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Baseline Hydrosoil Chemistry of the A-01 Wetland Treatment System, September 2001

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Executive Summary

The A-01 wetland treatment system was designed to remove metals from effluent from the A-01 NPDES outfall. Construction of the treatment system was completed in the summer of 2000 and all treatment cells were receiving A-01 effluent by July 2000. In September 2001, hydrosoil samples were collected from two of the treatment cells and analyzed for a suite of chemical parameters. The data indicate that copper and zinc are accumulating primarily in the surficial hydrosoils of the first treatment cells (A cells). Mercury was below the detection limit in most samples. However, the monthly data for mercury in water samples collected from the inflow and outflow of the treatment cells indicates that more mercury is removed in the A cells than in the B cells. The hydrosoils in the wetland treatment system have relatively low concentrations of organic carbon and a relatively low cation exchange capacity, due to the sandy nature of the hydrosoil and low organic content. Cation exchange capacity is expected to increase as organic matter produced by the wetland vegetation accretes in the wetland. Even though the wetland is removing metals from the A-01 effluent to concentrations that are below regulatory limits, as the treatment system matures, its ability to remove metals from the A-01 effluent is expected to increase.

1.0 Introduction

The A-01 wetland treatment system was designed to remove metals (primarily copper) from the A-01 effluent discharge. The treatment system consists of a stormwater retention basin, a splitter box, and 4 sets of two

treatment cells (Figure 1). Each treatment cell is a one-acre wetland that contains *Scirpus californicus* (giant bulrush) and has a 24 hour retention time. A-01 effluent flows from the retention basin to the splitter box, where it is distributed to the four A-cells. The effluent flows through the A-cells into the four B-cells and through the B-cells to the wetland outfall. When the wetland treatment cells were constructed, the hydrosoil was amended with organic matter (primarily coarse wood chips), fertilizer (Osmo-coat, 14-13-14 formula) at the rate of 3920 kg/hectare (1.75 tons/acre), and gypsum at the rate of 2240 kg/hectare (1 ton/acre). For the cells that were sampled in this investigation, a layer of hydrosoil was added to the cells, the amendments were added, an additional 6 inch layer of hydrosoil was added, and the soil was lightly disked to mix the amendments into the hydrosoil. The treatment system was constructed during the summer of 2000 and began receiving A-01 effluent in July 2000. In September 2001, hydrosoil samples were collected from one set of treatment cells (4-A and 4-B) and analyzed for a suite of chemical parameters in order to provide baseline data on metal concentrations and general hydrosoil chemistry early in the operational life of the treatment system. This report summarizes the hydrosoil chemistry data.

2.0 Sampling Locations/Methods

Hydrosoil cores were collected and analyzed using the methods described in Sections 2.1 and 2.2. Analytes included copper, zinc, mercury, iron, manganese, calcium, sulfate, sulfide, total organic carbon (TOC), and cation exchange capacity (CEC).

2.1 Field Methods

Hydrosoil samples were collected in cells 4A and 4B on September 18 and 19, 2001. Each cell was divided horizontally into 4 zones (A, B, C, and D), with Zone A being closest in the effluent inflow and Zone D being closest to the outflow from the cell (Figure 2). For all analytes but sulfide, 10 replicate hydrosoil samples were collected randomly within each zone by forcing a 5 cm diameter Plexiglas soil coring tube vertically into the sediment to a depth of 20 to 25 cm. Hydrosoil samples were slipped from the tubes and divided into a surficial sample and a bottom sample, based primarily on color and texture characteristics. Surficial samples were finer grained and softer than bottom samples. For copper, zinc, and mercury, a sub-sample of each surficial and bottom sample was placed in a labeled vial for analysis. The remainder of the 10 surficial and 10 bottom samples from each zone were composited in the field to provide one surficial composite and one bottom composite, which were analyzed for iron, manganese, calcium, DOC, CEC, and sulfate. The samples were placed into ziplock bags, iced, and shipped off-site to a laboratory for analyses. In addition to the 10 cores that were collected within each zone of a wetland cell, three cores were collected for sulfide analyses. Separate cores were collected for sulfide analyses, since it was essential that the cores be frozen immediately and shipped intact in order to prevent oxidation of the sulfide. Sulfide cores were quick-frozen in the field using dry ice and shipped while frozen. The off-site laboratory was supposed to divide the cores into top and bottom segments prior to analyzing for sulfide, but this step was inadvertently omitted. Therefore, sulfide measurements are reported for entire cores, rather than surficial and bottom segments.

