpret present-day pore water and solid sediment profiles, and as a prognostic tool to analyze As mobilization from the sediment under variable environmental scenarios.

Methods and Model Development

Study Site. Lake Tantare (47°04′15″N, 71°33′42″W) is a headwater oligotrophic lake located in an ecological reserve, 30 km northwest of Québec, a city of about 500,000 inhabitants in the Province of Québec, Canada. Atmospheric deposition is the only input of anthropogenic As to this lake, whose small, uninhabited watershed has been negligibly impacted by wood harvesting and wildfires. Lake Tantare has four basins separated by shallow sills; the data presented here are from the westernmost basin, which is acidic (pH 5.3–6.0), oligotrophic (Chl a 0.2–0.9 nm; (16)), and perennially oxygenated.

Sampling and Analyses. Water samples were obtained by in situ dialysis from 5 cm above the SWI to 10 cm below, using acrylic peepers designed to collect samples at 1-cm intervals; the peepers were deployed by divers at the deepest point of the basin (15 m) and left to equilibrate for 21 days. Peeper preparation and sampling procedures are described elsewhere (16). Pore water sampling occurred in July 2003, September 2003, and August 2004; near-bottom O2 concentrations was always >3.8 mg L–1. Three sediment cores were also collected by divers at the pore water sampling site using 9.5-cm internal diameter butyrate tubes and were extruded and sectioned within 2 h. One core, collected in July 2003, was analyzed for radionuclides, organic C, Fe, and As, while another core collected at the same time was analyzed for acid volatile sulfides (AVS). To minimize oxidation, sediment...
samples dedicated to AVS measurements were individually sealed in plastic bags and buried into a larger bag filled with anoxic sediment. The third core, collected in September 2007, was used to determine a vertical oxygen concentration profile across the SWI. The measurements were done within 30 min of core retrieval with an oxygen microelectrode (Unisense OX-100), which had a built-in reference electrode and a silver guard cathode (17). A two-point calibration was made between air-saturated water and anoxic sediment. The electrode position was controlled in two dimensions by a micromanipulator, and sensor currents were converted to voltages by a picocampere-millivolt converter (Unisense PA2000). After the measurements, the core was sectioned and the samples were stored in amber glass bottles and kept at anthesis for use in slurry incubations to measure the rates of OM mineralization.

Methods used for pore water (pH, As, Fe, sulfide (SS(II)), and SO₄²⁻) and solid phase (As, Fe, total organic carbon (Corg), ²¹⁰Pb, ¹³⁷Cs, and ²¹²Pb) analyses are described elsewhere (14). Sedimentary AVS concentrations were determined by acidizing wet sediment samples with 6 N HCl (18); the evolving sulfide gas was trapped in a NaOH solution and analyzed by colorimetry (19).

Rates of carbon mineralization were derived from the measured CO₂ accumulation during oxic incubation of sediment slurries (20) containing approximately 20 mL of wet sediment and 10 mL of filtered lake water that were placed in 100-mL glass vials sealed with rubber septa. The vials were shaken and their headspace was purged with air 3 times for 10 min. CO₂ concentration in the headspace was measured by gas chromatography (Perkin-Elmer Sigma 300; Porapak-Q column) at days 2, 4, 7, 14, 21, 28, 35, and 40. Note that, hereafter, [X] and (X) correspond to the concentration of species X in the aqueous and solid phases, respectively. Model formulation. Model development followed the general approach outlined by Van Cappellen and Wang (21). Mathematically, a set of partial differential equations (PDEs) defined a coupled transport–reaction system in which all the reactions were described by kinetic expressions; 13 reaction pathways and 11 chemical species are considered (Table 1). A detailed description of the transport–reaction model can be found in the Supporting Information (SI).

