

Technical note

Spatial distribution of acid-volatile sulfur in the sediments of Canadohta Lake, PA

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Abstract

Lake sediments are an important source of dissolved substances and can be the site of processes important to the biogeochemical cycling of nutrients and metals. Most studies which examine these processes, however, are based on the analysis of a single or a very few sediment cores taken at or near the deepest area of the lake. The implicit assumption is that lake sediments are spatially homogeneous and that extrapolations from such limited samples are representative of the lake sediments throughout the lake basin. We examined this assumption with respect to concentrations of acid volatile sulfides (S^{2-}_{vol}) – sulfur species which have been implicated in eutrophication, acid-neutralization, and heavy-metal toxicity. S^{2-}_{vol} concentrations measured in the surficial sediments of Canadohta Lake, PA, a lake of very simple morphometry, ranged from 0.07 to 30.32 $\mu\text{g g}^{-1}$ sediment dry weight. Concentrations were directly correlated with depth and inversely correlated with organic matter. These results suggest that results extrapolated from a few deep-water cores can lead to a serious overestimation of S^{2-}_{vol} in the lake sediments.

Introduction

Acid volatile sulfides (S^{2-}_{vol}) are operationally defined as those chemical species of S extractable by HCl digestion (Landers et al., 1983). Such species of reduced S are found in lake sediments as H_2S , a product of both dissimilatory sulfate reduction and the decomposition of organic S, as amorphous (FeS) and crystalline (e.g. pyrrhotite and mackinawite) iron monosulfides, and as greigite (Fe_3S_4). There are at least three reasons that sedimentary S^{2-}_{vol} concentrations are important in aquatic systems. First, dissimilatory SO_4^{2-} reduction is believed to play an important role in the generation of acid neutralizing capacity (Giblin et al., 1990; Cook et al., 1986). SO_4^{2-} reduction to H_2S can produce HCO_3^- creating a net alkalization

($2\text{CH}_2\text{O} + \text{SO}_4^{2-} \rightarrow \text{H}_2\text{S} + 2\text{HCO}_3^-$) that can ameliorate the effects of acid precipitation on surface-water pH. Second, H_2S reacts with Fe^{2+} to form relatively insoluble FeS_2 which removes Fe^{2+} from the sediment interstitial water thus preventing its coprecipitation with P under aerobic conditions. Removal of sufficient quantities of Fe can lead to increased ‘internal’ loading of P to the water column (Caraco et al., 1989, 1993) supporting dense populations of phytoplankton. Finally, the production of S^{2-}_{vol} may play an important role in the binding and precipitation of heavy metal cations (e.g. Cd, Cu, Hg, Ni, Pb and Zn) as insoluble sulfides. In the anoxic sediments of a lake, stronger divalent metal ions such as Cd may out-compete or displace Fe during the formation of metal monosulfides (DiToro et al., 1990; Hare et al., 1994).

Under this model free metal ions will not approach toxic concentrations until the FeS reservoir has been exhausted.

The concentration of S^{2-}_{vol} in lake sediments is a function both of the rate at which S^{2-} is produced, and the rate at which it is lost by oxidation or diffusion. Consequently, we should anticipate S^{2-}_{vol} concentrations to vary with those factors affecting the supply of organic matter, the rate of SO_4 reduction, and the redox status of the sediments. That is, S^{2-}_{vol} concentrations should be expected to vary both temporally with the seasonal variation in the supply of organic matter and stratification-induced hypolimnetic anoxia, and spatially with variations in sediment quality.

The temporal variability of S^{2-}_{vol} in lake sediments has only rarely been documented. Leonard et al. (1993) measured concentrations of S^{2-}_{vol} at a single station in each of three Minnesota lakes over a 16-month period. Their results indicate a two order of magnitude variation across season, with concentration significantly correlated with water temperature.

Spatial variability is almost equally unknown. Several studies have demonstrated that S^{2-}_{vol} increases (Smith & Klug, 1981; Herlihy & Mills, 1985), decreases (Nriagu & Soon, 1985; Leonard et al., 1993; Hadas & Pinkas, 1995) or increases then decreases (Davison et al., 1985) with sediment depth, but in most of these studies, results were based on only a single core taken at or near the deepest area of the lake, so within-lake variability cannot be addressed. In lakes where more than one core was taken, sites were selected on the basis of obvious heterogeneities caused by the effect of a major influent (Herlihy & Mills, 1985; Hadas & Pinkas, 1995).

