TREATMENT OF METAL CONTAINING GROUND AND SURFACE WATER IN PASSIVE SYSTEMS[1]

by

R.F. Mueller, W. Chatham, W. Drury, and F. Diebold[2]

Abstract. This study is part of a collaborative effort between Montana Tech and the Atlantic Richfield Company (ARCO) to find solutions for treating metal contaminated water (e.g., Cu, Zn, Cd, Mn, and Fe) from the Butte Hill as part of the remediation activities for the Clark Fork River Basin, in Southwestern Montana.

The field demonstration systems were constructed in 1995 and include anoxic horizontal flow gravel bed wetlands with cattail plants, horizontal flow gravel/organic substrate wetlands with cattail plants, and a vertical upflow gravel/organic substrate system without plants. Flow through operation was started in May 1996 with a total flow into the treatment systems of approximately 100 m^3/d. Hydraulic residence time for the test cells varies between 1.5 and 10 days. Results from the first year of operation including startup and performance through the winter with respect to hydrology, geochemistry, and microbiology within the test cells are presented. Metal removal efficiencies for the various technologies were determined.

Additional key words: Constructed wetlands, metal remediation, sulfate-reducing bacteria, field demonstration study.

Introduction

Storm water and ground water from Butte, Montana, are collected in the Butte Metro Storm Drain (MSD). The MSD channel is a tributary of Silver Bow Creek, which in turn is a tributary of the Clark Fork River. The Atlantic Richfield Company (ARCO) has initiated an investigation of the use of constructed wetlands for decreasing dissolved metal concentrations (Cu, Zn, Cd, Mn, Fe) within the MSD water before it enters Silver Bow Creek. The wetland demonstration study was intended to determine the relative efficiencies and capacities of three types of wetlands to treat this water over a three year time period. The geochemical, microbiological, physical, and hydrological properties of the various test cells are monitored. This is accomplished by sampling the water phase influents, effluents, and within the treatment cells.

Materials and Methods

Overall System Operation

Construction of the wetland demonstration site was completed in May 1996. The test cells were filled to design level with MSD water, and cattails (*Typha laifolia*) were planted with a spacing of 1 m centers. Cattails were chosen because of their dominance in all the nearby natural wetlands and their high primary production rates and good availability. Chunks of cattails, including several rhizomes and fresh shoots, were transplanted from a nearby natural wetland to the anoxic and aerobic wetland cells.

Flow through operation at design flow of 27 m^3/d to each of the test cells was started on May 27, 1996. Hydraulic residence time (HRT) for the test cells varied between 1.5 and 10 days. The operating conditions are presented in Table 1 and are further defined in Mueller *et al.*(1996). Two treatment trains are being tested (Figure 1):

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[2] Robert F. Mueller is Assistant Professor, of Chemistry and Geochemistry, William Drury is Associate Professor of Environmental Engineering, Frank Diebold is Professor of Chemistry and Geochemistry, and William Chatham is Assistant Professor of Chemistry and Geochemistry at Montana Tech of the University of Montana, 1300 West Park Street, Butte, MT 59701

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- Treatment train I consists of surge pond, followed by in parallel anoxic gravel cell 1, and anoxic gravel cell 4. The effluent from the two gravel cells are combined and serve as influents to aerobic cell 6.
- Treatment train II consists of surge pond, followed by in parallel anoxic compost/gravel cell #2, and anoxic compost/gravel cell #3. The effluent from the two compost/gravel cells is combined and serves as influent to aerobic cell 7.

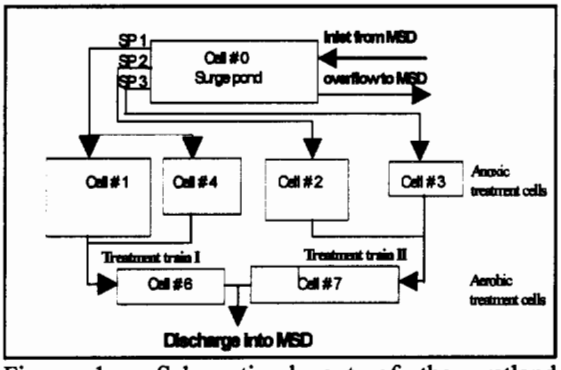

Figure 1. Schematic layout of the wetland demonstration system.