Briefly, the reaction network included three primary redox reactions describing the degradation of OM via oxic respiration (R1), dissimilatory iron reduction (R2), and sulfate reduction (R3) (Table 1). Nitrate reduction was not considered, because of the low values and poor precision of the NO₃⁻ concentration measurements. Manganese (Mn) oxyhydroxides were similarly excluded as potential electron acceptor, because neither the solid-phase nor the pore water Mn profiles showed evidence for significant Mn redox cycling in Lake Tantare (22). Possibly, authigenic Mn oxyhydroxides do not form due to the acidic conditions near the SWI (pH 5.3–6.0). An exponential decay function was imposed to describe the depth-dependent rate of total OM degradation, based on the mineralization rates measured in the sediment slurries (SI, Figure S2). Consumption of a given terminal electron acceptor (TEA = O₂, Fe(OH)₃(s), and SO₄²⁻) is coupled to the rate of OM oxidation through a Monod kinetic dependency on the TEA concentration, and an inhibition term limiting the rate of a respiratory pathway in the presence of stronger oxidants (SI). The vertical overlap between OM degradation pathways in lacustrine sediments has been successfully reproduced using this approach (23).

The secondary redox reactions considered were the oxidation of pore water Fe(II) by O₂, and of H₂S by O₂ and Fe(OH)₃(s) (R4, R5, and R6, respectively; Table 1). Bimolecular reaction rate laws were used for these reactions, thereby restricting their occurrence to depth intervals where both oxidant and reductant were present at nonzero concentra-

The rates of precipitation and dissolution of FeSO₄ (R7 and R−7, respectively) were explicitly dependent on the corresponding pore water saturation state. The rate of FeSO₄ precipitation (R8) was assumed to be proportional to the concentrations of pore water H₂S and of solid phase FeSO₄, and the rate of diagenetic sulfidization of sediment OM (R9) was assumed to depend on the concentrations of OM and pore water H₂S (24).

Sorption of As to Fe(OH)₃(s) (R10) and FeS(s) (R11) were treated as irreversible processes. Remobilization of sorbed As required the dissolution of Fe(OH)₃(s) (R12) and FeS(s) (R13), whereby stoichiometric release of the solid-bound As was assumed (Table 1). Formation of pure As oxides, As sulfides, and metal arsenates were not considered, because the pore waters remained undersaturated with respect to these mineral phases by several orders of magnitude (saturation index ≤ −10; SI). The model did not explicitly account for depth variations in [As] speciation; according to thermodynamic calculations >99% of [As] should be in the form of As(OH)₃ (SI).

The transport processes included in the one-dimensional conservation equations were molecular diffusion, bioirrigation, bioturbation, and sediment accumulation. The molecular diffusion coefficient for [As] was 5.8 × 10⁻⁶ cm² s⁻¹ (SI). Bioirrigation (α) and bioturbation (D_bio) coefficients were constrained independently from biological field surveys (25). α was assumed to decrease exponentially from a fixed boundary value at the SWI (α₀ = 4.6 × 10⁻¹⁰ s⁻¹) to zero at 10 cm depth, since no benthic animals were found below this depth in the sediments. The low value of D_bio (2.2 × 10⁻⁹ cm² s⁻¹) reflected the sparse benthic community (1690 ± 180 animals m⁻²; mostly chironomids) at the sampling site. The measured near-constant porosity, from the SWI to 30 cm depth, of 0.970 ± 0.002 was used in the calculations. Two average sedimentation rates (σ = 0.995 cm yr⁻¹ until 1962 and then 0.131 cm yr⁻¹) were derived from the sediment mass accumulation rates given in ref 14.