Since these studies, and among-lake comparisons indicate that S^{2-}_{vol} concentrations can vary across two orders of magnitude or more, presumably as some function of sediment quality, we might also expect significant variation within a single lake coincident with variations in its sediment quality. Hilton et al. (1986) have identified a number of common mechanisms that lead to quantitative heterogeneity of sediments within any lake, and Downing & Rath (1988) have demonstrated high qualitative variability even within lake regions which might otherwise be thought to be homogeneous.

Inferences about heavy metal precipitation, alkalinity generation, or FeS_2 formation in lake sediments that are based on a single or a few samples from the profundal zone may be misleading in light of this anticipated variation in sediment quality and quantity within

any lake basin. Only a small fraction of the total lake basin area is the recipient of focussed sediments, and experiences prolonged anoxia.

Shallower areas, even those within the hypolimnion, experience much shorter periods of anoxia, receive sediments of different quality and quantity, and make up a much larger fraction of the total lake basin area. We present data here to examine the spatial variability of S^{2-}_{vol} and some correlated characteristics in the surface sediments of a small lake of relatively simple morphometry.

Methods

All samples were collected from Canadohta Lake, Crawford County, Pennsylvania ($41^{\circ} 49'N$, $79^{\circ} 50'W$). The lake has a surface area of 68 ha, a maximum depth of 13.6 m, a mean depth of 5.5 m, and a basin of simple morphometry (Ostrofsky & McGee, 1991). Canadohta Lake is moderately eutrophic. It experiences seasonal stratification, and the hypolimnion becomes anoxic during the summer months. The watershed of the lake covers approximately 20 km² and is comprised mainly of agricultural land and deciduous forest. The lake's shore is extensively developed with summer cottages and camps.

Between 6 and 28 June, 1995, samples of surface sediment were collected at approximately 50 m intervals along ten parallel transects across the lake spaced approximately 200 m apart. At each sampling site, the depth was determined with an echo-sounder, and a sediment core was collected with a Wildco K-B corer. The surface 2.5 cm of each core was extruded in the field and collected in 2–20 ml capped, disposable, polypropylene syringes to minimize oxidation. Samples in sealed syringes were packed in ice, and returned to the laboratory. Analysis of the sediments began within two hours of collecting the samples.

Analysis of S^{2-}_{vol} was performed as a cold HCl digestion using an assembly described by DiToro et al. (1990). This apparatus consisted of a 125 ml digestion flask with an import tube, an export tube connected to a gas trapping flask, and an injection port, all of which entered the flask through a neoprene three-hole stopper. 5 cm³ of fresh sediment were injected into the purged digestion flask directly from the syringe used to collect the sample, followed by 12 ml of 8 N HCl. The sample was allowed to digest for one hour. Digestion resulted in the liberation of H_2S which travelled in a stream of N_2 carrier gas to the trapping solution at about

2 bubbles/second (gauged at the delivery tube) where it was trapped as ZnS. Once the digestion was complete, S^{2-}_{vol} concentrations were determined using the methylene blue colorimetric technique (Landers, et al., 1983). Results are expressed as $\mu\text{g g}^{-1}$ sediment dry weight. Sediment fresh weight/dry weight conversions were determined following oven-drying at 60 °C for 24 hr.

Total Fe in sediments was analyzed by atomic absorption spectrophotometry on $\text{HNO}_3/\text{H}_2\text{SO}_4$ digests of oven dried and weighed sediment. Results are expressed as mg g^{-1} dry sediment. Organic matter was determined using a LECO model 600 elemental analyzer, and is expressed as percent C. All analyses were done in triplicate, and untransformed means used in correlation and regression analysis.

Results

A total of 70 sediment samples were collected and analyzed from water depths ranging from 0.6 to 12.5 meters. Replication among triplicate samples was generally good; coefficient of variation for Fe and C analyses, for example, averaged less than 5%. Variability among the S^{2-}_{vol} triplicates was higher (median coefficient of variation = 25%) due to microscale heterogeneity in the sediments, to artifacts of the sampling, extraction, trapping and analysis technique, or to both. The means of all analyses are shown on Table 1. As anticipated, the samples revealed a high degree of spatial heterogeneity within the lake. Water content ranged from 6 to 42%, and dried sediment varied in C concentration from 3 to 42%. There was no relationship between water content of the sediments and depth (Table 2), but a significant relationship between depth and C. In general, sediments collected deeper than 4–5 meters had relatively constant C, but shallower sediments were highly variable, having either very high C (peaty samples from sheltered areas) or very low C (from exposed areas, or deltas composed of largely inorganic silt).

