SULFUR MINERALIZATION IN A WETLAND CONSTRUCTED TO TREAT ACID MINE DRAINAGE

Leslie S. Laudon

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Golden, Colorado

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Signed: Leslie A. Laudon

Leslie S. Laudon

Approved: Thomas R. Wildeman

Thomas R. Wildeman
Advisor

Golden, Colorado

Date: Jan. 9, 1989

S.R. Daniel, Head
Department of Chemistry and
Geochemistry

ABSTRACT

The various inorganic and organic forms of sulfur in a constructed wetland receiving acid mine drainage were studied over a ten month period. Samples collected after the system had been in operation for four months and samples of the original substrates were analyzed for total sulfur, acid volatile plus elemental sulfur, sulfate sulfur, disulfides and organic sulfur. Elemental sulfur and acid volatile could not be analyzed separately because the samples were air dried prior to analysis. Cores taken after ten months of operation were analyzed for all of the forms above including separate analyses for acid volatile and elemental sulfur. Results of the study showed no seasonal variations in the amounts of organic sulfur or disulfides. Acid volatile plus elemental sulfur showed a dramatic increase in the section of the wetland containing mushroom compost as the organic substrate. The section filled with manure, peat and decomposed wood products did not exhibit a similar increase. The large inputs of sulfate and ferrous iron from the mine drainage combined with the rich organic substrate encourages dissimilatory sulfate reduction and the permanently saturated conditions inhibit reoxidation of the sulfides once they form.

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Acknowledgments

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Introduction

The use of wetlands to treat acid mine drainage has received attention recently as a low cost alternative to conventional chemical treatment. The mechanisms controlling metal retention and pH adjustment operating in these systems have not been adequately identified or quantified. Emphasis has been placed on adsorption and oxidation as controlling processes whereas precipitation of metals in the reduced form has largely been ignored. A review of the chemistry of metal mine drainage formation and treatment by wetlands can be found in Wildeman and Laudon, 1988 (1). Sulfate reduction in most natural wetlands is limited by available sulfate (2,3), however, a wetland receiving acid mine drainage would have much higher than normal sulfate inputs. The other factors which can limit sulfate reduction and sulfide formation are useable organic matter and a reactive iron source (2,3). The wetland constructed at the Big Five tunnel, Idaho Springs, Colorado is receiving water with composition shown in Table 1. The substrates are rich in organic matter and the mine drainage is a source of iron and sulfate; dissimilatory sulfate reduction and precipitation of metals as sulfides should be an important mechanism in this system. To test this, cores were taken

Table 1. Big Five tunnel, Idaho Springs, Colorado

Water Characteristics

Subs.	Conc.	Subs.	Conc.
SiO_2	40 mg/L	Zn	10 mg/L
Al	18	Cd	0.03
Fe	50	Pb	0.01
Mg	150	Na	46
Ca	370	K	9.2
Mn	32	As	0.02
Cu	1.6	$SO_4^{=}$	2100

pH = 2.6 Cond. at 25°C = 2700

Temp = 13°C Flow = 0.045 CFS

after the system had been in operation for ten months and analyzed for total sulfur, acid volatile sulfides (AVS), acetone soluble sulfur (S°), chromium reducible sulfur, and organic sulfur. Samples collected from the original substrates and from the system after three months of operation were analyzed according to the same techniques to see if there were seasonal variations in the various sulfur fractions.

Site Description

The pilot system constructed at the Big Five tunnel, Idaho Springs, Colorado is divided into three 10 ft. x 20 ft. sections filled with A) mushroom compost, B) manure, peat, and decomposed wood products, and C) five inches of limestone gravel covered with the same organic material of section B. Plants from wetlands at similar elevation were transplanted into each section. Six wells were installed in each section for sampling water from different depths (Figure 1). Mine drainage from the Big Five tunnel was diverted into the system in October, 1987. The water inlet system was designed to disperse the water throughout the entire cross-section of each cell at a rate of one gallon per minute for each 200 ft^2 section. Howard et al. (4)

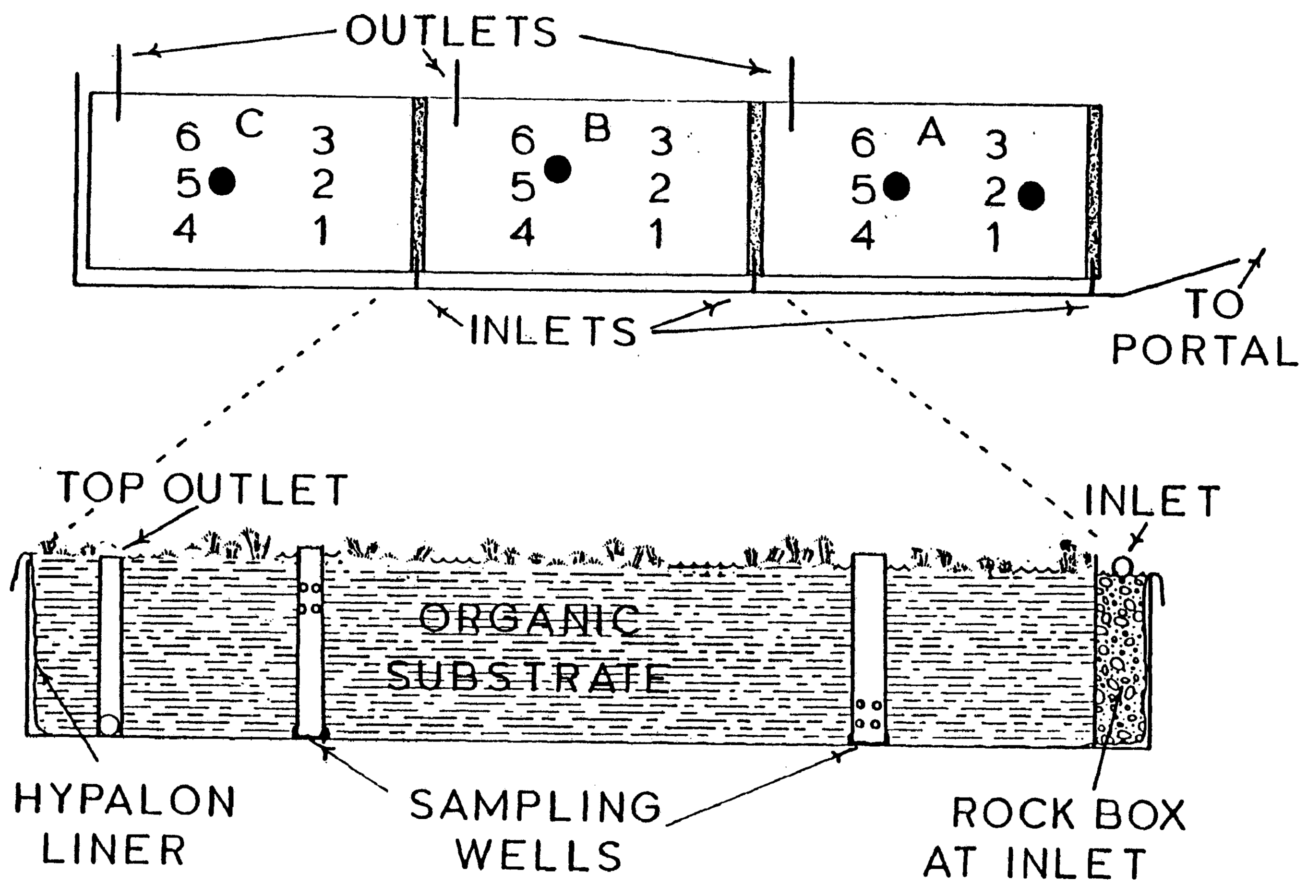

Figure 1. Schematic diagram of the Wetland System at the Big Five tunnel showing location of wells and samples.

contains a detailed description of the design and construction of the system.

Sulfur Geochemistry

Sulfur in soils, lake sediments, marine sediments and salt marshes occurs in many different organic and inorganic forms all intimately connected by microbial processes. The organic sulfur in soils and sediments is generally divided into two groups: carbon bonded sulfur and the organic esters of sulfuric acid or ester sulfate (5). C-bonded sulfur is produced by nearly all plants and microbes by assimilating sulfate, reducing it via sulfite to sulfide and incorporating it into the amino acids cysteine and methionine (5,6,7). The degradation products of C-bonded sulfur in soils are compounds such as H_2S, CH_3SH and $(CH_3)_2S$ which are gases and can escape from the soil or be oxidized back to SO_4^{2-}(6). C-bonded sulfur can also form by reaction of H_2S generated in the soil with organic matter (8,9,10, 11). Ester sulfate formation does not involve reduction of sulfate and is inhibited by its presence (12). Ester sulfate formation is offset by microbial production of sulfatase enzymes which hydrolyze SO_4^{2-} off of ester sulfates (10). This form of sulfur usually constitutes less than 10% of the organic sulfur in a soil or sediment (13).

The inorganic forms of sulfur are numerous due to the many possible oxidation states of the element. Sulfate is reduced and released to the environment as H_2S by dissimilatory sulfate reducing bacteria. The sulfate reduction reaction can be written as:

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$$

The generated H_2S can escape from the soil as a gas or react with metals precipitating metal sulfides. It also can be oxidized to a number of stable species such as elemental sulfur, sulfate and polythionate or unstable species such as sulfite and thiosulfate. Figure 2 shows the microbial sulfur cycle as depicted by Zinder and Brock (7).

The mineralization of sulfur is generally considered in terms of formation of iron minerals because iron is generally more available in these environments than other metals. Pyrite is the thermodynamically stable phase in reducing sediments but other iron sulfides can form. The following is a list of possible minerals taken from Tuttle (9):

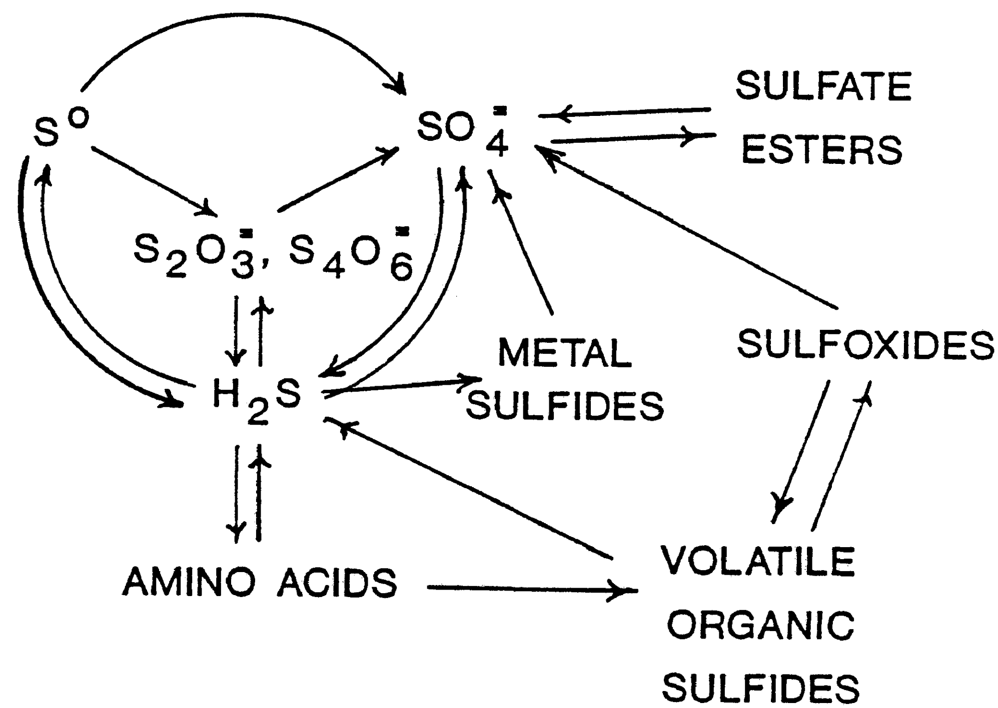

Figure 2. Microbial sulfur cycle

pyrite	FeS_2 (cubic)
*marcasite	FeS_2 (orthorhombic)
pyrrhotite	$Fe_{(1-x)}S$ ($0 \leq x \leq 0.125$)
*mackinawite	$FeS_{0.94}$
*greigite	Fe_3S_4 (cubic)
*smythite	Fe_3S_4 (hexagonal)

