Distribution of reduced inorganic sulfur compounds in lake sediments receiving acid mine drainage

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Abstract—The sediments of Lake Anna, Virginia, act as a major sink for incoming acid mine drainage (AMD) pollutants (Fe, SO_4^{2-}, H^+) due to bacterial sulfate reduction (SR). Acid-volatile sulfide (AVS), elemental S, and pyrite concentrations in the sediments of the polluted arm of the lake are significantly greater than those in unpolluted sections of the lake. Measurements of SR using $^{35}S-SO_4^{2-}$ showed that AVS and S^0 are the major short-term (48 h) products of SR in these sediments. Inorganic forms of S (AVS, S^0, and FeS_2) made up from 60 to 100% of the total sediment S concentration. Pyrite concentrations in the sediment were high but decreased exponentially with distance from the AMD source, suggesting that the pyrite was deposited as stream detritus from the abandoned mines. Iron monosulfide and elemental S concentrations were highest at a station 1 km away from the AMD inflow, indicating formation *in situ*. There was no evidence for the formation of organic S species. The results suggest that in Fe- and S-rich locations such as those contaminated with acid mine drainage, the distribution of end products of SR may vary substantially from those reported for more moderate environments.

INTRODUCTION

BACTERIAL sulfate reduction (SR) is an important alkalinity generating reaction that can partially counteract the acidification process in a variety of lakes receiving acidic pollution (COOK *et al.*, 1986; KELLY *et al.*, 1982; KING *et al.*, 1974; MILLS and HERLIHY, 1985; SCHINDLER and TURNER, 1982; TUTTLE *et al.*, 1969a,b). Oxidation of reduced S compounds consumes alkalinity and generates protons; thus in order for the effect of the alkalinity to be permanent, the sulfide formed during the reduction process must be held in the reduced form or removed from the system, such as by evolution of H_2S gas (SCHINDLER *et al.*, 1980). Because some forms of sulfide are more mobile than others and some forms are more readily oxidized by microorganisms, the identity of the compounds in which the reduced S is stored in the sediments plays a role in determining the importance of alkalinity generation from SO_4^{2-} reduction in lakes receiving anthropogenic S inputs from precipitation, mining activities, or industrial waste.

A further consideration in retention of reduced S in sediments is that biogenic S emissions may contribute to the acidity of precipitation in downwind areas at a later time (NRIAGU *et al.*, 1987). The emissions are largely H_2S and dimethylsulfide formed directly as a product of sulfate reduction or from the mineralization of organic S compounds. Formation of stable metal sulfides could reduce the potential for acid formation either in the water body or in the atmosphere either by biogenic S emissions or by reoxidation of the recently reduced SR endproducts.

Sulfur occurs in a variety of forms in sedimentary systems underlying both acidified and unacidified waters. The major inorganic forms of reduced S are amorphous metal sulfides, crystalline metal sulfides and disulfides (greigite, mackinawite, pyrite) and elemental S. Sulfur is also found in organic forms such as ester sulfates or carbon-bonded S (e.g. amino acids such as cysteine and methionine). The dominant forms of sedimentary S in unpolluted freshwater lakes are organic S compounds (DAVID and MITCHELL, 1985; KING and KLUG, 1982; MITCHELL *et al.*, 1981). NRIAGU and SOON (1985) reported elevated concentrations of reduced inorganic S in several freshwater lakes that receive heavy metal and acid rain deposition, but organic compounds still dominated the S present. RUDD *et al.* (1986) reported formation of substantial quantities of Fe monosulfide, pyrite, and organic S in epilimnetic lake sediments in Norway, the Adirondack Mountains, and at the Experimental Lakes Area in Manitoba. These authors concluded that while the immediate end products of SR were the inorganic forms, with time the most quantitatively important end product of SR was organic S.

Studies of SR in non-acidified habitats have examined the distribution of SR end products as they relate to the storage of energy within an ecosystem (HOWARTH, 1979, 1984; HOWARTH and TEAL, 1979). Results among various studies are not consistent. In some cases, formation of pyrite dominated the reactions (HOWARTH, 1979; HOWARTH and GIBLIN, 1983; HOWARTH and MERKEL, 1984), but other workers reported a greater importance of acid-volatile sulfide (AVS) and organic S (KING *et al.*, 1985). It is certain that the end-product distribution should not be expected to be identical at all sites, but at present

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there is little evidence to help determine why the differences occur.

Whereas most of the examinations of the relations between SR and lake buffering have been carried out in precipitation acidified lakes (or lakes that have been artifically acidified to simulate acidification by precipitation), the present study investigated SR and sediment S speciation in one arm of Lake Anna, an impoundment in central Virginia that receives acid mine drainage (AMD) from Contrary Creek which drains a series of abandoned pyrite mines and tailings piles. The concentrations of AMD pollutants in Contrary Creek are more concentrated than in unpolluted waters ($SO_4^{2-} \simeq 1$–20 mM, total dissolved Fe $\simeq 10$–50 ppm, pH $\simeq 2.5$–3.5), and the concentrations of the pollutants in the water and sediments of this arm of Lake Anna are substantially higher than those encountered in similar studies of precipitation acidified lakes.

Previous work on the sediments of this arm of Lake Anna has shown that SR rates and AVS concentrations are higher in the AMD-impacted section of the lake than in the unpolluted section (HERLIHY and MILLS, 1985). On an annual basis, 48% of the SO_4^{2-} entering from Contrary Creek is removed from the lake water by SR in the sediments within 2 km of the stream mouth (HERLIHY et al., 1987); the sediments of the Contrary Creek arm of Lake Anna act as a major S sink for the incoming AMD pollution. Organic matter is in abundance in the sediments; concentrations of organic matter range from 3 to 15%, and the average is about 5% throughout the study area.

The objective of the present study was to determine the dominant chemical form of the S sink in the sediments of the AMD-polluted Contrary Creek arm of Lake Anna, thereby elucidating the process of SO_4^{2-} removal and sediment S formation in a freshwater environment high in both Fe and S. Particular emphasis was given to understanding the nature and distribution of SR end-products in this Fe-rich system in contrast to reports in the literature of systems with lower concentrations of Fe. The results showed that Fe monosulfide and elemental S are the major products of SR in the sediments of the Contrary Creek Arm of Lake Anna, and that pyrite and organic S formation are of minor importance in these sediments.

