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**WASTEWATER TREATMENT AND HEAVY METALS REMOVAL  
IN THE A-01 CONSTRUCTED WETLAND  
2003 REPORT**

**Prepared**

**By**

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**August 2004**

Westinghouse Savannah River Company  
Savannah River Site  
Aiken, SC 29808

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DOC	dissolved organic carbon
DO	dissolved oxygen
EC	electrical conductivity
EXAFS	extended X-ray absorption fine structure spectroscopy
ICP-AES	inductively couple plasma - atomic emission spectroscopy
ICP-MS	inductively couple plasma – mass spectroscopy
Kd	distribution coefficient
NPDES	National Pollution Discharge Elimination System
OM	organic matter
PMF	potentially mobile fraction
RF	recalcitrant factor
SCDHEC	South Carolina Department of Health and Environmental Control
SEM	scanning electron microscopy
SREL	Savannah River Ecology Laboratory
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TOC	total organic carbon
U S EPA	United State Environmental Protection Agency
WTS	wetland treatment system
WD/XMP	wave dispersive X-ray microprobe spectroscopy

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## EXECUTIVE SUMMARY

The A-01 wetland treatment system (WTS) was designed to remove metals from the effluent at the A-01 NPDES outfall. The purpose of research conducted during 2003 was to evaluate 1) the ability of the A-01 wetland treatment system to remediate waste water, 2) retention of the removed contaminants in wetland sediment, and 3) the potential remobilization of these contaminants from the sediment into the water column. Surface water and sediment samples were collected and analyzed in this study.

The water data showed that Cu, Zn, and Pb concentrations in water were reduced as the water passed through each phase of the treatment system. Copper and Pb levels were typically reduced by 70% and 80% of the splitter box values after passing through the first cell, respectively. The removal process from water occurred very rapidly in the wetland system, with most removal already completed prior to exiting the first cell of the series. However, Fe and Mn data show the opposite pattern: the lowest concentrations of Fe and Mn were observed in the old A-01 outfall and the highest in the stream. Highest Fe and Mn concentrations in the stream water (~250 ppb and 120 ppb, respectively for Fe and Mn) indicates dissolution of the solid mineral phases of these two elements, very likely due to higher content of dissolved organic ligands and reducing conditions in the wetland cells.

In this study, sediment samples were collected from the primarily inorganic material below the highly organic surface detritus. Generally, metal concentrations in the inorganic sediment samples collected in 2003 were low. The highest concentrations of Cu (6.2 ppm) and Zn (10.3 ppm) were found in cell 1A. This distribution indicates that most of these metals were removed in the first wetland cell. Similar spatial distribution of these metals were observed in the samples collected in 2001; however, the values for 2003 were usually higher than 2001 values, which indicates that Cu and Zn have accumulated in the sediment over a period of two years.

Sequential extractions of wetland sediment were conducted to determine how strongly metals were bound to the wetland sediment. Only a very small percentage (less than 5 %) of Cu, Zn, and Pb was measured in the water or exchangeable step, indicating that under normal conditions (neutral pH and low ionic strength) metals are not expected to desorb from the sediment. The acid soluble and residual fractions made up the highest percentage of measured Cu, Zn, and Pb. Although the sequential extraction procedure used in this study is informative, it does not specifically account for metals bound to sulfides. Because the goal of this wetland is to precipitate metals from the water column and bind them as sulfide minerals in the sediment, the fraction of metals bound to sulfides is important. Due to lack of the sulfide fraction in the sequential extraction, very likely a large pool of metals that was found in the other fractions (e.g., residual fraction) is accounted for by the solid-sulfide phase.

The Potentially Mobile Fraction (PMF) is an indicator of the contaminant fraction that has the potential for entering into the mobile aqueous phase under changeable environmental conditions, such as pH, Eh, temperature and others. It is defined as the ratio of relatively mobile fractions of an element to the total concentration of the element in the sediment. Metals associated with the PMF are metals found in water, exchangeable, acid soluble,

organic, and amorphous Mn and Fe oxide fractions. Generally, the PMF values for Cu, Zn and Pb were about 20%. The low PMF values for Cu, Zn, and Pb in the A-01 WTS sediment indicate that most of the removed metals are in the very strongly bound phases and not easily extractable. The PMF values for these elements were higher than the pool of metals associated with the easily mobile fraction (i.e., a subset of the PMF consisting only of water and exchangeable fractions), indicating that remobilization and bioavailability of Cu, Pb and Zn were extremely low (1%, 2%, and less than 5% respectively, for Cu and for Zn and Pb). The PMF values for Fe and Mn showed an opposite trend. For both elements the PMF values were very high, about 70% or more for Fe and between 57 and 66 % for Mn. These high PMF values for Fe and Mn indicate high desorption of these elements from the sediment and high solubility of their solid phases.

The sequential extraction data was also used to calculate the recalcitrant factor (RF). The RF is the ratio of strongly bound fractions to the total concentration of elements in sediment (or the sum of all fractions). The meaning of the RF is opposite to the PMF; i.e., the RF indicates the virtually irreversible retention of metals by the solid phase. This construct provides an estimate of the percentage of a contaminant in the contaminated sediment that was resistant to remobilization; i.e., retention of contaminants in wetland sediments. The RF values were about 80% for Cu, Zn and Pb in cells 4A and 4B, indicating high retention of these elements in the sediment. The RF values for Fe and Mn were much lower than for Cu, Zn, and Pb. They ranged from 30 to above 40, respectively, for Fe and Mn.

## 1.0 INTRODUCTION

Constructed wetlands have the ability to remove pollutants from water that is directed through them and retain the pollutants in sediment. Removal mechanisms can act uniquely, sequentially, or simultaneously on each contaminant group or species. Processes controlling contaminant retention in constructed wetland sediments may be abiotic (physical/chemical) or biotic (microbial/phytological).

The primary abiotic processes that are responsible for contaminant immobilization in constructed wetland sediment involve a series of mechanisms: settling, sedimentation, sorption onto organic matter or mineral phases, oxidation and hydrolysis, formation of carbonates, formation of insoluble mineral phases, and binding to iron and manganese oxides. Settling and sedimentation achieve efficient removal of particulate matter and suspended solids. Sorption is a chemical process that results in either short-term retention or long-term immobilization of contaminants. It includes the combined processes of adsorption and absorption. Chemical precipitation involves the conversion of metals in the influent stream to an insoluble precipitate. These reactions represent an effective means for immobilizing toxic metals in the wetlands.

In addition to the abiotic processes, biotic processes like biodegradation and plant uptake can be major contributors to contaminant levels in wetland sediments. Some microbial/phytological processes taking place in wetlands are the following: aerobic/anaerobic biodegradation, phytoaccumulation/phytostabilization, and phytodegradation/rhizodegradation. Microbial metabolic processes play a significant role in the removal of organic compounds in aerobic/anaerobic environments of the wetland. The microbial transformation of metals and radionuclides occurs as the result of variety of mechanisms, and the products of these reactions are diverse. For example, many microbial species are capable of reducing Fe(III), U(VI), Cr(VI), and Mn(IV) (Ehrlich, 1996). Microbial reduction of U(VI) and Cr(VI) results in the less soluble U(IV) and Cr(III), while bacterial reduction of soluble Fe(III) ultimately results in Fe immobilization and mineral formation (Ehrlich, 1996). The formation of solid metal-sulfide precipitates, important for metal treatment in constructed wetland, represents another example of microbial reduction. In this process sulfide ( $S^{2-}$ ) is produced by sulfide reducing bacteria in anaerobic sediments during normal anaerobic respiration, a process that requires sulfate ( $SO_4^{2-}$ ) as a terminal electron acceptor. Formation of sulfide precipitates could be based on abiotic processes only or on both abiotic and biotic processes.

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 sequential, treatment cells (Figure 1). Each treatment cell is a one-acre wetland that contains *Schoenoplectus californicus* (giant bulrush) and has approximately a 24 hour retention time, depending on flow. 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 B-cells, through the B-cells to the wetland outfall (a new A-01 outfall), and into the Tim's Branch stream.

When the wetland treatment cells were constructed, the hydrosol 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) (Specht and Nelson, 2002). A layer of hydrosol was added to the cells, the amendments were added, an additional 6 inch layer of hydrosol was added, and the soil was lightly disked to mix the amendments into the hydrosol. The treatment system was constructed during the winter/spring of 2000 and began receiving A-01 effluent in July 2000. Since the beginning of the A-01 WTS operation, routine monitoring samples have been collected at the compliance point for monthly reporting. Additionally, as part of the research effort, water samples were collected from numerous locations from the inflow to the system through the discharge to the receiving stream in 2000 and 2001 (Nelson, et al., 2002). Sediment samples were collected and analyzed in order to provide baseline data on metal concentrations and general sediment chemistry early in the operational life of the treatment system in September, 2001 (Specht and Nelson, 2002). Additional water and sediment samples were collected in 2003 (July-August). A detailed description of 2003 sampling, analytical methods and results is presented below.

## 2.0 OBJECTIVE

The purpose of 2003 research work was to evaluate the removal of contaminants by the A-01 wetland treatment system. Of particular interest was the retention of the removed contaminants in wetland sediment and their potential to remobilize from the sediment into the water column. Removal and retention of contaminants in a constructed wetland is controlled by chemical and physical processes that occur in the wetland water and sediment. Therefore, the focus of this study was on chemical and physical characterization of the water and sediment samples to support the investigation of surface water and sediment metal concentrations, binding, and speciation. The results from the 2003 investigation will be used to evaluate the effectiveness of waste water remediation by the wetlands.

The objectives of the 2003 investigation were threefold:

- Evaluate the ability of the A-01 WTS to remove multiple constituents
- Compare metal concentrations in sediments to previous analyses conducted in 2001
- Assess the stability of sorbed metals with respect to the potential for subsequent remobilization.

### 3.0 MATERIALS AND METHODS

#### 3.1 SAMPLING

Samples were collected in four phases starting in July and continuing until August 2003. Water samples were collected in phases I and IV and sediment samples (cores) were collected in phases II and III (Figure 1 and 2).

