METAL REMOVAL EFFICIENCIES FROM ACID MINE DRAINAGE IN THE BIG FIVE CONSTRUCTED WETLAND ¹

by

Thomas R. Wildeman Steven D. Machemer Ronald W. Klusman Ronald R. H. Cohen Peter Lemke²

<u>Abstract.</u> 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 $(mg/day/m^2)$ 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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² Thomas R. Wildeman and Ronald W. Klusman are Professors of Chemistry and Geochemistry and Steven D. Machemer is a Graduate Student in the Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado 80401. Ronald R.H. Cohen is Assistant Professor of Environmental Sciences and Engineering Ecology and Peter Lemke is a Graduate Student in the Department of Environmental Sciences and Engineering Ecology, Colorado School of Mines, Golden, Colorado 80401.

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.

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 a]. 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 2 into three 6.1 m long cells with an area of 18.6 m.

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 HNO₃. 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 BaSO₄.

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 m².

		\$		\$		8		8	2.		flow
	Mn	dec.	Fe	dec.	Zn	dec.	Cu	dec.	SO4	pH	rate
				De	cembe	r 11,	1987				
Mine							1 0 0		1750	2 0	
Drainage	34	locaria e	32	100	10.6		1.02		1/50	2.0	
Output A	27	21	18	45	7.8	27	0.44	57	1560	4.0	4
				Fe	bruar	y 13,	1988				
Mine											
Drainage	28		28		8.2		0.89		1750	3.3	
Output A	27	4	18	36	5.9	28	0.14	84	1690	4.7	4
					May 3	1, 19	88				
Mine									1500	2.0	
Drainage	25		44		8.1		0.75		1500	3.0	
Output A	25	0	27	39	5.4	33	0.03	96	1330	4.3	4
100				A	ugust	19,	1988				
Mine											
Drainage	26		37		8.1		0.91		1460	2.9	
Output A	25	4	20	46	<0.1	100	0.17	81	650	5.5	1.9
				De	cenbe	r 18,	1988				
Mine			20				0 00		1710	2.0	
Drainage	29	1.020	38		9.2		0.80		1710	3.0	1 6
Output A	28	3	31	18	8.6	7	0.62	23	1/10	3.4	4.0
				Fe	bruar	y 21,	1989				
Mine					0.0		0 56		1960	3.0	
Drainage	27		36		9.5	= -	0.00	100	1600	5 1	1 1
Output A	22	19	12	63	4.5	52	<0.01	100	1050	5.1	***
					May	6, 19	89				
Mine	2.0				10.4		0 76		1760	3.0	
Drainage	30		42		10.4	25	10.70	100	1600	3.0	2.2
Output A	33	-10	28	33	7.8	25	<0.05	100	1030	3.5	5.5
				3	ugust	: 1, 1	1989				
Mine							0.75		1740	3.0	
Drainage	32		43		9.4	45	20.05	100	1200	4.1	1.1
Output A	31	3	39	9	5.2	45	<0.05	100	1700	4.1	
				De	cembo	er 3,	1989				
Mine					0.0		0 50		1700	3.0	
Drainage	29		43		9.0	14	<0.05	100	1690	6.0	1.1
Output A	30	-3	21	49	1.3	14	<0.05	100	1030	0.0	***

