

# Controls on Arsenic Speciation and Solid-Phase Partitioning in the Sediments of a Two-Basin Lake

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Arsenic (As) regeneration from sediments of Spy Pond, a two-basin lake near Boston, MA, continues to result in seasonally elevated As levels despite the several decades that have elapsed since the pond's historical contamination by a pulse input of As. Solid-phase speciation and partitioning of As in the sediments appear to be primary determinants of both potential As regeneration rate and, conversely, the rate at which long-term burial of the pond's As burden will occur. Although iron (Fe) chemistry often controls As speciation in lakes, a higher rate of As regeneration in the south basin, accompanied by the absence of a correlation between regenerated As and Fe in this basin, suggest that additional factors operate to control As cycling in this lake. Solid-phase As speciation was remarkably similar between sediments of the two basins of this lake, about 40% of sedimentary As in upper sediments being in relatively labile (ionically bound and strongly adsorbed) fractions and a larger fraction of As being associated with recalcitrant minerals, likely sulfides. Extraction, X-ray fluorescence, and acid-volatile sulfide data collectively suggest that sedimentary As cycling in both basins is largely controlled by the formation of sulfide minerals. An accounting of the size of sulfur (S) pools supports this conclusion, showing that sufficient S exists in the north basin to control both Fe and As, while the south basin has lower S levels resulting in seasonal accumulation of Fe in the porewater.

## Introduction

Arsenic (As) cycling in lakes is highly dependent on the redox environment (1–6) and lake trophic status (6, 7). In many systems, As cycling is controlled by iron (Fe). In oxic waters, solid Fe oxyhydroxides sorb As and settle, resulting in a net transport of As to the sediments (8, 9). Under anoxic

conditions, Fe(III) can be both abiotically and microbially reduced to Fe(II), releasing sorbed As to porewater and the water column (5, 10–14). However, decoupling of Fe and As cycling has also been reported (13, 15, 16), indicating that other processes in addition to sorption to Fe oxyhydroxides may control As partitioning in sediments.

Sulfidic sediments have also been identified as potential semi-permanent sinks for metals and metalloids (17–21). As conditions in sediments become increasingly reducing and sulfate-reducing conditions develop, As may be sequestered by precipitation of As-sulfide minerals (22), coprecipitation with Fe-sulfide minerals (11, 20), and sorption to Fe and other sulfide minerals (23, 24). Sorption to Fe-sulfide minerals can be an initial As sequestration mechanism, with conversion to more recalcitrant Fe–As–S minerals occurring over time (25). The Fe/S ratio has been hypothesized to determine which solid forms of As occur (26); precipitation of realgar (AsS) was predicted at higher Fe/S ratios, while orpiment (As<sub>2</sub>S<sub>3</sub>) formation was predicted for low Fe/S ratios. However, other work has indicated that As will occur preferentially in pyrite rather than form a separate As–S phase (17, 27–29).

Sequential extractions of As (30–33) have been used as a relatively simple means to obtain information on the likely speciation and mobility of As in wetland and river sediments (34), soils (33), mine tailings (35), contaminated drinking water aquifers (36–38), and in solids associated with water treatment (38, 39). Solid-phase As speciation in sediments is one determinant of arsenic's potential mobility. Arsenic in more labile phases can be readily mobilized by changing redox conditions or other chemical changes, while As that has become sequestered in mineral phases is unlikely to be mobilized by typical biogeochemical processes in sediments.

Spy Pond in Arlington, Massachusetts is an example of a hypereutrophic, two-basin, seasonally anoxic urban pond that is contaminated with As. In the 1950s and 1960s, both basins (north and south) of the pond were treated with arsenical herbicides. As a result, As concentration maxima (~2000 ppm in the north basin and ~3000 ppm in the south basin) are now present in sediments at a depth of 10–25 cm, and As concentrations in surface sediments (0–10 cm) remain significantly elevated above background (40).

Arsenic is readily mobilized to the water column of both basins during summer stratification. However, though the total As inventories of each basin are similar, dissolved As and Fe concentrations in the water column are often as much as 10 times greater in the south basin (41).

Further, unlike in many lakes (such as nearby Upper Mystic Lake, where Fe cycling alone appears to determine As remobilization (6)), As and Fe cycling can become seasonally decoupled in the water column of Spy Pond. In 1999, As levels in the hypolimnion of both basins initially increased but then plateaued during the summer, while Fe levels continued to increase.

The goal of this study was to gain a better understanding of the mechanisms controlling As and Fe remobilization and sequestration in sediments by characterizing sediment-side controls on Fe and As mobility in the two basins of Spy Pond. We tested three hypotheses: (1) the interbasin differences in water column As and Fe chemistry are mirrored by similar trends in the porewater concentrations; (2) solid-phase speciation rather than total amount in the solid phase determines the porewater concentrations of As; and (3) sulfur cycling plays an important role in controlling the porewater concentrations of As and Fe.