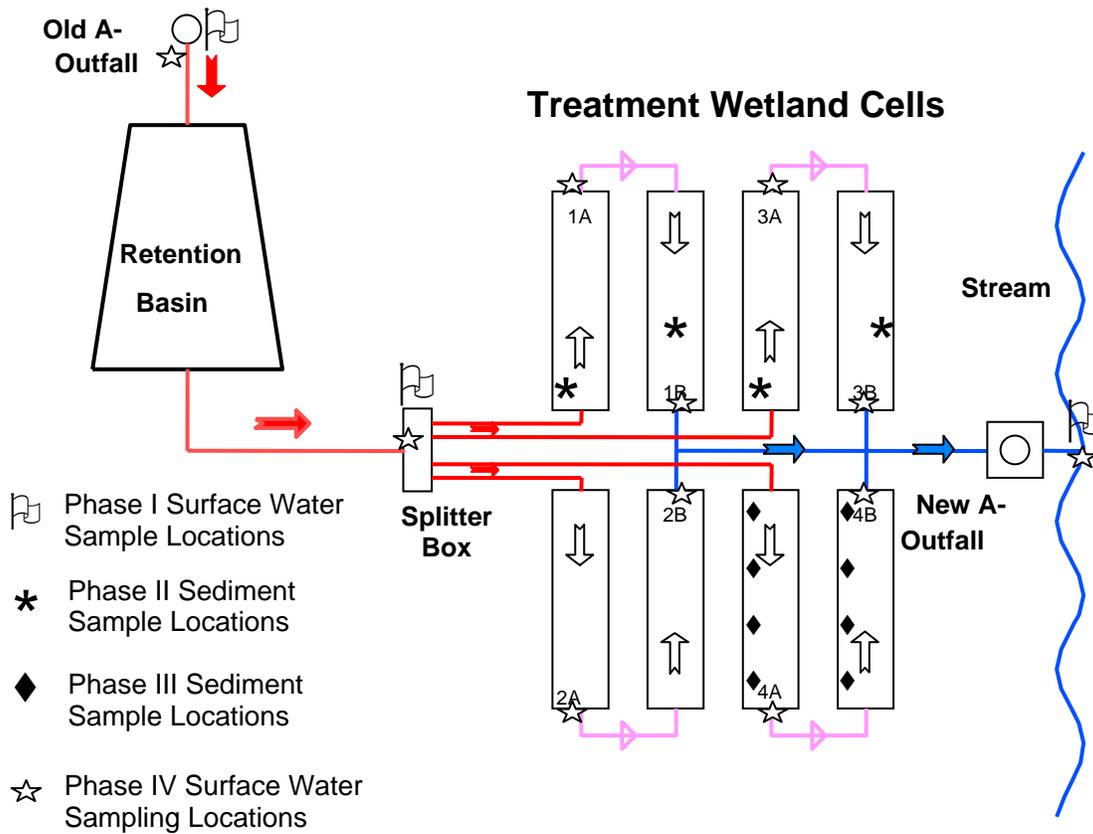


Figure 1. Schematic of the A-01 Wetland Treatment System and Sampling Locations

### **3.1.1 Surface Water in the A-01 Constructed Wetlands (Phase I)**

For Phase I sampling, five rounds of surface water samples were collected from three locations (Figure 1). Grab samples were collected on 7/16/03, 7/17/03, 7/18/03, 7/21/03, and 7/22/03 at the compliance point of the old A-01 outfall, the splitter box, and just below the new A-01 outfall (stream), for a total of 15 samples. These sample locations represent influent to the system, influent to the wetland cells, and effluent from the wetland cells. These locations were selected to evaluate the removal efficiency of the retention basin and the treatment cells.

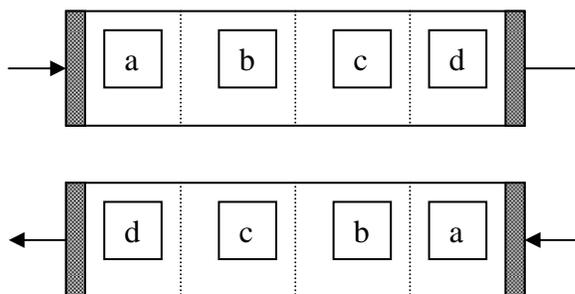
Prior to sample collection, sample containers were organized by sampling location and placed in appropriately sized plastic bags. Each plastic bag was labeled by location and sealed with masking tape. All sample containers were identified in accordance with the sample identification numbers on the chains-of-custody forms. Grab samples of surface water were collected from the selected A-01 sampling locations by immersing the sample container in the surface water or by using a 500 mL plastic beaker attached to a wooden rod.

### **3.1.2 Sediments in the A-01 Constructed Wetlands (Phase II)**

Sediment samples were collected only one time for the measurement of metal binding in the sediment. In Phase II, four sediment cores were collected in cells 1A, 1B, 3A and 3B, using Plexiglas core tubes with plastic caps on each end on 8/06/03 (Figure 1). The locations for Phase II were selected to evaluate metal retention by the sediment in the treatment cells. From each core, the layer composed of inorganic or mainly inorganic material, about 2 inch thick, from below the highly organic surface detritus was selected for further analysis.

### 3.1.3 Sediment Samples To Determine Spatial Partitioning in the A-01 Constructed Wetlands (Phase III)

Phase III sediment sampling generally followed the scheme implemented during sampling conducted in 2001 (Specht and Nelson, 2002) (Figure 1). Sediment sampling was conducted in cells 4A and 4B, with each cell being spatially divided into quarters along its long axis. Five cores were collected, as described above, from each quarter. Samples were assigned a letter designating sampling location: “A” locations were proximal to the influent progressing to “D” locations, which were distal, or at the discharge point of treatment cell (Figure 2). These locations were selected to observe the spatial distribution of metals in the sediment cell by comparing metal concentrations and speciation in the sediment close to the influent, the middle part of cell, and close to the discharge point of the treatment cell. Forty cores were collected and sent to the Savannah River Ecology Laboratory on 8/18/03 and 8/19/03 for analytical service. No samples were collected within approximately 20 ft of the end of the cells to avoid local effects attributable to inflow or outflow structures. As in Phase II, a 2 inch inorganic layer was selected and analyzed from each sediment core.



**Figure 2. Spatial Partitioning of 4A and 4B Cells for Phase III Sediment Sampling.**

### 3.1.4 Surface Water Samples To Determine Spatial Partitioning in the A-01 Constructed Wetlands (Phase IV)

To determine the spatial removal of contaminants throughout the wetland system, surface water samples were collected on 8/28/03 from the old A-01 outfall, the splitter box, the outflow of each cell, and below the new A-01 outfall (stream). The total number of samples collected for this phase was 11.

## 3.2 ANALYTICAL METHODS

### 3.2.1 Surface Water Sample Analysis

Surface water samples from the A-01 WTS, collected during phases phase I and IV were analyzed for pH and electrical conductivity (EC) immediately after receiving. Samples were acidified to a pH < 2 and analyzed for metal concentrations by inductively coupled plasma-mass spectroscopy (ICP-MS) using a Perkin Elmer Model Elan 6000. Additionally, phase IV samples were analyzed for dissolved organic carbon and anion concentrations.

### 3.2.2 Sediment Sample Analysis

The sediment samples were analyzed for total metal concentration with HNO<sub>3</sub> and HF acids according to EPA 3052 and analyzed for metals by inductively coupled plasma-mass spectroscopy (ICP-MS) using a Perkin Elmer Model Elan 6000. Additionally, an eight-step sequential extraction was performed on selected sediment samples. From phase II, one sediment sample from each cell and from phase III, one sediment sample from each quarter were selected for analysis. Sequential extraction was conducted on 1 g of sediment. Each step (fraction) was extracted with 30 mL of reagent (with the exception of the crystalline Fe oxide fraction for which 15 mL was used). Between each step, the weight of total reagent used was recorded for more precise calculations. The following extractions were conducted:

- Fraction 1:** Water soluble. Samples extracted with nanopure water for 16 hours.
- Fraction 2:** Exchangeable. Samples extracted with 0.50 M Ca(NO<sub>3</sub>)<sub>2</sub> for 16 hours.
- Fraction 3:** Acid soluble metals. Residue from the second fraction was extracted for 8 hours using 0.44 M acetic acid/ 0.1 M Ca(NO<sub>3</sub>)<sub>2</sub>.
- Fraction 4:** MnO<sub>2</sub> occluded metals were extracted for 30 minutes with 0.01M NH<sub>2</sub>OH-HCl/ 0.1 M nitric acid.
- Fraction 5:** Organically bound metals. The residue from the fourth extraction was extracted for 24 hours with 0.1 M Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>.
- Fraction 6:** Bound to amorphous Fe oxides. The residue from the fifth extraction was extracted with 0.175 M ammonium oxalate/ 0.1 M oxalic acid for four hours.
- Fraction 7:** Bound to crystalline Fe oxides. The extract in this step was 0.175 M sodium citrate/ 0.05 M citric acid/ Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>. Samples were extracted for 30 minutes.
- Fraction 8:** Residual phase. The samples were air dried and acid digested according to EPA 3052.

The extracts from each fraction were analyzed for metal concentrations by inductively coupled plasma-mass spectroscopy (ICP-MS) using a Perkin Elmer Model Elan 6000.

From the sediment phase III samples, porewater was extracted using Vectaspin tubes (10  $\mu\text{m}$ ). After separating the porewater at 10  $\mu\text{m}$ , it was further filtered using a 0.22  $\mu\text{m}$  nylon syringe filter. The pH and EC was immediately measured after extraction. An aliquot of the porewater was acidified to a pH < 2 for metals analysis. The remaining porewater sample was used for anion analysis.

## 4.0 RESULTS AND DISCUSSION

### 4.1 REMOVAL OF CONTAMINANTS FROM WASTE WATER AT A-01 WTS

#### 4.1.1 Characteristic and Chemistry of Surface Water from the A-01 WTS

The A-01 WTS generally operates at circumneutral pH (Specht and Nelson, 2002). The pH of wetlands ordinarily represents the amount of anaerobic decomposition and subsequent organic acid production vs. the amount of photosynthetic activity by algae. At the A-01WTS, effluent pH has not been identified as problematic since the beginning of its operation. The surface water pH values of the samples collected in phase IV are presented in Figure 3. The pH of surface water samples collected on August 28, 2003 was about 6.5; and it was steady through the treatment cells, new A-01 outfall, and below the new A-01 outfall (Figure 3).

Dissolved organic carbon (DOC) plays a major role in biogeochemistry processes in the wetland environment. It interacts with metal mobility and bioavailability, acid-base chemistry, and solubility-dissolution of metal ions. Mobility, bioavailability, and toxicity of Cu is largely controlled by the presence of DOC. Copper complexed with DOC is not immediately bioavailable (Kim et al., 1999). Organic carbon can also lead to both increases and decreases in mercury methylation. First, some forms of DOC are known sources of decomposable carbon substrates for microbial populations (Tranvik, 1988). Inputs of organic carbon may stimulate microbial activity and mercury methylation. Secondly, inorganic mercury is strongly bound by DOC, notably humic substances (Jackson 1989). This binding reduces the bioavailability of inorganic mercury to microbial methylators, thus decreasing methylmercury production. However, as conditions become more acidic, this mercury-DOC binding is reduced (Hintelmann et al., 1995). This increases mercury bioavailability to bacterial methylators and enhances methylation. Therefore, low pH and high DOC conditions are ideal for mercury methylation.

