

A SIMPLE FIELD TEST FOR ACID VOLATILE SULFIDE IN SEDIMENTS

ERIC F. ANDERSON AND DAVID J. WILSON

*Martin Luther King Magnet High School, 613 17th Avenue North, Nashville, TN 37203
Brown and Caldwell, 501 Great Circle Road, Nashville, TN 37228*

ABSTRACT—The presence of acid volatile sulfide (AVS) is of importance in reducing or eliminating toxicities of heavy metals in sediments in lakes and reservoirs. Acid volatile sulfide consists of the more soluble sulfides, principally FeS, when present as a solid phase in the sediment. The determination of AVS in sediments is of considerable practical interest because AVS can immobilize toxic heavy metals as highly insoluble sulfides. Present methods of analysis for AVS, although accurate, are costly and slow. A new, rapid, low-cost field test for AVS is described in which sediment samples are acidified in a closed jar, agitated, and the released hydrogen sulfide detected by the color produced on a paper moistened with lead nitrate solution. The detection limit is approximately 1 mg of sulfide, and sample sizes as large as 500 g can be analyzed.

Polluted sediments in lakes, reservoirs, waterways and bays across the United States constitute a serious problem (National Research Council, 1997). The Environmental Protection Agency has reported that 7% of the watersheds in the United States pose potential risk to people who eat fish from them (Chemical & Engineering News, 1998). Many of the sediments in these waters contain toxic heavy metals such as lead, cadmium, copper, and mercury. These metals may enter the aquatic food chain through bottom feeding organisms or by solution into the water column through diffusion and bioturbation.

Acid-volatile sulfide (AVS) is a pool of solid phase sulfides that may be present in the sediment and yields H₂S on treatment with hydrochloric acid. The AVS constitutes a reactive pool of sulfide that is available to immobilize toxic heavy metals as extremely insoluble metal sulfides (DiToro et al., 1990, 1991, 1992; Ankley et al., 1991, 1993; Carlson et al., 1991). Most AVS occurs naturally in the form of solid FeS in anaerobic sediments underlying many bodies of water. AVS is a major factor in controlling the bioavailability of heavy metals in sediments. The presence of AVS in sediments contaminated with heavy metals is therefore of great significance in reducing or eliminating the toxicities of these elements (Dilks et al., 1995). Howard and Evans (1993) have noted seasonal and spatial changes in sediment AVS in a seasonally anoxic lake.

Redox potentials in the hypolimnion may show drastic seasonal changes in the United States. During the summer, thermal stratification of water in lakes and reservoirs occurs, resulting in oxygen-rich water in the epilimnion and oxygen-poor or even anoxic water in the deeper hypolimnion (Cole, 1979; Miller, 1996). During this period of thermal stratification, the bottom sediments are in contact with anoxic water, and no AVS destruction occurs. In addition, microorganisms may use sulfate as an electron acceptor to generate AVS. During the fall, surface waters cool and become more dense. The resulting overturn of the body of water mixes oxygen-rich surface waters with the waters of the hypolimnion. During the period in which oxygen-rich water is in contact with the sediments, the AVS may be depleted or even

eliminated because of rapid reaction between oxygen and the AVS to form soluble sulfates (Fig. 1).

The heavy metal sulfides also can be oxidized to much more soluble sulfates by dissolved O₂, releasing the toxic metals and rendering them biologically available. All oxidations of heavy metal sulfides by oxygen to sulfates are thermodynamically spontaneous (Morgan et al., 1992; Zhuang et al., 1994). For example, the ΔG_0 for the reaction $\text{CuS(s)} + 2\text{O}_2 \rightarrow \text{Cu}^{+2}(\text{aq}) + \text{SO}_4^{-2}(\text{aq})$ is -625.6 kJ, which gives an equilibrium constant of 4×10^{110} (from Moeller et al., 1984).