METHODS

Sampling

To assess the nature of the S species in the sediments of Lake Anna, triplicate cores were collected at station C3 (Fig. 1) every 2–3 months from May 1985 to May 1986 and analyzed for SR rate, and concentrations of acid-volatile S (AVS), elemental S (S^0) pyrite, and total S. Sediment pore water was also collected and analyzed for pH, conductivity, and sulfate, Fe, and sulfide concentrations. Station C3 was selected for this study because it frequently had high rates of SR (HERLIHY and MILLS, 1985). For comparative purposes, cores were also collected from an unpolluted site (station F1, Fig. 1) in November 1985.

Interstitial water was obtained using sediment equilibrators (HERLIHY and MILLS, 1985) similar to those used by HESSLEIN (1976). After two weeks equilibration time, the equilibrators were removed from the sediment, and 10 ml of
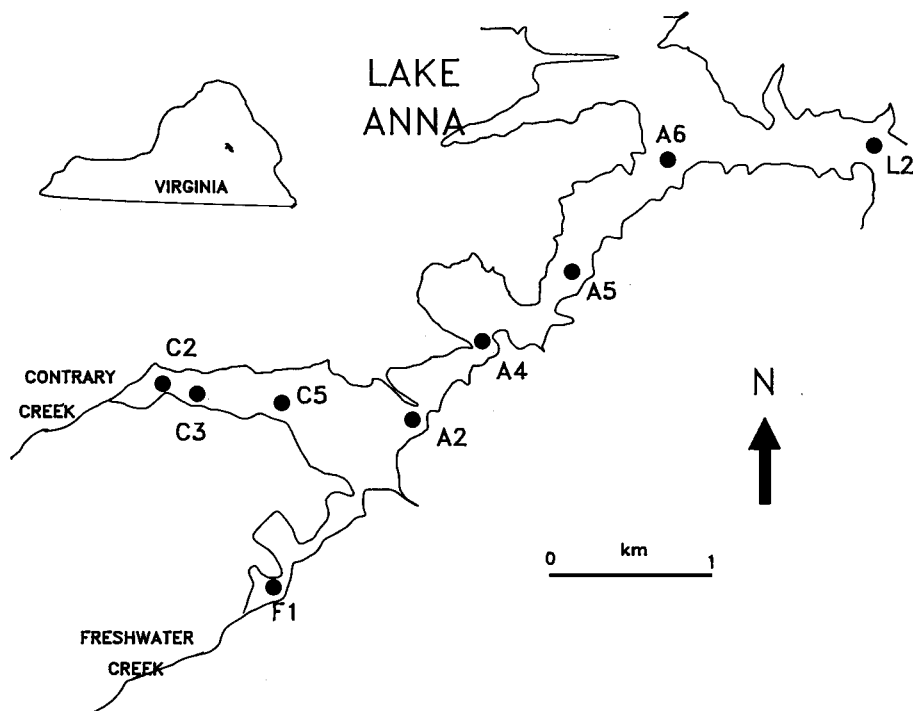

FIG. 1. Location of sampling stations in the Contrary Creek arm of Lake Anna.

pore water from each well was rapidly pipeted into a 15 × 120 mm test tube followed by the immediate addition of 1 ml of the colorimetric sulfide reagent (CLINE, 1969). The tube was capped with a butyl rubber stopper, inverted three times, and transported, in the dark, to the laboratory where the absorbance was read immediately upon return. The sulfide colorimetric reagent fixes the sulfide concentration as long as the samples are kept in the dark and analyzed within 24 h (KING, 1984).

Samples were taken for Fe and sulfate analyses by quickly pipeting 10 ml of the water in each well of the equilibrator into glass scintillation vials containing 100 μl of 6 N HCl. Acidifying the samples greatly retards the oxidation rate of ferrous Fe (MOSES et al., 1988); visual signs of Fe flocculation were seen within 15–30 min in unacidified samples.

The position of the equilibrator wells in the sediment was easily determined, because a bright orange band of Fe precipitated on the equilibrator at the sediment–water interface. The location of this orange band as the interface was confirmed by SCUBA divers who examined the equilibrators before removal.

Triplicate sediment cores were taken adjacent to the equilibrators at each station on each sampling trip in warm weather by SCUBA divers and in winter with a gravity corer (Wildco). Sediment temperature was determined by inserting a thermometer into a fresh sediment grab sample. The cores were transported to the laboratory in an insulated box and were held at the in situ temperature until processing (within 24 h).

Coring and collection of subsamples (subcores) with detipped, 10-ml plastic syringes was done as described elsewhere (HERLIHY and MILLS, 1985; HERLIHY et al., 1987). Subcores were taken at depths of 1, 3, 5, 7, and 9 cm in triplicate cores and used for analysis of SR rates and concentrations of several S species. After taking the sediment subcore, a detipped 1-ml syringe was inserted into the hole in the side of the core, and 0.5 ml of sediment was withdrawn for determination of porosity and total S content.

To assess the distribution of sediment S species throughout the AMD-contaminated arm of Lake Anna, depth-integrated concentrations of AVS, S^0 and FeS_2 (pyrite) were measured along a transect at stations C2, C3, C5, A2, A4, A5, A6, and L2 (Fig. 1). Stations A4, A5, and A6 were in the old Contrary Creek bed between the causeway bridge and the main body of the lake and had water depths of 9–10 m. Station L2 is in the main body of the lake downstream from the inflow of Contrary Creek in 12–13 m of water. Samples were collected in September, 1986, and processed in the field. Two sediment cores were collected at each station with a gravity corer (at stations > 10 m depth) or by a SCUBA diver. After siphoning off the bottom water, the top 8 cm of sediment of each core was extruded into another core liner (8 cm long) and separated from the rest of the core. A detipped 10-ml syringe barrel was then inserted vertically down the center of the core to obtain a subcore of the top 8 cm of sediment. The syringe barrel was stoppered at both ends so that there was no headspace, and the samples were transported on ice back to the laboratory where they were placed in a freezer and stored at −4°C until analysis.

To determine the SR endproducts resulting from longer term incubations of cores with $^{35}SO_4^{2-}$, 8 subcores, each containing 7 ml of homogenized surface sediment from station C3, were injected with 1 μCi of $^{35}SO_4^{2-}$ and incubated for 1.1, 10.5, 26, or 48 h (2 subcores taken at each time) at room temperature. The cores were then analyzed for AVS, S^0, and FeS_2 as described below.