Average dissolved organic carbon (DOC) concentrations for surface water were 7.8 ppm and 10.1 ppm for cells A and B, respectively (Figure 3). The lowest DOC concentrations were observed for the old A-01 outfall and the splitter box (Figure 3). The higher DOC concentrations in B cells is beneficial in binding metals, especially Cu, Hg, Pb, and Zn, as long as pH values remain circumneutral.

While, pH, DOC, redox, temperature, and salinity influence biogeochemistry of metals in wetlands, the factor that exerts the most control is sulfur chemistry and its link with sulfate-reducing bacteria. Sulfate reducers are obligate anaerobes that obtain energy for growth by oxidation of organic matter substrates, remove hydrogen atoms from the organic molecules, and use sulfate as the terminal electron acceptor, thus reducing sulfate to sulfide. Once in solution, sulfide forms strong bonds with cationic metals, such as, Cd, Cu, Hg, Pb, and Zn, making them unavailable for biological uptake (Perry 1995).

Sulfate concentrations for the surface water samples from phase IV are presented in Figure 4 and Table 1. Sulfate concentrations were rather steady though the entire system and ranged from 0.6 to 0.9 ppm (or 5.73 to 8.96  $\mu\text{M}$ ). These sulfate concentration data are consistent with the data from the mesocosm study (Harmon et al., 2004), where sulfate concentration in the control treatments ranged from 4.4 to 17.7  $\mu\text{M}$  and, after seven months in the low sulfate treated tanks, was 9.4  $\mu\text{M}$ . Harmon et al. (2004) indicated that the level of sulfate concentration in the control tanks (where sulfate as gypsum was not added to the system) was effective in removing metals from the water column while keeping mercury methylation low.

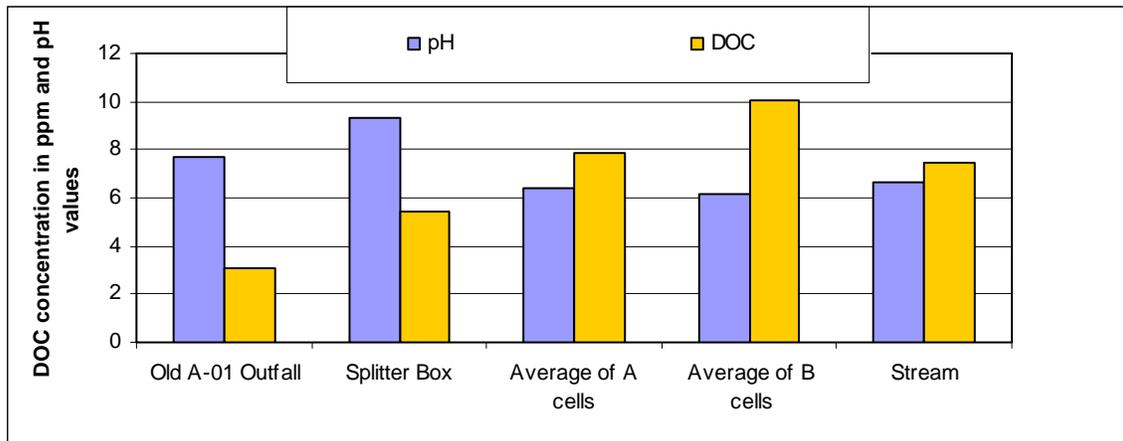


Figure 3. Concentration of DOC and pH values of surface water samples from A-01.

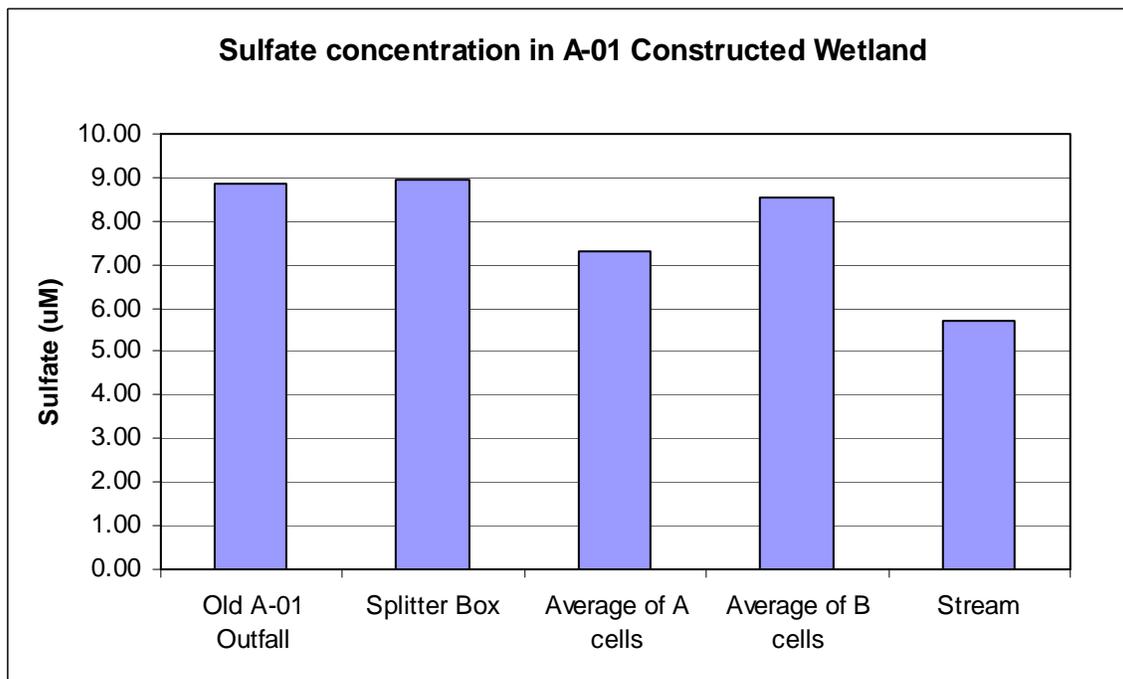


Figure 4. Concentration of sulfate ( $\mu\text{M}$ ) in surface water samples from the A-01.

**Table 1. Electric conductivity (EC) and anion concentrations in surface water samples from the A-01.**

Sampling Area	EC [uS/cm]	Chloride [ppm]	Bromide [ppm]	Nitrate [ppm]	Sulfate [ppm]
Old A-01 Outfall	38.0	4.4	< 0.05	0.70	0.9
Splitter Box	38.0	4.8	< 0.05	0.39	0.9
Average of A cells	36.2	4.6	< 0.05	0.08	0.7
Average of B cells	35.9	4.4	< 0.05	< 0.03	0.8
Stream	36.9	3.8	< 0.05	< 0.03	0.6

#### 4.1.2 Metals in Surface Water from the A-01 WTS

Copper, Zn, Pb, Fe, and Mn concentrations in surface water samples from influent and effluent collected on 7/16/03, 7/17/03, 7/18/03, 7/21/03, and 7/22/03 are graphed in Figures 5, 6, 7, 8, and 9 respectively. Copper concentrations in the surface water from the splitter box, and from the stream (below the new A-01 outfall) were consistent on each date and well below the NPDES permit limit (20.9 ppb). The lowest Cu concentrations were observed for the water samples from the stream (<5ppb). Zinc concentrations in most water samples were lower than 50 ppb. For Zn, there was less consistency among collecting locations than for Cu; for example, on July 16 and 18 the highest Zn concentrations were for water samples from the stream. For Pb, the same pattern was observed as for Cu; i.e., the lowest Pb concentration was for water samples from the stream, and the data were consistent throughout the trial (Figure 7).

The Fe and Mn show an opposite pattern from Cu, Zn, and Pb; i.e., Fe and Mn concentrations increased as water passed through the wetland (Figure 8 and 9). The average concentration of Mn for freshwater is 8 ppb with a wide range from 0.02 to 130 ppb (Bowen, 1979). The Mn concentrations observed in the stream are similar to the highest concentration of Mn observed in freshwater; i.e., they ranged from 90 to 120 ppb (Figure 9). High Fe and Mn concentrations in water samples from the stream indicate dissolution of the solid mineral phases of these two elements, very likely due to higher content of dissolved organic ligands in the wetlands cells (Figure 3) and reducing conditions of the wetland sediment.

Copper, Zn, Pb, Fe, and Mn concentrations in water samples collected at 11 locations (the old A-01 compliance point, the splitter box, the outflows of the eight wetland treatment cells, and stream on one sampling event (phase IV) are presented in Figures 10, 11, 12, 13, and 14. These data show that Cu, Zn and Pb levels in water are reduced as the water passes through each phase of the treatment system. However, Fe and Mn concentrations increased significantly in the 1A cells and remained at high concentrations throughout the system (Figure 13 and 14). Copper and Pb levels, after passing through the first cell, were typically reduced by 70% and 80%, respectively (Figure 10 and 12). Contaminant removal from water occurred very rapidly in the wetland system, with most removal completed prior to exiting the first cell of the series (see the Zn data, Figure 11).

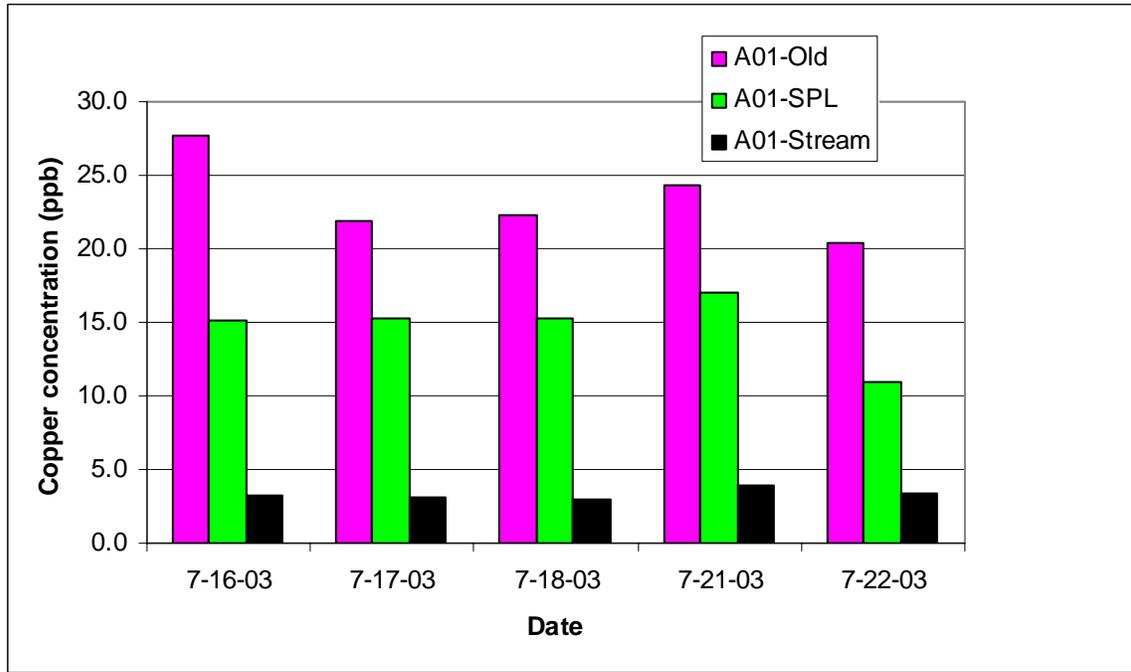


Figure 5. Copper concentration (ppb) in influent and effluent water.