It therefore becomes necessary to examine the seasonal behavior of AVS in contaminated sediments if one is to ascertain whether the binding of heavy metals as sulfides provides adequate protection. While molecular diffusion does not provide an efficient mechanism for mixing dissolved oxygen with sediments, bioturbation is much more effective (Thibodeaux, 1996), and in some circumstances can result in the production of oxic conditions in relatively thick layers of sediment during the winter and spring. Extensive testing of sediments for AVS would therefore seem advisable. Analysis of the chemical equilibria involved in the transformations of AVS and heavy metal sulfides has been presented by DiToro et al. (1991). Briefly, the presence of solid FeS at equilibrium in the sediments guarantees the immobilization of Ag, Cu, Cd, Hg, and Pb as insoluble sulfides, while the presence of dissolved O₂ guarantees the oxidation of all sulfides to much more soluble sulfates. However, for metals such as nickel and cobalt, the sulfides are more soluble, and may be mobile in the presence of solid FeS. In the presence of solid FeS the sulfide ion concentration is given by

$$[\text{S}^{-2}] = \left[\frac{K_{\text{FeS}}}{1 + ([\text{H}^+]/K_2) \cdot \{1 + ([\text{H}^+]/K_1)\}} \right]^{1/2}$$

where [H⁺] is the hydrogen ion concentration, K₁ and K₂ are the first and second ionization constants for H₂S, and K_{FeS} is the solubility product for ferrous sulfide. The solubility of a heavy metal M⁺² is then given by

$$[\text{M}^{+2}] = K_{\text{MS}}/[\text{S}^{-2}]$$

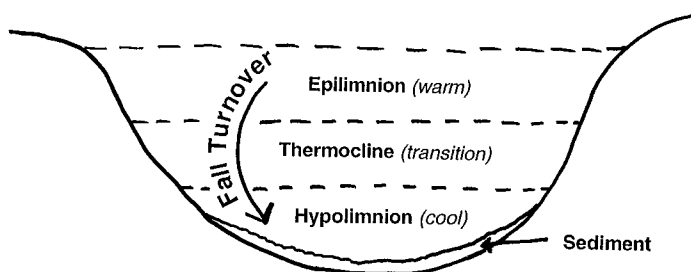


FIG. 1. Summer thermal stratification of lakes. In fall turnover, the oxygen-rich epilimnion layer is cooled and sinks to the bottom, exposing the sediments to oxygen-rich water. This may result in oxidation of sulfides formed in the sediment when it is anaerobic.

Heavy metal concentrations in equilibrium with solid FeS over the environmentally significant pH range are summarized in Table 1.

Unfortunately, the standard method currently used for the determination of AVS in sediments, although accurate, also is complex, time-consuming, and expensive. Acid volatile sulfide determination also requires a skilled technician and laboratory facilities, so cannot be used in the field (Allen et al., 1991; Allen et al., 1993). The method involves sediment sample treatment with hydrochloric acid, purging of the resultant H_2S , and H_2S capture by absorption in silver nitrate solution. The resulting silver sulfide is separated by filtration, dried, and weighed.

It would be desirable to have a low-cost, simple field test for AVS to supplement the laboratory analysis. A cheap field test could be widely used for screening, with the laboratory procedure employed as a quality control check and for analysis of particularly critical samples. In this way the seasonal dependence of AVS levels could be mapped out at greatly reduced expense.

We present a description of a simple AVS test, calibration results, and data taken on sediments from a pond in MetroCenter, Nashville, in the floodplain of the Cumberland River.