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
Output Concentrati Cu (mg/L) Fe (mg/L) Mn (mg/L) Zn (mg/L)	on 0.540 36.9 28.7	0.630 34.1 28.7	0.620 31.3 27.9	0.612 31.6 32.7		<0.05 18.9 27.8 4 86
SO4 (mg/L) Field Measurements	1690	1720	1710	1670		1660
Output pH Output Eh (mV)	3.3	3.4	3.4	3.3 740	3.3	5.1
Output Temp. (C) Input Flow (L/min) Absolute Decrease	4.75	9.0	8.1 4.57	4.72	4.0	1.06
Cu (mg/L) Fe (mg/L)	0.56	0.28	0.18	0.30		0.72
Mn (mg/L) Zn (mg/L)	0.5	0.9	0.7	-7.5		-4.9
SO4 (mg/L) Change in pH & Eh	60	10	0	10		120
Eh (mV decrease) Percent Decrease	100	65	18	10	35	180
Cu (%) Fe (%)	51 16	31 -21	23 18	33		100
Mn (%) Zn (%) SO4 (%)	2 17 3	3 16 1	2 7 0	-30 1 1		-21 46 7
Nass Removal Data Cu (mg/day/m2)	210	68	64	110		59
Fe (mg/day/m2) Mn (mg/day/m2)	2700 190	-1500 220	2400 250	-110		-400
2n (mg/day/m2) SO4 (mg/day/m2)	630 22000	370 2400	210	37 3700		9900
Sample Number Sampling Date	OPA-407 05-Mar-89	OPA-504 (19-Mar-89 (0PA-510 01-Apr-89	OPA-604 (16-Apr-89 (0PA-608 06-May-89	OPA-704 21-May-89
Sample Number Sampling Date Output Concentration Cu (mg/L)	OPA-407 0 05-Mar-89	OPA-504 (19-Mar-89 (<0.05	01-Apr-89	0PA-604 (16-Apr-89 (0.471	OPA-608 06-May-89 <0.05	0PA-704 21-May-89 0.580
Sample Number Sampling Date Output Concentration Cu (mg/L) Fe (mg/L) Mo (mg/L)	OPA-407 05-Mar-89 <0.05 18.5 27.8	<pre>OPA-504 (19-Mar-89 (<0.05 23.3 24.0</pre>	<pre>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>></pre>	0.471 31.3 31.6	<pre>OPA=608 06=May=89 </pre> <pre><0.05 28.3 32.5 </pre>	0.580 31.0 41.0
Sample Number Sampling Date Output Concentration Cu (mg/L) Fe (mg/L) Mn (mg/L) Zn (mg/L)	OPA-407 05-Mar-89 <0.05 18.5 27.8 4.76	<pre>OPA-504 0 19-Mar-89 0 <0.05 23.3 24.0 0.28</pre>	<pre>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>></pre>	0PA-604 0 16-Apr-89 0 0.471 31.3 31.6 8.5	<pre>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>></pre>	0.580 31.0 41.0 9.4
Sample Number Sampling Date Output Concentration Cu (mg/L) Fe (mg/L) Mn (mg/L) Zn (mg/L) SO4 (mg/L)	OPA-407 05-Mar-89 (0.05 18.5 27.8 4.76 1570	CODA-504 (0) 19-Mar-89 (0) 23.3 24.0 0.28 1530	<pre>>PA-510 (0) >1-Apr-89 (0) <0.05 (0) 17.1 (0) 30.1 (0) 4.58 (0) 1670 (0)</pre>	0PA-604 (0 16-Apr-89 (0 0.471 31.3 31.6 8.5 1730	2007-608 06-May-89 <0.05 28.3 32.5 7.8 1690	0PA-704 21-May-89 0.580 31.0 41.0 9.4 1700
