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An Aqueous and Sedimentalogical Model for Heavy Metal Contamination of Stream Systems Affected by Sulfide Mining in the Eastern United States

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Introduction

Disruption of a sulfide ore zone by underground mining and the subsequent dumping and accumulation of mill tailings into the stream valley adjoining the "Little Bob" sulfide mine has afforded an ideal situation for observation of the effects of sulfide ore mining on water quality within a restricted system

The purpose of the research is to establish trends for the accumulation and distribution of potentially toxic trace metals in fluvial systems that drain abandoned sulfide mineral mining operations. Evaluation of ecological parameters is also attempted.

The particular location and object of the study was chosen because it is one of a number of minor mining operations that occur along the strike of an extended sulfide bearing zone. It might well represent numerous such deposits across the nation (STANTON, 1972). It also contains all necessary comparative elements for our study: 1) Stream unaffected by pollution, 2) Water and sediments from a tailings pond, and 3) Stream eminating from the tailings pond. Analyses of this system should give an idea of the extent of water contamination in the studied stream and in similar, proximal systems.

Location of the Studied Site

The "Little Bob" mine is one of a series of mines and prospects located in a northeast striking sulfide mineral bearing zone. The zone extends from central Carrol County, Georgia (southwest of Atlanta) to Towns County, Georgia, some 240 km to the northeast. The zone is divided into six distinct units, one of which is the famous Creighton-Donlonega gold mining belt. The Geologic Survey of Georgia, Bulletin number 33 (1918) discusses the detailed extent and geology of these sulfide deposits.

The "Little Bob" mine is located in Paulding County in what is known as the "Paulding County Belt" of sulfide deposits. The old

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mine shaft is some 15 meters above the level of a stream that runs approximately 90 meters to the south (Fig. 1). During the period

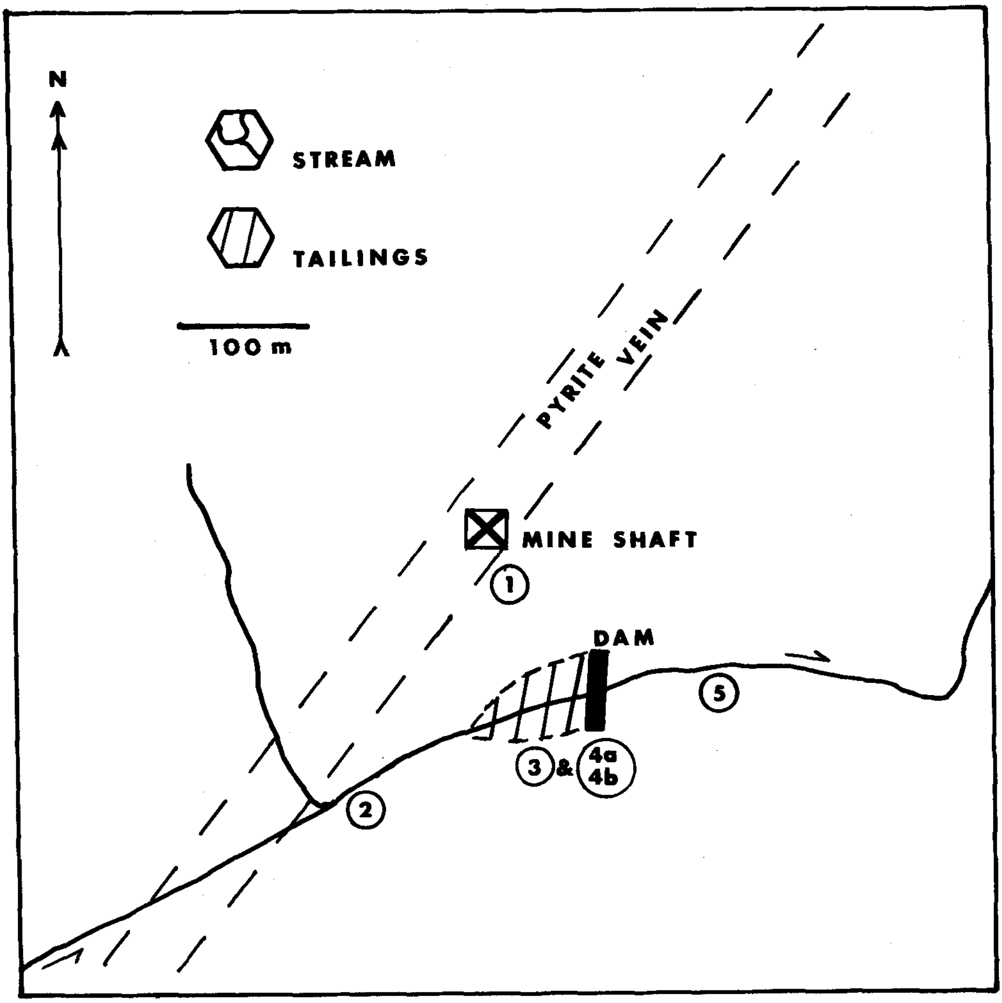

FIGURE 1. Index Map of Sample Locations, The Little Bob Mine, and the Sulfide Vein in Paulding County, Georgia.

of active mining between the middle 1800's and the early 1900's, water was pumped to the mine and mill from upstream and returned to the stream below the mill. As a result, the stream valley at that point became a tailings pond. It is from this stream, the tailings pond, and the sulfide ore at the mine that samples were taken for the present study.

