
Partitioning and Effects of Silver in Amended Freshwater Sediments

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The fate and effects of silver, amended as silver nitrate, silver chloride, and silver thiosulfate complex, in freshwater sediments with varying characteristics (e.g. diverse sand: silt/clay ratios, percent organic matter, etc.) were studied in static 10-d laboratory experiments. Partitioning of silver to particulates, overlying water and interstitial water was evaluated by measuring dissolved and total acid extractable silver concentrations over a 10 day period. Silver concentrations in the sand and silt/clay fractions were also measured. The results of silver nitrate amended sediments indicate that we can reasonably expect a factor of three difference in the affinity of particulates for silver, but over two orders of magnitude difference in aqueous ($< 0.45 \mu\text{m}$) silver concentrations were observed. Concentrations of silver in pore water varied widely. Concomitant variations in bioavailability were assessed using the amphipod *Hyalella azteca* Saussure. Ten-day LC_{50}s for *H. azteca* exposed for four sediments amended with silver as silver nitrate ranged from 1.6 to 397.7 mg Ag/kg dry sediment. In experiments with silver chloride amended sediments, *H. azteca* 10-d LC_{50}s were > 2560 mg Ag/kg dry sediment. *H. azteca* was also relatively insensitive to silver as silver thiosulfate complex with 10-d LC_{50}s > 569 mg Ag/kg dry sediment. These amendment experiments illustrate three primary principles: 1) sediment amendment procedures are dictated by the intrinsic characteristics (e.g. solubility) of the silver compounds; 2) silver nitrate, silver chloride and silver thiosulfate

complex differ in their affinity for sediments and partitioning in overlying waters and interstitial waters; and 3) bioavailability of silver compounds in sediments varied several orders of magnitude.

INTRODUCTION

As we transfer and transform metals in commerce, medicine and other activities around the globe, questions often arise concerning the consequences of local increases in metal concentrations or alterations of metal forms. Although silver has a predominately lithic biogeochemical cycle (Brookins 1988), the use of water in silver mining and industrial processes serves to alter aqueous and sediment silver concentrations in aquatic systems. Since "free" or bioavailable silver is relatively toxic to aquatic species (USEPA 1980), a clear understanding of the fate and effects of silver is required to accurately predict the potential risks of silver in aquatic systems. Like other metals with an affinity for particulates and sediments (e.g. Cu, Zn), only a fraction of the total silver found in sediment, interstitial or overlying water is bioavailable (LeBlanc *et al.* 1984). For aquatic systems, the presence of a particular concentration of silver in a sediment or water sample may be merely presumptive evidence of a potential problem. Currently, confirmatory evidence is derived from careful studies involving realistic exposures of biota that may be affected. Critical to any accurate risk assessment for silver in aquatic systems will be an understanding of bioavailability at a point in time, and through time. For purposes of this study, bioavailability is operationally defined as the ability of silver (element, compound, etc.) to concentrate in or on an organism and/or to elicit a response (adverse or beneficial)

as a result of exposure.

The laboratory experiments here were designed to accomplish the following objectives: 1) to determine the partitioning of silver introduced in water associated with sediments of varying characteristics (e.g. diverse sand: silt/clay ratios, % organic matter, etc.); and 2) to assess the bioavailability or effects of silver in sediment/water systems on *H. azteca* (a freshwater amphipod).

MATERIALS AND METHODS

Silver Partitioning to Sediments

Sediments for measurement of silver partitioning were selected based upon the following criteria: 1) representative of range in U.S. (pH 5-9, OC<1%-2.5%, Eh neg-pos); 2) characteristics that may be important in silver speciation and bioavailability (e.g., redox, pH, OC); 3) accessible: 1-2 h drive or colleague lives near by; 4) representative of both karst topography and granitic (quartz) topography; 5) sufficient volume to obtain pore water for analysis; 6) sediments must be unconfounded with toxicity; and 7) matching some current site with potential silver contamination. Based upon these selection criteria, seven sediments from throughout the US and a formulated sediment (Suedel and Rodgers 1994a, 1994b) were selected for the partitioning study (Table 1). These sediments represented the range of characteristics found in freshwater throughout the USA (Suedel and Rodgers 1991). Sediments were characterized by the methods of Allen *et al.* (1991), Black (1986), and Plumb (1981).

Three silver compounds, silver nitrate, silver chloride, and silver thiosulfate complex, were used for sediment partitioning experiments. Silver nitrate has a solubility of 2500 mg/ml (25°C) (Windholz *et al.* 1983). A stock solution of 10,000 mg Ag/L was prepared using Kodak silver nitrate crystals (173-1082). A series of silver concentrations were prepared by serial dilution from the silver nitrate stock, added to the sediments and homogenized to produce a range of sediment associated silver concentrations. Silver chloride (Sigma Brand silver chloride 7783-90-6) was amended directly to sediments in solid form due to its relatively low aqueous solubility (1.93 mg AgCl/L at 25°C) (Windholz *et al.* 1983). Silver thiosulfate complex is "relatively" insoluble and was also amended directly to sediments. Each sediment was amended with the calculated amount of silver compound to obtain the targeted (nominal) concentration.

Sediment amendment procedures involved homogenizing sediment and amended silver compounds with a spatula until thoroughly mixed. Sediments were amended and analyzed for silver periodically over a 10 day period. The contact period of ten days was chosen as the experimental duration since this would match the duration of the bioavailability experiments (Ingersoll and Nelson 1990; Tomasovic *et al.* 1995). Overlying water, pore water, and sediment samples were collected and analyzed for silver at 0d, 24h, 48h, 96h, 7d and 10d after initial silver amendment. Samples of sediment silt/clay fraction were also collected and analyzed for silver at 0d and 10d.

