

METAL REMOVAL EFFICIENCIES FROM ACID MINE  
DRAINAGE IN THE BIG FIVE CONSTRUCTED WETLAND<sup>1</sup>

by

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**Abstract.** An experimental constructed wetland in the Idaho Springs-Central City mining district of Colorado is providing data for metal removal efficiencies from acid mine drainage. The wetland is designed to passively remove the heavy metals found in the metal mine drainage flowing from the Big Five Tunnel. A number of different substrate compositions in the wetland have been used. The decrease of metal concentrations and the increase in pH is related to the rate of drainage flow through the wetland. For Fe and Zn, decreases in concentrations generally vary inversely with flow rate as do increases in pH. This information can be used in determining the maximum loading rate for any given metal removal efficiency. Mass removal data (mg/day/m<sup>2</sup>) indicate that there are some tendencies for greater metal removal rates and pH increases during the summer season than for the winter. No obvious relationships are found between mass removal data and flow rate for Fe, Zn, Cu, and Mn.

Additional Key Words: constructed wetland, low pH, heavy metals pollution.

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### Introduction

Research efforts over the past few years have contributed a great deal of knowledge towards designing constructed wetlands for the treatment of acid mine drainage (Hammer 1989). The Big Five wetland is one of the few built specifically to remove heavy metals from acid mine waters. It is located in Idaho Springs, Colorado, a region which produced a significant amount of precious metal ores around the turn of the century. Mine drainages in the region typically have low pH and high metal concentrations.

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The mine drainage flowing from the Big Five Tunnel was chosen to investigate the treatment of acid mine drainage with a constructed wetland system (Howard et al. 1989a). The design of the system was based on discussions with and findings of experienced investigators (Holm pers. comm., Kleinmann 1983 and pers. comm., Hiel and Kerins 1988). The system was built for a number of reasons including: to determine the fate of the metals in the system, to identify the organic substrates that function best in such systems, and, the primary focus of this paper, to determine the effectiveness of the system in decreasing the metal concentrations of the mine drainage.

In 1988, the clogging of the mine drainage flow lines inadvertently allowed observations of much larger increases in pH and larger decreases in metal concentrations with reduced flow. These observations led to further association of the metal removal efficiencies and increases in pH with different loading rates.

Initial studies suggested what kinds of metal removal processes may be important in the wetland, such as bacterially mediated sulfate reduction (Wildeman and Laudon 1989). Sulfate reducers were found to be dominant throughout the wetland

substrates whereas metal-oxidizing bacteria were found only very near the surface (Batal et al. 1989).

The objectives of this paper include (1) examining recent data to determine if processes such as bacterially mediated sulfate reduction are actually occurring, (2) determining if different perspectives on data analysis provide further insights on the metal removal processes taking place and, most importantly, (3) determining if there is a maximum loading rate for which metal removal processes will operate optimally. By relating different loading rates to removal efficiencies, the maximum loading rate for any given metal removal efficiency can be estimated.

### Materials and Methods

Materials, methods and procedures used in building and operating the Big Five treatment system are given in Howard et al. (1989a and 1989b). The treatment system has dimensions of 1.22 m in depth, 3.05 m in width, and 18.3 m in length. The structure is divided into three 6.1 m long cells with an area of 18.6 m<sup>2</sup>.

Water is piped from the tunnel portal to each of the cells through PVC piping which is fitted with valves to control the flow to each individual cell. Standpipes set at an overflow height of about 1 m act as drains in the cells.

Rock boxes were constructed at the upstream end of each of the cells to allow the mine drainage to contact as much cross-section of the organic substrate as possible. The boxes were filled with 10-15 cm rounded cobbles. The boxes were to force the flow downward into the substrate. These rock boxes, however, did not work well because the accumulation of metal hydroxides appeared to clog the downward flow of water into the substrate.

The cells contain an organic substrate to a depth of about 1 m. Cell A was filled with fresh mushroom compost, which consists of approximately 50 percent animal manure and 50 percent barley mash wastes from a local brewery. Cell B received a mixture of equal parts of peat, aged steer manure, and decomposed wood shavings and sawdust. Cell C was lined to a depth of 10-15 cm with 5-8 cm limestone rock, then filled to a 1 m depth with the same organic mixture as Cell B. Cattail, sedge, and rush species were transplanted from similar locations to each of the cells.

