SESSION 9: CONSTRUCTED WETLANDS

Page No.

Acidic Mine Drainage Abatement in an Anaerobic Sub-Surface Flow Wetland Environment - Case History of the Treatment System at Corsica, PA.
Jonathan M. Dietz, Dennis M. Stidinger 531

Chemical Characterization of Iron Oxide Precipitates from Wetlands Constructed to Treat Polluted Mine Drainage.
Caryl L. Fish, Robert S. Hedin, Jonna Partezana 541

The Bark Camp Run Demonstration Constructed Wetlands: Findings and Recommendations for Future Design Criteria.
William W. Hellier 550

Manganese and Trace Metal Removal in Successive Anaerobic and Aerobic Wetlands.
F.J. Sikora, L.L. Behrends, G.A. Brodie, M.J. Bulls 560

The Use of Overland Flow Wetland Treatment Systems to Remove Nickel from Neutral Mine Drainage.
Paul Eger, Jon Wagner, Glenn Melchert 580

Treatment of Metal Contaminated Groundwater in Passive Systems: A Demonstration Study.
R. F. Mueller, D.E. Sinkbeil, J. Pantano, W. Drury, F. Diebold, W. Chatham, J. Jonas, D. Pawluk, J. Figueira 590

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ACIDIC MINE DRAINAGE ABATEMENT IN AN ANAEROBIC SUB-SURFACE FLOW WETLAND ENVIRONMENT - CASE HISTORY OF THE TREATMENT SYSTEM AT CORSICA, PA[1]

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Abstract. Wetland Treatment Systems (WTS) have been constructed over the past decade for the treatment of Acidic Mine Drainage (AMD). Potential benefits of anaerobic sub-surface flow treatment were initially identified from attempts to improve effectiveness of a surface flow wetland at the Jennings Environmental Education Center in western Pennsylvania (Dietz and Stidinger 1993) which, although not completely successful, resulted in acidity removal rates two to four times greater than pre-modification rates. This study was conducted to investigate the potential benefits of sub-surface flow design, which utilizes a sub-surface collection system, in comparison to conventional surface flow design. Two field-scale WTS, each containing anaerobic surface flow and sub-surface flow treatment cells (approximately 100 m^2 each), were constructed along an existing AMD discharge, near Corsica, Pennsylvania, with a 3-4 pH, 250-400 mg/L (as $CaCO_3$) acidity, 20-40 mg/L iron, 15-40 mg/L manganese and 10-30 mg/L aluminum. Sampling of the WTS included two elements: a weekly monitoring program from March 1992 through November 1992 to collect discharge water quality data; and a post-monitoring pore water sampling program conducted on December 8, 1992. Sub-surface flow design was found to provide statistically greater acidity removal with an average rate of 61.8 grams per day per square meter (GDM), in comparison to surface flow which had an average rate of 4.78 GDM, and provided effluent alkalinities greater than 100 mg/L (as $CaCO_3$) and pH greater than 6.5 at the flows and loadings evaluated. Removal rates for iron and aluminum removal of 3.02 and 2.48 GDM in the sub-surface flow design were also significantly greater than surface flow design which had removal rates of 1.89 and 0.20 GDM, respectively. Manganese removal was ineffective in both surface and sub-surface flow designs. Based on pore water results of two sub-surface flow units receiving different AMD flow and loading, an acidity removal rate of 25 GDM is recommended for future wetland treatment systems constructed with the sub-surface flow design evaluated in this study.

Key Words: Acidic mine drainage, passive treatment, wetland treatment, water quality, remediation

Key Phrases: Acidic Mine Drainage remediation utilizing passive (wetland) treatment systems.

Introduction

Wetland Treatment Systems (WTS) have been constructed over the past decade for the treatment of Acidic Mine Drainage (AMD). These WTS have achieved variable and at times inconsistent success at improving and meeting established effluent limits. The variable success of WTS is attributable to differences in design, size and treatment material. Although treatment success is variable, all constructed WTS have, at a minimum, been successful in reducing chemical costs associated with AMD treatment and pollutant loading to receiving streams.

Recent investigations by Hedin *et al.* (1991) have proposed design (sizing) criteria for surface flow compost WTS based on removal rates for iron, manganese and aluminum. In a study by Dietz and Stidinger (1993) on constructed surface flow wetlands, the removal of acidity was correlated with the removal of iron and aluminum, but

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did not find any relationship between acidity removal and manganese removal. Based on these relationships and the consistency of acidity removal in the different wetlands, Dietz and Stidinger (1993) recommended the use of acidity as a design criteria.

Potential benefits of a new WTS design were originally identified at a WTS constructed at the Jennings Environmental Education Center (Dietz and Stidinger 1993). The system was originally constructed as a surface flow system; however, due to poor performance, the WTS was modified by placing limestone and drainline in trenches, to promote greater subsurface flow. The modifications decreased acidity, iron and aluminum and resulted in acidity removal rates 2 to 4 times greater than surface flow WTS.

The following is a summary of several components of the study "Technical Investigation of the Abatement of Acid Mine Drainage in a Sub-surface Wetland Environment" (Dietz *et al.* 1993). This study was to investigate the potential benefits of this WTS design, which utilizes a sub-surface collection system, in comparison to conventional surface flow WTS design and position (i.e., before or after) of surface flow when used in combination with the sub-surface flow systems.

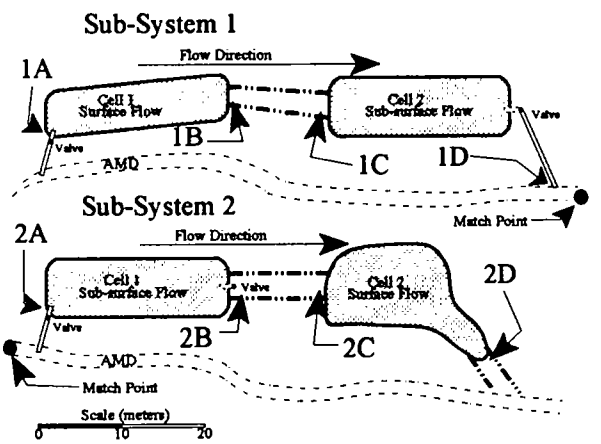

Figure 1. Plan view for the AMD wetland treatment system near Corsica, PA.

Wetland Design

The experimental system, designed to compare surface flow to sub-surface flow design and the two types of designs when used in combination, contained two wetland treatment systems, each containing a sub-surface and surface flow treatment cell. The order in the first treatment system (Sub-system 1) was surface flow followed by sub-surface flow. The order was reversed in the second treatment system (Sub-system 2) to permit evaluation of the two design combinations. Plan view of the two systems and cross-sections of surface flow and sub-surface flow units are contained on Figure 1 and 2.

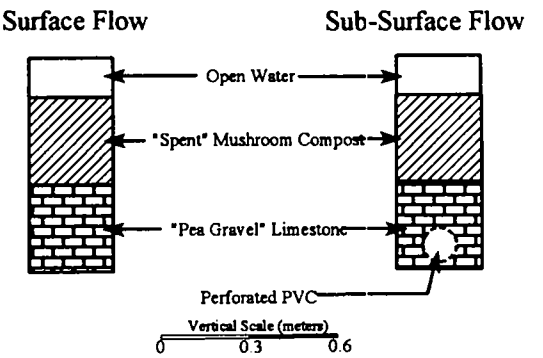

Figure 2. Typical cross-sections of units at the wetland treatment system near Corsica, PA.

The physical parameters of the treatment units consisted of at least 0.5 m of freeboard, a minimum slope of a 1:1 ratio for the inside and outside slopes, and 0.6 m berm width. The cell bottoms and banks of the treatment units were lined with clay found on-site during the excavation process. The surface area of Sub-system 1 totaled 303 m^2 with Cell 1 containing 113 ^{2}m and Cell 2 containing 130 m^2. The surface area of Sub-system 2 totaled 318 m^2 with Cell 1 containing 116 ^{2}m and Cell 2 containing 176 m^2.

After installation of the underdrain collection system in the sub-surface flow cells, "pea gravel" limestone purchased from Central Valley Aggregates was placed in each cell to a depth of 30 cm. The stone was covered with "spent" mushroom compost, obtained from Moonlight Mushrooms (Indiana, PA), to a depth of 30 cm. Once the compost was in place, the cells were allowed to fill and all areas disturbed by the construction activities were mulched and seeded with a grass/legume mix. After a two week waiting period the cells were planted by placing dug plant units, consisting of one mature cattail (*Typha latifolia*) and roughly a 30 cm

diameter of soil 25 cm thick, on approximately 0.6 m centers. Planting was completed in June of 1991.

Each sub-system received AMD from the same source and at the same flow rate of 11.4 L/min, which were controlled by intake gate valves. In addition to influent flow, gate valves and/or pipe weirs were located between treatment cells and at discharge locations to control and monitor flow through the WTS.

Sampling Program

The sampling program included several elements: a weekly monitoring program to collect discharge water quality data; and a pore water sampling program. The later program was conducted to evaluate wetland processes and functions. The different programs are discussed below.

Weekly Monitoring

For the weekly monitoring program, sampling stations were located in the two sub-systems to collect influent AMD, effluent from each sub-system and intermediate points between individual treatment units. Sampling stations, 1A through 2D on Figure 1, were located to sample influent, discharge, and intermediate locations in each sub-system at weirs and gate valves.

Sampling of the wetland was initiated in May of 1991; however, the severe drought during the early spring and summer of 1991 resulted in a loss of AMD flow in August. Flow did not return until early March of 1992 and normal water levels and sufficient AMD flow did not return until late March 1992. The weekly sampling was re-instated on March 25, 1992, continued through the spring, summer and fall of 1992 and was concluded on November 19, 1992. A total of 35 weekly samples were collected during the second year of the program.

Field measurements for temperature and flow were determined weekly at each sampling station. Temperature was measured with a YSI Model 51B Dissolved Oxygen meter. Estimates of flow were performed using a calibrated bucket (in liters) and a stop watch.

Water samples for laboratory analysis were collected weekly at each station, except influent stations in each sub-system, which were collected on alternating weeks. Samples were collected in 500 mL polyethylene bottles and, due to close proximity of the project (approximately 15 min.), transported to the laboratory in a cooler at the collected temperature. Water samples were analyzed for a number of parameters including: pH by electrometric method using an Orion (Ross) combination electrode; conductivity using a Markeson Model 10 and electrode cell; alkalinity and acidity by the potentiometric titration (H_2O_2) method; sulfate by the turbidimetric method; iron by the phenanthroline method; aluminum by the eriochrome cyanine R method; manganese by the periodate oxidation method; and calcium and magnesium (hardness), directly and indirectly, using the EDTA titrimetric method (APHA 1989 and HACH 1990).

Pore Water Monitoring

Pore water sampling was conducted on December 8, 1992 upon the completion of the weekly monitoring program. Pore water was extracted at the influent and effluent of each treatment pond at various depths from the compost layer; this was dependent on the depth of compost found at each sampling location. In general, pore water was extracted just below the surface, at 15 cm and 30 cm at each location. Cell 2 of Sub-system 2 contained only 15 cm of compost and could only be sampled at the surface and 15 cm depth.

Pore water samples were collected using a negative pressure apparatus that consisted of an 125 mL erlenmeyer flask, a hand held vacuum pump, and a variety of tubing, connectors and rubber stoppers. Collected pore water samples were numbered according to station and stored in air tight containers and transported to the laboratory. The samples were immediately analyzed (within 12 hours of collection) for Eh, pH, ferrous iron and sulfide. Eh was measured with an Orion combination redox electrode in a closed cell. Sulfide was measured on extracted water by the methylene blue method (APHA 1989). The remaining parameters, pH, alkalinity, acidity, total iron, ferrous iron, sulfate and conductivity were analyzed in accordance with procedures previously identified.

Results and Discussion

The results of the research project are summarized below. As reported earlier, a period of no flow

Table 1. Summary of averages and standard errors (in parenthesis) for water quality parameters of special interest monitored at the Corsica, PA wetland treatment system (n=35).

Sample Number	Lab pH	Alkal. mg/L	Acidity mg/L	Total Fe mg/L	Total Mn mg/L	Total Al mg/L	SO_4^{-2} mg/L	Ca mg/L	Mg mg/L
Sub-system 1									
Influent	3.41 (0.0002)	0 (0)	375 (96.8)	34.4 (12.7)	33.6 (6.80)	19.9 (8.55)	1579 (292)	315 (47.)	148 (33.)
Cell 1 Effluent	3.26 (0.0002)	0 (0)	340 (84.7)	20.1 (8.75)	31.8 (6.75)	18.4 (7.81)	1481 (294)	314 (61.)	144 (36.)
Cell 2 Influent	3.27 (0.0002)	0 (0)	232 (60.8)	15.8 (5.61)	32.4 (5.18)	10.8 (4.19)	1458 (285)	320 (47.)	134 (32.)
Cell 2 Effluent	6.76 (1e-7)	112 (21.0)	0 (0)	7.1 (5.44)	33.0 (4.29)	0.06 (0.03)	1351 (260)	377 (61.)	134 (35.)
Sub-system 2									
Influent	3.41 (0.0002)	0 (0)	375 (96.8)	34.4 (12.7)	33.6 (6.80)	19.9 (8.55)	1579 (292)	315 (47.)	148 (33.)
Cell 1 Effluent	6.62 (1.e-7)	112.3 (14.2)	0 (0)	11.13 (7.72)	38.21 (7.76)	0.055 (0.03)	1555 (288)	416 (67.)	160 (37.)
Cell 2 Influent	6.69 (1.e-7)	103.3 (13.7)	0 (0)	6.94 (6.04)	37.37 (7.62)	0.034 (0.02)	1537 (259)	422 (65.)	155 (34.)
Cell 2 Effluent	6.87 (8.e-8)	98.1 (16.5)	0 (0)	0.511 (0.32)	33.72 (5.93)	0.026 (0.02)	1496 (311)	408 (73.)	154 (40.)

occurred during the drought of 1991, which resulted in lowered water levels in several of the treatment units and caused air exposure to the mushroom compost and limestone layers. Therefore, only the data collected in the second year is included.

Effluent Water Quality

Discharge water quality is an important consideration in evaluating WTS performance and the ability of the treatment system to meet required effluent goals and regulatory limits (e.g., pH, iron, aluminum and manganese). The averages of the 35 samples collected for each of the monitoring stations for key parameters included in the sampling program are summarized in Table 1. To evaluate performance, effluent water quality from sub-systems and cells within sub-systems were statistically compared to influent water quality using an ANOVA procedure (Sokal and Rohlf 1981). A probability (p) of 0.05 was selected as the criteria for significant differences.

Temperatures monitored at stations within the sub-system averaged 13°C (55°F) during the monitoring program and varied over the course of the study from 4 to 26°C (40 to 79°F) in the treatment units. No significant effect of temperature was observed on discharge quality of any monitored parameter.

Three parameters that are closely related, pH, acidity and alkalinity, were similarly effected by the sub-systems. The pH in both Sub-systems increased significantly from influent pH of approximately 3 to effluent pH averages greater than 6.5, which is an almost complete removal of hydrogen ions by both sub-systems. The observed pH increases were associated with the sub-surface flow units, Cell 2 in Sub-system 1 and Cell 1 in Sub-system 2. Acidity followed a similar pattern as pH, significantly decreasing from influent concentrations of greater than 350 mg/L (as $CaCO_3$) to effluent aciditities of 0 mg/L in both sub-systems, with the majority of acidity decreases occurring in the sub-surface flow units. The remaining parameter, alkalinity, significantly increased across both sub-systems from 0 mg/L to approximately 100 mg/L (as $CaCO_3$) effluent alkalinity which entirely occurred in the sub-surface flow units of both sub-systems. Slight decreases

in alkalinity were observed across Cell 2, the surface flow unit in Sub-system 2, however, the decreases were not significant.

Two of three permit metals, iron and aluminum, decreased significantly across both sub-systems. Manganese, the third metal, did not significantly decrease across either sub-system; although slight increases and decreases of less than 2 mg/L were observed across individual units. Total iron decreased to approximately 7 mg/L in Sub-system 1 and less than 1 mg/L in Sub-system 2. With respect to individual treatment performance, total iron removal was similar across both units in each sub-system, ranging between 20 and 40 percent. A slight increasing trend in total iron was observed in effluent samples from sub-surface flow cells over the 35 weeks of the study, from initial concentrations of less than 5 mg/L to slightly greater than 10 mg/L. Total aluminum levels were found to decrease in both Sub-system 1 and 2 by almost 100 percent to effluent concentrations of less than 0.5 mg/L. Decreases in aluminum occurred in all treatment units, but predominately occurred in the sub-surface flow units and were directly related to the pH increases observed these units which is likely the result of aluminum pH dependent solubility (Stumm and Morgan 1981).

Calcium and magnesium were two metals monitored in the study to evaluate wetland processes. Calcium concentrations significantly increased across both sub-systesms by between 50 and 100 mg/L. The increases in calcium were associated with the sub-surface flow units in both sub-systems; no calcium concentration increases were observed across surface flow units. The observed calcium increases are likely the result of limestone dissolution in the sub-surface flow units, contributing at least 60 percent of the observed alkalinity increases from each sub-system. This alkalinity is important for the neutralization of acidity and hydrolysis and precipitation of metals. Conversely, magnesium concentrations were not significantly affected across either sub-system. Slight decreases of less than 15 mg/L were observed across Sub-system 1 and slight increases of less than 10 mg/L were observed across Sub-system 2, however, neither were significant. The magnesium data provide additional support that the increases in calcium were in fact due to limestone dissolution and not from some other process, such as evaporation.

Sulfate, monitored to evaluate processes within the wetland treatment system, was found to significantly decrease in Sub-system 1 by greater than 200 mg/L. Slight decreases of approximately 80 mg/L in Sub-system 2 were not significant. Sulfate exhibited decreases in both Cell 1 and Cell 2 in Sub-system 1 averaging decreases of approximately 100 mg/L in each cell. Seasonal increases and decreases in effluent sulfate concentrations were apparent in both sub-systems, however, influent sulfate data appeared to follow a similar seasonal change. The sulfate removal observed in the treatment units may reflect acidity removal processes (e.g., biological sulfate reduction) in the treatment systems which can be important for metal sulfide precipitation and alkalinity generation.

The effluent results indicate that the passive treatment systems remediate the majority of pollutants in the AMD. With respect to compliance levels associated with the mining industry, both sub-systems adequately reduced aluminum and raised pH to compliance levels. Only Sub-system 2, the sub-surface flow followed by surface flow configuration, adequately removed iron to levels below permit effluent limits. Neither sub-system lowered manganese which suggests additional treatment for manganese removal would be required to achieve compliance.

Removal Rates

Influent and effluent water quality data from each sub-system were used to determine loadings, removal rates and fluxes for each sub-system and units within each sub-system for iron, aluminum and acidity parameters. These three parameters were of interest since they were all significantly removed by the treatment systems. Loading rates, in grams per day (GPD) were calculated using influent concentration and flow data collected at each cell. Removal rates, also in GPD, were calculated using influent and effluent flow and concentration data. Average removal rates were adjusted to unit area rates or fluxes, in grams per day per square meter (GDM), using the surface areas of each unit.

Loading and removal rates for the sub-systems and individual units are contained in Table 2. The loading rates to the two sub-systems and surface flow unit, Cell 1 in Sub-system 1, and sub-surface flow unit, Cell 1 in Sub-system

2, were similar for all parameters, differing by less than 4 percent. Removal rates for each of the units were much more variable, differing by greater than 100 percent. A summary for each parameter is contained below.

Table 2. Average loading, removal, and flux rates for the Corsica, PA wetland treatment system.

Unit	Factor	Loading GPD	Removal Rate GPD	Flux Rate GDM
Sub-System 1				
Cell 1	Fe	528	214	1.89
	Al	295	22.5	0.20
	Acidity	5740	540	4.78
Cell 2	Fe	148	79.7	0.61
	Al	97.9	97.4	0.75
	Acidity	2170	3210	24.7
Total	Fe	528	338	1.12
	Al	295	187	0.62
	Acidity	5740	4760	15.7
Sub-System 2				
Cell 1	Fe	515	351	3.02
	Al	289	288	2.48
	Acidity	5530	7170	61.8
Cell 2	Fe	75.4	70.7	0.4
	Al	0.32	0.093	0.01
	Acidity	-1000	-42.7	-0.2
Total	Fe	515	465	1.46
	Al	289	288	0.91
	Acidity	5530	7030	22.1

Removal rates for acidity which reflect the addition of alkalinity to the effluent for Sub-system 2 were greater than Sub-system 1. The differences between sub-systems were not the result of differences in sub-system performance, but due to an uncontrollale loss of flow between Cell 1 and 2 of Sub-system 1, resulting in lower acidity loading and removal potential in the sub-surface flow unit (Cell 2). Removal rates adjusted for treatment area or fluxes for the sub-systems were similar, approximately 20 GDM, however, individual treatment unit fluxes were much more variable ranging from 0 to 60 GDM. As was indicated by the concentration results, acidity removal was predominately associated with the two sub-surface units. Fluxes for Cell 1 in Sub-system 2 (sub-surface flow) was 61 GDM, which was almost three times greater than the flux of 25 GDM for Cell 2 in Sub-system 1; however, the later unit received less than half the loading (2170 GPD vs. 6630 GPD). The surface flow unit from Sub-system 1 had a flux of 4.8 GDM which is similar to values obtained by other investigators (Dietz and Stidinger 1993 and Hedin *et al.* 1994) for anaerobic surface flow design. The removal rate for Cell 2 in Sub-system 2 is of limited value due to the absence of influent acidity.

Total iron removal rates were slightly greater in Sub-system 2, by slightly more than 100 GPD, than removed in Sub-system 1 which corresponds to slightly greater effluent iron measured from this sub-system (see Table 1). Total iron fluxes for Sub-system 2 were also slightly greater than Sub-system 1, 1.12 GDM versus 1.46 GDM, respectively. Fluxes were greatest in the first treatment units of both sub-systems and were coupled with the highest iron loadings. This relationship between iron removal and iron loading was alsc observed by Dietz and Stidinger (1993) in surface flow wetlands receiving various iron loadings.

Effluent total aluminum was essentially zero from both sub-systems, and differences in removal of aluminum, removal rates of 187 GPD for Sub-system 1 and 288 GPD for Sub-system 2, were due to previously discussed flow loss in Sub-system 1. Aluminum decreases across each sub-system were primarily associated with the sub-surface flow units, which had fluxes at least three times greater than the highest flux observed in the surface flow units, Cell 1 of Sub-system 1.

Pore Water Results

Pore water results from each treatment unit, average of influent and effluent samples, are summarized in Table 3. The pore water pH found in the compost of Cell 1, the surface flow unit in Sub-system 1, increased within the first several centimeters of compost depth from less than 4 to near 7. Cell 2, the sub-surface flow unit of Sub-system 1, did not have observable pore water pH increases until near the bottom of the compost layer which had

Table 3. Average of influent and effluent pore water results from the treatment units at the Corsica, PA wetland treatment system (n=2).

Cell	Depth cm	Eh mV	LAB pH	Alkal. mg/L	Acidity mg/L	Fe^{+2} mg/L	SO_4^{-2} mg/L	H_2S mg/L
Sub-System 1								
1	300	220	3.55	0	230	40.3	1000	0.84
	15	-275	6.45	460	0	16.7	1060	6.0
	30	-205	6.75	900	0	38.0	800	1.32
2	0	66.	4.41	2	244	7.7	785	0.84
	15	-168	4.49	2	236	10.5	1130	3.59
	30	-208	6.28	50	0	21.6	1250	0.78
Sub-System 2								
1	0	470	3.37	0	374	3.78	1350	0
	15	173	3.62	0	248	9.66	1300	0.55
	30	-55	4.20	0	332	15.0	1200	1.46
2	0	-67	6.53	159	0	25.5	1090	0.03
	15	-204	6.95	356	0	4.94	1190	3.21
	30	-197	7.11	826	0	5.46	955	0.67

pH levels near 6. Cell 1, the sub-surface flow unit of Sub-system 2, only had increases in pore water pH from slightly above 3 to approximately 4, less than a 1 unit pH increase. Similarly the increases in pore water pH in Cell 2 of Sub-system 1 were less than 1, however, surface water pH was well above 6 which did not allow for more substantial increases.

Pore water Eh, a measure of redox potential, decreased with depth in the compost in all units from values greater than 0 mV to less than -200 mV, except Cell 1 of Sub-system 2 which had decreases only to approximately -100 mV. The Eh decreases were fairly rapid occurring in the upper 15 cm of compost.

Acidity in pore waters tended to decrease with depth in the treatment units while alkalinity tended to increase with depth. Only pore waters from Cell 1 of Sub-system 2 contained acidity concentrations and no alkalinity at all depths. Surface flow units contained highest alkalinities in pore waters with maximum concentrations exceeding 800 mg/L. This is of particular interest for Cell 1 of Sub-system 1 since alkalinity was not measured in the effluent during the weekly monitoring program. Sub-surface flow units contained higher acidity concentrations and the lower alkalinity concentrations than surface flow units. This observed effect is likely the result of increased penetration of the AMD into the substrate, as a result of the underdrain systems, than would occur in surface flow design where diffusion across the water/compost barrier is relied upon.