Sampling and Analytical Procedures

The sampling scheme was designed to allow determination of the chemistry of unaffected stream waters, the relationships of water and sediment in the tailings pond, and the chemistry of the effluent below the pond (Fig. 1). Chemistry of the sulfide ore was determined in order to compare this metal source to the contents of the fluvial system.

Water samples were taken from above the tailings pond in the free flowing stream channel (#2), from semi-static water pools in the tailings pond (#3), and from free flowing water below the pond (#5) A sample was also taken from the sediment directly below the water sample in the tailings pond (#4A, #4B). A solid piece of pyrite ore (#1) was retrieved from the vein adjacent to the mine shaft. Sample sites are displayed in Figure 1.

The water samples were filtered through a .45 μm diameter mesh in the field. After suspended particulates were removed, the 1 pint samples were acidified with 5 drops of 2.0 N HCl. Acidification prevents plating of metals onto the sides of the sample container prior to analyses. All water and sediment samples were refrigerated while awaiting analyses.

PH values were measured and recorded at each of the sampling sites. A portable Orion 401 meter was used for these measurements.

Sediment samples (#4A and #4B) were taken from an accumulation of fine material in the pond. Sediment retrieval was accomplished by randomly selecting a grab sample in this area. The sediment was air dried, homogenized, and split into four subsamples. Two subsamples were selected from the set for duplicate analyses. The selected subsets were divided into two size ranges by sieving and centrifugation. The ranges were 105 to 5 μm (sand and silt) and 5 to .2 μm (fine silt and clay). See SCHRADER et al. (1977b) for methodology of separations.

Chemical analyses were performed on all of the samples by thermal neutron activation. A 5 percent replicate precision was obtained on the samples and a set of standard reagents. No interferences were observed; thus, no extractions were necessitated.

Results and Discussion

Table 1 represents the average metal concentrations obtained by neutron activation of the individual samples of this

TABLE 1.

Chemical Analyses in ppm (by Neutron Activation) of Water and Solid Samples from the "Little Bob" Mine Area, Georgia .

	Samples		
	1--Ore (pyrite)	2--H_2O Stream above mine)	3--H_2O (tailing pond)
Fe	3.5×10^5	0.05	1.20
Mn	470	0.02	1.18
Cd	0.06	0.004	0.08
Zn	90	0.03	1.06
Cu	190	0.008	0.08
Ni	0.01	---	0.09
Pb	230	0.009	0.10

	Samples		
	4A--Silt (pond-105 - 5 μ)	4B--Mud (pond-5 - 0.2 μ)	5--H_2O(below pond)
Fe	3.7×10^5	8.2×10^6	3.22
Mn	4.6×10^2	1.6×10^3	1.17
Cd	1.8	5.2	0.09
Zn	60	82	1.06
Cu	16	42	0.10
Ni	40	109	0.07
Pb	60	72	0.12

study. The water taken at site #2 is markedly less concentrated in all metals than the water from sites #3 and #4. The concentration of these metals at the latter two sites is obviously due to reaction of the stream waters with the tailings from the mining operations. The finer grained sediments (5 - 2 μ) are much more concentrated in the metals than either the sand-silt fraction or pyrite ore. Similar trace metal affinities for fine grained sediment was observed in North Carolina rivers by SMOCK et al. (1971).

Illite, kaolinite and montmorillonite comprise the finest grained, clay fraction of the sediment. The cation sorption capacity of these clay minerals probably accounts for the elevated metal concentrations (JACKSON, 1958; SCHRADER et al., 1977b). There is no available structural site in the silicate lattices of these clays in which significant quantities of the trace metals might become incorporated.

Amorphous Fe-Mn oxides are abundant in the pond, both suspended in the water and coating the underlying sediment. These oxyhydroxides are effective concentrators of trace metals (POSSELT et al., 1968; SMOCK et al., 1971; APPALACHIAN REGIONAL COMMISSION, 1969; SCHRADER et al., 1977b, SCHRADER, 1977a). Thus, the coatings of this material on the silt and sand sized sediment (105 - 5 μ m) are possible sites for heavy metal accumulation. The clay sized sediment has no such coating.

The effectiveness of this concentrating mechanism in the studied stream system is attested to by the heavy metals associated with the 105 - 5 μm sediment fraction (Table 1). Since mineralogically this fraction of the sample is mostly calcite and quartz, no ion sorption or ion exchange mechanism can be proposed for the heavy metal capture. Samples of these coarser grains were acid washed to remove the oxides and analyzed. Virtually no heavy metals were then observed. Thus, the concentration of heavy metals in the coarser sediments is probably a function of the amorphous coating.

