TREATMENT OF ACID MINE DRAINAGE WITH A COMBINED WETLAND/ANOXIC LIMESTONE DRAIN:
A COMPARISON OF LABORATORY VERSUS FIELD RESULTS

John Cliff
Pat Sterner
Jeff Skousen
Alan Sexstone

Division of Plant and Soil Sciences
West Virginia University

Introduction

Acid mine drainage (AMD) treatment requires the addition of a base to raise pH and to cause precipitation of metals. The most common bases used for AMD neutralization are NaOH, Na_2CO_3, NH_4OH, and $Ca(OH)_2$. Equipment for application and reagent costs are expensive when considered over 10 to 20 years of water treatment. Passive systems attempt to raise pH and precipitate metals without the continual addition of chemicals. These systems often are more economical in terms of total costs, but generally provide only partial treatment and have limited longevity.

Anoxic limestone drains (ALDs) may provide economical passive treatment of AMD. To maximize successful water treatment, application of this technology is currently thought to be restricted to AMD low in aluminum, low in dissolved oxygen (<I mg/L DO), and containing predominately reduced ferrous iron (Skousen 199 1). ALDs are thought to fail in two ways: clogging of limestone pores due to precipitation of insoluble metal compounds, and armoring of limestone by ferric hydroxides thus hindering carbonate dissolution. Water passing through an ALD causes limestone dissolution, raising pH and adding alkalinity. A pH of no greater than 6.0 is attained in closed limestone systems. Therefore, ferrous hydroxides do not precipitate, and armoring or coating of the limestone by ferrous iron is limited. However, aluminum hydroxides precipitate above pH 5.0 and plug the drain with time. Upon exiting the anoxic drain, aeration causes the ferrous iron to oxidize and ferric hydroxides precipitate in a settling basin. The alkalinity provided by the drain buffers the solution to dramatic drops in pH.

Artificial wetlands provide passive treatment of AMD by adsorption and oxidation reactions, but these systems can also generate anaerobic conditions in saturated sediments leading to microbial reduction processes. Microbial removal of DO and iron reduction may promote solubility of ferrous iron and/or retain iron precipitates in wetland sediments (Lovley 1993). This paper reports the treatment effectiveness of a combination wetland/ALD treatment system under two different conditions. The system was designed to increase the current application of ALDs by pre-treating AMD in an anaerobic wetland before introducing it into an ALD.

Materials -and-Methods

Two experimental wetland/ALDs have been monitored for more than one year. The first system was constructed at the Douglas Highwall abandoned mine land (AML) site and a second system was constructed in a greenhouse at West Virginia University. Diagrams and dimensions of the Douglas and greenhouse systems are presented in Figures 1 and 2.

Douglas System

The Douglas System is located near Douglas, WV, on a 60-acre AML site reclaimed by the West Virginia Division of Environmental Protection in 1991-1993 (Skousen 1995). One deep mine portal historically discharged large volumes of AMD into the North Fork of the Blackwater River approximately 2 miles upstream from its confluence with the mainstem of the Blackwater River. Construction of the wetland/ALD consisted of a concrete bulkhead at the AMD portal that diverted 100 to 3 00 gpm of AMD into the constructed wetland/ALD. The total length of the system is 2700 ft and is lined on the bottom and sides with a PVC liner. After exiting the portal, AMD flows into the wetland portion of the system (Cell I). Dimensions of Cell I are 1200 x 8 x 6 ft (L x W x D) and consists of a 2-ft base of high quality (>90%) $CaCO_3$ limestone (3/4 to I V2 inch size) covered by 4 ft of organic material (peat/hay/soil; 50/30/20) (Figure 1). The limestone and organic material are separated by a permeable erosion control material (Curlex Excelsior) to keep organic matter from filtering into the limestone. Cell I also has top and bottom baffles installed in an alternating pattern every 100 ft that are designed to increase contact with the organic substrate. Top baffles extend from above the surface of the wetland to the top of the limestone. Bottom baffles extend from the base of the wetland to within 2 ft of the surface.

Cell II is 1500 x 30 x 8 ft (L x W x D) and consists of 5 ft of high quality (>90%) $CaCO_3$ limestone (3/4 to 11/2 inch size) covered by 3 ft of organic material separated by Curlex material. Top barriers only have been installed every 300 ft starting at the beginning of Cell II. These barriers are designed to maximize water contact with the limestone.

Water sampling devices were installed approximately every 200 ft in Cell I and every 300 ft in Cell II for a total of 13 sampling devices. These devices consist of 8 ft long by I 0-inch diameter PVC pipe capped at the bottom end and inserted vertically to the bottom of the cell. Within each device, small sampling ports were constructed so as to extract water at varying depths. Cell I sampling ports are fixed at depths of 2, 3, 4, 5, and 6 ft. Flexible tygon tubing extends from each port to the top of the sampling device, and suction can be placed on the tube to extract water samples. Cell II sampling devices are similar to those in Cell I except they are 9 ft long and have sampling ports at depths of 1.6, 3, 5.5, and 7.5 ft. The wetland/ALD has been planted with a limited number of Typha (cattails) and other wetland species, and it has been extensively colonized by volunteer plant species. A sedimentation basin to collect metal hydroxide flocs is immediately downstream of Cell II. Its dimensions are

82 x 30 x 4 ft (L x W x D). The Douglas System was allowed to equilibrate with river water for one month prior to treating approximately 240 gpm of AMD since July 1994.

Greenhouse System

A greenhouse scale model of the Douglas system was constructed at West Virginia University. Dimensions of the wetland/ALD being 38 x 1.6 x 2.6 ft (L x W x D) (Figure 2). The frame for the wetland/ALD is constructed of lumber and lined with four layers of 6-mil polyethylene sheeting. The bottom of the wetland/ALD is sloped to 1%.

The wetland/ALD is divided into two separate cells. Cell I is 16 ft long and consists of a 10-inch base of high quality (>90%) $CaCO_3$ limestone (3/4 to 11/2 inch size) covered by 1.8 ft of organic material. Cell II is 20 ft long and consists of a 1.6-ft base layer of 3- to 4-inch, high quality (>90%) $CaCO_3$ limestone covered by 1.2 ft of organic material. The organic substrate consists of a mix of peat moss, hay, and soil (4/4/1). Commercially available landscape cloth separates the organic matter and the limestone in both cells. Cell I is divided by alternating top and bottom baffles which are designed to increase flow in the organic matter. Three top baffles extend from approximately 1 inch above the substrate to 6 inches above the limestone. Bottom baffles extend from the bottom to the top of the limestone. A 1.7-ft baffle divides Cell I from Cell II. Within Cell II, a series of four evenly-spaced, 1.4-ft deep top baffles directs the water to the limestone.