Sulfate concentrations in the pore water of the two surface flow units were similar. Concentrations increased by less than 100 mg/L from surface concentrations to the 15 cm depth before decreasing to well below surface water concentrations at the 30 cm depth. Sulfate concentrations in the sub-surface flow units differed from each other and the surface flow units. Cell 2 of Sub-system 1 contained increasing concentrations of sulfate with depth, whereas pore water sulfate in Cell 1 of Sub-system 2 decreased by approximately 150 mg/L throughout the 30 cm compost depth. Sulfide

concentrations, the other sulfur form monitored, were detected at depths in the compost in all treatment units with maximum concentrations ranging between 2 and 8 mg/L. Maximum sulfide concentrations tended to occur at the middle depth of 15 cm.

The low Eh (less than -100 mV) and elevated pH (greater than 4) in pore waters collected from the treatment units indicate that conditions are conducive for biological sulfate reduction (Dietz 1989). Sulfate was found to decrease with respect to depth in several units which, in combination with the elevated sulfide concentrations, clearly indicates this process occurs in the units. The processes benefits in improving AMD quality are reflected in the higher pH and alkalinity observed in pore waters.

The differences in pore water data between surface flow and sub-surface flow design are apparent for all the parameters evaluated. Surface flow units contained higher pH, lower Eh, higher alkalinity and higher sulfide in pore waters than sub-surface flow units. The differences are likely the result of increased interaction of AMD with the compost layer in sub-surface flow units from directing the AMD through the compost with the underdrain system. The importance of this greater interaction is apparent in effluent results from the sub-surface flow units which had effluent higher in pH, lower in acidity, and higher in alkalinity than the surface flow unit.

Differences in sub-surface flow unit pore water Eh, pH and acidity were also observed. These differences are likely the result of differences in AMD loading to the two units, as identified in the previous section (see Table 2), where Cell 1 in Sub-system 2 received higher AMD loading than Cell 2 in Sub-system 1.

Sub-surface Flow vs. Surface Flow Comparison

A statistical analysis was conducted to compare water quality monitoring data from surface flow design (Sub-system 1 - Cell 1) and sub-surface flow design (Sub-system 2 - Cell 1) in order to evaluate the beneficial effects of the sub-surface flow treatment design over conventional surface flow design. The analysis consisted of comparing water quality monitoring data for individual parameters using an ANOVA procedure (Sokal and Rohlf 1981). Parameters included in this analysis were selected based on effluent requirements of wetland systems (i.e., pH, acidity, alkalinity, total iron, total manganese, and aluminum) and wetland processes (i.e., sulfate, calcium and magnesium).

The average pH discharged from the sub-surface flow design was significantly ($p<0.001$) higher, greater than 3 units, than the average pH discharged from the surface flow design. In comparison to surface flow, which discharged significantly ($p<0.001$) higher concentrations of acidity and no alkalinity, sub-surface flow discharged significantly ($p<0.001$) greater concentrations of alkalinity and no acidity. Iron and aluminum concentrations discharged by sub-surface flow were also significantly ($p<0.001$) lower than the surface flow units; iron and aluminum concentrations were approximately 10 mg/L and 20 mg/L lower, respectively. Conversely, manganese concentrations were significantly higher, approximately 6 mg/L, from sub-surface flow than surface flow. Calcium, analyzed to evaluate processes, was significantly different between the two designs. Calcium measured significantly ($p<0.001$) greater, approximately 100 mg/L, in the discharge from sub-surface flow than surface flow. The remaining two parameters, sulfate and magnesium, had averages that were slightly different between flow designs; however, the differences were not significant.

This comparison clearly indicates the anaerobic sub-surface flow design has superior AMD remediation capabilities than surface flow design for this type of AMD discharge. Water quality improvements were significantly better for all parameters evaluated except manganese, however, neither design afforded any measurable decreases in manganese concentrations. In addition, the superior effluent water quality results in higher removal rates for most of the parameters, except manganese, in sub-surface flow which would be reflected in reduced treatment area for sub-surface flow design. The improved effluent water quality from sub-surface flow may be, in part, the result of improved interaction of the AMD with the compost. In addition, the importance of higher calcium concentrations from sub-surface flow, which are the result of limestone solubilization, may be the result of improved contact of the AMD with the limestone layer.

Sub-System Comparison

A statistical analysis was also conducted, similar to the sub-surface flow and surface flow comparison, to compare water quality monitoring data from Sub-system 1 to Sub-system 2 to determine which configuration afforded better effluent water quality; see Table 1 for comparison of effluent means.

The average pH values discharged from the sub-systems were not significantly different. Both systems provided complete removal of acidity throughout the monitoring program. A slightly higher (approximately 14 mg/L) average alkalinity was discharged by Sub-system 1 in comparison to Sub-system 2; this was found to be significant ($p<0.005$). Sub-system 2 exhibited an average total iron of less than 1 mg/L, which was significantly ($p<0.001$) lower than the 7.1 mg/L average total iron exhibited by Sub-system 1. In addition, the average aluminum concentration from Sub-system 2 was significantly ($p<0.001$) lower than the level from Sub-system 1; however, in both sub-systems the average aluminum levels were well below 1 mg/L. The remaining metal analyzed, manganese, was not significantly different between the two sub-systems.

Sulfate, a process parameter, was significantly ($p<0.025$) different between the two sub-systems. On average, sulfate concentrations were approximately 150 mg/L lower in Sub-system 1 than in Sub-system 2. The remaining two parameters, calcium and magnesium, had averages that were slightly higher for Sub-system 2 than Sub-system 1; however, the differences were not significant.

The only effluent water quality parameter effected by placement of the sub-surface and surface flow units was iron. The Sub-system 2 configuration, sub-surface flow followed by surface flow, yielded iron concentrations significantly lower than Sub-sytem 1 and to levels necessary to meet compliance concentrations. This suggests sub-surface flow followed by surface flow will be the preferred configuration in a two cell treatment design.

Summary

Wetland design has been evolving over the past decade. Recent studies have begun to recommend sizing criteria that are intended to provide guidance in designing wetland systems (e.g., Hedin *et al.* 1994 and Dietz and Stidinger 1993), however, this design information has been limited to surface flow designs. The results from this research treatment project provided water quality and design information regarding sub-surface flow design. In addition, the study provided guidance with respect to placement of sub-surface flow and surface low treatment units when used in combination.

The water quality monitoring data clearly indicated that sub-surface flow design produces water quality that is superior to surface flow design for a number of parameters that include pH, iron, aluminum, acidity and alkalinity. Neither wetland design significantly removed manganese; however, manganese removal would not be expected in strongly reducing environments, as is found in compost wetland treatment systems, where solubility of manganese tends to increase (Stumm and Morgan 1981).

The water quality monitoring data also identified the appropriate alignment of a two cell system utilizing sub-surface and surface flow units. Water quality was similar between the two sub-systems for pH, aluminum, acidity and alkalinity. Effluent iron levels (approximately 0.5 mg/L) in Sub-system 2 were significantly lower than effluent iron levels (approximately 7 mg/L) in Sub-system 1 which indicates sub-surface flow followed by surface flow is the better alignment.

Processes in the wetlands important for remediating the high acidity in AMD were qualitatively evaluated. Alkalinity generating processes identified in the wetlands were sulfate reduction and limestone dissolution. Based on calcium increases in sub-surface flow units limestone dissolution accounted for greater than 60 percent of the alkalinity generated.

Acidity removal rates, identified by Dietz and Stidinger 1993 as the most reliable design parameter for determining size of wetland systems constructed for AMD treatment, were 24.7 GDM and 61.8 GDM in the two sub-surface flow cells. Lower pH, higher Eh, and higher acidities observed in pore water collected in the compost of the sub-surface flow cell in sub-system 2, which had a flux rate of 61.8 GDM, suggest the cell may have been overloaded. Therefore, a design criteria of 25 GDM for acidity removal, based on acidity flux measured in Cell

2 of Sub-system 1, is recommended for predicting size of future sub-surface flow wetland treatment systems.

The intent of the study was not to evaluate life expetancy of the sub-surface flow design. Life expetancy of sub-surface flow systems will likely be affected by a number of factors associated with the chemistry of the AMD, materials placed in the sub-surface flow system and design features (e.g., aerobic pre-treatment) intended to reduce excessive precipitation of metals in sub-surface flow systems. Long-term operational data from systems based on the above design guidance will be required to assess long-term effectiveness of the sub-surface flow design.

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CHEMICAL CHARACTERIZATION OF IRON OXIDE PRECIPITATES FROM WETLANDS CONSTRUCTED TO TREAT POLLUTED MINE DRAINAGE[1]

by

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Abstract. The passive treatment of abandoned mine drainage using wetlands will produce a significant amount of iron rich sludge which will require costly removal and disposal. An alternative to disposal may be the use of this iron oxide material as pigments which could defray some of these costs. In this research, iron deposits from five alkaline mine drainage wetlands were collected and a series of standard tests were run. The tests included loss on ignition, moisture, pH, acid soluble metals, oil absorption, and water soluble matter. The results of these tests were compared to those acheived using commercially available natural and synthetic iron oxides. The results indicate that iron oxides from constructed wetlands have chemical properties that are intermediate to those of natural and synthetic iron oxide products.

Additional Key Words: Acid mine drainage, constructed wetlands, iron oxides

Introduction

Passive methods of treatment for iron contaminated mine waters have been developed in recent years (Hedin et al. 1994). The principle technique used to treat this mine drainage is to pass the water through a constructed wetland, where the iron precipitates as iron oxide. Because passive methods are cost effective when compared to chemical alternatives (Brodie 1990), many private companies, public reclamation agencies, and non-profit conservation organizations are adopting this technology. Interest in passive techniques has been tempered, however, by concerns about the long-term costs of managing the iron oxide sludge that collects in the wetlands. It is anticipated that mine operators and reclamation groups will need to remove the metal-rich precipitates from passive systems every 5 to 20 years (the period depends on the design of the individual systems). Since the sludges are not classified as hazardous, they can be legally disposed of in an active mine backfill or in a public landfill. The costs associated with collecting and legally disposing of the iron oxide wastes, however, may be substantial.

The possible recovery and utilization of iron oxides from passive treatment systems has not been previously considered in detail. A significant iron oxide industry exists in the United States. In 1990, 123,000 mtons of iron oxides were

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produced for use as pigments in construction materials and coatings, as industrial catalysts, in foundry sands and in animal feeds. These iron oxides were produced from natural sources, by synthetic processes, and as a by-product of steel manufacturing. Natural iron oxides are produced by mining hemitite, geothite, or magnetite deposits. Synthetics are produced through the oxidation and neutralization of solutions containing ferrous or elemental iron, or as a by-product of analine production. Because synthetics are of higher purity than the natural iron oxides, they demand a higher price (Mauney 1994, Templeton 1990).

The purpose of this study was to evaluate precipitates from alkaline mine drainage wetlands as a potential source for iron oxide. The study focused on alkaline mine water (pH > 6.0) due to its faster precipitation rates, existing treatment sites, and potential for future wetlands construction. In Western Pennsylvania, constructed wetlands are currently being designed for several discharges that will precipitate more than 250,000 pounds of iron oxide per year. These wetlands will provide a large source of passively precipitated iron oxides.

Experimental

Sample Collection

Samples were collected during July 1995 from five alkaline mine drainage wetlands (Table 1) which were either natural or constructed wetlands used for the treatment of abandoned mine

Table 1:Descriptions of Sampling Sites

Site	Year	Builder	Design	Flow gal/min	Iron Conc. (mg/L) Influ.	Iron Conc. (mg/L) Efflu.	Substrate	Water Source	Coal Seam
Bubbler	1970	Unknown	Bore Hole	300	80	80	Wood	Deep Mine	Pgh.
Saint Vincent	1982	Boy Scout Troop	Natural	30	80	5	Soil	Deep Mine	Pgh.
Cedar Grove	1989	Natural Resource Conservation Service	Settling Pond 2-3 Wetlands LS Cell	41.2	92	41	Clay	Deep Mine	Pgh.
Howe Bridge	1991	Mill Creek Coalition	ALD Ditches 2 Ponds	34	265	185	Clay LS SMC	Abandoned Well	Clarion
Morrison	1990	Glacial Mining Company	ALD Ditch Settling Pond 2 Cells	1.7	151	56	Clay Manure	Surface Mine	Clarion
Tennessee	1992	Confidential Company	Pump Discharge Ditch	750	45	<1	Clay	Surface Mine	Sewanee

Pgh. - Pittsburgh
LS - Limestone
SMC - Spent Mushroom Compost
ALD - Anoxic Limestone Drain

drainage. Four of these sites (Saint Vincent, Cedar Grove, Howe Bridge, and Morrison) are located in western Pennsylvania. The Tennessee wetland is located near Chattanoga, TN. A sixth site (locally known as the Bubbler) was a wooden weir receiving mine drainage from a bore hole. It was chosen to determine the effect of precipitation in a non-vegetative area.

In each wetland site, three sampling areas were chosen: one close to the influent point of the wetland, one in the center of the wetland, and one near the effluent point of the wetland. A flow of water was present at each sampling point. Grab samples of the solid iron oxide precipitates were collected and placed into two gallon polyethylene bags. Two bags were collected at each sampling area. Each bag was filled with precipitate and water from one third to one half of its capacity. The Bubbler sample was taken directly from the first and second sections of the weir.

Commercial Iron Oxides

Samples of commercial iron oxides were obtained from the Bayer Corporation, (Pittsburgh, PA) and Hoover Color Corporation (Hiwasee, VA). The Bayer samples, Bayferrox 130M and Bayferrox 940, were synthetics produced by the analine process. The Hoover samples, 202RS Raw Sienna and 308BS Burnt Sienna, were natural iron oxides.

Sample Preparation

All samples were air dried in a greenhouse (maximum daytime temperatures 38° - 47° C) for 5-7 days. Once dried, the samples were crushed to a powdery consistency using a pestle. Most of the plant debris was removed by passing the samples through a 0.850 mm The sieved material was then further ground to pass through a 0.425 sieve. The fine material resulting from this sieving was placed in polyethylene bags and sealed for future use.

Analytical Methods

American Standard Test Methods (ASTM) procedures for pigments were done in duplicate to test the precipitates (Table 2) and the commercial iron oxide.

Table 2: ASTM Pigment Methods

Designation	**Title**	**Procedure**
D 1280-84	Standard Test Methods for Common Properties of Certain Pigments	4. Loss on Ignition and Ash 5. Matter Soluble in Water 6. Hydrogen IonConcentration*
D 280-81	Standard Test Method for Hygroscopic Moisture (and Other Matter Volatile Under the Test Conditions) in Pigments	Method A-For Pigments that do not Decompose at 110°C
D 1483-84	Standard Test Method for Oil Absorption of Pigments by Gardner-Coleman Method	
D 185-84	Standard Test Method for Coarse Particles in Pigments, Pastes, and Paints	Insoluble Dry Pigments, Except Metallic Aluminum and Bronze Powders

* Revisions in this method are noted in text.

Revisions were made to method D 1280-84 (Procedure 6 - Hydrogen Ion Concentration) upon consultation with an iron oxide manufacturer. The electrode used was an Orion Ag/AgCl Sure-Flow Electrode, Model number 9172BN. First, the cool sample solution was stirred with a glass stir rod sixty times. It was then allowed to settle for two minutes. After that time, the electrode was placed into the sample, stirred slightly and allowed to sit for an additional two minutes. The pH reading was taken after the two minute wait.

Metal Analysis

Sample Digestion. Each solid sample was digested by adding 100 ml of concentrated nitric acid (69.0-70.0% Baker Analyzed Nitric Acid) to a weighed portion of the precipitate in a 400 ml beaker and heated on a hot plate to induce boiling. The solution was reduced to 25 ml or less and filtered through Whatman 40 ashless filter paper to remove the acid insoluble material from the solution. The residue was then air dried and weighed to determine the percentage of acid insoluble found within the iron oxide sample. During filtering, the solution was transferred into a volumetric flask and diluted to 100 ml. After dilution, the flasks were sealed, labeled, and placed into a 3-5 °C refrigerator for storage.

Analysis. The sample digestates were analyzed for iron and twelve trace metals - cobalt, nickel, lead, aluminum, calcium, manganese, chromium, magnesium, sodium, zinc, copper and cadmium. The analysis was done using the inductively coupled plasma atomic emission spectrophotometer (ICP-AES) (Varian Liberty 200). All of the samples were analyzed in duplicate on the ICP. A standard curve for each element was determined at the beginning of each run using two multi-element standards.(Table 3) Since the ICP is linear over several orders of magnitude only two standards were necessary. The standard concentrations were determined from trial runs with representitive precipitated iron oxide. Wavelengths for each element were chosen to minimize interference from the high concentrations of iron.

Table 3:Elemental Wavelengths and concentrations of Standards

Element	Wavelength (nm)	Standards (ppm)
Co	345.350	1,10
Ni	352.454	1,10
Pb	368.348	1,10
Al	396.152	1,10
Ca	317.933	50,100
Mn	257.610	5,10
Fe	260.709	100,500
Cr	267.716	1,10
Mg	279.553	5,100
Na	588.995	5,10
Zn	213.856	1,10
Cu	324.754	1,10
Cd	228.802	1,10

A control check was also run for each set of samples. To analyze for iron, the samples were diluted 1 to 100.

Results and Discussion

Pigment Tests

The dried and sieved (0.425 mm sieve) precipitates were subjected to a variety of pigment tests similar to those used in the pigment industry to test the commercial iron oxide. The results from these tests on the wetland precipitate are shown in Table 4. The results from commercial iron oxide are given in Table 5. Loss on ignition for the wetland precipitates is in the same range as the yellow iron oxide (Bayferrox 940) and much higher than the red iron oxide (Bayferrox 130M). Since this test is in part an indication of the purity of the iron oxide, it is encouraging. The oil absorption test is also encouraging since this is an indication of the suitability of the precipitates pigments in paint applications. For the most part the wetland precipitates are very similar to the commercial iron oxides in terms of oil absorption.

Table 4: Pigment Tests for Wetland Precipitates

	Bubbler	Saint Vincent	Cedar Grove	Howe Bridge	Morrison	Tennessee
0.850 Sieve (% retained)		$3.16^{0.23}$	$11.56^{5.76}$	$20.08^{13.99}$	$17.14^{12.19}$	41.68^{nd}
Ignition Loss (% lost)	$13.74^{0.04*}$	$16.82^{2.13}$	$16.83^{0.35}$	$16.68^{0.31}$	$16.98^{0.17}$	$14.79^{0.95}$
Soluble Matter (%)	$0.80^{0.09}$	$1.00^{0.05}$	$0.95^{0.05}$	$1.00^{0.09}$	$0.36^{0.10}$	$0.65^{0.11}$
pH	$6.38^{0.04}$	$6.82^{0.06}$	$6.94^{0.07}$	$5.26^{0.13}$	$6.06^{0.42}$	$7.20^{0.11}$
Oil Absorp. (%)	$118.80^{2.88}$	$83.90^{7.91}$	$88.60^{2.14}$	$81.40^{10.47}$	$81.19^{3.63}$	$65.50^{10.24}$
Moisture (%)	$9.08^{1.76}$	$5.17^{0.54}$	$8.25^{1.65}$	$8.74^{4.12}$	$2.90^{0.40}$	$6.24^{3.72}$
0.045 mm sieve (% retained)	21.00^{nd}	$17.33^{6.87}$	$10.40^{10.07}$	$18.60^{16.68}$	$10.85^{11.04}$	$9.12^{5.31}$

Superscripts are 95% confidence limits

Table 5: Pigment Tests for Commercial Iron Oxide

	Bayferrox 130M	Bayferrox 940	Hoover 308BS	Hoover 202RS
Ignition Loss (% lost)*	0.6	13		
Soluble Matter (%)*	0.2	0.25		
pH	$6.47^{0.09+}$	$4.1^{0.02}$	$7.07^{0.12}$	$6.97^{0.02}$
Oil Absorption (%)	$37.84^{0.84}$	$89.4^{0.72}$	$64.1^{3.43}$	$45.9^{6.09}$
Moisture (%)*	0.4	0.25		
0.045 mm sieve*	0.002	0.04	0.1	0.05

*Taken from product literature
+Superscripts are 95% Confidence limits

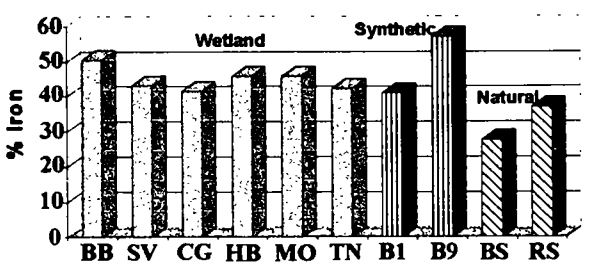
The meaning of the two sieve tests should be clarified. The 0.850 mm test is not a pigment test but a measurement of the miscellaneous material that is found in the wetland precipitates and is removed with a large size sieve. This material included leaves, grass and other biotic material. The 0.045 mm test is a critical test for the pigment industry since the particle size must be consistent to provide consistent blending by the customers. However, it should be noted that this is a test for final product iron oxide that is sold to the customer and the wetland precipitates were not processed except in a rudimentary fashion. Further processing (i.e. grinding) would certainly decrease the values for this test.

The final two tests (moisture and water soluble matter) also have much higher values for the wetland precipitates than the commercial iron oxide. Once again the results from these tests would change considerable with some simple processing such as rinsing the precipitates and then more thoroughly drying them.

Metals Analysis

The results of the metal analysis for the precipitates are shown in Table 6 and the commercial iron oxides in Table 7. The most important metal analysis is, of course, the percent iron in the precipitates. As can be seen in Figure 1, the percent iron is similar in the precipitates to the synthetic iron oxide and somewhat higher than the natural iron oxide.

Figure 1: Concentration of Iron in Precipitates. BB = Bubbler, SV = Saint Vincent, CG = Cedar Grove, HB = Howe Bridge, MO = Morrison, TN = Tennessee, B1 = Bayferrox 130M, B9 = Bayferrox 940, BS = Hoover 308BS, and RS = Hoover 202RS .



Results from four of the other metals analyzed are shown in Figure 2. For aluminium and manganese the concentrations are somewhat higher than the synthetic iron oxide but lower than the natural. The analysis for copper shows all the wetland precipitates to be lower than both the synthetic and natural iron oxides. The zinc results indicate some diversity in the wetlands with zinc concentrations from the Bubbler, Saint Vincent, Cedar Grove and Tennessee sites being lower than the concentrations in the commercial iron oxide. The values from the Howe Bridge site are close to the concentrations of the high zinc commercial products. The Morrison site is substantially higher in zinc concentration than any of the other samples. This illustrates that there is some diversity in the wetland precipitates and that critical commercial applications may require careful screening of the precipitates used.

Metals in the mine drainage are most likely the source of the trace metals in the precipitates. Therefore, mine drainage with high concentrations of metals would produce precipitates with high metal concentrations. The water soluble matter is probably associated with ions such as Na^+, SO_4^{2-}, and Cl^- present as water soluble salts. The concentration of sodium in the Bubbler, Saint Vincent, and Cedar Grove sites is much higher than at the other sites. The water soluble matter is also much higher at these sites. The Howe Bridge site does not fit into this pattern, however, with relatively low sodium concentrations and high water soluble matter.