Boundary Conditions. Zero concentration gradients were used as lower boundary condition for all solutes and solids. An average deposition flux of reactive Fe oxyhydroxides f_e Fe(OH)₃ (SI) = 6.7 µmol cm⁻² yr⁻¹) was imposed as upper boundary value at the SWI. This value was obtained using particulate matter accumulation data from eight sediment traps deployments in the hypolimnion of the lake basin between 1997 and 1999 (SI); the trap material was extracted with a reducing agent (NH₄OH) to estimate the Fe(III) oxyhydroxides content. The measured bottom water concentrations of solutes, except that of [SO₄²⁻], were also imposed as upper boundary values at the SWI (SI, Table S1). Time-dependent variation in bottom water [SO₄²⁻] was assumed to parallel the increasing sulfate deposition from 1940 until the mid-1980s and the subsequent drop since then, which has been reported for lakes from eastern North America (15). Accordingly, the variation over time (t) in [SO₄²⁻] at the SWI (ySO₄) was described by the following bell function (26):

\[
y^{SO_4} = y_{0}^{SO_4} + a \cdot e^{-\left[0.5 \times \frac{t - t_{max}}{b}\right]^2}
\]

where ySO₄ (10 µM) is the preindustrial lake water [SO₄²⁻], t_max (1985) is the year of peak SO₄²⁻ atmospheric deposition, a (60 µM) defines the maximum [SO₄²⁻] at t_max and b (6 yr) defines the width of the peak. The variation in particulate As deposition flux at the SWI (f_{dep,PS}) was also described by eq 1, replacing ySO₄ by yPS and f_{dep,PS} by f_{dep,PA}, respectively. The values of t_max (1950), a (2.5 mmol cm⁻² yr⁻¹), and b (8 yr) were calculated by assuming that f_{dep} parallels the historical trend in atmospheric As during the last century, as reconstructed by Couture and associates (14) through inverse modeling of [As] and [As] profiles measured in an adjacent, seasonally anoxic basin.
of Lake Tantare. The value of $J_{\text{dep,0}}$ (2.1 nmol cm$^{-2}$ yr$^{-1}$) is the estimated background flux of As deposited at the SWI of our study site (14). It should be noted that $J_{\text{dep}}$ comprises both the As deposited from the atmosphere and As recycled in the water column, i.e., As that escapes the bottom sediments and is redeposited with settling particles. The transient boundary conditions for $[\text{SO}_4^{2-}]$ and As deposition are shown in Figure 1g and h.

Results and Discussion

Depth Profiles of Key Geochemical Variables. The rate of OM mineralization decreased exponentially from 465 µmol C cm$^{-2}$ yr$^{-1}$ in the upper 0.5 cm of sediment to <60 µmol C cm$^{-2}$ yr$^{-1}$ at 10 cm depth (SI, Figure S2). Pore water $O_2$ was depleted within the uppermost 0.5 cm of sediment (Figure 1a). Pore water concentrations of dissolved Fe(II) and As were higher than those in the overlying water (Figure 1b and e). Pore water $[\text{SO}_4^{2-}]$ concentrations decreased with depth below the SWI, whereas $[\Sigma S(-II)]$, which were near or below detection in the overlying water, increased below 2–6 cm sediment depth (Figure 1c and d). The pore water data showed significant variability from one sampling time to another (Figure 1b–e), illustrating the sensitivity of pore water profiles to seasonal variations in biogeochemical activity due to, for example, the seasonality of the deposition flux and reactivity of OM at the SWI. The observed subannual fluctuations in the pore water distributions, as well as the likely fluctuation in $O_2$ penetration and in the deposition flux of OM, however, are beyond the scope of the model.

<table>
<thead>
<tr>
<th>TABLE 1. Reaction Network and Kinetic Formulations Used in the Model (See SI for Further Details)</th>
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<td><strong>description</strong></td>
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<td>aerobic respiration</td>
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<td>Fe oxide reduction</td>
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<td>sulfate reduction</td>
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<td>Fe(II) oxidation by $O_2$</td>
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<td>$H_2S$ oxidation by $O_2$</td>
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<td>$H_2S$ oxidation by Fe oxide</td>
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<td>$\text{FeS}_{(s)}$ dissolution$^a$</td>
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<td>$\text{FeS}_{(s)}$ precipitation</td>
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<td>pyrite precipitation</td>
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<td>OM sulfidization</td>
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<td>As sorption to $\text{Fe(OH)}_{3(s)}$</td>
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<td>As sorption to $\text{FeS}_{(s)}$</td>
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<td>As release during dissolution of $\text{Fe(OH)}_{3(s)}$</td>
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$^a$ $[\Sigma S(-II)] = [\text{H}_2\text{S}] + [\text{HS}^-]$. $^b$ $\Omega_{f_{\text{FeS}}} = [\text{Fe(III)}][\Sigma S(-II)]^2 k_{f_{\text{FeS}}}$. 