Silver Bioavailability in Sediment Experiments

Four sediments (Sediments 1, 3, 6 and 7) encompassing a broad range of

characteristics were selected for silver amendment and bioavailability experiments (Table 1). *H. azteca* (1-2 weeks old) were exposed in 250-ml beakers to 70 g of sediment amended with aqueous silver nitrate, solid silver chloride, or solid silver thiosulfate complex. UMBFS filtered pond water was added as the overlying water in a ratio of 4:1 water to sediment volume. Experiments were conducted in light (16 h light/8 h dark) and temperature (21° +/- 1°C) controlled incubators. During the 10 d exposures, water characteristics [temperature (°C), pH, dissolved oxygen (mg/L), alkalinity (mg/L as CaCO₃), hardness (mg/L as CaCO₃) and conductivity (µmhos/cm)] were measured at the beginning and end of each experiment. Temperature, pH, dissolved oxygen, and conductivity were also measured at 24h, 48h, 96h, and 7 d of the experiment. Experiments were initiated by adding 10 juvenile *H. azteca* to each of 4 replicate beakers per concentration. As a food source *H. azteca* were given 4 leached maple leaf disks (7 mm diameter each) per beaker at the beginning of each test. All organisms were obtained from cultures maintained at the University of Mississippi Department of Biology laboratory (Lawrence 1981).

Sediment toxicity tests were conducted with Sediments 1, 3, 6, and 7 amended with solutions of silver nitrate in a series of silver concentrations and an unamended control (Nebeker *et al.* 1984). Silver chloride was amended directly to Sediments 1, 3, 6 and 7 in a concentration series as in the partitioning experiments described above. Ten day sediment toxicity tests were also conducted by amending these sediments with solid silver thiosulfate complex. A single nominal concentration of 2000 mg Ag (as silver thiosulfate complex)/kg dry sediment was amended to all four sediments with an unamended

sediment sample as a control. The silver thiosulfate complex used in sediment toxicity testing contained 0.598% silver. Two replicates of control and treatment were used for each silver thiosulfate sediment experiment. Prior to the addition of *H. azteca*, the overlying water in beakers containing silver thiosulfate were aerated for a period of 10 minutes to oxidize excess thiosulfate. Samples of sediment, overlying water, and pore water were collected and analyzed for silver concentrations as described below.

Analytical and Statistical Procedures

Overlying water from experimental beakers was collected and acidified to pH <2 with 15-16N redistilled nitric acid. Water samples were then filtered through a 0.45 µm Gelman Metricel membrane filter and analyzed for total acid extractable silver using flame atomic absorption spectrophotometer (AA). Sediment samples were collected from each beaker and centrifuged in a Beckman model J2-21 centrifuge at 10,000 rpm for 10 minutes to extract pore water. Pore water was acidified to pH <2 with 15-16N redistilled nitric acid, filtered (0.45 µm Gelman metricel membrane filter) and analyzed for total acid extractable silver using AA.

Approximately 5g of sediment from each centrifuged sediment sample were dried in aluminum weigh boats for 24 hours at 75°C. Dry sediment (2g) was then acidified with 10 ml of 15-16N redistilled nitric acid and heated for 5h at 200°C to extract sediment associated silver. Samples were cooled and vacuum filtered through a 0.45 µm Gelman Metricel membrane filter. Samples were brought to volume (25ml) with Milli-Q® water and analyzed for total acid extractable silver by flame atomic absorption spectrophotometer.

Additional sediment samples were separated into sand and silt/clay fractions by specific gravity, and analyzed for silver according to the same procedure. Biological endpoints for toxicity experiments included LC50s and 95% confidence intervals (CI) calculated using methods described in Stephan (U.S. Environmental Protection Agency 1985) or the trimmed Spearman-Kärber method, as appropriate.

RESULTS AND DISCUSSION

The divergent characteristics of the sediments selected for this research are readily apparent (Table 1). The pH of these sediments ranged from 6.0 to 7.9. Sediments ranged from slightly oxidized (+62 mv) to reduced (-300 mv). Organic carbon content (0.03%-2.54%) spanned a range that would be expected to encompass most sediments in the U.S. Organic matter ranged from 0.29% to 6.05%. Ratios of organic carbon:organic matter ranged from 1.71% to 62.1%. Cation exchange capacity ranged from 0.11 to 14.29 meq/100g. Acid volatile sulfides (AVS) were not detectable in two sediments and were as high as 133.5 $\mu\text{mol/g}$ of dry sediment. The bulk density of sediments ranged from 80 to 44% sediment. The coarse (sand) fraction of these sediments constituted 28 to 96% of these samples. The fine fractions (silt and clay) similarly ranged widely with silt ranging from 4 to 37% and clay from nondetectable (<0.01%) to 3.1% of the sample. With this range in characteristics, these sediments should permit a thorough evaluation of the potential for sediments to interact with silver and alter bioavailability.

Partitioning of silver compounds (AgNO_3 and AgCl) was evaluated using these

sediments (Figs. 1-6). The test systems were amended with silver compounds as mentioned previously and the concentrations of silver were determined in overlying water, pore water, and particulate fraction or compartments. The solubilities of the silver compounds necessitate adjusting the amendment procedures for the various compounds. Silver nitrate can be amended to sediment in an aqueous solution with a concentration of up to 2500 g/L in the solution. Silver chloride and silver thiosulfate complex have to be amended in solid forms.

For AgNO_3 amended sediments, silver concentrations associated with particulates ranged from $<50 \mu\text{g Ag/kg}$ for Sediment 2 to $>150 \text{ mg Ag/kg}$ for Sediment 4 (Fig. 1). After an initial contact period of 10d, the results indicate that we can reasonably expect a factor of 3 difference in the affinity of particulates for silver for sediments. Total silver concentrations in overlying water ranged more widely (Fig. 2). Total silver concentrations in overlying water ranged from $<0.25 \text{ mg Ag/L}$ to $>8 \text{ mg Ag/L}$. The two orders of magnitude difference in total aqueous silver concentration was not readily attributed to a specific sediment or aqueous characteristic. Similarly, silver concentrations range from a low of approximately 9 mg Ag/L , to a high pore water concentration of $>35 \text{ mg Ag/L}$ in Sediment #5.