Sampling of the mine drainage water and of the cell outputs was done about twice monthly with more frequent samplings in the summer season. Water samples were filtered in the field and preserved with HNO<sub>3</sub>. At least two duplicate water samples were taken monthly. Duplicate output water samples were taken from the same sample during the filtering

process and duplicate mine drainage water samples were taken as separate samplings from the mine drainage. For reporting purposes, data for the duplicates have been averaged. The relative difference between duplicates for metal determinations are generally within a few percent and within one percent or less for sulfate values.

Metal analyses were done by flame atomic adsorption and sulfate determinations were made gravimetrically by precipitation of BaSO<sub>4</sub>.

### Water Quality of the Big Five Mine Drainage and Wetland Outputs

The most abundant heavy metals in the Big Five Tunnel mine drainage are Fe, Mn, Zn, and Cu. The analytical results of these metal concentrations and of sulfate in the cell output waters and mine drainage show promising results for the Big Five treatment system (Table 1). Metal concentration decreases range from basically none for Mn to essentially complete removal for Cu. Decreases in concentrations for Fe of up to 63 percent and for zinc of up to 100 percent are found. Decreases in sulfate concentrations of about 10% are typical in Cell A.

### Relationships Between Loading Rates and Metal Concentrations

After about 24 months of operation, the mushroom compost in Cell A shows a much better capability to remove metals and raise the pH than the substrates in the other two cells at similar flow rates (Howard et al. 1989b, Wildeman and Laudon 1989). Because of the higher metal removal efficiency and effluent pH, the focus in this paper is on the results from Cell A.

The Big Five wetland is operated as closely as possible to a passive, natural system. Consequently, events of nature such as freeze-thaw cycles cause fluctuation in the removal processes that produce fluctuations in the output concentrations. Because of this, loading rates should be considered as rough guidelines.

Metal removal data for different loading rates were gathered by adjusting flow rates two days to one week prior to sampling in order to allow for the wetland to equilibrate. Retention time is inversely proportional to the flow rate. Thus, at higher flow rates, less time is required for equilibration. A retention time of about 70 hours is estimated for a flow rate of 4 L/min. Table 2 contains the flow rates of mine drainage through Cell A at the time of sampling. In addition, changes in pH (unit increase) and Eh (decrease in mV) are given as well as the amount of decrease in sulfate concentration.

Table 1. Metal and sulfate concentrations (mg/L) and pH in the Big Five mine drainage and Cell A output water are given below. Percentages of the decrease in metal concentration in the Cell A output water relative to the mine drainage is also given. The Cell A input flow rate is given in liters/minute. The area of Cell A is 18.6 m<sup>2</sup>.

		% Mn dec.	% Fe dec.	% Zn dec.	Cu mg/L	% Cu dec.	SO <sub>4</sub> <sup>2-</sup> mg/L	pH	flow rate
December 11, 1987									
Mine Drainage		34	32	10.6	1.02		1750	2.8	
Output A		27	18	7.8	0.44	57	1560	4.6	4
February 13, 1988									
Mine Drainage		28	28	8.2	0.89		1750	3.3	
Output A		27	18	5.9	0.14	84	1690	4.7	4
May 31, 1988									
Mine Drainage		25	44	8.1	0.75		1500	3.0	
Output A		25	27	5.4	0.03	96	1330	4.3	4
August 19, 1988									
Mine Drainage		26	37	8.1	0.91		1460	2.9	
Output A		25	20	<0.1	0.17	81	650	5.5	1.9
December 18, 1988									
Mine Drainage		29	38	9.2	0.80		1710	3.0	
Output A		28	31	8.6	0.62	23	1710	3.4	4.6
February 21, 1989									
Mine Drainage		27	32	9.3	0.56		1860	3.0	
Output A		22	12	4.5	<0.01	100	1690	5.1	1.1
May 6, 1989									
Mine Drainage		30	42	10.4	0.76		1760	3.0	
Output A		33	28	7.8	<0.05	100	1690	3.5	3.3
August 1, 1989									
Mine Drainage		32	43	9.4	0.75		1740	3.0	
Output A		31	39	5.2	<0.05	100	1700	4.1	1.1
December 3, 1989									
Mine Drainage		29	43	9.0	0.58		1700	3.0	
Output A		30	21	1.3	<0.05	100	1690	6.0	1.1

Table 2. Output concentrations, field measurements, flow rates, and mass removal data for Cell A from November 1988 to August 1989. Missing data represents output and/or mine drainage samples which were not collected on those dates.