* metastable phases

Pyrite formation occurs according to two distinct mechanisms: indirectly via an acid volatile intermediate which subsequently reacts with elemental sulfur or polysulfides to form pyrite or directly from precipitation of ions in solution. The reactions for the two mechanisms are (2,14):

Indirectly through monosulfide intermediate:

$$Fe^{2+} + H_2S \longrightarrow FeS + 2H^+$$

$$FeS + S^\circ \longrightarrow FeS_2$$

Indirectly through greigite intermediate:

$$3FeS + S^\circ \longrightarrow Fe_3S_4$$

$$Fe_3S_4 + 2S^\circ \longrightarrow 3\ FeS_2$$

Directly:

$$Fe^{2+} + S^\circ + H_2S \longrightarrow FeS_2 + 2H^+$$

Directly through polysulfides:

$$Fe^{2+} + S_5S^{2-} + HS^- \longrightarrow FeS_2 + S_4S^{2-} + H^+$$

The direct precipitation mechanism is thought to be the cause of single crystal pyrite formation and requires that the solution be undersaturated with respect to acid volatile sulfides (low H_2S concentration). Single crystal pyrite also can form from reaction of mackinawite with elemental sulfur without going through a greigite intermediate. When a greigite intermediate is involved, the resulting pyrite exists in framboidal form (2).

Pyrite formation in most sediments is limited by the rate of sulfate reduction or iron availability. Sulfate reduction in turn is limited by the supply of sulfate or useable organic material (2,3). Sulfate reduction is generally limited by organic matter in marine sediments and by sulfate availability in freshwater systems. Since each of the above mechanisms require elemental sulfur or polysulfides, pyrite formation is also affected by the availability of a source of slightly oxidized sulfur. Because of this requirement a rapid pyrite mineralization zone is often seen at the oxic-anoxic interface or around oxidizing and reducing microenvironments associated with roots where sulfides generated by sulfate reduction become oxidized to elemental sulfur or polysulfides (15,16).

In freshwater wetlands and saltmarshes seasonal variations in sulfide formation and sulfate retention are often observed (10,14,17,18,19). A similar phenomenon is observed in laboratory studies measuring sulfate reduction rates (17,18,20,21). As sulfate becomes a limiting reactant or as redox conditions change, sulfides oxidize completely and become a source of sulfate. Sulfides are viewed as the short term end products of sulfate reduction because with time they will become incorporated into the organic sulfur fraction when the source of sulfate is eliminated and sulfides are oxidized to provide a source of sulfate (8,10,17,18,19,20). If reducing conditions and a source of sulfate are maintained iron monosulfides and pyrite are the end products of sulfate reduction (15,17,21,22).

Based on the above cycles, the following seasonal variations in the sulfide content of saltmarsh sediments are interpreted by Cutter and Velinsky (14):

Spring to early summer: photosynthesis injects O_2 into the upper 15 cm of sediment which oxidizes Fe sulfides and precipitates Fe oxides and S°.

Autumn: 0_2 infusion slows and SO_4^{2-} reduction predominantes, Fe oxides and S° are reduced and reprecipitated as Fe sulfides.

Winter: oxidation and reduction rates slow but Fe sulfides continue to precipitate due to upward diffusion of porewater H_2S and Fe(II).

Wieder et al. (10) observed that Big Run Bog, West Virginia was a source of SO_4^{2-} to receiving streams during periods of low flow and a sink for SO_4^{2-} during high flow periods corresponding to the water saturation status of the wetland. Water levels vary seasonally in most freshwater wetlands and the redox front moves up and down according to the saturation level. In addition, Sphagnum has been shown to inhibit SO_4^{2-} reduction due to the root mass creating a large oxidizing zone in the soil (21).

Conditions at the Big Five tunnel constructed wetland favor the formation and retention of sulfides. Water levels and chemistries do not fluctuate throughout the year (23). A deep reducing zone was maintained during the study. The supply of SO_4^{2-} and reactive iron is abundant (Table 1) as is the supply of organic matter. The quality of the organic matter as a source of nitrogen and phosphorus for the plants and bacteria is assumed to be adequate.

Methods

The extraction sequence for the various forms of sulfur determined in this study is shown in Figure 3. The scheme is modified from Tuttle et al. (24), and Wieder et al. (25). A detailed description of the procedures is provided in Appendix A .

Total sulfur: Total sulfur was determined on a one gram split of the dried and lightly ground sample according to ASTM method D-3177 (26). The sample was fused with four times its weight Eschka mixture, the liberated sulfur is precipitated as $BaSO_4$ and determined gravimetrically.

Acid volatile sulfur (AVS): Samples were placed in a glove bag filled with N_2 and then transferred into the reaction flask of a Johnson-Nishita distillation apparatus (27). The apparatus was connected, purged with N_2 and 80 ml of de-aerated (bubbled with N_2 for 5 minutes) 6N HCL added to the reaction flask. The H_2S evolved from the AVS was passed through a buffer solution (pH 4.0) and collected as Ag_2S in 0.1M $AgNO_3$.

H_2S: H_2S was only present in one sample (#1A2) and was collected by bubbling N_2 through the sample and collecting the H_2S as Ag_2S. H_2S was titrated iodometrically (28) in

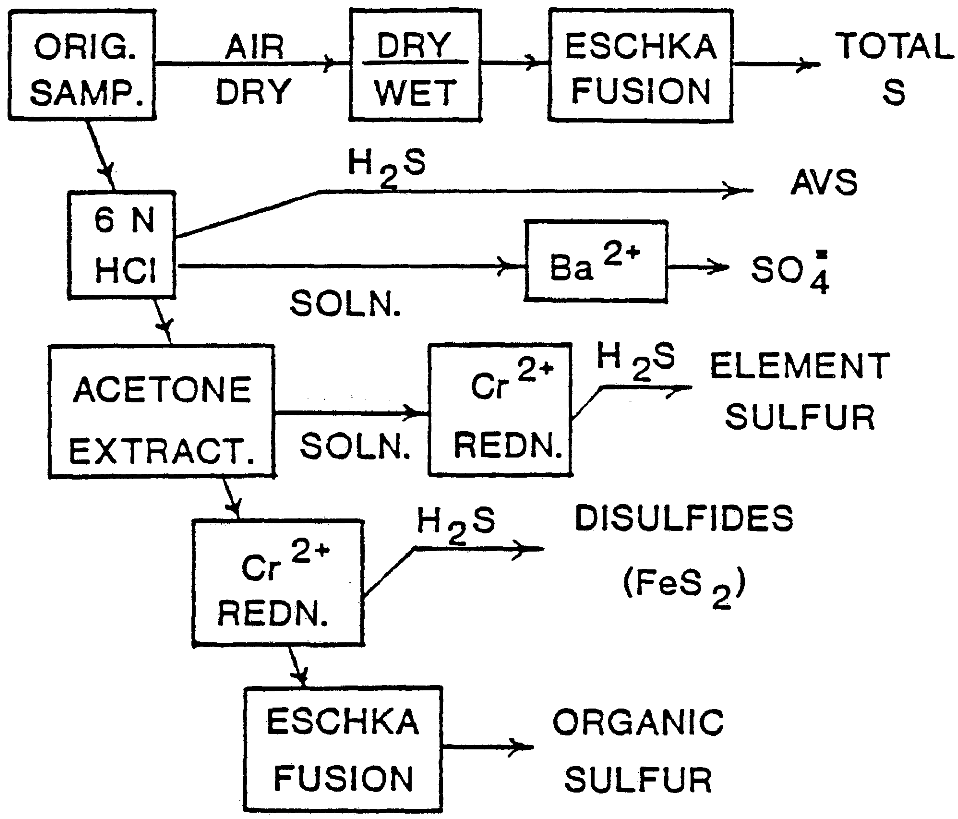

Figure 3. Extraction sequence

well water samples to verify its presence prior to soil analyses.

Acetone soluble sulfur (S°): The dried residue from the AVS determination was extracted overnight (16 hr) on a rotary shaker in 100 ml analytical grade acetone. The sample was filtered through a 0.45u Nucleopore polycarbonate filter. The filtrate was transferred to the reaction flask, the apparatus connected, purged with N_2, and 20 ml concentrated HCl and 50 ml of Cr^{2+} solution (1 M $CrCl_3 \cdot 6H_2O$ in 0.1N HCl passed through a Jones reductor to reduce Cr^{3+} to Cr^{2+} (29)) added through the dropping funnel. The solution was boiled and the evolved H_2S collected as Ag_2S.

Sulfate sulfur: 10 ml of 100g/L $BaCl_2$ was added to the acid filtrate from the AVS step to precipitate the SO_4^{2-} as $BaSO_4$. The precipitate was heated with doubly distilled HNO_3 to remove contaminants, filtered, dried and weighed.

Pyritic sulfur: The residue from the acetone soluble fraction was transferred to the distillation apparatus and treated the same way the acetone extraction.

Organic sulfur: The residue from the pyritic fraction was subjected to an Eschka fusion in the same manner as with total sulfur.

Cores were taken from the back part of each section near well 5 (see Figure 1) and from the front of section A

July 21 and 25, 1988 using a WILDCO #2420 corer with disposable tubes. The cores were immediately transported back to the lab (30 minutes) in an upright position to maintain water covering the core. Due to the unconsolidated nature of the sediments, the cores settled within minutes of sampling until only six to eight inches of core remained covered with approximately 12 to 18 inches of water. The water was syphoned off to within two inches of sediment and the cores extruded in a glove bag filled with N_2. Since it was not possible to obtain samples by depth within the core, a composite sample was analyzed. The top and bottom inch of each core was discarded and the remainder of the core mixed. One split was transferred to the distillation flask for AVS + H_2S analysis and the other split was weighed to get a moisture determination.

Sulfur analyses were also performed on the original substrate materials as well as samples collected in January, 1988 from the top six inches of substrate near wells A5 and B5. Duplicates were run on samples of the cores taken near wells A5 and B5. Because all of these samples were air dried and acid volatile sulfides oxidize quickly when exposed to air, the AVS fraction could not be recovered separately. In these cases AVS is reported as AVS + S°.