The effluents from the two aerobic treatment cells are combined and discharged back into the MSD channel. To avoid the discharge of nutrients during startup, water from the discharge pump was recycled to the surge pond for one month after startup before continuos discharge was begun July 1, 1996. The recirculation increased the supply of macro nutrients such as P and N fertilizing the plant growth in the anoxic gravel wetlands.

Chemical Sampling and Analyses

For chemical and microbiological data monthly influent and effluent samples were taken. Test cell effluent samples were taken at a depth of approximately 20 cm above the bottom of the outlet control structures to eliminate exposure to atmospheric oxygen and degassing of the sample.

Iron, manganese, zinc, copper, cadmium, lead, nickel, and arsenic, were measured in filtered (0.45 µm) and unfiltered samples by ICP.

Organic and inorganic carbon were analyzed on a Shimadzu total organic carbon analyzer; short chain fatty acids, phosphate, nitrate, and sulfate were analyzed in filtered samples on a Dionex ion chromatograph; hydrogen sulfide was analyzed using the methylene blue method (Cline, 1969), pH, and dissolved oxygen were measured on site. Sampling and analyses followed American Public Health Association, (1995).

Microbial Analysis

Acridine orange direct counts (AODC) were determined by staining the water sample with a 0.01 % acridine orange, filtered through a 0.22 µm pore size black filter, and counting by epi-fluorescence microscopy. Heterotrophic plate counts (HPC) were performed on R2A agar media. Colonies were counted after incubating for 48 hours at 25°C. General anaerobic bacteria (GAB) were determined by the most probable number (MPN) method using fluid thioglycolate medium (DIFCO) and incubating for 21 days at 25°C. Sulfate-reducing bacteria (SRB) were determined by the most probable number (MPN) method using Postgate media B and incubating for 21 days at 25°C (Postgate, 1984).

Table 1. Design parameters for the anoxic and aerobic test cells.

Unit cell #	flow rate [m^3/d]	flow dir.	HRT[1] [d]	lxwxd[2] [mxmxm]	volume [m^3]	porosity [-]	eff.Vol[3] [m^3]	comp./grav.[4] [-]
Surge pond	327	hor.	4.6	18x36x1.8	1512	-	1512	-
Anaerob 1	27.2	hor.	10	31x31x0.75	764	0.38	290	0/100
Anaerob 2	27.2	hor.	6	14x27x1.2	455	0.36	164	20/80
Anaerob 3	27.2	vert.	1.5	9x9x1.5	122	0.34	67	50/50
Anaerob 4	27.2	hor.	5	22x22x0.75	355	0.38	135	0/100
Aerobic 6	54.5	hor.	0.5		28[5]		28[5]	soil mix
Aerobic 7	54.5	hor.	1.6		90[5]		90[5]	soil mix

[1] Hydraulic residence time; [2] Length x width x depth;[3] Effective volume (total cell volume x porosity); [4] Compost/gravel ratio, 3/4" washed river gravel plus 20 % calcite gravel (3/4") was used; [5] Volume calculated assuming a 15 cm free water surface of the aerobic cells.

Results and Discussion

System Hydraulics

Hydraulic conductivities in the anoxic test cells ranged from 6 to >10 cm/s for the horizontal flow gravel wetlands (Table 2). The horizontal flow cell 2, with a 20/80 v/v% compost/gravel composition exhibited a significantly lower hydraulic conductivity than the pure gravel cells. Similar to other upflow passive treatment systems (Cohen, 1995), cell 3 experienced a drastic decrease in hydraulic conductivity after approximately 5 month of operation. Whether this decrease was due to settling and a subsequent decrease of hydraulic conductivity of the lower portion of the substrate or was caused by plugging of the inlet pipes cannot be concluded at this time. The flow rate through cell 3 decreased to approximately 1/3 of its original design flow.