Sample Number Sampling Date Output Concentration Cu (mg/L) Fe (mg/L) Mn (mg/L) Zn (mg/L) SO4 (mg/L) Field Measurements Output pH	OPA-407 05-Mar-89 (0.05 18.5 27.8 4.76 1570 5.5	<pre>>PA-504 (0 19-Mar-89 (0 <0.05 23.3 24.0 0.28 1530 6.5</pre>	<pre>>PA-510 0 D1-Apr-89 </pre> <0.05 17.1 30.1 4.58 1670 5.4	0PA-604 (0 16-Apr-89 (0 0.471 31.3 31.6 8.5 1730 3.9	2000-608 26-May-89 <0.05 28.3 32.5 7.8 1690 3.5	0PA-704 21-May-89 0.580 31.0 41.0 9.4 1700 3.8
Sample Number Sampling Date Output Concentration Cu (mg/L) Fe (mg/L) Mn (mg/L) Zn (mg/L) SO4 (mg/L) Field Measurements Output pH Output Eh (mV)	OPA-407 05-Mar-89 (0.05 18.5 27.8 4.76 1570 5.5 260	COLORA-504 COLOS 23.3 24.0 0.28 1530 6.5 130	<pre>>PA-510 0 D1-Apr-89 </pre> <0.05 17.1 30.1 4.58 1670 5.4 465	0PA-604 (0 16-Apr-89 (0 0.471 31.3 31.6 8.5 1730 3.9 630	2000-000 20.05 28.3 32.5 7.8 1690 3.5 600	0PA-704 21-May-89 0.580 31.0 41.0 9.4 1700 3.8 600
Sample Number Sampling Date Output Concentration Cu (mg/L) Fe (mg/L) Zn (mg/L) SO4 (mg/L) Field Measurements Output pH Output Eh (mV) Output Temp. (C) Input Flow (L/min)	OPA-407 05-Mar-89 (0.05 18.5 27.8 4.76 1570 5.5 260 1.8 0.79	2022-504 19-Mar-89 <0.05 23.3 24.0 0.28 1530 6.5 130 7.1 0.22	<pre>>PA-510 0 01-Apr-89 <0.05 17.1 30.1 4.58 1670 5.4 465 6.5 1.81</pre>	0PA-604 (0 16-Apr-89 (0 0.471 31.3 31.6 8.5 1730 3.9 630 10.0 2.07	OPA-608 06-May-89 <0.05 28.3 32.5 7.8 1690 3.5 600 10.0 3.32	0PA-704 21-May-89 0.580 31.0 41.0 9.4 1700 3.8 600 16.5 2.30
Sample Number Sampling Date Output Concentration Cu (mg/L) Fe (mg/L) Zn (mg/L) SO4 (mg/L) SO4 (mg/L) Field Measurements Output PH Output Eh (mV) Output Temp. (C) Input Flow (L/min) Absolute Decrease Cu (mg/L)	OPA-407 05-Mar-89 (0.05 18.5 27.8 4.76 1570 5.5 260 1.8 0.79	0PA-504 19-Mar-89 <0.05 23.3 24.0 0.28 1530 6.5 130 7.1 0.22 0.73	<pre>>PA-510 0 >1-Apr-89 </pre> <0.05 17.1 30.1 4.58 1670 5.4 465 6.5 1.81 0.76	0PA-604 16-Apr-89 0.471 31.3 31.6 8.5 1730 3.9 630 10.0 2.07 0.23	2007 2005 28.3 32.5 7.8 1690 3.5 600 10.0 3.32 0.76	0.580 31.0 9.4 1700 3.8 600 16.5 2.30 0.27
Sample Number Sampling Date Output Concentration Cu (mg/L) Fe (mg/L) Zn (mg/L) SO4 (mg/L) SO4 (mg/L) Field Measurements Output Eh (mV) Output Eh (mV) Output Temp. (C) Input Flow (L/min) Absolute Decrease Cu (mg/L) Fe (mg/L)	OPA-407 05-Mar-89 (0.05 18.5 27.8 4.76 1570 5.5 260 1.8 0.79	0PA-504 19-Mar-89 <0.05 23.3 24.0 0.28 1530 6.5 130 7.1 0.22 0.73 17 -1.8	<pre>>PA-510 0 >1-Apr-89 </pre> <0.05 17.1 30.1 4.58 1670 5.4 465 6.5 1.81 0.76 21 0.0	0PA-604 16-Apr-89 0.471 31.3 31.6 8.5 1730 3.9 630 10.0 2.07 0.23 7.3 -2.3	2007 2005	0PA-704 21-May-89 0.580 31.0 9.4 1700 3.8 600 16.5 2.30 0.27 17 2.7