Sample Number Sampling Date	OPA-106 19-Nov-88	OPA-108 01-Dec-88	OPA-201 18-Dec-88	OPA-303 21-Jan-89	OPA 02-Feb-89	OPA-404 21-Feb-89
<b>Output Concentration</b>						
Cu (mg/L)	0.540	0.630	0.620	0.612		<0.05
Fe (mg/L)	36.9	34.1	31.3	31.6		18.9
Mn (mg/L)	28.7	28.7	27.9	32.7		27.8
Zn (mg/L)	8.2	8.0	8.6	10.8		4.86
SO4 (mg/L)	1690	1720	1710	1670		1660
<b>Field Measurements</b>						
Output pH	3.3	3.4	3.4	3.3	3.3	5.1
Output Eh (mV)	535	625	665	740	633	540
Output Temp. (C)	2.0	9.0	8.1	6.7	4.0	1.5
Input Flow (L/min)	4.75	3.13	4.57	4.72	1.81	1.06
<b>Absolute Decrease</b>						
Cu (mg/L)	0.56	0.28	0.18	0.30		0.72
Fe (mg/L)	7.2	-6.0	6.8	-0.3		19
Mn (mg/L)	0.5	0.9	0.7	-7.5		-4.9
Zn (mg/L)	1.7	1.5	0.6	0.1		4.1
SO4 (mg/L)	60	10	0	10		120
<b>Change in pH &amp; Eh</b>						
pH (unit increase)	0.4	0.5	0.4	0.5	0.4	2.1
Eh (mV decrease)	100	65	18	10	35	180
<b>Percent Decrease</b>						
Cu (%)	51	31	23	33		100
Fe (%)	16	-21	18	-1		50
Mn (%)	2	3	2	-30		-21
Zn (%)	17	16	7	1		46
SO4 (%)	3	1	0	1		7
<b>Mass Removal Data</b>						
Cu (mg/day/m2)	210	68	64	110		59
Fe (mg/day/m2)	2700	-1500	2400	-110		1600
Mn (mg/day/m2)	190	220	250	-2700		-400
Zn (mg/day/m2)	630	370	210	37		340
SO4 (mg/day/m2)	22000	2400	0	3700		9900

Sample Number Sampling Date	OPA-407 05-Mar-89	OPA-504 19-Mar-89	OPA-510 01-Apr-89	OPA-604 16-Apr-89	OPA-608 06-May-89	OPA-704 21-May-89
<b>Output Concentration</b>						
Cu (mg/L)	<0.05	<0.05	<0.05	0.471	<0.05	0.580
Fe (mg/L)	18.5	23.3	17.1	31.3	28.3	31.0
Mn (mg/L)	27.8	24.0	30.1	31.6	32.5	41.0
Zn (mg/L)	4.76	0.28	4.58	8.5	7.8	9.4
SO4 (mg/L)	1570	1530	1670	1730	1690	1700
<b>Field Measurements</b>						
Output pH	5.5	6.5	5.4	3.9	3.5	3.8
Output Eh (mV)	260	130	465	630	600	600
Output Temp. (C)	1.8	7.1	6.5	10.0	10.0	16.5
Input Flow (L/min)	0.79	0.22	1.81	2.07	3.32	2.30
<b>Absolute Decrease</b>						
Cu (mg/L)		0.73	0.76	0.23	0.76	0.27
Fe (mg/L)		17	21	7.3	14	17
Mn (mg/L)		-1.8	0.0	-2.3	-2.5	2.7
Zn (mg/L)		8.0	5.2	1.3	2.6	1.1
SO4 (mg/L)		180	80	10	70	20
<b>Change in pH &amp; Eh</b>						
pH (unit increase)	2.6	3.5	2.4	1.2	0.5	0.5
Eh (mV decrease)	450	510	200	5	40	15
<b>Percent Decrease</b>						
Cu (%)		100	100	32	100	32
Fe (%)		42	56	19	33	35
Mn (%)		-8	0	-8	-8	6
Zn (%)		97	53	13	25	10
SO4 (%)		11	5	1	4	1
<b>Mass Removal Data</b>						
Cu (mg/day/m2)		12	110	36	200	48
Fe (mg/day/m2)		280	3000	1200	3600	3000
Mn (mg/day/m2)		-31	0	-370	-650	480
Zn (mg/day/m2)		140	730	210	670	200
SO4 (mg/day/m2)		3100	11000	1600	18000	3600

Table 2 (continued). Output concentrations, field measurements, flow rates, and mass removal data for Cell A from November 1988 to August 1989. Missing data represents output and/or mine drainage samples which were not collected on those dates.