MATERIALS AND METHODS

AVS Test Procedure—The field AVS test is simple. Dilute HCl is mixed with a given wet weight or volume of sediment sample to liberate gaseous H_2S from acid-soluble metal sulfides (principally FeS) which may be present. The H_2S is detected with a paper strip moistened with lead nitrate or lead acetate solution. A black precipitate of PbS is formed on the paper if AVS is present. For field use it is more convenient to measure a volume

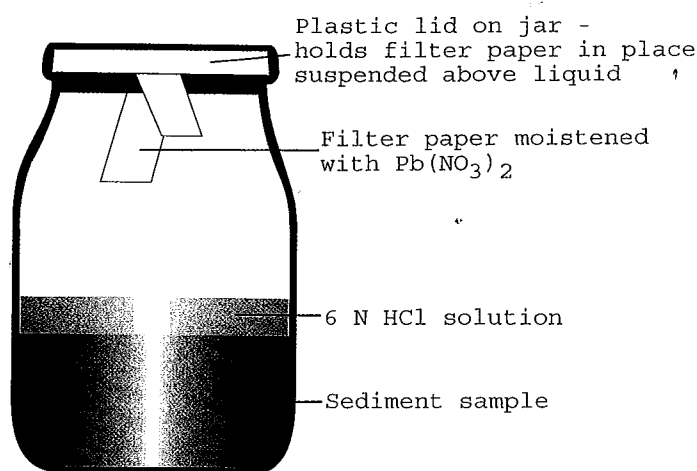


FIG. 2. Diagram of setup for acid volatile sulfide field test.

of sediment than to measure a weight. Sediment samples should never be dried because of possible loss of AVS during drying.

A strip of lead nitrate paper is prepared by adding 6 drops of a saturated lead nitrate solution to one end of a strip of filter paper. Then 250 ml of sediment is placed in a one-quart glass jar. Fifty ml of dilute (approximately 6 M) HCl is added to the sediment in a fume hood or out of doors and the jar is quickly closed with the lead nitrate paper strip suspended in the top of the jar. The paper strip is held in place by pinching the dry end of the paper between the jar lid and the mouth of the jar (Fig. 2).

After approximately 15 sec the jar is gently swirled to mix the acid with the sediment and increase the rate of liberation of H_2S . Care must be taken to prevent the muddy slurry from coming into contact with the paper strip. The filter paper is left in contact with the headspace gas for two minutes. The jar is opened and the filter paper strip removed for examination. If the paper is blackened by the formation of PbS, a significant concentration of AVS is present in the sediment. If little or no AVS is present, the paper will show a light grey-brown stain or no color change at all.

A positive test may be made semiquantitative by repeating with progressively smaller quantities of fresh sediment (100, 50, 25, 10, etc., ml) until the test no longer yields a darkening of the filter paper. AVS can then be estimated by using a sensitivity constant and the volume of the smallest sediment sample that yielded a color change in the paper strip.

The sensitivity of the test was determined as follows. Known amounts of sulfide (as freshly-prepared 0.0156 M Na_2S solution)

TABLE 1. Heavy metal concentration (mg/l) in equilibrium with solid FeS

Metal sulfide	K_{ep}	pH 5	pH 6	pH 7	pH 8	EPA criteria
CdS	2×10^{-28}	2.0×10^{-10}	2.1×10^{-11}	2.8×10^{-12}	6.6×10^{-13}	1×10^{-2}
PbS	1×10^{-28}	1.9×10^{-10}	1.9×10^{-11}	2.6×10^{-12}	6.1×10^{-13}	5×10^{-2}
CuS	6×10^{-36}	3.4×10^{-18}	3.6×10^{-19}	4.8×10^{-20}	1.1×10^{-20}	1.0
HgS	4×10^{-53}	7.2×10^{-35}	7.5×10^{-36}	1.0×10^{-36}	2.4×10^{-37}	1.5×10^{-4}
Ag ₂ S	6.3×10^{-50}	6.9×10^{-32}	7.2×10^{-33}	1.3×10^{-33}	2.3×10^{-34}	5×10^{-2}

were added to 50 g of AVS-free sediment. Two types of samples were studied. The first was pond sediment that had been allowed to thoroughly air dry and was then exposed to air for three months in a shallow pan with frequent mixing. The second type of sample was black surficial topsoil which was treated by the same procedure as used to prepare the sediment samples. The spiked sediments were then tested by the new method. The amount of sulfide added to the sediment was decreased until the test no longer yielded a positive result (no color change of the strip). The sensitivity of the test was calculated using the minimum quantity of sulfide for which a positive test was obtained.