Table 2. Anoxic test cell hydraulic conductivities.

Cell #	Composition v/v% compost/ gravel	k (cm/s)
1	0/100	> 6.0
4	0/100	> 10.2
2	20/80	≈ 0.8
3	50/50	< 0.005

Water evaporation rates were measured at 0.1m/month for cells #1 and #4 and 0.2 m/month for cell #2. Cell #3 was covered with geotextile for thermo insulation and no evaporation rates were measured.

Frost penetration was measured beginning January 1996 after several nights of subzero (F) temperatures. The maximum observed frost penetration was observed in test cell #2 at 22 cm depth. The minimum observed frost penetration was 3 cm measured in cell #1. The average frost penetration depth was 12 cm. A 40 cm high snow cover and a shallow ground water level aid in winter operation of the test cells.

Water Chemistry

Trace metal immobilization in the tested wetland treatment systems increased during the first two months of operation. The trace metal removal occurred almost completely in the anoxic test cells. The aerobic cells contributed very little to the overall trace metal removal. However, they were effective in oxydizing sulfides and organic carbon. Small amounts of iron and copper were removed from the aqueous phase in the surge pond (Table 3). The primary removal mechanism for iron in the surge pond, where high oxygen concentrations were present may have been the oxidation to Fe(III) and subsequent precipitation. The small amount of copper that was removed in the surge pond might have been due to coprecitation with the iron. Other tested constituents did not exhibit a significant change in concentrations between the MSD water and the surge pond effluent.

Approximately two months after startup, the trace metal removal efficiency in the anoxic treatment cells appeared to reach a steady level for zinc, copper, and cadmium. Similar trace metal removal efficiencies, based on filtered samples were observed in the two compost-amended anoxic treatment cells #2 and #3 (Table 3). Significant differences were apparent for the two anoxic gravel cells. Cell #1 has been operated at a HRT of 10 days, and cell #4 has been operated at a HRT of 5 days. The effluent zinc concentrations from cell #1 and #4 (unfiltered sample) for August, September and October 1996 ranged from 6-31 and 352-488 µg/l, respectively. A similar trend was observed for copper. Zinc and copper sulfides could be formed at similar effectiveness in both treatment cells, but due to the higher dilution rate in cell #4 the zinc sulfides were not effectively immobilized within the cell and were transported with the effluent to the subsequent aerobic cell. This transport phenomenon became more distinct with increasing flow rates (data not reported). No significant transport of undissolved metals from cell #1, #2 or #3 was observed. This might be due to the higher hydraulic residence time in cell #1 and the compost fraction of cells #2 and #3, improving the overall filtration effect for suspended solids of these treatment cells. Both anoxic gravel wetlands exhibited a significantly higher iron removal in comparison to the compost amended cells (Table 4). However, treatment train II was more effective in overall iron removal. The reason for this might be an increased activity of iron oxidizing bacteria in the aerobic cell #7 due to a higher dissolved oxygen concentration (data not reported). Manganese removal efficiencies were similar for all tested anoxic cells. The removal efficiency of iron and manganese increased due to the aerobic treatment in cell #7 where high dissolved oxygen concentrations were present but remained constant in cell #6 where oxygen was deficient.

Table 3. Trace metal effluent concentrations (µg/l) and the calculated removal efficiencies (based on concentration) from the anoxic and aerobic test cells. Reported concentrations are averages of August, September and October 1996.