There are two permanent sampling devices in Cell I at a distance of 4.6 and 16 ft from the influent end. Each sampler is constructed of 10-inch diameter PVC pipe that is approximately 3 ft long and capped at the bottom end. Four water/sediment sampling ports are located at depths of 3 and 16 inches, and a single water sampling port made from 5/8-inch tygon tubing surrounded by PVC pipe can collect water samples at the median depth in the limestone (2.3 ft). Cell II has one permanent sampler located 10 ft from its influent end and is identical to the Cell I samplers except that the water and sediment samplers are at a depth of 10 inches, and the limestone water sampling port is at a depth of 17 inches. Samplers allow water and sediment to be obtained anaerobically. The inflow of each wetland/ALD is divided into three parallel inflow ports at median depth in the organic matter. Water exits each wetland/ALD at the median depth of Cell II limestone (2.3 ft) and is diverted via a '/2-inch PVC pipe to a series of settling basins. The organic substrate was inoculated with anaerobic sediments from natural wetlands treating AMD. One week after filling the systems with water, cattails and other rootstocks of wetland species were planted into the wetland/ALD. This system was allowed a one-month establishment period before approximately 0.04 gpm (53 gal/day or 200 L/day) of AMD was introduced.

Sampling Regime

The Douglas wetland/ALD was sampled monthly from June to November 1994, and quarterly thereafter until September 1995. The greenhouse system was sampled on a monthly basis from August 1994 to September 1995.

Chemical Analyses

Water samples were taken from sampling ports by allowing water to flow into a container prior to pumping through a YSI Model 3500 sample chamber containing pH, Eli, electrical conductivity, and temperature probes. Water samples for elemental analysis were filtered (0.45 um), acidified (2% volume) with concentrated HCl (12N), and stored in sealed vials at 4^0C until analyzed. Iron, manganese, aluminum, calcium, and magnesium were quantified using inductively coupled plasma spectrometry (ICP). Ferrous iron was quantified using a modified ferrozine photometric assay (Stookey 1970). Total acidity and alkalinity were determined by fixed-end-point titration to a pH of 8.3 or 4.2, respectively, by an automatic titrator. Sulfate was analyzed using single column ion chromatography (HPLC).

Results

Douglas System

Average, maximum, and minimum values are given for influent and effluent water quality in Tables 1 and 2. Figures 3-5 show ferrous iron, ferric iron, and aluminum concentrations across sampling dates at influent, effluent, and at the bottom sampling port of the last sampling device in Cell II. These data indicate that the system effectively treated water from a pH of 3.0 to a pH of 6.6, decreased average acidity by 94%, and produced an average net alkalinity of 127 mg/L. However, no iron or aluminum are exiting the drain, so both iron and aluminum must be precipitating in the drain (Figures 3-6). At present, we do not know the iron oxidation state when precipitation occurs. We have, however, observed overland flow and high Eh and DO readings throughout the wetland (data not shown) suggesting that the Douglas system primarily oxidized rather than reduced iron as it was originally designed to perform. Therefore, even though pH and alkalinity are increased and metals are removed by the system, metal precipitation in the limestone theoretically will result in decreased longevity of AMD treatment.

Greenhouse System

Average, maximum, and minimum influent and effluent water quality parameters are presented in Tables 3 and 4. In contrast to the Douglas system, the greenhouse system was fed AMD of much poorer quality. The acidity value of this AMD averaged 2,400 mg/L as compared to 430 mg/L in the Douglas system. Despite the fact that both systems were designed similarly, the greenhouse system exhibited preferential flow through the limestone as opposed to overland flow. This was due to higher organic substrate hydraulic conductivity as well as a reduced flow rate in the greenhouse system compared to Douglas, thereby allowing the water to percolate to the limestone. The water was also introduced subsurface in the greenhouse system compared to releasing the water at the surface at Douglas. As indicated in Figure 7, pH increased in the greenhouse system from 2.8 to 6.0 for the first seven months followed by a substantial drop in pH after seven months. Total acidity decreased an average of 1,259 mg/L throughout the study period (Figure 8). However, in contrast to Douglas, the greenhouse never generated net alkaline water (Figure 9). It is clear from alkalinity and aluminum data (Figures 9 and 10) that the greenhouse system showed signs of failure after June 1995. No aluminum exited the drain from August 1994 to July 1995, but the drain only retained 17% of the aluminum on September 1995. Since July 1995, alkalinity has been less than 20 mg/L. Influent and effluent iron data (Figure 11) indicate that the greenhouse system only retained about 10% of the total added iron load. Iron retention is nearly opposite of that reported for the Douglas system which acted as an iron sink, retaining all the iron. These data demonstrate that the greenhouse wetland/ALD functioned in a manner more in keeping with its original design. However, there was no clear pattern of overall iron oxidation or reduction between influent and effluent data in the system.

Discussion

Despite similar design characteristics, the Douglas system and the greenhouse system performed differently. While the Douglas system treated water effectively for nearly a year, the system did not function as designed. Observations of extensive overland flow as well as erratic Eh and DO readings throughout the wetland indicate insufficient hydraulic conductivity in the organic matrix. It appears that the Douglas system functioned as an iron oxidizing metal sink. Conversely, relatively little of the iron introduced into the greenhouse system precipitated in the drain. High concentrations of ferric iron were observed in the circumneutral effluent from the greenhouse system. One possible explanation for this phenomenon is chelation of Fe" by organic acids leached from the substrate or exuded by plant roots. If this hypothesis proves true, this phenomenon may enhance drain life by preventing precipitation and limestone armoring in the drain. Chelation may also enhance availability for microbial iron reduction (Lovley et al. 1996).

Despite our ability to measure microbial reduction in laboratory assays of wetland sediments, neither system exhibited significant net iron reduction. It is possible that detention time was insufficient in low Eli areas in the wetland substrate for significant net iron reduction to occur. However, iron reduction may have been nutrient limited since it is primarily a microbially-mediated reaction. In either case, future designs utilizing this treatment technology for AMD with high DO or high dissolved ferric iron should take into consideration the saturated hydraulic conductivity of the organic matter and the detention time of the water in contact with organic matter. If significant rates of iron reduction are to occur, longer periods of time are needed for microbial iron reduction.

Acknowledgments

Special thanks go to the West Virginia Division of Environmental Protection. Appreciation is extended to former Director David Callaghan, David Broschart, and David L. Smith of WVDEP. Breckenridge Corporation was the AML contractor on the site and thanks go to Alan Shreve and Tim Stump for allowing WVU employees to be on site at various times during construction. Funding for conducting research on this project was obtained from the U.S. Bureau of Mines and the National Mine Land Reclamation Center.