Conclusion

In general the wetland precipitates have many similar characteristics to commercial iron

Table 6: Concentration of Metals in Wetland Precipitates

Metals	Bubbler	Saint Vincent	Cedar Grove
Co (ppm)	23.66 +/- 40.32	45.77 +/- 12.60	51.66 +/- 7.86
Ni (ppm)	20.71 +/- 2.70	16.86 +/- 1.94	22.70 +/- 25.05
Pb (ppm)	27.24 +/- 1.94	72.88 +/- 36.92	68.28 +/- 34.71
Al (ppm)	259.9 +/- 8.6	3322 +/- 1639	820.1 +/- 57.12
Ca (ppm)	3825 +/- 113	5310 +/- 664.1	5004 +/- 287.4
Mn (ppm)	328.4 +/- 11.4	735.2 +/- 386.7	144.1 +/- 37.43
Cr (ppm)	2.97 +/- 0.07	74.04 +/- 136.3	0.18 +/- 0.35
Mg (ppm)	347.6 +/- 11.1	728.6 +/- 216.1	359.2 +/- 25.6
Na (ppm)	422.1 +/- 4.6	1141 +/- 1182	1284 +/- 137
Zn (ppm)	125.0 +/- 5.1	93.44 +/- 9.06	69.71 +/- 5.05
Cu (ppm)	18.87 +/- 1.56	22.24 +/- 1.71	15.34 +/- 0.75
Cd (ppm)	< 0.10	<0.10	3.01 +/- 1.96
%Fe	50.45 +/- 0.08	43.11 +/- 6.44	41.41 +/- 2.28

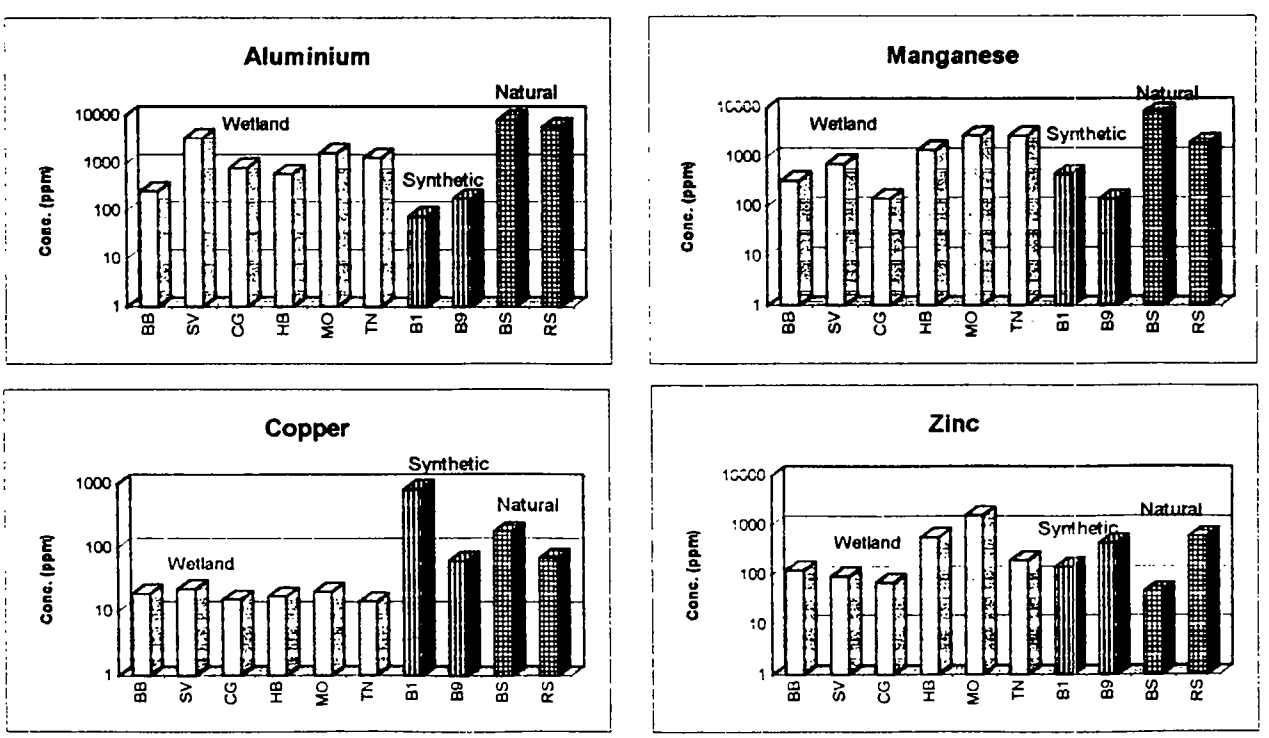
Metals	Howe Bridge	Morrison	Tennessee
Co (ppm)	72.13 +/- 20	276.4 +/- 28.0	108.3 +/- 9.5
Ni (ppm)	156.16 +/- 63.53	325.3 +/- 73.8	200.6 +/- 24.5
Pb (ppm)	86.97 +/- 35.85	84.76 +/- 34.86	17.93 +/- 20.71
Al (ppm)	600.0 +/- 180.6	1660 +/- 511	1321 +/- 894
Ca (ppm)	1060 +/- 31.20	1401 +/- 203	6038 +/- 1392
Mn (ppm)	1383 +/- 193	2716 +/- 278	2694 +/- 715
Cr (ppm)	<0.10	0.15 +/- 0.30	1.35 +/- 1.74
Mg (ppm)	343.8 +/- 50.20	355.9 +/- 42.4	586.8 +/- 164.5
Na (ppm)	73.88 +/- 17.24	88.17 +/- 9.80	40.95 +/- 5.50
Zn (ppm)	569.4 +/- 108.2	1570 +/- 184	195.6 +/- 45.9
Cu (ppm)	17.10 +/- 1.68	20.21 +/- 1.80	14.21 +/- 0.62
Cd (ppm)	0.05 +/- 0.097	<0.10	<0.10
%Fe	45.88 +/- 4.68	45.74 +/- 10.58	42.30 +/- 8.67

Table 7: Concentration of metals in commercial iron oxide

Metals	Bayferrox 130M	Bayferrox 940	Hoover 308BS	Hoover 202RS
Co (ppm)	43.62 +/- 15.25	42.29 +/- 6.06	62.21 +/- 2.01	45.48 +/- 6.74
Ni (ppm)	182.6 +/- 38.7	34.93 +/- 7.38	146.2 +/- 21.2	173.13 +/- 4.20
Pb (ppm)	34.50 +/- 1.89	45.61 +/- 1.64	73.39 +/- 15.8	69.17 +/- 22.43
Al (ppm)	77.21 +/- 18.46	183.7 +/- 16.9	8153 +/- 268	5757.8 +/- 94.7
Ca (ppm)	152.5 +/- 45.7	259.5 +/- 23.8	7512 +/- 210	1264.9 +/- 108.4
Mn (ppm)	450.6 +/- 89.0	143.1 +/- 10.7	8094 +/- 69	1958.4 +/- 57.6
Cr (ppm)	479.6 +/- 86.5	105.1 +/- 13.0	159.6 +/- 1.3	190.7 +/- 3.2
Mg (ppm)	20.07 +/- 4.47	76.08 +/- 5.74	10343 +/- 156	10577 +/- 303
Na (ppm)	160.4 +/- 15.4	622.1 +/- 23.7	393.5 +/- 1.5	264.4 +/- 1.0
Zn (ppm)	145.7 +/- 17.6	434.9 +/- 29.9	46.99 +/- 2.94	597.7 +/- 308.5
Cu (ppm)	826.6 +/- 73.6	61.69 +/- 3.60	177.9 +/- 2.1	69.09 +/- 0.10
Cd (ppm)	<0.10	0.50 +/- 0.35	68.52 +/- 0.36	1.58 +/- 2.79
%Fe	40.99 +/- 0.97	57.11 +/- 0.83	27.63 +/- 0.47	37.06 +/- 0.44

Figure 2: Selected Metals Concentrations in Wetland Precipitates and Commercial Iron Oxide.

Wetland: BB = Bubbler, SV = Saint Vincent, CG = Cedar Grove, HB = Howe Bridge, MO = Morrison, TN = Tennessee
Synthetic: B1 = Bayferrox 130M, B9 = Bayferrox 940
Natural: BS = Hoover 308BS, RS = Hoover 202RS



oxide. The iron concentrations, oil absorption, and ignition loss are all reasonably close to the commercial iron oxide. Several of the other parameters such as moisture, 0.045 mm sieve, and water soluble matter are significantly different. However, this difference may be due to a lack of processing such as grinding, washing, or vigorous drying. The inclusion of some of these processing steps may bring these values closer to the commercial products.

The results of the metal analysis are interesting in that they show the precipitates to be between the synthetic and the natural iron oxides in concentration for several metals. They are also significantly lower in copper and chromium concentration than both the natural and the synthetic material.

These results are encouraging and would indicate that the wetland precipitates do have some potential as a raw material for commercial iron oxide. There is some additional processing that will be necessary to make a consistent product, but additional evaluations are justified.

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THE BARK CAMP RUN DEMONSTRATION CONSTRUCTED WETLANDS: FINDINGS AND RECOMMENDATIONS FOR FUTURE DESIGN CRITERIA

by

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Abstract The performance of six wetlands built to ameliorate acid mine drainage has been analyzed over 806 days. The wetlands are each 52 m x 8 m at the water surface, with a 5 cm surface water column and 60 cm depth of substrate consisting of horse manure mixed with an equal volume of SiO_2 stone. Each wetland has a 1 mm polyethylene liner and wooden deflectors every 2 m to promote uniform flow. The dominant macrophyte is *Typha latifolia*. Flows are ~10 m^3/d. Median influent pH = 3.0; acidity = 202 mg/L as $CaCO_3$; $[Fe^{+3}]$ = 22.9 mg/L; $[Fe^{+2}]$ = 0.8 mg/L; [Al] = 10.9 mg/L; [Mn] = 2.0 mg/L; and $[SO_4^{-2}]$ = 592 mg/L. Water quality was determined biweekly for each wetland's influent and final effluent and at 84 internal sampling stations built to sample at depths 5, 25, 45, and 60 cm below the water surface. Tracer studies showed that the mine drainage flows through both the surface water column and the substrate, and a one-dimensional flow model appears satisfactorily to explain the performance of the wetlands. Wetlands should be designed to achieve uniform flow and to maintain flow through the substrate A polishing area of a few m^2 with a substrate consisting only of limestone chips appears to be helpful in maintaining effluent alkalinity. Simple mathematical models were developed to assess the performance of the constructed wetlands. Removal of Fe^{+3} is by hydrolysis, followed by reduction to Fe^{+2} and incorporation into the substrate. Removal of Al^{+3} is by hydrolysis. The observed removal rates of 1g d^{-1} m^{-2} for Fe^{+3} and 0.5g d^{-1} m^{-2} for Al^{+3}, combine with concurrent neutralization of the resulting H^+, to give an acidity removal rate of 5.5g d^{-1} m^{-2}. A zero-order rate law can be used to describe the observed rate of Fe^{+3} removal First-order rate laws also produce good representations for the rates of Fe^{+3} and Al^{+3} removal. Effluent Mn concentration > influent [Mn], and declines in accordance with a first-order rate law, indicative of desorption of Mn^{+2} initially present in the substrate. This may explain past difficulties in assessing Mn removal in anaerobic constructed wetlands.

Additional Key Words: water pollution abatement, constructed wetlands design, mathematical modeling.

Introduction

The PA Department of Environmental Protection (DEP 1988) has reported that discharges from coal and clay mining operations account for pollution of approximately 2700 km of Pennsylvania's streams. At least 794 discharges are being treated by current coal operators to conform to effluent limits (Hellier, *et al.* 1994). A large number of discharges are from operations that were abandoned before current mining laws were passed; for example, the Muddy Run watershed receives 15.75 metric tons of acid per

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day from abandoned mines (Skelly and Loy 1972). To restore the quality of the polluted streams, a technologically feasible and cost-effective means must be found to abate the pollution from these discharges.

The United States Environmental Protection Agency (EPA 1982) has approved chemical treatment for mine discharges; however, because of the cost, passive treatment methods, including constructed wetlands, are also being used to treat mine discharges of different qualities. While there have been several studies and reports on the subject of constructed wetlands, and design guidance manuals have been published (Hedin *et al.* 1994), there is little theoretical discussion on the basis for the design of constructed wetlands.

Objectives

The objectives of this study were: (1.) To study the performance of wetlands built to take advantage of anaerobic processes in treating a mine discharge with moderate acidity and moderately elevated metals; (2.) To obtain transient and long term water quality data at key sample points in the wetlands.; (3.) To determine flow patterns within the wetlands; (4.) To assess the effects of moderate pretreatment of the wetland influents with anhydrous NH_3; (5.) To develop simple mathematical models from the data obtained, upon which future designs can be based; and (6.) To compare the design criteria produced by the mathematical models to previous design criteria, and to compare the performance of the demonstration wetlands to the performance of existing wetlands.

Site Selection

The site of the abandoned Bark Camp #1 and #2 deep mines and coal processing facility was selected for the study because: (1.) The discharge had a moderate acidity of < 300 mg/L as $CaCO_3$ and a moderate Fe concentration of < 30 mg/L, indicating a reasonable likelihood of successful treatment and that there was a reasonable chance to improve the quality of the degraded stream; (2.) The landowner, the Pennsylvania Bureau of Forestry, approved of the project and provided assistance; and (3.) It was within reasonable travel time of the office.

Bark Camp Run is located in Huston Township, Clearfield County, PA, and has been impacted by the abandoned mining operation. as shown by the following results obtained 9/4/90, before the study was initiated: pH = 5.5; acidity = 22 mg/L as $CaCO_3$ (alkalinity = 3 mg/L); $[Fe^{+3}]$ = 7.1 mg/L; [Al] =2.7 mg/L; [Mn] = 0.9 mg/L; $[SO_4^{-2}]$ = 186 mg/L; no fish are present.

Upstream of the study area, the respective parameters were: pH = 6.9; acidity = 0 mg/L as $CaCO_3$ (alkalinity = 18 mg/L); $[Fe^{+3}]$ = 0.2 mg/L; [Al] = 0.2 mg/L; [Mn] = 0.1 mg/L; $[SO_4^{-2}]$ = 161 mg/L, and around 50 trout/km were found. Bennetts Branch Sinnemahoning Creek, to which Bark Camp Run is tributary, is stocked with trout by the PA Fish and Boat Commission.

The Bark Camp Run watershed area is 726 ha, and the stream flow is on the order of 7000 m^3/day downstream of the study area. The combined mine discharges from the study area contribute nearly 700 m^3/day of this flow. During the study, the following median values were found for the discharge: pH = 3.0; acidity = 202 mg/L as $CaCO_3$; $[Fe^{+3}]$ = .22.9 mg/L; $[Fe^{+2}]$ = 0.8 mg/L; [Al] = 10.9 mg/L; [Mn] = 2.0 mg/L; and $[SO_4^{-2}]$ = 592 mg/L.

Constructed Wetlands Design

Six constructed wetlands were built, each with a 1mm polyethylene liner on the bottom and 2 (horizontal) :1 (vertical) in-slopes to prevent groundwater exchange. The wetlands were 52 m long and 8 m wide at the water surface. The design freeboard is 35 cm, surface water column depth 5 cm, and substrate depth 60 cm. The top 5 cm of substrate is topsoil, and the remaining 55 cm is a mixture that is 50% by volume horse manure and 50% by volume river gravel with approximately 5 cm

dimension and composed primarily of SiO_2. This rock, rather than limestone, was added to the substrate in order to assess the effects of allowing all the alkalinity to be generated through dissolution from the substrate and by biological reactions, without supplementation of the substrate with limestone. The manure itself had been freshly generated over the past winter and had a measured alkalinity of approximately 15000 mg $CaCO_3$ equivalent per kg dry weight. The substrate in the initial 2m length at the influent barrel consisted of the aforesaid stone alone, while the substrate in the last 2m immediately preceding the effluent barrel consistent of crushed limestone of about 1.5 cm dimension.

From three manhole/mixing chambers, influent was directed into pairs of wetlands via a barrel around whose bottom 15 cm periphery were drilled 6 mm holes. The effluent barrels were of the same design. Wooden deflectors were built every 2m along the wetlands' length to promote uniform flow. Sample stations were built to measure water quality at depths of 5 cm, 25 cm, 45 cm, and 60 cm after 128 m^2, 256 m^2, and 384 m^2 of wetland area for all six wetlands; also after 96 m^2 for wetland #2 and after 48 m^2 for wetlands #4 and #6. The dominant macrophyte was *Typha latifolia*. Figure 1 is a plan view of the wetlands. The areas given are the cumulative wetland areas from the inlet to the sample stations depicted.

Anhydrous ammonia was used for a one year period to adjust influent pH. Mixing chamber pH was adjusted in an effort to deliver an influent having pH = 3.0 to wetlands #1 and #2; pH = 4.0 to wetlands #3 and #4; and pH = 5.0 to wetlands #5 and #6.

Methods

Biweekly water quality samples were obtained upstream and downstream of the study area and from the final treatment basin, at the wetland influent and effluent, and at the 12 internal sample points of the odd numbered wetlands and 16 internal sample stations of the even numbered wetlands. Each sample was separated into two aliquots to facilitate laboratory processing; one aliquot to be analyzed for pH , alkalinity, acidity, and $[SO_4^{-2}]$ and the other to be analyzed for $[Fe^{+2}]$, total [Fe], [Mn], [Mg], and [Al]. The latter aliquot was acidified to pH < 2.0. Additionally, the effluents were analyzed for Cl^-, P, K, BOD, and forms of N. The samples were put into iced containers and transported to the Department's laboratory in Harrisburg, where they were analyzed following EPA approved methods (APHA 1992).

Influent flows were measured with a beaker and stop watch on most occasions when the water quality samples were taken. When influent flow rates were not measured, they were estimated by interpolation between measured values. Because influent flows remained very steady from measurement to measurement, the instantaneous measurement was considered to be representative. Effluent flow rates, while measured, proved less representative because they were more sensitive to daily evaporation and rainfall.

A tracer study was conducted to determine flow patterns in the wetlands (Donahue 1994). On June 9, 1993, 11.6 kg of NaBr was dissolved in water and poured into the influent barrels of wetlands #1 and #2 during one half hour. Over 68 days, samples from all of the two wetlands' sample points were analyzed at the Pennsylvania State University for $[Br^-]$, and breakthrough curves of $[Br^-]$ as a function of time were developed.

Results and Discussion

The performances of the six wetlands are illustrated and discussed in the report to EPA (Hellier 1996). Flows varied over time, but usually were less than 15 m^3/day. The effluent pH was usually near 6.0, contrasted with an influent pH of 3.0. The wetlands tended to impart alkalinity as shown by an effluent which was alkaline to neutral as contrasted with an influent with a median acidity of 202

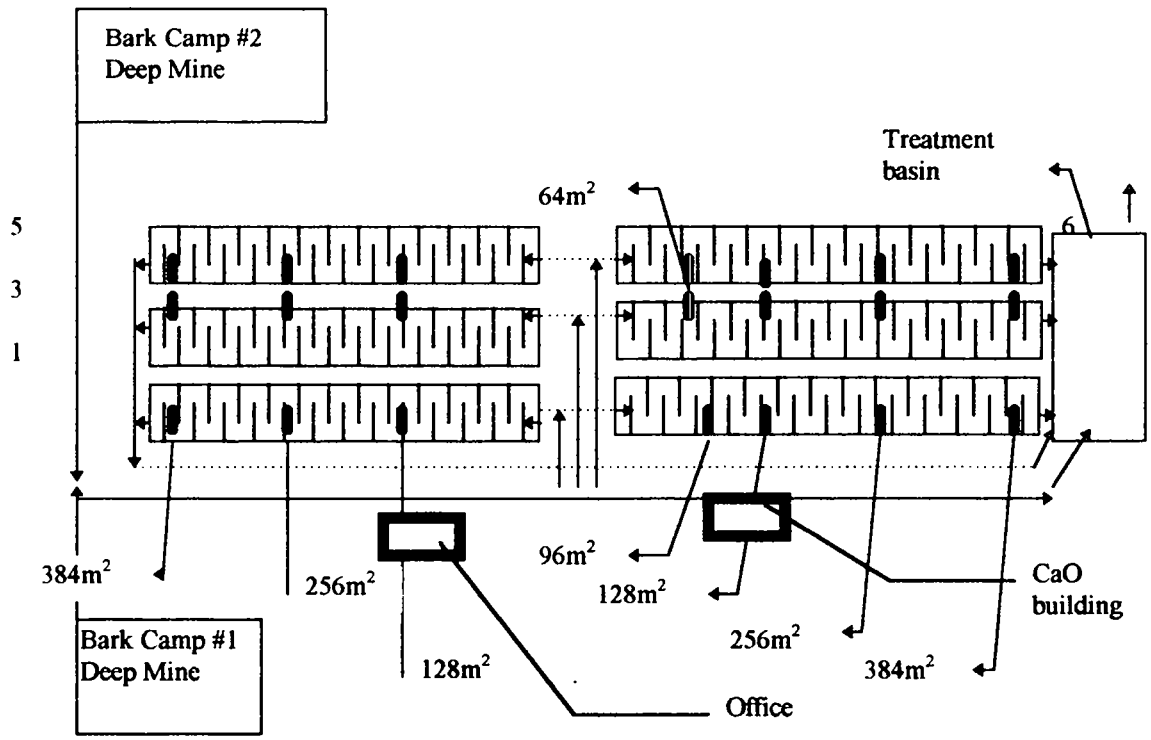

Figure 1.Plan View of Bark Camp Run Constructed Wetlands.

mg/L. Effluent [Fe^{+3}] tended to be about an order of magnitude lower than influent [Fe^{+3}], and most of the effluent Fe was Fe^{+2}. Total Fe removal was effective for the period from about 130 days to 400 days. After 400 days, Fe continued to be removed, although not as efficiently. The wetlands have been effective in removing Al, but effluent [Mn] has consistently exceeded influent [Mn]. For the purpose of illustration, the overall performance of wetland #1 is shown (Figure 2).

Graphs were made of the pollution indicators as a function of time at constant depth in the substrate for the different cumulative treatment areas, and at constant cumulative treatment area for the four different depths within the substrate. For the present discussion, Figure 3 presents the [Fe^{+3}] data for wetland #1. The results for the indicators are summarized as follows: (1) Net acidity tended to decline and pH to increase with increasing depth, although no regular pattern is apparent. Deeper parts of the substrate tended to maintain alkaline conditions better over time compared to the surface water column and the shallower parts of the substrate. (2) Total [Fe] tended to decline with depth, with [Fe^{+3}] being lowered relative to influent [Fe^{+3}] and [Fe^{+2}] being elevated; (3) [Al] tended to be lowered relative to influent concentrations, but (4) [Mn] was elevated relative to influent concentrations; (5) [SO_4^{-2}] fluctuated, and no apparent pattern was observed.

The tracer breakthrough curves at the four different depths at a cumulative treatment area of 128 m^2 are shown for wetland #1 (Figure 4). Based on the breakthrough curves, detention times were calculated. The flow characteristics of wetland #1 were assumed to apply to wetlands #3 and #5; the characteristics of wetland #2, to wetlands #4 and #6. To apply the results to a given water quality sampling period, detention time was assumed to be proportional to influent flow. Detention times behaved regularly

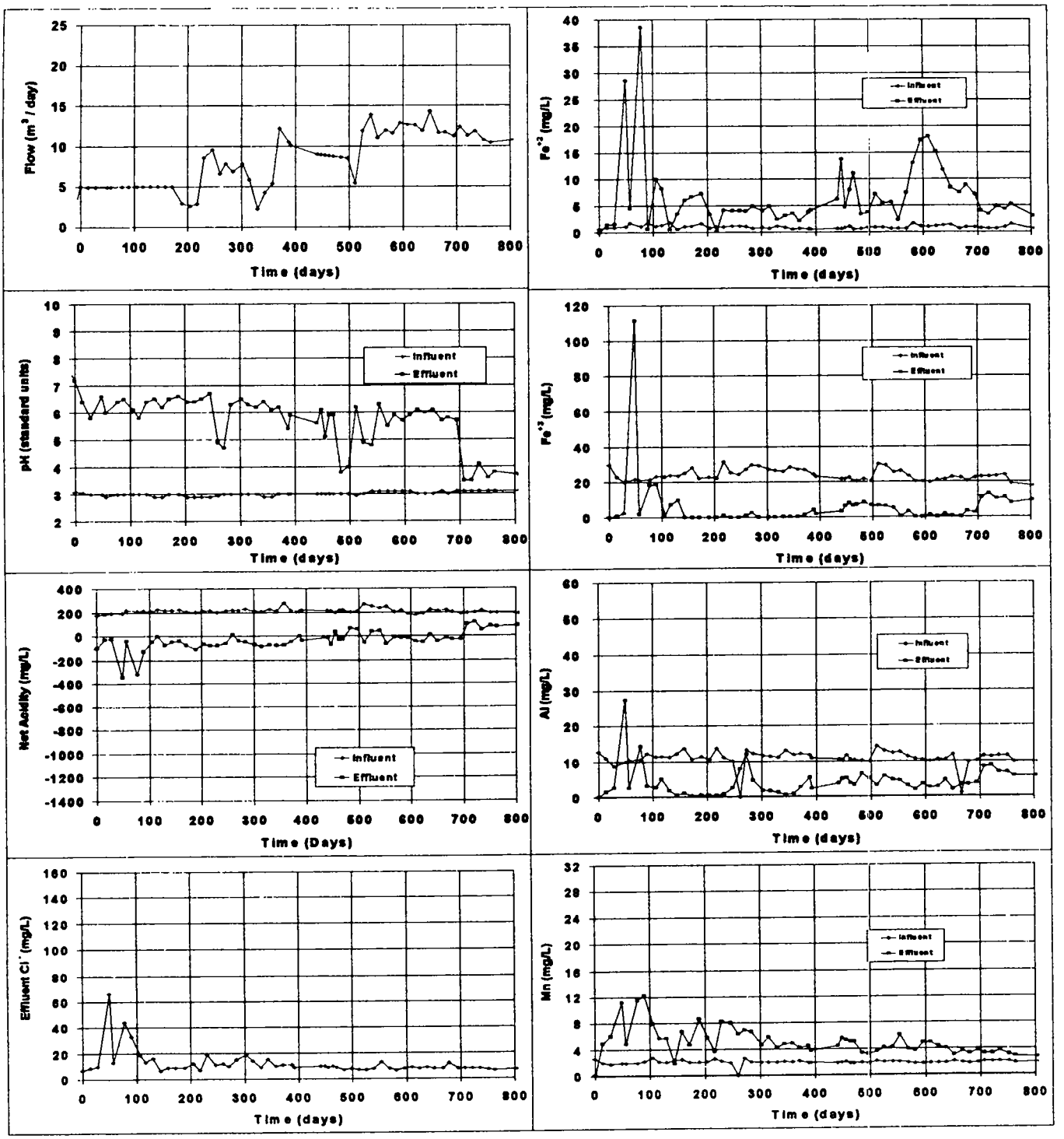

Figure 2. Overall Performance of Wetland #1.