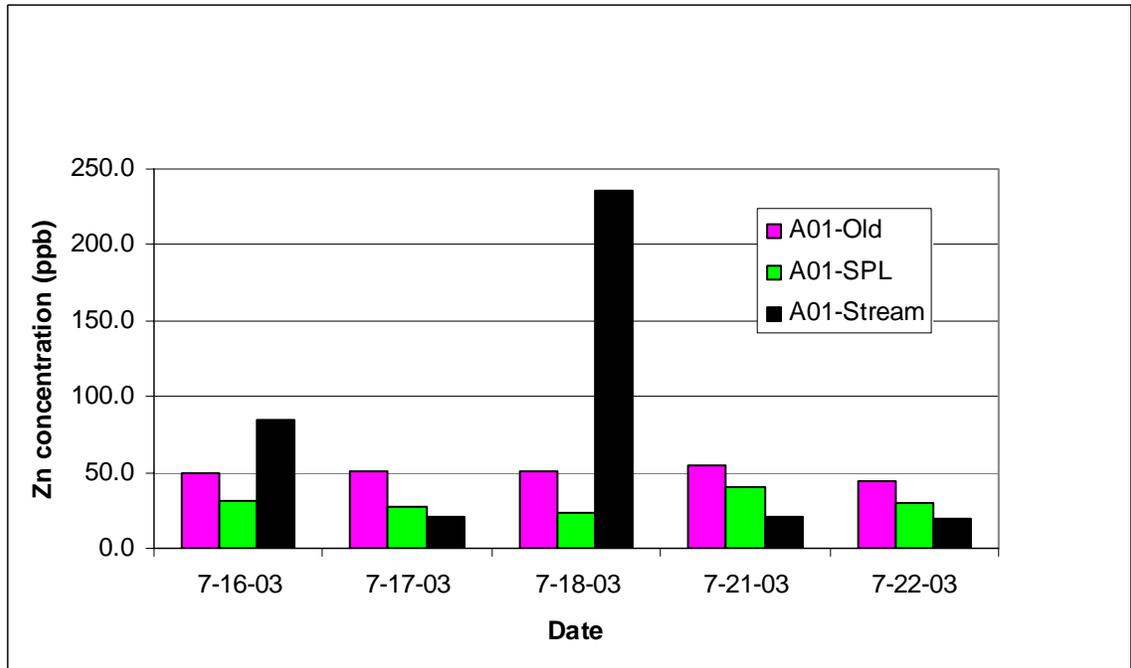


Figure 6. Zinc concentration (ppb) in influent and effluent water.

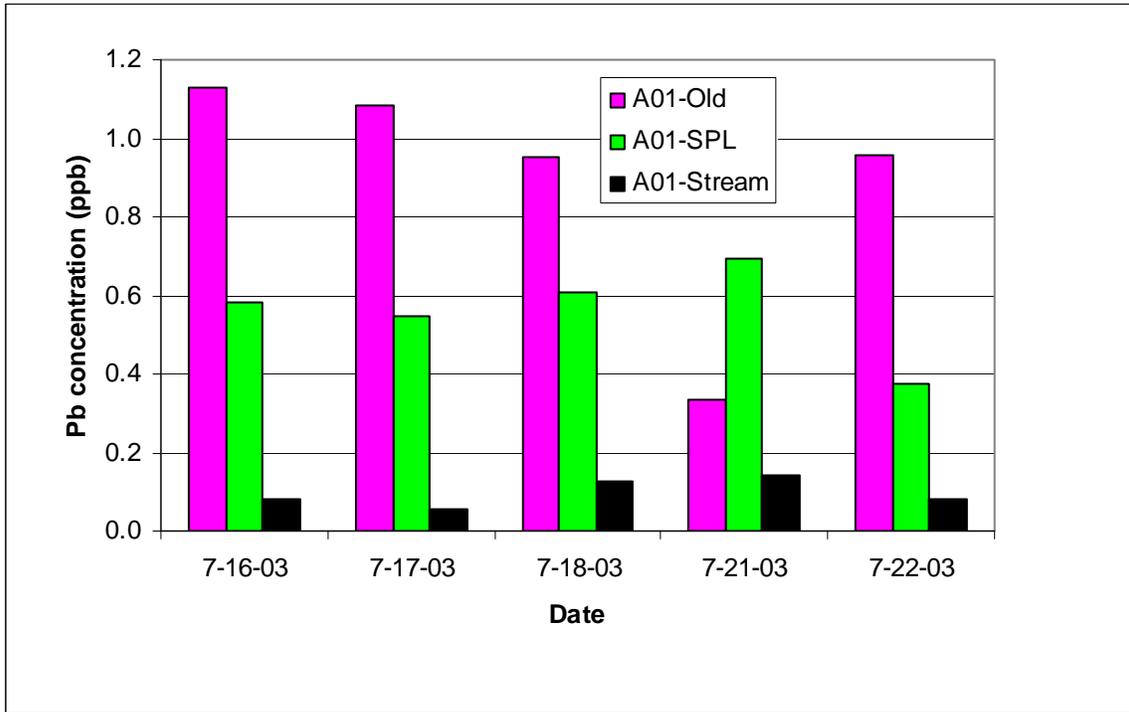


Figure 7. Lead concentration (ppb) in influent and effluent water.

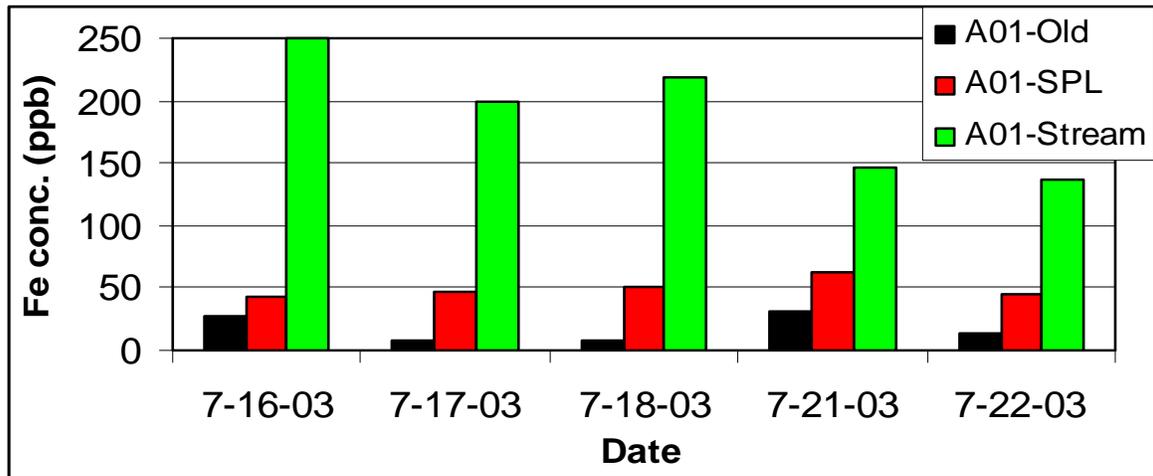


Figure 8. Fe concentration (ppb) in influent and effluent water.

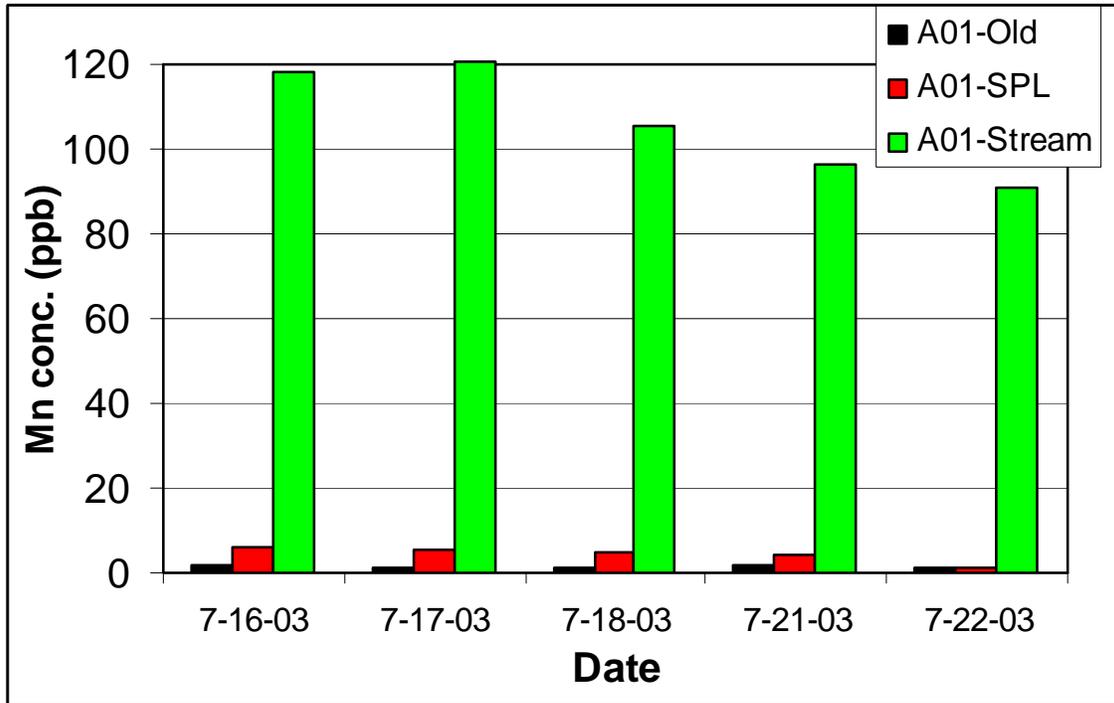


Figure 9. Mn concentration (ppb) in influent and effluent water.