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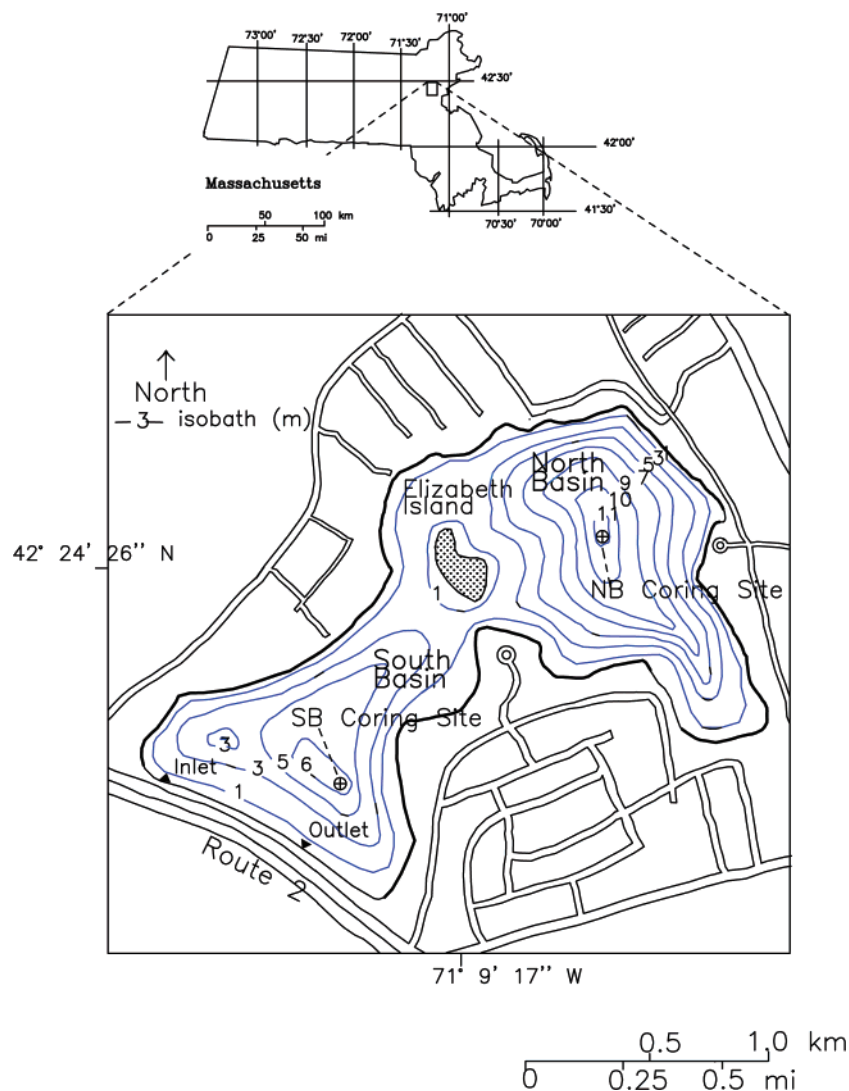


FIGURE 1. Map of Spy Pond, Arlington, Massachusetts.

## Materials and Methods

**Site Description.** The north and south basins of Spy Pond are separated by a shallow sill (Figure 1). Forty storm drains deliver surface water to the pond. The largest of these drains a major highway (Massachusetts Route 2) and during the winter carries salty runoff into the south basin. Salt accumulation in the bottom waters of the south basin has led to incomplete mixing of the water column in the spring. The north basin is typically well-mixed in April, and stratification and oxygen depletion in the hypolimnion proceeds throughout late spring.

**Sampling and Core Processing.** Sediment cores were collected on January 8, March 3, July 25, and October 3, 2001 from the deepest parts of the two basins using a previously described freeze-core method (42). The cores were wrapped in plastic wrap and held in a cooler on dry ice for transport. Upon arrival at the lab, the top 10 cm of each core was cut into five 2-cm lengths using a hot tungsten-wire saw in an argon-flushed anaerobic chamber. Frozen sections were placed in 250-mL polycarbonate Sep-Cor bottles with rubber O-ring seals (argon headspace). Thawed samples (covered and sealed) were removed from the chamber and centrifuged at 11 000g for 25 min. Porewater was decanted and filtered (0.2- $\mu$ m syringe filter) in the anaerobic chamber.

**Porewater Analysis.** Total As and Fe in the porewater (and extractions) were determined by graphite furnace atomic absorption spectroscopy (Perkin-Elmer 4100Z, detection

limits (dl) = 5  $\mu$ g/L and 1  $\mu$ g/L for As and Fe, respectively). Palladium and magnesium nitrate were matrix modifiers. Fe(II) was measured using the ferrozine method (dl = 10  $\mu$ M) and sulfide was determined using the methylene blue spectrophotometric method (dl = 1  $\mu$ M) (43). Chloride was determined by ion chromatography (Dionex 16).

**Solid-Phase Analyses.** To measure acid-volatile sulfides in the solid phase, 0.5 g of wet sediment together with 50 mL of 1 N HCl was slowly bubbled with nitrogen for 1 h. Sulfide liberated to the gas phase was trapped as ZnS in two consecutive traps containing 0.2 M zinc acetate/0.12 sodium acetate solution and quantified with the methylene blue method (dl = 1  $\mu$ g sulfide/g sediment).