References

Lovley, DR. 1993. Dissimilatory metal reduction. Annual Rev. Microbiol. 47:263-290.

Lovley, DR., J.C. Woodward, F.H. Chapelle. 1996. Rapid anaerobic benzene oxidation with a variety of chelated Fe(III) forms. Appl. Env. Micro. 62:288-29 1.

Skousen, J. 1991. Anoxic limestone drains for acid mine drainage treatment. Green Lands

21:30-35.

Skousen, J. 1995. Douglas abandoned mine land project: Description of an innovative acid mine drainage treatment system. Green Lands 25:29-38.

Stookey, L.L. 1970. Ferrozine - A new spectrophotometric reagent for iron. Anal. Chem. 42:779-781.

	Average	Maximum	Minimum
Temperature (c°)	10.8	12.6	10
pH	3.0	3.7	2.7
Eh (mV)	497	540	423
EC (S/m)	.09	1.4	.04
Acidity (mg/L as $CaCO_3$ eq)	431	529	394
Alkalinity (mg/L as $CaCO_3$ eq)	0	0	0
Total iron (mg/L)	20	25	17
Ferrous iron (mg/L)	5	9	0
Ferric iron (mg/L)	20	25	20
Manganese (mg/L)	6	7	5
Aluminum (mg/L)	35	54	28
Calcium (mg/L)	64	116	48
Magnesium (mg/L)	42	46	35
Sulfate (mg/L)	530	606	460

Table 1. Influent averages, maximums, and minimums of water quality parameters at Douglas Highwall (July, 1994 - September, 1995).

	Average	Maximum	Minimum
Temperature (C')	13.6	17.5	8.1
pH	6.6	7.3	5.2
Eh (mV)	164	299	57
EC (S/m)	0.11	0.14	0.10
Acidity (mg/L as $CaCO_3$ eq)	25	54	0
Alkalinity (mg/L as $CaCO_3$ eq)	152	294	1
Total iron (mg/L)	0	0	0
Ferrous iron (mg/L)	0	0	0
Ferric iron (mg/L)	0	0	0
Manganese (mg/L)	3	14	0
Aluminum (mg/L)	1	2	0
Calcium (mg/L)	202	378	132
Magnesium (mg/L)	82	318	19
Sulfate (mg/L)	445	517	249

Table 2. Effluent averages, maximums, and minimums for selected water quality parameters at Douglas Highwall (July, 1994 - September, 1995).

	Average	Maximum	Minimum
Temperature (C)	23.1	26.2	18.1
pH	2.8	3.0	2.5
Eh (mV)	415	437	374
EC (S/m)	0.47	0.48	0.46
Acidity (mg/L as $CaCO_3$ eq)	2402	2711	2033
Alkalinity (mg/L as $CaCO_3$ eq)	0	0	0
Total iron (mg/L)	661	963	485
Ferrous iron (mg/L)	444	612	312
Ferric iron (mg/L)	217	352	132
Manganese (mg/L)	5	7	4
Aluminum (mg/L)	173	239	125
Calcium (mg/L)	451	552	289
Magnesium (mg/L)	171	219	132
Sulfate (mg/L)	3010	3925	1769

Table 3. Influent averages, maximums, and minimums of water quality parameters for the greenhouse wetland/ALD September, 1994 - September, 1995).

	Average	Maximum	Minimum
Temperature (c°)	20.4	25.1	16.5
pH	5.6	6.4	4.1
Eh (mV)	13	197	-75
EC (S/m)	0.44	0.46	0.42
Acidity (mg/L as $CaCO_3$ eq)	1153	1688	707
Alkalinity (mg/L as $CaCO_3$ eq)	153	344	12
Total iron (mg/L)	663	1446	423
Ferrous iron (mg/L)	440	552	340
Ferric iron (mg/L)	208	969	10
Manganese (mg/L)	8	12	5
Aluminum (mg/L)	18	121	1
Calcium (mg/L)	653	980	363
Magnesium (mg/L)	191	320	135
Sulfate (mg/L)	2262	3158	1470

Table 4. Efffluent averages, maximums, and minimums for selected water quality parameters for the greenhouse wetland/ALD (September, 1994 - September, 1995).