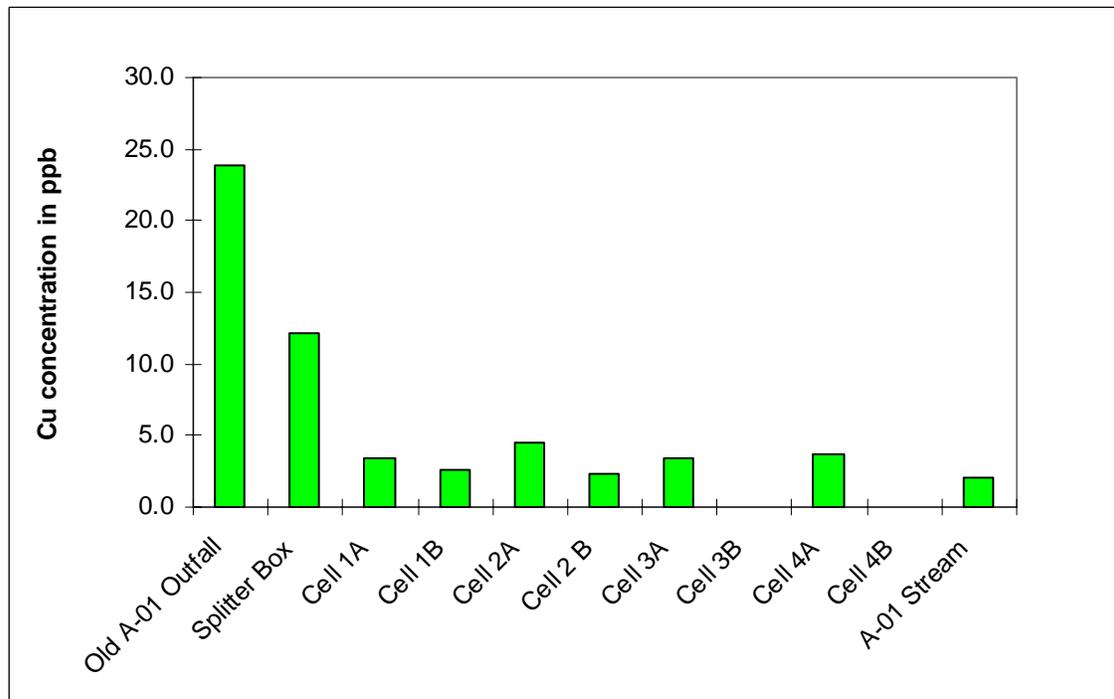


Figure 10. Copper concentration (ppb) in surface water samples.

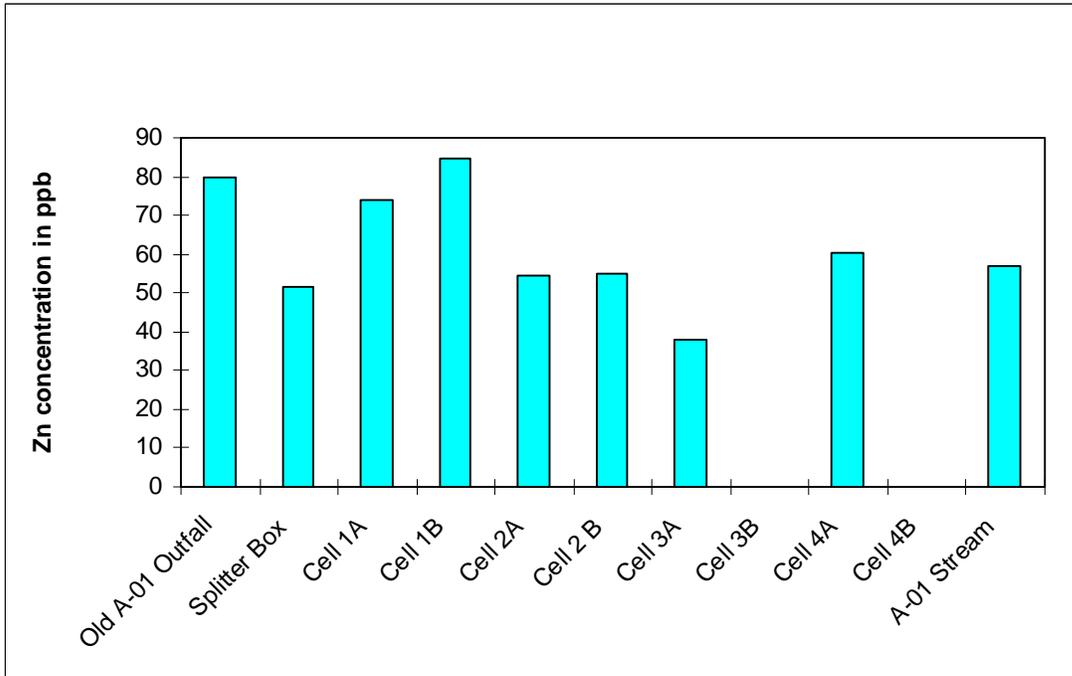


Figure 11. Zinc concentrations (ppb) in surface water samples.

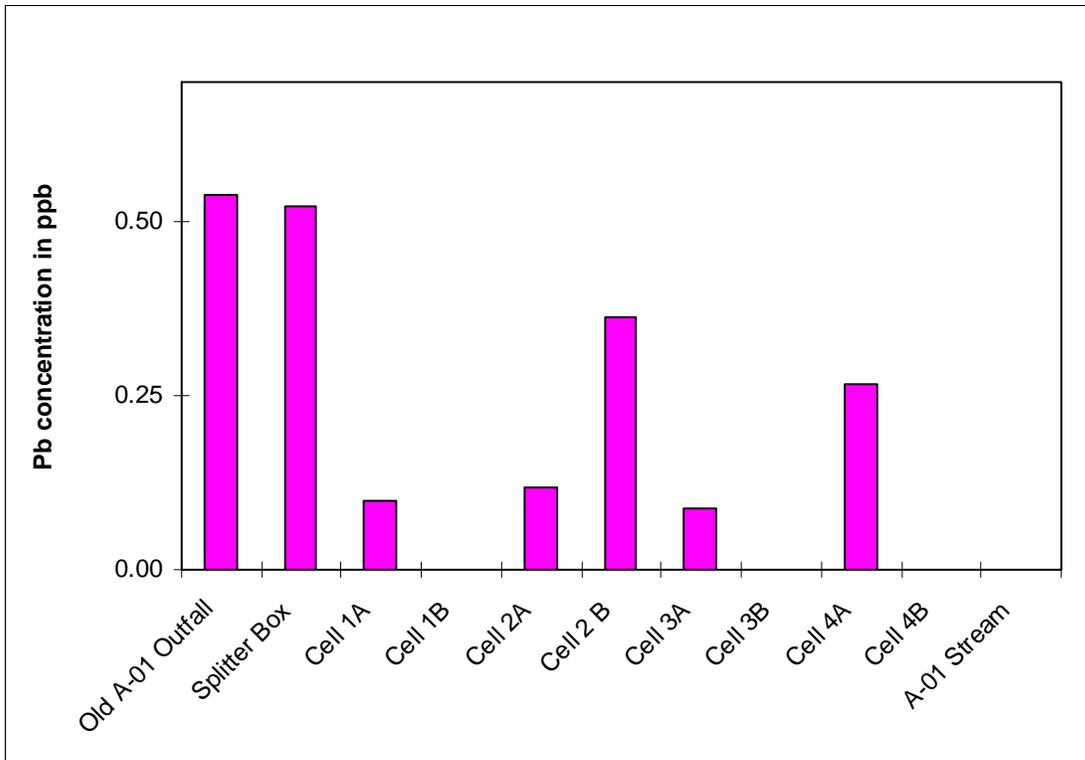


Figure 12. Lead concentration (ppb) in surface water samples.

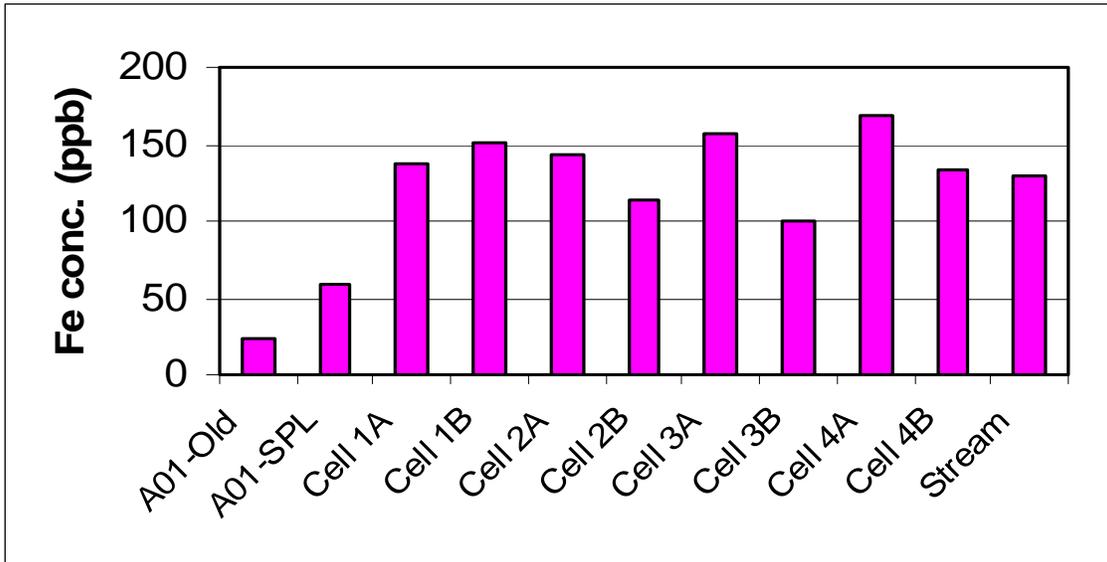


Figure 13. Iron concentration (ppb) in surface water samples.

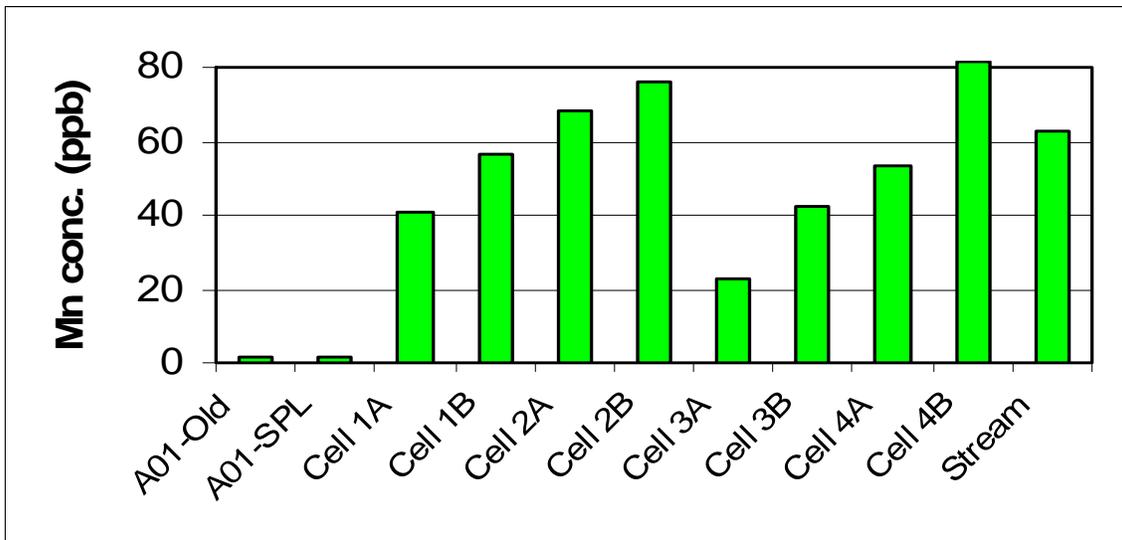


Figure 14. Manganese concentration (ppb) in surface water samples.