Analytical methods

Sulfate concentration in the interstitial water was determined by ion chromatography (MOSES et al., 1984). Hydro-

gen sulfide concentration was measured colorimetrically following the method of CLINE (1969). Ferrous and ferric Fe concentrations were determined by the ferrozine method (STOOKEY, 1970; GIBBS, 1979) and by an ion chromatographic technique (MOSES et al., 1988).

Sediment porosity was determined by weight loss on drying at 105°C for 24 h to determine water content. It was assumed that the density of the water was 1 g/ml and that the water volume equaled the pore volume. Total S concentration was determined on dried sediment using the alkaline hypobromite technique of TABATABAI and BREMNER (1970) as modified for freshwater sediments by KING and KLUG (1980). SR rates were measured using the ^{35}S–SO_4^{2-} tracer method (JORGENSEN, 1978) as modified by HERLIHY (1987). The subcores were analyzed for the S fractions as described below, and the amount of ^{35}S label in each S fraction was determined by liquid scintillation counting. SR rates were calculated by multiplying the SO_4^{2-} turnover rate constant (^{35}S trapped as reduced $S/^{35}S$ injected/incubation time) by the interstitial SO_4^{2-} pool (in μmol/ml sediment) as shown in Eqn (1)

$$\text{SR rate} = \frac{^{35}S\text{-sulfide}}{^{35}SO_4^{2-}} * [SO_4^{2-}] * t_{inc}^{-1} * 1.06 \qquad (1)$$

where 1.06 is the isotope correction factor (KAPLAN et al., 1963; SOROKIN, 1962) and t_{inc} is the incubation time.

AVS, elemental S, and pyrite concentrations were determined sequentially on each sediment subcore using the techniques of ZHABINA and VOLKOV (1978) and WIEDER et al. (1985). AVS was measured by adding 2 ml of concentrated HCl and 20 ml of deionized water (DIW) to the frozen sediment subcore and purging the released sulfide with N_2 gas into two, 20-ml 0.2 N NaOH traps. The traps were then combined and analyzed for sulfide colorimetrically (CLINE, 1969). This procedure yields the concentration of the aqueous sulfides (H_2S, HS^-, and S^{2-}) along with the monosulfides such as FeS. Because the concentrations of aqueous sulfides were determined separately (described above) and found to be absent or insignificant in concentration compared with total AVS, the AVS fraction is considered to be only FeS. The term AVS will be used, however, to denote the possibility of metals other than Fe included in AVS. No determinations of such elements were made.

Elemental S was determined by filtering the sediment remaining from the AVS determination and extracting it with acetone for 4 h in a soxhlet extractor. The acetone was placed in the distillation apparatus and 10 ml of 1 M $CrCl_2$ and 8 ml of concentrated HCl were added to reduce and volatilize the S. The liberated sulfide was purged, trapped, and analyzed as described for the AVS technique. The reduced Cr solution was prepared immediately before use by passing a 1-M $CrCl_3 \cdot 6H_2O$ solution made up in 0.5 N HCl through a Jones reduction column (8–30 mesh amalgamated Zn, Fisher).

Pyrite concentration was determined on the residual sediment from the S^0 analysis. The sediment was placed in a modified Johnson–Nishita distillation-reflux apparatus (WIEDER et al., 1985) together with 16 ml of freshly reduced 1M $CrCl_2$ solution, 8 ml concentrated HCl, 10 ml ethanol, and 50 ml DIW. The mixture was boiled for 1 h and the liberated sulfide trapped and analyzed as described above.

Recovery efficiencies were determined for the total S and Cr-reduction techniques. For the latter, fine-grained pyrite samples were washed (3 times in boiling 6 N HCl followed by boiling acetone), dried, weighed and analyzed for S by the Cr-reduction procedure as outlined above. Almost all (86.0%, SEM = 2.67%, $n = 6$) of the pyrite S was recovered as Cr-reducible S (a pyrite stoichiometry of FeS_2 was assumed). For uncleaned pyrite samples, the recovery was only 58.3% (SEM = 5.35%, $n = 4$). Analysis of SO_4^{2-} and cysteine (a S-containing amino acid) solutions showed that
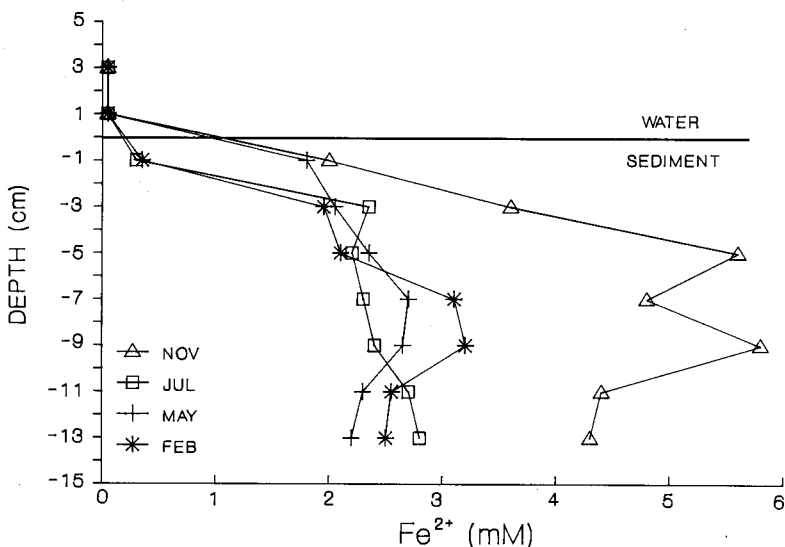
FIG. 2. Depth profiles of Fe^{2+} concentration (mM in pore water) at station C3 from July 1985 to May 1986. Data points represent the mean of duplicate samples. Standard deviations were usually between 10 and 40% of the mean.

<0.1% of these forms of S were recoverable by the Cr-reduction assay (HERLIHY, 1987).

To determine the recovery of total S, samples of pyrite (fine-grained, cleaned as above), thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$), and L-cysteine hydrochloride [$HSCH_2CH(NH_2)COOH \cdot HCl \cdot H_2O$] mixed and analyzed by the hypobromite methodology to determine the recovery rate, which was 105% (SEM = 8.30%, n = 6). In earlier work, it was reported that recovery rates of aqueous sulfides in the distillation apparatus were very high (97–100%), and recovery of labeled sulfide added to sediment samples as AVS was 88.3% (SEM = 4.37%, n = 7) (HERLIHY and MILLS, 1985). These recovery values are presented to indicate the efficiency of the techniques, but sediment concentration data were not corrected for recovery efficiency. The values reported here are similar to those of WIEDER et al. (1985).