	Cadmium			Copper			Zinc		
Cell #	avg.	stdev	η	avg.	stdev	η	avg.	stdev	η
MSD f[1]	66	15	-	271	79	-	17559	3874	-
MSD u[2]	56	19	-	414	192	-	15194	5407	-
0 f	68	14	-0.030	246	94	0.092	19019	4664	-0.083
0 u	57	21	-0.018	306	124	0.261	15424	5766	-0.015
1 f	1	2	0.982	2	3	0.993	71	56	0.995
1 u	0.1	0.3	0.998	2	2	0.993	17	14	0.999
2 f	1	1	0.982	2	2	0.993	93	49	0.994
2 u	1	1	0.982	3	2	0.990	41	21	0.997
3 f	1	2	0.982	2	2	0.993	156	141	0.990
3 u	0.3	1	0.995	4	3	0.987	32	25	0.998
4 f	1	1	0.982	3	2	0.990	153	120	0.990
4 u	1	1	0.982	16	32	0.948	420	68	0.973
6 f	1	1	0.982	6	6	0.980	121	80	0.992
6 u	1	1	0.982	27	30	0.912	237	151	0.985
7 f	1	1	0.982	13	4	0.958	129	91	0.992
7 u	0.4	1	0.993	20	13	0.935	19	9	0.999

Table 4. Iron, magnesium, and manganese effluent concentrations (µg/l) and removal efficiencies (η) from the anoxic and aerobic test cells. Reported concentrations are averages of August, September and October 1996.

	Iron			Manganese		
Cell #	avg.	stdev.	η	avg.	stdev.	η
MSD f[1]	27	53		11091	1580	
MSD u[2]	1257	516		10736	3129	
0 f	215	440	0.829	12426	2228	-0.157
0 u	2319	1138	-0.845	9644	2132	0.102
1 f	447	404	0.807	5653	3209	0.414
1 u	263	219	0.887	4836	3351	0.499
2 f	372	556	0.840	3519	2423	0.635
2 u	1715	386	0.260	5462	1435	0.434
3 f	105	92	0.955	7170	252	0.257
3 u	862	651	0.628	5175	3584	0.463
4 f	191	109	0.918	8235	1255	0.146
4 u	346	101	0.851	8181	1106	0.152
6 f	143	147	0.938	5462	1428	0.434
6 u	888	390	0.617	6687	1346	0.307
7 f	34	17	0.985	5952	898	0.383
7 u	320	199	0.862	4787	2134	0.504

[1] Reported values based on filtered samples. Removal efficiency η was based on filtered surge pond ($c_{A,SP,f}$) and filtered test cell effluent concentrations ($c_{A,\,e,f}$); ($\eta_{A,f} = 1 - c_{A,\,e,f}/c_{A,SP,f}$).

[2] Reported values based on unfiltered samples. Removal efficiency η was based on unfiltered surge pond ($c_{A,SP,u}$) and unfiltered test cell effluent concentration ($c_{A,\,e,u}$); ($\eta_{A,u} = 1 - c_{A,\,e,u}/c_{A,SP,u}$).

Sulfate Reduction

The anoxic gravel wetlands exhibited a higher sulfate removal efficiency than did the compost amended cells #2 and #3. The sulfate removal efficiency was significantly higher for gravel cell #1 (10 day HRT) as compared to cell #4 (5 day HRT), and 32% and 20%, respectively, of the incoming sulfate concentration was reduced. Both compost amended cells exhibited a similar sulfate removal efficiency of 14%.

Based on averaged data from August, a total concentration of 288 µmol/l of divalent trace metals (Zn+Cu+Cd) were measured in the influents to the anoxic test cells. Assuming a 1:1 stoichiometric ratio between divalent trace metals and sulfide, the measured averaged sulfate reduction rate (SRR) was significantly greater than the amount required to precipitate Cu, Cd, and Zn sulfides (Table 5). This was the case in all tested anoxic treatment cells. Hence, the trace metal removal could be explained due to metal sulfide precipitation. However, other sorption related processes might still be occurring simultaneously.

Increase in pH and Alkalinity

The pH increased significantly due to the treatment (Figure 2). The observed pH increase in the anoxic cells with subsequent aerobic treatment resulted in a final discharge of approximately one pH unit above the MSD water. Alkalinity increased significantly in all treatment cells, most likely due to the microbially produced inorganic carbon (Table 6). Little variation in alkalinity was observed over the report period. The alkalinity was highest in the effluent of gravel cell #1, indicating a high microbial activity in this cell. Both gravel wetlands produced a higher alkalinity than did the compost amended treatment cells.