Sample Number Sampling Date	OPA-708 01-Jun-89	OPA-804 16-Jun-89	OPA-807 22-Jun-89	OPA-810 29-Jun-89	OPA-814 05-Jul-89
<b>Output Concentration</b>					
Cu (mg/L)	<0.05	<0.05	<0.05	0.470	<0.05
Fe (mg/L)	26	25.8	20.6	29.8	20.6
Mn (mg/L)	34.2	33.6	33.5	34.4	34.3
Zn (mg/L)	6.3	4.44	2.15	7.4	2.79
SO4 (mg/L)	1680	1620	1610	1680	1600
<b>Field Measurements</b>					
Output pH	4.3	4.6	5.1	3.4	6.0
Output Eh (mV)	380	520	285	630	245
Output Temp. (C)	16.0	18.0	16.0	25	22
Input Flow (L/min)	2.83	1.73	1.25	1.66	0.38
<b>Absolute Decrease</b>					
Cu (mg/L)	0.88	0.76		0.24	0.71
Fe (mg/L)	20	22		15	20
Mn (mg/L)	0.9	-4.2		-6.7	-7.1
Zn (mg/L)	2.3	3.2		-0.4	3.7
SO4 (mg/L)	70	80		20	160
<b>Change in pH &amp; Eh</b>					
pH (unit increase)	1.4	1.6		0.4	3.0
Eh (mV decrease)	250	130		10	350
<b>Percent Decrease</b>					
Cu (%)	100	100		34	100
Fe (%)	43	46		34	50
Mn (%)	3	-14		-24	-26
Zn (%)	27	42		-5	57
SO4 (%)	4	5		1	9
<b>Mass Removal Data</b>					
Cu (mg/day/m2)	190	100		31	21
Fe (mg/day/m2)	4400	3000		2000	600
Mn (mg/day/m2)	200	-570		-870	-210
Zn (mg/day/m2)	510	430		-49	110
SO4 (mg/day/m2)	15000	11000		2600	4700

Sample Number Sampling Date	OPA-818 09-Jul-89	OPA-821 11-Jul-89	OPA-904 14-Jul-89	OPA-907 20-Jul-89	OPA-911 01-Aug-89
<b>Output Concentration</b>					
Cu (mg/L)	0.490	0.071	<0.05	0.490	<0.05
Fe (mg/L)	25.6	21.9	17.3	29.6	39.0
Mn (mg/L)	29.1	28.7	30.0	30.3	30.8
Zn (mg/L)	6.87	3.58	0.25	7.7	5.19
SO4 (mg/L)	1700	1640	1630	1730	1700
<b>Field Measurements</b>					
Output pH	3.2	5.5	5.7	3.4	4.1
Output Eh (mV)	590	385	210	560	225
Output Temp. (C)	20	18	17	18.5	16.5
Input Flow (L/min)	5.25	1.13	1.17	3.89	1.06
<b>Absolute Decrease</b>					
Cu (mg/L)		0.68	0.72		0.75
Fe (mg/L)		25	24		3.7
Mn (mg/L)		2.8	-0.3		1.4
Zn (mg/L)		5.3	8.7		4.2
SO4 (mg/L)		60	110		
<b>Change in pH &amp; Eh</b>					
pH (unit increase)	0.2	2.6	2.7		1.1
Eh (mV decrease)	70	280	390		450
<b>Percent Decrease</b>					
Cu (%)		91	100		100
Fe (%)		53	58		9
Mn (%)		9	-1		4
Zn (%)		60	97		45
SO4 (%)		4	6		2
<b>Mass Removal Data</b>					
Cu (mg/day/m2)		60	66		62
Fe (mg/day/m2)		2200	2200		300
Mn (mg/day/m2)		250	-27		110
Zn (mg/day/m2)		470	790		350
SO4 (mg/day/m2)		5300	10000		3300

Concentration decreases in the output water relative to the input water can be compared to the inlet flow rate, since the mine drainage concentrations are relatively consistent with time making the flow rate roughly proportional to loading (Table 2). Positive values indicate a decrease in concentration, whereas negative values indicate an increase in concentration.