Sample Number Sampling Date Output Concentration Cu (mg/L) Fe (mg/L) Zn (mg/L) SO4 (mg/L) SO4 (mg/L) Field Measurements Output Eh (mV) Output Eh (mV) Output Temp. (C) Input Flow (L/min) Absolute Decrease Cu (mg/L) Fe (mg/L) En (mg/L) Zn (mg/L)	OPA-407 05-Mar-89 (0.05 18.5 27.8 4.76 1570 5.5 260 1.8 0.79	0PA-504 19-Mar-89 <0.05 23.3 24.0 0.28 1530 6.5 130 7.1 0.22 0.73 17 -1.8 8.0	<pre>>PA-510 0 >1-Apr-89 </pre> <0.05 17.1 30.1 4.58 1670 5.4 465 6.5 1.81 0.76 21 0.0 5.2	0PA-604 16-Apr-89 0.471 31.3 31.6 8.5 1730 3.9 630 10.0 2.07 0.23 7.3 -2.3 1.3	DPA-608 06-May-89 <0.05 28.3 32.5 7.8 1690 3.5 600 10.0 3.32 0.76 14 -2.5 2.6	0PA-704 21-May-89 0.580 31.0 9.4 1700 3.8 600 16.5 2.30 0.27 17 2.7 1.1
Sample Number Sampling Date Output Concentration Cu (mg/L) Fe (mg/L) Zn (mg/L) SO4 (mg/L) SO4 (mg/L) Field Measurements Output Eh (mV) Output Eh (mV) Output Temp. (C) Input Flow (L/min) Absolute Decrease Cu (mg/L) Fe (mg/L) Mn (mg/L) SO4 (mg/L)	OPA-407 05-Mar-89 (0.05 18.5 27.8 4.76 1570 5.5 260 1.8 0.79	0PA-504 19-Mar-89 <0.05 23.3 24.0 0.28 1530 6.5 130 7.1 0.22 0.73 17 -1.8 8.0 180	<pre>>PA-510 0 >1-Apr-89 </pre> <0.05 17.1 30.1 4.58 1670 5.4 465 6.5 1.81 0.76 21 0.0 5.2 80	0PA-604 16-Apr-89 0.471 31.3 31.6 8.5 1730 3.9 630 10.0 2.07 0.23 7.3 -2.3 1.3 10	DPA-608 06-May-89 <0.05 28.3 32.5 7.8 1690 3.5 600 10.0 3.32 0.76 14 -2.5 2.6 70	0PA-704 21-May-89 0.580 31.0 9.4 1700 3.8 600 16.5 2.30 0.27 17 2.7 1.1 20
Sample Number Sampling Date Output Concentration Cu (mg/L) Fe (mg/L) Zn (mg/L) SO4 (mg/L) SO4 (mg/L) SO4 (mg/L) SO4 (mg/L) Output Temp. (C) Input Flow (L/min) Absolute Decrease Cu (mg/L) Fe (mg/L) Mn (mg/L) Zn (mg/L) SO4 (mg/L) Change in pH & Eh pH (unit increase) Eh (mV decrease)	OPA-407 05-Mar-89 30 4.76 4.76 1570 5.5 260 1.8 0.79 2.6 450	00000000000000000000000000000000000000	<pre>>PA-510 0 >1-Apr-89 </pre> <0.05 17.1 30.1 4.58 1670 5.4 465 6.5 1.81 0.76 21 0.0 5.2 80 2.4 200	0PA-604 16-Apr-89 0.471 31.3 31.6 8.5 1730 3.9 630 10.0 2.07 0.23 7.3 -2.3 1.3 10 1.2 5	>PA-608 >06-May-89 <0.05	0PA-704 21-May-89 0.580 31.0 9.4 1700 3.8 600 16.5 2.30 0.27 17 2.7 1.1 20 0.5 15