The total solid-phase content of a suite of elements was determined for sediment depth increments in the top 10 cm of the January samples by X-ray fluorescence (XRF) using a Spectro Analytical X-Lab 2000 spectrometer. Five grams of dried sample was ground with a tungsten carbide mill, blended with copolymer, and pressed into circular disks. Performance of the instrument was tested regularly with National Institute of Standards and Technology standard reference material 2709 (San Joaquin soil) (dls ranged from 0.2 to 1 ppm, precision = 3%).

To characterize the phases of As and Fe present, sediment solids were sequentially extracted using a protocol developed for arsenic speciation (34). Table 1 provides a description of each extraction step and its particular significance for

**TABLE 1. Extraction Steps, Targeted As Phases, and Significance of Each Phase for Spy Pond**

extractant	target phase	significance for this study
1 M MgCl <sub>2</sub> 1 M Na <sub>2</sub> HPO <sub>4</sub> 1 N HCl	ionically bound As strongly adsorbed As As coprecipitated with very amorphous Fe oxyhydroxides, AVS, carbonates	mobilizable by increased ionic strength, such as from road salt competing anions such as phosphate could mobilize As reduction of most easily reducible Fe oxides will liberate As
0.2 M ammonium oxalate/oxalic acid 0.05 M Ti(III)–citrate–EDTA–bicarbonate 10 M HF	As coprecipitated with amorphous Fe oxyhydroxides As coprecipitated with crystalline Fe oxyhydroxides As oxides and As coprecipitated with silicates	reduction of more crystalline phases of Fe oxides will mobilize As  this fraction of Fe oxides is less readily reduced
16 N HNO <sub>3</sub>	As coprecipitated with pyrite and amorphous As <sub>2</sub> S <sub>3</sub>	potential long-term sink
16 N HNO <sub>3</sub> + 30% H <sub>2</sub> O <sub>2</sub>	orpiment and remaining recalcitrant As minerals	potential long-term sink

evaluating mobility in Spy Pond sediments. The method was rigorously tested by Keon et al. (34) using standard reference materials. There is a possibility that some As extracted in the later steps may be an artifact, formed during the HCl extraction by precipitation with AVS (44). This potential artifact might be important if there is sufficient sulfide liberated to enable precipitation of appreciable As sulfides compared to the concentrations found in the final extraction steps.

**Geochemical Modeling.** The equilibrium geochemical model PHREEQCI Version 2 (45) was used to model the hypolimnion and porewater in both basins to test effects of water chemistry changes on the precipitation of As. The MINTEQ database was used since it contains constants for As speciation, precipitation, and surface complexation. The following reaction for amorphous arsenopyrite (FeAsS<sub>(amorphous)</sub>) formation was added to the MINTEQ database: FeAsS(am) + 3H<sub>2</sub>O = H<sub>3</sub>AsO<sub>3</sub> + 2H<sup>+</sup> + HS<sup>−</sup> + Fe<sup>2+</sup> + 3e<sup>−</sup>, log K = −18.06 (46, 47). Two models for aqueous thioarsenite formation were added to the database and run separately: one predicting AsS<sub>2</sub><sup>−</sup> and HAsS<sub>2</sub> (48) and the other predicting As(OH)<sub>2</sub>(SH), As(OH)<sub>2</sub>S<sup>−</sup>, As(OH)S<sub>2</sub><sup>2−</sup>, AsS<sub>3</sub>H<sup>2−</sup>, AsS<sub>3</sub><sup>3−</sup>, and As(SH)<sub>4</sub><sup>−</sup> (49). Results for saturation indices (SI) of minerals of interest varied only slightly between the two models.

Equilibrium constants of the sorption reactions for two carbonate surface species (surfFeOCO<sub>2</sub>H and surfFeOCO<sub>2</sub><sup>−</sup>) were added (50). Arsenic sorption to iron oxyhydroxide was modeled for two types of binding sites with differing affinities for As (Ks were taken from MINTEQ database). The weak site is generally more abundant and may be important for As. Water column data (total As, total P, pH, S(−II)T, Fe(II), total Mn, dissolved oxygen, and temperature) were obtained from a previous Spy Pond study (41). Na<sup>+</sup> and Cl<sup>−</sup> concentrations were calculated from measured specific conductivity (assuming specific conductance derives mostly from NaCl) using a relationship developed for Spy Pond (unpublished). Typical freshwater values were used for less abundant ions such as K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>, and model results were not particularly sensitive to the concentrations of these constituents (51). Total carbonate in the water was determined using PHREEQCI based on the charge balance constraint (total carbonate was adjusted so that the error was <0.1%). Solid formation and surface complexation were modeled with PHREEQCI.

## Results

**Sediment Porewater As and Fe.** Figure 2 depicts the porewater concentrations for both Fe and As throughout the year. Levels of porewater As were not significantly different between the two basins at any time, with average concentrations of about 4 μM (300 ppb) for January, March, and July (Figures 2a and b). In both basins, porewater As concentrations were highest in October. Fe(II) concentrations increased with sediment depth in both basins, but south basin

concentrations were up to five times greater than those in the north basin (Figure 2c and d), as was hypothesized from water column data.