Concentrations of silver associated with AgCl amended sediments ranged from about 30 mg Ag/kg to $>65 \text{ mg Ag/kg}$. Thus, concentrations in nature might be expected to range by a factor of two. Similarly, the dissolved silver found in the pore water was an order of magnitude less than for AgNO_3 amended sediments. Pore water concentrations of silver ranged from 0.025 mg Ag/L to 0.25 mg Ag/L . This order of magnitude range in

pore water concentration of silver should translate into differences in toxicity. The concentration of total silver in samples of the overlying water from AgCl tests ranged from 0.036 mg Ag/l to 0.084 mg Ag/L. These overlying water concentrations of silver are two orders of magnitude less than those observed for AgNO₃ amended sediments.

Relatively little change in silver concentrations in the three fractions (particulate associated, pore water, and overlying water) was observed over the ten days of this experiment. Silver concentrations were relatively stable after the initial 2 hours of contact for both AgNO₃ and AgCl amended sediments. For both AgNO₃ and AgCl amended sediments, an affinity of silver for the silt/clay fraction is apparent. Enrichment of silver concentrations in the silt/clay fraction relative to the sand fraction ranged from two to approximately one hundred fold.

The 10-d LC₅₀ values for *H. azteca* sediment toxicity experiments with silver nitrate are shown in Table 2. *H. azteca* tested in Sediment 3 had a 10 d LC₅₀ of 1.6 (95% CI 1.5-1.7) mg Ag/kg, whereas organisms in Sediment 7 had a 10-d LC₅₀ over two orders of magnitude higher at 397.7 (95% CI 345-417) mg Ag/kg.

In 10d *H. azteca* experiments with silver thiosulfate complex, sediments were amended with a nominal concentration of 2000 mg Ag/kg of silver thiosulfate complex. Analytical measures of silver as silver thiosulfate in sediments were 1126, 648, 569 and 682 mg Ag/kg in sediments 1, 3, 6 and 7, respectively. There was no detectable concentration (detection limit = 13 µg Ag/L) of silver in the overlying water after 24 hours of contact time, or at the end of the 10d experiment. In 10d-exposures of *H. azteca*, survival was 90% or greater in all test sediments. Survival of control organisms was 100%.

The 10-d LC₅₀ for Sediment 1 was >1126, for Sediment 3 was >648, Sediment 6 was >569, and Sediment 7 was >682 mg Ag/kg.

Four sediments were amended with silver nitrate and the bioavailability of silver was evaluated using *H. azteca*. A change in sediment characteristics had a dramatic effect on silver partitioning relative to bioavailability with *H. azteca* 10-d LC₅₀s ranging from 1.5 mg Ag/kg to 397.7 mg Ag/kg. Upon examination of individual sediment characteristics, it does not appear that any one parameter is predominantly influencing silver partitioning, but observed partitioning is the result of an interaction of several characteristics that determine the fraction of bioavailable silver. For example, Sediment 3 and Sediment 7 had similar particle size characteristics and redox (Table 1) and yet *H. azteca* in Sediment 3 had a 10-d LC₅₀ of 1.5 mg Ag/kg and in Sediment 7 had a 10d LC₅₀ of 442 mg Ag/kg. These sediments however, have different pH values, a factor which can alter the speciation of silver. The sediment with the lower pH is predicted to have a higher percentage of free silver ion. An additional parameter that differed between these two sediments was percent organic carbon (and organic matter). Sediment 3 had an order of magnitude less organic carbon and organic matter than Sediment 7. Cation exchange capacity (CEC) also varied by an order of magnitude between the two sediments. Sediment 7 had 0.6% clay and a CEC of 2.4 meq/100 gm dry sediment, which would provide binding sites for silver ions, removing them from the water column. AVS is another characteristic that was different between the two sediments. Sediment 7 with 2.2 μmols AVS/g dry weight should have had sufficient AVS to sequester most of the amended silver (as silver nitrate) (Allen *et al.* 1993). Indeed, the toxicity of silver amended to this

sediment was significantly less than the toxicity observed for the other sediments.

The data for silver amended Sediments 1 and 6 are somewhat enigmatic. The parameters that are suspected to influence bioavailability and toxicity of silver in sediments (pH, redox, organic carbon, organic matter, cation exchange capacity, and fraction of silt/clay) would indicate that Sediment 1 should be more toxic with the same concentration of silver than Sediment 6. This was not the case; in fact, the observed toxicity did not differ significantly for these two sediments.

CONCLUSIONS

These sediment amendment experiments illustrate three primary principles: (a) sediment amendment procedures must be adjusted based upon the solubility of the silver compounds studied; (b) silver compounds differ greatly in their affinity for sediments and their compartmentalization into pore water and overlying waters; and (c) diverse sediments vary widely in their affinity for silver and their ability to bind silver. This was reflected in differing bioavailabilities of silver amended sediments to *H. azteca* (measured as LC_{50S}).

Bioavailability to *H.azteca* of silver, as silver nitrate, amended to sediments with varying characteristics (i.e., organic matter and acid volatile sulfide) is not equal from one sediment to another. Sediment characteristics significantly affected the bioavailability of silver nitrate. When the source of silver as a variable is examined by sediment toxicity experiments with *H. azteca*, clearly AgCl when amended to sediments is orders of magnitude less toxic than AgNO₃. Sediments amended with silver thiosulfate complex are

similar in toxicity to AgCl amended sediments with 10-d LC₅₀s in excess of 2000 mg Ag/kg. These results have serious and obvious implications for risk assessments of silver in aquatic ecosystems.