The sum of the concentration of the reduced inorganic S species (AVS, S^0, and FeS_2) and the interstitial SO_4^{2-} concentration was subtracted from the total S concentration to yield the concentration of residual S. The residual S represents organic S and any solid phase or bound SO_4^{2-} forms.

RESULTS

The Fe^{2+} concentration in the interstitial water (1.5–6.0 mM) was much higher than the concentration in the lake water (30–100 μM) (Fig. 2). In the sediment, little or no ferric Fe was detected, while in the lake water the Fe^{2+}/Fe^{3+} ratio was roughly 1:1 (HERLIHY, 1987). Depth profiles of ferrous Fe concentration in the sediment pore waters were very similar in July 1985, February 1986, and May 1986 while higher concentrations were observed in November 1985 (Fig. 2).

No H_2S was observed in the water column of Lake Anna at any time (Fig. 3), nor was any detected in the pore waters during the February 1986 sampling trip. During the November, May, and July trips, low

interstitial H_2S concentrations (0.5–4 μM) were observed in the upper 1–5 cm of sediment, while maximum concentrations of 5–12 μM were observed between 7–9 cm depth.

The sulfate turnover rate constant (^{35}S-sulfide formed/$^{35}SO_4^{2-}$ added) in station C3 sediments in May 1986, was low at the 1 cm level but had increased rapidly by 3 cm depth (Fig. 4). The bar diagram shows the partitioning of the reduced ^{35}S label between the AVS, S^0, and FeS_2 S fractions. The majority of the reduced ^{35}S label was recovered in the AVS fraction (41–80%). Most of the remaining label was recovered in the S^0 fraction. A minor portion of the reduced label was recovered in the FeS_2 fraction. A large proportion of the total reduced label was observed in the more oxidized S fractions (S^0 and FeS_2) nearer the sediment surface (59% at 1 cm). Only 20% of the label was recovered as S^0-plus-FeS_2 at 9 cm depth. Similar depth profiles of the ^{35}S distribution as expressed by the turnover rate constant were observed during the other sampling trips. SR rates were highest at the sediment surface, despite the low surface turnover rate constant, due to the much higher sulfate concentrations there (HERLIHY and MILLS, 1985; HERLIHY, 1987). No SR was observed below 5 cm due to the depletion of sulfate below that depth.

In the homogenized surface sediment samples from station C3, 98.3% of the added ^{35}S-SO_4^{2-} label was recovered in reduced inorganic form (either AVS, S^0, or pyrite) after 48 h (Fig. 5). Most of the label was recovered as AVS. The amount of label recovered as pyrite was small (2.7–6.7% of the total added) and did not change over the course of this experiment. The amount of S^0 recovered after 1.1 h of incubation (4.7%) was also low; however, it increased steadily
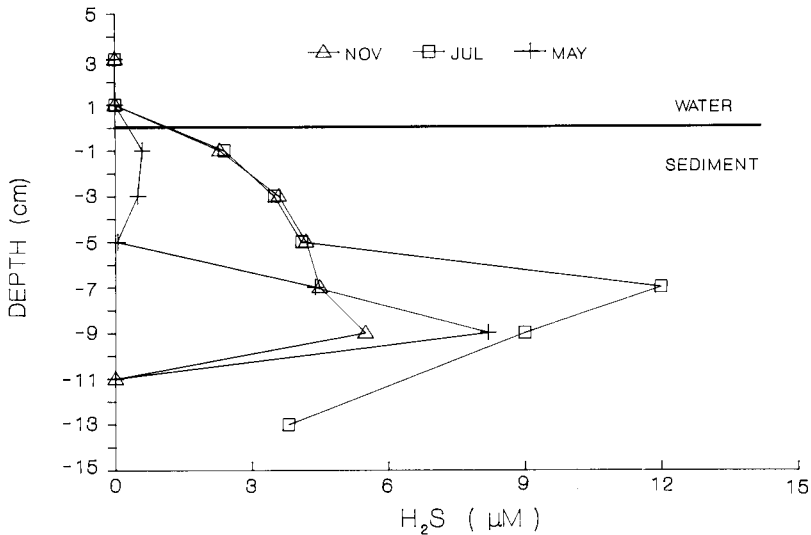
FIG. 3. Depth profiles of aqueous sulfide concentration (μM) at station C3 from July 1985 to May 1986. No sulfide was detected at any depth in February 1986. Data points represent the mean of duplicate samples. Standard deviations were usually between 30 and 100% of the mean.

with time so that after 48 h it accounted for 21.8% of the added ^{35}S.

The concentrations of the different S species in the sediments at station C3 in May 1986, showed the highest amount of total S at 1 cm depth (Fig. 6). Concentrations of pyrite and residual S were highest at the sediment surface and decreased with depth. Residual S was below the detection limit at 9 cm depth. Conversely, AVS and S^0 concentrations were low at the sediment surface and increased with depth. The dissolved SO_4^{2-} concentration in the sediment pore water is not shown on this figure, because even at the sediment surface (where it is the highest) it is one to two orders of magnitude lower than the con-

centrations of the other S species. The sediment S concentrations observed in February 1986, were very similar to those observed in May 1986, and the S distributions in May and July 1985, were also similar to these except that very little or no residual S was present at any depth.