## 4.2 RETENTION OF THE CONTAMINANTS IN THE SEDIMENT

### 4.2.1 Total Concentration of Metals in Sediment from the A-01 WTS

The metal concentrations in the sediment samples collected from cell 1A, 3A, 1B, and 3B are presented in Table 2. The highest Cu and Zn concentrations were in cell 1A (10.1 and 14.3 ppm, respectively, for Cu and Zn). Concentrations in the remaining samples from this cell, and from other cells were rather steady, about 4 and 8 ppm, respectively, for Cu and Zn. Lead concentrations in the sediment samples were rather consistent in the tested cells, with an average value of about 4.5 ppm for cell 1A, 3A, and 3B. Iron concentrations were highest in cell 1B (5963 ppm), and Mn concentrations were highest in cell 3A (50.8 ppm). Fe and Mn concentrations were relatively consistent in the other cells, averaging between 2500 and 3500 ppm for Fe and between 25 and 40 ppm for Mn (Table 2 and 4).

**Table 2. Total metal concentrations in the inorganic sediment from the A-01 WTS.**

<b>Sample ID</b>	<b>Al</b>	<b>As</b>	<b>Cr</b>	<b>Cu</b>	<b>Fe</b>	<b>Mn</b>	<b>Ni</b>	<b>Zn</b>	<b>Pb</b>
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
1A1	4433	1.5	13.9	10.1	3054	33.1	3.7	14.3	4.9
1A2	3440	1.2	8.9	3.7	2314	29.5	2.9	7.7	4.7
1A3	4226	1.1	8.7	3.3	2237	27.5	2.9	7.3	4.3
1A4	4972	1.0	7.8	7.7	2264	27.6	3.1	12.2	4.1
<b>Avg</b>	<b>4268</b>	<b>1.2</b>	<b>9.8</b>	<b>6.2</b>	<b>2467</b>	<b>29.4</b>	<b>3.1</b>	<b>10.3</b>	<b>4.5</b>
<b>Stdev</b>	<b>635</b>	<b>0.2</b>	<b>2.7</b>	<b>3.3</b>	<b>393</b>	<b>2.6</b>	<b>0.4</b>	<b>3.4</b>	<b>0.4</b>
1B1	5557	1.1	7.9	3.4	2313	34.9	3.2	7.4	4.4
1B2	9442	9.4	181.7	4.6	16094	24.2	5.2	7.8	12.4
1B3	5165	1.2	9.1	3.9	2520	20.0	3.2	7.9	4.5
1B4	4963	1.3	10.2	3.9	2923	21.4	4.0	8.0	5.5
<b>Avg</b>	<b>6282</b>	<b>3.2</b>	<b>52.2</b>	<b>3.9</b>	<b>5963</b>	<b>25.1</b>	<b>3.9</b>	<b>7.8</b>	<b>6.7</b>
<b>Stdev</b>	<b>2121</b>	<b>4.1</b>	<b>86.3</b>	<b>0.5</b>	<b>6759</b>	<b>6.7</b>	<b>0.9</b>	<b>0.3</b>	<b>3.8</b>
3A1	4590	1.1	8.3	3.9	2360	38.6	3.3	8.6	4.2
3A2	3437	1.0	8.3	3.8	2417	46.8	3.2	7.7	4.1
3A3	5274	1.4	9.4	4.0	2811	67.2	3.6	8.5	5.2
<b>Avg</b>	<b>4434</b>	<b>1.1</b>	<b>8.7</b>	<b>3.9</b>	<b>2530</b>	<b>50.8</b>	<b>3.3</b>	<b>8.3</b>	<b>4.5</b>
<b>Stdev</b>	<b>929</b>	<b>0.2</b>	<b>0.6</b>	<b>0.1</b>	<b>245</b>	<b>14.7</b>	<b>0.2</b>	<b>0.5</b>	<b>0.6</b>
3B1	6298	1.4	10.1	5.0	3468	30.4	5.0	9.9	4.8
3B2	3753	1.5	11.4	4.8	3428	26.7	5.3	10.2	4.9
3B3	4090	1.2	9.3	4.3	3126	23.4	4.2	9.3	4.2
3B4	4589	1.4	10.9	4.9	3489	31.2	6.8	10.2	4.6
<b>Avg</b>	<b>4682</b>	<b>1.3</b>	<b>10.4</b>	<b>4.7</b>	<b>3377</b>	<b>27.9</b>	<b>5.3</b>	<b>9.9</b>	<b>4.6</b>
<b>Stdev</b>	<b>1131</b>	<b>0.1</b>	<b>0.9</b>	<b>0.3</b>	<b>170</b>	<b>3.6</b>	<b>1.1</b>	<b>0.4</b>	<b>0.3</b>

The data for the second set of sediment samples collected from cells 4A and 4B (phase III), are presented in Table 3. The Cu and Zn data were compared to data collected in 2001 (Specht and Nelson, 2002) (Figure 15 and 16). Generally, the Cu concentrations for the samples collected in 2003 were higher in cell 4A than in cell 4B. A similar pattern was observed for Cu concentrations in the samples collected in 2001; however, the values for 2003 are usually higher than 2001 values (Figure 15). This data set indicates that Cu and Zn have accumulated in the inorganic sediment layer over a period of two years.

**Table 3. Total metal concentrations (ppm) in the inorganic sediment from the A-01 WTS (n = 5 for each quarter and n = 20 for each cell).**

<b>Location</b>		<b>Al</b>	<b>Cr</b>	<b>Ni</b>	<b>Cu</b>	<b>Zn</b>	<b>As</b>	<b>Sb</b>	<b>Pb</b>
A01-4AA	Mean	7193	17.02	4.60	5.05	11.29	2.06	0.18	5.41
	St Dev	3556	4.46	0.42	0.80	1.41	0.37	0.01	0.58
A01-4AB	Mean	5272	14.26	5.52	6.64	11.27	2.20	0.21	6.16
	St Dev	835	0.74	0.74	1.48	1.03	0.10	0.01	0.26
A01-4AC	Mean	5655	13.49	5.07	8.57	12.07	1.91	0.26	6.96
	St Dev	1302	1.60	0.39	4.81	2.80	0.13	0.01	0.41
A01-4AD	Mean	5004	12.13	5.04	5.61	9.98	1.70	0.24	6.24
	St Dev	1259	1.67	0.63	1.29	1.14	0.25	0.03	0.51
<b>A01-4A</b>	<b>Mean</b>	<b>5781</b>	<b>14.22</b>	<b>5.06</b>	<b>6.47</b>	<b>11.15</b>	<b>1.97</b>	<b>0.22</b>	<b>6.19</b>
	<b>St Dev</b>	<b>2063</b>	<b>2.96</b>	<b>0.61</b>	<b>2.77</b>	<b>1.77</b>	<b>0.29</b>	<b>0.04</b>	<b>0.70</b>
A01-4BA	Mean	4822	10.06	3.93	4.80	9.12	1.28	0.21	5.19
	St Dev	790	1.10	0.49	1.04	0.63	0.19	0.01	0.54
A01-4BB	Mean	6132	10.92	4.35	4.85	9.76	1.50	0.23	5.88
	St Dev	2799	0.68	0.45	1.01	0.68	0.23	0.03	0.68
A01-4BC	Mean	4706	9.42	3.53	3.64	8.32	1.15	0.20	4.92
	St Dev	644	1.40	0.70	0.69	1.25	0.23	0.02	0.52
A01-4BD	Mean	4757	11.04	4.10	4.42	9.15	1.43	0.23	5.59
	St Dev	490	2.47	0.78	1.40	1.34	0.52	0.04	1.01
<b>A01-4B</b>	<b>Mean</b>	<b>5104</b>	<b>10.36</b>	<b>3.98</b>	<b>4.43</b>	<b>9.09</b>	<b>1.34</b>	<b>0.22</b>	<b>4.94</b>
	<b>St Dev</b>	<b>1514</b>	<b>1.58</b>	<b>0.65</b>	<b>1.09</b>	<b>1.08</b>	<b>0.33</b>	<b>0.03</b>	<b>2.41</b>

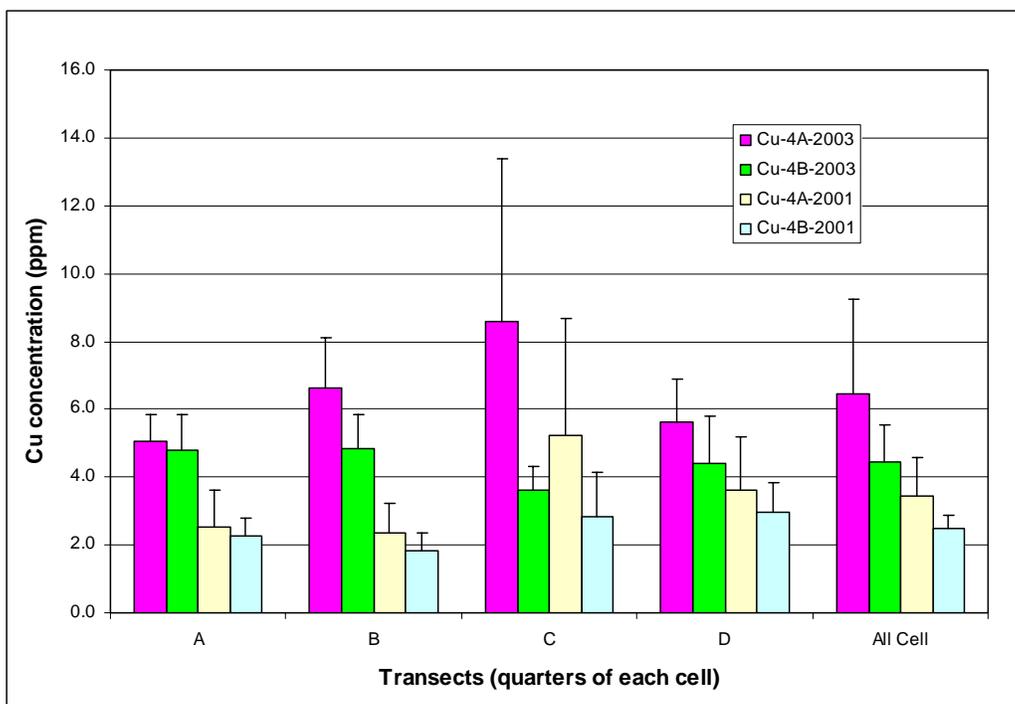


Figure 15. Comparison of Cu concentrations in the sediment samples collected in 2001 (Specht and Nelson, 2002) and 2003.