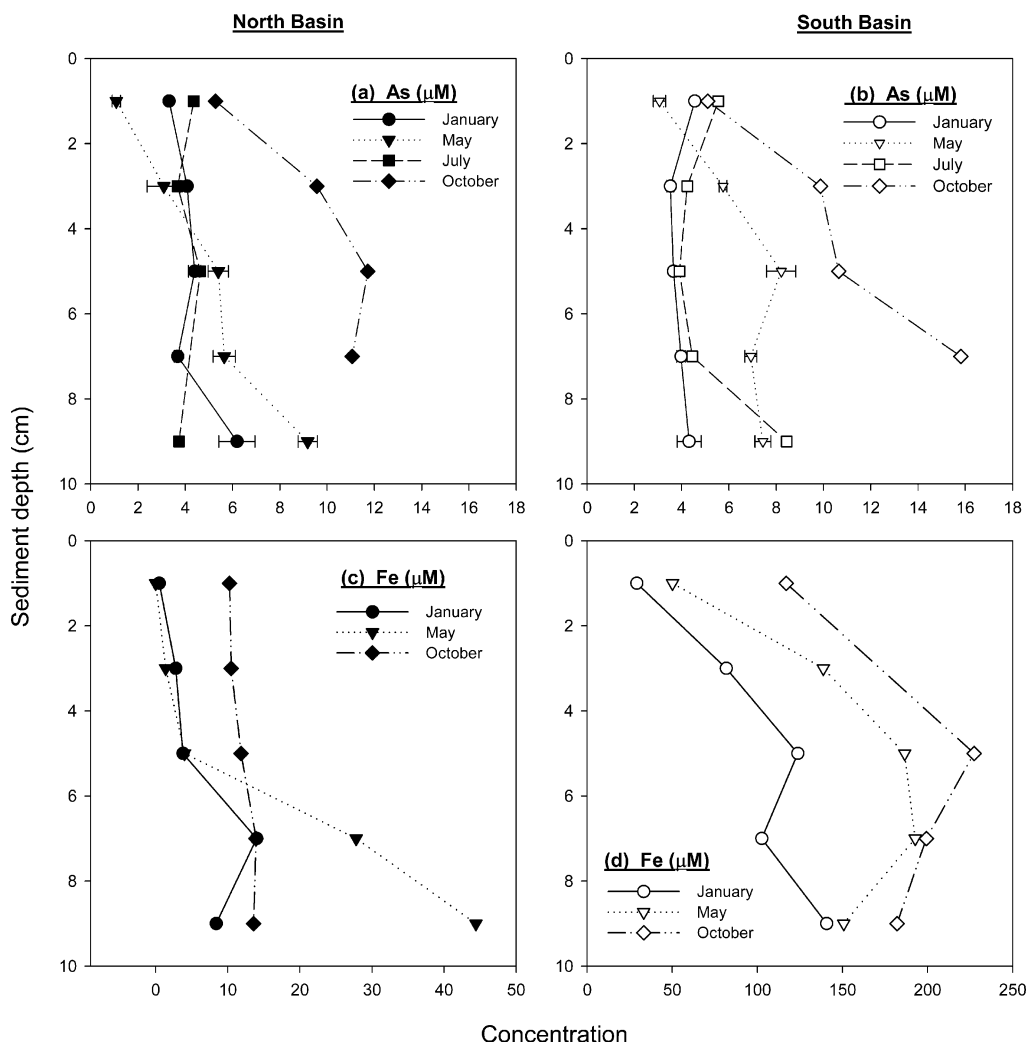
**Solid-Phase Element Profiles.** Figure 3 compares the solid-phase total concentrations of a suite of elements in the north and south basins. While solid-phase concentrations of As and Fe are similar between the two basins (Figure 3a and b), the percentage of S in the solid phase was approximately a factor of 2 higher in the north basin (Figure 3e). Concentrations of C, Na, and Zr (Figure 3c, d, and f) as well as Mg, Al, and K (data not shown) were consistently higher in the surface sediments of the south basin. The elevated concentrations of Na and Cl in the south basin compared to the north appear to reflect road salt in highway runoff that disproportionately impacts the south basin. P and Pb levels are similar between basins (Figure 3g and h).

**Solid-Phase Speciation of As.** Sequential extractions of sediments indicate that most of the As is coprecipitated in recalcitrant minerals with Fe and/or S (Figure 4). Approximately 50% and 75% (annual averages) of As in the north and south basins, respectively, was present in the HNO<sub>3</sub>-extractable fractions (Figure 5), which target pyrite (FeS<sub>2</sub>), orpiment (As<sub>2</sub>S<sub>3</sub>), and other Fe- or S-rich recalcitrant mineral phases. In general, the magnitude of the more labile fractions of As is similar between the basins (Figure 4). There was greater As in labile fractions for both basins in October, which corresponds to the higher porewater As concentrations observed for that month. Yearly averages for ion-exchangeable (MgCl<sub>2</sub>) and strongly complexed (PO<sub>4</sub>-extractable) As fractions were 15–20% and 24% of the total, respectively.