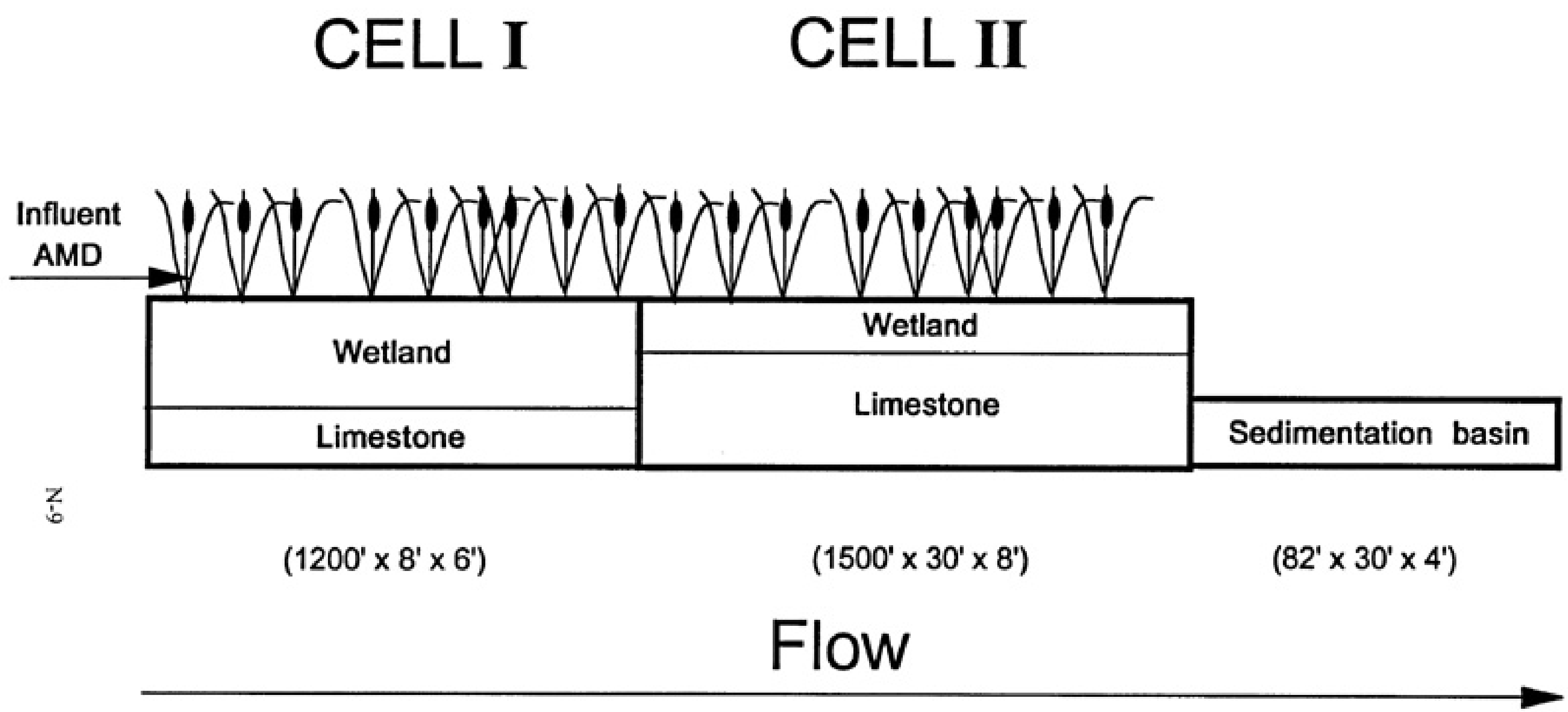


Figure 1. Schematic representation of the Douglas Highwall wetland/ALD system.

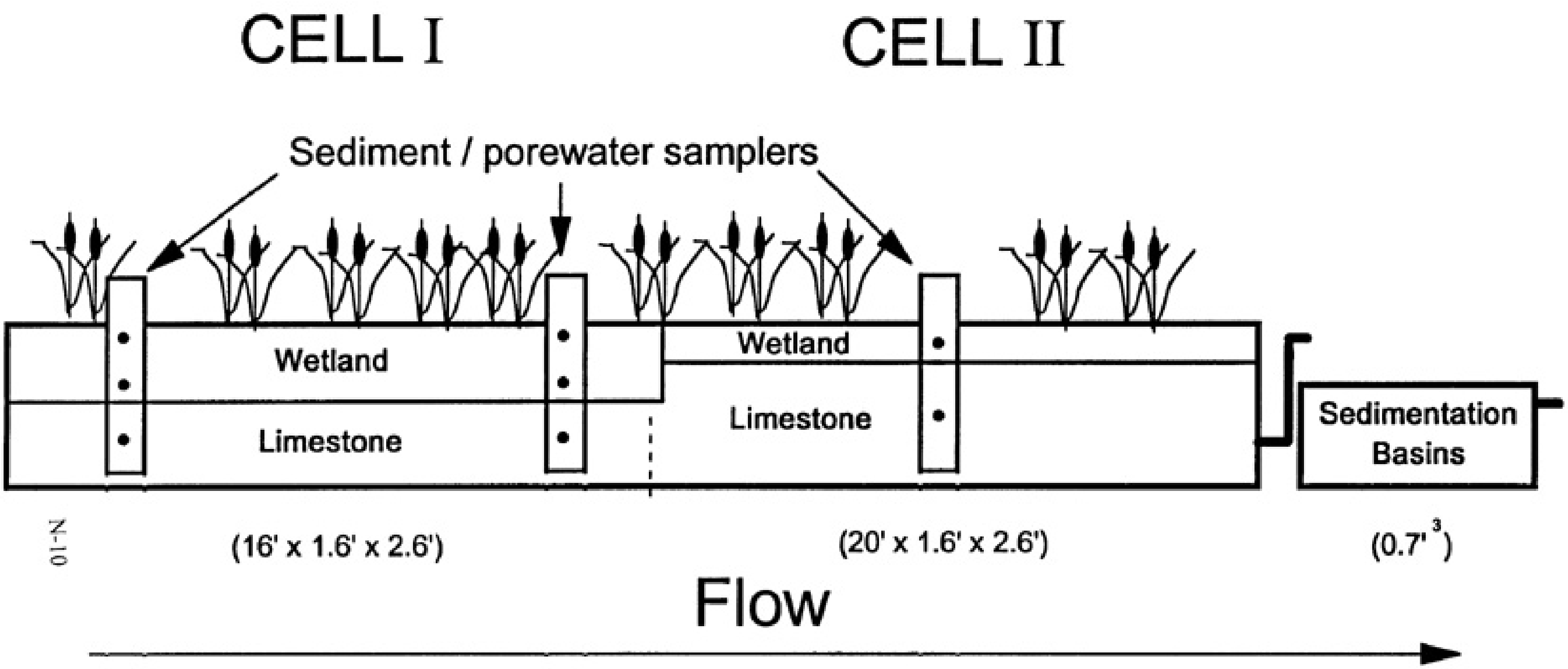
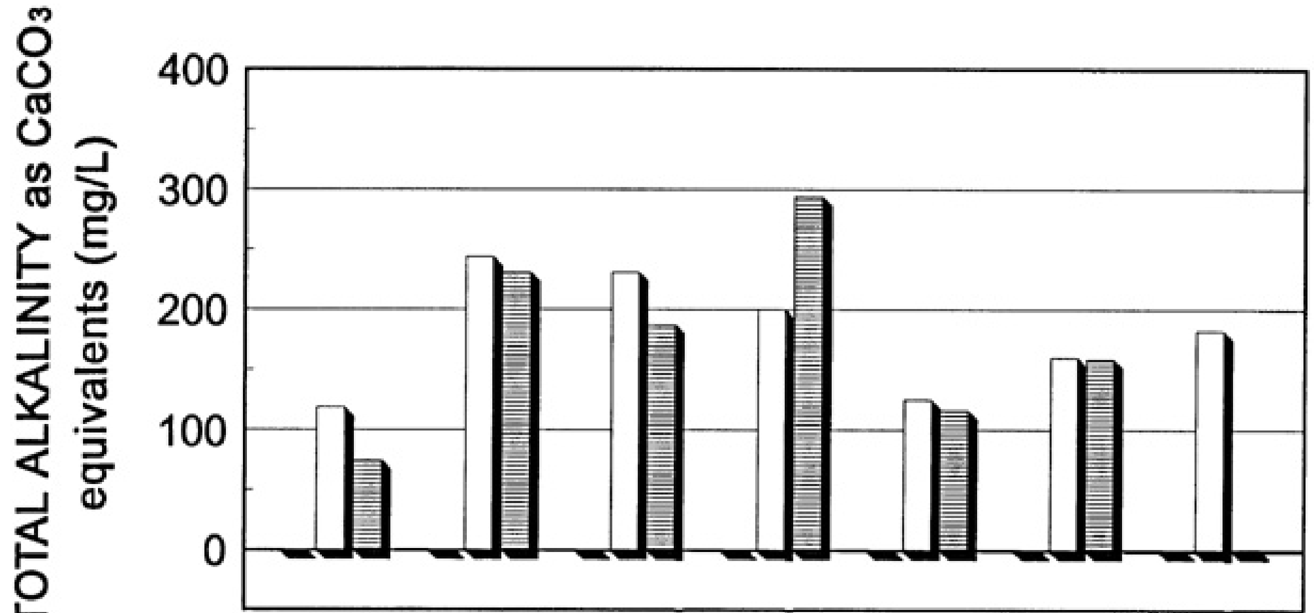
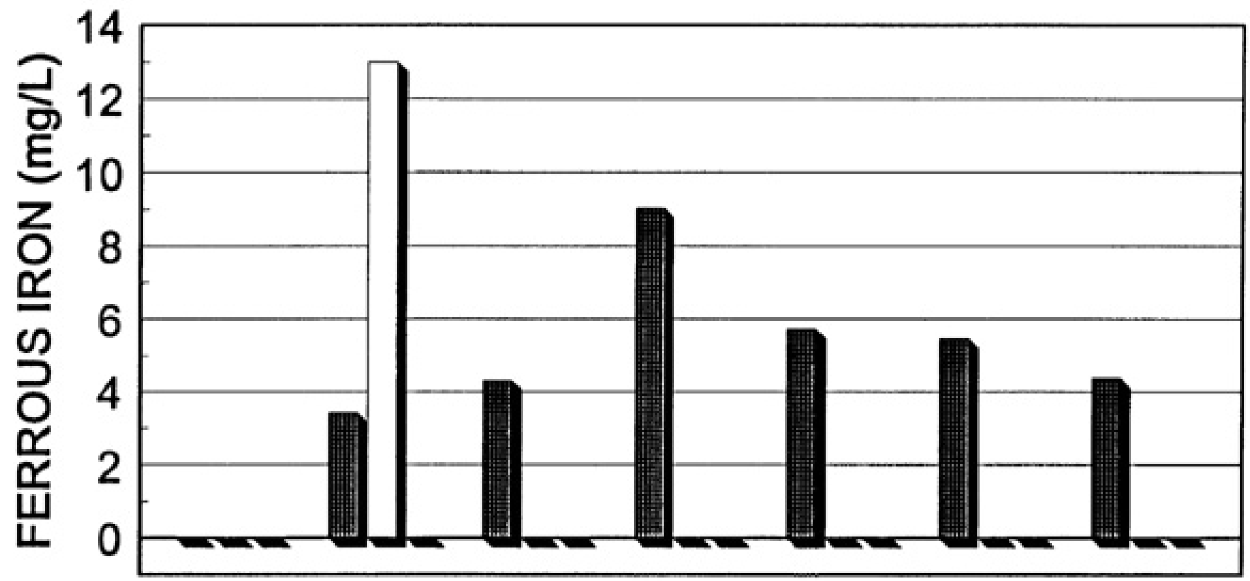