The sediment S concentrations at station F1, the unpolluted site, In November 1985 (Fig. 7), were an order of magnitude lower than the concentrations observed at station C3 at the same period of time. Except at the 1 cm depth, the highest concentration of S was observed in the residual S fraction. S^0 and FeS$_2$ concentrations were low and constant with depth.
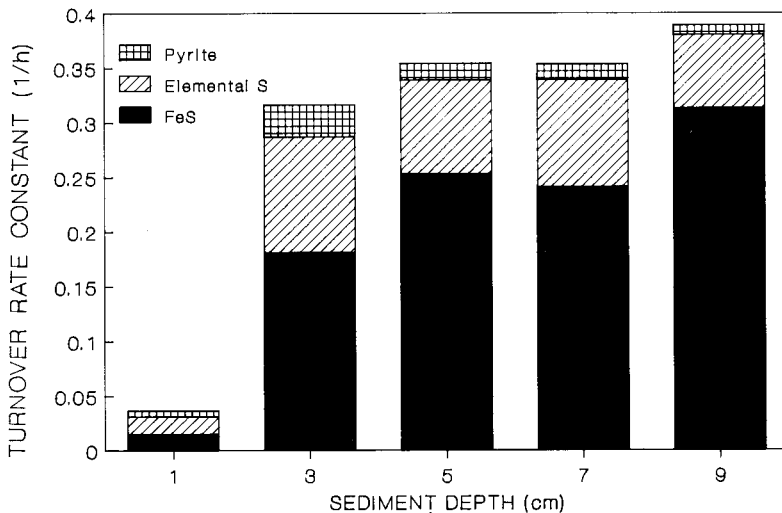

FIG. 4. $^{35}SO_4^{2-}$ turnover rate constant (1/h) with depth in the sediment at station C3 in May 1986, showing the relative importance of AVS (FeS), S^0, and FeS$_2$ to the total turnover. Data are the mean of triplicate subcores. Standard deviations were usually between 20% and 40% of the mean.
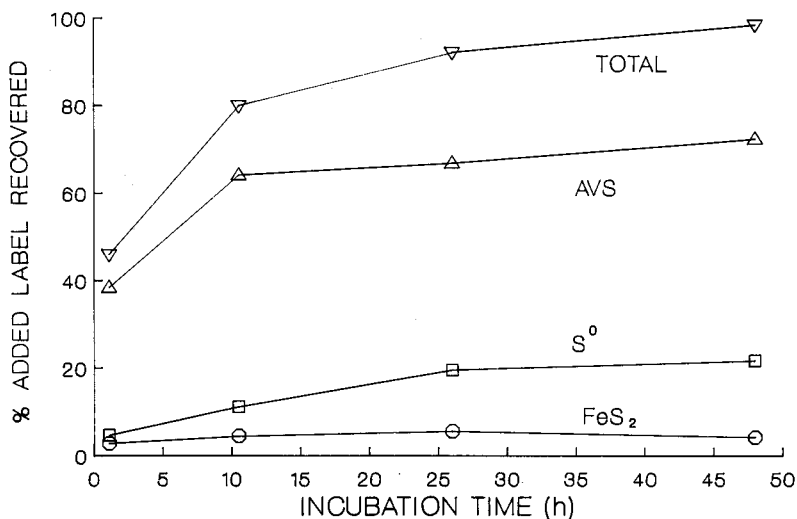
FIG. 5. Recovery of added $^{35}SO_4^{2-}$ label as AVS, S^0, or FeS_2 with time in homogenized station C3 surface sediments. Data points represent the mean of duplicate samples.

SR rates and sediment S concentrations were integrated with depth so that the differences between sampling trips could be more easily observed (Table 1). Note that the values reported after August 1985, were from a totally new sediment layer. In August 1985, 30 cm of rain from Hurricane Danny fell at Lake Anna, and 8–12 cm of new sediment was deposited at station C3. Details on the changes that occurred in the sediment (pH, alkalinity, AVS, S^0, and FeS_2 concentrations) immediately after the storm are reported elsewhere (BELL *et al.*, in review). The fresh sediment had high concentrations of pyrite and elemental S and almost no AVS.

The pre-storm samples (May and July 1985) contained higher AVS and S^0 concentrations than the post-storm samples (Table 1). Following the storm (November 1985 to May 1986), AVS and S^0 concentrations increased with time in the sediment. There was also a much higher amount of residual S in post-storm samples than in pre-storm samples. Pyrite and total S concentrations stayed relatively constant over the study period. The amount of S in dissolved SO_4^{2-} was very small (<1% of the total S) at all times except November. The high SO_4^{2-} and SR rates in November were due to the large amounts of SO_4^{2-} input in the August storm. By February, SO_4^{2-} was depleted to pre-storm levels.

The maximum amount of pyrite in the lake sediments along a transect away from Contrary Creek is at station C2 near the mouth of the creek (Fig. 8). The

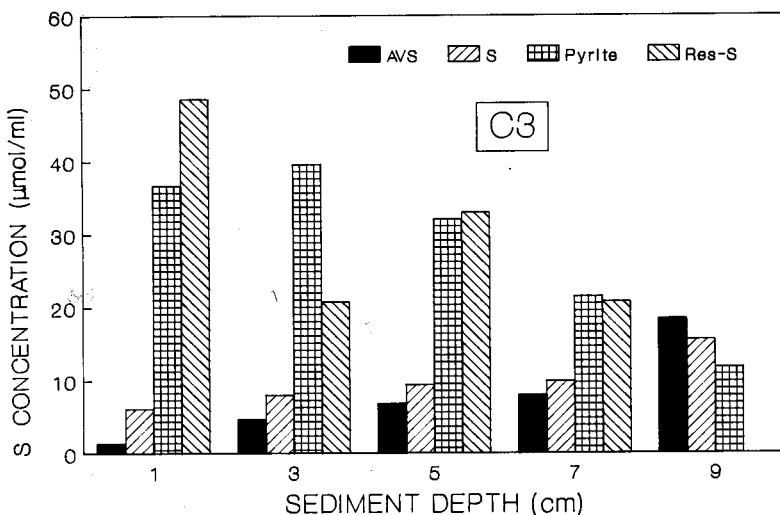FIG. 6. Sediment S concentrations (μmol/ml sediment) at station C3 in May 1986. Residual S (Res-S) calculated as described in the text. Data points represent the mean of triplicate subcores. Standard deviations were usually between 10 and 30% of the mean.
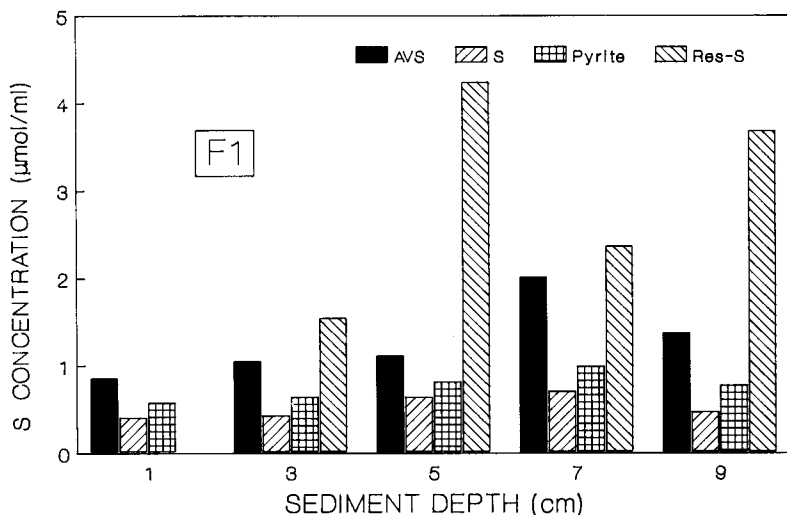
FIG. 7. Sediment S concentrations (μmol/ml sediment) at station F1 in November 1985. Residual S (Res-S) calculated as described in the text. Data points represent the mean of duplicate subcores.