Solid-phase Fe speciation was similar between the two basins (Figure 6). In the January cores from both basins, approximately 60% of the Fe was in the Mg- or PO<sub>4</sub>-extractable phases, which are the more labile phases. Less than 5% of the Fe was found in the nitric acid extraction steps, which target crystalline iron sulfides. Overall, a higher percentage of the Fe was in more labile fractions compared to As.

**Porewater Sulfide and Solid-Phase Acid-Volatile Sulfides.** Acid-volatile sulfides (Figure 7) in the sediments were similar (approximately 20 μmol/g wet sediment) for both basins for the May, July, and October sampling dates. In contrast, AVS concentrations were 2–5 times higher in the south basin during the January sampling date. Porewater sulfide was not detected in any samples from either basin.

**Geochemical Modeling.** A geochemical model of the porewater predicts that at sulfide concentrations from 1 nM to 10 mM, the saturation index (SI = log(Ion activity product/K<sub>sp</sub>)) for orpiment (As<sub>2</sub>S<sub>3</sub>) is higher than that for all Fe-sulfides. At very low sulfide concentrations (1 nM), 150 μM Fe(II), and pe = −4, the SI for orpiment is 2.8 while SIs for pyrite (FeS<sub>2</sub>) and amorphous arsenopyrite (FeAsS<sub>(am)</sub>) are 1.2 and 1.3, respectively. FeS is undersaturated with a SI of −0.73. At sulfide concentrations of greater than 1 mM, the SI for orpiment is approximately 5 orders of magnitude higher than



**FIGURE 2.** Porewater concentrations of arsenic (a, b) and iron (c, d) in sediments from the north and south basins. For As, error bars represent standard deviations of triplicates. Fe data do not have error bars, as for most samples only a single reading was taken. Ten percent of the samples were conducted in duplicate, and the method precision is approximately 2%.

that for pyrite. However, a lower SI does not necessarily predict the absence of a mineral; rather, it may indicate that the mineral has already formed in the environment. The SIs were very sensitive to pe; however, the ratios between the minerals of interest remained similar at reducing pe values.

In a model of the water in the hypolimnion, the effect of salinity on the SIs for arsenic minerals between the two basins was tested by increasing the NaCl concentration of the north basin to reflect the higher salinity measurement in the south basin. With this modification, the SIs decreased by 0.04 to 0.1. The resulting SI for arsenopyrite was  $-0.09$ , indicating that with higher salinity it no longer tended toward precipitating. These modeling results show that, in general, a slight increase in the solubility of minerals may result from the higher salt concentrations in the south basin porewater compared to the north basin. Although increased salinity in the south basin does increase the solubility of minerals, changes in SI of this order correspond to at most a 25% difference in ion product, which is not sufficient to explain order-of-magnitude inter-basin concentration differences.

## Discussion

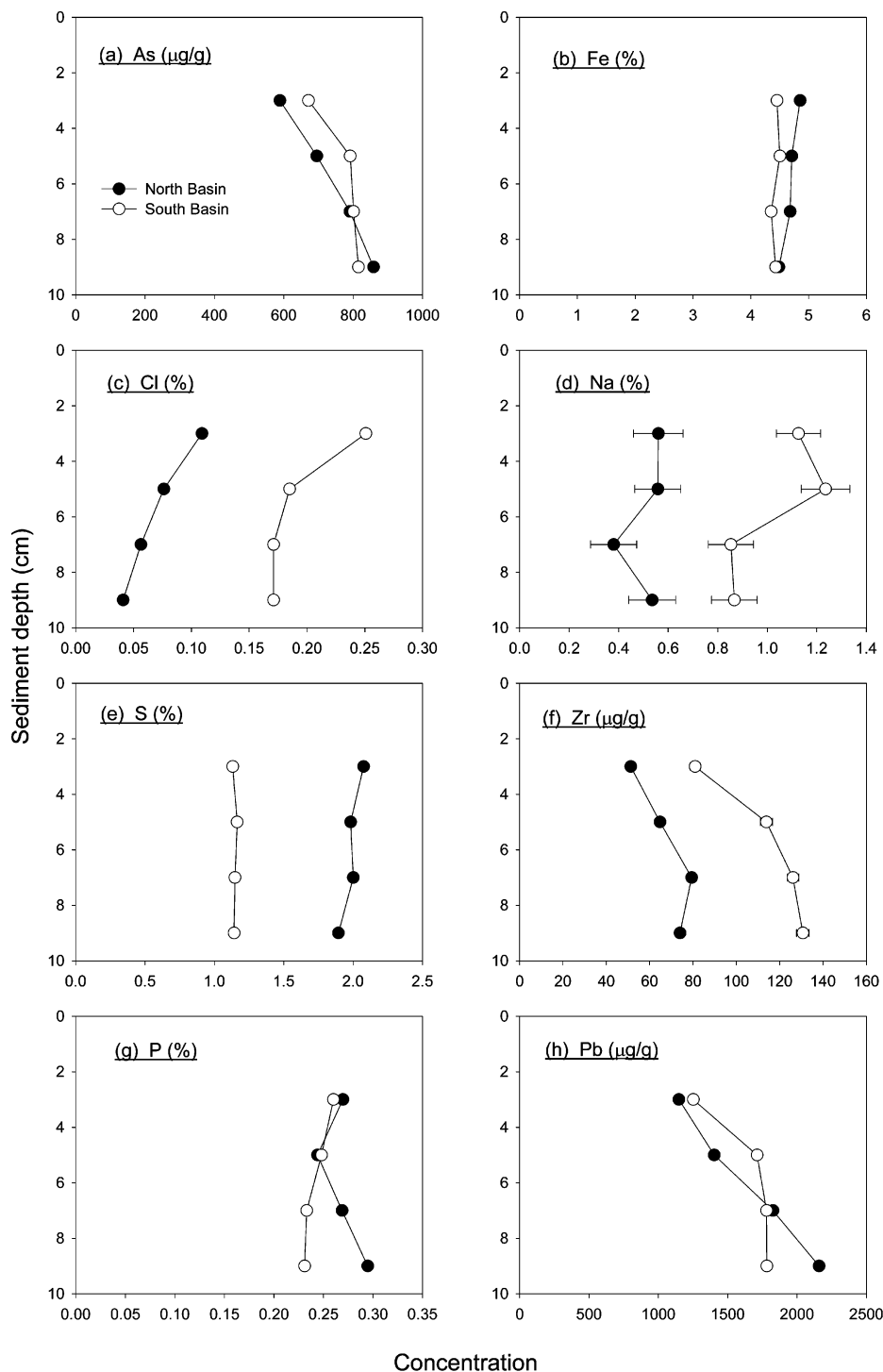
We hypothesized that the dramatically higher hypolimnion concentrations previously observed for As and Fe in the south basin would also be observed in the porewater. To test this hypothesis, we analyzed the porewater as a function of depth in the surface sediment from both basins for all sampling