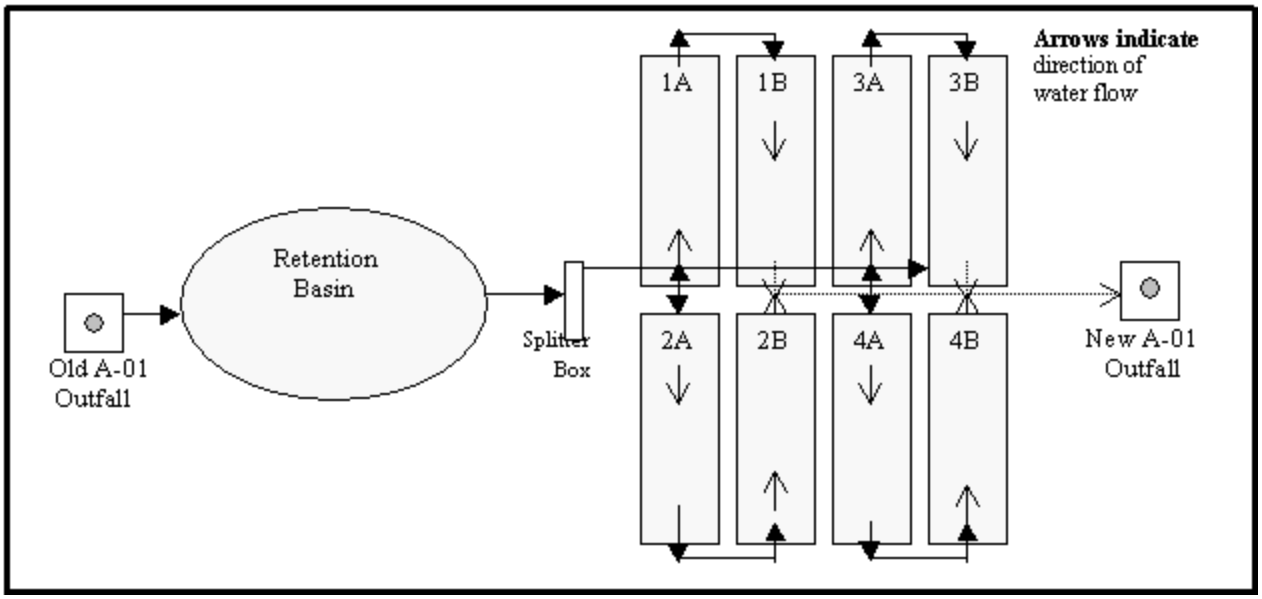

Figure 1. Schematic of the A-01 Wetland Treatment System

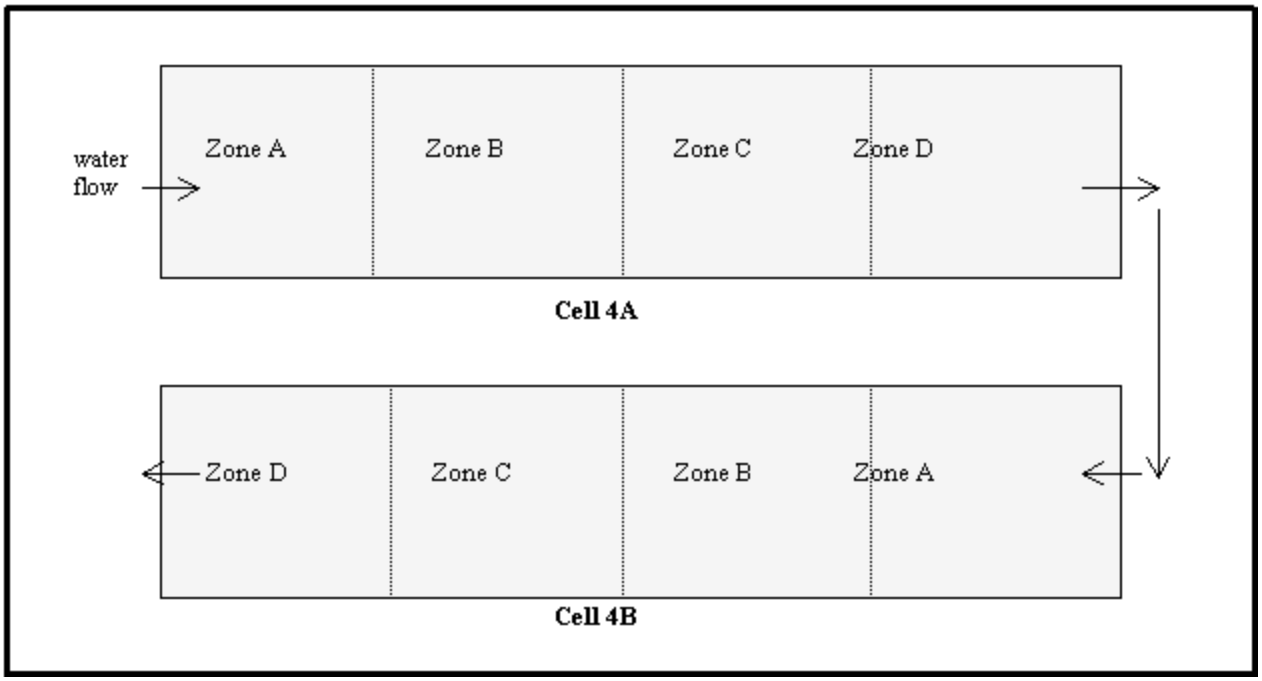

Figure 2. Location of Sampling Zones within Cells 4A and 4B

2.2 Laboratory Methods

All Chemical analyses were performed by ETT Environmental (SCDHEC Certification #23104). All results are reported on a dry weight basis as mg/kg, except cation exchange capacity, which is reported as milliequivalents/100 g. The following methods of analysis were used.

Table 1. Methods Used for Chemical Analysis of Hydrosoil Samples

Analyte	Method

Copper, zinc, calcium, iron, manganese	SW 846 Method 3050B Acid digestion of sediments with HNO_3 and H_2O_2, followed by analysis using EPA Method 2007 (ICP-AES)
Mercury	EPA 245.1 Cold Vapor Technique
Sulfate	EPA 375.4 Turbidimetric Method
Sulfide	SW 846 Method 9031. Extractable Sulfides
Total Organic Carbon (TOC)	EPA 415.2. Persulfate oxidation method
Cation Exchange Capacity (CEC)	SW 846 Method 9081. Sodium acetate method

3.0 Results

The results for copper and zinc are graphed in Figures 3 and 4, respectively. Raw data can be found in Appendix 1. Copper and zinc concentrations exhibited a longitudinal gradient in the surficial (top) samples collected from Cell 4-A. Copper concentrations in the surficial samples collected from Cell 4-A, Zone A averaged 20 mg/kg; Zones B and C were about 10 mg/kg, and Zone D was about 7 mg/kg. Surficial sediment concentrations in Cell 4-B were <5 mg/kg, except for Zone D, which was slightly higher (6 mg/kg). The higher average for Zone D was due primarily to one high value (18.1 mg/kg). Copper concentrations in the bottom samples were much lower than in the top samples, averaging 1.8 to 5.2 mg/kg. The copper concentrations in the bottom samples should be representative of the baseline concentrations of the wetland hydrosoil before A-01 effluent began discharging to the treatment system.