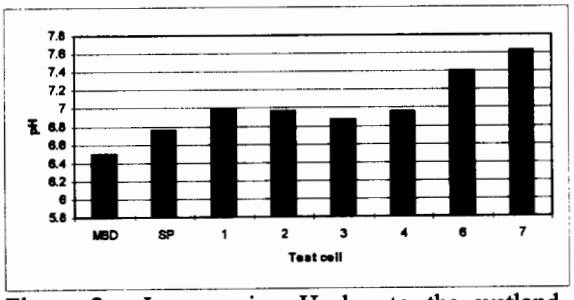

Figure 2. Increase in pH due to the wetland traetment of MSD water. The plotted pH values represent averages of July and August.

Table 5. Required and actual occurring sulfate reduction rate (SRR) to immobilize the combined trace metal influent rate of zinc, copper, and cadmium in the test cells.

cell #	metal influent rate[1] (mmol/m^{3}d)	required SPR[2] (mmol/m^{3}d)	SRR [3] (mmol/m^{3}d)
1	28.8	28.8	182
2	48	48	128
3	192	192	547
4	57.6	57.6	230

[1] Sum of the divalent trace metals influent rate ($c_{Me,in}$(II)/HRT).
[2] Required sulfide production rate (SPR) for stoichiometric metal sulfide precipitation.
[3] observed sulfate reduction rate (SRR).

Table 6. Average alkalinity data in mg $CaCO_3$/l from the test cell effluents from July and August. Data were calculated from inorganic carbon and pH analyses.

Cell #	average alkalinity Treatment train I	average alkalinity Treatment train II
MSD	63.33	63.33
0	65.83	65.83
1		257.55
2	131.15	
3	119.73	
4		164.35
6		230.57
7	152.07	

Kinetics of Trace Metal and Sulfate Removal

For estimation of reaction rates for metal and sulfate removal within the anoxic treatment cells, first order rate coefficients were used based on ideal plug flow reactor (PFR) behavior. Levenspiel (1993) introduced a finite effluent concentration that was applied to wetland analysis by Kadlic and Knight (1996).

$$\ln (c_{A,e} - c_A^*)/(c_{A,in} - c_A^*) = - k\Theta_t$$

where: $c_{A,in}$: influent conc. of constit. A [g/ m^3]
$c_{A,e}$: effluent conc. of constit. A [g/ m^3]
c_A^*: background conc. of A [g/ m^3]
r_A: reaction rate of constit. A [g/ m^{3}d]
Θ_t: HRT of the treatment cell[d]
k: first order rate coefficient [1/d]

The first order rate coefficient for sulfate removal was in the range of 0.03 to 0.06 d^{-1}. First order rate coefficients for zinc, copper and cadmium were in the range of 0.8-1.2, 2-15, and 0.7-2 d^{-1}, respectively. Concentration profiles were developed for the anoxic test cells based on the estimated first order rate coefficients and compared to actual measurements from various sample ports located inside the anoxic test cells. Reasonable correlations between observed and simulated data were observed (Figure 3). A well designed tracer test may help to evaluate and to predict species transport and reaction within the test cells.