Fe and Zn generally show a greater removal as the flow rate is decreased but Cu and Mn are not easily related. If one tries to choose an optimum flow below which the removal efficiency appears to be more consistent, the results for Cu and Zn provide the best number (Table 2). Below a flow of about 1.5 L/min, Cu is uniformly removed and below this flow appreciable Zn is always removed from the mine drainage. It appears that below 1.8 L/min, Mn is not removed from solution, and in fact, may be redissolved. If this is the case, the processes affecting Mn in a wetland system require further study. If metal removal occurs through sulfide formation, Cu removal may also occur at higher flow rates because copper sulfides are very insoluble. However, the Cu removal process is not consistent.

In Table 2, pH and sulfate removal values vary with flow. In these cases, there appears a general relationship of better removal of hydrogen ions and sulfate as the flow is decreased. Figure 1 shows the relationship between flow rate and the decrease in sulfate concentration. A linear regression analysis on flow rates below 2.3 L/min and the decrease in sulfate concentrations gives an  $R^2$  value of 82%.

In Figure 2, a plot of sulfate removal with Eh shows that as Eh decreases, generally greater amounts of sulfate are removed, presumably due to sulfate reduction. A linear regression on these data gives an  $R^2$  value of 77%. The relationships in Figures 1 and 2 also implies that Eh generally decreases with flow rate. Linear regressions on other sets of data result in much lower correlation coefficients.

These data indicate that processes in the substrate affecting pH, Eh, and sulfate concentration operate at much greater efficiencies below a certain flow rate. These three parameters are related to microbiological processes in the wetland. The product of these processes is dissolved sulfide. Dissolved sulfide has been measured at around 5 mg/L in Cell A. Sulfide may precipitate with and remove metals from solution. Microbial sulfate reduction processes are sensitive to the presence of oxygen, tying their efficiencies to lower Eh conditions. Higher flow rates may introduce more oxygen into the system than can be removed by microbial processes leaving Eh values high.

#### Relationships Between Mass Removal Data and Seasonal Cycles

To take advantage of our flow rates for optimizing treatment efficiency in other wetlands, conversion to

metal loading rates should be made. The resulting values apply to a wetland with mushroom compost as described above and a size of 18.6 m<sup>2</sup>. It is very possible that other substrates will have different loading rates. In addition, it is important to consider how the water is to penetrate, flow through, and be collected from the complete cross-sectional area of the substrate.

Mass removal data was calculated based on discussions with Hedin (pers. comm.) as follows:

$$([M_{md}] - [M_{op}])(FR)(CF)/(A)$$

where:

[M] = concentration of metal or sulfate  
 md = mine drainage  
 op = wetland output  
 FR = flow rate into wetland  
 CF = conversion factor = (1440 min/day)  
 A = area of wetland = (18.6 m<sup>2</sup>)

In Cell A, it has been found that transpiration and evaporation account for at most a 10 % reduction in flow between the inlet and outlet (Dietz, pers. comm. 1989). Consequently, it is assumed that the flow out equals the flow in and the resulting units are: mg/day/m<sup>2</sup>.

The mass of metal removed from solution per day per square meter of wetland has been calculated for samples analyzed and is also given in Table 2. Mass removal data indicate that there are some tendencies for greater metal removal rates and pH increases during the summer season than for the winter. However, as expected, Mn shows no trend.

These tendencies probably reflect the generally lower temperatures found in the wetland during the winter (Table 2). Lower temperatures should result in lower microbial activity in the substrate. Sulfate reducing bacteria, however, will still function at 3-4°C (Batal et al. 1989). With lower microbial activity, less metal removal is expected due to a slow down of the processes that the microbes mediate.

If mass removal data are compared with flow rates, it is not the case that the greatest removals of a pollutant occur at low flow. This is particularly evident for the Cu data. The reason for this is that the above equation multiplies the decrease by the flow rate, and at flow rates below 1.5 L/min, all of the Cu is essentially removed from solution. For the other metals, this effect of low mass removal at low flow, is not as prominent. This observation implies that a passive wetland system has to be operated with an obvious margin of safety to insure satisfactory removal results.