The zinc data showed a similar longitudinal trend, averaging 29 mg/kg in 4A, Zone A, top; about 15 mg/kg in Zones B and C, top; and about 13 mg/kg in Zone D, top. Mean zinc concentrations in the samples collected from Cell 4-B were considerably lower than in 4A, averaging 7 to 11 mg/kg. Zinc concentrations in the bottom samples collected from both the 4A and 4B cells were much lower than in the top samples, averaging 5.5 to 9.4 mg/kg. The zinc concentrations in the bottom samples should be representative of the baseline concentrations of the wetland hydrosoil before A-01 effluent began discharging to the treatment system. The results for copper and zinc indicate that the metals present in the wetland inflow are being rapidly removed from the water column as the water enters the upper end (Zone A) of the first set of cells. The data suggest that most of the removal is occurring in the first set of treatment cells.

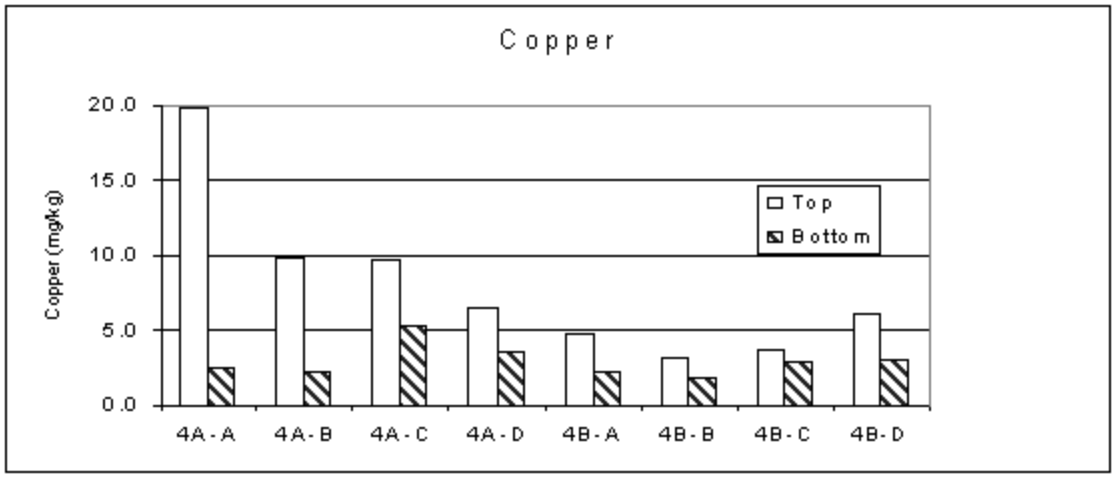

Figure 3. Copper Concentrations in the Hydrosoil of the A-01 Wetland Treatment System, September 2001

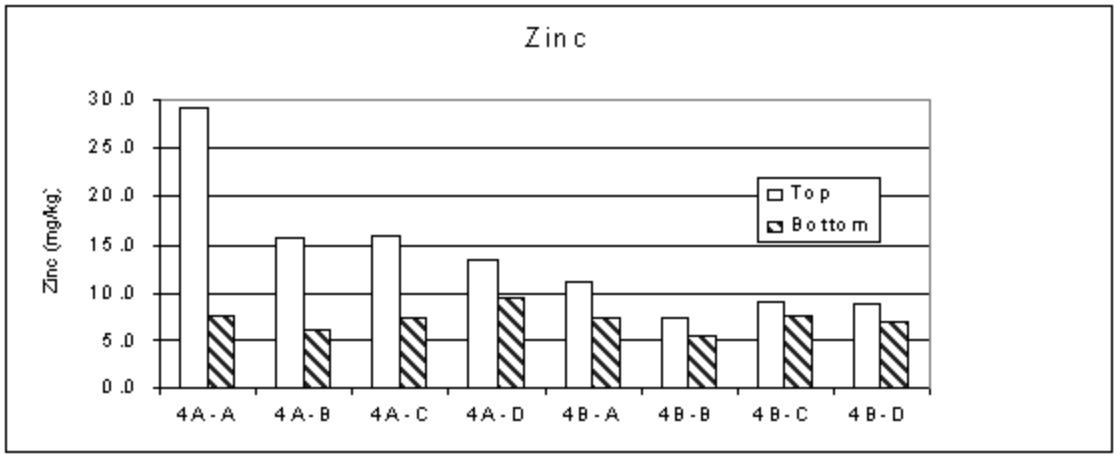

Figure 4. Zinc Concentrations in the Hydrosoil of the A-01 Wetland Treatment System, September 2001

In most of the samples, mercury concentrations were below the detection limit of 0.08 mg/kg (Appendix 1). In cell 4-A, mercury was detected in only one of 80 samples, but the one sample where mercury was present was relatively high (0.353 mg/kg). In cell 4-B, mercury was detected in 13 of 80 samples, with concentrations ranging from 0.08 to 1.14 mg/kg. In 4-B, mercury was most often detected in the wetland soils of Zone D (8 of 20 samples), which is closest to the wetland exit. In Zone D, mercury was detected in both the surficial and the bottom samples, which suggests that the source of the mercury may be the hydrosoil that was added to the cell, rather than deposition from the water column. Mercury analyses performed on water samples collected from the splitter box and the wetland treatment cells indicate that most of the mercury removal is occurring in the A treatment cells, rather than in the B cells (Figure 5).