Figure 2. Schematic representation of the greenhouse wetland/ALD system at West Virginia University.



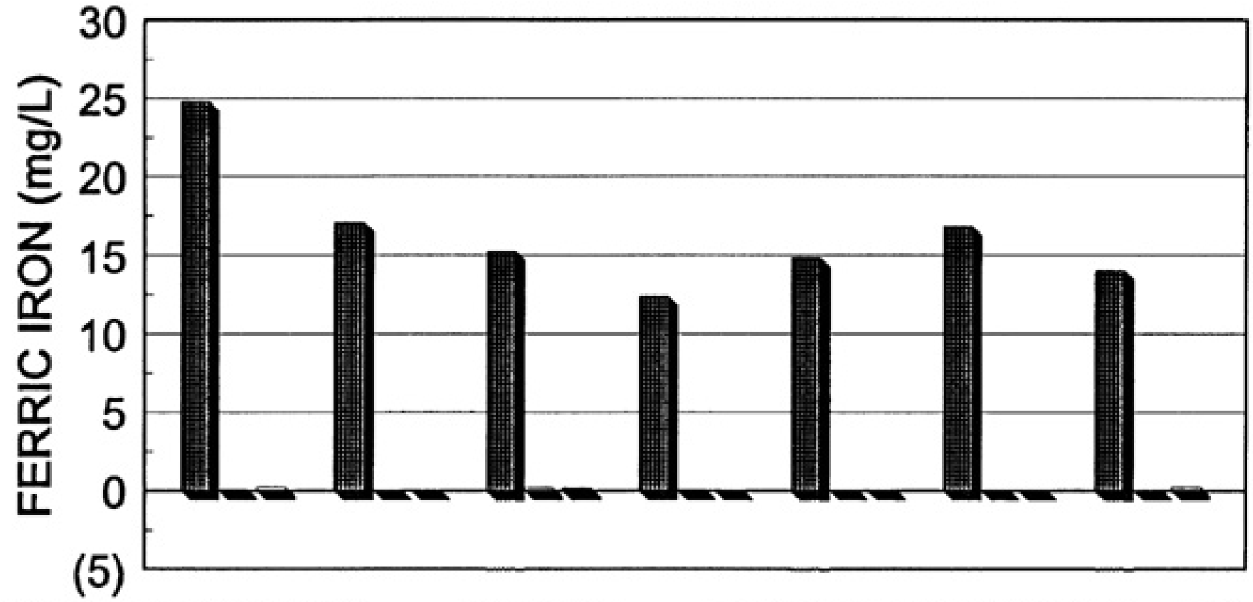
DATE	8-17-94	9-15-94	10-28-94	11-18-94	3-7-95	6-13-95	9-8-95
INFLUENT	0	0	0	0	0	0	0
BOTTOM SAMPLER	119	244	231	200	125	160	182
EFFLUENT	75	231	188	294	117	159	1

Figure 3. Influent and effluent alkalinity at Douglas Highwall.