Results

Descriptions of sample locations are provided in Table 2 and results of the soil sulfur analyses are provided in Table 3. H_2S water analyses results are presented in Table 4. Wieder et al. (25) verified the analysis scheme by testing recoveries of certified standards by each of the methods used. The results of their tests are summarized in Table 5. Pyrite recoveries were 93% but the minimum guaranteed purity of the standard was only 85% FeS_2. The sulfur in these experiments was titrated iodometrically rather than recovered as Ag_2S.

Tuttle et al. (24) developed a similar procedure and verified the recoveries using Mossbauer spectroscopy and chemical determinations on iron. In addition, particle size of the oil shale samples used by Tuttle was found to affect recovery efficiencies. Also tested was the effectiveness of $AgNO_3$ as a trapping agent for H_2S. Yields were 97.8-100.7% for pure pyrite standards.

Table 6 shows the results of duplicate and triplicate analyses and the calculated relative percent differences (RPD) and relative standard deviations (RSD). Values for RPD are quite high ranging from 5-66%. This is often due to values being low, so small differences cause large differences in RPD. Also Tuttle et al. (24) showed that

Table 2. Description of Sample Locations

Abbreviation	Description
CS	Compost substrate: initial material used in cell A.
TA5*	Top 6" of substrate collected near well A5
#5(A5)*	Second core collected; near well A5
#1(A2)*	First core collected; near well A2
P/M/WP	Peat, manure, wood products: initial material in cells B and C
TB5*	Top 6" of substrate collected near well B5
B(B5)*	Core collected in cell B near well B5
C(C5)*	Core collected in cell C near well C5

* See black dots of Figure 1 for sample location.

Table 3. Forms of S in substrate samples and NBS Coal 1635. All values in %S.

Sample	Date Collected	S_{TOT}	S_{AVS}	$S_{S°}$	S_{FeS_2}	S_{ORG}	S_{SO_4}
TAS	1/88	0.83		0.45*	0.05	0.21	0.17
#2(A5)	7/88	1.39#	0.83	0.16	0.09+	0.22+	0.08+
#1(A2)	7/88	1.61	0.31	0.49	0.24	0.35	0.07
P/M/WP	8/87	0.61	<.02	0.05	0.34	0.14	0.16
TB5	1/88	0.59	--	0.09*	0.25	0.15	0.15
B(B5)	7/88	0.67#	.08	0.09	0.42+	0.20	0.02
C(C5)	7/88	0.73+	0.19	0.13	0.40	0.19	0.07
NBS Coal 1635		0.32	<0.03	0.02	<0.02	0.35	<0.02

* AVS + S°

\# average of 3 values

\+ average of 2 values

S_{TOT} = Total Sulfur

S_{AVS} = Acid volatile sulfur

$S_{S°}$ = Acetone soluble sulfur

S_{FeS_2} = Disulfides

S_{ORG} = Organic sulfur

S_{SO_4} = SO_4^{2-} sulfur

Table 4. Results of H_2S titration on well water samples

Well	Screened Interval	mg/L S as H_2S
A3	1'	20
A4	1'	< 1
A5	2'	79
B4	1'	49
C5	3'	9

Table 5. Percent recoveries of S additions (from Wieder et al.)

Procedure	Average % recovery of S added as							
	Na_2SO_4	$Na_2S_2O_3$	$Na_2S_2O_4$	S°	FeS_2	FeS	PNPS*	methionine
AVS	1.1	38.2	90.0	1.4	5.4	92.2	0	0.2
Cr^{2+} reducible	3.31	99.6	93.4	94.4	92.8	95.4	0	2.5
Acetone soluble	3.0	2.5	1.6	97.6	2.4	3.4	0	0

* PNPS =paranitrophenylsulfate

Table 6. Result of replicate S analyses on Big 5 substrates

Sample	Procedure*	Values	RPD+	RSD#
#2(A5)	S_{TOT}	1.48		
		1.35		
		1.35		7.5%
B(B5)	S_{TOT}	0.78		
		0.65		
		0.59		9.7%
C(C5)	S_{TOT}	0.74		
		0.71	4	
#2(A5)	AVS+S°	0.99		
		1.21	20	
B(B5)	AVS+S°	0.23		
		0.17	30	
#2(A5)	FeS_2	0.12		
		0.06	66	
B(B5)	FeS_2	0.31		
		0.53	52	
#2(A5)	S_{ORG}	0.16		
		0.17	4	
B(B5)	S_{ORG}	0.19		
		0.20	5	
#2(A5)	S_{SO_4}	0.07		
		0.09	25	

* Detection limits for these procedures were determined by Tuttle (9) to be 0.01 wt. % S for a 5 gram sample

+ $RPD = \frac{(C_1-C_2)\times 100\%}{(C_1+C_2)/2}$ C_1 = larger of the 2 observed values

C_2 = smaller of the 2 observed values

$RSD = (S/\bar{X})X100\%$ S = standard deviation

$\bar{X}$ = mean

grain size had an effect on sulfur recoveries in oil shale samples. The samples in the Big Five tunnel study were not ground.

Table 7 shows the calculated sum of sulfur fractions compared with the total sulfur as determined by the Eschka fusion. Agreement is generally within 20% except for low values and often the sum of individual fractions is higher than the total. This is probably due to the rigorous treatment of the samples in the separation scheme and the possibility that grain size has more effect on the Eschka determination. It was expected that the total of the individual forms would generally be less than the total analyses due to slight losses of Ag_2S in filtering and incomplete recovery from the distillation apparatus (sticking to tubes and bubbler tips).

The agreement of duplicate runs is considered to be good when accounting for the heterogeneity of the samples. In an attempt to overcome this problem, the first run on all cores used a much larger sample weight (20-30 g) compared to the second run on the air dried samples (5 g).

The possible presence of carbonates in the sample is another source of error in this method that would affect the analyses. In this case, loss of carbonates would occur during the AVS analysis enriching the sample in the

Table 7. Comparison of Total S analyses and sum of individual fractions

Sample	S_{TOT}	S_{Frac}
CS	0.15	0.30
TA5	0.83	0.88
#2(A5)	1.48	1.44
#3(A5)dup	1.35	1.53
#1(A2)	1.61	1.46
P/M/WP	0.61	0.69
TB5	0.59	0.64
B(B5)	0.78	0.74
B(B5)dup	0.65	0.92
C(C5)	0.74	0.98
Coal 1635	0.32	0.37

remaining sulfur forms. Carbonates would fizz or froth when the HCl was added and this was not observed in any of the analyses.

Discussion

The preliminary results from the H_2S titrations indicated sulfate reduction and H_2S generation was occurring in cell A and was most intense near well 5.

The compost substrate (CS) initially had a low total S content (0.15%) which was mainly organic S. The sample taken from cell A well 5 (TA5)in January after the mine drainage had been entering the system for three months had a higher total S content (0.83%) and essentially the same organic S content (0.21%) as the original material. The sulfur increase was in the form of AVS + S°. The pyritic and organic S did not change significantly. The core taken in the front of cell A close to where the mine drainage enters the system had a lower AVS content and higher S° and organic S than the core taken near the back of the cell (near well 5) close to the drain. The high organic S content may be due to the presence of algae in the sample.

Sulfur forms in cell B showed little change over the ten month period. Total S did not increase as in cell A. AVS + S° increased slightly but not nearly as dramatically as in the compost substrate. Results for the sulfur analyses in cells A and B are shown graphically in Figures 4 and 5. The results from the core taken from cell C were very similar to those from cell B.

Mushroom compost appears to be a better medium for the growth and activity of the sulfate reducing bacteria. Counts of the bacteria have consistently been higher in cell A than the other two cells (30). Cell A is also the only one converting sulfur to sulfides to any extent. The rapid increase in total S mainly as AVS and S° in cell A represent the existence of favorable conditions for the formation of pyrite. However, pyrite is not forming in the substrate.

The removal of metals in the system is not limited to iron. Figures 6 to 9 show the concentration of metals (Cu, Fe, Mn, and Zn,) in the output waters from each cell compared to the mine drainage for the ten months of operation. Appendix B contains the tabulated results of the output water analyses performed by the Environmental Protection Agency's Contract Laboratory Program. Cu is being effectively removed from cell A but not from cells B and C. However, Fe is being removed from the mine drainage in all the cells. Fe can be precipitated as an oxide or sulfide and can be seen precipitating as an oxide in all the cells. It is possible that the removal mechanism for Fe is

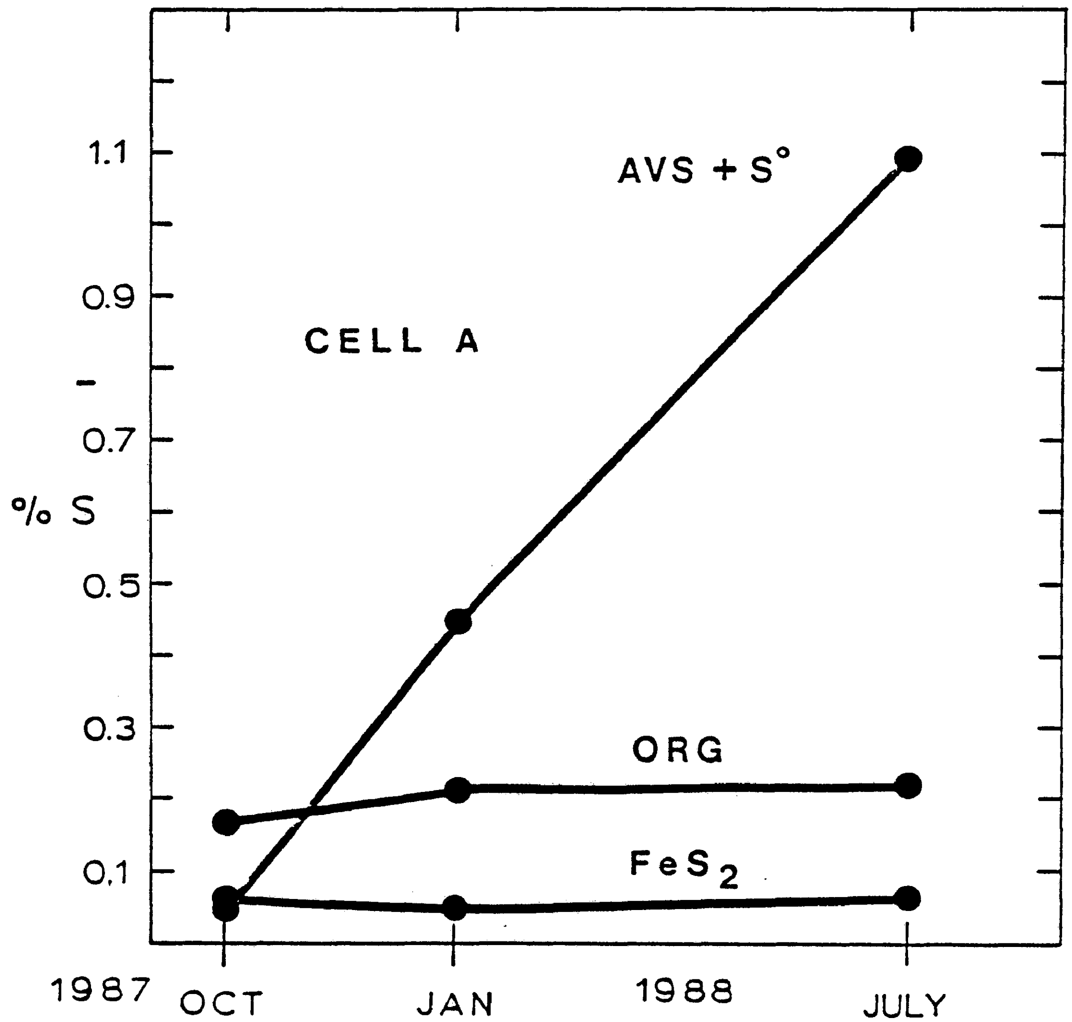

Figure 4. Changes in sulfur content of substrate in Cell A over 10 months of operation.