dates. Figure 2 shows that similar concentrations of As were present in the sediment porewater of both basins, while the concentrations of Fe were much higher in the porewater of the south basin. This indicates that the mobilization of As from the solid phase is not simply dependent on the reduction of iron oxides, in agreement with the decoupled summer hypolimnetic profiles.

We sought to explain why the porewater concentrations of Fe, but not As, would differ between the basins. The molar ratios of the two elements in the solid-phase in both basins were compared, but no significant differences between the basins were observed. The ratio of the labile fractions of Fe and As was determined (from Figures 4 and 6), but again no significant inter-basin differences were found. Thus, neither the amount of Fe and As in the solid-phase nor its speciation among various fractions could explain the markedly different mobilization between the two basins for Fe.

A mass balance on sulfur was calculated to test the hypothesis that the concentrations of dissolved Fe and As are controlled by sulfide. The total sulfur contents of the north and south basin sediments were 630 and 312  $\mu\text{mol S/g}$  dry sediment, respectively. From sequential extraction data, 5  $\mu\text{mol S/g}$  dry sediment may be precipitating as As-S or As-Fe-S phases such as orpiment and realgar (however, the method cannot distinguish As-S phases from As-Fe-S phases). Figure 3 shows total Fe concentrations of 860 and 820  $\mu\text{mol Fe/g}$  dry sediment in the north and south basins,





**FIGURE 3.** Total element concentrations in the solid phase as determined by X-ray fluorescence. When not visible, error bars are smaller than the width of the symbol.

respectively; and ~25% of the total Fe (215 and 205  $\mu\text{mol/g}$  dry sediment) is likely bound in recalcitrant sulfidic phases, based on sequential extraction data (i.e., the last three extraction steps). Assuming that the most likely iron-sulfide species to form would be  $\text{FeS}_{2(s)}$  (this mineral has a higher SI than  $\text{FeS}_{(s)}$ ), we can subtract the S precipitating as pyrite from the total S. In the north basin, under this scenario, there would be sufficient S to bind all of the Fe appearing in the recalcitrant sulfidic phases ( $630 - 5 - (2 \times 215) = 195$ ) if no other metal-sulfide phases are considered, while the south basin ( $312 - 5 - (2 \times 205) = -103$ ) would have insufficient sulfide to precipitate all of the available Fe. Thus, additional Fe would not be precipitated with sulfide, and to

the extent it remains in solution, Fe would accumulate in the dissolved phase and be subject to possible transport to the water column. It is important to note that if  $\text{FeS}$  formation was favored (52), sufficient S would be available to bind all recalcitrant Fe in both basins. Indeed, the fact that there is insufficient S to bind all recalcitrant Fe as  $\text{FeS}_2$  suggests as an alternative hypothesis that  $\text{FeS}$  may be an important product under these conditions.