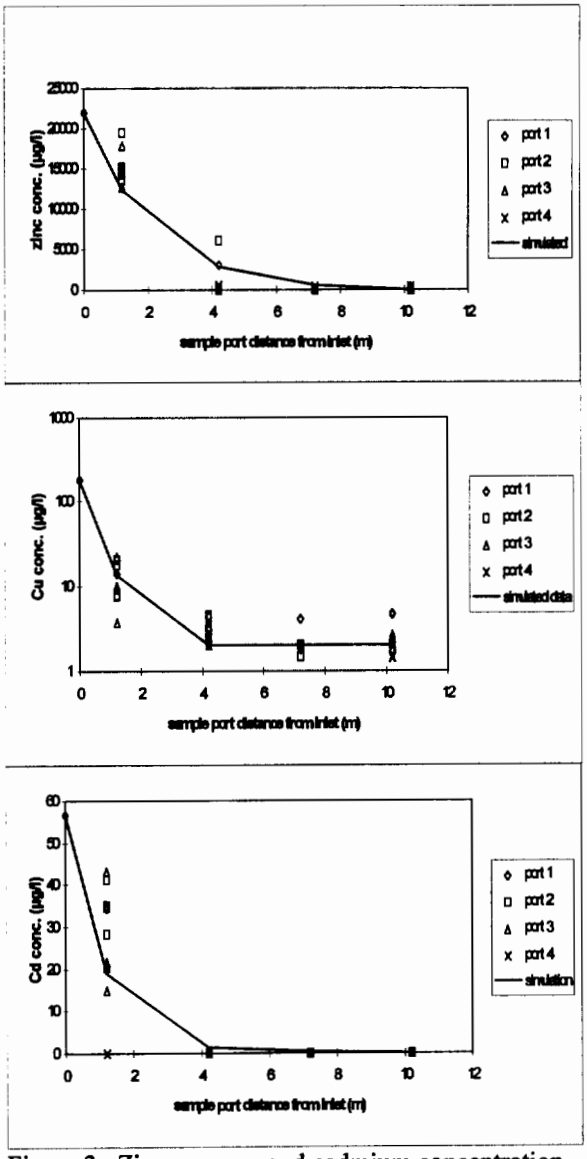

Figure 3. Zinc, copper, and cadmium concentration profiles (filtered acidified samples) within the anoxic treatment cell 2. The measured data was compared to a first order kinetic PFR model.

Nutrient Availability

Total organic carbon (TOC) was between 5 and 10 mg/l in the MSD water. The TOC concentration increased in all anoxic treatment cells (Figure 4). A similar effluent concentration was observed in the two anoxic gravel cells. Aerobic cell #6 reduced the TOC to approximately half of its influent concentration, aerobic cell #7 did not indicate an overall TOC removal. The final TOC discharge concentrations from treatment train I and II were not significantly different. The TOC measurements may indicate that the anoxic gravel cells were not carbon limited and the observed higher sulfate reduction rate in treatment train I as compared to II could possibly be explained by the greater availability of bioavailable organic carbon. Total dissolved phosphorous varied between 12 and 79 µg/l (data for July and August) in the surge pond effluent. All cell effluents exhibited an increase in dissolved phosphorous, indicating that phosphorous was non limiting in any of the treatment cells. The most significant phosphorous increase was observed from the cells with compost addition. Ammonia-nitrogen was present in the MSD water at a range of 0.2 to 1.1 mg-N/l. In August and September, the effluent ammonia concentrations of the two gravel cells #1 and #4 were below the detection limit of 0.05 mg/l. This may indicate a nitrogen growth limitation of the anoxic gravel cells and of the subsequent aerobic cell #6. Effluents of aerobic cells #6 and #7 were consistently below detection limit for ammonia-nitrogen.

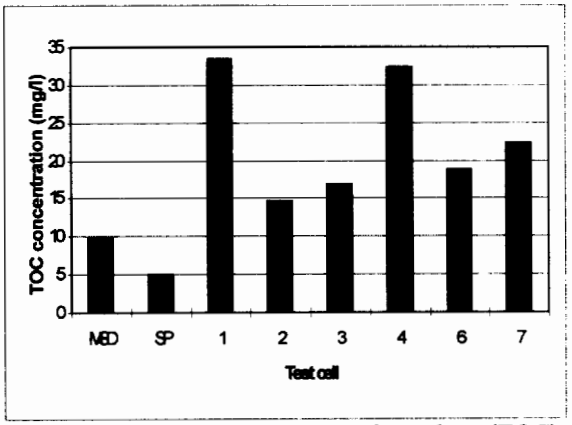

Figure 4. Change in total organic carbon (TOC) concentration due to the wetland treatment of MSD water. The plotted concentrations are averages of July and August.