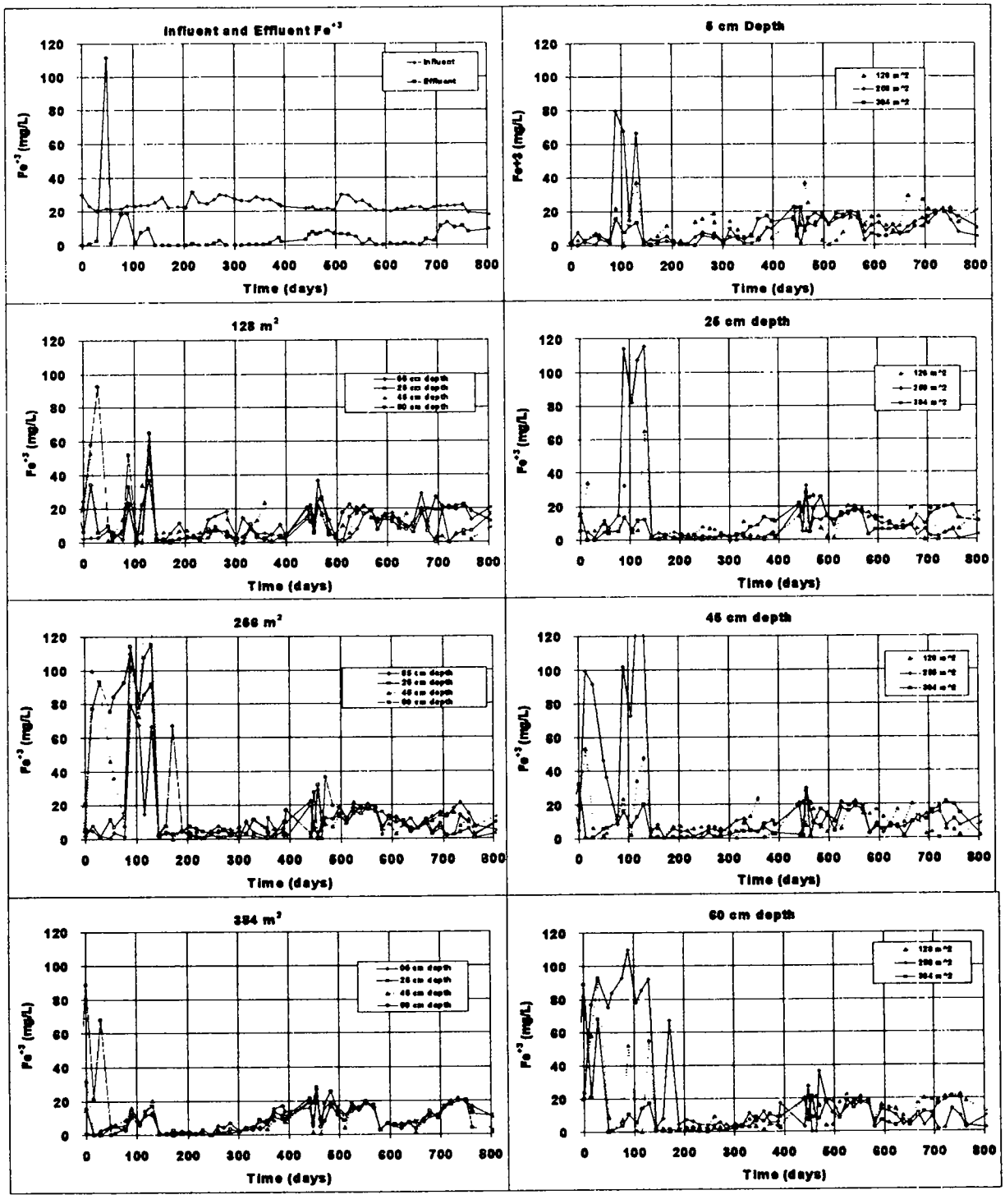

Figure 3. Wetland #1 Removal of Fe^{+3}.

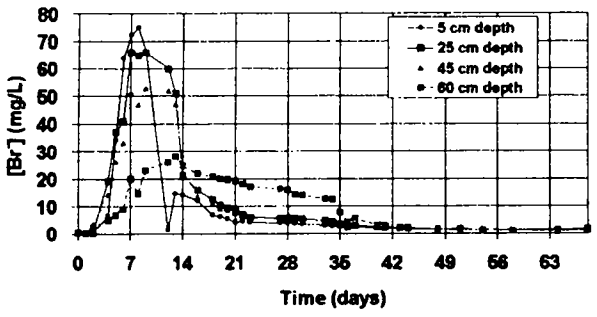

Figure 4: Wetland #1 [Br⁻] after 128 m² Area

and increased with increasing depth, suggesting the first approximation of a one-dimensional flow pattern in which flow was uniform and varied only in the vertical direction throughout most of the wetlands. The irregularities exhibited near the influent can be attributed to a drawdown effect resulting from the effluent being taken from the bottom of the effluent barrels.

The study period appears to be divided into three phases: (1.) A transient startup period in which the wetland acclimates to the mine drainage flow and reaches steady operation. During this phase, the effluent exhibits elevated [Cl^-] and [Fe], indicative of possible desorption and flushing from the substrate. The transient period is not identical for all pollutants; for example, [Mn] continues a downward trend. (2.) A steady period in which the wetlands generate alkalinity, remove acidity, and are very effective in removing Fe; (3.) A declining effectiveness period in which the wetlands begin to lose their alkalinity generation capabilities and Fe removal becomes less effective. During this period, the limestone chip polishing area appears to remove between 30% and 100% of the Fe^{+3}. The declining wetland effectiveness may be due to the loss of the alkaline material originally present in the horse manure. Both of these facts suggest that limestone, rather than inert stone (SiO_2), should be incorporated into the substrate to maintain the performance of the wetlands.

The anhydrous NH_3 addition accelerated the deposition of FeOOH at the entrance to the wetlands, as evidenced by the coloration of the substrate surface: wetlands #1 and #2 had no coloration; wetlands #3 and #4 had some coloration; and wetlands #5 and #6 had substantial coloration. Influent pH in all six wetlands returned almost instantaneously to 3.0 as the Fe^{+3} was hydrolyzed.

Mathematical models

The development of a comprehensive mathematical model to explain the behavior of all pollutant indicators is beyond the scope of this report. Model development will be illustrated by considering the removal of Fe in the first 128 m^2 of treatment area during the steady phase of the study.

The 22.90 mg/L median influent [Fe^{+3}] accounts for 96% of the influent Fe. Mechanisms of Fe^{+3} removal from the water include (1) Hydrolysis of Fe^{+3} followed by precipitation as FeOOH from the surface water column and retention as a solid on the surface of the substrate; (2) Hydrolysis of Fe^{+3} and retention of the resulting FeOOH within the substrate; (3) Reduction of Fe^{+3} to Fe^{+2} within the substrate, followed by its Fe^{+2} retention in the substrate as organically bound Fe^{+2}, FeS, or $FeCO_3$.

The following assumptions were made to develop a simple model: (1.) The transient startup period having passed, on any sample day during the steady period of operation, the influent flow and indicator concentrations are steady. (2.) Plug flow conditions apply in the surface water column and within the substrate. This assumption is justified by considering that the flow is low relative to the wetland volume, and that the deflectors and the *Typha latifolia* enhance uniform, plug flow. (3.) Flow components in the x direction (along the length of the wetland) are large relative to flow components in the y or z directions; (4.) To permit the use of differential equations, the water column and the substrate are

considered mathematically to be continuous media; (5.) The rate expression for a given indicator depends only on the concentration of that indicator.

Zero order model

Historically, expressions of rate for removal of pollutants in constructed wetlands have been simple linear representation based on the mass of pollutant removed per unit area per unit time; i.e., g day^{-1} m^{-2} (US Bureau of Mines, *op. cit.)*. If the wetland depth is constant, or if an average depth is used, this representation considers the removal rate *independent* of concentration:

$$d[Fe^{+3}]/dt = -k_0 \quad (1)$$

The zero-order rate constant k_0 is given by:

$$k_0=([Fe^{+3}]_{in}-[Fe^{+3}])/(\tau-\tau_{in}) \quad (2)$$

where the subscript "in" stands for conditions at the beginning of the wetland section being considered, and τ stands for detention time as determined from the tracer breakthrough time (Figure 4) and influent flow rate. For each wetland, the rate constant k_0 was determined between sampling stations at the different depths, (Figure 3), removal rates were calculated at those depths, and the composite rate of removal in each section of the wetland was calculated by averaging among the rates at the four depths. The rate of Fe^{+3} removal, g day^{-1} m^2 is shown in Table 1. The removal rate for the first 128 m^2 of the wetlands is consistent with removal rates that DEP has observed in other wetlands receiving acidic influents. However, the calculated removal rates in this first one-third of the wetland is sensitive to the position within the wetland. This suggests, particularly for the first 128 m^2 of the wetland, that a different rate expression might be more valid. The calculated removal rates in the remainder of the wetland are less consistent, and may indicate a change in mechanism to which a different model must be applied.

First-order model

The use of a first-order rate law to describe pollutant removal is common practice in sanitary engineering. The first order rate expression:

$$d[Fe^{+3}]/dt = -k_1[Fe^{+3}] \quad (3)$$

can be combined with the simplifying assumptions given above to calculate the first-order rate constant k_1:

$$k_1=\ln([Fe^{+3}]_{in}/[Fe^{+3}]_{out})/(\tau-\tau_{in}) \quad (4)$$

The procedure for calculating removal rates in g day^{-1} m^{-2} was similar to that used for the zero-order model. The removal rates are given in Table 2. They are again sensitive to the position in the wetland. The tendency of the removal rate to decline as the position of a particular treatment area of the wetland becomes further removed from the influent suggests that the removal rate does depend on $[Fe^{+3}]$ and lends credence to a first or higher order model.

The removal of Al was also considered, using a first-order rate expression, (Table 3). The behavior of [Mn] (Fig. 2) indicates that desorption from the substrate is occurring, possibly in accordance with a first-order rate law.

Conclusions

The procedures outlined above give a reasonable, simple predictive tool for the design of constructed wetlands. If a conservative figure of 1.0 g day^{-1} m^{-2} removal rate is taken for Fe^{+3} and the similarly derived 0.5 g day^{-1} m^{-2} removal rate is taken for Al^{+3}, and both removals are converted into acidity equivalents:

$$\text{Acidity equivalent} = 2.6883\ Fe^{+3}] + 5.5643\ [Al^{+3}] \quad (5)$$

an acidity removal rate of 5.5 g day^{-1} m^{-2} as $CaCO_3$ equivalent is calculated for the Bark Camp Run wetlands. This agrees well with the US Bureau of Mines (Hedin *et al.* 1994) guideline of 5.0 g day^{-1} m^{-2} as $CaCO_3$ and the 6 g day^{-1} m^{-2}

Table 1. Removal Rate (g day^{-1} m^{-2}) for Fe^{+3} Using Zero-order Model.

Cumulative Treatment Area

Wetland	64 m^2	96 m^2	128 m^2	256 m^2	374 m^2
1	nd	nd	1.01	+0.03	1.34
2	nd	3.04	1.21	+0.87	1.13
3	nd	nd	1.15	-0.03	2.92
4	2.90	nd	1.72	-.036	0.35
5	nd	nd	1.25	+0.55	1.67
6	1.93	nd	0.35	-0.45	12.10

Table 2. Removal Rate (g day^{-1} m^{-2}) for Fe^{+3} Using First-order Model.

Cumulative Treatment Area

Wetland	64 m^2	96 m^2	128 m^2	256 m^2	374 m^2
1	nd	nd	1.08	+0.04	0.71
2	nd	4. 93	0.38	+0.85	0.79
3	nd	nd	1.47	-0.02	0.52
4	5.90	nd	4.44	-0.33	0.17
5	nd	nd	3.78	-0.03	0.77
6	1.28	nd	0.81	-0.03	0.54

Table 3: Removal Rate (g day^{-1} m^{-2}) for Al^{+3} Using First-order Model.

Cumulative Treatment Area

Wetland	64 m^2	96 m^2	128 m^2	256 m^2	374 m^2
1	nd	nd	4.42E-01	-2.42E-02	-1.50E+00-
2	nd	3.09E+00	2.20E-01	-1.07E-02	-2.93E-01
3	nd	nd	4.58E-01	-2.30E-03	-1.19E+00
4	3.64E+00	nd	5.58E-01	+1.22E-01	-4.13E-01
5	nd	nd	2.08E+00	-1.66E-03	-1.30E-01
6	9.80E-01	nd	3.89E-02	+7.28E-02	-7.85E-01

In all three tables, the symbol "nd" means "not determined."

guideline given by Dietz *et al.* (1994). We conclude that the sizing guidelines for a system of this type receiving acidic influent can be explained by simple kinetic models. The designer is cautioned that the wetlands will experience a transient startup period, during which a steady model will not apply. Desorption of pollution indicators from the substrate during the transient startup period, particularly Mn, appears to be important, and the simplified models should not be applied to this period.

The declining performance of the wetlands indicated that the acid neutralizing properties of a substrate fashioned only of horse manure and inert, preponderantly SiO_2 stone will not be sustained for more than about 1 to 1½ year.

The performance of wetlands designed in a specific way to take advantage of anaerobic processes for treating a mine discharge with moderate acidity and moderately elevated metals has been studied. Water quality data

have been presented representing the first 806 days of operation, including transient startup conditions and short term performance following startup. Long-term data continue to be collected. The flow patterns in the wetlands were studied with a Br^- tracer, and the presence of flow through the substrate was demonstrated. Anhydrous NH_3 as pretreatment has the effect of accelerating the hydrolysis of Fe^{+3} and thus has the advantages of chemical treatment with other alkaline materials. The simple mathematical models we have developed compare favorably with previous design criteria. Further modeling efforts continue, and the results of this effort will be presented at a later time.

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MANGANESE AND TRACE METAL REMOVAL IN SUCCESSIVE ANAEROBIC AND AEROBIC WETLANDS

by

F.J. Sikora, L.L. Behrends, G.A. Brodie, and M.J. Bulls

Abstract. A microcosm study was conducted to evaluate the use of anaerobic wetlands preceding aerobic wetlands for removal of Mn, Cu, Ni, Zn, and Pb in wastewater. Initial concentrations for Mn, Cu, Ni, Pb, and Zn were 20, 2.0, 1.5, 2.1, and 2.0 mg/L, respectively. Each experimental unit consisted of three cattle-feeding troughs (cells) set in series. The first cell was anaerobic and the last two were aerobic. Water was delivered to the wetland cells at 20 mL/min for a period of 380 days starting August 24, 1994. The anaerobic wetlands consisted of three treatments replicated two times. The aerobic wetlands consisted of two treatments replicated three times. One anaerobic treatment contained organic matter and limestone (SP). Another anaerobic treatment contained organic matter, limestone, and canarygrass (SP&CG). The third anaerobic treatment consisted of canarygrass planted in river gravel (RG). Water flowed into the top and was discharged from the bottom of each anaerobic wetland. The aerobic treatments consisted of reciprocating or not reciprocating water between two cells containing river gravel. The anaerobic troughs with organic matter were effective in reducing sulfate to sulfide and producing alkalinity in the range from 80 to 300 mg/L. Manganese removal in the anaerobic systems decreased with time with the effluent anaerobic waters near equilibrium with respect to MnS and $MnCO_3$ toward the end of the experiment. Removal of Cu, Ni, Zn, and Pb was very effective in the anaerobic cells with organic matter due to precipitation of metal sulfides. Since Mn removal was ineffective in the long-term in the anaerobic system, aerobic wetlands would be necessary for further water treatment. Manganese removal in the reciprocating aerobic cells was quicker than in the nonreciprocating aerobic cells with removal due to precipitation of Mn oxides. Coupled anaerobic-aerobic wetlands appear to hold promise for removing trace metals via metal sulfide precipitation and Mn via Mn oxide precipitation.

Additional Key Words: alkalinity, compost, copper, lead, nickel, sulfate, sulfide, lead, zinc.

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[3] Publication in this proceedings does not prevent authors from publishing their manuscript, whole or in part, in other publication outlets.

INTRODUCTION

Due to federal limits placed on Fe and Mn concentrations in acid mine drainage effluent, considerable research has been conducted on the use of wetlands for removal of these metals. Monthly averages for Fe and Mn concentrations generally must be below 3 and 2 mg/L, respectively (Code of Federal Regulations, 1995). Both aerobic and anaerobic surface-flow wetlands have been used. Aerobic wetlands consist of a layer of water over soil with O_2 supplied via diffusion. Iron and Mn removal occurs via precipitation of metal oxides. Anaerobic wetlands consist of a layer of organic matter placed on top of soil. Anaerobic conditions are imposed with high C in the organic layer and rapid depletion of available O_2. Anaerobic conditions promote sulfate reduction to sulfide and subsequent precipitation of metal sulfides.

Removal rates for Fe and Mn in surface flow wetlands range from 10 to 20 and 0.5 to 1 $g/m^2/d$, respectively (Hedin et al., 1994). The reason for less efficient removal of Mn is due to slower kinetic processes in the oxidation of Mn^{2+} (Stumm and Morgan, 1981). Ferrous Fe readily oxidizes to ferric Fe at pH above 3.5 with rapid precipitation of ferric Fe oxyhydroxides. Uncatalyzed Mn^{2+} oxidation does not occur readily until pH >10 (Brezonik, 1994). Manganese oxidation can occur quicker at lower pH from 6 to 9 with autocatalysis from Mn sorption onto Mn oxide precipitates (McBride, 1994), catalysis via microorganisms (Ghiorse, 1984; Bender et al., 1994), or Mn sorption onto other solids (Davies and Morgan, 1989). Another process that limits Mn removal is the reduction of oxidized Mn in the presence of ferrous Fe. Ferrous Fe will readily reduce oxidized Mn precipitated as oxides, keeping Mn in solution (Hedin et al., 1994; Burdige et al., 1992). Due to the disadvantageous interaction between Fe and Mn, Mn removal in acid mine drainage does not occur significantly until Fe is reduced to low concentrations.

Passive Mn removal has been studied in a number of systems. Gordon (1989) and Gordon and Burr (1989) found Mn oxidation to be related to a black microbial coating found on rock surfaces. Adequate Mn removal occurred in rock bed filters with a similar black coating observed on rock surfaces (Thornton, 1995) and with gravel beds supporting a green algae-microbial mat consortium (Phillips et al., 1994). Manganese removal in both systems was purported to be biotically controlled. Biotic mediation in the algae mat may have been due to O_2 release and CO_2 uptake from the algae, maximizing Mn oxide precipitation in aerobic alkaline microenvironments (Bender et al., 1994). McMillen et al. (1994) studied the use of unsaturated vertical flow wetlands to provide conditions for Mn oxidation and precipitation and found effective Mn removal at initial Mn concentrations ranging from 0.5 to 60 mg/L. When a biocide was added, Mn removal remained high which indicated that abiotic catalysis of Mn oxidation and precipitation was the controlling factor for Mn removal. Contrary results were obtained in lake water samples with an initial Mn concentration of 2 mg/L where rate constants for Mn oxidation in poisoned samples were 10 to 100 times less than rate constants in unpoisoned samples (Johnson et al., 1995). Gordon and Burr (1989) also concluded microbial processes may play a vital role in Mn oxidation by studying Mn removal via microbial black slime on rock surfaces.

Iron and Mn have been the focus for metals removal in acid mine drainage. However, removal of trace metals in acid-mine drainage and other metal-laden wastewater will

receive more attention in the future due to impending limits on effluent concentrations via the Clean Water Act. Concentrations of Fe and Mn in acid mine drainage can range from 2 to greater than 150 mg/L, while concentrations of trace metals such as Cu, Ni, Pb, and Zn are usually less than 2 mg/L. An appropriate passive technology for trace metal removal is anaerobic wetlands since many of the trace metals of concern form metal sulfides with very low solubility. The disadvantage with surface-flow anaerobic wetlands is the anaerobic conditions are limited to the water-sediment interface with not all of the water being exposed to the reducing conditions. Improvement of treatment efficiency can occur by forcing water downward through an organic layer as done with successive alkalinity producing systems (SAPS) (Kepler and McCleary, 1994). A typical SAPS design consists of a surface layer of 1.6 to 1.9 m of water, 45 cm of compost below the water, and a 45 to 60 cm layer of limestone rock below the compost. The system provides reducing conditions and adds alkalinity to the water from sulfate reduction and limestone dissolution.

The objective of the current study was to ascertain mechanisms involved in the removal of Mn, Cu, Ni, Pb, and Zn in water treated by anaerobic and aerobic wetlands. The water used in the study was simulated acid mine drainage pretreated by an anoxic limestone drain and surface-flow aerobic wetlands where most of the Fe was removed. The anaerobic cells were hypothesized to remove the trace metals via sulfide precipitation. The aerobic cells were hypothesized to remove Mn via oxide formation.

MATERIALS AND METHODS

The study was conducted inside a greenhouse at the TVA Environmental Research Center in Muscle Shoals, AL. The cells used to simulate anaerobic and aerobic wetlands were insulated cattle feeding troughs that measured 1.1 x 0.6 x 0.6 m^3. The troughs were lined with a 40 mil plastic liner to prevent metal leakage from the galvanized steel. Each experimental unit consisted of 3 troughs placed in series with the first trough being the anaerobic cell and the second two troughs being the aerobic cells (Fig. 1). The troughs were plumbed with PVC pipe so water entered the surface of the first cell, exited at the bottom of the first cell, entered the second cell at the bottom, exited the surface of the second cell, entered the surface of the third cell, and exited on the bottom of the third cell. Surface area of one trough and one experimental unit was 0.5 and 1.5 m^2, respectively. Volume of one trough and one experimental unit was 0.3 and 0.9 m^3, respectively.

The experiment included 6 experimental units with 3 anaerobic treatments and 2 aerobic treatments. The anaerobic treatments consisted of canarygrass (CG) (*Phalaris arundinacea*), SAPS (SP) (12), and a SAPS+canarygrass combination (CG&SP). The SP treatment had a bottom 10 cm layer of crushed limestone gravel, a 30 cm mid-layer of composted chicken litter, and an 18 cm surface layer of water. The CG treatment consisted of canarygrass planted in 58 cm of river gravel. The CG&SP treatment consisted of river gravel on top of compost and limestone as set in the SP system and canarygrass planted in the gravel. Size distribution of the river gravel was 4% <6.7 mm, 66% 6.7 to 19 mm, 25% 19 to 25 mm, and 5% >25 mm. Size distribution of the limestone gravel was 4% <4.7 mm, 7% from 4.7 to 6.7 mm, 81% from 6.7 to 19 mm, and 8% from 19 to 25 mm. Size

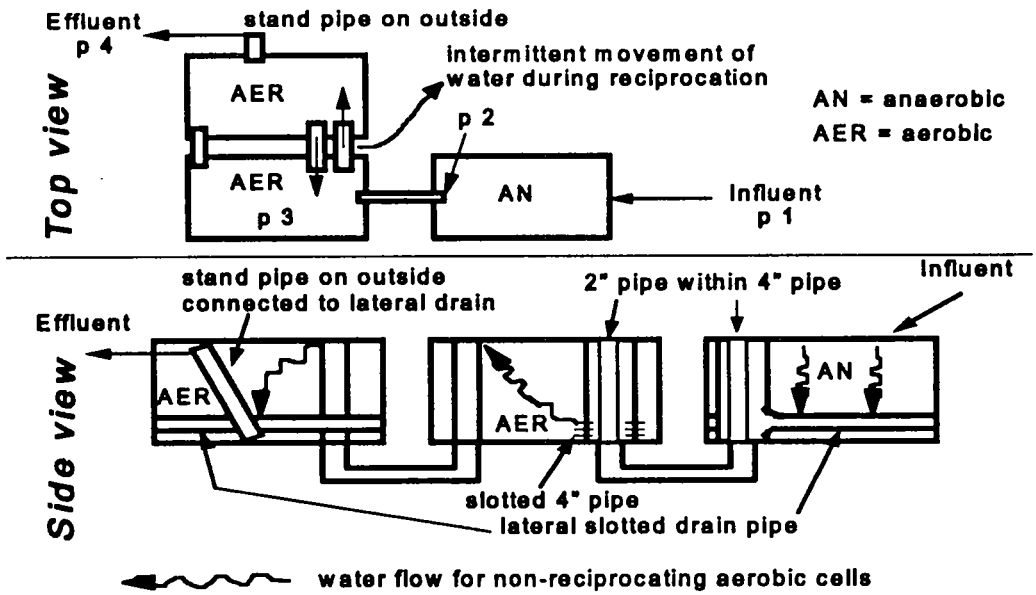

Figure 1. Diagram of one experimental unit used in the study. The four sampling positions are identified in Top view as p1, p2, p3, and p4.

distribution of the compost was 14% <0.4 mm, 3% from 0.4 to 0.6 mm, 8% from 0.6 to 1 mm, 3% from 1 to 1.2 mm, and 72% >1.2 mm.