Pore water concentrations of dissolved Fe(II) and As were higher than those in the overlying water (Figure 1b and e). Pore water $\text{SO}_4^{2-}$ concentrations decreased with depth below the SWI, whereas $[\Sigma S(-II)]$, which were near or below detection in the overlying water, increased below 2–6 cm sediment depth (Figure 1c and d). The pore water data showed significant variability from one sampling time to another (Figure 1b–e), illustrating the sensitivity of pore water profiles to seasonal variations in biogeochemical activity due to, for example, the seasonality of the deposition flux and reactivity of OM at the SWI. The observed subannual fluctuations in the pore water distributions, as well as the likely fluctuation in $O_2$ penetration and in the deposition flux of OM, however, are beyond the scope of the model.
simulations, which focus on the effects of historical changes in atmospheric deposition of As and SO$_4^{2-}$ at a yearly resolution.

Solid-phase As concentration decreased with depth in the upper 2 cm of the sediment, then increased to reach a local maximum at a depth of about 5.5 cm, and decreased again (Figure 1h). The concentrations of reactive Fe(III) oxyhydroxides concentration were estimated as the excess Fe concentration over the constant Fe concentration (200 µmol g$^{-1}$) measured below 15.5 cm. Concentrations of FeS$_{(s)}$ (assuming that AVS $\approx$ FeS$_{(s)}$; Figure 1g) were too low to contribute significantly to the excess Fe, while the pore waters were highly undersaturated with respect to other Fe(II) solids, such as FeCO$_3(s)$ and Fe(OH)$_2(s)$. Fortin et al. (27) further provided direct evidence for the presence of poorly crystalline ferrihydrite and lepidocrocite near the SWI at the sampling site, which is consistent with the observation that the major part of Fe settling to the sediments could be extracted with the mild reagent hydroxylamine hydrochloride (SI). Figure 1f shows that {Fe(OH)$_3$} dropped sharply in the top 2 cm and then decreased more gently below this horizon. The {Fe(OH)$_3$} depth profile closely matched those measured at the same site in earlier studies (22, 28; Figure S1). A distinctive subsurface maximum in {FeS} was observed at about 5 cm depth (Figure 1g).

**Baseline Simulation.** The baseline simulation was carried out with the boundary conditions described above, and aimed at reproducing the general trends observed in the pore water and solid sediment depth profiles. Initial guesses for the values of the reaction parameters were taken from the literature, and their values were further adjusted to fit the experimental data while taking into account the parameter ranges reported in the literature, when available (SI; Table S2). In addition, a 500 yr model spin-up prior to 1850 was performed to ensure a steady state at the start of the baseline simulation.

The model is able to reproduce the observed [O$_2$] and [SO$_4^{2-}$] pore water profiles (Figure 1a and c), as well as the general trends in those of [Fe] and ΣS(II) (Figure 1b and d). Note that the {Fe(OH)$_3$} profile, which reflects the intense redox cycling of Fe, is particularly well captured (Figure 1f). The model predicts that most of the dissolved Fe is released to the overlying water column and that only a small fraction of the deposited reactive Fe is ultimately buried as FeS$_{(s)}$ (Figure 2).