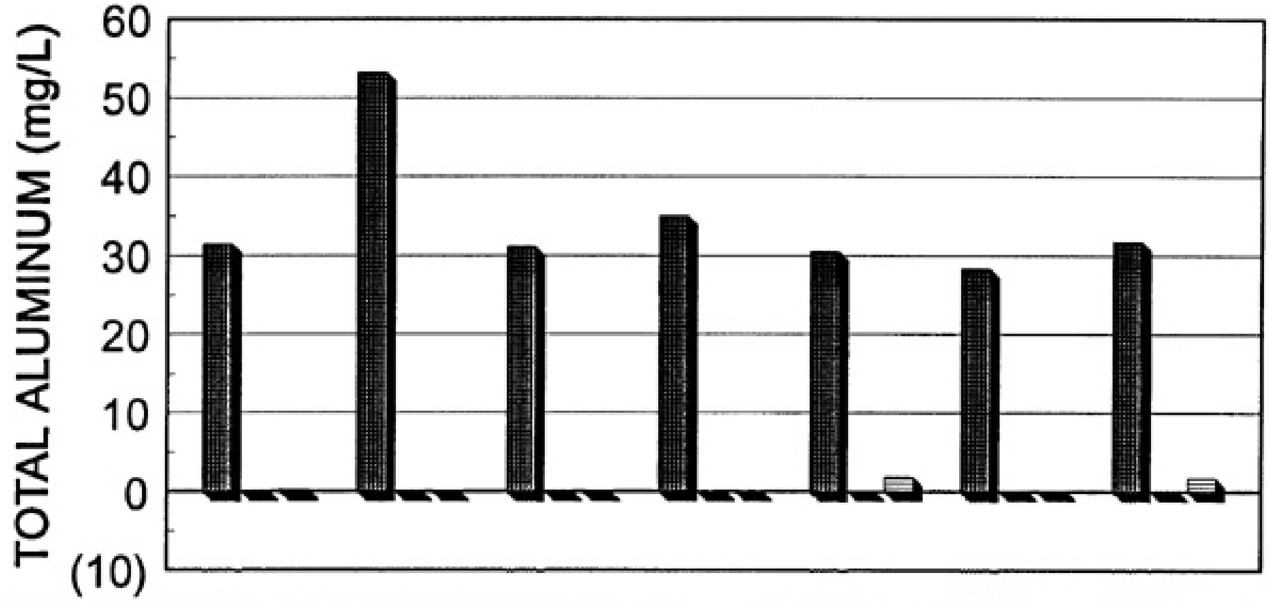
DATE	8-17-94	9-15-94	10-28-94	11-18-94	3-7-95	6-13-95	9-8-95
INFLUENT	0	3.4	4.3	9.0	5.7	5.5	4.4
BOTTOM SAMPLER	0	13.0	0	0	0	0	0
EFFLUENT	0	0	0	0	0	0	0

Figure 4. Influent and effluent ferrous iron concentrations at Douglas Highwall.



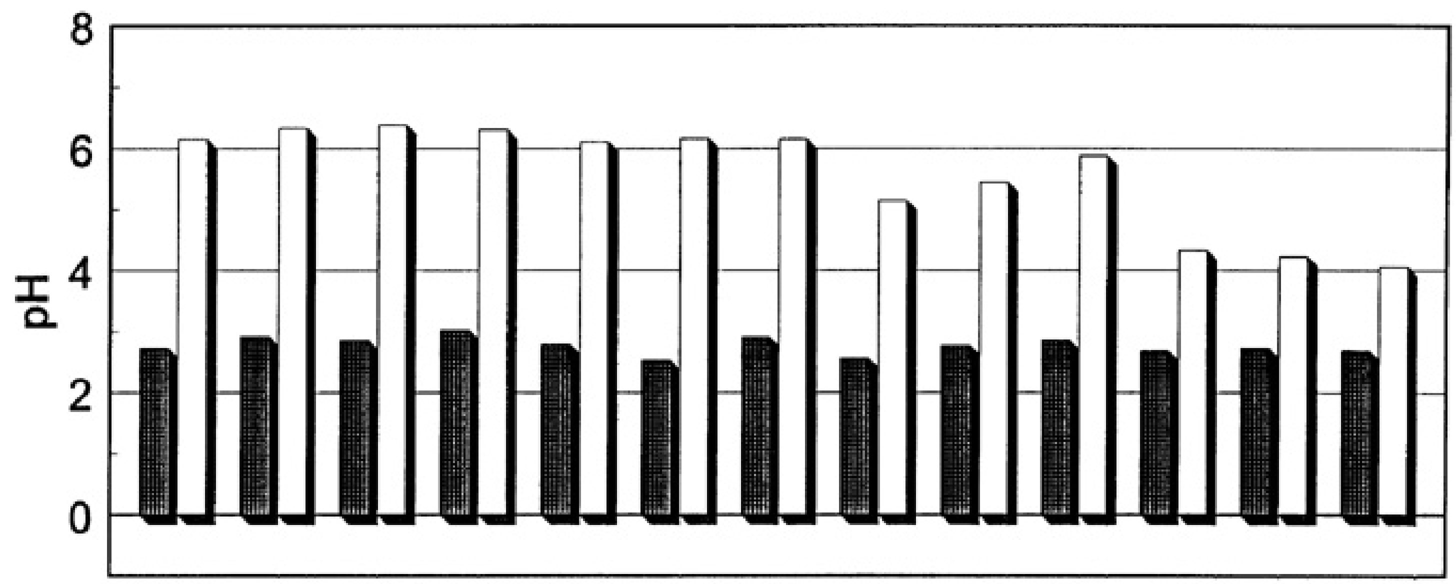
DATE	8-17-94	9-15-94	10-28-94	11-18-94	3-7-95	6-13-95	9-8-95
INFLUENT	24.8	17.1	15.3	12.4	14.8	16.8	14.0
BOTTOM SAMPLER	0.1	0	0.2	0.1	0	0	0
EFFLUENT	0.3	0.1	0.2	0	0	0	0.3

Figure 5. Influent and effluent ferric iron concentrations at Douglas Highwall.