RESULTS AND DISCUSSION

Sensitivity—The test consistently detected 1 mg of sulfide (2 ml of 0.0156 M $\text{Na}_2\text{S} = 1 \text{ mg S}^{-2}$). With 50 g of sediment, this corresponds to 20 mg S^{-2} /kg of wet sediment as the limit of detection. It also was possible to detect 1 mg of sulfide in a 250 g sediment sample, giving a limit of detection of 4 mg/kg. No difference in sensitivity was observed between experiments carried out on the two types of samples. We therefore take the sensitivity constant for the test as 1 mg of sulfide.

To illustrate, if the smallest sediment sample that yields a positive result weighs 75 g, then the AVS concentration in this sediment is approximately $1 \text{ mg}/0.075 \text{ kg} = 13 \text{ mg/kg}$.

Only two varieties of samples were investigated, so we feel that one would be well-advised to verify the sensitivity of the test on site-specific samples to improve confidence in the test results.

Possible interference from iron—Several AVS-free sediment (topsoil) samples were spiked with Na_2S and excess ferrous ammonium sulfate to see if the presence of excess ferrous ion (possibly from FeCO_3) caused interference. No significant differences were seen.

Destruction of AVS by exposure to air—Sediment from the anaerobic bottom of a pond in Metrocenter, Nashville, in the floodplain of the Cumberland River, was known to contain $\geq 100 \text{ mg/kg}$ of AVS. A portion of this sediment was spread out on a flat surface (cookie sheet) in a layer about 2.5 cm thick and allowed to air-dry without mixing. Samples were taken monthly for AVS testing. Within three months tests for AVS in this aerated sediment were negative, indicating that atmospheric oxygen destroys AVS relatively rapidly.

AVS in an overturned pond—Sediment samples were taken from the pond mentioned above during the summer, fall, winter, and early spring of 1997–98, and dissolved oxygen (D.O.) was monitored from the end of August, 1997, until the end of March, 1998. Fall overturn apparently occurred in mid-November, as indicated by D.O. concentrations measured at a depth of about 0.7–0.8 m. Sediment AVS concentrations and D.O. levels (measured with a Hach test kit by the Winkler method) are reported in Table 2.

The sediment AVS levels in grab samples (estimated to be from the top 8 cm of the sediment) remained high through January, but by the end of March had dropped to undetectable ($< 10 \text{ mg/kg}$). Evidently the movement of oxygen down into the sediments in this pond is a relatively slow process, since fall overturn occurred in November. Risk assessments for heavy metals based on the AVS levels through January would miss the potentially toxic “window” which occurred later and during which AVS is not available to provide protection by immobilizing these toxic metals. These results indicate the importance of experimentally ascertaining the seasonal dependence of AVS by

TABLE 2. Sediment acid volatile sulfide (AVS) and dissolved oxygen concentrations from a pond at Fountain Square, MetroCenter, Nashville, Tennessee.

Sediment AVS		Dissolved oxygen ¹	
Date sampled	Concentration (mg S^{-2} /kg sediment)	Date sampled	Concentration (mg/l)
8/29/97	100	10/14/97	1
11/7/97	100	11/7/97	2
12/16/97	100	11/20/97	12
1/18/98	100	1/18/98	9
3/23/98	none detected (<10)	3/27/98	11

¹ Sampling depth 0.7–0.8 m.

means of a set of tests distributed over the period of overturn, rather than by relying on tests made on only one or two occasions.