The anaerobic treatments were replicated 2 times. Three replications of each of the two aerobic treatments were placed after a complete set of anaerobic treatments (Table 1). The two aerobic treatments consisted of reciprocating the top 20 cm of water from one cell to another (w/recip) or not reciprocating (wo/recip) (Behrends et al., 1993). The water was air-lifted by pumping air to the bottom of each of 2 paired aerobic cells through 5 cm diameter pipes. Air was intermittently pumped to each 5-cm pipe at 15 minute intervals. The pumped air moved the top 20 cm of water from one cell to another which exposed rock surface biofilms to air and provided aeration of the water.

After putting the appropriate media in the cells, 2 L of septic tank effluent were added to the composted chicken litter and on the surface of the planted gravel in order to inoculate the system with sulfate reducing bacteria. Nutrient solution was flowed through the anaerobic cells at 20 mL/min for a period of 1 month to nourish the canarygrass and sulfate-reducing bacteria. The nutrient solution contained 112, 137, 55, 12, 46, 2.3, 3.6, and 186 mg/L NH_4-N, Ca, K, P, Mg, Na, Cl, and S, respectively. Micronutrients in the solution consisted of 11, 59, 55, 17, 13, 3.2 and 296 ug/L B, Co, Mn, Mo, Zn, Cu, and Fe, respectively.

Acid mine drainage that simulated water pretreated with an aerobic wetland was passed through the experimental cells beginning on August 24, 1994 after the cells were acclimated with nutrients. August 24 was considered the initial time of the experiment and represented as day 0 in the figures. The salts $MnSO_4 \cdot H_2O$, $FeSO_4 \cdot 7H_2O$, $NiSO_4$, $CuSO_4$

Table 1. Outline of experimental treatments.

Experimental unit	Anaerobic treatment	Anaerobic rep	Aerobic treatment	Aerobic rep
1	CG	1	w/recip	1
2	SP	1	w/recip	2
3	CG&SP	1	w/recip	3
4	CG	2	wo/recip	1
5	SP	2	wo/recip	2
6	CG&SP	2	wo/recip	3

$\cdot 5H_2O$, $PbSO_4$, $ZnSO_4 \cdot 7H_2O$, $CaSO_4$, and $MgSO_4 \cdot 7H_2O$ were added to 1135 L resulting in expected concentrations of 20, 1.5, 2, 2, 2, 2, 90, 90, and 209 mg/L of Mn, Fe(II), Ni, Cu, Pb, Zn, Ca, Mg, and S, respectively. The solution was delivered to the first trough in each experimental unit at a rate of 20 ml/min. This flow rate resulted in loading rates of 0.82 and 0.12 $g/m^2/d$ for Mn and Fe, respectively, and a loading rate of 0.08 $g/m^2/d$ for the trace metals Cu, Ni, Pb, and Zn. Assuming the effluent water from TVA aerobic wetlands (Brodie, 1993) were treated by an equivalently sized wetland system for Mn removal, the Mn loading rates would range from 0.03 to 1.73 $g/m^2/d$ with an average of 0.34 $g/m^2/d$.

During May, 1995, the canarygrass was showing symptoms of N deficiency with very pale green leaves. Fertilizer was added on June 2, 1995 (day 282) to supply nutrients to canarygrass. To equalize effects of fertilizer addition on the anaerobic processes, fertilizer was added to all anaerobic treatments including the SP treatment that did not contain canarygrass. Fertilizer was added as N, P, and K as 34-0-0, 0-40-0, and reagent grade KCl at 60, 10, and 10 g, respectively, to each anaerobic cell. Fertilizer was mixed and added as a solid to the surface of each cell. In the gravel wetlands (CG and SP&CG), gravel was dug out to allow fertilizer to be added to the water. If the fertilizer was fully diluted with the water in the anaerobic wetlands, solution concentrations would be 154 mg/L N, 15 mg/L P, and 40 mg/L K.

Based on rock and compost porosity, the average pore volume in the cells was 40%, the retention time through each cell was 4.2 days and the retention time through the experimental unit was 12.5 days. Retention time through the organic layer in the anaerobic cells was approx. 2.1 days. This retention time was less than the retention times of 5 to 10 d reported to be maximum required for adequate sulfate reduction (Eger, 1992). The retention time through the limestone layer in the SAPS was approx. 0.7 d which was greater than the retention time of 0.5 d required for maximum alkalinity production (Hedin et al., 1994). The hydraulic load for the whole experimental unit was 1.9 cm/d and was within the range of hydraulic loads of 0.9 to 27 cm/d reported for wetland systems treating acid mine drainage (Hedin et al., 1994; Brodie, 1993).

Approximately once a month for a total of 11 sampling periods, water samples were collected for chemical analyses. Samples were collected in 4 locations at the influent (p1), effluent of anaerobic cells (p2), a 10 cm diameter well in the first aerobic cell (p3), and final effluent from the aerobic cell (p4) (Fig. 1). Water samples for metal analyses were acidified with 0.5 mL HNO_3 per 50 mL and refrigerated until analysis. Samples were analyzed for Fe, Mn, Ni, Cu, Pb, Zn, Ca, and Mg by inductively coupled plasma spectrophotometer (ICP). Detection

limits were 0.003, 0.003, 0.005, 0.004, 0.03, and 0.003 mg/L for Fe, Mn, Ni, Cu, Pb, and Zn, respectively. Another set of water samples were frozen until analyses for SO_4-S, C, NH_4-N, NO_3-N, and PO_4-P. Sulfate was determined by ion chromatography. Nonpurgeable organic C was determined by a Dohrmann DC 190 TOC analyzer. Ammonium, NO_3-N, and PO_4-P were determined with LACHAT flow-injection analysis. Alkalinity, pH, and sulfide were determined in water immediately after sampling. After measuring pH with a glass electrode, total alkalinity was determined via titration to pH 4.5 with NaOH using the pH electrode to monitor the endpoint. Water was sampled directly into an Orion SAOB solution at a ratio of 10 mL sample to 10 mL SAOB solution and analyzed with a sulfide ion-selective electrode.

Probes were placed into access wells to monitor dissolved oxygen (DO), temperature, electrical conductivity (EC), and redox. Dissolved oxygen and temperature were monitored with a YSI probe and meter. Electrical conductivity was determined with an Orion probe and meter. Platinum-tipped copper wire electrodes were kept in place for redox measurements. Two redox electrodes were placed into the effluent sump of each anaerobic cell 7.5 cm from the bottom (p2, Fig. 1) and one redox probe was placed in a well in the first aerobic cell 15 cm from the bottom (p3, Fig. 1). Another redox probe was placed in a well in the second aerobic cell 15 cm from the bottom near the subsurface effluent header (see Fig. 1). The redox measured from this redox probe was assumed to be the redox of the effluent water (p4). The redox probes were checked every 3 months by placing the probes in a standardized redox solution (0.1 M Fe^{2+}, 0.1 M Fe^{3+}, and 1 M H_2SO_4) that should have yielded a 432 mV reading at 22 °C using a saturated calomel reference electrode. Greater than 90% of the probes tested yielded values that were within ± 30 mV of the standard mV reading. If the probe tested fell outside of this range, it was replaced. The reference electrode used for redox determination was a saturated calomel electrode. The measured redox potentials were adjusted in reference to a standard H_2 reference electrode by adding 244 mV to the electrode readings (Stumm and Morgan, 1981).

There were six experimental units as outlined in Table 1 that were randomly laid out in the study. Data from the anaerobic and aerobic wetlands were analyzed separately to first discern differences among the three anaerobic treatments and then to discern differences among the two aerobic treatments. In an overview of the whole system (Table 2), data was averaged across the two replications for each anaerobic treatment and across the three replications for each aerobic treatment. Since the anaerobic effluent water from CG and the treatments with organic matter (SP and CG&SP) were very different, the effectiveness of the aerobic treatments was further evaluated (Table 3) for treating effluent only from anaerobic cells containing organic matter. The aerobic treatments were thus averaged across aerobic replications 2 and 3 as shown in Table 1.

Total alkalinity determined from titration also included HS^- and HPO_4^{2-} in the waters tested in addition to HCO_3^-. Therefore,

$$A_T = A_C + [HS^-] + [HPO_4^{2-}]$$

where A_T is total alkalinity and A_C in carbonate alkalinity (Butler, 1991). The unit for alkalinity in the above equation is mole/L. Rearranging and solving for $[HS^-]$ and $[HPO_4^{2-}]$ to equal total sulfide and phosphorus concentrations yields:

$$A_C = [HCO_3^-] = A_T - \frac{10^{-7.02} S_T}{10^{-7.02} + 10^{-pH} a_{HS}} - \frac{10^{-7.2} P_T}{10^{-7.2} + 10^{-pH} (a_{HPO4}/a_{H2PO4})}$$

where S_T and P_T are total sulfide and phosphate concentrations, respectively, in mole/L and $10^{-7.02}$ and $10^{-7.2}$ are proton dissociation constants for H_2S and $H_2PO_4^-$, respectively. The activity coefficients (a_i) were calculated from Davies equation using electrical conductivity to estimate ionic strength (Lindsay, 1979). The carbonate alkalinity shown as mole/L HCO_3^- in the above equation was converted to $CaCO_3$ alkalinity with units of mg/L by:

$$A_C\ (100{,}000\ \text{mg}\ CaCO_3 / 2\ \text{mole}\ HCO_3^-)$$

Predicted carbonate alkalinity produced from calcite dissolution was calculated from the increase in Ca concentration observed from the influent to the effluent of the anaerobic wetlands. Assuming the Ca increase was due solely to calcite dissolution, 2 moles of alkalinity are produced for every mole of Ca dissolved:

$$2\ H^+ + CaCO_3 \longrightarrow Ca^{2+} + 2\ HCO_3^-$$

The alkalinity was calculated in terms of $CaCO_3$ alkalinity in mg/L as:

$$\frac{(\text{Ca increase, mg/L})}{(40.1\ \text{mg}\ Ca^{2+}/\text{mmol})} \times (2\ \text{mmol}\ HCO_3^- / \text{mmol}\ Ca^{2+}) \times (100\ \text{mg}\ CaCO_3 / 2\ \text{mmol}\ HCO_3^-)$$

For sulfate reduction, 2 moles of alkalinity are produced for every mole of sulfide produced:

$$2\ CH_2O + SO_4^{2-} \longrightarrow S^{2-} + 2\ HCO_3^-$$

Predicted alkalinity from sulfate reduction was calculated in terms of $CaCO_3$ alkalinity in mg/L as:

$$\frac{(\text{S conc., mg/L})}{(32.1\ \text{mg S/mmol})} \times (2\ \text{mmol}\ HCO_3^- / \text{mmol}\ S^{2-}) \times (100\ \text{mg}\ CaCO_3 / 2\ \text{mmol}\ HCO_3^-).$$

Activities of chemical components were calculated from solution concentrations using MINEQL$^+$ (Schecher and McAvoy, 1991). The activites were used to determine the potential existence of various solid phases that would support determined metal activity levels assuming equilibrium conditions existed. For evaluation of potential Mn solid phases in the anaerobic wetlands, saturation indices were calculated for Mn solid phases as:

$$\text{Log (SI)} = \text{Log (IAP} / K_{sp})$$

where SI is the saturation index, IAP is the ion activity product in solution, and K_{sp} is the theoretical solubility product for the solid phase in question (Sposito, 1989). If Log (SI) were greater than 0, the solution was supersaturated with respect to the solid phase. If Log (SI) were less than 0, the solution was undersaturated with respect to the solid phase. In both these cases, the existence of the solid phase was not likely. If Log (SI) were equal to 0, the solution was in equilibrium with the solid phase and the existence of the solid phase in question was likely.

For evaluating the potential Cu, Ni, Pb, and Zn solid phases in the anaerobic wetlands and potential Mn solid phases in the aerobic wetlands, metal activities were plotted versus pe+pH and compared to solubility lines for known solid phases. The pe was determined as redox (mV)/59.2 (Lindsay, 1979). The

pH was added to pe to obtain pe+pH. Since the reducing or oxidizing potential of an aquatic environment is affected by both pe and pH, the pe+pH is a useful parameter to define the oxidizing potential of the water. For comparison, another scale is presented for redox in mV at the average pH levels of the waters analyzed.

The Log (CO_2, atm) was calculated using the HCO_3^- activity calculated from MINEQL$^+$ and pH as:

$$\text{Log}(CO_2, \text{atm}) = 7.82 - \text{pH} + \log(HCO_3^-).$$

Results and Discussion

Overview of Coupled Anaerobic and Aerobic Cells

Table 2 displays average water chemistry data across all sampling periods and replications for effluent waters from each anaerobic and aerobic treatment. In the anaerobic effluent waters, pH and alkalinity were greater in the SP and CG&SP treatments compared to the CG treatment (Table 1). The organic matter in the SP and CG&SP treatments was effective in producing highly anaerobic conditions as evidenced by redox less than -170 mV, DO less than 4% saturation, and sulfide concentrations from 19 to 21 mg/L in the effluent waters. The high alkalinity produced in these anaerobic waters resulted in CO_2 partial pressures that were supersaturated with respect to atmospheric CO_2 of $\log(CO_2) = -3.52$ (Table 2). As the water was treated by the aerobic cells, the CO_2 degassed from the water more effectively in the reciprocating treatment compared to the non-reciprocating treatment which resulted in lower alkalinity, lower CO_2 partial pressures, and higher pH in the effluent from the reciprocating treatment compared to the nonreciprocating treatment.

Calcium concentrations in the effluent of the anaerobic cells increased from the influent concentrations due to dissolution of calcite (Table 1). Calcite was added to the SP and CG&SP treatments as limestone. Since river gravel was the only medium used in the CG treatment, an increase in Ca concentration in this treatment is indicative of some calcite present in the river gravel. Batch titrations with HCl has shown the river gravel to have a calcium carbonate equivalence of 0.35%.

Manganese concentration was decreased approximately 50% in the anaerobic cells with further reduction to levels below 0.3 mg/L in the aerobic cells (Table 1). The SP and CG&SP treatments of the anaerobic cells were very effective in reducing concentrations of Cu, Ni, Pb, and Zn to levels near the detection limits of the ICP. The CG anaerobic treatment was less effective with concentrations ranging from 0.06 to 0.44 mg/L for Cu, Ni, and Zn.

The addition of compost in the SP and CG&SP anaerobic treatments resulted in greater NH_4-N and PO_4-P concentrations in the anaerobic effluent waters compared to the CG treatment (Table 1). The reciprocating aerobic wetland was very effective at reducing NH_4-N levels below analytical detection. However, both reciprocating and nonreciprocating aerobic treatments only reduced PO_4-P concentrations to 2.9 and 2.4 mg/L, respectively, with an average 3.6 mg/L aerobic influent concentration.

Table 2. Water chemistry of the influent and effluent of anaerobic cells and effluent of aerobic cells.

		Anaerobic effluent			Aerobic effluent	
Parameter †	*Influent*	*CG*	*SP*	*CG&SP*	*w/recip*	*wo/recip*
pH	4.9(0.5)‡	6.7(0.2)	7.2(0.1)	7.0(0.1)	7.7(0.2)	7.4(0.4)
Alkalinity	0	81(33)	142(44)	193(59)	57(18)	118(41)
log(CO_2, atm)		-1.73(0.13)	-1.96(0.26)	-1.64(0.21)	-2.88(0.19)	-2.12(0.37)
Redox		304(357)	-172(120)	-174(93)	584(136)	532(163)
DO	98(14)	11(11)	3(3)	1.8(1.8)	92(18)	30(19)
Ca	90(5)	120(15)	122(10)	133(17)	127(14)	142(14)
Mg	93(5)	96(3)	99(3)	98(4)	89(14)	92(18)
Mn	20(1)	11(8)	10(5)	10(6)	.04(.04)	.24(.24)
Cu	2.0(0.2)	.06(.06)	.009(.009)	.005(.002)	.005(.003)	.03(.03)
Ni	1.5(0.3)	0.44(0.41)	.016(.016)	.008(.008)	.005(.004)	.006(.003)
Pb	2.0(0.3)	.04(.03)	< .03	.03(.01)	< .03	< .03
Zn	2.1(0.1)	.30(.30)	.009(.009)	.01(.01)	.006(.005)	.007(.007)
Fe	1.0(1.2)	1.2(1.2)	.062(.062)	.073(.072)	.005(.005)	.009(.009)
S	< .02	.10(.10)	19(9)	21(9)	< .02	< .02
SO_4-S	207(36)	211(31)	193(36)	182(33)	209(42)	198(31)
org-C	1.7(1.0)	2.2(1.6)	5.3(1.8)	5.2(2.1)	3.5(1.8)	3.7(2.1)
EC	1.12(.04)	1.23(.06)	1.24(.04)	1.27(.08)	1.18(.17)	1.26(.07)
NH_4-N	<.02	.28(.28)	2.2(2.2)	1.6(1.6)	<.02	.8(.8)
NO_3-N	.23(.06)	.04(.04)	<.02	<.02	3.5(3.5)	2.0(2.0)
PO_4-P	<.03	.04(.04)	4.8(3.9)	6.0(5.0)	2.9(2.9)	2.4(2.4)

† Units for all parameters are in mg/L except for pH and log (CO_2), which are unitless, redox is in mV, DO is % saturation, and EC is mS/cm.

‡ Data is averaged across sampling time and replications. Values in parenthesis represent standard deviations.

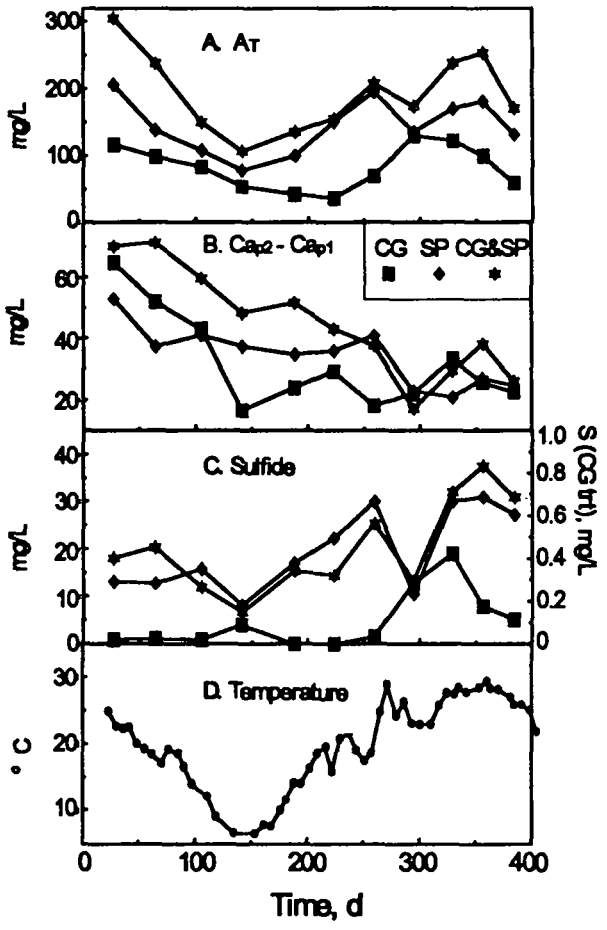

Figure 2. Total alkalinity, A_T (A), Ca increase (B), sulfide (C), and water temperature (D) changes with time in the effluent waters from the anaerobic wetland cells for the canarygrass (CG), SAPS (SP), and canarygrass+SAPS combination (CG&SP) treatments. Calcium increase is the difference in Ca concentrations in the effluent and influent waters of the anaerobic cells (Ca increase = Ca_{out} - Ca_{in}).

Anaerobic Wetland Cells

Alkalinity in the effluent waters of the anaerobic cells was correlated fairly well with water temperature (Fig. 2A). Alkalinity was greater with higher water temperatures. Alkalinity generation was greater in the anaerobic treatments containing compost (SP and CG&SP) compared to CG. The alkalinity from CG&SP was greater than SP alkalinity during the warmest times of the year at the initiation of the experiment (day 0 to day 60) and during the summer (day 320 to day 360).

A chemical parameter that has a relationship to alkalinity generation is Ca concentration difference between effluent and influent waters (Fig. 2B). If the Ca difference can be assumed to be due solely to calcite dissolution, some conclusions on calcite dissolution effectiveness can be made in these systems. Calcite dissolution was greatest at the initiation of the experiment and continually declined with time for all anaerobic treatments. Calcite dissolution declined more rapidly in the CG treatment probably due to a limited amount of calcite present in the river gravel. Calcite dissolution did not show seasonal trends. For example, the Ca difference continually declined during the warming time of the year from day 200 to day 400. The decline in calcite dissolution may have been due to calcite particles being continually coated by organic matter and inorganic precipitates.

Another chemical parameter related to alkalinity generation is sulfide concentrations as shown in Fig. 2C. Sulfide was much greater in the treatments containing compost (SP and CG&SP) compared to the treatment without compost (CG). The increase in sulfide concentrations was correlated well with increased water temperatures that must have increased productivity of sulfate reducing bacteria. At day 290 sampling, there was a drastic decline in sulfide concentration in SP and CG&SP. The systems were fertilized with N, P and K at day 282. The decline in S may have been due to sulfate-reducing bacteria unsuccessfully competing with other heterotrophic bacteria that may have flourished after adding supplemental nutrients.

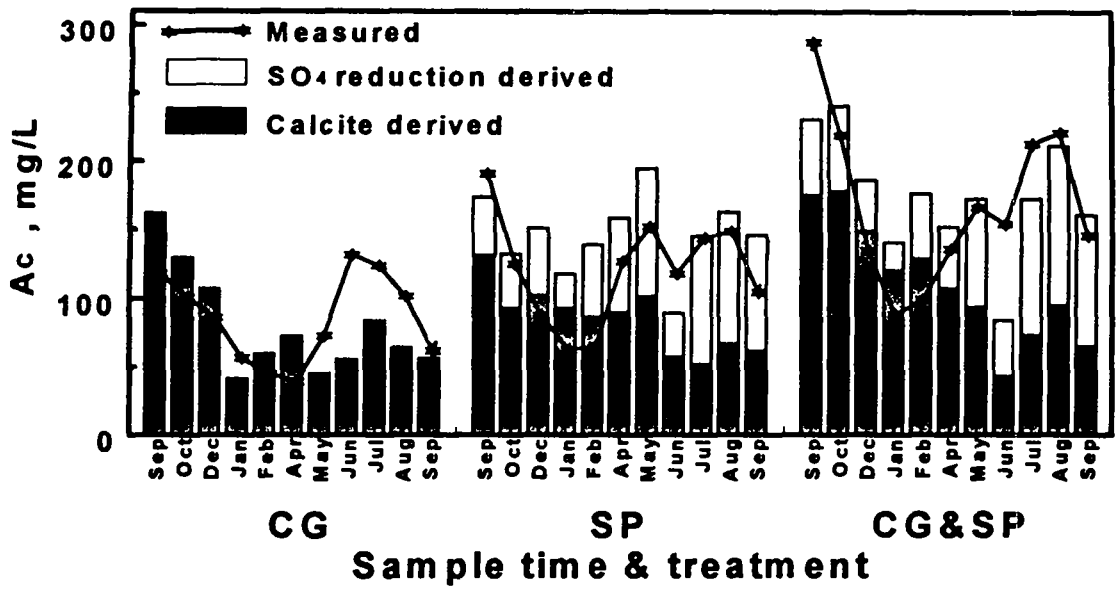

Figure 3. Calculated carbonate alkalinity (A_C) based on calcite dissolution and sulfate reduction compared to measured carbonate alkalinity in effluent waters from the anaerobic wetland cells for the canarygrass (CG), SAPS (SP), and canarygrass + SAPS combination (CG&SP) treatments.

The expected carbonate alkalinity produced from calcite dissolution and sulfate reduction was calculated and compared to carbonate alkalinity from measured total alkalinity (see Materials and Methods) (Fig. 3). Alkalinity calculated from calcite dissolution and sulfate reduction followed a trend similar to measured alkalinity with lower alkalinity during colder periods of the year and higher alkalinty during warmer periods. However, there were discrepancies between measured alkalinity and total alkalinity predicted from calcite dissolution and sulfate reduction. The overestimated alkalinity predicted from calcite dissolution and sulfate reduction can be due to an increase in Ca concentration related to chemical processes that do not release HCO_3^- into solution, such as exchangeable Ca or dissolution of non-carbonate Ca minerals such as gypsum. Another possible explanation is that pure calcite was not present so the assumption that 2 moles of HCO_3^- was released for each mole of Ca dissolved may have overestimated alkalinity calculated from Ca dissolution. Yet another explanation is that HCO_3^- released from calcite dissolution precipitated with other metals, such as Mn, leaving Ca in solution while HCO_3^- was removed.