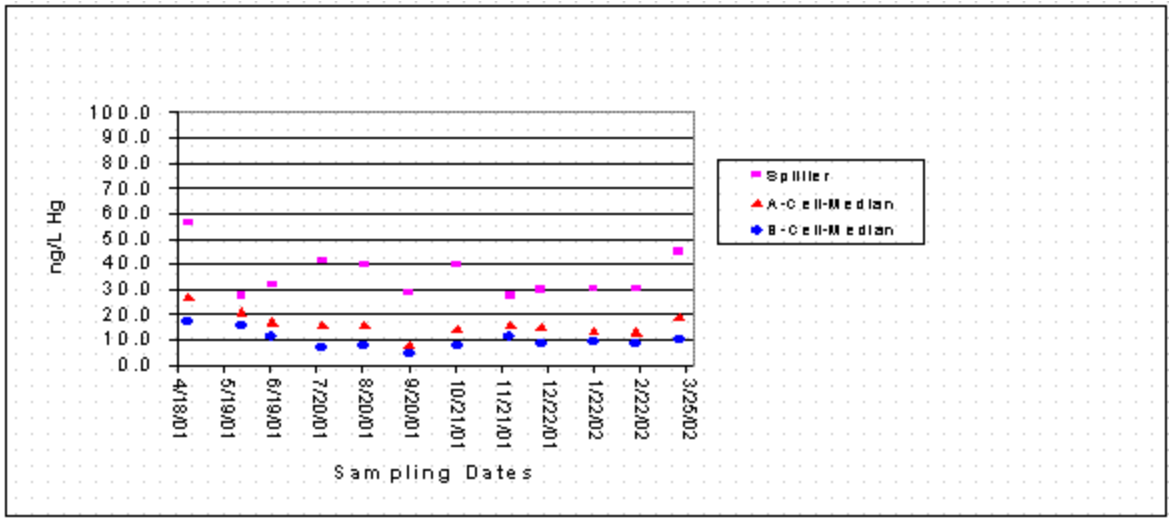

Figure 5. Concentrations of Total Mercury in Water Samples Collected from the Splitter Box and Wetland Treatment Cells

Concentrations of calcium in the wetland sediments were somewhat variable, ranging from 0.171 to 0.733 mg/kg, but there were no consistent differences between top and bottom samples and no longitudinal gradient was observed in either cell 4-A or 4-B Figure 6; Table 2).

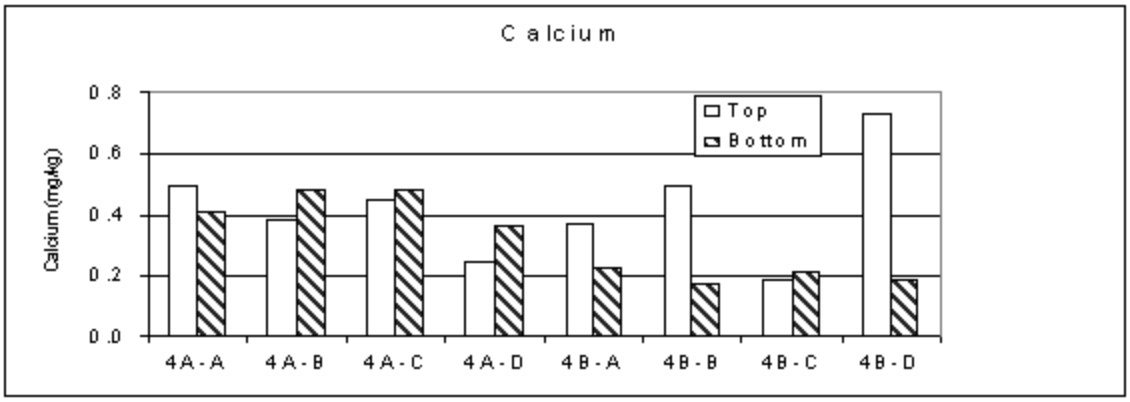

Figure 6. Calcium Concentrations in the Hydrosoil of the A-01 Wetland Treatment System, September 2001

Manganese concentrations in the top samples ranged from 0.035 to 0.093 mg/kg, while the bottom samples ranged from 0.073 to 0.111 mg/kg (Table 2). At most locations, manganese concentrations were higher in the bottom samples than in the surficial samples (Figure 7). The solubility of manganese increases under reducing conditions (Hem, 1985), and it is likely that some manganese in the top samples has become soluble and has been lost to the water column.

Table 2. Concentrations of Calcium, Iron, Manganese, Sulfate, TOC and CEC in A-01 Wetland Hydrosoils, September 2001

Location*	Calcium	Iron	Manganese	Sulfate	TOC	CEC
4A-A-T	0.493	8.96	0.093	<188	346	2.85
4A-A-B	0.406	4.59	0.077	<188	399	2.93
4A-B-T	0.381	5.06	0.051	<188	322	2.49
4A-B-B	0.482	5.94	0.095	<188	458	3.24
4A-C-T	0.450	5.83	0.050	<188	284	2.89
4A-C-B	0.482	6.39	0.090	<188	410	3.85
4A-D-T	0.243	5.07	0.049	<188	411	2.67
4A-D-B	0.359	5.42	0.102	<188	390	3.88
4B-A-T	0.370	6.62	0.072	<188	292	2.61
4B-A-B	0.226	3.84	0.111	<188	347	2.93
4B-B-T	0.494	5.31	0.075	<188	498	3.22
4B-B-B	0.171	3.35	0.089	<188	338	2.04
4B-C-T	0.184	2.88	0.035	<188	353	4.04
4B-C-B	0.212	7.02	0.100	<188	363	3.50
4B-D-T	0.733	5.36	0.086	<188	233	3.58
4B-D-B	0.190	3.28	0.073	<188	374	2.58

All units are mg/kg, except Cation Exchange Capacity, which is reported as meq/100 g of soil.
*Location is designated by cell number, zone, and depth (T = top; B = bottom)