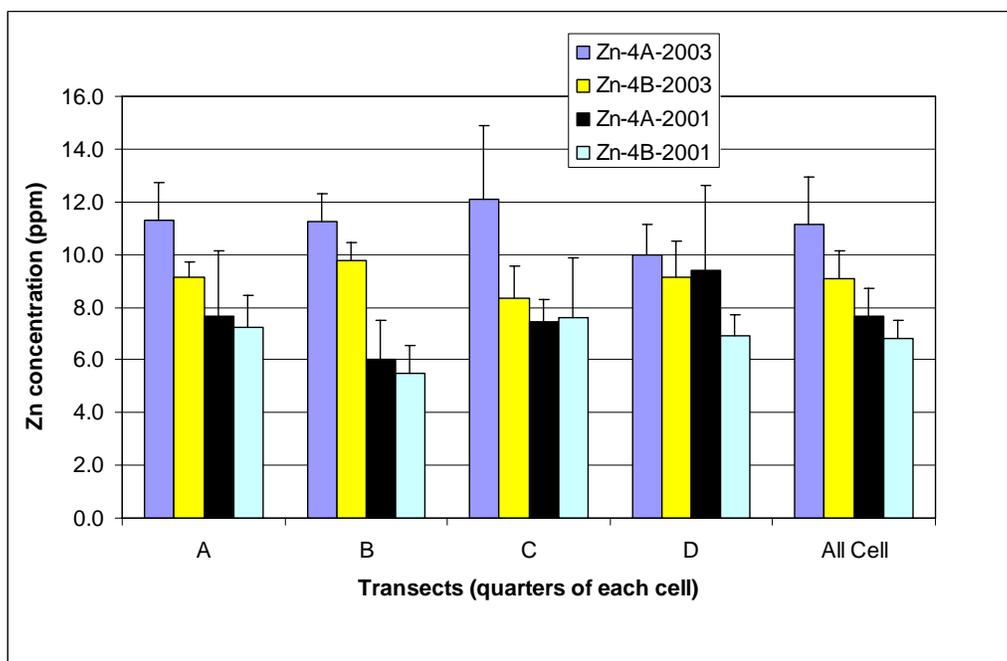


Figure 16. Comparison of Zn concentrations in the sediment samples collected in 2001 (Specht and Nelson, 2002) and 2003.

**Table 4. Total concentration of Fe and Mn in sediment samples from cell 4A and 4B, A, B, C, and D stand for transect. Five sediment samples were collected from each transect (A-D) for a total of 20 samples per cell.**

Location		Mn ppm	Fe ppm
4AA	Mean	39	3381
	St Dev	10	457
4AB	Mean	29	3908
	St Dev	11	122
4AC	Mean	30	4236
	St Dev	12	199
4AD	Mean	37	3700
	St Dev	19	578
<b>4A</b>	<b>Mean</b>	<b>34</b>	<b>3806</b>
	<b>St Dev</b>	<b>13</b>	<b>477</b>
4BA	Mean	35	3054
	St Dev	14	278
4BB	Mean	39	3608
	St Dev	11	222
4BC	Mean	50	2869
	St Dev	12	537
4BD	Mean	37	3292
	St Dev	15	744
<b>4B</b>	<b>Mean</b>	<b>40</b>	<b>3206</b>
	<b>St Dev</b>	<b>13</b>	<b>533</b>

#### 4.2.2 Porewater Chemistry

Porewater from wetlands is a medium that is characterized by sulfidic and low oxygen conditions, therefore, anoxic and sulfidic processes play major roles in this environment. The porewater collected from inorganic sediment from cells 4A and 4B had a pH of about 6 and high electrical conductivity (161 and 80uS/cm, respectively) (Table 5). The porewater sulfate concentration was 100 times higher than in surface water; i.e., 569.5  $\mu\text{M}$  (54.7ppm) in cell 4A and 653  $\mu\text{M}$  (62.7 ppm) in cell 4B (Table 1 and 5, and Figure 4). Similarly, Harmon et al. (2004) found that the sulfate level in porewater was 100 times higher than the sulfate concentration in porewater from control treatments (i.e., where no sulfate addition). Porewater sulfate is of particular importance because of its relationship with sulfate-reducing bacteria and the sediment's ability to sequester metals. High level of sulfate in porewater was not likely a limiting factor for bacterial metabolism. Gilmour and Henry (1991) speculated that the optimal sulfate concentration for mercury methylation by sulfate-reducing bacteria in sediments was in the range of 200-500  $\mu\text{M}$ . Above this concentration, sulfide would inhibit methylation, while at lower sulfate levels, sulfate reduction and hence methylation would be limited by available sulfate.

The predominant factors governing dissolved metal speciation and reactivity in porewaters are metal oxidation state and metal complexes including inorganic and organic ligands. In fact, little is known about metal speciation from experimental research primarily because of the small sample volumes obtained for analysis and because of dramatic changes which can occur on the millimeter vertical scale (Luther, 1995).

Concentrations of Fe in the porewater from the sediment from cell 4A and 4B were high, 6532 and 4633 ppb, respectively (Table 6). Manganese concentrations in the porewater samples were also high, 2070 ppb and 1776 ppb, respectively for cell 4A and 4B. The release of Mn and/or Fe to water depends on the redox chemistry of these two elements as well as the solubility of the solids formed under the redox potential present in the wetland sediment. Mineral  $\text{Fe}(\text{OH})_3$  controls the release of  $\text{Fe}^{3+}$ , while the other two minerals  $\text{FeCO}_3$  and  $\text{Fe}(\text{OH})_2$  control the release of  $\text{Fe}^{2+}$ . Under reducing conditions,  $\text{FeCO}_3$  and  $\text{Fe}(\text{OH})_2$  are stable in the pH range of 7 to approximately 10, as carbonate solid rather than hydroxide solid (Evangelou, 1998). The pH of the porewater was about 6 (Table 5) indicating that  $\text{FeCO}_3$  and  $\text{Fe}(\text{OH})_2$  were dissolved. The stability of Mn species is also Eh and pH dependent (Evangelou, 1998). Under reducing conditions, the solids controlling the release of  $\text{Mn}^{2+}$  are  $\text{MnCO}_3$  and  $\text{Mn}(\text{OH})_2$ , which are stable in the pH range of 7.5 to approximately 11.2. High Mn concentrations could also be related to high concentration of  $\text{Fe}^{2+}$ . Manganese precipitates will return to solution in the presence of ferrous iron ( $\text{Fe}^{2+}$ ) (Stumm and Morgan, 1981). Bacteria play an important role in the dissolution of Mn solid phases (oxides) too, since they accelerate the oxidation of  $\text{Mn}^{2+}$  to  $\text{Mn}^{4+}$ .

**Table 5. Characteristic of porewater from the sediment collected in cells 4A and 4B (the letters A, B, C, and D represent quarters, the letters A and B represent the wetland cells; n = 5 for each quarter, n = 20 for each cell).**

Location		EC uS/cm	pH	Chloride ppm	Bromide ppm	Nitrate ppm	Sulfate ppm
A01-4AA	Mean	130.9	6.3	15.2	BD	0.1	71.6
	St Dev	49.3	0.8	2.9	BD	BD	37.4
A01-4AB	Mean	122.3	6.0	15.8	BD	0.1	61.1
	St Dev	15.8	0.1	10.5	BD	0.0	57.1
A01-4AC	Mean	283.5	6.5	12.1	BD	0.1	34.6
	St Dev	419.7	0.4	1.9	BD	0.0	58.5
A01-4AD	Mean	98.0	6.2	14.8	20.2	0.1	42.8
	St Dev	68.3	0.6	9.4	BD	0.0	52.9
<b>A01-4A</b>	<b>Mean</b>	<b>161.0</b>	<b>6.2</b>	<b>14.5</b>	<b>20.2</b>	<b>0.1</b>	<b>54.7</b>
	<b>St Dev</b>	<b>215.8</b>	<b>0.6</b>	<b>7.0</b>	<b>BD</b>	<b>0.0</b>	<b>50.6</b>
A01-4BA	Mean	62.6	5.7	17.6	BD	0.2	62.5
	St Dev	26.6	0.7	9.4	BD	0.0	49.4
A01-4BB	Mean	109.0	6.3	19.0	BD	0.1	65.9
	St Dev	44.1	0.8	4.6	BD	0.0	55.1
A01-4BC	Mean	87.2	5.7	13.8	BD	BD	43.3
	St Dev	42.5	0.4	2.8	BD	BD	27.1
A01-4BD	Mean	65.0	6.2	15.8	BD	0.4	73.1
	St Dev	42.5	0.4	5.3	BD	0.5	59.1
<b>A01-4B</b>	<b>Mean</b>	<b>80.3</b>	<b>6.0</b>	<b>16.8</b>	<b>BD</b>	<b>0.2</b>	<b>62.7</b>
	<b>St Dev</b>	<b>42.1</b>	<b>0.6</b>	<b>5.9</b>	<b>BD</b>	<b>0.3</b>	<b>47.4</b>

**Table 6. Total concentrations (ppb) of some elements in porewater from the sediment collected in cells 4A and 4B (the letters A, B, C, D represent quarters, the letters A and B represent the wetland cells; n = 5 for each quarter, n = 20 for each cell).**