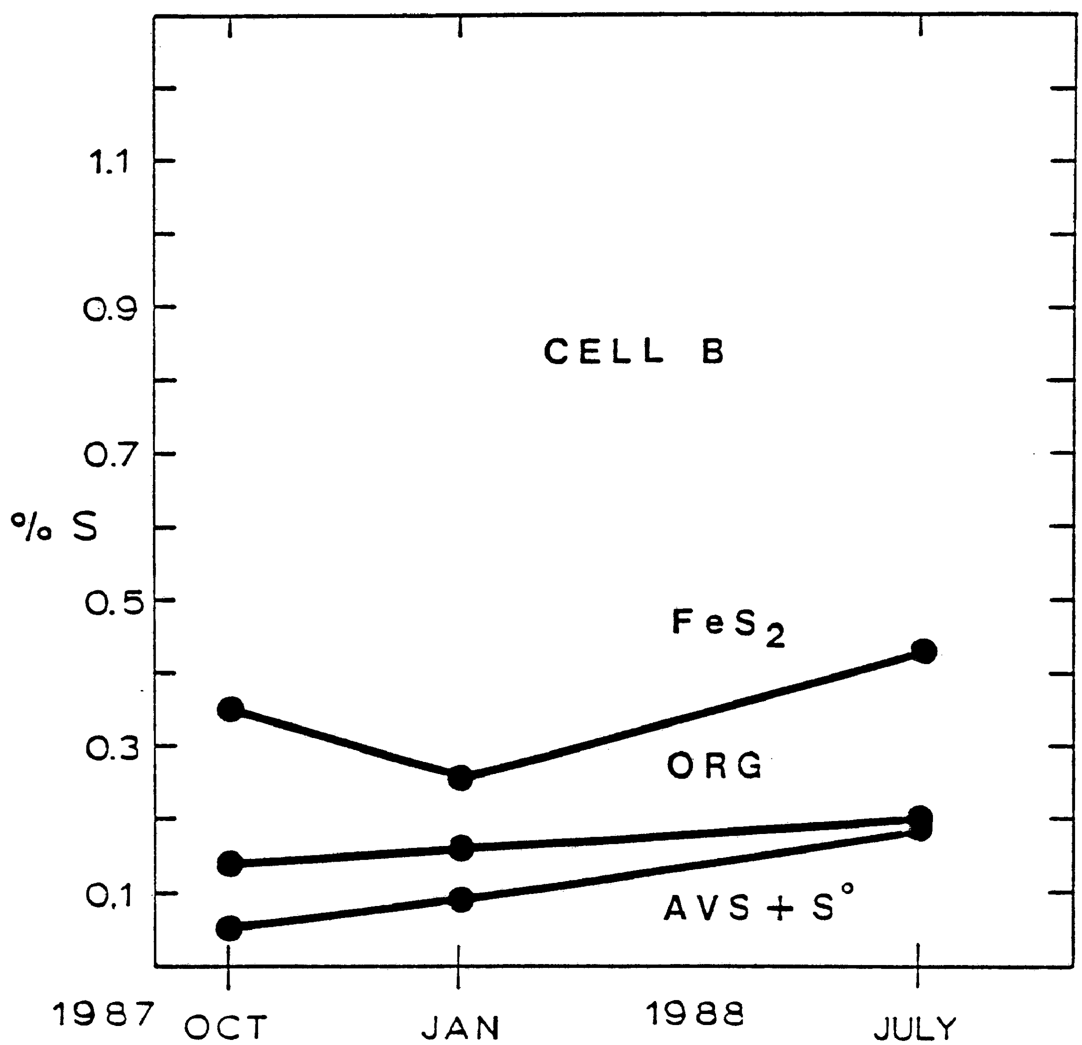

Figure 5. Changes in sulfur content of substrate in cell B over 10 months of operation.

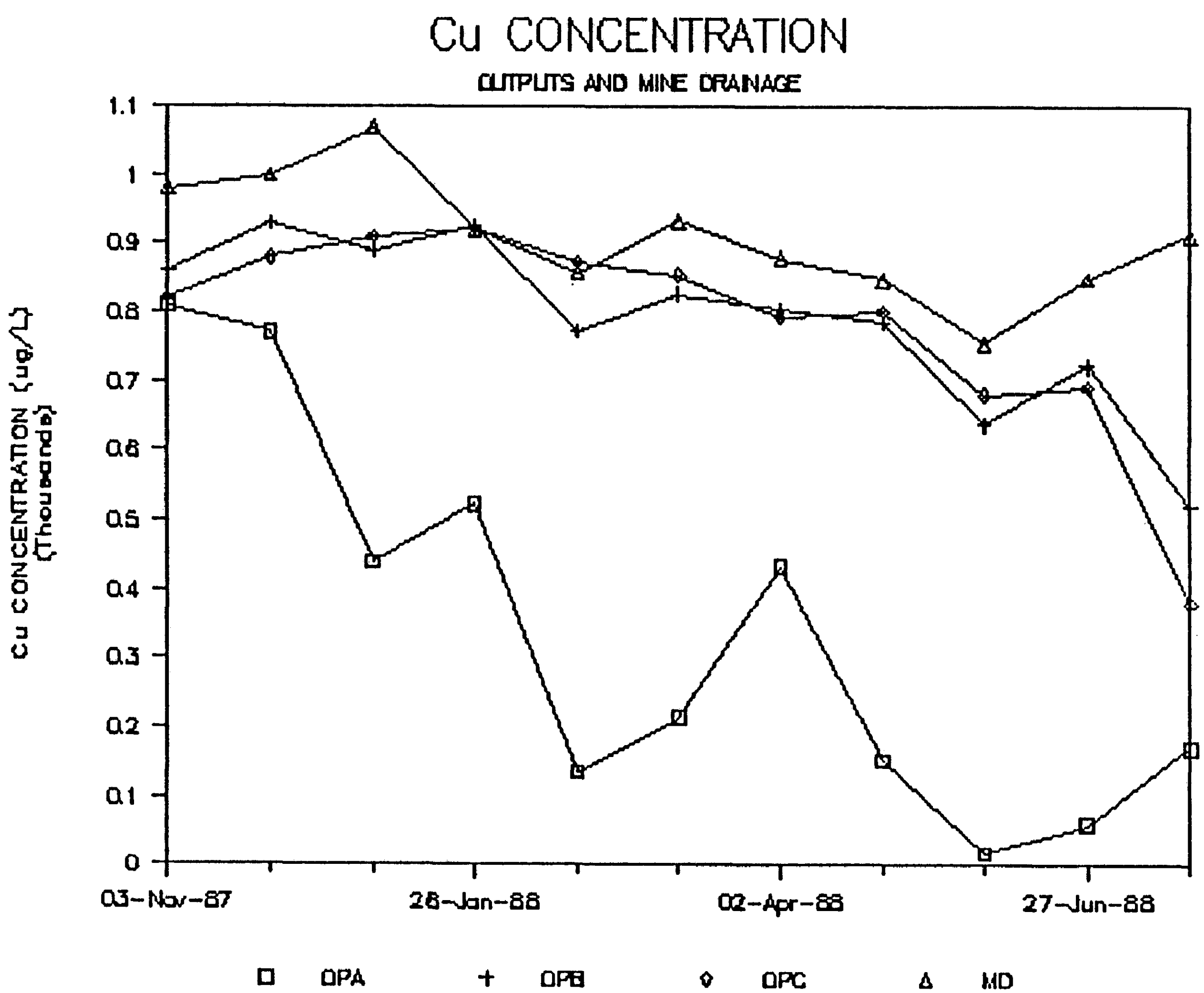

Figure 6. Cu content of output waters and mine drainage.

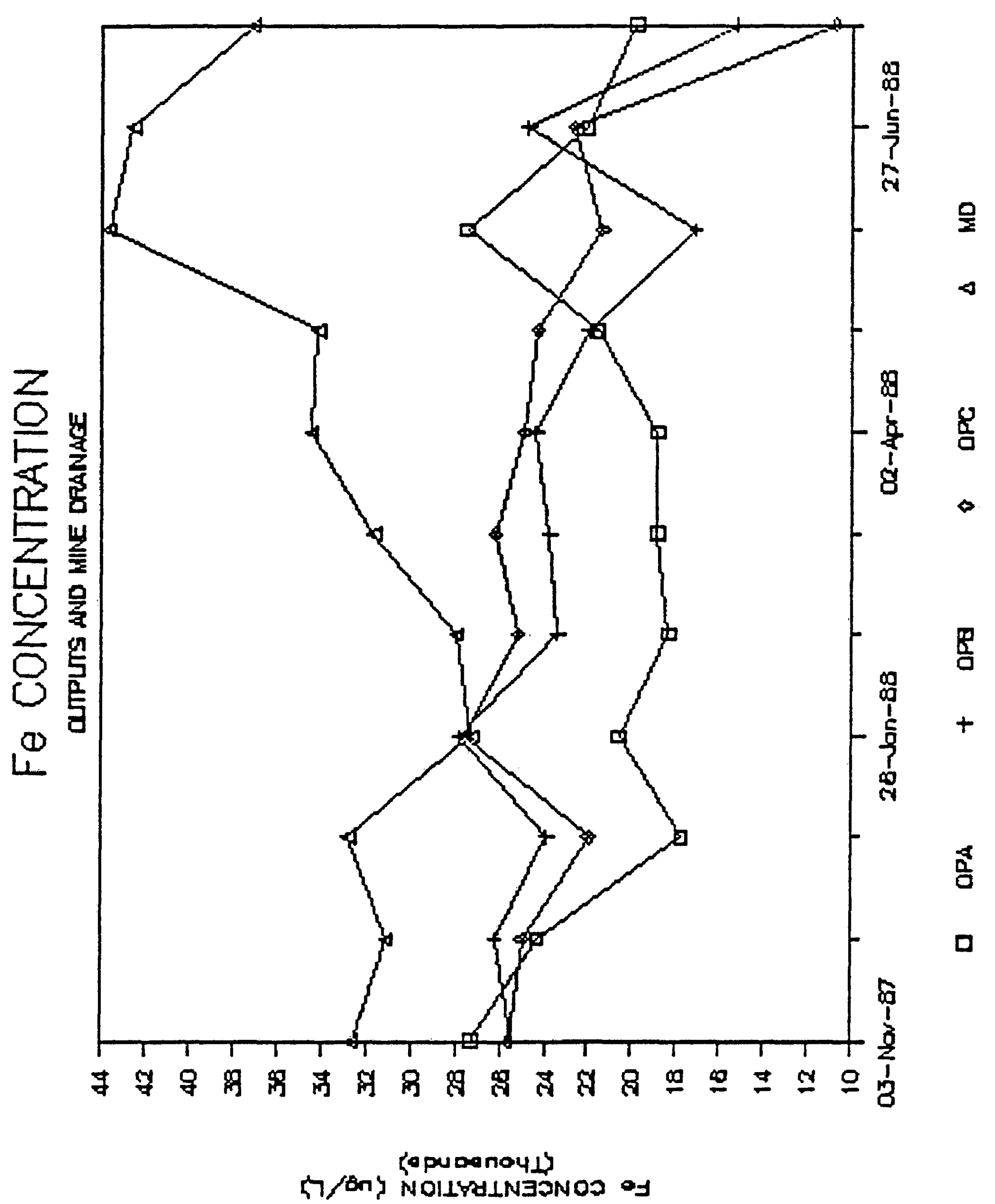

Figure 7. Fe content of output waters and mine drainage.