Other factors may be influencing the mass removal data trend with seasonal cycles besides seasonal changes and loading rate fluctuations. Mass removal

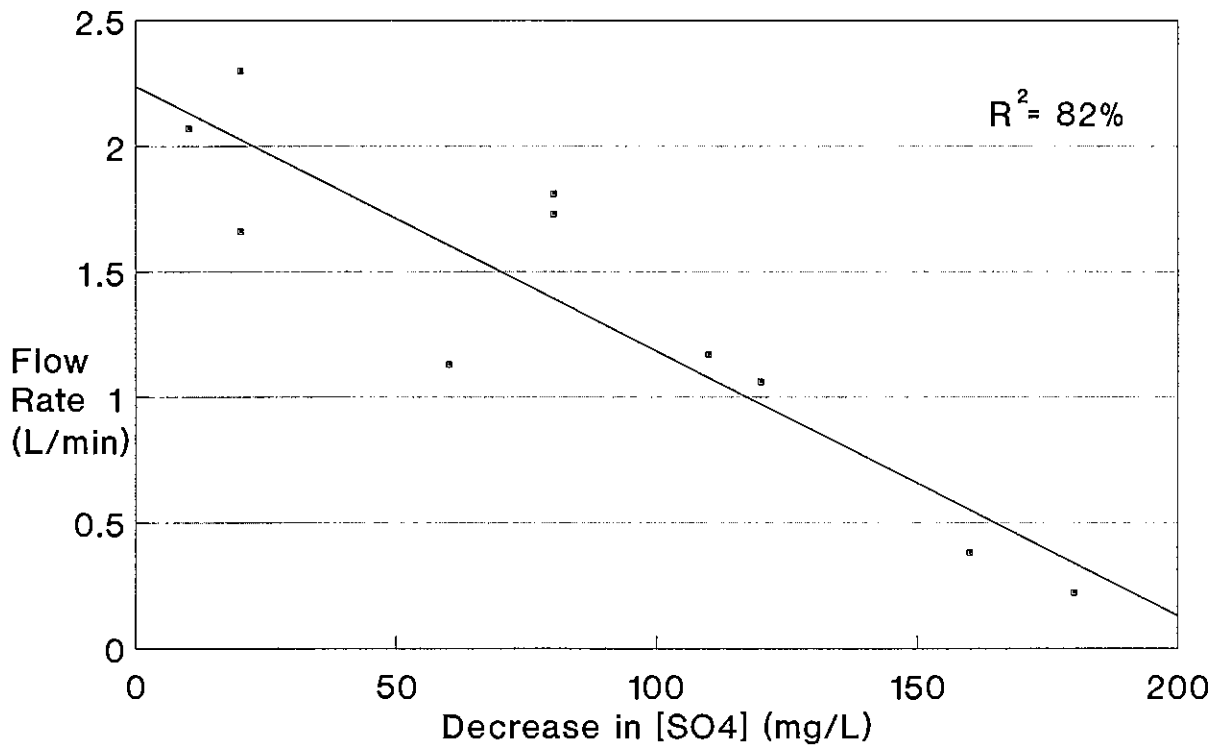


Figure 1. Decrease in sulfate concentration versus flow rate for Cell A.