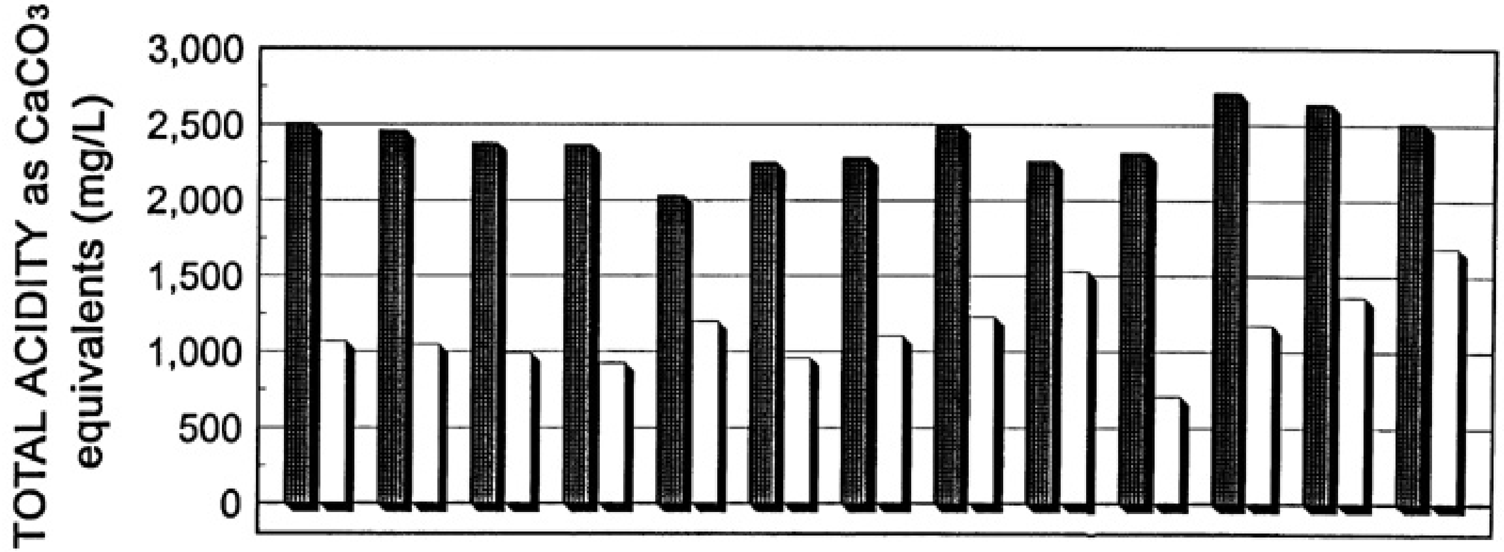
DATE	8-17-94	9-15-94	10-28-94	11-18-94	3-7-95	6-13-95	9-8-95
INFLUENT	32	53	31	35	31	28	32
BOTTOM SAMPLER	0	0	0	0	0	0	0
EFFLUENT	0	0	0	0	2	0	2

Figure 6. Influent and effluent total aluminum concentrations at Douglas Highwall.



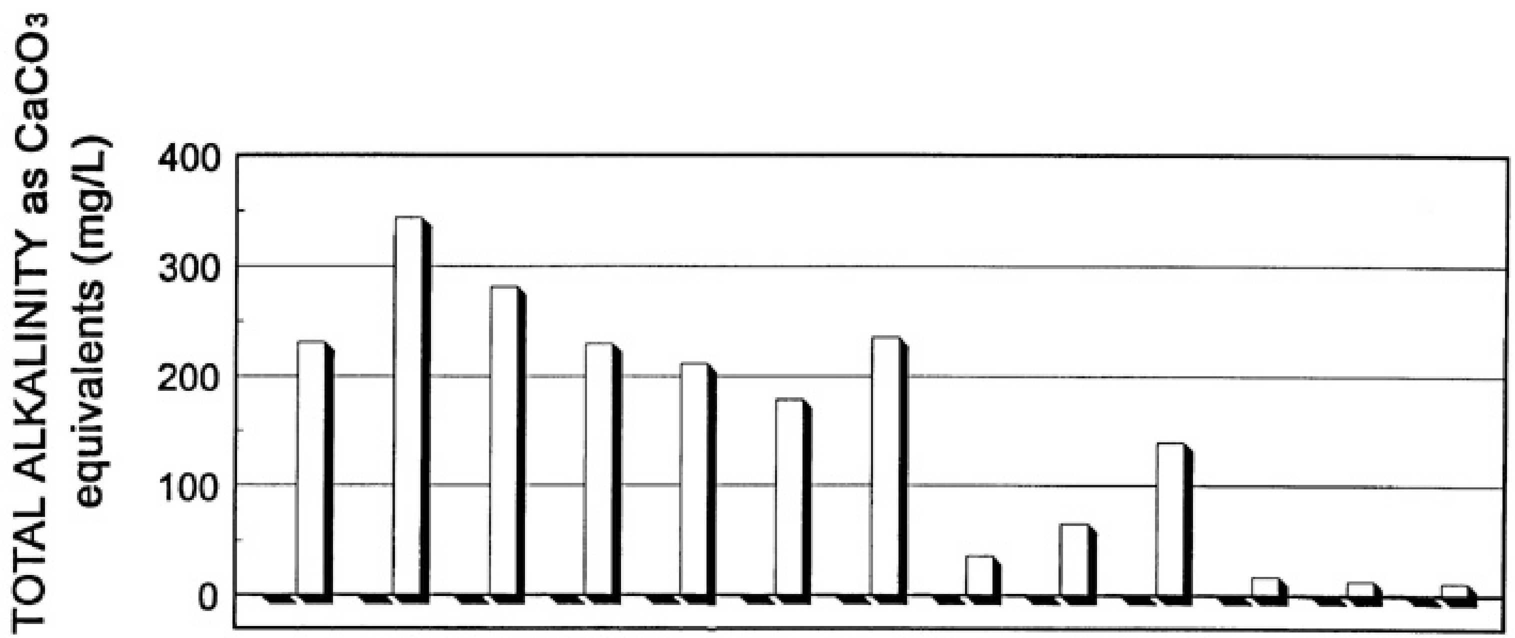
DATE	9-26-94	10-25-94	12-2-94	12-15-94	1-27-95	2-24-95	3-31-95	4-28-95	5-23-95	6-21-95	7-26-95	8-25-95	9-29-95
INFLUENT	2.7	2.9	2.9	3.0	2.8	2.5	2.9	2.6	2.8	2.9	2.7	2.7	2.7
EFFLUENT	6.2	6.3	6.4	6.3	6.1	6.2	6.2	5.2	5.4	5.9	4.3	4.2	4.1

Figure 7. Influent and effluent pH in the greenhouse wetland/ALD.