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Table 1. Characterization of sediments selected for silver partitioning and bioavailability experiment

Parameters	Sed. 1	Sed. 2	Sed. 3	Sed. 4	Sed. 5	Sed. 6	Sed. 7	Sed. 8
pH	6.00	6.95	6.80	6.87	7.90	7.30	7.48	7.38
Redox	+57.0	+62.0	-232.0	-168.1	-248.5	-297.0	-291.0	-300.0
O.C.	0.38%	0.03%	0.18%	2.54%	0.08%	0.45%	1.02%	ND
O.M.	1.68%	1.75%	0.29%	6.05%	0.47%	3.94%	2.31%	4.56%
CEC	1.50	1.58	0.11	14.29	0.67	7.77	2.40	6.91
AVS	4.63	0.79	0.36	6.81	NM	NM	70.75	133.52
%Sed.	72.95	80.15	76.70	43.70	78.11	55.40	69.52	51.70
%Sand	75.90	77.05	94.47	28.50	95.59	60.31	95.19	91.38
%Silt	21.40	22.95	5.53	71.50	4.23	36.51	4.25	8.27
%Clay	2.7	NM	NM	NM	0.18	3.18	0.56	ND

Redox (mV), CEC = cation exchange capacity (meg/100g dry sed.), AVS = acid volatile sulfide ($\mu\text{mol/g}$ dry sed.), O.C. = organic carbon, O.M. = organic matter, ND = not determined, NM = not measured (AVS detection limit = 0.01 $\mu\text{moles/g}$ dry sed, %Clay detection limit = 0.01%)

Table 2. Results of 10-d sediment bioavailability experiments with *H. azteca* in sediments amended with silver nitrate. LC50s are based on total acid extractable silver concentration in sediments (mg Ag/kg).

Sediment Sample	10-d LC50 (95% CI)
Sediment #1	60.7 (55.7- 66.1)
Sediment #3	1.62 (1.5-1.74)
Sediment #6	45.4 (34.1-79.8)
Sediment #7	379.7 (345-417)

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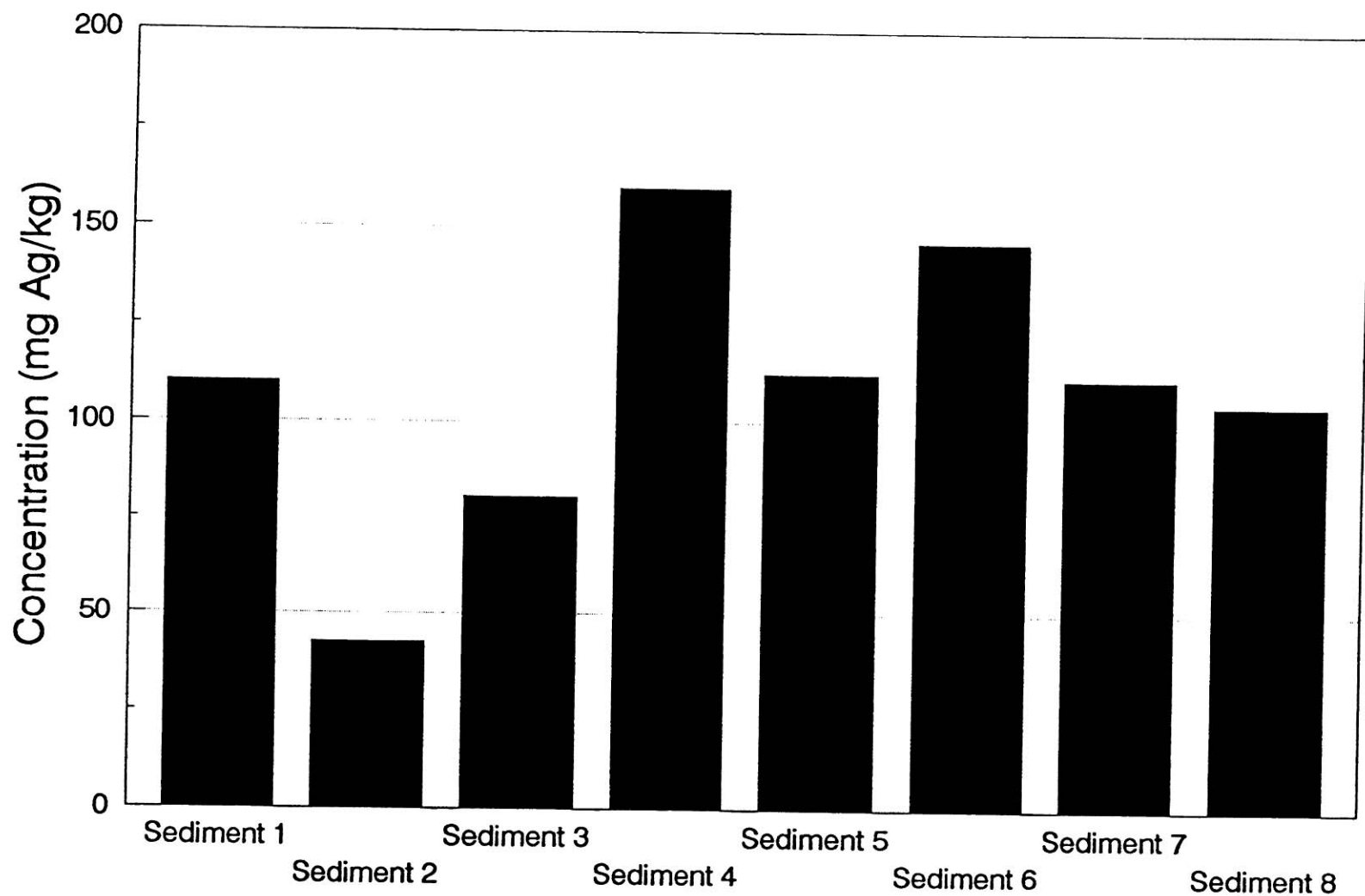


Fig.1 Concentration of acid extractable silver in particulate fraction of sediments. Sediments amended with 320 mg Ag/kg as silver nitrate.