O'Day et al. (26) characterized 1  $\mu\text{mol}$  reactive Fe/g dry sediment as Fe-poor and 100  $\mu\text{mol}$  reactive Fe/g dry sediment as Fe-rich. In Spy Pond sediment, approximately 500  $\mu\text{mol}$  Fe/g dry sediment is extractable by just the first two extractants; thus, according to this classification, Spy Pond

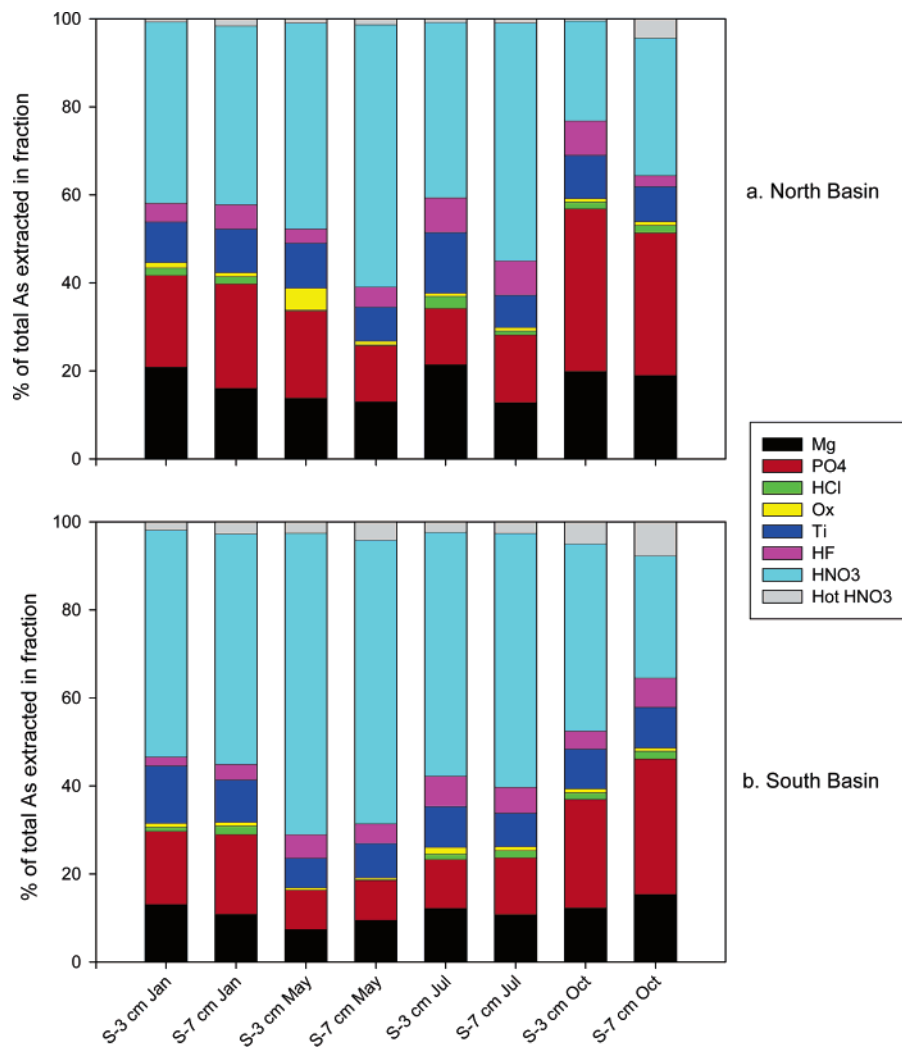


FIGURE 4. Solid-phase speciation of arsenic as determined by sequential extraction in the north (a) and south (b) basins.

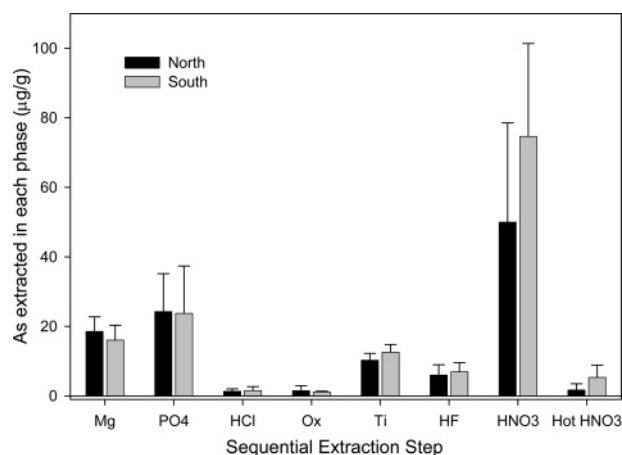


FIGURE 5. Yearly averages for arsenic extracted in each phase in sediments from the north and south basins.

sediments are Fe-rich. However, Fe(II) and S(II) interact through the very low solubility of FeS and FeS<sub>2</sub>, and the Fe/S ratio for Spy Pond sediments is relatively small. The ratios of total Fe to total S are 1.3 and 2.6 in the north and south basins, respectively, while the ratio of reactive Fe/total S are 0.8 and 1.7. These ratios are consistent with the Fe/S ratios calculated for sediment characterized as S-controlled. AVS was detected in sediments from both basins, indicating sulfur-reducing conditions. Also, the very small fraction of As

released in the extraction of amorphous Fe oxyhydroxide is consistent with the characterization of this environment as S-controlled, rather than Fe-controlled. In contrast, sequential extraction data in more oxic environments has revealed that As coprecipitated with amorphous Fe can comprise the largest fraction (53).

Other recent studies have applied sequential extraction results with other metrics (Fe/S ratios and the presence of AVS) to identify controls on As mobility (26, 54). In general, higher Fe/S ratios were observed in environments characterized as Fe-controlling with respect to As, usually determined as a result of numerous supporting observations (e.g., geochemical modeling and direct observation of As phases). Conversely, lower Fe/S ratios and the presence of AVS typically indicated that As was controlled by sulfidic phases unless the concentration of sulfur was so low as to not enable precipitation of As sulfides.