Fe concentration of the sediment ranged from 6 to 36.3 mg g^{-1} dry wt. There was a significant correlation between Fe and depth (Table 2) although the predictive power of this relationship was weak.

S^{2-}_{vol} varied from 0.07 to 30.32 $\mu\text{g g}^{-1}$ sediment dry weight, and even with the single low outlier removed, varied from 1.08 to 30.32 $\mu\text{g g}^{-1}$. S^{2-}_{vol} concentrations were very strongly correlated with depth (Table 2, Figure 1), and inversely correlated with C,

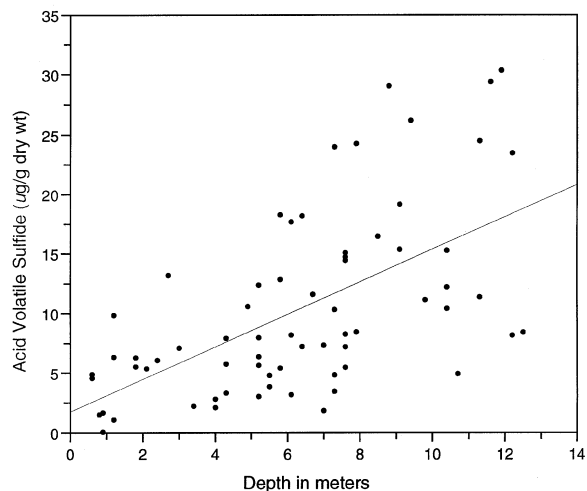


Figure 1. Acid volatile sulfides in the surface sediments of Canadohta Lake as a function of water depth. $S^{2-}_{vol} = 1.74 + 1.36(\text{depth})$, $r = 0.59$, $n = 68$.

although the C data were not normally distributed. Natural log transformation of both S^{2-}_{vol} and C (Figure 2) gave a much stronger correlation ($r = -0.36$). There was no relationship between S^{2-}_{vol} and either Fe or water content. In an attempt to better explain the distribution of S^{2-}_{vol} we performed a stepwise multiple regression (Zar, 1974). The resulting model,

$$S^{2-}_{vol} = 16.40 + 1.65(\text{depth}) - 4.98\ln(\text{Fe}) \quad r^2 = 0.43,$$

is very highly significant ($p < 0.001$) but has only modest predictive power.

Discussion

Concentrations of S^{2-}_{vol} measured in Canadohta Lake (mean $S = 10.3 \mu\text{g g}^{-1}$ sediment dry wt) are similar to concentrations reported from oligotrophic Ennerdale Water, UK (Davison et al., 1985), northern Ontario Batchawara and Turkey lakes (Nriagu & Soon, 1985), and the unaffected station in Lake Anna, Virginia (Herlihy & Mills, 1985). Comparisons with hypereutrophic Wintergreen Lake are difficult since results there were reported as mass/volume rather than mass/mass, but assuming a sediment specific gravity of 1.0, the results are very similar here as well (Smith & Klug, 1981).

Canadohta Lake S^{2-}_{vol} concentrations are very much lower, however, than those reported from mesoeutrophic Windermere and Blelham Tarn, UK (Davison et al., 1985); Caribou, Fish and Pike Lakes, Min-

Table 1. Sediment Characteristics – Dry weight is expressed as percent of fresh sediment weight, carbon is expressed as percent of dry sediment weight, S_{vol}^{2-} is expressed as $\mu\text{g/g}$ dry weight sediment and Fe values are expressed in mg/g dry weight sediment.