The underestimation of alkalinity during the months from May to August in CG and from June to July in CG&SP may have been due to active canarygrass roots releasing HCO_3^- during anion uptake (Mengel and Kirkby, 1982), which would be an unaccounted source of alkalinity. The SP treatment did not contain canarygrass, but did contain algae in the surface water. Lower CO_2 and higher pH were observed in the SP treatment compared to the CG and CG&SP treatments (Table 2). Algae absorbs CO_2 during photosynthesis which increases pH (Vymazal, 1995), but these processes counterbalance

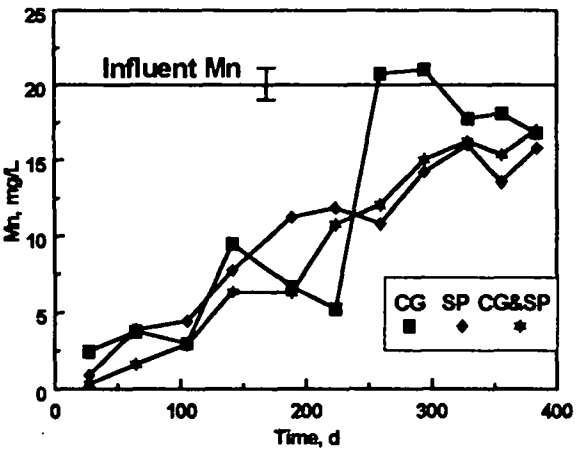

Figure 4. Manganese concentrations in effluent waters from the anaerobic wetland cells for the canarygrass (CG), SAPS (SP), and canarygrass+SAPS combination (CG&SP) treatments with time.

one another with no change in alkalinity (Butler, 1991). Therefore, large differences were not observed between measured and predicted alkalinity in SP during the summer months.

The anaerobic cells effectively removed Mn in influent waters with low effluent Mn concentrations observed at the beginning of the experiment (Fig. 4). However, as time progressed Mn removal efficiency declined as Mn concentrations approached influent concentration of 20 mg/L. Similar trends in Mn removal were observed by Wildeman et al. (1993) and Stark et al. (1995). In Wildeman et al. (1993), bench-scale studies of anaerobic systems have shown greater than 95% Mn removal from 24 to 71 days of operation. However, in a pilot-scale anaerobic wetland with influent Mn concentration of 31 mg/L, Mn removal efficiency was near 50% during the first 3 months with removal efficiencies declining to 10% from 6 to 24 months of the study. In Stark et al. (1996), results similar to Fig. 4 were obtained with Mn concentrations slowly increasing in effluent of anaerobic wetlands with 50% removal efficiency occurring at approximately 120 day.

As anaerobic wetlands are initiated there may be plentiful sorption sites on organic matter and limestone for Mn to sorb onto. Although the affinity of organic functional groups for Mn is low (McBride, 1994; Wildeman et al., 1994), some sorption of Mn onto abundant carboxyl and hydroxyl functional groups in the compost should be expected. Manganese sorption onto limestone may occur via surface displacement of Ca^{2+} for Mn^{2+} to form a solid solution or precipitation of a $MnCO_3$ solid phase at the surface (Evangelou, 1995). Once Mn sorption capacities were reached on both compost and limestone media and no other important removal mechanism existed, Mn concentrations in effluent water from anaerobic wetlands would be expected to increase as observed in Fig. 4.

To determine what Mn solid phases were controlling Mn in the water of the anaerobic cells, saturation indices were calculated and are plotted in Fig. 5. Throughout the experiment, the water was very much undersaturated with respect to MnOOH. The Mn oxide solid phases contain Mn in an oxidized state. The reducing conditions of the anaerobic wetlands keep Mn in the reduced manganous state (Mn^{2+}), making formation of Mn oxides extremely unlikely.

The anaerobic waters were undersaturated with respect to $MnCO_3$ at the beginning of the experiment. From day 220 to day 400, water from the SP and CG&SP treatments was near equilibrium to supersaturated with respect to $MnCO_3$. From day 300 to day 400, water from CG was near equilibrium to undersaturated with respect to $MnCO_3$. Similar Log (SI) values were reported for $MnCO_3$ in effluent waters from anoxic limestone

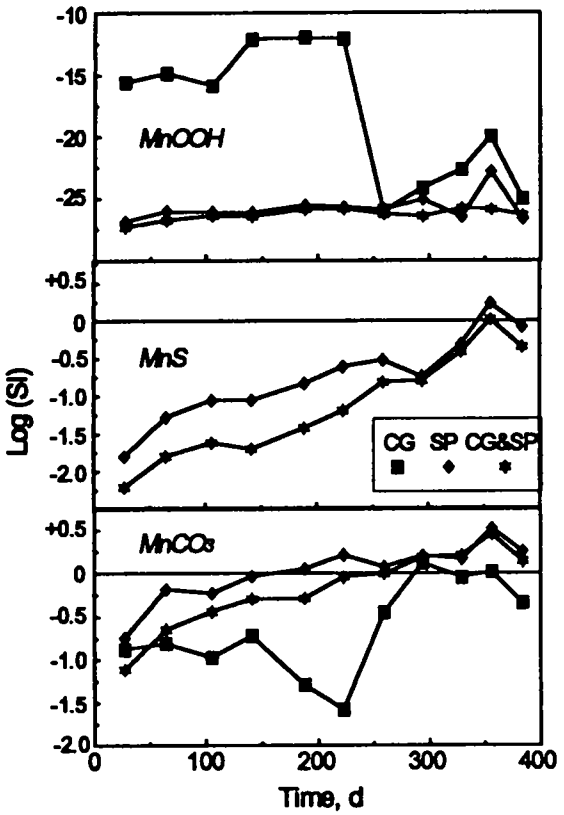

Figure 5. Logarithm of saturation indices (Log (SI)) for MnOOH(s), MnS(s), and $MnCO_3$(s) in effluent waters from the anaerobic wetland cells for the canarygrass (CG), SAPS (SP), and canarygrass+SAPS combination (CG&SP) treatments with time.

drains (Hedin and Watzlaf, 1994) where limited Mn removal in the waters occurred. The Log (SI) values indicated conditions existed for $MnCO_3$ to form and may exert some control on Mn concentration in water toward the end of the experiment. The supersaturation levels that existed may have been due to kinetic limitations on $MnCO_3$ precipitation.

The waters from the treatments with organic matter (SP and CG&SP) were undersaturated with respect to MnS for most of the study until day 350 when the solutions were near equilibrium with this mineral. Saturation indices was not calculated for the CG treatment since sulfide was not detected in most of the samples. The solubility of MnS is fairly high compared to other metal sulfides. Therefore, removal of Mn in anaerobic wetlands via MnS formation is not very effective.

The data in Fig. 5 further supports the hypothesis that Mn was being sorbed onto compost and limestone at the beginning of the experiment when the waters were undersaturated with respect to MnS and $MnCO_3$. As the sorption sites filled, Mn concentrations rose to a high enough level so MnS and $MnCO_3$ could begin to control Mn solubility. The advantage of removing Mn via precipitation as $MnCO_3$ or MnS is that the anion precipitating with Mn is in constant supply from the sulfate reduction process. This is contrary to Mn removal via sorption where the component removing Mn (sorption sites) has a finite availability. A disadvantage of Mn being removed as $MnCO_3$ or MnS is that the solubilities of the minerals are so high that they support Mn concentrations in water that are unacceptable for discharge (Fig. 4). Therefore, a subsequent oxidation of the Mn to form Mn oxides is required in an aerobic wetland.

The concentrations of Cu, Ni, Pb, and Zn in the effluent from the anaerobic cells containing organic matter (SP and SP&CG) were always near the detection limit for the ICP (Table 2). However, the Ni and Zn concentrations in the anaerobic effluents from the CG treatment increased to 1.1 to 1.2 mg/L after 120 days and subsequently decreased (Fig. 6).

The redox in the treatments with organic matter were always at very low values (approx. -200 mV) throughout the experiment, whereas the redox in the effluent stream from the CG treatment was >400 mV up to day 240 and then drastically dropped to maintain redox levels between -200 and 200 mV. The decrease in the

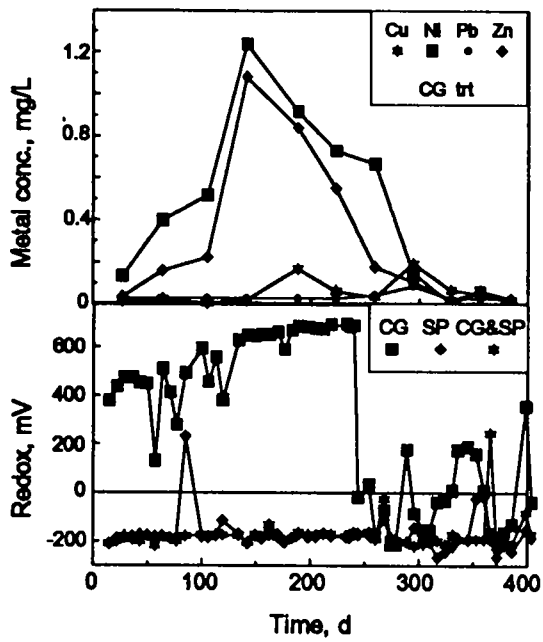

Figure 6. Concentrations of Cu, Ni, Pb, and Zn and redox in effluent waters from the anaerobic wetland cells for the canarygrass (CG), SAPS (SP), and canarygrass+SAPS combination (CG&SP) treatments with time.

redox in the CG treatment coincided with the spring growth of the canarygrass in late April 1995. As in this study, canarygrass growth has been observed to reduce redox levels to very low values in gravel bed wetlands (Zhu and Sikora, 1995; Steinberg and Coonrod, 1994). Because of this ability to reduce redox levels, canarygrass was chosen for this experiment to determine if sulfide could be produced in a plant-rock system without organic matter. Even though redox levels were low (<200 mV), there must still have been limitations to sulfate reduction due to the low sulfide concentrations observed (Fig. 2). The limitation was probably a lack of available C.

To determine what solid phases may have been controlling concentration of trace metals in the anaerobic wetland effluents, stability diagrams were constructed with log of metal activities plotted versus pe+pH (Fig. 7). The data represented in the figure is only from samples in which the metal was detected above analytical detection limits of the ICP. This represented 33, 30, 8, and 42 % of the samples collected for Cu, Ni, Pb, and Zn, respectively. The data for the treatments with organic matter (SP and CG&SP) were combined since there was very little difference between these treatments. The Cu activities were undersaturated with respect to $CuCO_3$. Except for some data from the CG treatment, there was an observable trend that Cu activities were drastically reduced with a decrease in pe+pH due to precipitation of CuS. Most of the CG data at higher pe+pH indicate Cu may be controlled by a Cu oxide solid phase. Nickel activity levels were undersaturated with respect to $NiCO_3$ and $Ni(OH)_2$ indicating some other solid phase or sorption was controlling this metal in solution. At low pe+pH, data clustered around the NiS solubility line. From the limited data available for Pb, $Pb(OH)_2$ appeared to control Pb activities at high pe+pH and PbS controlled Pb activity at low pe+pH. For Zn, solubility appeared to be controlled by $ZnCO_3$ in the CG data at high pe+pH and by ZnS at low pe+pH for all treatments. Figure 7 is only useful as a qualitative predictor of what minerals may control metal activities in solution because indirect analysis of what solid phases may be present is made from solution chemistry. Other solid phases not considered or sorption of metals onto Fe and Mn oxides (McBride, 1989) may have also controlled metal solution activities.

The similarity in the solubility diagrams of Fig. 7 is that metal sulfides precipitate and reduce metal activities to very low levels in solution at low pe+pH. The pe+pH value at which the metal sulfide solubility line begins to decline depends on the solubility of the

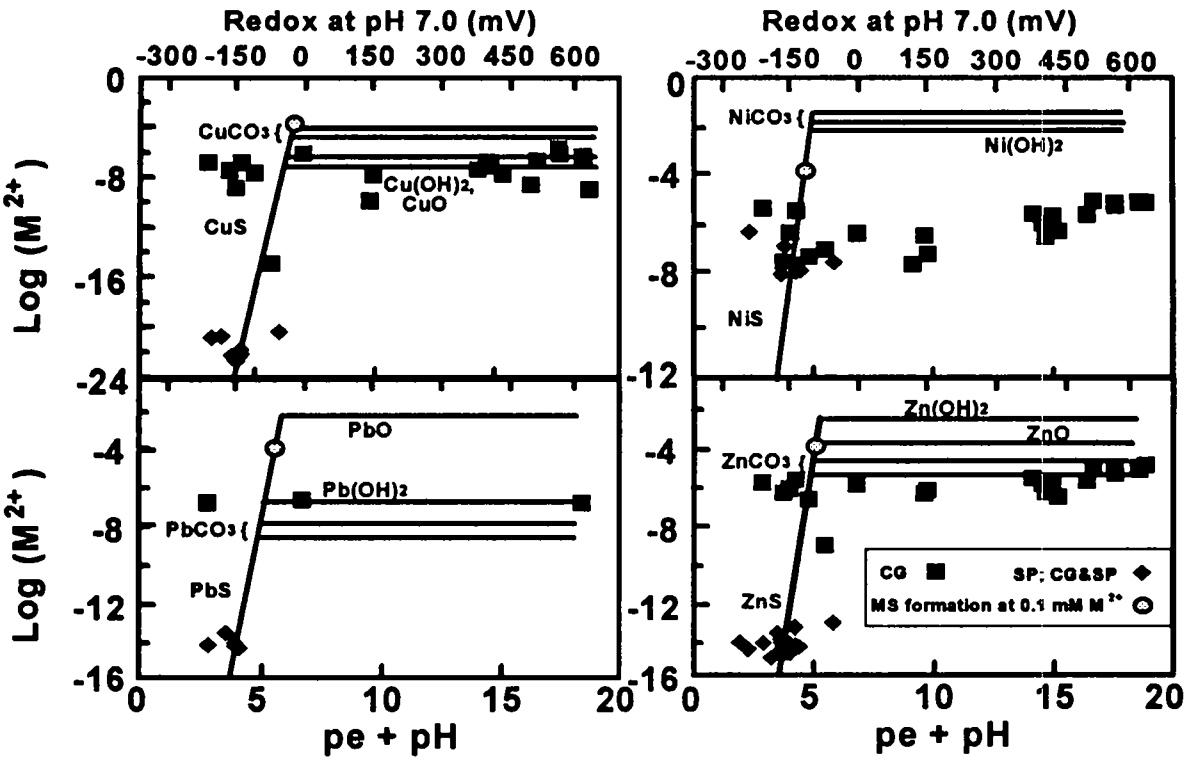

Figure 7. Metal activities as a function of pe + pH for Cu, Ni, Pb, and Zn in effluent waters from the anaerobic wetland cells for the canarygrass (CG), SAPS (SP), and canarygrass+SAPS combination (CG&SP) treatments. Symbols represent experimental data. Lines represent solubility of known solids. The two lines for $MnCO_3$ represents the range of $MnCO_3$ solubility for low measured alkalinity (upper line) and high measured alkalinity (lower line). The upper x axis is the equivalent redox value for the average pH level of 7.0.

metal sulfide. The greater the solubility, the lower the pe+pH has to be before precipitation of the metal sulfide begins. The redox levels at pH 7 required to reduce metal activities below 0.1 mM are -24, -62, -94, and -114 mV for Cu, Pb, Zn, and Ni, respectively (shown as shaded circles in Fig. 7). Although not shown in Fig. 7, the required redox at pH 7 to reduce Mn activities below 0.1 mM via MnS formation is -175 mV. Therefore, the affinity of metals to form metal sulfides decreases in the order Cu>Pb>Zn>Ni>Mn. The same trend for metal sulfide formation can be presented by comparing solubility products of the metal sulfides (Hedin et al., 1994). Both the anaerobic treatments with organic matter (SP and CG&SP) produced very low redox levels, which were adequate in precipitating Cu, Ni, Pb, and Zn as metals sulfides and reducing solution concentrations of the metals to very low levels (Table 1).

The stability diagrams for Ni and Zn concentrations in the CG treatment in Fig. 7 can be used to explain observed changes in Ni and Zn concentrations (Fig. 6). At higher pe+pH, $ZnCO_3$ appeared to control Zn solubility (Fig. 7). At the beginning of the experiment, alkalinity was high which would be expected to lower Zn concentrations

Table 3. Water chemical parameters affected by reciprocation in aerobic treatments. Only the aerobic cells treating effluent from the SP and CG&SP anaerobic treatments are considered.

Parameter †	Anaerobic effluent	First aerobic cell		Aerobic effluent	
		w/recip	wo/recip	w/recip	wo/recip
pH	7.1	7.7(0.2)‡	7.2(0.1)	7.7(0.2)	7.3(0.4)
Alkalinity	168	63(19)	149(62)	63(16)	127(46)
Log(CO_2)	-1.8	-2.85(0.10)	-1.91(0.20)	-2.85(0.13)	-2.17(0.46)
Redox	-173	544(124)	-195(87)	588(112)	509(155)
DO	2.4	94(14)	2.3(2.3)	93(14)	11(11)
Mn	10	0.31(0.88)	6.2(3.4)	0.05(0.08)	0.35(0.35)

† Units for pH and Log (CO_2,atm) are unitless, alkalinity is in mg/L, redox is in mV, DO is in % saturation, and Mn is in mg/L.

‡ Data is averaged across sampling time and replications. Values in parenthesis represent standard deviations.

due to $ZnCO_3$ precipitation. As time progressed, alkalinity declined (Fig. 1) resulting in subsequent increase in Zn concentrations (Fig. 6). The redox of the CG effluent water dramatically dropped at day 240 (Fig. 6) which resulted in a decrease in pe+pH to levels that predicted ZnS and NiS controlled (Fig. 7) and lowered Zn and Ni concentrations (Fig. 6).

Aerobic Wetland Cells

There were little differences in Mn concentrations in the effluent waters from the aerobic cells treating water from the anaerobic cells containing organic matter when comparing reciprocating and non-reciprocating treatments (Table 3). However, considerable differences were observed for these parameters in waters taken from the first aerobic cells (Table 3). The cells with reciprocation resulted in higher DO, redox, and pH levels in the first aerobic cells compared to non-reciprocating cells. The high redox and pH levels most likely resulted in lower Mn concentrations in the first reciprocating aerobic cells compared to the first nonreciprocating cells (Table 3) due to greater likelihood for Mn oxide precipitation to occur. The long retention time of 9 days in the aerobic cells was ample for adequate removal of Mn in the final effluent whether the cells were reciprocating or not.

A plot of log Mn activity vs pe+pH was constructed (Fig. 8) for predicting what solid phases may have been controlling Mn concentrations in the aerobic wetlands. The lines are predictive solubility lines for MnS, $MnCO_3$, MnOOH, Mn_2O_3, and Mn_3O_4. Without reciprocation, most of the waters in the first aerobic cells had low pe+pH values and the Mn

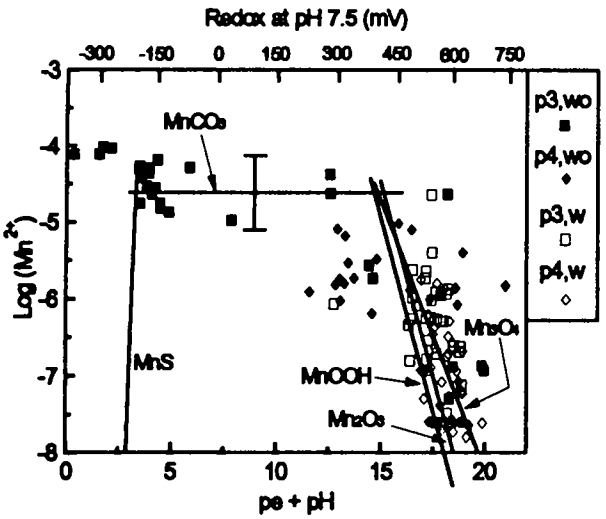

Figure 8. Manganese activities as a function of pe + pH in water sampled from p3 and p4 (see Fig. 1) in the aerobic wetland cells for treatments without reciprocation (wo) and with reciprocation (w). Symbols represent experimental data. Lines represent solubility of known solids. The error bar for $MnCO_3$ represents the range of $MnCO_3$ solubility for low measured alkalinity (upper boundary) and high measured alkalinity (lower boundary). The upper x axis is the equivalent redox value for the average pH level of 7.5.

activities appeared to be controlled by a combination of MnS and $MnCO_3$. In the effluent waters of the nonreciprocating treatment, the pe+pH levels increased and the Mn activities approached solubility with Mn oxides. The pe+pH levels were high at both sampling positions in the reciprocating treatment with Mn activities clustered around the Mn oxide solubility lines.

It is difficult to ascertain whether the mechanism for Mn oxidation was biotic or abiotic since poisoned abiotic treatments were not included in the experiment. However, a conclusion can be made that producing an environment that thermodynamically favors Mn^{2+} oxidation and precipitation as Mn oxides is the first requirement for Mn removal from solution. Such an environment is produced with pe+pH above 15 or redox above 400 mV at pH 7.5. A second requirement may be that an appropriate type and quantity of bacteria needs to be present to increase the rate of Mn oxidation. The influent waters to the aerobic systems were highly anaerobic which may have exaggerated the utility of having a reciprocating aerobic wetland to rapidly increase pe+pH to allow for rapid Mn oxidation and subsequent precipitation. For waters that already have higher pe+pH, aerating the water may not be that critical. Although aeration occurred via reciprocating water in a gravel bed in the current experiment, aeration by passing the water over a riprap may also suffice in increasing pe+pH levels to allow for rapid Mn oxidation and precipitation.

CONCLUSIONS

The data collected the first year of this study has shown decreased calcite dissolution and Mn removal efficiencies with time in anaerobic wetlands. Alkalinity generation was observed to be seasonal with greater alkalinity in the warmer time of the year. Mn removal was very effective in aerobic wetlands following anaerobic wetlands. Aeration of effluent waters from anaerobic wetlands is required for raising pe+pH to high enough levels to allow for rapid oxidation of Mn to form Mn oxide precipitates. Trace metal removal was very effective in the anaerobic treatments with organic matter due to precipitation of metal sulfides. The study is being con- ducted for another year to determine long term efficiencies of the wetland systems and to develop scaled-up design criteria.

ACKNOWLEDGMENTS

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THE USE OF OVERLAND FLOW WETLAND TREATMENT SYSTEMS[1] TO REMOVE NICKEL FROM NEUTRAL MINE DRAINAGE

by

Paul Eger, Jon Wagner, Glenn Melchert[2]

Abstract. In 1992, two overland flow wetland treatment systems were built in existing natural wetlands in northeastern Minnesota to remove copper, nickel, cobalt and zinc from neutral mine drainage. Typical input metal concentrations ranged from 2 - 5 mg/L for nickel, to less than 0.1 mg/L for copper, cobalt and zinc. Flow rates were on the order of 75 L/min for both systems. The treatment systems covered 4200 m^2 and 7000 m^2 and contained a series of soil berms installed across the wetland, and about a 30 cm layer of a mixture of peat and peat screenings (a waste material generated during the processing of horticultural peat). Although these systems have been successful in removing about 70 - 90% of the input metals, output nickel concentrations in one of the wetlands exceeded the discharge standard by as much as a factor of four. Average flow rates were greater than the design value by a factor of two, and the wetland was unable to adequately treat this flow volume. In 1993 and 1994, changes made to reduce the hydraulic gradient and minimize channeling improved performance, but nickel concentrations still exceeded permit requirements during periods of high flow and during the fall as temperature decreased. In 1995, the mining company constructed an additional 10,000 m^2 of wetland to provide additional treatment. After the expansion, the discharge was in compliance with permit requirements, until high flows and decreasing temperatures in the fall caused nickel concentrations to exceed standards.

Additional keywords: copper, cobalt, zinc, passive treatment, stockpile runoff

Introduction

Wetlands have been used to address a variety of water quality problems, including those arising from agricultural, municipal and industrial sources (Hammer 1989, Moshiri 1993). Wetlands have also been successful in treating coal mine drainage, and are being examined for their ability to treat metal mine drainage (Hedin and Nairn 1993, Eger et al. 1993, Wildeman et al. 1993). The use of wetlands to treat mine drainage is an attractive alternative to more conventional treatment methods. Wetlands are less costly to build than the conventional treatment systems, use processes which naturally occur in wetlands to remove metals from the water (e.g. adsorption, filtration), and offer a system that ideally should operate with little to no maintenance for extended periods of time.

LTV Steel Mining Company operates several taconite mines in northeastern Minnesota. At their Dunka Mine, located

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near Babbitt, surface drainage with elevated copper, nickel, cobalt, and zinc is generated as water infiltrates stockpiles of mineralized Duluth Complex (an igneous intrusive rock formation which contains disseminated copper and nickel sulfides). In the mid-1980's, LTV began an extensive program to evaluate various options for mitigating the problems at this mine. The company's preferred option was a combination of passive alternatives which would reduce flow emanating from their stockpiles, and which would use wetland treatment to remove metals from the resulting drainage. In 1988, four overland flow test cells were built to investigate methods to optimize metal removal and to provide design data for the ultimate implementation of wetland treatment at this facility. Based on the results of this study, two full-scale wetland treatment systems were built in the winter of 1992. This paper discusses the performance of those two systems.

Methods

General Construction

Each of the two treatment systems was built in existing wetlands. Construction began in the winter of 1992. The wetland systems were designed by STS Consultants, Ltd., and built by LTV Steel Mining Company (Frostman 1992).