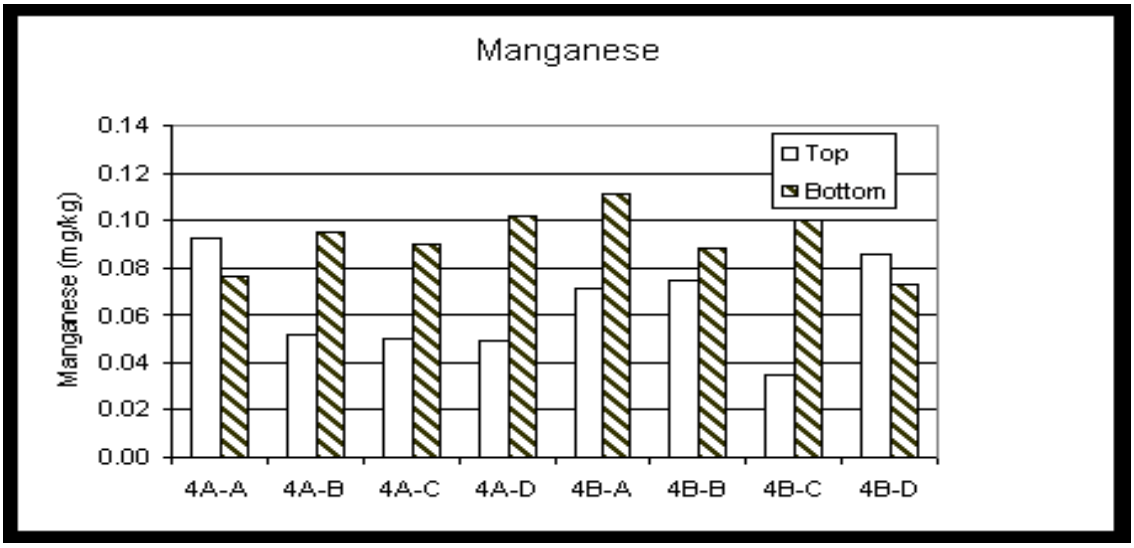

Figure 7. Manganese Concentrations in the Hydrosoil of the A-01 Wetland Treatment System, September 2001

Concentrations of iron in the wetland soils ranged from 2.88 to 8.96 mg/kg (Table 2). Although iron concentrations were somewhat variable, no obvious patterns of distribution were observed (Figure 8). Total organic carbon (TOC) ranged from 233 to 498 mg/kg (Table 2). No obvious vertical or longitudinal patterns of distribution were observed (Figure 9). Cation exchange capacity (CEC) of the wetland soils was relatively low, ranging from about 2 to 4 meq/100 g (Table 2). Typically, CEC values for sandy textured soils are between 2 and 10 meq/100 g (Buckman and Brady, 1969). Like iron and TOC, no obvious trends of distribution were observed (Figure 10). Concentrations of sulfate were below the detection limit of 188 mg/kg at all locations (Table 2).

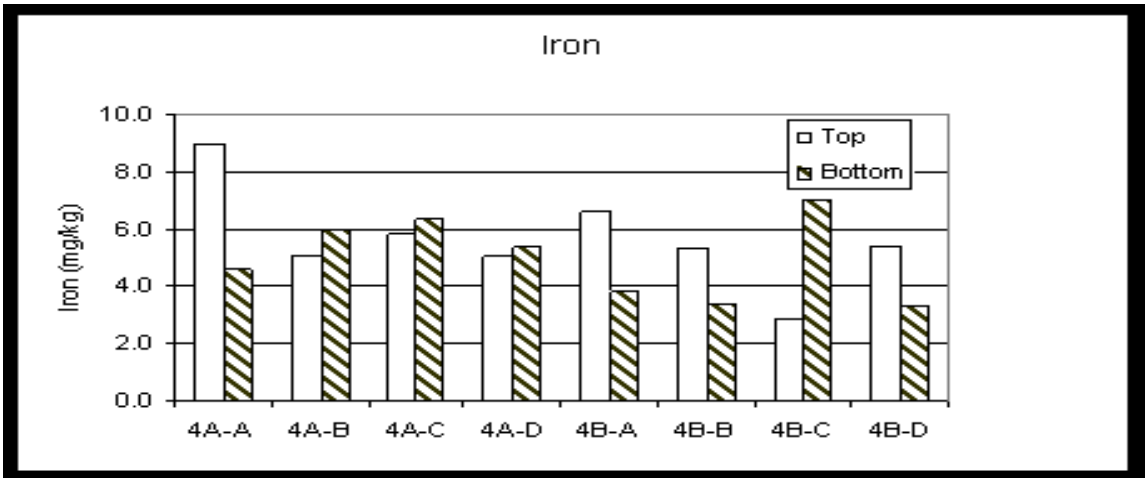

Figure 8. Iron Concentrations in the Hydrosoil of the A-01 Wetland Treatment System, September 2001