Sample Number Sampling Date Output Concentration Cu (mg/L) Fe (mg/L) Zn (mg/L) SO4 (mg/L) SO4 (mg/L) SO4 (mg/L) Output PH Output Eh (mV) Output Flow (L/min) Absolute Decrease Cu (mg/L) En (mg/L) SO4 (mg/L) Change in pH & Eh pH (unit increase) Eh (mV decrease) Percent Decrease Cu (%)	OPA-407 05-Mar-89 18.5 27.8 4.76 1570 5.5 260 1.8 0.79 2.6 450	<pre>>PA-504 (0 19-Mar-89 (0 > 23.3 24.0 0.28 1530 6.5 130 7.1 0.22 0.73 17 -1.8 8.0 180 3.5 510 100</pre>	<pre>>PA-510 0 01-Apr-89 <0.05 17.1 30.1 4.58 1670 5.4 465 6.5 1.81 0.76 21 0.0 5.2 80 2.4 200 100</pre>	0PA-604 (0 16-Apr-89 (0 0.471 31.3 31.6 8.5 1730 3.9 630 10.0 2.07 0.23 7.3 -2.3 1.3 10 1.2 5 32	DPA-608 D6-May-89 <0.05 28.3 32.5 7.8 1690 3.5 600 10.0 3.32 0.76 14 -2.5 2.6 70 0.5 40 100 133	0PA-704 21-May-89 0.580 31.0 9.4 1700 3.8 600 16.5 2.30 0.27 17 2.7 1.1 20 0.5 15 32
Sample Number Sampling Date Output Concentration Cu (mg/L) Fe (mg/L) Zn (mg/L) So4 (mg/L) Field Measurements Output pH Output Eh (mV) Output Eh (mV) Output Temp. (C) Input Flow (L/min) Absolute Decrease Cu (mg/L) Fe (mg/L) So4 (mg/L) Change in pH & Eh pH (unit increase) Eh (mV decrease) Percent Decrease Cu (%) Fe (%) Mn (%)	OPA-407 05-Mar-89 27.8 4.76 1570 5.5 260 1.8 0.79 2.6 450	0.05 23.3 24.0 0.28 1530 6.5 130 7.1 0.22 0.73 17 -1.8 8.0 180 3.5 510 100 42 -8	2007 201-Apr-89 20.05 17.1 30.1 4.58 1670 5.4 465 1.81 0.76 2.1 0.00 5.2 80 2.4 200 100 56 0	0PA-604 (0 16-Apr-89 (0 0.471 31.3 31.6 8.5 1730 3.9 630 10.0 2.07 0.23 7.3 -2.3 1.3 10 1.2 5 32 19 -8	DPA-608 D6-May-89 <0.05 28.3 32.5 7.8 1690 3.5 600 10.0 3.32 0.76 14 -2.5 2.6 70 0.5 40 100 3.3 -8	0PA-704 21-May-89 0.580 31.0 9.4 1700 3.8 600 16.5 2.30 0.27 17 2.7 1.1 20 0.5 15 32 35 6
Sample Number Sampling Date Output Concentration Cu (mg/L) Fe (mg/L) So4 (mg/L) So4 (mg/L) So4 (mg/L) So4 (mg/L) Field Measurements Output Eh (mV) Output Eh (mV) Output Eh (mV) Output Temp. (C) Input Flow (L/min) Absolute Decrease Cu (mg/L) So4 (mg/L) Change in pH & Eh pH (unit increase) Eh (mV decrease) Percent Decrease Cu (%) Fe (%) Mn (%) Zn (%) So4 (%)	OPA-407 05-Mar-89 30 4.76 1570 5.5 260 1.8 0.79 2.6 450	00000000000000000000000000000000000000	<pre>>PA-510 0 >1-Apr-89 </pre> <0.05 17.1 30.1 4.58 1670 5.4 465 6.5 1.81 0.76 21 0.0 5.2 80 2.4 200 100 56 0 53 5	0PA-604 16-Apr-89 0.471 31.3 31.6 8.5 1730 3.9 630 10.0 2.07 0.23 7.3 -2.3 1.3 10 1.2 5 32 19 -8 13 1 1	DPA-608 06-May-89 <0.05 28.3 32.5 7.8 1690 3.5 600 10.0 3.32 0.76 14 -2.5 2.6 70 0.5 40 100 33 -8 25 4	0PA-704 21-May-89 0.580 31.0 9.4 1700 3.8 600 16.5 2.30 0.27 17 2.7 1.1 20 0.5 15 32 35 6 10 1