Microbiology

The presence and activity of GAB as well as SRB are of importance to the performance of anoxic wetlands for metal remediation (Eger, 1992; Wildeman, 1993). The presence and activity of heterotrophic bacteria and algae is of importance for the removal of organic carbon and other macronutrients in the aerobic treatment cells (Portier, 1989; Wetzel, 1993). Hydrogen sulfide was produced in all four anoxic treatment cells and effluent concentrations ranged from 2 to 9 mg-$S^{=}$/l. Sulfate reducing bacteria were detected in all four anoxic treatment cells. The cell numbers for SRB range from 10^2 to 10^4 cell#/ml. Approximately 1% of the total cell number (AODC) in the anoxic cell effluents were viable SRB capable of growing between 10 and 20°C. The total number of organisms measured by the AODC method ranged between 10^5 and 10^7 colony forming units/ml.

Various organic substrates were tested for microbial sulfate-reduction in laboratory batch experiments. After incubation with solids obtained from the upflow treatment system, increased sulfate reduction was observed when acetate or butyrate (200 mg/l initial concentration) were added to the samples (data not reported). However, only acetate was detected in small concentrations up to 10 mg/l in the anoxic test cells.

Plant Recovery and Animal Activity

Approximately 90-95 % of the planted cattails recovered from the transplant in the anoxic cells. A lower recovery rate (70 - 80 %) was observed in the aerobic cells due to drowning or floating of some of the plants because of periodical occurring high water levels.

Ducks, pigeons, and a family of killdeers regularly visit the wetlands. A kingfisher has also been seen at the site. The surge pond, and the aerobic cells contain a number of aquatic beetles. Adult midges (Chironomidae) and damsel flies have been seen on the aerobic cells.

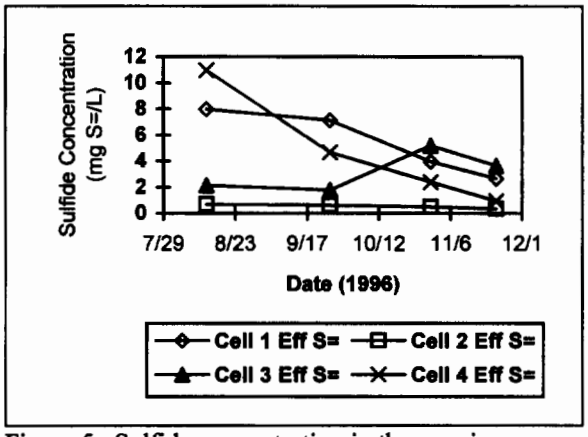

Figure 5. Sulfide concentration in the anoxic treatment cell effluents.

Summary

High removal efficiencies for zinc, copper, and cadmium were achieved in the tested anoxic passive treatment systems. Restricted flow was observed in the upflow system, possibly a result of plugging in the lower portion of this test cell.

Similar trace metal removal based on filtered samples was observed in all four anoxic treatment cells. Significant differences were apparent for unfiltered samples especially when comparing two anoxic gravel wetlands at different hydraulic residence times. Cell 1 has been operated at a HRT of 10 days and cell 4 has been operated at a HRT of 5 days. The effluent zinc concentration from cell 1 and cell 4 (unfiltered sample) for August and July 1996 ranged from 26-35 and from 328-494 µg/l, respectively. This may indicate that metal sulfides were formed at similar effectiveness in both treatment cells, but due to the higher dilution rate in cell 4, metal sulfides were not effectively immobilized within the cell and were transported with the effluent to the subsequent aerobic cell. This transport phenomenon became more distinct with increased flow rates. No significant transport of undissolved metals from cell 1, 2 or 3 was observed. This might be due to the lower dilution rate in cell 1 and overall filtration and sorption mechanisms due to the compost fraction of cells 2 and 3. No significant removal of zinc, copper, or cadmium was observed in the aerobic treatment cells. However, small amounts of iron and copper were removed in the surge pond.

Sulfate-reducing bacteria were present in all anoxic treatment cells, in the surge pond, and in

the MSD water. Hydrogen sulfide was produced in all anoxic treatment cells. Viable sulfate reducing bacteria made up 1% of the total number of viable + non viable organisms detected in the effluents of the anoxic treatment wetlands.

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