The pH values at each sampling site are reported in Table 2.

TABLE 2

Recorded pH Values at Each Sampling Site

	Sample Number					
	1	2	3	4A*	4B*	5
pH	---	6.5	5.2	2.0	2.0	5.1

*pH taken by inserting probe into undisturbed sediment.

The pH values of the water, 5.1 to 6.2, are consistent with surrounding streams and many other streams in the Southeast which drain sulfide bearing areas (SCHRADER and RULE, 1975).

However, the lower pH values within the sediment reflect the breakdown of pyrite (FeS_2) and $FeSO_4$ by the coupled reactions:

$$2FeS_2 + 2H_2O + 7O_2 \rightleftarrows 2(FeSO_4) + 2(H_2SO_4)$$

$$2(FeSO_4) + 3H_2O \rightleftarrows Fe(OH)_3 + H_2SO_4 + H^+$$

(FURBISH and SCHRADER, 1976).

Crystalline and amorphous Fe-oxides become unstable at pH values below approximately 2.5 (WHITTEMORE and LANGMUIR, 1975; BROWN, 1971; FURBISH, 1963). Consequently, a low pH below the sediment-water interface allows the dissolution of heavy metal-laden oxyhydroxides and liberates these metals to the aqueous media. However, the higher pH above the interface allows precipitation of these same compounds if dissolved, ionic concentrations permit. Thus, a constant cycle of precipitation of hydrous oxides at the sediment surface and subsequent dissolution (after burial) of these oxides below the interface is the proposed semi-static equilibria model. Since the water is not static, metals are continuously carried away from the site of precipitation and dissolution. These metals, removed from the chemical cycling, are transported by the waters downstream and out of the tailings pond. In Table 1 the similarity of the water in the tailings pond and downstream can be observed. The main difference between the two samples is the elevated Fe content in the sample below the pond (#5). These higher concentrations can be understood since most of the filtered particulates below the pond are Fe-rich hydrous oxides transported, as are the dissolved species, away from the ponded areas.

The analyzed ore samples consisted of the sulfide, pyrite, with minor amounts of other sulfides, chalcopyrite, sphalerite and galena. Quartz and calcite were abundant with minor hornblende, garnet, and magnetite. No distinct cadmium or nickel bearing minerals were observed. The bulk composition of the ore, as noted above, can change on strike and at depth (SHEARER and HALL, 1918), so the sulfide ore acts simply as a metallic ion source rather than donating a specific amount of heavy metals to the system. Any ground water discharge from such a sulfide body would reflect the gross composition of the ore body but would change as the sulfide composition changed, all other factors equal.

The bulk metallic ion content of the unexposed sulfide ore is, within limits, reflected by a water sample (No. 2, Table 1) taken from the stream above the tailing pond. It in no way reflects the results of mining, but rather, of a normal chemical anomaly of ground water from an area containing sulfides.

Table 3 lists the E. P. A. recommended maximum levels of certain toxic metals for public water sources. The water samples obtained upstream (No. 2, Table 1) contains no metal in excess of the suggested maximum level for human use; however, both in the tailings pond and downstream Fe, Mn, Cd, and Pb levels all exceed the safety standards for human consumption. We feel that the semi-static, ionic cycling model proposed above accounts for the elevated metal concentrations in this discharge. Since small farms and rural communities use this stream and others like it for water supplies, a definite health hazard is suggested. The levels suggested by the E. P. A. for human use are much higher than that which will affect aquatic life (floral and faunal). Thus, the elevated metal contents as dissolved species and suspended, particulate oxyhydroxides may significantly alter the ecology of the stream system. Since the contamination of these fluvial systems depends strongly on the pH at critical points in the chemical cycle, possible external controls could be easily implemented. Buffering of the system to above 2.5 would prevent dissolution of the Fe-Mn oxyhydroxides. The heavy metals then would be concentrated into filterable particulates that might be mechanically removed from settling ponds.

TABLE 3.

E. P. A. Suggested Metal Levels (in ppm) for Public Water Sources (Dr. R. Horton, Environmental Protection Agency, Personal Communication).

	Fe	Mn	Cd	Zn	Cu	Ni	Pb
ppm	.3	.05	.01	5.0	1.0	---	.05

At the present time, however, these small stream systems are rarely or never monitored by state, federal, or private organizations; thus, the potential human health and natural ecological hazards are virtually unknown and untested.

Conclusions

Small streams in the southeastern U. S. can be significantly contaminated by abandoned mining operations. Heavy metal contamination of such stream systems may be a function of the cyclic precipitation and dissolution of Fe-Mn oxyhydroxides. Since these mines are no longer operative and many of the original companies defunct, no private company is willing to regulate the rates of metal accumulation in stream waters. The unregulated waters pose a hazard for rural communities and natural ecological systems within the drainage basins.

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