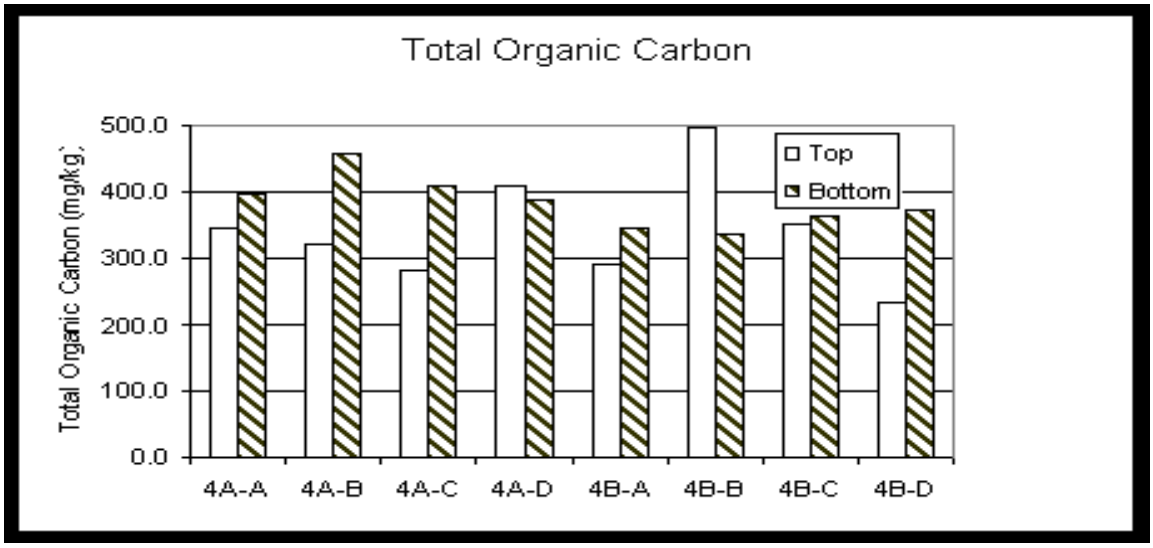

Figure 9. Total Organic Carbon Concentrations in the Hydrosoil of the A-01 Wetland Treatment System, September 2001

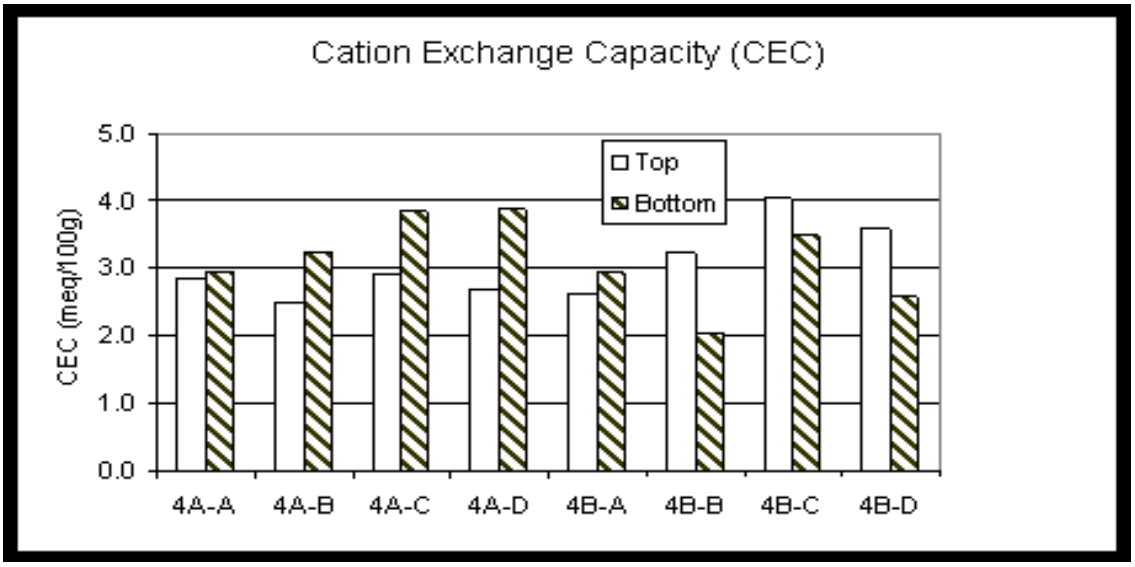

Figure 10. Cation Exchange Capacity of the Hydrosoil of the A-01 Wetland Treatment System, September 2001

Sulfide concentrations in the hydrosoil samples were extremely variable, ranging from 6.07 to 174 mg/kg (Table 3). Mean sulfide concentrations within a sampling zone (N=3) ranged from about 30 to about 105 mg/kg (Figure 11). The variability is probably due to a combination of the patchy distribution of the gypsum that was applied to the hydrosoil and patchy redox conditions resulting from proximity to plant roots.

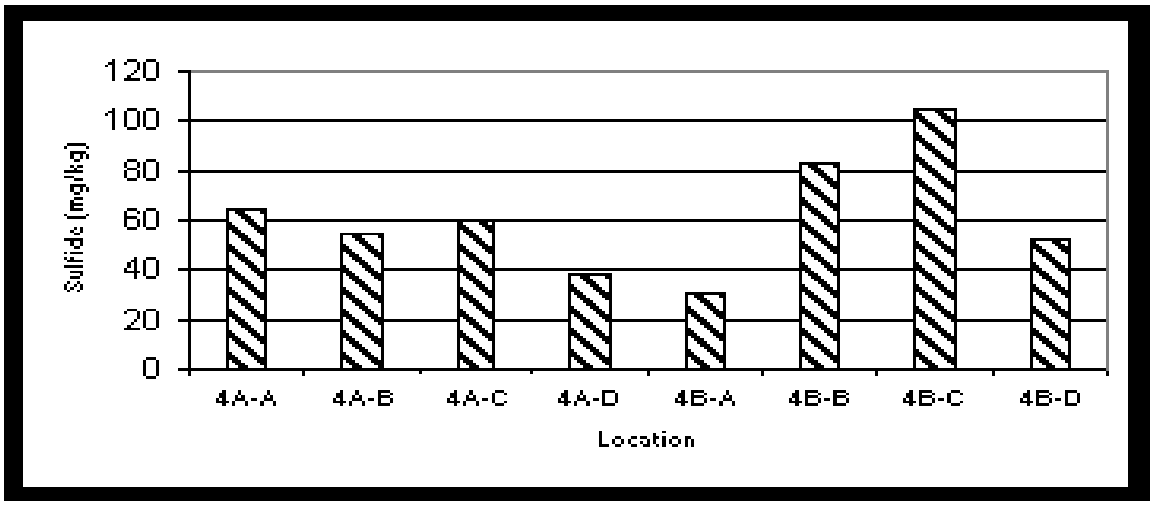

Figure 11. Sulfide Concentrations in the Hydrosoil of the A-01 Wetland Treatment System, September 2001.