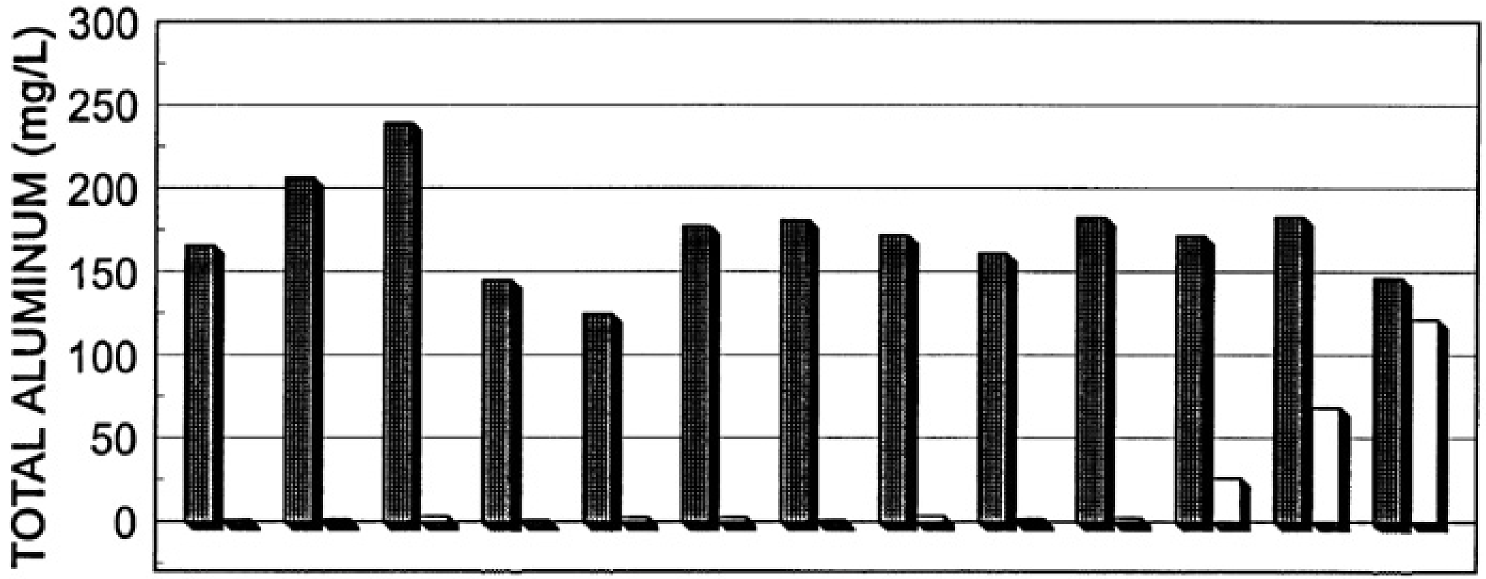
DATE	9-26-94	10-25-94	12-2-94	12-15-94	1-27-95	2-24-95	3-31-95	4-28-95	5-23-95	6-21-95	7-26-95	8-25-95	9-29-95
INFLUENT ■	2,506	2,463	2,381	2,369	2,034	2,253	2,283	2,494	2,261	2,316	2,711	2,639	2,513
EFFLUENT □	1,069	1,044	988	925	1,200	960	1,102	1,232	1,532	707	1,175	1,363	1,688

Figure 8. Influent and effluent total acidity in the greenhouse wetland/ALD.



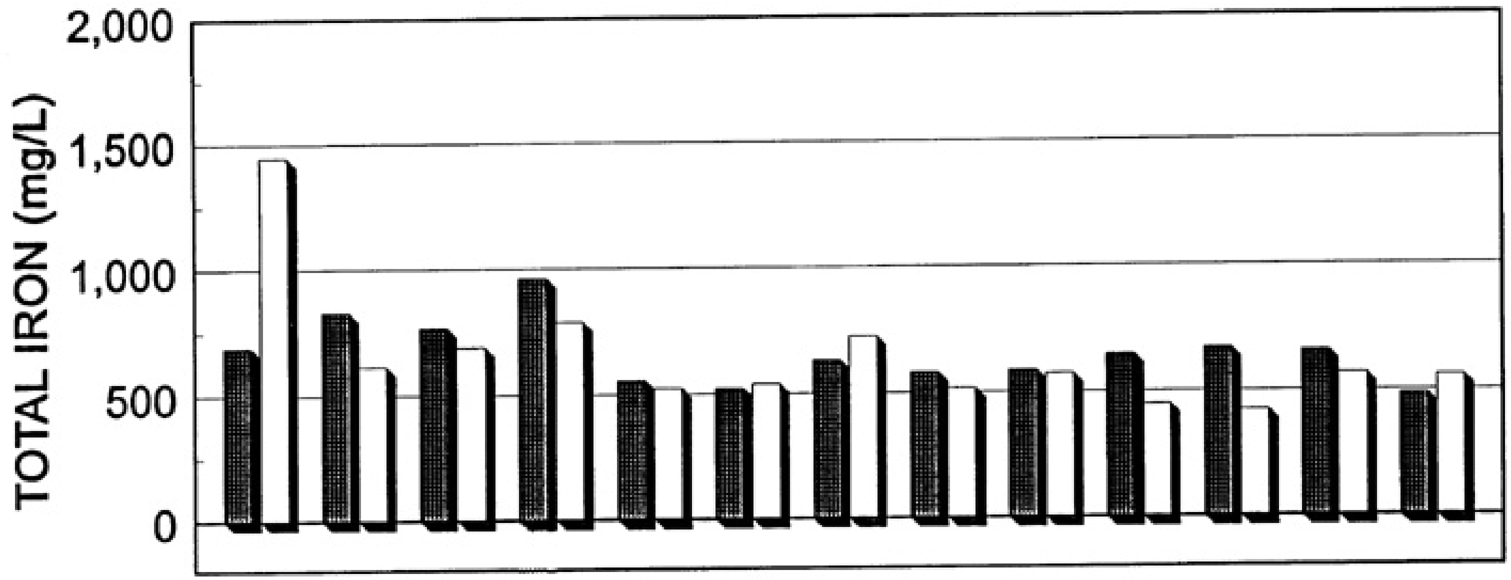
DATE	9-26-94	10-25-94	12-2-94	12-15-94	1-27-95	2-24-95	3-31-95	4-28-95	5-23-95	6-21-95	7-26-95	8-25-95	9-29-95
INFLUENT	0	0	0	0	0	0	0	0	0	0	0	0	0
EFFLUENT	231	344	281	230	211	178	235	36	66	139	17	14	12

Figure 9. Influent and effluent total alkalinity in the greenhouse wetland/ALD.



DATE	9-26-94	10-25-94	12-2-94	12-15-94	1-27-95	2-24-95	3-31-95	4-28-95	5-23-95	6-21-95	7-26-95	8-25-95	9-29-95
INFLUENT ▦	165.7	206.0	239.0	144.7	124.6	177.2	180.5	171.8	160.8	182.1	171.3	182.6	145.9
EFFLUENT □	1.0	1.4	2.8	0.8	2.3	2.4	0.8	3.4	1.6	2.3	25.9	68.3	120.8

Figure 10. Influent and effluent aluminum concentrations in the greenhouse wetland/ALD.



DATE	9-26-94	10-25-94	12-2-94	12-15-94	1-27-95	2-24-95	3-31-95	4-28-95	5-23-95	6-21-95	7-26-95	8-25-95	9-29-95
INFLUENT	694	830	769	963	554	520	632	581	585	647	671	660	485
EFFLUENT	1,446	616	691	789	522	538	725	515	572	447	423	568	557

Figure 11. Influent and effluent total iron concentrations in the greenhouse wetland/ALD.