The baseline simulation yields a {FeS} maximum at 5–6 cm depth (Figure 1g). Preliminary simulations, where OM sulfidization was omitted, predicted {FeS} concentrations 1...
order of magnitude higher than the measured values. Another study, using a similar modeling approach, also overpredicted lake sediment (FeS) (23). One way to reduce production of FeS in the model simulations is to increase the oxidation rate of ZS(-II) (R5 and R6). However, this approach generates a subsurface [SO₄²⁻] peak that does not appear in the measured profiles (Figure 1c). Alternatively, it has been proposed that a significant proportion of dissolved sulfide in acidic, organic-rich lake sediments is consumed by the sulfidization of OM (29); we therefore included this reaction in our model. To reproduce the (FeS) profile and the trends in the ZS(-II) profiles (Figure 1d and g), OM sulfidization (R9) must then represent the main sink for sulfide in Lake Tantare sediment. Further investigations will be required to independently confirm the major role of OM sulfidization as a removal mechanism for sulfide in the sediments. It should also be noted that the model predicts that FeS₂₀₀ is not an important sink for reactive Fe and sulfides (<10⁻⁴ µmol g⁻¹), because of the combination of a relatively low rate constant for pyrite precipitation and low pore water sulfide concentrations.

In the reactive transport model, the [As] and [As] distributions are completely determined by the redox transformations of carbon, oxygen, iron, and sulfur, and by the upper boundary conditions for transformations of carbon, oxygen, iron, and sulfur, and by distributions are completely determined by the redox transformations. For pyrite precipitation and low pore water sulfide concentrations, because of the combination of a relatively low rate constant for pyrite precipitation and low pore water sulfide concentrations.

The effects of anthropogenic SO₄²⁻ and As loadings on the depth distribution of [As] are shown in Figure 1i. Keeping the water column [SO₄²⁻] constant at its estimated preindustrial value (i.e., ySO₄ = 10 µM) leads to an attenuation of the [As] peak at ~5.5 cm depth and to lower [As] at greater depths, relative to the baseline simulation. Keeping ySO₄ constant at the preindustrial value of 2.1 nmol cm⁻² yr⁻¹ nearly completely suppresses the diagenetic [As] peak at the depth where [FeS] is maximum. Individually, neither of these two simulations accurately reproduces the [As] profile recorded in Lake Tantare sediments.

Depth-integrated reaction rates and fluxes (Figure 2) from the baseline simulation indicate that about 10% of As currently deposited at the SWI is buried in the form of FeS₀₉₉₉ bound As whereas 75% is transported to the overlying water, suggesting that the remaining 15% of is trapped in the redox loop associated with the Fe(OH)₃₃₉₉₉₉ recycle. Careful inspection of Figure 2, however, reveals imbalances in the integrated rates and fluxes, because the sedimentary cycles of Fe, As, and S have yet to reach steady state. That is, the biogeochemical reaction system is still recovering from the high SO₄²⁻ and As inputs of the past.

As Remobilization From the Sediment. In the baseline simulation, the benthic flux of [As] from the sediment to the water column (J⁺_{SWI} = J_{diffusion} + J_{bioirrigation}) reaches its maximum value 26 yr after the particulate As deposition flux peaked, i.e., in 1976 rather than in 1950 (Figure 3a). In other words, a lag time of more than two decades separates the benthic remobilization of As from its original input into the lake system. A similar delay in the benthic release of As has been reported for a lake impacted by a pulse addition of particulate As (30). A noteworthy feature of Figure 3a is that, after reaching its peak value, J⁺_{SWI} drops sharply becoming even lower than the preindustrial level around the year 2006. Somewhat unexpectedly, this minimum value of J⁺_{SWI} occurs at the time [Fe(OH)₃] reaches a minimum at the SWI (Figure 3a). All else being equal, low concentrations of Fe(OH)₃ should promote the escape of dissolved As to the water column. The decreasing As sorption capacity of Fe(III) oxyhydroxides, however, is offset by the increase in that of FeS (reaction R11), which is fueled by anthropogenic SO₄²⁻ deposition (3I). The model further predicts a lag time of about 21 yr between the peak input of SO₄²⁻ to the lake in 1985 and the minimum in As efflux from the sediments.