pyrite concentration along the transect decreases in an exponential fashion with distance from the creek mouth. The highest concentrations of AVS and S^0 were observed at station C5. AVS and S^0 concentrations tended to follow each other and rapidly decreased with distance away from C5. Depth integrated AVS, S^0 and pyrite concentrations at station L2 were 1.5–2 times higher than they were at station F1 in November.

DISCUSSION

^{35}S label distribution

Sulfate entering the sediments in the Contrary Creek arm of Lake Anna was rapidly reduced to sulfide by bacterial SR. At greater depths of the sediment (5–9 cm) most of the labeled S formed over the 0.5–2 h incubation was recovered as AVS, while in the surface sediments more than half of the label was recovered as S^0 and pyrite (Fig. 4). This would indicate that the more oxidizing conditions near the sediment surface result in a rapid transformation of the bacterially reduced sulfide to more oxidized products such as S^0 or pyrite. ^{35}S was recovered as S^0 at all depths sampled, even though the deeper samples were from a reducing zone with a low enough sediment Eh (below 0 mV; HERLIHY, 1987) so that it was unlikely that oxygen would have been present. Culturable sulfide-oxidizing bacteria (*Thiobacillus spp.*) have been observed throughout the top 10 cm of sediment in this arm of Lake Anna (counts of $\simeq 10^3$ bacterial/ml sediment, McINTIRE and MILLS, unpub-
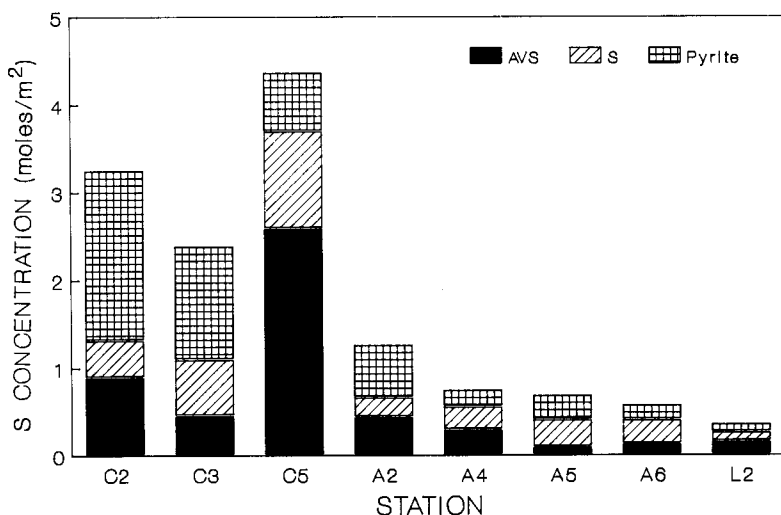

FIG. 8. Depth integrated (0–8 cm) S concentrations (moles/m^2 sediment) in Lake Anna sediments in a transect away from the mouth of Contrary Creek. See Fig. 1 for map of the sampling stations.

Table 1. Mean depth-integrated (0–8 cm) sediment S concentrations (mmol/m^2) and sulfate reduction rates (mmol/m^2/d^1) at station C3

		May 30 1985	July 13* 1985*	Nov. 8 1985	Feb. 19 1986	May 14 1986
AVS	mean	1150	1350	165	363	425
	min.	790	1050	136	270	391
	max.	1460	1650	193	456	478
S^0	mean		1470	293	356	674
	min.		1260	283	309	606
	max.		1680	303	445	756
		3630† 3390–3840				
Pyrite	mean		1760	1370	1490	2600
	min.		1510	1240	1470	2420
	max.		1910	1500	1530	2870
Total sulfur	mean	5400	4620	—	4630	6180
	min.	4670	4350		4330	4810
	max.	6560	5090		5180	8640
Residual sulfur	mean	660	−170	—	2510	2480
	min.	76.8	−160		1890	946
	max.	1440	−180		3120	5000
SO$_4^{2-}$ (pore water)	mean	15.8	7.7	133	14.8	5.9
SR rate	mean	10.4	27.7	99.2	0.72	13.0
	min.	8.8	20.2	63.9	0.46	8.6
	max.	11.8	32.3	134	1.17	19.3

*On August 18, 10 cm of fresh sediment was deposited at station C3.

†In May 1985 the S^0 and pyrite fractions were not measured separately. This number is the sum of S^0 + pyrite.

lished data) and could be responsible for the sulfide oxidation. Sulfide can also be chemically oxidized to S^0 in the presence of ferric Fe without oxygen being present.

There was very little ^{35}S label recovered as pyrite during SR rate measurements. Its presence could indicate pyrite formation, but other supportive evidence is missing. There were no significant increases in sediment pyrite concentrations with time over the course of the study. Inability to remove all of the acetone from the sediment before Cr reduction or incomplete acetone extraction could result in a small amount of elemental S occurring in the pyrite fraction. This error is relatively minor in the determination of concentration but was magnified when measuring label activity in samples where only a small percentage of the added sulfate label was reduced. Surface sediment had low SO$_4^{2-}$ turnover rate constants and thus a small amount of label recovered as reduced S. A very low activity of elemental S in the pyrite fraction could cause a large overestimate in pyrite formation. Over the short term, pyrite formation is probably unimportant in these sediments.

The highest rate of SR occurred at the sediment surface because of the high pore water sulfate concentrations there despite a low surface turnover rate constant. Because most of the SR occurred at the 1 cm level, a great deal of S^0 was formed at this depth, and therefore S^0 was an important S sink for the incoming AMD-derived sulfate.