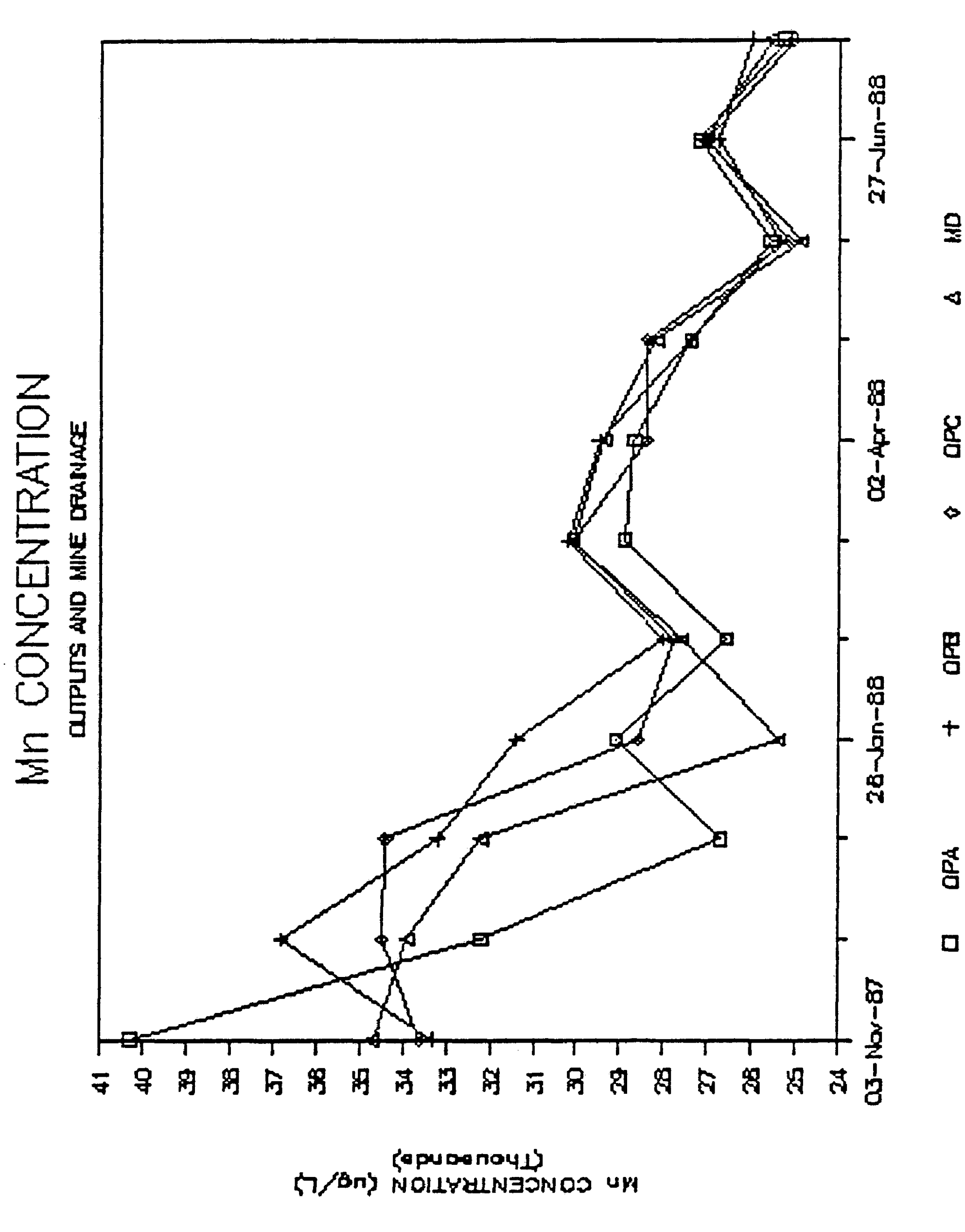

Figure 8. Mn content of output waters and mine drainage.

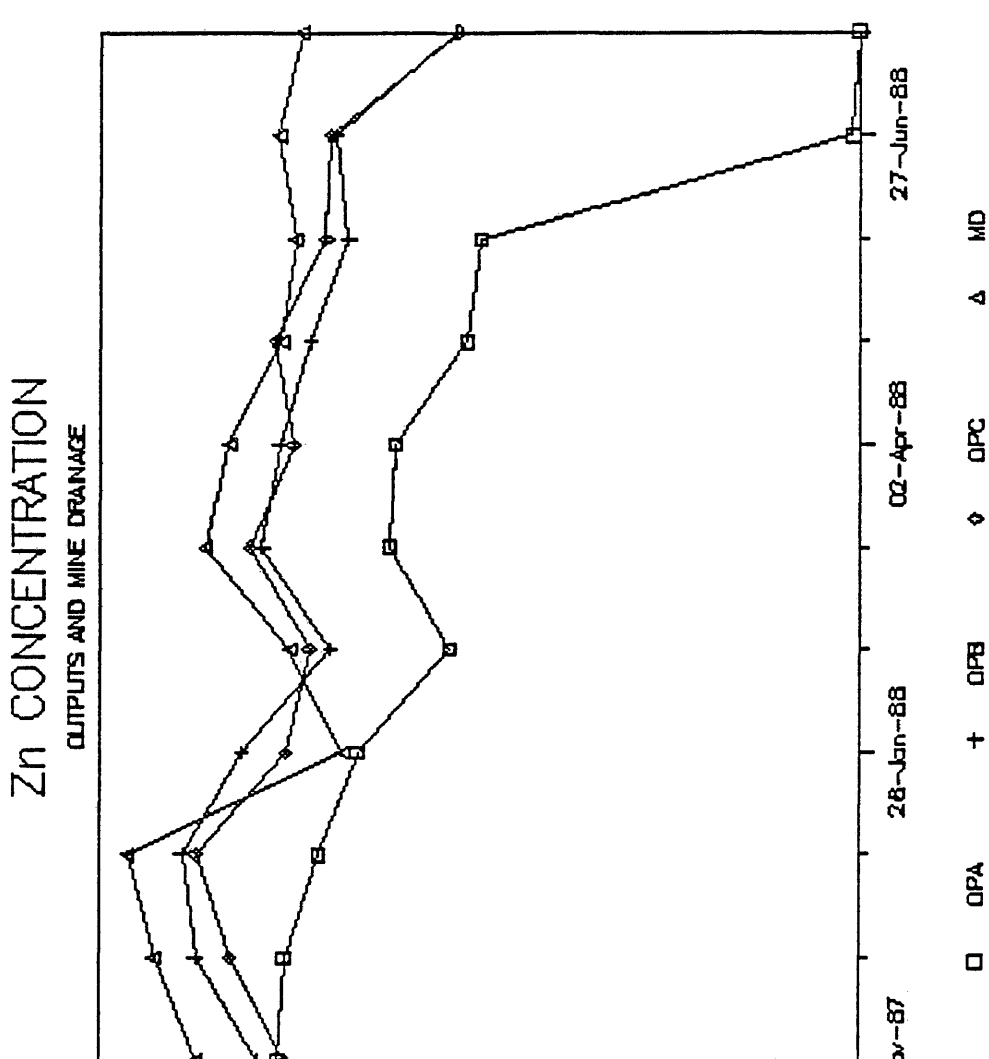

Figure 9. Zn content of output waters and mine drainage.

precipitation as an oxide and other metals are precipitating as sulfides. This would explain why pyrite is not forming in the system.

If the AVS forming is an Fe sulfide, the maintenance of reducing conditions could prevent the formation of S° or polysulfides and inhibit pyrite formation. The samples analyzed from the cores were composite samples so no depth relationship could be determined. It is possible that the S° that does form in the system is not being mixed and does not react with the AVS.

An attempt was made to confirm the existence of an iron monosulfide by Mossbauer spectroscopy in sample #2(A5) which had 0.81% AVS. The spectrum did not pick up iron monosulfides or pyrite. There was a peak for some Fe(II) mineral. It is possible that iron sulfides are forming but are too fine grained to be analyzed by Mossbauer (31).

Conclusions

It is obvious from the results of all the analyses performed throughout the ten months of operation of the wetland treatment system at the Big Five tunnel that different mechanisms are operating in the different types of substrates. Mushroom compost is much more effective at drainage. These metals are the ones that make this site and many others in Colorado more difficult to treat than coal mine drainage sites. The difference in mechanism appears to be the formation of metal sulfides via dissimilatory sulfate reduction in the cell with the mushroom compost compared with little sulfide formation in the peat, manure and wood products sections. Metal removal in these sections is limited mainly to iron and is probably due to precipitation as oxides and adsorption of other metals.

Suggestions for Further Work

At this point it is unclear exactly what metals are associated with the sulfides which are forming. If the metal is iron it is too fine grained to be analyzed by Mossbauer spectroscopy and therefore by X-ray diffraction (XRD). Other metal sulfides which might be forming probably also would be too fine grained or totally amorphous to detect using XRD. There is also a good chance that what is forming is a mixed phase containing several metals. This problem was not foreseen at the beginning of the project or precautions could have been taken to determine the composition of the monosulfides before or in addition to the destructive sulfide analysis. The metals associated with the acid volatile sulfides could be determined by removing the pore water by thorough rinsing of the sample prior to the AVS treatment and analyzing the metals extracted into the HCl. The metals could be easily analyzed using atomic adsorption spectroscopy. The difficult task would be the rinsing of the sample because all transfers of sample or pore water would have to be conducted under N_2 so the AVS fraction would not oxidize.

A study is currently being conducted to determine which metals in the substrates are organically bound, oxide bound, water soluble, exchangeable and precipitated. These fractions also are operationally defined but will give some insight into how metals are retained in the wetland system.

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Appendix A

Detailed Descriptions of Analytical Procedures

Total and Organic Sulfur:

Reagents:

Barium chloride solution: Dissolve 100 g of $BaCl_2*2H_2O$ and dilute to 1L.
Eschka mixture: commercially available or mix 2 parts by weight of light calcined MgO with 1 part anhydrous Na_2CO_3.
HCl concentrated.
Sodium hydroxide solution: Dissolve 100 g of NaOH in 1 L of water.
Methyl orange solution: Dissolve 0.02 g methyl orange in 100 ml of hot water and filter through Whatman 40 paper.