Sample site	Depth (m)	Dry wt.%	% Carbon	S_{vol}^{2-} $\mu\text{g/g}$ dry wt. sediment	Fe mg/g dry wt. sediment
A1	0.9	42.02	2.94	1.67	17.0
A2	1.2	33.57	4.96	1.08	13.1
A3	4.0	7.531	12.15	2.80	31.0
A4	5.5	15.99	8.61	4.78	31.1
A5	7.3	8.061	8.51	3.45	–
A6	9.8	9.205	7.53	11.13	–
A7	10.4	8.436	10.69	12.20	35.6
A8	7.6	18.39	6.76	14.71	34.5
A9	3.0	11.08	9.29	7.09	24.9
A10	0.6	27.97	4.45	4.87	13.8
B1	0.6	10.63	38.59	4.55	12.4
B2	2.7	11.48	15.08	13.19	31.5
B3	4.9	17.39	8.48	10.57	36.3
B4	7.9	13.47	8.38	24.27	34.6
B5	10.7	20.23	6.74	4.91	33.0
B6	9.1	–	5.79	15.34	33.0
B7	7.3	18.19	5.81	4.82	25.1
B8	1.2	–	–	9.84	–
C1	0.9	9.935	41.82	0.07	33.0
C2	4.3	13.96	9.75	3.31	36.1
C3	7.9	14.09	8.13	8.43	34.8
C4	12.2	13.04	7.97	23.47	33.5
C5	11.3	17.78	6.94	11.36	34.8
C6	8.5	21.15	6.31	16.44	–
D1	4.3	14.99	11.80	5.75	29.2
D2	7.0	12.45	8.73	7.33	–
D3	7.6	14.47	7.09	8.25	34.4
D4	4.3	6.01	11.24	7.90	20.5
E1	1.2	9.893	20.45	6.33	23.0
E2	6.4	20.67	10.28	7.22	24.6
E3	10.4	33.97	8.98	10.39	17.0
E4	12.5	14.7	4.36	8.40	31.4
E5	12.2	21.76	6.78	8.14	30.5
E6	10.4	10.6	9.04	15.25	33.6
E7	7.6	14.81	8.75	5.46	35.5
E8	5.2	16.15	40.64	5.64	24.9
E9	2.4	–	–	6.07	–
F1	0.8	12.24	43.19	1.51	14.3
F2	6.1	13.13	7.84	17.67	33.7
F3	9.1	9.112	7.92	19.15	30.7
F4	7.6	15.21	8.66	15.06	35.3
G1	2.7	12.06	–	–	–
G2	5.8	7.853	10.32	18.27	33.4
G3	5.5	11.3	10.52	3.84	28.0
G4	1.8	30.38	11.44	5.52	27.6

Continued on p. 83

Table 1. Continued

Sample site	Depth (m)			S_{vol}^{2-}	Fe
		Dry wt.%	% Carbon	$\mu\text{g/g}$ dry wt. sediment	mg/g dry wt. sediment
H1	3.4	9.884	14.82	2.21	31.4
H2	5.2	9.887	11.22	3.02	32.0
H3	5.2	27.36	11.54	6.37	33.3
H4	6.7	9.616	10.29	11.60	35.7
H5	7.6	6.242	10.04	7.20	26.6
H6	7.6	13.87	8.54	14.43	25.6
H7	5.8	6.675	9.35	12.85	29.3
H8	1.8	12.73	15.66	6.28	14.3
I1	3.7	–	–	–	–
I2	8.8	17.48	7.73	29.04	6.6
I3	9.4	15.42	7.26	26.20	30.2
I4	11.3	12.98	7.36	24.49	33.0
I5	11.9	7.948	9.20	30.32	35.2
I6	11.6	11.74	7.69	29.39	33.0
I7	7.3	11.87	7.69	24.00	6.0
I8	5.2	9.807	10.72	7.96	32.4
I9	2.1	14.01	51.03	5.35	12.0
J1	4.0	10.33	11.38	2.09	36.7
J2	6.1	7.895	8.46	8.17	32.4
J3	7.0	10.29	9.31	1.83	35.4
J4	7.3	8.111	10.27	10.31	35.3
J5	6.4	9.958	9.61	18.18	33.3
J6	6.1	10.98	9.80	3.17	33.4
J7	5.8	8.125	11.10	5.40	36.2
J8	5.2	9.584	11.03	12.38	32.3
J9	3.7	9.753	13.81	–	31.1
Mean		14.15	11.77	10.29	28.9
Standard deviation		7.04	9.44	7.56	8.09
Coefficient of variation		0.49	0.80	0.73	0.28

nesota (Leonard et al., 1993), and of course the lakes receiving elevated sulfur by way of acid mine drainage – Lake Anna, Virginia, affected station (Herlihy & Mills, 1985), or atmospheric fallout – McFarlane and Kelly Lakes, Ontario (Nraigu & Soon, 1985).

Comparisons with these and other lakes may not be appropriate for at least two reasons. First, the Canadota Lake data were collected from surficial sediments (top 2.5 cm) whereas the above data were collected from the top 10, 15 or 20 cm, or from an unspecified interval. We have already noted the variability of S_{vol}^{2-} with depth in the sediment profile. Second, given the reported two order of magnitude seasonal variation in

Table 2. Correlation matrix of sediment characteristics. Double and triple asterisks represent $p < 0.01$ and $p < 0.001$, respectively.