A sensitivity analysis was conducted to determine the dependency of J⁺_{SWI} on the various model parameters (see SI). This exercise revealed that J⁺_{SWI} is most sensitive to parameters that influence the OM degradation rates and the abundance of Fe(OH)₃₃₉₉₉₉. Hence, imposing higher rates of OM degradation increases As release to the hypolimnions, because of the upward migration of the oxic–anoxic boundary in the sediment and the reduced availability of Fe(III).
oxyhydroxides close to the SWI (Figure 3b). Maximum release also occurs slightly earlier than in the baseline simulation. This is consistent with previous findings for a mine-impacted lake where increased lake productivity (and therefore increased OM degradation in the sediments) amplified As remobilization from the sediments (32, 33). Conversely, decreasing the OM degradation rates results in a thicker oxic zone near the SWI and, thus, a greater capacity to trap upward diffusing As by Fe(III) oxyhydroxides, thereby lowering and delaying the dissolved As efflux from the sediment.

The complex effects of water column [SO$_4^{2-}$], another key forcing parameter, on $R_{80}$ are illustrated in Figure 3c. Simulations are provided for preindustrial [SO$_4^{2-}$] that have been increased or decreased by a factor of 2 relative to the baseline scenario. Such variations in natural background sulfate level are expected for lakes located closer to or further from the ocean, respectively, compared to Lake Tantaré. Both the doubling and halving of the background lake water [SO$_4^{2-}$] generally decrease the efflux of dissolved As to the overlying lake water, although the departure from the baseline scenario remains relatively small. The higher preindustrial [SO$_4^{2-}$] increases As retention in the sediment because of higher FeS$_3$ production, while the lowering of $R_{80}$ when preindustrial [SO$_4^{2-}$] is decreased reflects the increased abundance of ferric iron oxyhydroxides near the SWI, which act as a barrier against upward migrating pore water As. Such an increase in Fe(OH)$_3$ when water column [SO$_4^{2-}$] is lowered derives from a decreased intensity in Fe(OH)$_3$ reduction by porewater S(-II) (see Figure 2 and Table 1). The different water column [SO$_4^{2-}$] scenarios differ mainly by their effect on the maximum value of $R_{80}$, which is similar to that of the baseline simulation for the lower preindustrial [SO$_4^{2-}$] but significantly lower than that of the baseline simulation for the higher preindustrial [SO$_4^{2-}$]. In fact, increasing the lake water [SO$_4^{2-}$] concentration dampens the response of $R_{80}$ to the historical maximum in the deposition flux of As. Note that, in contrast to the OM degradation rate, variations in lake water [SO$_4^{2-}$] have no effect on the timing of maximum As release. Overall, FeS$_3$ formation in Lake Tantaré sediments acts as a buffer against benthic remobilization of anthropogenic As. This is in line with earlier work, which has shown that binding to iron sulfides may control As sequestration in anoxic sediments (e.g., refs 7 and 34).

In summary, our findings show that the solid-phase As profile in the sediments of Lake Tantaré records both the historical changes in As pollution and the postdepositional redistribution of this element. The latter, in turn, is sensitive to the time-dependent variations in atmospheric deposition of sulfate to the lake, as binding to iron sulfides represents the main sedimentary sink for As. Because reactive transport modeling allows one to separate the effects of atmospheric deposition of As and sulfate from those of early diagenetic transformations and transport processes, it should be useful in supporting not only scientific research aimed at better understanding the fate of As in the environment, but also the management of As contaminated sediments.

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Supporting Information Available

Determination of reactive Fe(III) deposition fluxes, depth-profiles of reactive Fe(III) oxyhydroxides, formulation of the reactive transport model, determination of the OM mineralization rates, list of model parameters, equilibrium speciation calculations, and sensitivity analyses. This information is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(20) Dawwe, B.; Middelburg, J. J.; Herman, P. M. J. Effect of oxygen on the degradability of organic matter in subtidal and intertidal