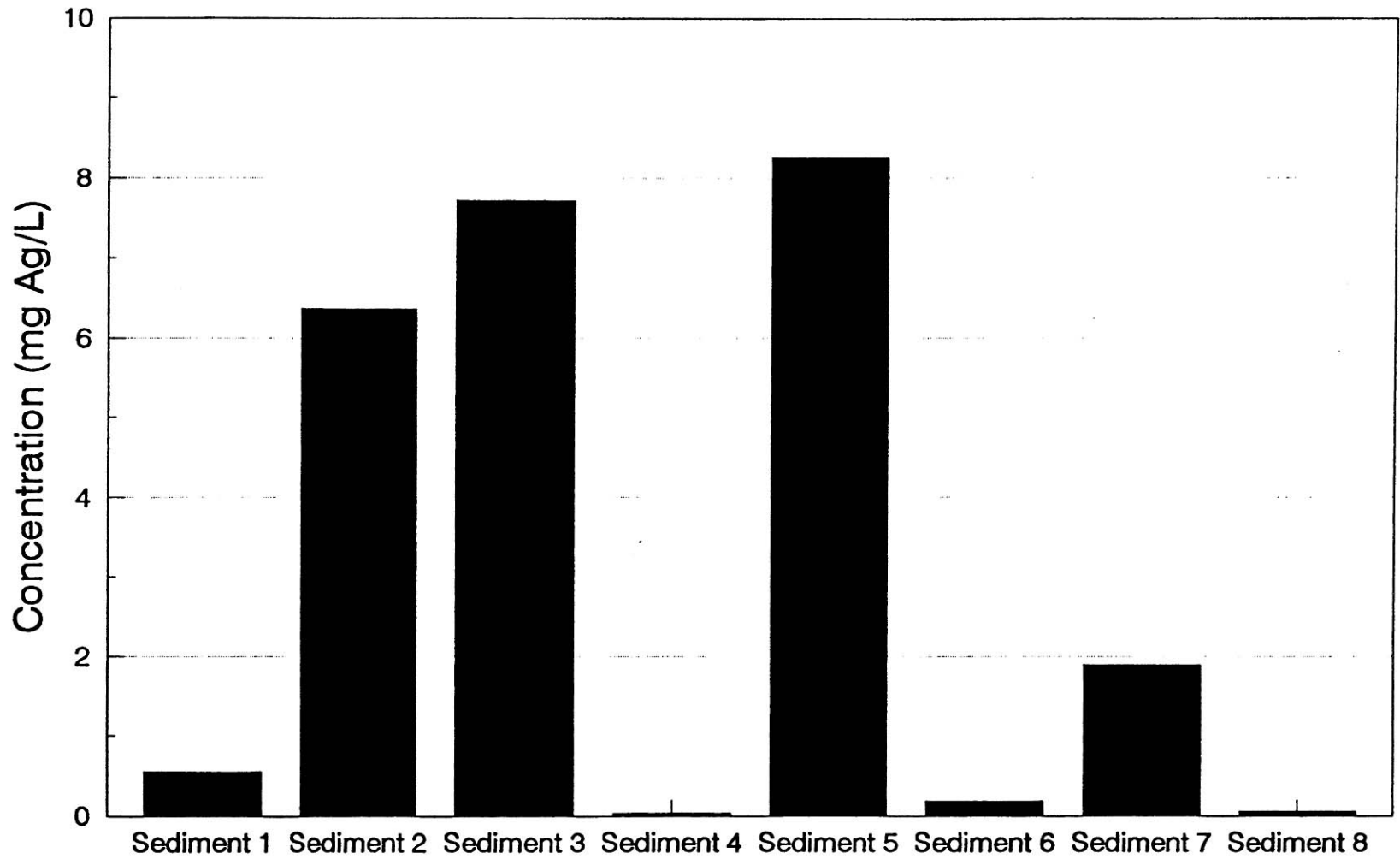


Fig.2 Concentration of dissolved (<0.45 μm) silver in overlying water. (Sediments amended with 320 mg Ag/kg as silver nitrate)