Weigh 1 gram of sample onto weighing paper, record exact weight. Mix well with 3 grams of Eschka mixture and place mixture in a crucible. Cover mixture with an additional 1 gram of Eschka mixture. Place crucible in a cold oven and raise the temperature to 800°C over 1 hour. Leave samples in the 800°C oven for 2 hours. Remove samples from oven and dump contents of crucible into a 250 ml beaker: add 100 ml hot DI water and digest on hotplate (do not boil) for 1/2 hour. Filter samples using Whatman 40 filter paper into 600 ml beakers washing with hot DI water until filtrate volume is 250 ml. Add a few drops of methyl orange. If the sample turns pink add NaOH solution until the sample turns yellow, if the sample turns yellow add con HCl and boil samples on the hotplate. Using a glass pipet add 10 ml of $BaCl_2*2H_2O$ (100g/L). Boil the solution for 15 minutes. Reduce the heat to below boiling and continue heating samples for 3 hours. Cool and filter $BaSO_4$, precipitate through (preweighed) .45 millipore filters. Rinse the precipitate with a small amount of absolute ethanol. Dry the filters and precipitate overnight in a desicator. Weigh the filter and precipitate and calculate the %S as:

$$\%S = \frac{(A-B) \times 13.737}{C}$$

where:

A = grams of $BaSO_4$ precipitated.
B = grams of $BaSO_4$ correction due to blank.
C = grams of sample used.

Acid volatile sulfide:

Reagents:

6N HCl: Dilute concentrated HCl 1:1 with DI water.
0.1 M $AqNO_3$: Dissolve 4.2475 g $AGNO_3$ in 250 ml DI water.

pH 4.0 buffer

Weight distillation flask with a rubber stopper in the neck. With the flask and core inside the glove bag transfer the sample into the flask and stopper it tightly. Weigh the flask with the sample inside to obtain the sample weight. Obtain a wet:dry weight ratio by placing a split of the sample in a preweighed dish, weigh the wet sample, allow the sample to dry and weigh it again. Set up the distillation apparatus with the dropping funnel, buffer tube with about 25ml of pH 4.0 buffer in it, and the collection tube with 25-50ml of 0.1 M $AgNO_3$ in it. Quickly attach the flask containing the sample to the apparatus and purge the system with N_2 trying to minimize any contact between the sample and the air. Add 80ml 6N HCl to the dropping funnel and open the stopcock slightly so the N_2 bubbles through the HCl for 5 minutes. Apparatus may vary slightly so the procedure may have to be slightly altered to accommodate different setups. Disconnect the buffer tube from the apparatus and open the dropping funnel stopcock to allow the acid to enter the distillation flask. Quickly reattach the buffer tube to minimize loss of H_2S. Slowly heat the sample to a setting of 90 on the Variac, boil for 5 minutes, and reduce the heat to a setting of 70. Allow the reaction to proceed until H_2S is no longer being evolved. Test this by placing a piece of filter paper wetted with $AgNO_3$ in the gas stream between the buffer and the $AgNO_3$. Filter the Ag_2S onto preweighed polycarbonate .45 filters and dry to a constant weight. Filter the sample mixture rinsing well with DI water. Dry the residue and save it for acetone extraction. Save the filtrate for SO_4 analysis. The AVS is calculated as:

$$\%S = \frac{A \times 12.938}{B}$$

where A = weight of Ag_2S

B = dry weight of sample.

Acetone soluble sulfur:

Reagents:

0.1 M $AgNO_3$: see AVS procedure.

Acetone: analytical grade.

HCl: concentrated.

Cr(II) solution: Dissolve 133g $CrCl_3 * 6H_2O$ in 500 ml of 0.1 M HCl. Pass the solution through a Jones reductor to reduce the Cr(III) to Cr(II).

pH 4.0 buffer.

Weigh approximately 5 grams (record exact weight) of the dried residual solid from the AVS analysis into a 250 ml Erlenmeyer flask, add 100 ml analytical grade acetone and cover with parafilm. Shake gently (so that the acetone does not splash onto the parafilm) on a rotary shaker for 16 hours. Filter through a .45 polycarbonate filter and transfer the filtrate to the reaction flask. Set up the distillation apparatus and purge the system with N_2. Add 50 ml of reduced Cr solution and 20 ml of concentrated HCl through the dropping funnel. Heat the mixture to boiling, then reduce the heat and allow the reaction to go to completion (see AVS). Collect the Ag_2S in 0.1 M $AgNO_3$ as with the AVS. Retain the residue from the acetone extraction for disulfide analysis.

Disulfides (pyritic sulfur)

Reagents:

Cr(II) solution: see acetone soluble sulfur.

HCl: concentrated.

0.1 M $AgNO_3$: see AVS.

pH 4.0 buffer.

Place the weighed, dried residual sample from the acetone extraction in the distillation flask. Connect the apparatus and purge it with N_2. Add 50 ml Cr(II) solution and 20 ml con HCl through the dropping funnel. Heat the solution to boiling, continue boiling until H_2S is no longer evolving. Filter the Ag_2S as with the AVS. Filter the residual sample for organic S analysis.

Sulfate Sulfur

Reagents:

Barium Chloride solution: see total sulfur.

Nitric acid: concentrated, doubly distilled.

Adjust the volume of the HCl filtrate from AVS analysis to 250 ml with DI water. Bring solution to a boil and add 10 ml $BaCl_2$ solution. Reduce heat to just below boiling and heat for three hours. Cool samples and filter precipitate (using teflon coating filters). Transfer filter and precipitate to a teflon beaker. Add 5 ml doubly distilled HNO_3 and heat in covered beakers, rinsing four times with 5 ml portions of DI water. Filter the precipitate and dry overnight in a desicator. Calculate the sulfate as with total sulfur.

H_2S in Well Waters

Dialysis bags were filled with deaerated deionized water and suspended in the wells at the screening depth on June 27 (wells were pumped out before bags were inserted). The bags were removed July 14. If a precipitate was obvious in the bag it was placed in a jar filled with 0.1 M sodium dithionate and transported to the lab for filtering and Mossbauer analysis. Bags without precipitate were rinsed with DI water, punctured with a needle and 90 or 40 ml of the water was added to 10 ml of 10% zinc acetate solution in a capped graduated cylinder.

Reagents:

Hydrochloric Acid, 6N.

Standard Iodine solution, 0.0250 N: dissolve 20 to 25 g KI in a little DI water and add 3.2 g iodine. After the iodine has dissolved, dilute to 1000 ml and standardize against 0.0250N $Na_2S_2O_3$.

Dissolve 6.205g $Na_2S_2O_3 \cdot 5H_2O$ in DI water and add 0.4 g olid NaOH. Dilute to 1000 ml.

Starch solution: dissolve 2g soluble starch and 0.2 g salysilic acid in 100 ml hot DI water.

Contents of the graduated cylinder were rinsed into a 250 ml Erlenmeyer flask. Iodine solution was added until excess iodine was present as indicated by a yellow color. The pH was adjusted to 3-5 with HCl and the samples titrated with $Na_2S_2O_3$.

Calculate as:

$$mg/l\ S = \frac{a+b}{c} \times 32046$$

a = ml iodine added x molarity of iodine solution

$$b = \frac{\text{ml } Na_2S_2O_3 \text{ added x molarity of } Na_2S_2O_3 \text{ solution}}{2}$$

c = sample volume

Appendix B

Water analysis data for outputs from each section of the constructed wetland at the Big Five tunnel, Idaho Springs, CO.

Key to abbreviations

OPA: output water from cell A

OPB: output water from cell B

OPC: output water from cell C

MD: mine drainage

ITR: EPA's inorganic traffic report

The number following OPA, OPB, OPC, MD in the table refers to the sampling event (1-12).

	OPA-1 MHJ 518 13-Oct-87	OPA-2 MHJ 510 03-Nov-87	OPA-3 MHJ 538 21-Nov-87	OPA-4 MHJ 592 11-Dec-87
Minor & Trace Elements				
Al ug/L	<82	5000	4600	2700
Sb ug/L	<50	160	<50	<50
As ug/L	3.6	<3	<3	<3
Ba ug/L	<100	<100	<100	<100
Be ug/L	<.3	1.8	1.7	<.3
B ug/L	<5	<5	<5	<5
Cd ug/L	<4	39	41	18
Cr ug/L	<6	66	<6	12
Co ug/L	<29	100	110	120
Cu ug/L	18	810	770	440
Fe ug/L	3800	27300	24300	17800
Pb ug/L	9.1	36	46	<3
Mn ug/L	390	40300	32200	26700
Hg ug/L	<.2	<.2	<.2	<.2
Ni ug/L	<22	100	97	<22
Se ug/L	<3	<30	<30	<30
Ag ug/L	9	150	140	160
Tl ug/L	<2	<2	<2	<20
V ug/L	<14	<14	<14	<14
Zn ug/L	100	8400	8300	7800
Major Cations				
Ca ug/L	18700	340000	311900	345400
Mg ug/L	7900	130500	122700	134700
K ug/L	51300	18600	22300	55200
Na ug/L	12400	48000	43000	53800
Major Anions				
HCO3 mg/L	143	<5	<5	15
CO3 mg/L	<5	<5	<5	<5
Cl mg/L	23	8.7	7.1	20.9
F mg/L	5.4	<.1	0.88	0.89
SO4 mg/L	2.1	1730	1960	1560
Nutrients				
NO3/NO2 mg/L	1.4	7.2	<.05	<.5
NH4 mg/L	21	2	7	27
Lab Determinations				
TDS mg/L	442	2520	2620	2657
TSS mg/L	20	16.8	74	100
Acidity	<5	4070	139	54.4
TOC mg/L	170	17	36	98
Field Determinations				
pH	6.7	3.1	3.5	4.6
Eh mv	340	670	588	410
Conductivity	761	2618	2506	2523
Temperature	13	11.5	8.1	5
Dissolved O2	6.5	7.3	6.75	8.5

	OPA-5 MHL 669 26-Jan-88	OPA-6 MHL 702 13-Feb-88	OPA-7 MHL 709 09-Mar-88	OPA-8 MHN 098 02-Apr-88
Minor & Trace Elements				
Al ug/L	5050	2730	4210	4660
Sb ug/L	22	41	<15	<15
As ug/L	<10	<10	<10	<10
Ba ug/L	45	30	24	24
Be ug/L	2.4	1.1	1.9	1.6
B ug/L	68	72	60	33
Cd ug/L	27	16	17	17
Cr ug/L	<5	<5	<5	<5
Co ug/L	96	82	84	82
Cu ug/L	523	135	214	433
Fe ug/L	20600	18400	18900	18900
Pb ug/L	21	<5	<5	5.9
Mn ug/L	29100	26600	28900	28700
Hg ug/L	<.2	<.2	<.2	<.2
Ni ug/L	187	168	180	180
Se ug/L	<5	<25	<5	<25
Ag ug/L	<5	<5	<5	<5
Tl ug/L	<10	<10	<10	<10
V ug/L	<3	<3	<3	<3
Zn ug/L	7240	5940	6780	6710
Major Cations				
Ca ug/L	368000	328000	343000	354000
Mg ug/L	135000	121000	131000	130000
K ug/L	41500	47700	31500	19800
Na ug/L	50400	48000	46200	45300
Major Anions				
HCO3 mg/L	5.6	<5	<5	<5
CO3 mg/L	<5	<5	<5	<5
Cl mg/L	17.4	20.2	11.5	6.5
F mg/L	0.99	1.03	0.09	0.05
SO4 mg/L	1730	1690	1660	1840
Nutrients				
NO3/NO2 mg/L	<.01	0.04	0.61	<.01
NH4 mg/L	25	21.3	11.9	4.99
Lab Determinations				
TDS mg/L	2410	2390	2420	2450
TSS mg/L	65	74	51	31
Acidity	108	79.5	109	111
TOC mg/L	88.3	92.4	39.8	15.4
Field Determinations				
pH	4.6	5.25	4.2	4.2
Eh mv	440	330	690	505
Conductivity	2511	2555	2487	2564
Temperature	4	5.2	2	8.3
Dissolved O2	7.6	8.6	8.8	7.8