Table 3. Sulfide Concentrations (mg/kg) in A-01 Wetland Hydrosoil Samples

Cell 4-A	Sulfide (mg/kg)	Cell 4-B	Sulfide (mg/kg)
4A-A-1	74.4	4B-A-1	14.3
4A-A-2	106	4B-A-2	70.9
4A-A-3	<12.5	4B-A-3	8.08
4A-B-1	*	4B-B-1	130
4A-B-2	50.8	4B-B-2	36
4A-B-3	<60	4B-B-3	<56.2
4A-C-1	52.3	4B-C-1	16.6
4A-C-2	67.4	4B-C-2	174
4A-C-3	*	4B-C-3	125
4A-D-1	<52.3	4B-D-1	6.07
4A-D-2	50.8	4B-D-2	*
4A-D-3	25.5	4B-D-3	97.5

*Sample containers were broken in transit.

4.0 Conclusions

Based on data from the bottom hydrosoil samples, background concentrations of copper in the hydrosoil prior to being inundated with A-01 effluent were about 2 to 4 mg/kg and background zinc concentrations were about 5 to 10 mg/kg. Copper and zinc concentrations are considerably higher in the surficial hydrosoil, and were highest in the surficial hydrosoil near the inflow to cell 4A and decreased with increasing distance from the inflow. In cell

4A, Copper concentrations in the surficial hydrosoil averaged 20 mg/kg in Zone A, about 10 mg/kg in Zones B and C, and <6 mg/kg in Zone D and in all four zones of cell 4B. Zinc averaged about 29 mg/kg in cell 4A, zone A, about 16 mg/kg in zones B and C, and about 13 mg/kg in Zone D. Zinc was slightly elevated in the surficial hydrosoil of Cell 4B, Zone A (11.1 mg/kg), but was <9 mg/kg in the remaining 3 zones of cell 4B. These results suggest that the most of the copper and zinc present in the A-01 effluent is being bound to the hydrosoil quickly as the effluent flows into the A cells. Mercury was below the detection limit in most of the hydrosoil samples. However, the monthly data for mercury in water samples collected from the inflow and outflow of the treatment cells indicates that more mercury is removed in the A cells than in the B cells.

With the exception of manganese, no other longitudinal or vertical trends were noted in the data. Manganese concentrations were generally lower in the surficial hydrosoil than in the deeper hydrosoil. The solubility of manganese increases under anoxic conditions, and it is likely that manganese in the surficial hydrosoil is being lost to the water column and transported out of the wetlands.

When the wetland was constructed, approximately 4% organic matter was added to the wetland cells. This organic matter was primarily in the form of coarse wood chips. Based on the TOC data, percent organic matter in the wetland hydrosoil is < 1%. The wetland was designed as a system that would accrete organic matter over time, from the decaying *Scirpus*. The data from September 2001 shows no evidence of surficial accretion, since TOC concentrations in the surficial and bottom hydrosoil samples are very similar. However, in September 2001, the *Scirpus* had experienced only one full growing season and had not undergone winter senescence. It is anticipated that TOC concentrations in the surficial hydrosoils will increase over time as the wetland matures. The cation exchange capacity of the wetland hydrosoils was relatively low, due to the sandy composition of the soil and low organic content. Since organic matter is expected to accrete in the wetland, it is anticipated that CEC in the surficial hydrosoil will increase over time.

5.0 References

1. Buckman, H.O. and N.C. Brady. 1969. The Nature and Properties of Soils. Macmillan Company, New York.
2. Hem, J.D. 1985. Study and Interpretation of the Chemical Characteristics of Natural Water. U.S. Geological Survey Water-Supply Paper 2254.

Appendix 1. Concentrations of Copper, Zinc and Mercury in A-01 Wetland Hydrosoil Samples, September 2001

Location	Copper		Zinc		Mercury	
	Top	Bottom	Top	Bottom	Top	Bottom
4A-A-1	35.30	2.16	45.20	6.80	<0.08	<0.08
4A-A-2	8.64	2.24	16.10	6.40	<0.08	<0.08
4A-A-3	27.70	2.56	37.80	8.64	<0.08	<0.08
4A-A-4	36.20	2.16	48.70	7.28	<0.08	<0.08
4A-A-5	14.40	2.40	25.80	6.32	<0.08	<0.08
4A-A-6	35.40	1.84	44.50	5.76	<0.08	<0.08
4A-A-7	5.12	2.40	11.70	7.04	<0.08	<0.08
4A-A-8	6.48	5.52	15.80	14.20	<0.08	<0.08
4A-A-9	5.28	2.08	11.80	8.08	<0.08	<0.08
4A-A-10	24.80	1.92	34.50	6.00	<0.08	<0.08
4A-A mean	19.90	2.53	29.20	7.65		
4A-A standard deviation	13.32	1.07	14.70	2.47		