	S_{vol}^{2-}	%C	%H ₂ O	Fe
%C	–0.30**			
%H ₂ O	–0.16	–0.18		
Fe	0.08	–0.32**	–0.35**	
Depth	0.59***	–0.49***	–0.11	0.41***

Minnesota lakes (Leonard et al., 1993) such between-lake comparisons would be valid only if sediments were collected at comparable times.

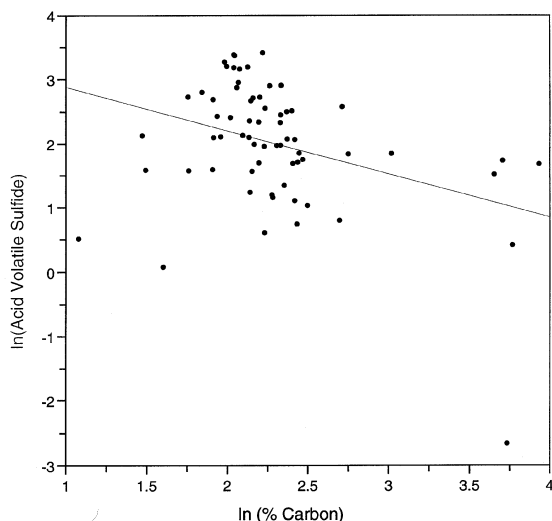


Figure 2. Natural log of S^{2-}_{vol} in the surface sediments of Canadohta Lake as a function of natural log of %C in sediment. $\ln(S^{2-}_{vol}) = 3.56 - 0.68 \ln(\%C)$, $r = -0.36$, $n = 66$.

In the studies cited above, all data were derived from a single core, presumably collected from the deepest area of the lake. While these studies demonstrated seasonal variation, or variation with depth within any core, none has addressed the question of spatial variability within a lake basin. S^{2-}_{vol} concentrations in Canadohta Lake spanned almost three orders of magnitude ($S = 0.07 - 30.32 \mu\text{g g}^{-1}$ dry wt), with sediments from deeper waters having greater concentrations. Using the coefficient of variation (s/mean , Table 1) as a comparative measure of heterogeneity, sediment S^{2-}_{vol} concentrations were more highly variable in Canadohta Lake than sediment moisture or Fe concentrations. Further, S^{2-}_{vol} concentrations were more variable than sediment total P or several other P species (Ostrofsky & McGee, 1991). A highly significant pattern in this variation is the increase in S^{2-}_{vol} concentrations with increasing water depth. Although the deep-water sediments of Canadohta Lake have, in general, less organic matter than shallow-water sediments, this organic matter may be of higher quality, derived from settling plankton rather than from more refractory allochthonous material typical of shallow sediments. At the time of sampling, the deeper areas of the hypolimnion were anoxic, and SO_4 reduction was probably in progress very near the sediment surface. As a consequence, the production of S^{2-}_{vol} in the deeper sediments was probably greater than in shallower sediments, and the absence of active circulation prevented

the formation of steep diffusion gradients between the surficial sediments and the overlying water.

One consequence of this variation is that it would be easy to overestimate the S^{2-}_{vol} of any lake if only one or a few samples from the deepest regions were analyzed and used to make whole-lake projections of S^{2-}_{vol} concentrations. For example, if we estimated S^{2-}_{vol} from our deepest samples (depth >10 m) we could make an estimate of alkalinity-generating capacity, or of heavy metal binding capacity based on an average S^{2-}_{vol} of $16.21 \mu\text{g g}^{-1}$. However, given the variability even within this limited area, the 95% confidence interval about this mean ranges from $S = 10$ to $22 \mu\text{g g}^{-1}$. Further, the majority of the lake sediments lie much shallower than 10 m and have much less S^{2-}_{vol} . The volume-weighted mean sediment S^{2-}_{vol} concentration for the whole lake is $9.8 \mu\text{g g}^{-1}$, approximately half of the concentration from sediments greater than 10 m in depth. We would be attributing to the system a capacity that only a small fraction of the sediments actually have. We propose, therefore, that any studies of S^{2-}_{vol} , or any monitoring take into account spatial variability, and collect samples from a number of locations within each lake representing the full range of depths available.

Clearly, the biogeochemical cycling of sulfur in lakes represents a collection of important processes with consequences for eutrophication, acid-neutralization and metal toxicity. It is widely recognized that within lakes, sediment chemistry often exhibits a large degree of spatial variability (e.g. Downing & Rath, 1988; Ostrofsky & McGee, 1991). Much of the S work to date has not accounted for the variability that can occur, and likely overestimates concentrations of S^{2-}_{vol} and other S species within lakes.

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