Both areas were originally a combination of emergent (wet meadow) and scrub-shrub type wetlands, and the majority of the woody vegetation, which consisted primarily of alder, was removed from the site. The basic design for each system included the construction of a series of soil berms, which were built to control water levels and to maximize contact between the drainage and the substrate (Figure 1). Soil berms were built with glacial till (sandy silt) available from a surface overburden stockpile on the property. After the berms were constructed, a one-foot layer of a mixture of local peat and peat screenings was applied. The screenings are a waste material generated during the processing of horticultural peat and consist mostly of wood fragments and long peat fibers. This material was selected to increase the permeability of the peat to at least 10^{-3} cm/sec and to provide available organic carbon. In the spring of 1992, the berms were hand-seeded with Japanese Millet, while the open water areas were seeded with cattails. To obtain the cattail seeds, cattail heads were placed in a container of water with a small amount of liquid soap and several large bolts, and then the mixture was agitated until the heads broke and the seeds were dispersed. The slurry was then broadcast over the wetland.

W2D/3D system

This system covers 4200 m^2, contains 6 berms, and treats the drainage from two seepages which are associated with waste rock stockpile 8031 (Figure 2). One of the seeps is diffuse with an undefined channel (Site W2D), while only limited flow data exists for the other seep (Site W3D). The average flow from the stockpile has been estimated to be on the order of 75 L/min. From 1992-94, the input to the wetland was estimated to have an average pH of 7, with mean metal concentrations of 1.92 mg/L nickel, 0.05 mg/L copper, 0.05 mg/L zinc and 0.02 mg/L cobalt (Table 1).

W1D system

The majority of the flow to this system originates from the base of the 8018 stockpile, although additional seepage from the 8031 stockpile also drains to this area (Figure 2). V-notch weirs were installed to provide continuous measurement of the input and output flows. Annual average flows, from 1986-94, ranged from 75 - 150 L/min, with peak flows exceeding 750 L/min. Water quality samples of the inflow and outflow were colleted twice per month during the period of flow (generally March - December). Samples were collected within the system about once per month (Figure 2). From 1992-94, the input to the

Table 1. 1992-94 water quality data for the W1D and W2D/3D wetland treatment systems.

	W2D/3D input	W2D/3D output	W2D/3D standards	W1D input	W1D output	W1D standards
pH	7.0	7.0	6.5-8.5	7.1	7.1	6.5-8.5
Copper	0.050	0.006	0.023	0.068	0.010	0.023
Nickel	1.92	0.124	0.213	3.94	0.38	0.484*
Cobalt	0.017	<0.001	0.050	0.032	0.010	0.050
Zinc	0.054	<0.01	0.343	0.051	0.012	0.343

All Concentrations are in mg/L except pH, which is in standard units.
* Nickel standard increased from 0.213 in 1995.

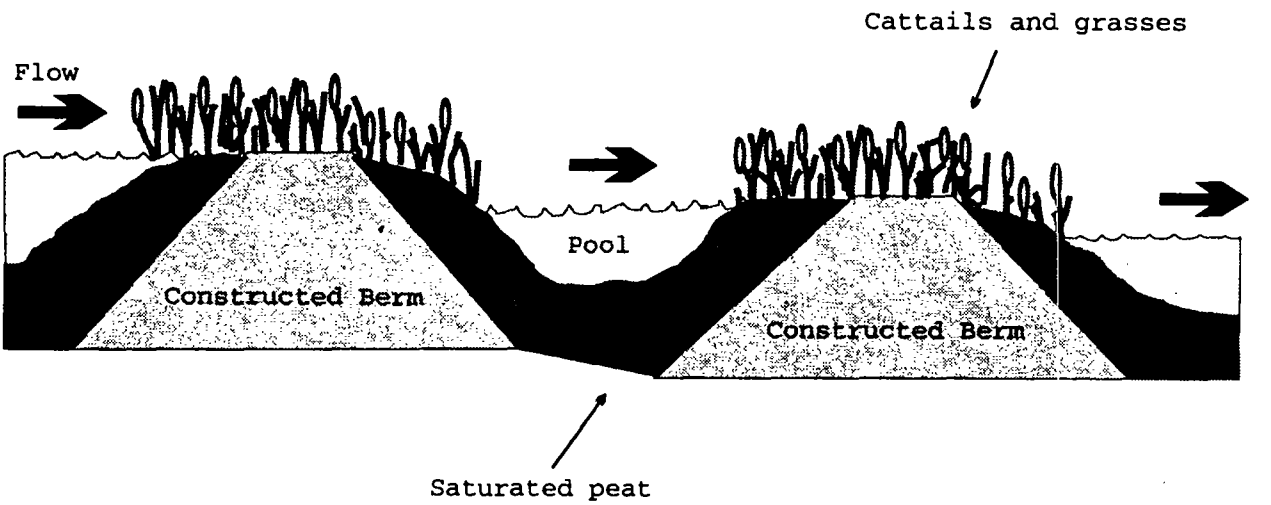

Figure 1. Cross section of typical berms (schematic).

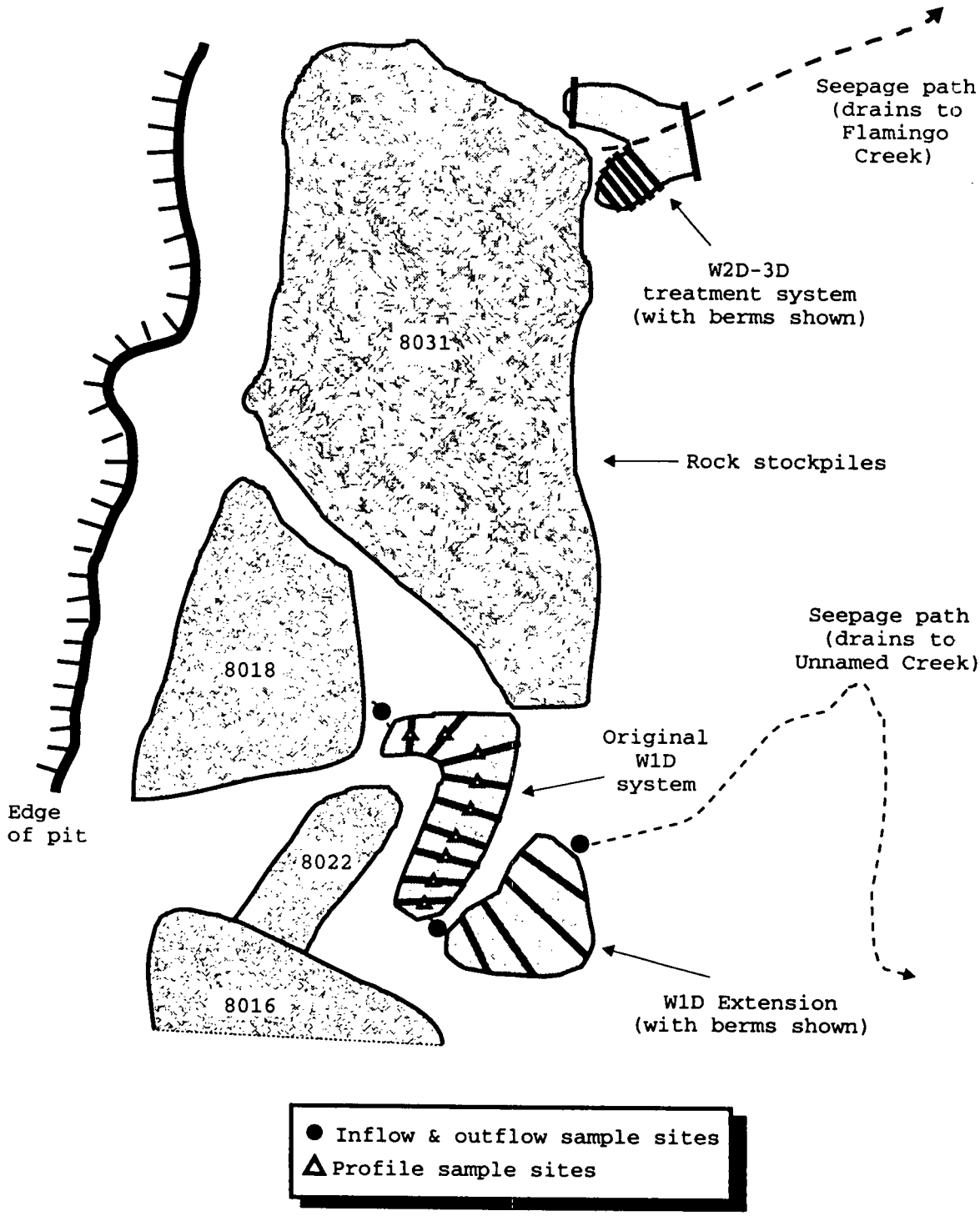

Figure 2. Dunka Pit site map showing locations of the W1D and W2D/3D wetland treatment systems and surrounding waste rock stockpiles.

wetland had an average pH of 7.1, and contained 3.94 mg/L nickel, 0.07 mg/L copper, 0.05 mg/L zinc and 0.03 mg/L cobalt (Table 1).

The original W1D treatment system, constructed in the spring of 1992, covered 7000 m^2 and contained a series of 9 berms. In 1993 and 1994, changes were made to the system to disperse flow, minimize channeling and improve contact between the drainage and the substrate. In 1995, the system was expanded by 10,000 m^2, and included an alternating series of overflow and underflow berms (Figure 3). Prior to construction of these berms, the original organic soils were removed; the berms were then built on the mineral soil base and compacted to minimize any future settling.

Results

This paper will focus on the results from the W1D system. This site has higher flows, higher concentrations of trace metals, and a steeper slope than the W2D/3D system. The W2D/3D system has been in compliance with permit requirements since it was constructed in 1992 (Table 1).

Limited data collected prior to construction indicated that the metal concentrations were reduced to acceptable levels in the natural wetland even before the system was constructed (Lapakko and Eger 1987). The construction of the system and the addition of new substrate has made the system more efficient and increased the length of time the system should be capable of providing treatment.

W1D Flow

For the period 1992-94, the input flow rates were similar to the long term average for the site, with average annual flows of 110 - 150 L/min. Daily input flows ranged from 0 in the winter to around 750 L/min during periods of heavy precipitation. In general, outflow was greater than or equal to inflow, except during those periods of the summer when precipitation was low.

Water quality

Overall, the wetland was effective in reducing metal concentrations. All metal concentrations decreased, ranging from 70% for cobalt to 90% for nickel. Outflow levels of copper, cobalt, and zinc consistently met water quality standards (Table 1). Despite an overall 90% decrease in concentration, nickel exceeded the water quality standard, particularly during high flow periods in the summer and when temperatures decreased in the fall (Figure 4). Nickel concentrations to less than 0.2 mg/L after the size of the system was increased in the spring of 1995. Outflow concentrations were in compliance until October, when concentrations exceeded the effluent limit of 0.484 mg/L (Figure 4).

Mass Removal

Overall metal mass removal in the wetland, from 1992-94, has ranged from 4.5 kg for zinc to 453 kg for nickel. These correspond to areal rates of removal ranging from 1 to 96 $mg/m^2/day$ (Table 2).

Discussion

Trace metal removal in a wetland is influenced by a large variety of physical, chemical and biological processes (Hammer 1989). Physical processes, such as filtration and sedimentation, are important in removing particulate metals, while it is the chemical and biological processes that provide for the removal of dissolved metals. The majority of trace metal removal in wetland treatment systems is associated with the substrate (Wildeman 1993, Gersberg 1984). Data from the test cells constructed at the Dunka mine, indicated that over 99% of the metal removal was associated with the peat, with only about 1% being removed by the vegetation (Eger et al. 1994).

Table 2. Mass removal and areal removal rates, W1D wetland treatment system 1992-94.

	Mass Removed (kg)	Areal Removal Rate * (mg/ m^2 /day)
Copper	6.1	1.3
Nickel	453	96
Cobalt	6.7	1.4
Zinc	4.5	1.0

* Calculated by dividing the total mass removed by the area of the wetland and the number of days of flow

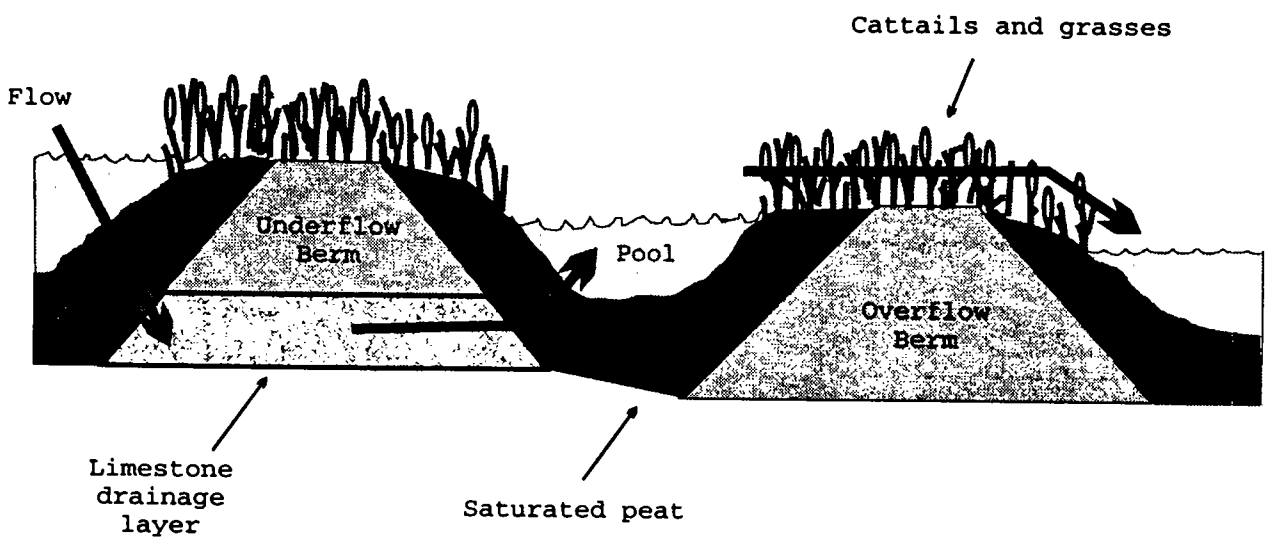

Figure 3. Cross section of an underflow/overflow berm system (schematic).

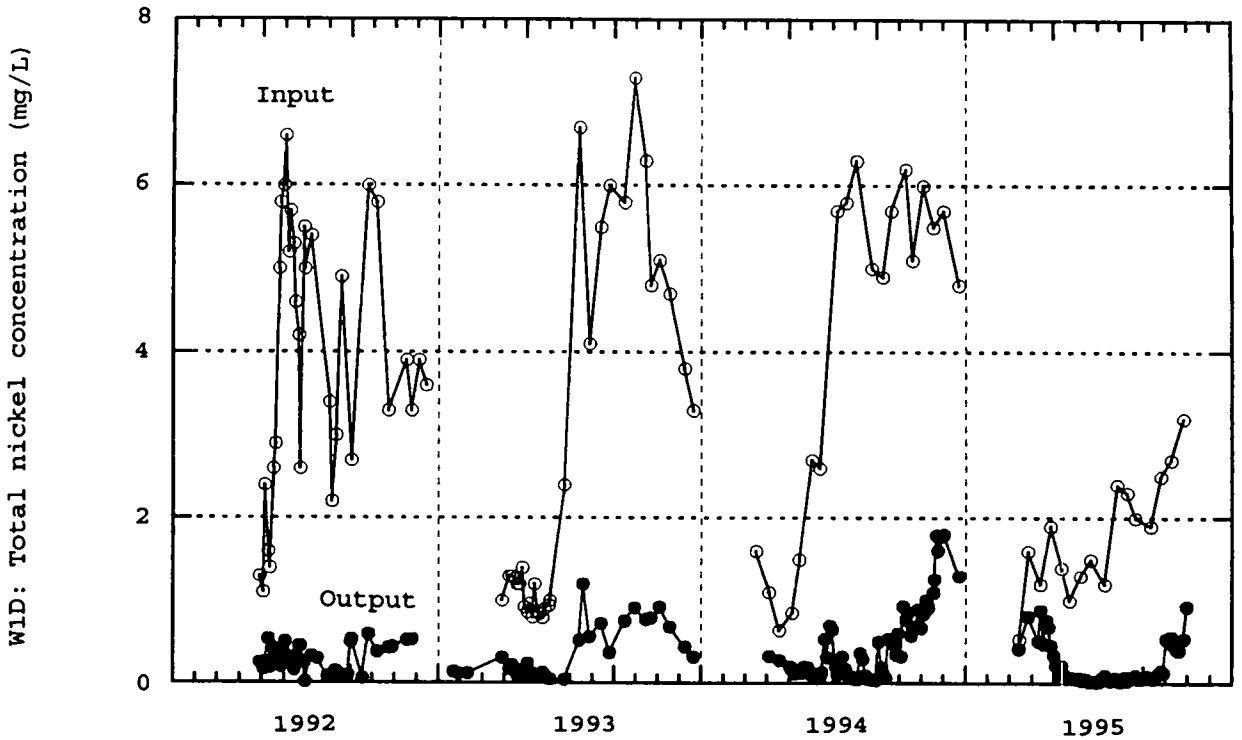

Figure 4. W1D input and output nickel concentrations, 1992-1995.

(Vegetation can enhance overall removal by dispersing flow, increasing the hydraulic conductivity of the organic substrate, and providing a source of new organic material.) Therefore, any full-scale system should be designed to maximize the contact of the drainage with the substrate. Metal removal in the test cells with a water depth of 5 cm was significantly greater than in those where the water depth was 15 cm (Eger et al. 1993). Removal in the test cells also increased as residence time increased, with a minimum of two days needed to achieve optimum removal.

Important factors in the design of a wetland treatment system to remove metals include detailed characterization of the drainage, the effluent standards that must be met, and performance data for the type of wetland to be constructed (Eger and Melchert 1992). Two of the most important design parameters are the residence time and the rate of metal removal in the wetland. Both of these factors are needed to determine the appropriate size of the wetland system.

Using the results from the test cells, an initial size for the W1D system was determined (Eger and Melchert 1992). The required treatment area was calculated based on: 1) the minimum required residence time needed to achieve compliance with permit standards and 2) the measured rate of metal removal expressed per unit area (Table 3). Since the area of the wetland must be of sufficient size compliance with permit standards to satisfy both the residence time and metal removal criteria, the

Table 3. Comparison of the actual constructed wetland size to the site required based on initial design calculations, for the W1D and W2D/3D systems.

	W2D/3D Design Values	W2D/3D[a] Actual Values 1992-94	W1D Design Values[b]	W1D Actual Values 1992-94
pH	7.0	7.0	7.1	7.1
Nickel (mg/L)	2	1.92	5.4	3.9
Flow (L/min)	75[c]	75[c]	75[d]	150
Required Size (m^2)	3700	4200	6300(12,600)[e]	7000(17,000)[f]
• Based on Flow	3700	NAp	3700 (7400)[e]	NAp
• Based on Metal loading	2500	NAp	6300 (12,600)	NAp

a: Concentration values are based on samples from site W3D
b: Average Values, 1980-91.
c: Estimated.
d: Average, 1990-91.
e: Value in parentheses based on long term flow value, 1986-1991
f: Wetland site was expanded to 17,000 m^2 in the spring of 1995
NAp: Not applicable

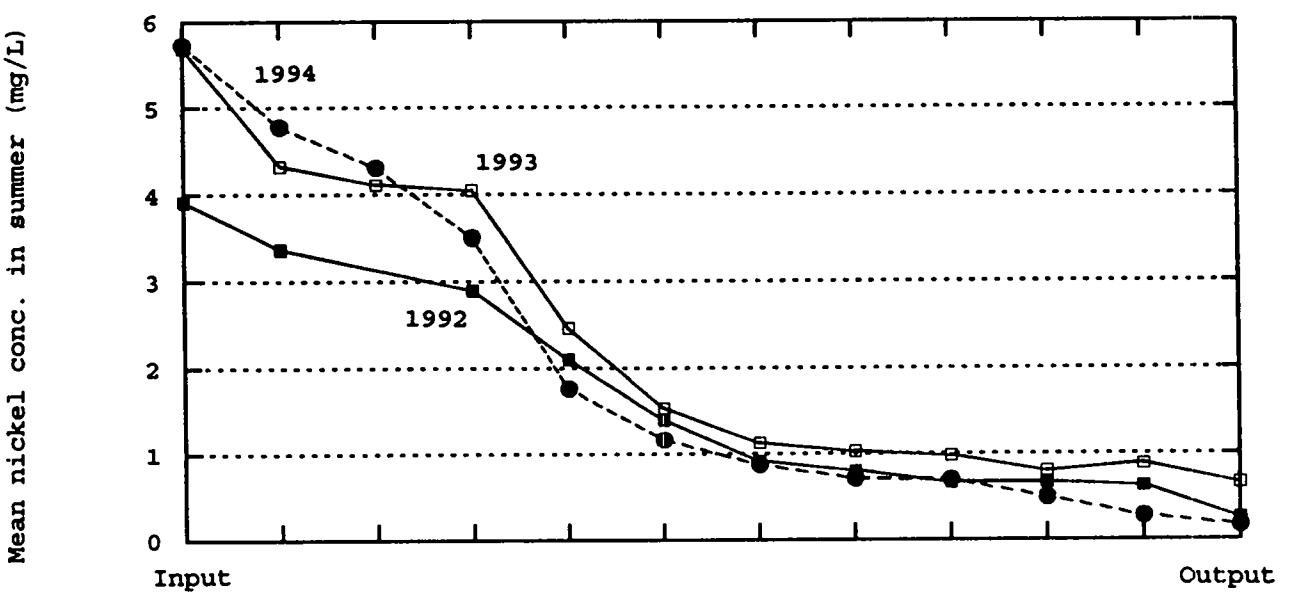

Figure 5. Nickel concentrations within the W1D wetland treatment system during the summer periods of 1992-1994. The values shown for each site are the means of the available summer data.

larger of the two calculated areas should be used as the basis for the design. Assuming an average input flow of 150 L/min (long term average), a residence time of two days, water depth of 5 cm, and good flow dispersion, the wetland size based on residence time was 7400 m^2, and 12,600 m^2 based on the rate of metal removal. Since these calculations use only the average flow, additional area or storage should be included if higher flows are to be treated adequately. Table 3 compares the size of the original W1D system and the W2D/3D system with the initial estimates made from the test cell data.

The initial size of the W1D system was substantially smaller than the area calculated from the test cell data, while the size of the W2D/3D system exceeded the calculated area. There were two reasons for the reduced size of the original W1D system. Since the company was modifying a natural wetland to provide treatment, the Minnesota Pollution Control Agency wanted to minimize the extent of wetland disturbance. The company had also made some changes to the watershed around the stockpiles. They believed that the average flow for the two years immediately preceding construction, although lower than the long term average, was representative of future flow and they based their design on this assumption. If the average input flow had been 75 L/min, the area would have satisfied the criteria developed from the test cells.

The inability of the W1D wetland to produce water which consistently satisfies the effluent requirements is primarily due to its small size and inadequate flow dispersion. Performance is particularly poor during periods of high flow. Flow channels have developed in the wetland, particularly in the lower half of the system, decreasing the contact between the drainage and the substrate. The average measured flow during 1992 to 1994 was essentially the same as the long-term average, and as a result the wetland was undersized by about a factor of two. Water samples collected from within the wetland indicated that metal removal was particularly low in those areas with significant channelization (Figure 5). Dye studies confirmed the lower contact and shorter residence time in this section (McCarthy et al. 1994).

Once the system was enlarged, concentrations decreased to levels below standards until October 1995, when concentrations increased dramatically and exceeded discharge limits (Figure 4). Unusually large rains (13 cm) at the end of September dramatically increased inflow at a time when wetland performance typically decreases due to decreasing temperatures. Additional data will be collected and analyzed to better determine the cause of the lack of treatment efficiency during this time.

Conclusions

Wetland treatment has been successful in reducing trace metal concentrations in stockpile drainage by over 90%. Design criteria derived from test cells provided a reasonable estimate of required wetland size. Measured rates of metal removed expressed per unit area of wetland ranged from 1 $mg/m^2/day$ for zinc to 96 $mg/m^2/day$ for nickel. Enlarging the W1D system improved metal removal and generally produced effluent which met water quality standards. Additional work is planned to investigate the poor performance of the system in the fall of 1995, metal removal within the wetland, and the total metal removal capacity of the wetland.

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TREATMENT OF METAL CONTAMINATED GROUNDWATER IN PASSIVE SYSTEMS: A DEMONSTRATION STUDY[1]

by

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Abstract. A pilot scale field test on passive treatment systems for metal and sulfate removal from ground water and surface runoff, is being conducted in Butte, Montana. This study is 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, and Fe). The field demonstration systems include anaerobic horizontal flow gravel bed wetlands with plants, horizontal flow gravel/organic substrate wetlands with plants, and vertical upflow gravel/organic substrate system without plants. The experimental design for sulfate and metal removal will be presented as well as the hydraulic design criteria used. Results from this test will be used to estimate system economics, long term performance and the life expectancy for these systems. Studies on mesoscale passive treatment systems such as 1.5 m high vertical upflow gravel/organic substrate columns are also presented. The parameters describing system performance are: hydraulic conductivity, volumetric sulfate-reduction rate, and metal immobilization rate.