It is notable that forty years after the pulse input of highly mobile arsenate and arsenite ions, only approximately 60% of the As in sediments is precipitated as recalcitrant sulfides. Sufficient quantities of As have remained in a labile form to result in remobilization with seasonal anoxia, leading to hypolimnetic concentrations comparable to those of lakes receiving current inputs.

**Implications for Spy Pond.** In this study, As cycling in both basins of As-contaminated Spy Pond was shown to be largely controlled by the formation of sulfide minerals. The evidence for this is the substantial percentage of As (~60%) found in the extractions targeting sulfide minerals, the

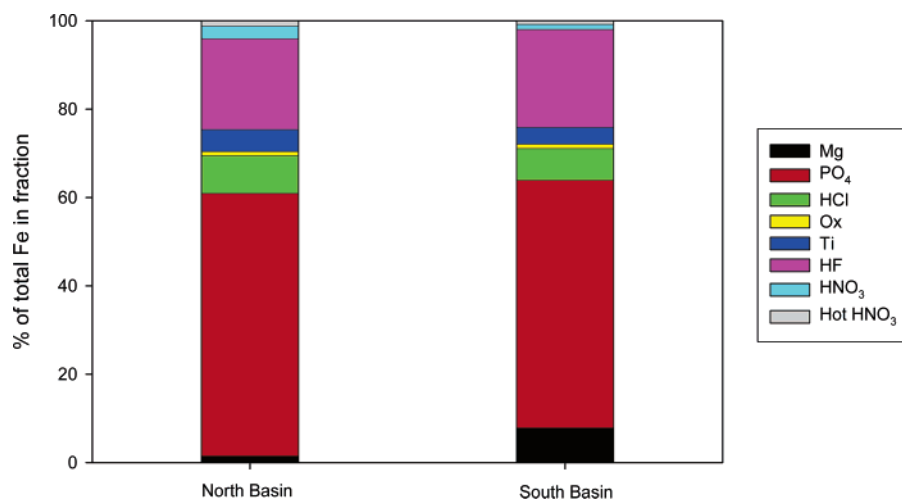


FIGURE 6. Fe speciation in the January cores from the north and south basins.

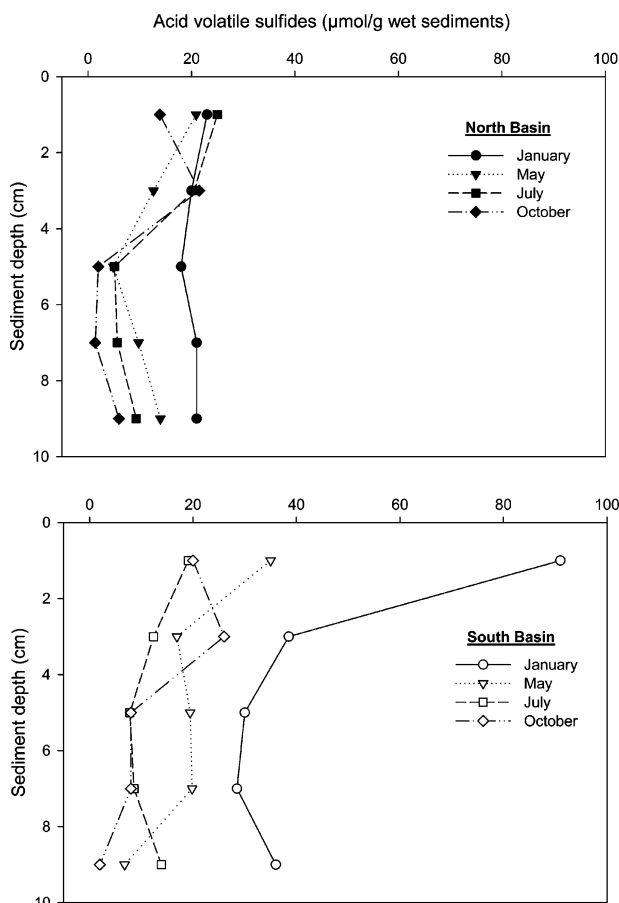


FIGURE 7. Acid-volatile sulfide concentrations in sediment porewater in the north and south basins.

presence of AVS, and low Fe/S ratios. In addition, a S mass balance revealed differential controls on Fe in the two basins. While sufficient S exists in the north basin to control both Fe and As, the south basin has lower S, and, apparently as a result, Fe accumulates in the porewater. These findings complement other studies evaluating controls on As mobility in lacustrine sediments and provide evidence of natural As immobilization mechanisms in an urban, As-contaminated lake.

Although there has been a substantial shift toward relatively recalcitrant sulfide mineral phases over decades of burial and persistent sulfate-reducing conditions, there remains a sizable pool of readily mobilizable As. This As is

primarily surface-complexed by solids. Thus, seasonal anoxia in the hypolimnion continues to mobilize As and cause the accumulation of high (200–2000 nM) levels of As in the water column.

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