The results of the 48 h-label incubation study on homogenized surface sediment (Fig. 5) demonstrated that all of the added label was reduced within 48 h, and that all of the reduced label was recovered in inorganic forms. The immediate product of SR was mostly AVS and a small amount of S^0. More of the reduced S was recovered in the S^0 fraction with time. Thus the initial product of SR in these sediments was AVS. With time, part of the AVS was converted to S^0. Formation of pyrite appears to be relatively minor over a period of 48 h. Because all of the added label was accounted for in inorganic forms, organic S production from sulfate was negligible in these sediments.

KING et al. (1985) recovered an average of 50.2% of their label as AVS, 36.6% as S^0, and 13.2% was pyrite in the top 10 cm of sediment collected in the Great Sippewissett Salt Marsh. More label as recovered as S^0 nearer the sediment surface due either to a more oxidized surface sediment or because of the release of more ferric Fe during the AVS distillation, thereby causing an artificial increase in S^0 due to oxidation of sulfides. From their data, KING et al. (1985) could not confirm either hypothesis. In a coastal marine sediment (Limfjorden, Denmark) HOWARTH and JORGENSEN (1984) found most of the ^{35}S label in the AVS fraction (67–89%). Significant percentages of label were also recovered as elemental S (5–27%) and pyrite (4–12%). As in the salt marsh, more S^0 and pyrite were recovered nearer the sediment surface. In contrast to KING et al. (1985), HOWARTH and GIBLIN (1983) found that the majority of the reduced S label in several salt marsh sediments was recovered as pyrite (50–90%) and concluded that pyrite formation was the most important S end prod-

uct in the Great Sippewissett Marsh. More pyrite formation might be expected in salt marsh sediment due to a more rapid input of oxygen into the sediment from the marsh grass rhizosphere. The discrepancy between the work of King's group and Howarth's group has not yet been satisfactorily explained. The conclusions of the present study agree with those of KING et al. (1985), i.e. that AVS is the major end product of SR (at least in Lake Anna) and that pyrite is of relatively minor importance.

Errors in analyses

It has been reported that the AVS analysis may cause an overestimate in S^0 due to the oxidation of FeS to S^0 by ferric Fe released during the acidification (KING et al., 1985). This problem may have caused a slight overestimate of S^0 and underestimate in AVS in this study. Nevertheless, the error should be small for three reasons. First, recovery of known amounts of AVS from sediment subcores showed a mean recovery of 88% (HERLIHY and MILLS, 1985). Thus, in the worst case, only 12% of the AVS could have been oxidized to S^0. Second, HOWARTH and JORGENSEN (1984) found that artificially produced ^{35}S-labeled elemental S accounted for up to 5% of the total reduced label in the top sediment and only 1–2% of the total at all lower depths in a coastal marine sediment. Corrections for this artifact in calculating AVS and S^0 formation from SR rates were minor at all depths except the surface sediment where it increased estimates of AVS formation by 7.8%. Third, the results of the sediment S analyses during the first two weeks after a major storm event (BELL et al., in review) showed a large amount of S^0 with almost no AVS present. The S^0 from this time period could not be formed from AVS during the analysis because there was no AVS to start with. Therefore, although the AVS distillation can cause problems in the analyses, it seems unlikely that it could have a large effect on the results of this study. At worst the estimates of AVS and S^0 would be underestimated and overestimated, respectively, by about 10%.

HOWARTH and JORGENSEN (1984) suggested that isotope exchange could cause misleading results in ^{35}S label studies; it is possible that the presence of label in the different S fractions could be the result of isotopic exchange rather than chemical transformations. In the present study, no isotope exchange occurred between pyrite and the other S forms during a 48 h period. The amount of label recovered as pyrite was small and did not increase with time even though there was a large pool of unlabeled pyrite in the sediment in contact with a large amount of labeled AVS (Fig. 5). While not conclusive with respect to other S species, these data suggest that isotope exchange was not a major problem, especially with the short incubation times used in this study. Differences in the results obtained by HOWARTH and

JORGENSEN (1984) and those reported here may be due to the high concentration of Fe^{2+} present in Lake Anna sediments. Although speculative in nature, it may be that the excess of available Fe reduces the number of options for reactions in the S pool and the relative ease with which those reactions occur, thereby reducing or eliminating the exchange of isotopes. Clearly, more work on this phenomenon is needed to prove the usefulness of ^{35}S-label studies in studying S transformations in various sediments.

Sediment sulfur concentrations

Concentrations of AVS in the sediment at station C3 (Fig. 6) were in the range 1–20 μmol/ml sediment and were greater with increasing depth in the sediment. These concentrations are similar to the AVS concentrations of 5–20 μmol/ml sediment observed in coastal marine sediments (TROELSEN and JORGENSEN, 1982; HOWARTH and JORGENSEN, 1984). AVS concentrations in unpolluted freshwater lakes are reported in the range 1–3 μmol/ml (SMITH and KLUG, 1981; NRIAGU and SOON, 1985), lower than the concentrations observed at C3. In contrast, McFarlane Lake in Ontario, which receives extensive pollution (SO_4^{2-}, H^+, and metals) from the smelters in Sudbury, had higher AVS concentrations than station C3 (259 μmol/g dry wt; NRIAGU and SOON, 1985); to convert values from C3 to a per gram dry weight basis multiply the values by a factor of ~4.5.

S^0 concentrations in sediments at C3 were similar to those reported for coastal marine sediments (2–14 μmol/ml; HOWARTH and JORGENSEN, 1984), greater than those reported for unpolluted freshwater lakes (0.1–0.7 μmol/ml; SMITH and KLUG, 1981), and less than those for polluted McFarlane Lake (343 μmol/g dry wt; NRIAGU and SOON, 1985). Pyrite concentrations at station C3 were of the order of 10–30 μmol/ml sediment (Fig. 8), similar to the 50–75 μmol/ml sediment observed by KING et al. (1985) in the Great Sippewissett Salt Marsh. Values in polluted McFarlane Lake were also similar (122 μmol/g dry sediment, NRIAGU and SOON, 1985) to the C3 values, while pyrite concentrations in coastal marine sediments (Limfjorden) were higher (20–200 μmol/ml wet sediment, HOWARTH and JORGENSEN, 1984). The total inorganic S concentrations in the Contrary Creek arm of Lake Anna (station C3) were of the same order as the total S concentrations found in other high sulfate aquatic systems.