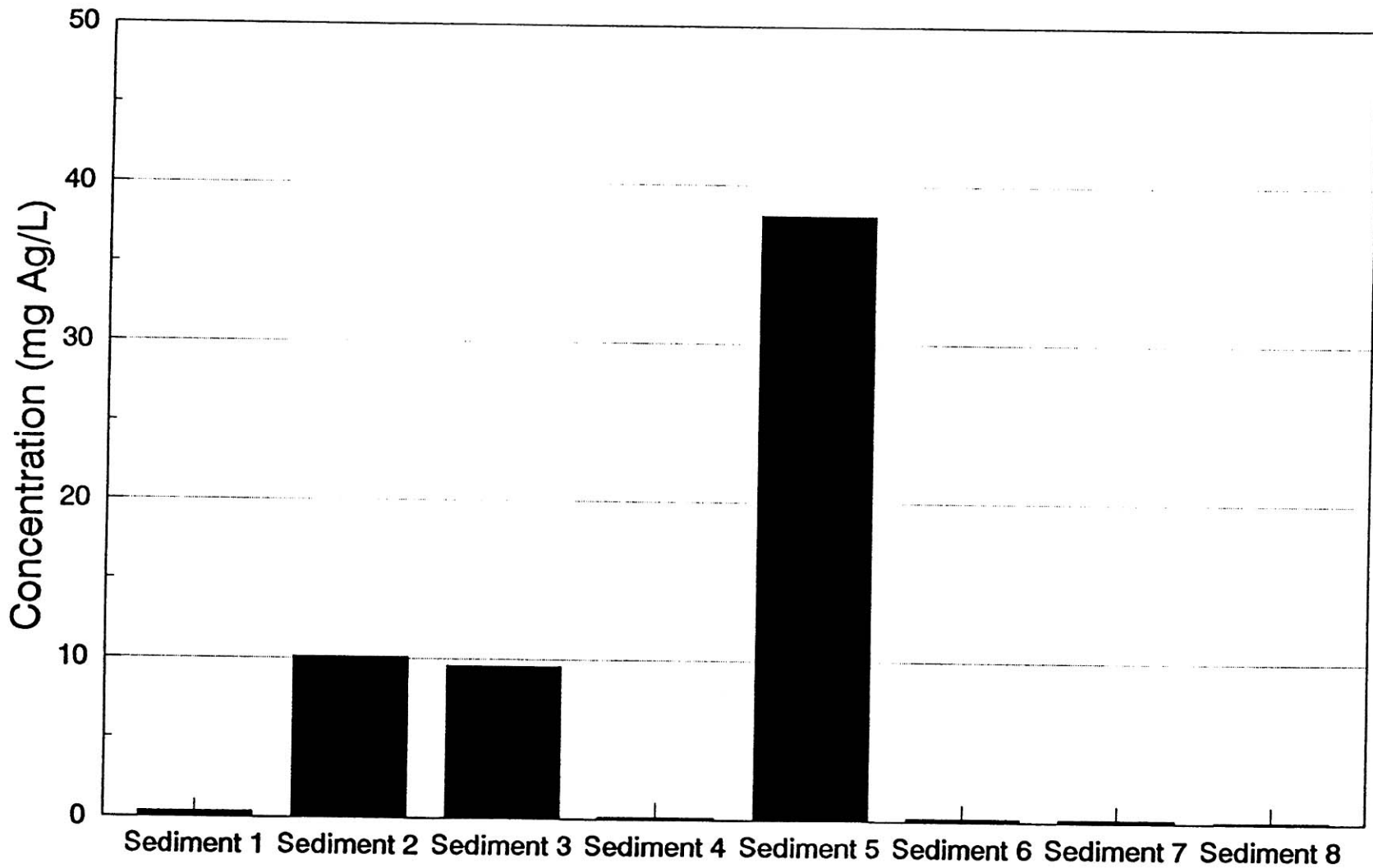


Fig. 3 Concentration of dissolved (<0.45 μm) silver in pore water. (Sediments amended with 320 mg Ag/L as silver nitrate)

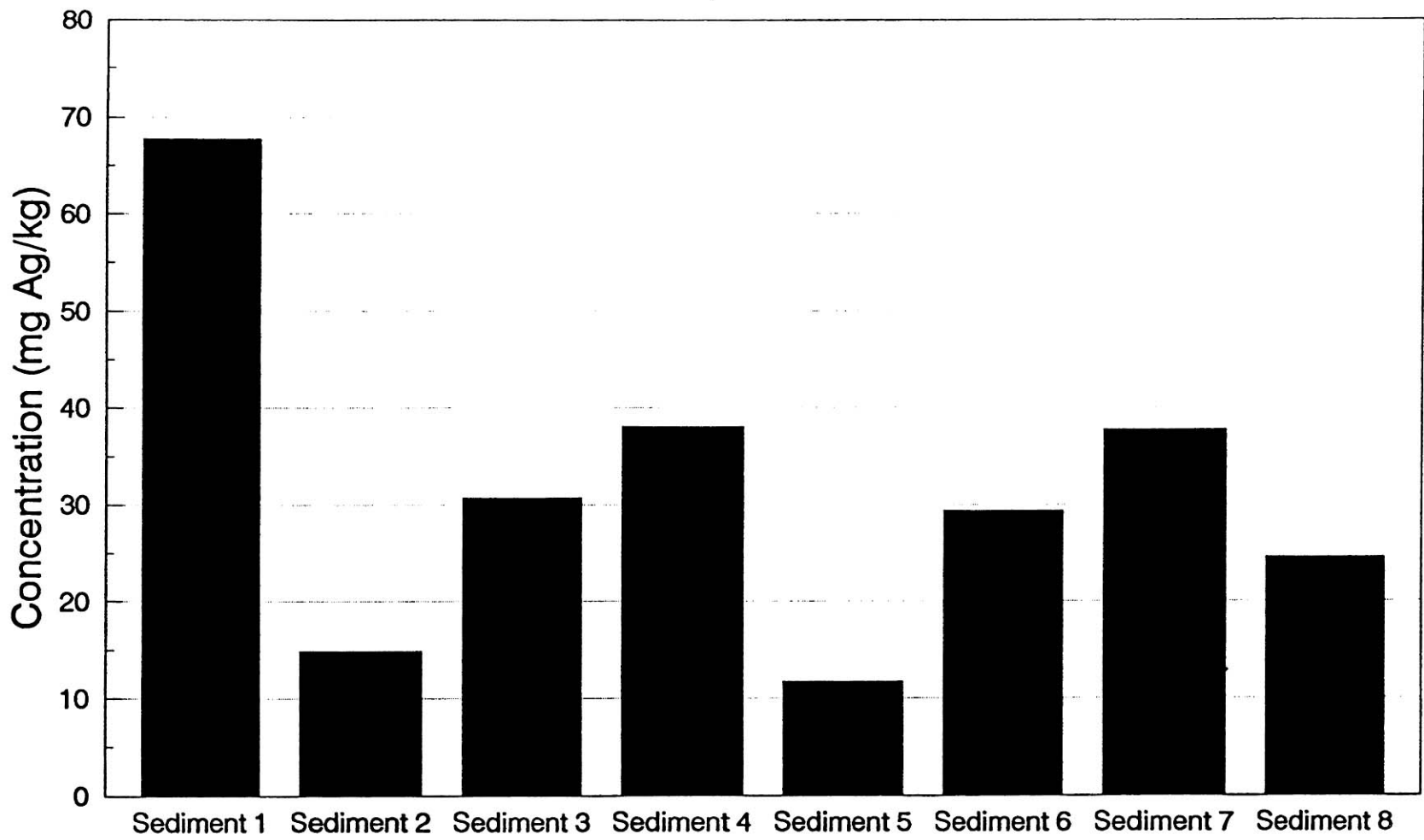


Fig. 4 Concentration of acid extractable silver in particulate fraction of sediments. Sediments amended with 320 mg Ag/kg as silver chloride.