Sample Number Sampling Date Output Concentration Cu (mg/L) Fe (mg/L) Mn (mg/L) SO4 (mg/L) SO4 (mg/L) SO4 (mg/L) Field Measurements Output Eh (mV) Output Eh (mV) Output Eh (mV) Output Eh (mV) Output Temp. (C) Input Flow (L/min) Absolute Decrease Cu (mg/L) SO4 (mg/L) Change in pH & Eh pH (unit increase) Eh (mV decrease) Percent Decrease Cu (%) Fe (%) Nn (%) Zn (%) SO4 (%) Mass Removal Data	OPA-407 05-Mar-89 30 30 30 30 30 30 30 30 30 30 30 30 30	00000000000000000000000000000000000000	<pre>>PA-510 0 >1-Apr-89 </pre> <0.05 17.1 30.1 4.58 1670 5.4 465 6.5 1.81 0.76 21 0.0 5.2 80 2.4 200 100 56 0 53 5	0PA-604 16-Apr-89 0.471 31.3 31.6 8.5 1730 3.9 630 10.0 2.07 0.23 7.3 -2.3 1.3 10 1.2 5 32 19 -8 13 10 2.6	OPA-608 06-May-89 <0.05	0PA-704 21-May-89 0.580 31.0 9.4 1700 3.8 600 16.5 2.30 0.27 17 2.7 1.1 20 0.5 15 32 35 6 10 1
Sample Number Sampling Date Output Concentration Cu (mg/L) Fe (mg/L) Mn (mg/L) SO4 (mg/L) SO4 (mg/L) SO4 (mg/L) Field Measurements Output Eh (mV) Output Eh (mV) Change in pH & Eh pH (unit increase) Eh (mV decrease) Percent Decrease Cu (%) Fe (%) Mass Removal Data Cu (mg/day/m2) Fe (mg/day/m2)	OPA-407 05-Mar-89 30 30 30 30 30 30 30 30 30 30 30 30 30	DPA-504 19-Mar-89 <0.05 23.3 24.0 0.28 1530 6.5 130 7.1 0.22 0.73 17 -1.8 8.0 180 3.5 510 100 42 -8 97 11 12 280	2002 2002 2005 2005 17.1 30.1 4.58 1670 5.4 465 6.5 1.81 0.76 21 0.0 5.2 80 2.4 200 100 56 0 53 5 110 3000	OPA-604 16-Apr-89 0.471 31.3 31.6 8.5 1730 3.9 630 10.0 2.07 0.23 7.3 -2.3 1.3 10 1.2 5 32 19 -8 13 10 1.2 5 32 19 -8 13 10 10 1.3 10 1.3 10 1.3 10 1.3 10 10 10 10 10 10 10 10 10 10	DPA-608 D6-May-89 <0.05 28.3 32.5 7.8 1690 3.5 600 10.0 3.32 0.76 14 -2.5 2.6 70 0.5 40 100 33 -8 25 4 200 3600	0PA-704 21-May-89 0.580 31.0 9.4 1700 3.8 600 16.5 2.30 0.27 17 2.7 1.1 20 0.5 15 32 35 6 10 10 1 48 3000
Sample Number Sampling Date Output Concentration Cu (mg/L) Fe (mg/L) Mn (mg/L) SO4 (mg/L) SO4 (mg/L) SO4 (mg/L) Field Measurements Output Eh (mV) Output Eh (mV) SO4 (mg/day/m2) Fe (mg/day/m2) Mn (mg/day/m2)	OPA-407 05-Mar-89 30 30 30 30 30 30 30 30 30 30 30 30 30	DPA-504 19-Mar-89 <0.05 23.3 24.0 0.28 1530 6.5 130 7.1 0.22 0.73 17 -1.8 8.0 180 3.5 510 100 42 -8 97 11 12 280 -31	2002 2002 2005 17.1 30.1 4.58 1670 5.4 465 6.5 1.81 0.76 21 0.0 5.2 80 2.4 200 100 56 0 53 5 110 3000 202	OPA-604 16-Apr-89 0.471 31.3 31.6 8.5 1730 3.9 630 10.0 2.07 0.23 7.3 -2.3 1.3 10 1.2 5 32 19 -8 13 10 1.2 5 32 19 -8 13 10 10 1.3 10 1.3 10 1.3 10 1.3 10 10 10 10 10 10 10 10 10 10	DPA-608 D6-May-89 <0.05 28.3 32.5 7.8 1690 3.5 600 10.0 3.32 0.76 14 -2.5 2.6 70 0.5 40 100 33 -8 25 4 200 3600 -650 -650	0PA-704 21-May-89 0.580 31.0 41.0 9.4 1700 3.8 600 16.5 2.30 0.27 17 2.7 1.1 20 0.5 15 32 35 6 10 10 1 48 3000 480