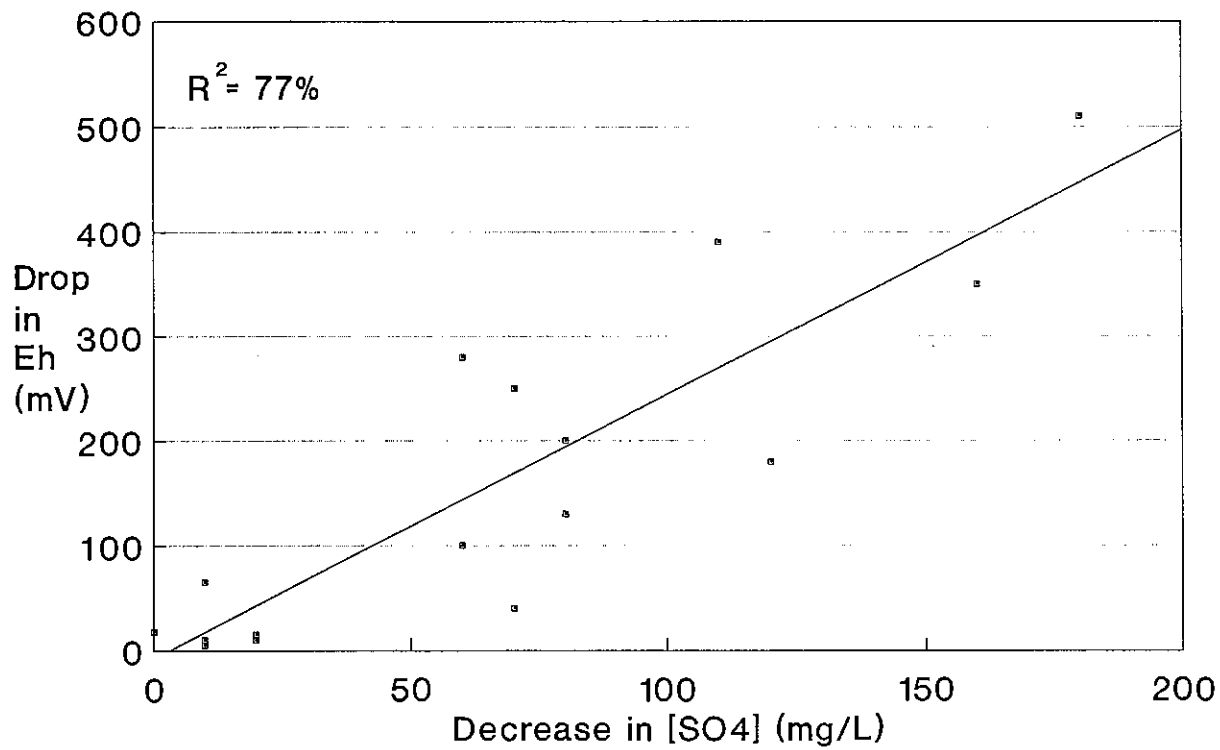


Figure 2. Decrease in sulfate concentration versus decrease in Eh for Cell A.

data for Cu, Zn and sulfate show similar fluctuating trends which are most evident in the spring. Some of the variation may be explained by a drop in metal removal efficiencies at higher loading rates as discussed above.

Another explanation for this variation may be large fluctuations in temperature which occur particularly in the spring. This is when some of the largest fluctuations in the mass removal data occur. Small changes in temperature of 3-4°C can cause the interdependent community of microbes operating in a reducing system to go dormant for several days until the microbes are able to readjust to the different temperature (Updegraff, pers. comm.). Such a variable could greatly affect seasonal trends, and it may produce the greatest instability in the fall and spring when temperature fluctuations are the largest. Determining if these factors can cause temporary failures certainly is a future research objective.

#### Summary

Research conducted at the Big Five wetland shows that the Eh of the effluent and the decrease in sulfate concentration is very responsive to changes in flow rate. Data indicate that processes in the substrate affecting pH, Eh, and sulfate concentration operate at much greater efficiencies below flow rates of about 1.5 L/min. These three parameters are related to microbial sulfate reduction in the wetland where the dissolved sulfide produced may precipitate with and remove metals from solution.

An important result of these tests is the delineation of metal removal efficiencies and pH increases with flow rate. Consistently good results for Cu, Fe and Zn removal from the Big Five mine drainage are obtained using a substrate of fresh mushroom compost with flow rates less than 1.5 L/min in a system with an area of 18.6 m<sup>2</sup>. This corresponds roughly to a loading rate of 100, 1000, and 4000 mg/day/m<sup>2</sup> for Cu, Fe and Zn, respectively. For Cu, decrease in concentration is not as strongly linked to flow rate as is found for sulfate and pH changes. This may be due to some other process, such as complexation by humic acids, that is also important to copper removal. For Mn, no removal with flow is detected and it appears that at low flows Mn is added to solution. This implies that if Mn removal is an objective it will have to be accomplished in later stages in the wetland after the pH is raised and the other heavy metals have been removed.

Mass removal data does not appear to be as good an indicator of how well a wetland is removing pollutants. This appears to be due to the need to maintain the loading rate at a value that is low enough to allow a margin of safety for the natural misfortunes that occur.

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