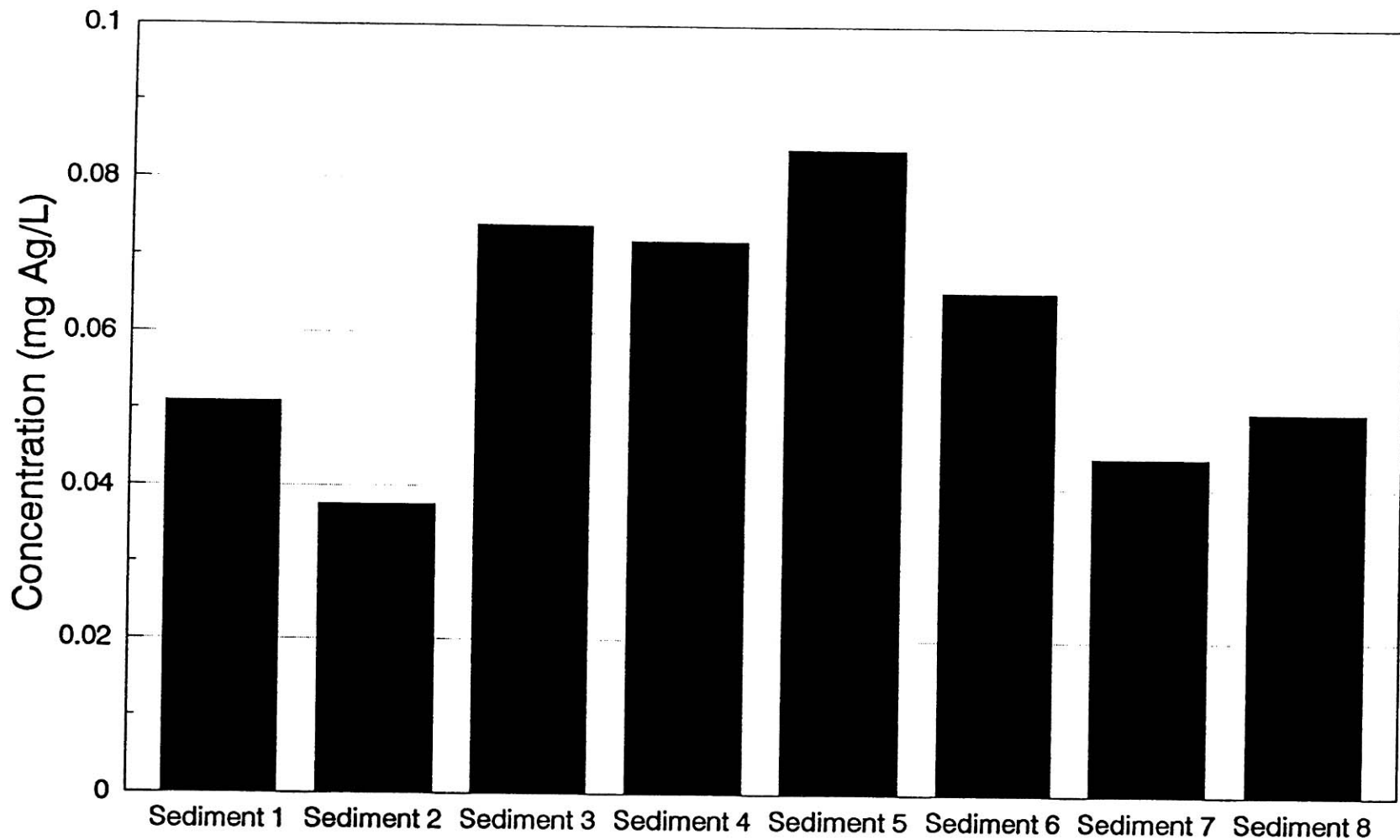


Fig. 5 Concentration of dissolved (<0.45 μm) silver in overlying water. (Sediments amended with 320 mg Ag/kg as silver chloride)