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

Introduction

Acid mine drainage affects natural waters by decreasing water quality, stream aesthetics, and and the productivity of fisheries and other aquatic biota.

Natural and constructed wetlands have been used for many decades mainly in Europe, as a low cost, low maintenance waste water treatment system. In recent years constructed wetland systems have been adapted to treat AMD in the U.S. Passive anaerobic treatment of AMD was successful in immobilizing metals and increasing pH of the water (Wildeman, 1992).

One of the aims for the remediation effort in Butte, Montana (USA) is the emplacement of wetlands for the treatment of storm water runoff and near surface groundwater from the Metro Storm Drain (MSD) (Figure 1). Suspended and dissolved metals are being transported with the MSD water into Silver Bow Creek and eventually into the Clark Fork River. This research project is part of the ARCO remediation activities in the Clark Fork River Basin, in Southwestern Montana.

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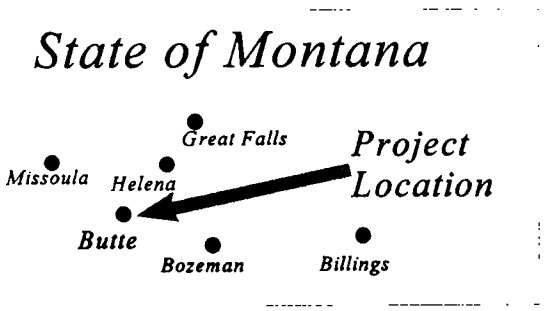


Figure 1. Location of the passive treatment demonstration site.

GOALS AND OBJECTIVES OF THE DEMONSTRATION STUDY

The overall goal of this demonstration study is to demonstrate the effectiveness of passive treatment systems for metal contaminated groundwater in Montana's alpine climate. Within this demonstration study the capabilities of three different passive treatment system designs are being evaluated based on hydraulic, chemical, microbial, and biological performance. An excessive monitoring system is in place to monitor hydraulic conductivity, water chemistry, and solids composition within the cells as well as in influent and effluent for each of the systems. Mechanistic and empirical models are being developed to increase our understanding of the fundamental processes occurring within these systems, including system performance, economy, and life expectancy. This information is essential for up scaling to a larger full scale operation.

MECHANISMS FOR METAL REMOVAL IN ANAEROBIC WETLANDS

Abiotic Processes

A pH increase in the aqueous phase due to the acid neutralizing capacity of the substrate can cause a consequent precipitation of dissolved metals and nonmetals. These pH induced precipitations can also indirectly cause other dissolved species to be removed from the aqueous phase. All of these pH initiated processes depend upon the acid neutralizing capacity, i.e. the alkalinity, of the substrate. If the alkalinity of the substrate will not be sustained, pH induced processes are short term.

Biotic Processes

Biotic initiated processes in anaerobic wetlands are the only long term self sustaining processes that will have a significant effect upon the effectiveness of the wetlands in treating acid metal and sulfate containing waters (Bolis *et al.* 1992). Sulfate reducing bacteria (SRB) will become active and produce hydrogen sulfide when exposed to a low redox potential (<-100 mV) and the presence of other required nutrients, such as short chain organic carbon compounds, nitrogen, phosphorous, and other required trace elements (Widdel, 1988). The presence of sulfide in anaerobic environments results in the formation of the corresponding metal sulfides which are extremely insoluble (Table 1) (Lawrence and McCarty, 1965). Many free metal ions can be inhibiting or toxic to the microbial consortium, whereas precipitated metal sulfides do not have a negative effect on microbial and acivity (Mueller and Steiner, 1992). These metal sulfide precipitates remain stable in anaerobic environments.

In most constructed wetlands for AMD a temperature between 4 and 20 °C is expected. Hence, the rate of microbial conversion will be slow and hydraulic residence times should be in the order of days to achieve sufficient microbial sulfate reduction from a complex substrate.

The microbial processes occurring in a natural or a constructed wetland are summarized in Figure 2. Complex organic carbon sources such as composts, or wood waste products are inexpensive and common energy sources. The carbon and energy inputs into the wetland system are present either from an external source (e.g., compost) or from plants within the system. This complex organic carbon is decomposed and converted microbially into suitable carbohydrates for fermentative organisms. Fermentative organisms

Table 1. Solubility of Heavy Metal Sulfides at 18 °C (Lawrence and McCarty, 1965).

Sulfide Salt	Solubility prod.	Solubility (mg/l)
CuS	$8.5\ 10^{-45}$	$9\ 10^{-18}$
Cu_2S	$2.0\ 10^{-47}$	$3\ 10^{-11}$
PbS	$3.4\ 10^{-28}$	$4\ 10^{-9}$
ZnS	$1.2\ 10^{-23}$	$3\ 10^{-7}$
FeS	$3.7\ 10^{-19}$	$5\ 10^{-5}$

further degrade these compounds into shorter chain volatile fatty acids and hydrogen that can be utilized by sulfate reducing bacteria. In the absence of sulfate or in the presence of inhibitors specific for sulfate reduction, methane could be produced (Loveley *et al.* 1982). Hence, a high sulfate concentration is desired to effectively suppress methane production.

System Design

Surge pond

The following is descibing design of systems presented in Figure 3 which is currently under construction. For most applications a surge pond or equalization pond is required to equalize water flow and water chemistry in the inlet water to the treatment systems. Another important function of the surge pond is solid settling. Since only minor fluctuations in water chemistry were observed for the MSD water and only a fraction of the total water flow is being treated, the main design criteria for the surge pond were its settling characteristics and its solid accumulation rate. Additionally the pond must hold a sufficient supply of MSD water to supply water to the treatment systems during a dry period.

Sediment settling tests in a 1.2 m high settling column were performed. After 30 hours a total suspended solids (TSS) reduction of 90% was observed. Multiplying by a safety factor of 3 and adjusting to a temperature of 2°C for increased water viscosity the resulting hydraulic retention time was 6.4 days.

Anaerobic treatment systems

The paradigm for successful treatment in a passive system includes three major components. The flow characteristics must be maintained within prescribed boundaries throughout the life of the system, the specific microbiological environment must be maintained, and heavy metals must be immobilized and permanently removed from the water phase. If any of these requirements are not met the system will be non functional with regard to effective metal removal.

The total required sulfate reduction may be calculated from the following based on metals and acid loading of the water (Eger, 1992):

$$M_{SO4} = \sum [Me^{2+}] + 1.5 \sum [Me^{3+}] + 0.5\,10^{-pH}$$

The volume of the constructed wetland has to provide sufficient sulfate removal to immobilize the metal loading and neutralize the acid loading. The required sulfate reduction rate (SRR) is dependent on flow rate and the total required sulfate reduction for metal removal in the contaminated ground water.

$$SRR = F \times M_{SO4}$$

The volumetric sulfate reduction rate (VSSR) is driven by the organic fraction of the system and can be calculated after the sulfate reduction potential (SRP) for a chosen substrate has been experimentally determined.

$$VSRR = SRP \times f_{co}$$

The total wetland volume (V_t) can then be calculated:

$$V_t = \frac{SRR}{VSRR}$$

Where:

F: flow rate [m^3/d];

f_{Co}: volumetric fraction of compost in the system [-];

SRP: sulfate reduction potential per volume substrate [$mole/m^3/d$];

M_{SO4}: stoichiometric amount of sulfate required to be reduced for complete metal immobilization and acid neutralization [mol/ m^3];
SRR: sulfate reduction rate for total metal immobilization and acid neutralization [mol/d];
VSRR: volumetric sulfate reduction rate per total system volume [mol/m3/d];
V_t: total wetland volume including inert gravel [m^3];

The effectiveness of the sequestering will impact the operational lifetime of the wetland. Information will be obtained by taking intact core samples and analysing the rate of metal accumulation in the systems, the form of the sequestered metals, and their stability.

Hydraulic considerations

The hydraulic residence time (HRT) of a gravel bed system can be calculated when the porosity (P) of the media is known:

$$HRT = \frac{V_t \times P}{F}$$

Hydraulic conductivity (K) is a critical parameter for a flow through a porous media and for the design of any wetland system. Most failures in the field have occurred because of inadequate knowledge of the short term and long term consequences of flow characteristics. K can be determined from Darcy's Law:

$$F = A_c \times K \times \frac{dh}{dl}$$

Where:
HRT: hydraulic residence time [d];
P: porosity [-]
A_c: crossectional area [m^2]
dh/dl: hydraulic gradient [-]
K: hydraulic conductivity [m/d]

There are several limits that will constrain the engineering choices that will be available. There will be a minimum allowable hydraulic conductivity, or alternatively for a fixed flow, there will be a maximum allowed hydraulic loading to the system to avoid fracturing, channeling, or short-circuiting around the wetland. As the fraction of organic material approaches zero (100 % gravel system) the fuel for the biological activity is eliminated, and this may adversely affect the microbial performance and the resulting metal removal efficiency.

Test Cell Dimensions and Layout

The tested passive treatment systems are two anaerobic gravel substrate wetlands sustaining horizontal flow of MSD water (Type 1 and 1A), an anaerobic organic compost - limestone gravel substrate wetland sustaining horizontal flow of MSD water (Type 2) and an anaerobic organic compost - limestone gravel substrate passive system sustaining upward flow of MSD water (Type 3) (Figure 3). The Type 1A wetland will have identical substrate as Type 1 but will be sized 50% smaller by volume. Each of the test systems are receiving MSD water from the surge pond. The effluent from each of these primary treatment systems passes through an aerobic wetland, designed to further, reoxidize and to remove iron and excess organic materials that have leached out from the compost systems. The surge pond effluent is distributed via underground pipes into each of the anaerobic test cells at a flow rate of 27.2 m^3d^{-1} to each unit. The effluents of cell 1 and 1A are combined and treated in an aerobic wetland. The effluents of cell 2 and 3 are combined and treated in a separate aerobic wetland. The effluents from the two aerobic wetlands are combined and discharged back into the MSD channel. Cell dimensions, hydraulic residence time, substrate/gravel composition, and the hydraulic conductivities are summarized in Table 2.

Complex Organic Substrates

Fermentative Organisms

Volatile Fatty Acids + HCO_3^- + H_2

Sulfate Reducing Bacteria ← SO_4^{-2}

$[HCO_3^-]$; $[OH^-]$; $[H_2S]$; $[CO_2]$

- In the absence of sulfate, methane is produced

<u>Metal Sulfide Precipitation</u>

$H_2S + Me^{2+}$ $MeS + 2H^+$

Figure 2. *Metabolic Pathways in anaerobic wetland systems.*

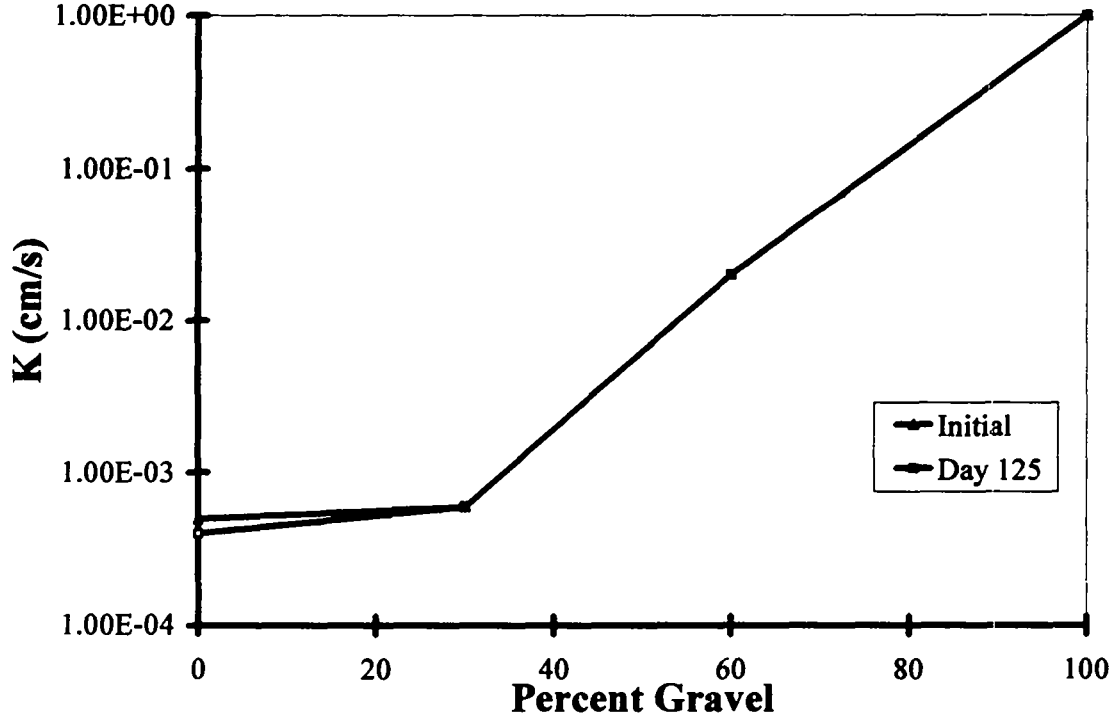


Figure 4. *Changes in hydraulic conductivity over time.*

Table 2. Design parameters for the anaerobic and aerobic test cells.

Unit Cell#	HRT [d]	flow [m³/d]	lxwxd [mxmxm]	vol m³	porosity [-]	compost/gravel [%/%]	hydraulic conductivity [cm/s]
Pond	7.0	154	20x36x1.5	1080	-	-	-
An 1	10.0	27.2	31x31x0.75	721	0.38	0/100	1-10
An 1a	5.0	27.2	22x22x0.75	370	0.38	0/100	1-10
An 2	6.0	27.2	14x27x1.2	453	0.36	20/80	0.1-0.5
An 3	1.5	27.2	9x9x1.5	122	0.34	50/50	0.01-0.06
A 1	2.8	54.5	28x8x0.7	157	NT	soil mix	NT
A 2	8.0	54.5	49x13x0.7	446	NT	soil mix	NT

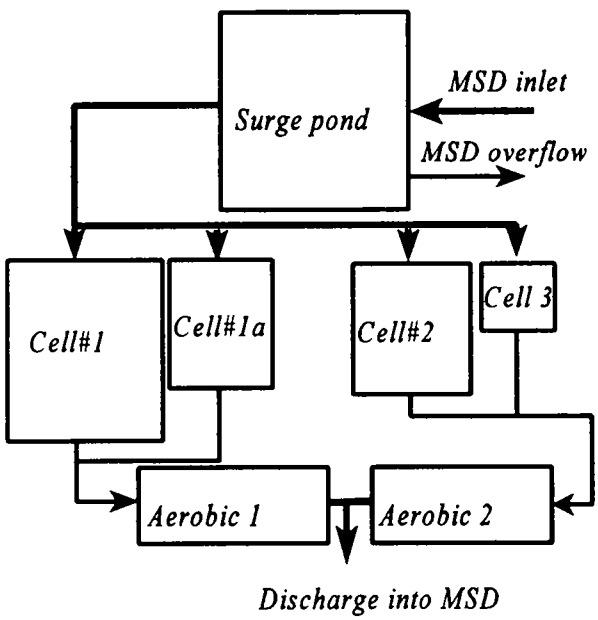


Figure 3. Schematic layout of the demonstration system.

Laboratory Results with Anaerobic Upflow Columns

Hydraulic Performance

Four 1.5 m high and 25 cm diameter upflow columns were operated over 6 months to test for hydraulic performance, sulfate reduction capacity, and metal removal efficiency. These tests columns were identical in height to the actual field system. Different ratios of compost to gravel were placed in each of the columns (Table 3). The hydraulic residence time was set at 1.5 days in all four columns. The hydraulic conductivity decreased significantly with a higher compost content in the columns. Table 3 indicates the

Table 3. Hydraulic conductivity values (K) measured in various gravel/compost mixt substrate.

C#	RG [%]	CG [%]	compost [%]	K [cm/s]
1	0	0	100	$7.8\ 10^{-4}$
2	10	20	70	$7.4\ 10^{-4}$
3	40	20	40	3.210^{-2}
4	80	20	0	1.0

dependence of hydraulic conductivity on substrate composition. The hydraulic conductivity was a function of substrate composition ranging from 100% compost to 100% gravel. A higher gravel fraction increased the hydraulic conductivity, causing the hydraulic conductivity value to asymptotically approach the performance of a pure gravel system as the pore size created by the gravel dominated the flow regime. Changes in hydraulic conductivity during 4 months of operation were not statistically significant for any of the tested

substrates (Figure 4).

Table 4. Chemical Composition of the Organic Compost Used in this Study

Constituent	value
pH (1:4 DI water)	6.7
alkalinity	23 mg $CaCO_3$/g dry weight
moisture	57 % by weight
organic content	80 % by dry weight
total organic carbon	46 % by dry weight
total Kjeldahl nitrogen	1.6 % by dry weight
SIN*	1713 ppm per dry weight
C/N - ratio	29.7
phosphate-P	276 ppm per dry weight
Cu	28 ppm per dry weight
Cd	<1 ppm per dry weight
Zn	114 ppm per dry weigh
Fe	272 ppm per dry compost

SIN: soluble inorganic nitrogen ($NH_4^+ + NO_3^- + NO_2^-$).

Chemical and microbial performance

Organic Substrate. To screen for a source of organic substrate to be used in an anaerobic passive treatment system for AMD the following criteria were applied: The total organic carbon content in the substrate should be high, the metal content should be low (most of the metals present will ultimately contribute to the overall metal load into the system), the buffering capacity should be high to raise the pH of the AMD, and other required nutrients for SRB growth and metabolism should be present at the required concentration ratios, e.g. carbon:nitrogen:phosphorous at approximately 100:10:1 by weight (Widdel, 1988). However, leaching of nutrients from the organic substrate should be relatively slow in order to avoid discharging nutrients and to supply a long lasting nutrient source for SRB and subsequent metal removal. The organic substrate used was a mixture of composted sewage sludge and wood chips.The chemical composition of this compost is presented in Table 4. Within approximately 10 residence times, the chemical oxygen demand (COD) dropped to a level of <100 ppm (eq. to a BOD of 40 ppm).

Sulfate reduction and Metal removal. A significant reduction in sulfate was observed after approximately 10 residence times in the upflow columns (Figure 5). On average a reduction rate of 100 to 200 mmol Sulfate per m^3 compost and day were observed. For comparison, a sulfate removal rate of 300 mmoles sulfate per cubic meter of compost per day by an active SRB consortium was observed by Wildeman (1993).

Metal removal was observed as soon as operation started. The initial removal of metals was most likely due to adsorption onto particulate organic matter (Angelidis and Gibbs, 1989). Metal concentrations in the effluent of the various gravel/compost columns were similar for all columns containing compost, and the metal removal efficiencies were on average 99 % for zinc, 90% for copper and 90% for cadmium (Table 5). Copper and cadmium were present at much smaller concentrations in the MSD water and the removal rate was defined by the analytical detection limit. Zinc concentration measurements

Table 5. MSD water chemistry before and after treatment in anaerobic vertical upflow columns

Constituent	MSD water (Influent)	Column effluent	Units	treatment efficiency %
Cu	80-900	10-70	µg/l	88-99
Cd	40-120	10-40	µg/l	75-92
Zn	8000-11000	90-250	µg/l	97-99
Mn	8500-9000	8000-9500	µg/l	0
Fe	40-100	900-1000	µg/l	0
pH	6.6-6.8	6.8-7.0	-	-
Sulfate	127-270	119-255	mg SO4-S/l	ND
TSS	5-2500	NT	mg/l	-

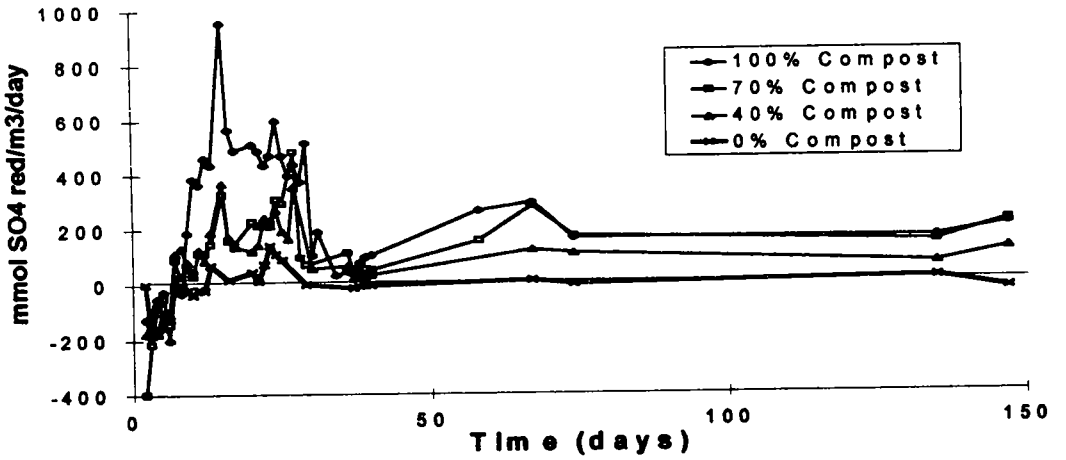
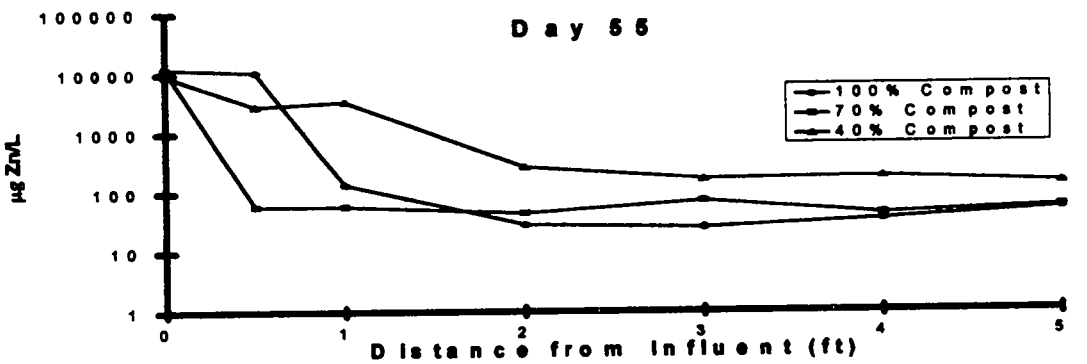
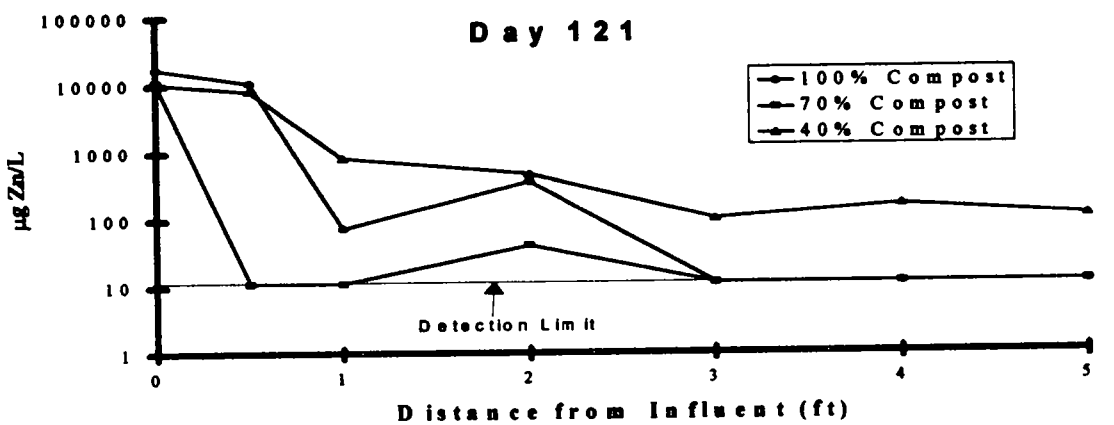


Figure 5. Sulfate removal rate was plotted over time. Significant sulfate reduction was observed in all columns with organic content.



(a)



(b)

Figure 6. Zinc concentrations over the lengths of the columns at day 55 (a), and day 121 (b). Zinc was removed faster in the columns with higher organic compost fractions.

were taken at various location of the column after 3 month of continuous operation. A shorter column length was necessary to remove zinc for the columns with a higher organic compost fraction (Figure 6). Little or no metal removal was observed in the 100% gravel columns (data not presented).

Conclusions

Laboratory experiments were used to design field test systems for metal removal from contaminated ground and surface water in Butte, Montana. The design calculations were based on the metal and acidity load of the MSD water, the potential sulfate reduction rate, the hydraulic conductivity for the chosen substrate (as observed in laboratory experiments), and on the total flow rate. The field system is being brought on line in May of 1996.

Successful zinc, copper, and cadmium removal were achieved in 1.5 m high upflow mixed substrate columns. The long term removal of these metals were based on the microbial sulfate reduction within the column substrate.

The hydraulic conductivity of the substrates controlled the flow regime of the upflow columns. Hydraulic conductivity was increased successfully by increasing the gravel/compost ratio.

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