Sulfur concentrations in C3 sediments were an order of magnitude higher than those in the unpolluted sediments at station F1 (Fig. 7). The low concentrations of AVS, S^0, and pyrite observed at F1 indicate that the high concentrations of reduced S in the polluted arm of Lake Anna were caused by the AMD inflow and were not normal concentrations in sediments in this area. The residual S in F1 sediments was almost certainly organic S because sulfate con-

centrations were very low (<150 μM) in this part of the lake. The large amount of residual S compared to inorganic S in these sediments was not surprising because organic forms of S usually dominate the element in unpolluted freshwater lake sediments (MITCHELL et al., 1981; KING and KLUG, 1982).

Due to the analytical methods used in this study, the residual S represents organic S and/or solid or adsorbed sulfate species. The November through May residual S concentrations at station C3 (10–50 μmol/ml sediment) were much larger than the residual S concentrations at station F1 (2–3 μmol/ml sediment). Because no organic S was formed from labeled SO_4^{2-} (Fig. 5) there is no reason to believe that the amount of carbon-bonded S at C3 should be greater than that at F1. Therefore, if station F1 represents the typical carbon-bonded S concentration in the lake, it is unlikely that the large amount of residual S at C3 is carbon-bonded S. Because more ester sulfate would form in higher sulfate water it is possible that some of the residual S is in the form of ester sulfate. However, due to the high sulfate concentrations at station C3 and the large amount of Fe oxyhydroxide floc, the majority of the residual S probably represents sulfate adsorbed onto or co-precipitated with solid materials. SIGG and STUMM (1981) have shown that sulfate can adsorb onto FeOOH surfaces under the acidic conditions that are present in Lake Anna waters. These sulfate containing materials drop out of the water column and accumulate in the lake bed. These adsorbed sulfates would not be detected by the equilibrators because they are not dissolved in the pore water. Sulfate in this bound fraction would be released when the Fe hydroxides are reduced to ferrous Fe in the reducing portion of the sediment. This would explain why the residual S concentration decreased with depth in the sediment and was below detection limits at 9 cm depth. By 9 cm depth, the ferric Fe would have been reduced and the sulfate would be released and rapidly reduced due to the high sulfate turnover rate constant at depth in the sediment. If the residual S was ester sulfate, a similar type of mechanism would explain the depth profile. Ester sulfates would form in the water column and then accumulate in the sediments. Once in the sediments, sulfate would be slowly released upon hydrolysis of the ester.

The maximum concentrations of AVS observed in the transect study were found at station C5 (Fig. 8). S^0 concentrations were also highest at station C5. Because there were higher sulfate concentrations nearer the mouth of Contrary Creek at stations C2 and C3, it was expected that the highest AVS and S^0 concentrations would occur there. One possible explanation for these results is that AVS and S^0 forming on or just below the sediment surface were moved downstream as bed load sediment by the current along the lake bottom. A noticeable bottom water current exists in this arm of the lake, and gentle scouring is often observed. Data on the net sedimen-

tation rate showed a small loss of sediment during certain times of the year (HERLIHY, 1987). It is also possible that more sulfide and S tend to accumulate at station C5 than at the more upstream stations due to less bottom water turbulence or some other biogeochemical factor that preserves the reduced sulfides from oxidation.

The concentration of pyrite decreased rapidly with distance from the mouth of Contrary Creek (Fig. 8). This suggests that the pyrite fraction represents pyrite that is carried in from the abandoned mines on Contrary Creek. The pyrite is likely carried in from the creek during storm events and is deposited in the lake near the mouth of the creek as the current velocity decreases. Thus little pyrite would be carried far from the mouth of the creek.

Significant changes in almost all S species were observed between July 1985 and the post-storm event sampling (November–May 1986, Table 1). The only species that did not demonstrate any significant changes was pyrite, indicating that pyrite concentrations in the lake sediments were stable over time and were the result of pyrite carried in from Contrary Creek. Also, the freshly deposited sediment in the polluted arm of Lake Anna had large amounts of S^0 and pyrite, indicating a significant allochthonous input of these materials. Therefore, separating out the pyrite- and S^0-loading to the sediments from pyrite and S^0 formation in the sediments was impossible. Negligible amounts of AVS were carried in from the creek so that accumulation of AVS in the new sediment layer can be attributed to in situ formation.

AVS and S^0 concentrations in July 1985, were higher than they were at any time after the storm event. Thus even in the nine months following the storm, AVS and S^0 concentrations had not returned to pre-storm levels. The high July S^0 concentration suggests that S^0 accumulation does occur in the sediment because it is significantly higher than the background sediment concentration brought in by the storm. Also, the spatial pattern of S^0 concentrations (with depth and along the transect) varies with the pattern of AVS concentration and not with pyrite concentration indicating that a significant fraction of the S^0 is formed in the sediments rather than carried in from the creek.

CONCLUSIONS

Both the distribution of ^{35}S label and the observed spatial and temporal pattern of sediment S concentrations showed that the major end products of SR in these sediments were FeS and to a lesser extent elemental S (S^0). There was no strong evidence for the formation of pyrite or organic S over the course of this study. Sedimentation events play a major role in transporting S into these sediments, probably by the absorption of sulfate onto settling Fe oxyhydroxides and other solid particles. Sedimentation events

caused increases in pore water sulfate, residual S, and the subsequent formation and accumulation of Fe monosulfides.

Pore water contained high concentrations of ferrous Fe and very little dissolved sulfide due to the rapid precipitation of FeS. Inorganic forms of S (FeS, S^0, and FeS_2) made up from 60% to 100% of the total sediment S concentration in the polluted arm of the lake. Organic S was the predominant form in the unpolluted arm of the lake. Sediment pyrite concentrations were high and decreased exponentially with distance from the AMD source indicating that the pyrite is stream detritus. AVS and S^0 concentrations were highest at a station 1 km downstream from the AMD inflow, indicating in situ formation. No evidence was observed for the formation of organic S species. This study showed that in an Fe- and S-rich freshwater system the major pathway of S storage in the sediment is through inorganic S species, rather than through organic S as reported for other acid-impacted freshwater systems. Burial of reduced S as stable, relatively immobile products, suggests that the alkalinity generated in the sediments by sulfate reduction represents a permanent neutralization of the acid pollution.

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