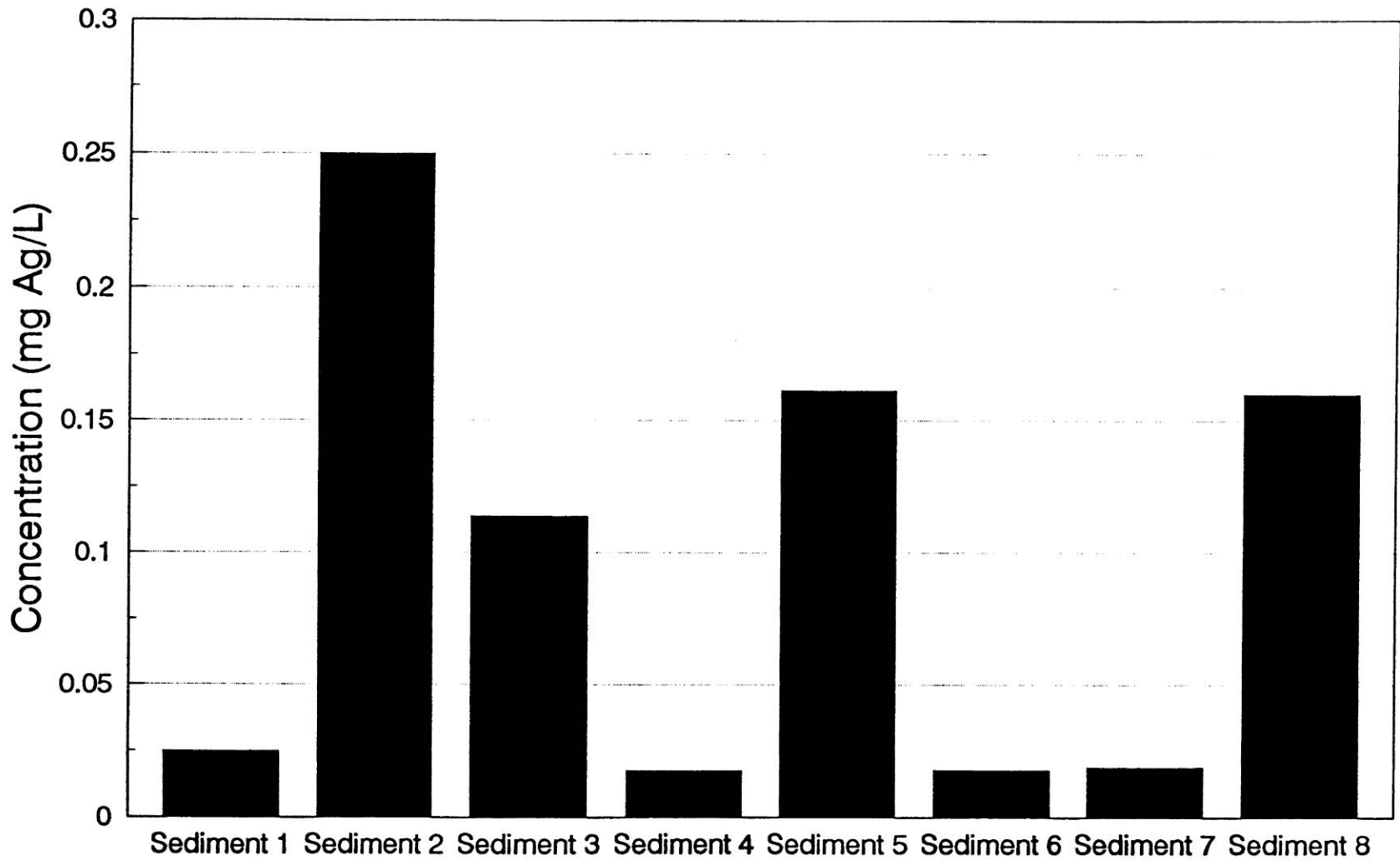


Fig. 6 Concentration of dissolved (<0.45 μm) silver in pore water.
(Sediments amended with 320 mg Ag/kg as silver chloride)

Questions & Answers: Partitioning and Effects of Silver in Amended Freshwater Sediments

- Q. DOMINIC DI TORO (Manhattan College): I noticed that the acid-volatile sulfide (AVS) in your sediments was quite low. I was wondering if you dried your sediments?
- A. No, we took surficial sediments where the organisms are found and one of the things we're interested in is the toxicity of AVS to organisms. We've done a few experiments and we found that they are fairly sensitive to AVS. In other words, they both behaviorly avoid AVS and give up in terms of life when they don't.
- Q. Did you show toxicity effects or behavior? We haven't seen that in the sediment quality criteria work that's been going on for five years.
- A. Do you find AVS in the areas where the organisms are active?
- Q. Absolutely.
- A. Well, I guess we could spend hours or even days talking about the sources of volatile sulfides and so on. What we found is that the AVS, when exposed to diatomic oxygen, were all oxidized and at a fairly rapid rate. So these organisms were tolerating AVS where there's no diatomic oxygen. These are aerobes, in sort of loose terms, and they have an absolute requirement for diatomic oxygen. So where you find benthic organisms that are not aerobes, if you will, you then will likely find that the AVS is pretty small.
- Q. This is absolutely untrue. The normal set in sediment is that you find obligate aerobes, whatever, and it poses AVS via concentration, that's the normal. If you oxygenate them and deplete the oxygen you are absolutely right, that would leave an anaerobic environment, but it's common finding that obligate aerobes live in there, too. In special areas, of course, but in close proximity to all these sulfidic sediments, and the reason they survive is because they aerate themselves.
- A. In terms of the whole of silver required to elicit response in the organism?
- Q. Yes, except for the one case where you have, like 1 ppm — was that the sediment with zero AVS by chance?
- A. No, that was the sediment with fairly low AVS and fairly low organic carbon.
- Q. Right, and did you see any contravention or a notion that the molar ratio of silver to AVS is less than one or less than 0.5 in this case? Did you see any toxicity in that case?
- A. As we load these sediments and as we exceed the molar capability of AVS we do see the onset of toxicity, but it's not completely explained by AVS so there are other factors.
- Q. I guess the question is the other way, when you have enough AVS have you ever seen toxicity?
- A. Yes.
- Q. You have seen toxicity in the presence of excess AVS?
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- A. Yes, and I think the reason is that AVS for a bulk sediment isn't necessarily evenly distributed. Which AVS do you use to even represent one beaker, do you use the AVS for a bulk sample from that sediment and does that represent what the animals actually see?
- Q. I will tell you what we do but I'm curious to see that experiment because that would be unusual.
- Q. ANDERS ANDREN (Univ. of Wisconsin): From what I understand, as you mix your solid silver chloride, you mix that into the sediment, is that correct?
- A. We do that and then allow it to reestablish negative redox and so on.
- Q. How do you know that you don't change the AVS?
- A. You can measure the AVS before and after and you see similar values. You don't see exactly the same values.
- Q. But you mix it in anoxic conditions?
- A. No. We mix it under water and it rapidly reestablishes. If it's pretty strongly negative redox, in about 24-48 hours it will reestablish the negative redox.
- Q. I know you have some amendments where you have 2,000 mg/kg silver or 3,000 mg/kg. Now, I would suspect that you have solubility product controls at much lower levels than that, so then it wouldn't really matter whether you have 2,000 mg/kg or 3,000 mg/kg as far as the water concentration goes. It seems it would be the same if it's controlled by some sort of the insoluble phase. So then, why should there be a difference in toxicity?
- A. In fact, there wasn't in a lot of cases. Once you exceed a certain minimum concentration for the solubility product control you don't see any difference in toxicity. I mean, for a lot of these organisms we've illustrated the need to have the techniques to measure bioavailable metal. For example, in chrome work we can precipitate chrome and allow these animals to build their cases out of chrome, a major part would be made of chrome, essentially, total chrome. So you can take, essentially, pure silver or pure copper or whatever and if it's not bioavailable the animals don't know it's there, and likely, you can digest or biodegrade it and measure it but that measurement does not mean anything.
- Q. What do you mean by pure silver? Metallic?
- A. Yes. An example I was going to show and hesitated to show to this group because I wasn't sure how it would be received is one showing that 18.3 pounds of metallic silver were deposited at the lower end of the Mississippi River in a sinking ship. In theory, if all of that was bioavailable you would have had mortality for miles of the river. But it's simply not bioavailable.
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