Table 2 (continued). Output concentrations, field measurements, flow rates, and mass removal data for Celt 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
Output Concentrat: Cu (mg/L) Fe (mg/L) Mn (mg/L) Zn (mg/L) SO4 (mg/L)	<pre><0.05</pre>	<0.05 25.8 33.6 4.44 1620	<0.05 20.6 33.5 2.15 1610	0.470 29.8 34.4 7.4 1680	<0.05 20.6 34.3 2.79 1600
Field Measurement: Output pH Output Eh (mV) Output Temp. (C) Input Flow (L/min)	4.3 380 16.0 2.83	4.6 520 18.0 1.73	5.1 285 16.0 1.25	3.4 630 25 1.66	6.0 245 22 0.38
Cu (mg/L) Fe (mg/L) Mn (mg/L) Zn (mg/L) SO4 (mg/L)	0.88 20 0.9 2.3 70	0.76 22 -4.2 3.2 80		0.24 15 -6.7 -0.4 20	0.71 20 -7.1 3.7 160
Change in pH & Eh pH (unit increase) Eh (mV decrease)	1.4	1.6	5	0.4	3.0
Percent Decrease Cu (冬) Fe (冬) Mn (冬) Zn (冬) S04 (冬)	100 43 27 4	100 40 -14 42		34 34 -24 -5	100 50 -26 57 9
Mass Removal Data Cu (mg/day/m2) Fe (mg/day/m2) Mn (mg/day/m2) 2n (mg/day/m2) S04 (mg/day/m2)	190 4400 200 510 15000	100 3000 -570 430 11000		31 2000 -870 -49 2600	21 600 -210 110 4700
Sample Number Sampling Date	OPA-818 OF 09-Jul-89 1	PA-821 0 1-Jul-89 1	PA-904 0 4-Jul-89 2	PA-907 00 0-Jul-89 00	PA-911 1-Aug-89
Output Concentration Cu (mg/L) Fe (mg/L) Mn (mg/L) Zn (mg/L) SO4 (mg/L)	0.490 25.6 29.1 6.87 1700	0.071 21.9 28.7 3.58 1640	<0.05 17.3 30.0 0.25 1630	0.490 29.6 30.3 7.7 1730	<0.05 39.0 30.8 5.19 1700
Field Measurements Dutput pH Dutput Eh (mV) Dutput Temp. (C) Input Flow (L/min)	3.2 590 20 5.25	5.5 385 18 1.13	5.7 210 17 1.17	3.4 560 18.5 3.89	4.1 225 16.5 1.06
Absolute Decrease Cu (mg/L) Fe (mg/L) Mn (mg/L) Zn (mg/L) SO4 (mg/L)		0.68 25 2.8 5.3 60	0.72 24 -0.3 8.7 110		0.75 3.7 1.4 4.2
Change in pH & Eh pH (unit increase) Eh (mV decrease)	0.2	2.6 280	2.7		1.1 450
rercent becrease Cu (%) Fe (%) Mn (%) Zn (%) SO4 (%)		91 53 60 4	100 58 -1 97 6		100 9 4 45 2
Mass Removal Data Cu (mg/day/m2) Fe (mg/day/m2) Mn (mg/day/m2) Zn (mg/day/m2) SO4 (mg/day/m2)		60 2200 250 470 5300	66 2200 -27 790 10000		62 300 110 350 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 chose 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 R² 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 2 described above and a size of 18.6 m. 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 = (118.6 m²)

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([M<sub>md</sub>] - [M<sub>op</sub>])(FR)(CF)/(A)
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where: [M] = concentration of metal or sulfate md = mine drainage op = wetland output FR = flow rate into wetland CF = conversion factor = (1440 min/day) $A = \text{area of wetland} = (18.6 \text{ m}^2)$

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/m².

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 3-4⁰C (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 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.



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



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

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 $3-4^{0}$ 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 (Updegraf, 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^2 . This corresponds roughly to a loading rate of 100, 1000, and 4000 mg/day/m² 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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