	OPA-9 MHL-764 04-May-88	OPA-10 MHL 769 31-May-88	OPA-11 MHJ 211 27-Jun-88	OPA-12 MHQ-601 19-Aug-88
Minor & Trace Elements				
Al ug/L	4280	3050	168	475
Sb ug/L	<17	<17	<17	<24
As ug/L	<3	<3	<3	<4
Ba ug/L	22	25	31	<49
Be ug/L	<2	<2	<2	<2
B ug/L	<10	<10	18	<10
Cd ug/L	27	13	<5	<5
Cr ug/L	10	15	18	13
Co ug/L	74	72	60	63
Cu ug/L	152	18	60	170
Fe ug/L	21600	27500	22100	19900
Pb ug/L	16	1.9	<1	<1
Mn ug/L	27400	25600	27200	25300
Hg ug/L	0.3	<.2	<.2	<.2
Ni ug/L	48	54	19	21
Se ug/L	<20	<20	<2	<2
Ag ug/L	8.6	14	118	15
Tl ug/L	<7	<2	<7	<6
V ug/L	<4	<4	<4	<7
Zn ug/L	5690	5480	125	30
Major Cations				
Ca ug/L	309000	316000	343000	321000
Mg ug/L	27400	123000	137000	130000
K ug/L	13800	12200	13600	27000
Na ug/L	38400	39700	46700	45800
Major Anions				
HCO3 mg/L	<2	<5	14	
CO3 mg/L	<2	<5	14	
Cl mg/L	8.49	24.8	9.9	
F mg/L	1	1.08	0.284	
SO4 mg/L	1980	1140	14	
Nutrients				
NO3/NO2 mg/L	<.1	0.35	0.1	
NH4 mg/L	0.6	2.7	0.48	
Lab Determinations				
TDS mg/L	1854	2397	2910	
TSS mg/L	83	79	77	
Acidity	111	104	51	
TOC mg/L	18	4.9	3	
Field Determinations				
pH	3.65	4.3	3	5.48
Eh mv	445	447	300	415
Conductivity	2470	2501	2415	2431
Temperature	12	15	18.8	20.5
Dissolved O2	7.2	6	5.4	2.5

	OPB-1 MHJ 525 15-Oct-87	OPB-2 MHJ 506 03-Nov-87	OPB-3 MHJ 540 21-Nov-87	OPB-4 MHJ 593 11-Dec-87
Minor & Trace Elements				
Al ug/L	<82	5600	5900	5000
Sb ug/L	<50	<50	<50	<50
As ug/L	<3	<3	<3	<3
Ba ug/L	<100	<100	<100	<100
Be ug/L	<.3	2.1	2.6	1
B ug/L	<5	<5	<5	<5
Cd ug/L	<4	44	54	25
Cr ug/L	<6	58	<6	<6
Co ug/L	<29	110	140	120
Cu ug/L	18	860	930	890
Fe ug/L	3800	25500	26200	23900
Pb ug/L	73	38	57	19.7
Mn ug/L	340	33300	36800	33200
Hg ug/L	<.2	<.2	<.2	<.2
Ni ug/L	<22	110	150	<22
Se ug/L	<3	<30	<30	<30
Ag ug/L	12	160	150	160
Tl ug/L	<2	<2	<2	<20
V ug/L	<14	<14	<14	<14
Zn ug/L	210	8700	9600	9800
Major Cations				
Ca ug/L	17700	342200	327900	349800
Mg ug/L	8100	128300	127300	133000
K ug/L	33700	11400	11200	23300
Na ug/L	19500	46700	42900	55800
Major Anions				
HCO3 mg/L	187	<5	<5	<3
CO3 mg/L	<5	<5	<5	<2.5
Cl mg/L	36	5.7	7.1	22
F mg/L	<.1	<.1	0.95	1.04
SO4 mg/L	32	1750	1670	1430
Nutrients				
NO3/NO2 mg/L	5.4	4.5	0.24	0.47
NH4 mg/L	<2	<2	1	3.6
Lab Determinations				
TDS mg/L	232	2460	2610	2621
TSS mg/L	16	4.8	38	42
Acidity	<5	3383	166	125
TOC mg/L	42	2	4	8.5
Field Determinations				
pH	6.1	2.8	3.1	3.13
Eh mv	145	700	640	640
Conductivity	377	2636	2641	2649
Temperature	12	11	7.9	4.7
Dissolved O2	6.5	8	7.35	8.5

	OPB-5 MHL 671 26-Jan-88	OPB-6 MHL 704 13-Feb-88	OPB-7 MHL 710 09-Mar-88	OPB-8 MHN 093 02-Apr-88
Minor & Trace Elements				
Al ug/L	6520	5610	5820	5720
Sb ug/L	58	40	<75	<15
As ug/L	<10	<10	<10	<10
Ba ug/L	24	16	14	16
Be ug/L	3.4	1.6	2.7	2.3
B ug/L	68	49	42	22
Cd ug/L	33	25	23	22
Cr ug/L	<5	<5	<5	<5
Co ug/L	106	91	91	92
Cu ug/L	925	772	826	804
Fe ug/L	27800	23400	23800	24400
Pb ug/L	48	30	32	38
Mn ug/L	31400	28000	30200	29500
Hg ug/L	<.2	<.2	<.2	<.2
Ni ug/L	196	170	187	183
Se ug/L	<5	<25	<5	<5
Ag ug/L	<5	<5	<5	<5
Tl ug/L	<10	<10	<10	<10
V ug/L	<3	<3	<3	<3
Zn ug/L	8940	7630	8640	8380
Major Cations				
Ca ug/L	313000	339000	340000	36100
Mg ug/L	122000	122000	126000	130000
K ug/L	10900	16100	12500	13400
Na ug/L	48500	46500	45800	46100
Major Anions				
HCO3 mg/L	<5	<5	<5	<5
CO3 mg/L	<5	<5	<5	<5
Cl mg/L	9	11.5	9.1	8.9
F mg/L	1.07	0.96	0.07	0.05
SO4 mg/L	1780	1610	1680	2020
Nutrients				
NO3/NO2 mg/L	0.06	0.01	0.29	<.01
NH4 mg/L	1.07	1.79	0.87	0.74
Lab Determinations				
TDS mg/L	2420	2290	2430	2460
TSS mg/L	1	15	6	14
Acidity	169	37.9	159	170
TOC mg/L	3.48	6.31	3.87	3.68
Field Determinations				
pH	3.4	3.65	3.2	3.15
Eh mv	515	425	710	615
Conductivity	2599	2532	2458	2676
Temperature	3	3	0	7
Dissolved O2	8.5	9.4	11	9.6

	OPB-9 MHL 767 04-May-88	OPB-10 MHL 771 31-May-88	OPB-11 MHJ 209 27-Jun-88	OPB-12 MHQ-603 19-Aug-88
Minor & Trace Elements				
Al ug/L	5510	4660	4950	5290
Sb ug/L	<17	<17	<17	<24
As ug/L	3.5	<3	4.5	<4
Ba ug/L	20	15	47	<49
Be ug/L	<2	<2	2.7	2.3
B ug/L	<10	37	<10	16
Cd ug/L	29	28	26	18
Cr ug/L	5.7	12	23	11
Co ug/L	86	82	87	77
Cu ug/L	785	637	722	520
Fe ug/L	22000	17200	24800	15300
Pb ug/L	44	29	43	4.9
Mn ug/L	27400	25400	26800	26000
Hg ug/L	0.8	<.2	<.2	<.2
Ni ug/L	76	58	64	32
Se ug/L	<2	<20	<20	7.7
Ag ug/L	17	9	16	48900
Tl ug/L	<70	<2	<7	<6
V ug/L	<4	<4	<4	<7
Zn ug/L	7920	7380	7560	5840
Major Cations				
Ca ug/L	320000	309000	323000	334000
Mg ug/L	127000	119000	127000	134000
K ug/L	13900	11200	9400	15200
Na ug/L	41300	38800	44300	48900
Major Anions				
HCO3 mg/L	<2	<5	<5	
CO3 mg/L	<2	<5	<5	
Cl mg/L	10	33.7	11	
F mg/L	1.09	1.12	0.31	
SO4 mg/L	1530	1570	26	
Nutrients				
NO3/NO2 mg/L	<.1	0.35	0.1	
NH4 mg/L	1.2	0.3	<.1	
Lab Determinations				
TDS mg/L	1891	2535	2840	
TSS mg/L	30	20	43	
Acidity	175	166	130	
TOC mg/L	5.7	2.35	<2	
Field Determinations				
pH	3.1	3	2.95	3.3
Eh mv	715	680	625	625
Conductivity	2742	2759	2791	2705
Temperature	10.4	13.9	19.2	17.5
Dissolved O2	8	6.4	5.8	4.1

	OPC-1 MHJ 515 15-Oct-87	OPC-2 MHJ 503 03-Nov-87	OPC-3 MHJ 541 21-Nov-87	OPC-4 MHJ 594 11-Dec-87
Minor & Trace Elements				
Al ug/L	<82	5200	5700	5000
Sb ug/L	<50	<50	<50	<50
As ug/L	5.2	<3	<3	<3
Ba ug/L	<100	<100	<100	<100
Be ug/L	<.3	2	2.2	1
B ug/L	<5	<5	<5	<5
Cd ug/L	<4	39	48	30
Cr ug/L	<6	43	<6	33
Co ug/L	<29	97	120	120
Cu ug/L	27	820	880	910
Fe ug/L	5200	25600	25000	22000
Pb ug/L	9.1	41	57	19.3
Mn ug/L	550	33600	34500	34400
Hg ug/L	<.2	<.2	<.2	<.2
Ni ug/L	<22	90	110	<22
Se ug/L	<3	<30	<30	<30
Ag ug/L	12	150	130	160
Tl ug/L	<2	<2	<2	<20
V ug/L	<14	<14	<14	<14
Zn ug/L	100	8300	9100	9600
Major Cations				
Ca ug/L	25000	317800	307400	357200
Mg ug/L	9600	119900	119300	134100
K ug/L	80900	10600	13700	21500
Na ug/L	20900	44500	41100	54800
Major Anions				
HCO3 mg/L	473	<5	<5	<3
CO3 mg/L	<5	<5	<5	<2.5
Cl mg/L	44	8	12	18.8
F mg/L	1.4	<.1	0.88	0.96
SO4 mg/L	3.7	1740	1780	1520
Nutrients				
NO3/NO2 mg/L	<.1	7	0.1	<.05
NH4 mg/L	32	<2	2	3.6
Lab Determinations				
TDS mg/L	540	2450	2590	2614
TSS mg/L	33	7.4	58	46
Acidity	<5	2790	153	119.6
TOC mg/L	212	3	5.7	6.5
Field Determinations				
pH	6.5	3.1	3.25	3.3
Eh mv	285	690	635	610
Conductivity	765	2704	2429	2681
Temperature	13.5	11	5.3	5
Dissolved O2	7.1	8.1	8.1	9.4