LITERATURE CITED

- ALLEN, H. E., G. FU, W. BOOTHMAN, D. M. DiTORO, AND J. D. MAHONY. 1991. Draft analytical method for determination of acid volatile sulfide in sediment. EPA 821/R91–100, Dec.
- ALLEN, H. E., G. FU, AND B. DENG. 1993. Analysis of acid-volatile sulfide (AVS) and simultaneously extracted metals (SEM) for the estimation of potential toxicity in aquatic sediments. *Environ. Toxicol. Chem.*, 12:1441–1463.
- ANKLEY, G. T., V. R. MATTSON, E. N. LEONARD, C. W. WEST, AND J. L. BENNETT. 1993. Predicting the acute toxicity of copper in freshwater sediments: evaluation of the role of acid-volatile sulfide. *Environ. Toxicol. Chem.*, 12:315–331.
- ANKLEY, G. T., G. L. PHIPPS, E. N. LEONARD, D. A. BENOIT, V. R. MATTSON, P. A. KOSIAN, A. M. COTTER, J. R. DIERKES, D. J. HANSEN, AND J. D. MAHONY. 1991. Acid-volatile sulfide as a factor mediating cadmium and nickel bioavailability in contaminated sediments. *Environ. Toxicol. Chem.*, 10:1299–1308.
- CARLSON, A. R., G. L. PHIPPS, V. R. MATTSON, P. A. KOSIAN, AND A. M. COTTER. 1991. The role of acid-volatile sulfide in determining cadmium bioavailability and toxicity in freshwater sediments. *Environ. Toxicol. Chem.*, 10:1309–1320.
- CHEMICAL & ENGINEERING NEWS. 1998. EPA finds 7% of watersheds have polluted sediments. 76(4):27.
- COLE, G. A. 1979. *Textbook of limnology*. C. V. Mosby, St. Louis.
- DILKS, D. W., J. S. HELFAND, AND V. J. BIERMAN JR. 1995. Development and application of models to determine sediment quality criteria-driven permit limits for metals. *Proc. Toxic Substances Water Environ.: Assess. Control*, Cincinnati, Ohio.
- DiTORO, D. M., J. D. MAHONY, D. J. HANSEN, K. J. SCOTT, A. R. CARLSON, AND G. T. ANKLEY. 1992. Acid volatile sulfide predicts the acute toxicity of cadmium and nickel in sediments. *Environ. Sci. Technol.*, 26:95–102.
- DiTORO, D. M., J. D. MAHONY, D. J. HANSEN, K. J. SCOTT, M. B. HICKS, S. M. MAYR, AND M. S. REDMOND. 1990. Tox-

- icity of cadmium in sediments: the role of acid volatile sulfide. *Environ. Toxicol. Chem.*, 9:1487-1495.
- DITORO, D. M., C. S. ZARBA, D. J. HANSEN, W. J. BERRY, R. C. SVHWARTZ, C. E. COWAN, S. P. PAVLOU, H. E. ALLEN, N. A. THOMAS, AND P. R. PAQUIN. 1991. Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. *Environ. Toxicol. Chem.*, 10:1541-1558.
- HOWARD, D. E., AND R. D. EVANS. 1993. Acid-volatile sulfide (AVS) in a seasonally anoxic mesotrophic lake: seasonal and spatial changes in sediment AVS. *Environ. Toxicol. Chem.*, 12:1051-1058.
- MILLER, G. T. 1996. *Living in the environment—principles, connections, and solutions*. Wadsworth Publishing, New York.
- MOELLER, T., J. C. BAILAR, J. KLEINBERG, C. O. GUSS, M. E. CASTELLION AND C. METZ. 1984. *Chemistry with inorganic qualitative analysis*, 2nd ed. Academic Press, New York.
- MORGAN, J. R., R. W. HOLMAN, AND D. J. WILSON. 1992. Oxidation of heavy metal sulfides in relation to the environment. *J. Tennessee Acad. Sci.*, 67:90-92.
- NATIONAL RESEARCH COUNCIL. 1997. Quoted in hidden hazard: toxic mud. *Nat. Wild.*, Aug./Sept.
- THIBODEAUX, L. J. 1996. *Environmental chemodynamics*, 2nd ed. Wiley-Interscience, New York.
- ZHUANG, Y., H. E. ALLEN, AND G. FU. 1994. Effect of aeration of sediment on cadmium binding. *Environ. Toxicol. Chem.*, 13:717-723.