4A-B-1	3.68	4.40	8.48	9.04	<0.08	<0.08
4A-B-2	6.08	2.80	10.70	7.36	<0.08	<0.08
4A-B-3	28.90	1.76	37.40	5.12	<0.08	<0.08
4A-B-4	14.30	1.20	22.00	4.00	<0.08	<0.08
4A-B-5	12.50	2.08	19.00	6.00	<0.08	<0.08
4A-B-6	6.80	2.64	11.40	6.72	<0.08	<0.08
4A-B-7	4.88	2.56	8.88	6.72	<0.08	<0.08
4A-B-8	4.88	2.32	9.04	5.60	<0.08	<0.08
4A-B-9	4.32	2.08	9.28	4.80	<0.08	<0.08
4A-B-10	12.40	1.60	20.30	4.72	<0.08	<0.08
4A-B mean	9.87	2.34	15.65	6.01		
4A-B standard deviation	7.73	0.88	9.25	1.50		
4A-C-1	10.20	4.00	16.80	7.20	<0.08	<0.08
4A-C-2	4.88	4.64	8.08	8.24	<0.08	<0.08
4A-C-3	13.50	3.36	21.60	8.00	<0.08	<0.08
4A-C-4	8.32	4.32	14.50	8.32	<0.08	<0.08
4A-C-5	15.30	3.92	25.20	7.28	<0.08	<0.08
4A-C-6	6.08	14.20	10.20	7.60	<0.08	<0.08
4A-C-7	10.50	5.60	16.30	8.40	<0.08	<0.08
4A-C-8	13.00	3.28	23.00	7.28	<0.08	<0.08
4A-C-9	4.96	3.84	9.04	6.24	<0.08	<0.08
4A-C-10	8.96		13.60	6.16	<0.08	<0.08
4A-C mean	9.60	5.24	15.80	7.47		
4A-C standard deviation	3.63	3.43	5.95	0.81		
4A-D-1	8.32	3.12	16.70	8.72	<0.08	0.353
4A-D-2	4.16	4.16	8.88	9.20	<0.08	<0.08
4A-D-3	2.08	2.56	4.56	7.12	<0.08	<0.08
4A-D-4	9.28	6.08	16.60	13.90	<0.08	<0.08
4A-D-5	4.96	5.36	13.00	13.60	<0.08	<0.08
4A-D-6	9.20	1.76	17.10	5.60	<0.08	<0.08
4A-D-7	3.52	1.76	7.44	5.92	<0.08	<0.08
4A-D-8	9.76	5.20	17.90	13.70	<0.08	<0.08
4A-D-9	6.08	3.84	13.70	8.96	<0.08	<0.08
4A-D-10	8.88	2.32	17.40	7.44	<0.08	<0.08
4A-D mean	6.62	3.62	13.34	9.42		
4A-D standard deviation	2.81	1.56	4.78	3.21		

Appendix 1, continued

Location	Copper		Zinc		Mercury	
	Top	Bottom	Top	Bottom	Top	Bottom
4B-A-1	7.60	2.32	16.30	7.28	<0.08	<0.08
4B-A-2	4.48	2.96	10.20	8.96	<0.08	0.222
4B-A-3	2.56	1.84	8.08	6.40	<0.08	<0.08
4B-A-4	6.40	1.44	13.70	6.08	<0.08	0.088
4B-A-5	5.44	2.56	12.80	7.20	0.145	<0.08
4B-A-6	6.00	1.92	12.20	6.08	0.232	<0.08

4B-A-7	4.24	2.88	10.30	9.28	<0.08	<0.08
4B-A-8	4.56	2.08	9.92	6.40	<0.08	<0.08
4B-A-9	2.80	1.92	7.28	6.48	<0.08	<0.08
4B-A-10	4.32	2.88	10.20	8.24	<0.08	<0.08
4B-A mean	4.84	2.28	11.10	7.24		
4B-A standard deviation	1.56	0.52	2.69	1.19		
4B-B-1	2.88	2.32	7.76	6.88	<0.08	<0.08
4B-B-2	1.60	1.44	5.52	5.20	<0.08	<0.08
4B-B-3	1.92	1.76	5.84	5.12	<0.08	<0.08
4B-B-4	1.92	2.48	5.52	6.24	<0.08	<0.08
4B-B-5	4.24	1.60	8.88	5.52	<0.08	<0.08
4B-B-6	3.76	1.76	8.16	5.60	<0.08	<0.08
4B-B-7	3.44	1.84	7.84	5.28	<0.08	0.087
4B-B-8	1.76	1.52	4.88	5.28	<0.08	<0.08
4B-B-9	6.64	2.72	12.96	6.72	<0.08	<0.08
4B-B-10	3.60	0.96	5.92	3.20	<0.08	<0.08
4B-B mean	3.18	1.84	7.33	5.50		
4B-B standard deviation	1.54	0.53	2.40	1.03		
4B-C-1	3.60	1.60	9.60	6.16	<0.08	<0.08
4B-C-2	6.24	4.00	13.80	8.88	<0.08	<0.08
4B-C-3	5.36	2.56	11.30	6.16	<0.08	<0.08
4B-C-4	2.72	4.88	7.52	11.30	<0.08	<0.08
4B-C-5	2.56	1.68	6.88	5.20	<0.08	<0.08
4B-C-6	2.24	4.32	6.32	10.60	<0.08	<0.08
4B-C-7	3.76	1.44	9.52	5.28	<0.08	<0.08
4B-C-8	1.76	1.76	5.92	5.76	<0.08	<0.08
4B-C-9	3.04	2.00	8.08	6.88	<0.08	<0.08
4B-C-10	6.00	3.92	11.10	9.60	<0.08	<0.08
4B-C mean	3.73	2.82	9.00	7.58		
4B-C standard deviation	1.60	1.32	2.53	2.30		
4B-D-1	4.16	2.72	8.64	6.96	<0.08	<0.08
4B-D-2	6.32	3.52	10.60	7.44	<0.08	0.128
4B-D-3	18.10	2.72	6.08	6.48	<0.08	<0.08
4B-D-4	2.32	1.92	7.12	6.24	0.08	<0.08
4B-D-5	3.68	4.40	7.44	7.76	<0.08	<0.08
4B-D-6	9.04	2.88	15.40	7.28	0.088	<0.08
4B-D-7	7.84	3.92	13.20	6.64	0.629	<0.08
4B-D-8	2.40	2.48	6.00	5.92	0.088	<0.08
4B-D-9	4.16	1.76	8.08	6.32	0.096	0.112
4B-D-10	2.56	3.44	6.56	8.32	<0.08	1.14
4B-D mean	6.06	2.98	8.92	6.94		
4B-D standard deviation	4.83	0.84	3.19	0.76		