	OPC-5 MHL 672 26-Jan-88	OPC-6 MHL 705 13-Feb-88	OPC-7 MHL 711 09-Mar-88	OPC-8 MHN 095 02-Apr-88
Minor & Trace Elements				
Al ug/L	6370	5720	5870	5460
Sb ug/L	88	38	<75	<15
As ug/L	<10	<10	<10	<10
Ba ug/L	19	15	17	18
Be ug/L	3.2	2	2.8	2.2
B ug/L	43	48	78	20
Cd ug/L	34	25	26	26
Cr ug/L	<5	<5	<5	<5
Co ug/L	100	92	91	90
Cu ug/L	922	874	854	794
Fe ug/L	27600	25200	26200	24900
Pb ug/L	50	33	32	25
Mn ug/L	28600	27800	30100	28400
Hg ug/L	<.2	<.2	<.2	<.2
Ni ug/L	179	175	188	174
Se ug/L	<25	<25	<5	<5
Ag ug/L	6.3	<5	<5	<5
Tl ug/L	<10	<10	<10	<10
V ug/L	4.4	<3	<3	<3
Zn ug/L	8280	7940	8810	8180
Major Cations				
Ca ug/L	322000	332000	344000	341000
Mg ug/L	126000	119000	128000	124000
K ug/L	5620	15400	16200	18300
Na ug/L	46600	45900	47700	46800
Major Anions				
HCO3 mg/L	<5	<5	<5	<5
CO3 mg/L	<5	<5	<5	<5
Cl mg/L	9.8	13.8	13.1	14.9
F mg/L	1.08	1.05	0.06	0.05
SO4 mg/L	1700	1580	1670	1800
Nutrients				
NO3/NO2 mg/L	0.06	0.26	0.02	0.16
NH4 mg/L	0.85	1.58	1.93	2.04
Lab Determinations				
TDS mg/L	2490	2310	2460	2410
TSS mg/L	18	16	13	27
Acidity	177	86.5	158	157
TOC mg/L	2.37	4.23	6.72	6.72
Field Determinations				
pH	3.4	3.6	2.9	3.25
Eh mv	510	445	655	625
Conductivity	2658	2578	2490	2454
Temperature	2	1.2	1	6
Dissolved O2	8.4	9.9	10.2	8.8

	OPC-9 MHL 768 04-May-88	OPC-10 MHL 772 31-May-88	OPC-11 MHJ 208 27-Jun-88	OPC-12 MHQ-605 19-Aug-88
Minor & Trace Elements				
Al ug/L	5890	4810	5110	5070
Sb ug/L	<17	<17	<17	<24
As ug/L	3.6	<3	5.3	<4
Ba ug/L	21	41	27	<49
Be ug/L	<2	<2	<2	2.3
B ug/L	<10	<10	<10	55
Cd ug/L	36	30	29	23
Cr ug/L	9.7	10	16	11
Co ug/L	92	83	89	79
Cu ug/L	800	680	691	380
Fe ug/L	24300	21400	22700	10800
Pb ug/L	51	14	56	3.5
Mn ug/L	28400	25200	27000	25100
Hg ug/L	0.4	0.2	<.2	<.2
Ni ug/L	82	68	65	34
Se ug/L	<2	<20	<20	<2
Ag ug/L	72	13	5.6	11
Tl ug/L	<7	<2	<7	<6
V ug/L	<4	<4	<4	<7
Zn ug/L	8440	7700	7630	5810
Major Cations				
Ca ug/L	336000	308000	328000	326000
Mg ug/L	134000	119000	129000	130000
K ug/L	14900	12100	10100	22800
Na ug/L	42800	39600	45100	51300
Major Anions				
HCO3 mg/L	<2	<5	<5	
CO3 mg/L	<2	<5	<5	
Cl mg/L	12.5	16.8	11	
F mg/L	1.1	1.13	0.3	
SO4 mg/L	1600	1220	15	
Nutrients				
NO3/NO2 mg/L	<.1	<.1	<.1	
NH4 mg/L	0.6	1.4	<.1	
Lab Determinations				
TDS mg/L	1414	2489	3160	
TSS mg/L	35	38	41	
Acidity	173	197	119	
TOC mg/L	6.7	3.51	<2	
Field Determinations				
pH	3.1	3.05	3	3.45
Eh mv	685	661	650	583
Conductivity	2470	2734	2689	2621
Temperature	14	13.8	18.8	15.5
Dissolved O2	7.6	5.9	5.4	4.5

	MD-1 MHJ 505 15-Oct-87	MD-2 MHJ 521 03-Nov-87	MD-3 MHJ 539 21-Nov-87	MD-4 MHJ 595 11-Dec-87
Minor & Trace Elements				
Al ug/L	5900	6000	5800	5600
Sb ug/L	<50	<50	<50	<50
As ug/L	<3	<3	<3	<3
Ba ug/L	<100	<100	<100	<100
Be ug/L	2.2	2.4	2.2	1.2
B ug/L	<5	<5	<5	<5
Cd ug/L	46	50	50	27
Cr ug/L	63	61	<6	39
Co ug/L	110	110	120	120
Cu ug/L	970	980	1000	1070
Fe ug/L	31000	32600	31100	32800
Pb ug/L	56	43	66	28.2
Mn ug/L	37400	34700	33900	32200
Hg ug/L	<.2	<.2	<.2	<.2
Ni ug/L	110	130	120	<22
Se ug/L	<30	<30	<30	<30
Ag ug/L	150	160	140	170
Tl ug/L	<2	<2	<2	<20
V ug/L	<14	<14	<14	<14
Zn ug/L	9100	9600	10200	10600
Major Cations				
Ca ug/L	334200	347000	317800	352100
Mg ug/L	126100	132000	123700	134600
K ug/L	8000	8200	7500	8200
Na ug/L	46200	47500	42800	48600
Major Anions				
HCO3 mg/L	<5	<5	<5	<3
CO3 mg/L	<5	<5	<5	<2.5
Cl mg/L	7.4	6	5	4
F mg/L	<.1	<.1	0.98	0.96
SO4 mg/L	1600	1780	2000	1580
Nutrients				
NO3/NO2 mg/L	8.5	70	1.4	<.05
NH4 mg/L	<2	<2	0.22	3
Lab Determinations				
TDS mg/L	2470	2480	2590	2638
TSS mg/L	24	10.8	32	42
Acidity	434	3587	154	149
TOC mg/L	<2	<2	<1	<1
Field Determinations				
pH	2.85	2.75	2.92	2.75
Eh mv	610	685	635	625
Conductivity	2679	2709	2651	2743
Temperature	14.5	14	12.5	12.5
Dissolved O2	9.9	8.2	7.42	9.7

	MD-5 MHL 674 26-Jan-88	MD-6 MHL 700 13-Feb-88	MD-7 MHL 712 09-Mar-88	MD-8 MHN 097 02-Apr-88
Minor & Trace Elements				
Al ug/L	6060	5860	5970	5830
Sb ug/L	36	38	<75	<75
As ug/L	<10	<10	<10	<10
Ba ug/L	22	14	8.2	10
Be ug/L	2.6	1.5	2.6	2.3
B ug/L	54	39	40	22
Cd ug/L	28	25	30	29
Cr ug/L	<5	<5	<.5	<5
Co ug/L	84	95	96	98
Cu ug/L	921	859	933	879
Fe ug/L	27300	28000	31700	34500
Pb ug/L	41	28	35	28
Mn ug/L	25400	27600	30100	29400
Hg ug/L	<.2	<.2	<.2	<.2
Ni ug/L	153	170	198	199
Se ug/L	<5	<10	<5	<25
Ag ug/L	<5	<5	<5	<5
Tl ug/L	<10	<10	<10	<10
V ug/L	<3	<3	<3	<3
Zn ug/L	7460	8240	9460	9120
Major Cations				
Ca ug/L	296000	332000	333000	34200
Mg ug/L	119000	120000	124000	124000
K ug/L	<489	8520	7030	8060
Na ug/L	45000	42900	43400	43400
Major Anions				
HCO3 mg/L	<5	<5	<5	<5
CO3 mg/L	<5	<5	<5	<5
Cl mg/L	5.6	6.05	5.7	6.2
F mg/L	1.04	1.09	0.06	0.05
SO4 mg/L	1730	1750	1760	1810
Nutrients				
NO3/NO2 mg/L	0.07	0.14	1.41	0.26
NH4 mg/L	0.25	0.12	0.15	0.16
Lab Determinations				
TDS mg/L	2390	2380	2470	2450
TSS mg/L	3	16	9	7
Acidity	196	187	205	196
TOC mg/L	0.94	0.91	0.9	0.93
Field Determinations				
pH	3.2	3.3	2.8	3.25
Eh mv	540	470	710	635
Conductivity	2661	2642	2698	2718
Temperature	11.5	11.6	9	10.9
Dissolved O2	8.3	7.6	8.1	6.5

	MD-9 MHL 766 04-May-88	MD-10 MHL 773 31-May-88	MD-11 MHJ 212 27-Jun-88	MD-12 MHQ-606 19-Aug-88
Minor & Trace Elements				
Al ug/L	5700	4820	5350	5800
Sb ug/L	<17	<17	<17	<24
As ug/L	<3	<3	3.5	<4
Ba ug/L	13	8	22	<49
Be ug/L	2.5	3.3	<2	2
B ug/L	<10	<10	<10	<10
Cd ug/L	41	39	35	34
Cr ug/L	10	12	14	9
Co ug/L	89	86	90	93
Cu ug/L	848	754	850	912
Fe ug/L	34200	43700	42600	37100
Pb ug/L	37	51	47	5.3
Mn ug/L	28200	24900	27100	25600
Hg ug/L	0.2	<.2	0.6	<.2
Ni ug/L	64	79	85	73
Se ug/L	<2	<20	<2	<2
Ag ug/L	26	12	<5	<5
Tl ug/L	<70	<2	<7	<6
V ug/L	<4	<4	<4	<7
Zn ug/L	8350	8140	8400	8060
Major Cations				
Ca ug/L	309000	296000	326000	325000
Mg ug/L	119000	115000	129000	132000
K ug/L	9400	9100	7400	9000
Na ug/L	38200	36600	43500	45900
Major Anions				
HCO3 mg/L	<2	<5	<5	
CO3 mg/L	<2	<5	<5	
Cl mg/L	6	16	7.4	
F mg/L	1.1	1.15	0.3	
SO4 mg/L	1580	1500	14	
Nutrients				
NO3/NO2 mg/L	<.1	0.04	<.1	
NH4 mg/L	0.7	0.5	<.1	
Lab Determinations				
TDS mg/L	1551	2482	3250	
TSS mg/L	20	76	42	
Acidity	210	261	164	
TOC mg/L	<2	1.51	<2	
Field Determinations				
pH	2.96	3.02	3	2.9
Eh mv	655	609	610	662
Conductivity	2735	2754	2760	2797
Temperature	12.3	14.5	15.3	15.4
Dissolved O2	6.65	7.9	5.8	4.9