Location		Mn	Fe	Ni	Cu	Zn	As	Pb
		ppb	ppb	ppb	ppb	ppb	ppb	ppb
A01-4AA	Mean	1362.0	3329.2	3.8	2.5	446.6	6.3	3.0
	St Dev	794.7	2681.4	3.2	1.3	95.3	2.3	2.5
A01-4AB	Mean	2634.0	10193.4	3.4	38.4	296.2	6.2	3.6
	St Dev	1719.4	3180.9	3.9	74.3	51.0	1.1	4.1
A01-4AC	Mean	2019.5	8101.8	15.1	3.9	351.0	3.8	1.4
	St Dev	1664.9	10588.8	24.6	2.7	128.8	0.8	NA
A01-4AD	Mean	2375.7	5589.5	2.3	7.1	244.6	6.0	1.3
	St Dev	2050.4	4289.7	1.0	5.4	111.4	3.6	1.3
<b>A01-4A</b>	<b>Mean</b>	<b>2069.6</b>	<b>6532.5</b>	<b>6.6</b>	<b>12.5</b>	<b>335.3</b>	<b>5.5</b>	<b>2.6</b>
	<b>St Dev</b>	<b>1607.6</b>	<b>6222.9</b>	<b>13.3</b>	<b>35.6</b>	<b>123.5</b>	<b>2.3</b>	<b>2.6</b>
A01-4BA	Mean	1463.7	9271.5	6.9	11.8	60.8	5.5	7.3
	St Dev	1184.9	10268.1	7.6	10.0	21.0	2.4	6.4
A01-4BB	Mean	2027.3	2588.6	4.8	11.1	57.4	2.8	3.9
	St Dev	1374.5	5475.9	4.9	11.2	35.1	1.8	5.9
A01-4BC	Mean	2790.8	3025.9	4.3	5.7	73.1	4.4	2.9
	St Dev	1922.8	4551.3	5.4	3.9	24.8	3.0	4.0
A01-4BD	Mean	861.6	4401.4	2.9	4.8	244.7	6.4	4.3
	St Dev	661.2	3010.8	1.9	4.6	107.4	2.3	5.0
<b>A01-4B</b>	<b>Mean</b>	<b>1775.6</b>	<b>4633.9</b>	<b>4.9</b>	<b>8.6</b>	<b>98.8</b>	<b>4.6</b>	<b>4.8</b>
	<b>St Dev</b>	<b>1487.0</b>	<b>6300.0</b>	<b>5.2</b>	<b>8.2</b>	<b>88.1</b>	<b>2.4</b>	<b>5.1</b>

### 4.2.3 Metal Speciation

Solid phase chemical speciation is critical to understanding and modeling metal-removing systems, because the particular distribution of metal compounds and their interaction with the native matrix under aqueous conditions determines their environmental mobility, bioavailability, and retention. A variety of approaches have been attempted to determine the speciation of metals in solids, including sequential selective chemical extractions (Tessier et al., 1979 and Miller et al., 1986), wave dispersive X-ray microprobe spectroscopy (WD/XMP), and extended X-ray absorption fine structure spectroscopy (EXAFS) (Brown, et al., 1995). The sequential chemical extraction procedure is essentially operational and may give rise to difficulties if this is not kept in mind (Nirel and Morel, 1990). Nevertheless, despite the dangers of uncritical acceptance of results from sequential extractions analysis, the procedure is still widely used because it is a useful first approach for assessing the likelihood of mobilization and retention of metals in soils or sediments.

The main intent of conducting sequential extractions in this study was to determine how strongly metals were bound to the wetland sediment. Early extraction steps (water soluble, exchangeable, acid soluble metal, amorphous oxides, and organic fractions) tend to recover metal fractions that are less strongly bound than the fractions collected in the later extractions steps (crystalline oxides, sulfides, and residue fractions). Therefore, if the removed metals are retained by the wetland sediment, they very likely would be found in the strongly bound fractions. The sequential extraction data for Cu, Zn, and Pb in the sediment samples from phase II are presented in Table 7 and Figure 17. From phase II sampling, four sediment samples were selected for sequential extraction: 1A4, 3A1, 1B2, and 3B2. Unfortunately, percent recovery (the difference between the total amount of metal in soil and sum of metal fractions) was satisfactory only for the sample from 3A1 (more than 90% for Cu and Zn, respectively, and 71% for Pb, Table 7). Therefore, only the results of 3A1 samples will be discussed for phase II. The main focus will be on phase III data, where eight sediment samples were analyzed and percent recovery was satisfactory for all samples.

**Table 7. Concentration of Cu, Zn, and Pb (ppm) in various fractions in the sediment samples.**

Sample ID	Water	Exch.	Acid Soluble	MnO2 Occluded	Organic	Am FeO	Cry. FeO	Residual	Sum of 8 steps	Total digestion	Recovery
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	%
<b>Cu</b>											
1A4	0.071	0.162	1.641	0.890	0.568	0.364	0.507	0.110	4.314	7.700	56
3A1	0.045	0.055	0.252	0.177	0.140	0.108	0.367	2.438	3.582	3.900	92
1B2	0.062	0.106	0.176	0.170	0.109	0.080	0.381	0.056	1.140	4.600	25
3B3	0.067	0.078	0.194	0.102	0.082	0.069	0.389	0.286	1.267	4.300	29
<b>Avg</b>	<b>0.061</b>	<b>0.100</b>	<b>0.566</b>	<b>0.335</b>	<b>0.225</b>	<b>0.155</b>	<b>0.411</b>	<b>0.722</b>	<b>2.576</b>	<b>5.125</b>	<b>51</b>
<b>Stdev</b>	<b>0.012</b>	<b>0.046</b>	<b>0.717</b>	<b>0.372</b>	<b>0.230</b>	<b>0.140</b>	<b>0.065</b>	<b>1.148</b>	<b>1.613</b>	<b>1.740</b>	<b>31</b>
<b>Zn</b>											
1A4	0.129	1.312	2.308	0.572	0.649	0.160	0.105	0.728	5.963	12.200	49
3A1	0.067	0.246	0.457	0.096	0.272	0.058	0.064	6.571	7.831	8.600	91
1B2	0.168	1.340	0.455	0.115	BD	0.052	0.057	1.384	3.569	7.800	46
3B3	0.088	0.327	0.187	0.118	BD	0.021	0.092	2.323	3.156	9.300	34
<b>Avg</b>	<b>0.113</b>	<b>0.806</b>	<b>0.852</b>	<b>0.226</b>	<b>0.460</b>	<b>0.073</b>	<b>0.080</b>	<b>2.751</b>	<b>5.130</b>	<b>9.475</b>	<b>55</b>
<b>Stdev</b>	<b>0.045</b>	<b>0.601</b>	<b>0.979</b>	<b>0.231</b>	<b>0.267</b>	<b>0.061</b>	<b>0.023</b>	<b>2.629</b>	<b>2.185</b>	<b>1.917</b>	<b>25</b>
<b>Pb</b>											
1A4	0.011	0.011	0.719	0.242	0.076	0.031	0.008	0.332	1.430	4.100	35
3A1	0.017	0.103	0.880	0.217	0.081	0.038	0.005	1.737	3.078	4.200	73
1B2	0.063	0.351	0.808	0.205	0.093	0.043	0.006	0.476	2.044	12.400	16
3B3	0.008	0.177	0.480	0.157	0.053	0.027	0.009	0.421	1.332	4.200	32
<b>Avg</b>	<b>0.025</b>	<b>0.161</b>	<b>0.721</b>	<b>0.205</b>	<b>0.076</b>	<b>0.034</b>	<b>0.007</b>	<b>0.742</b>	<b>1.971</b>	<b>6.225</b>	<b>39</b>
<b>Stdev</b>	<b>0.026</b>	<b>0.144</b>	<b>0.174</b>	<b>0.036</b>	<b>0.017</b>	<b>0.007</b>	<b>0.002</b>	<b>0.666</b>	<b>0.802</b>	<b>4.117</b>	<b>24</b>

The sequential extraction of sediment sample 3A1 yielded only a minimal amount of water extracted Cu, Zn, and Pb. The majority of the metals were associated with residual fractions (more than 50% of the total) (Figure 17). The next most abundant fraction was the acid soluble fraction. The extraction in this step aims to solubilize acid volatile sulfides, carbonates, and pH-dependent phases.

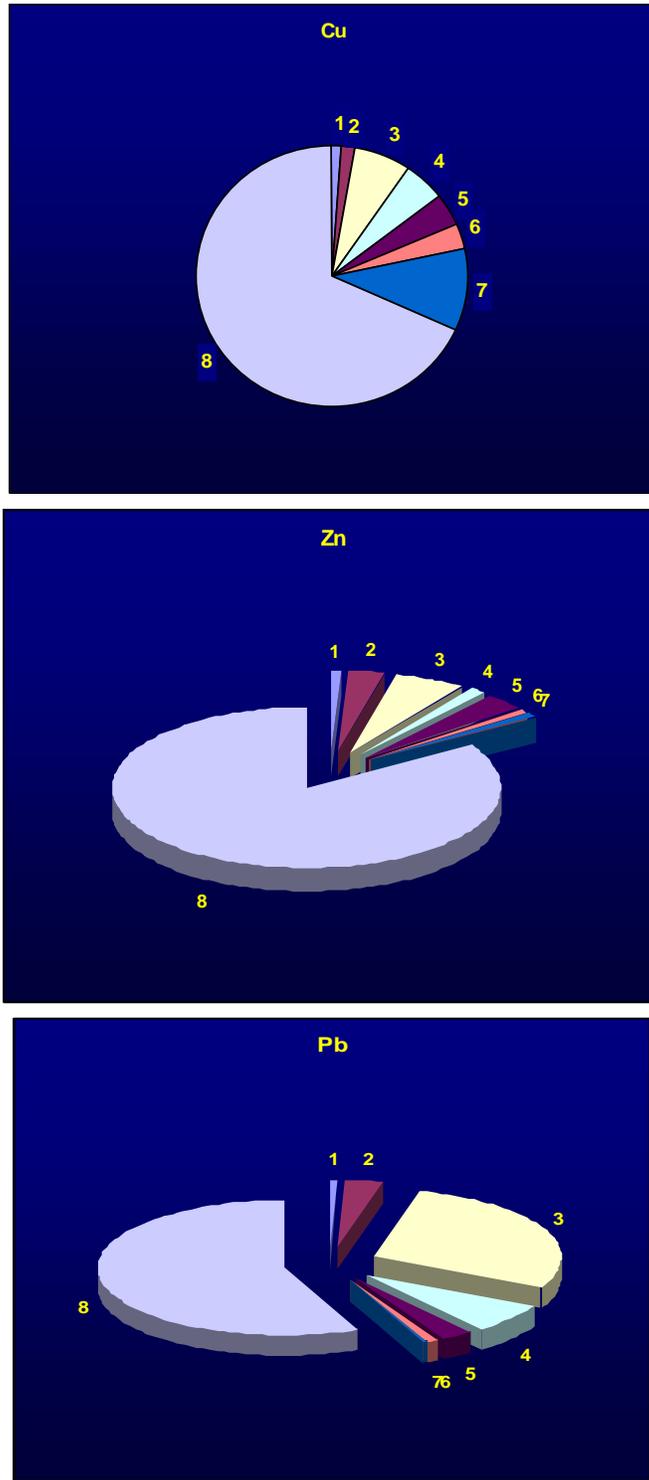


Figure 17. Sequential chemical extraction of Cu, Zn, and Pb in sediment (in %) from 3A1; the sequential extraction steps:1 - water, 2 - exchangeable, 3 – acid soluble, 4 - MnO<sub>2</sub> occluded, 5 – organically bound, 6 – amorphous Fe oxides, 7 – crystalline Fe oxides, 8 – residual.

The sequential extraction data for the phase III sediment samples are presented in Tables 8, 9, 10, 11, and 12 and Figures 18, 19, and 20. The distribution of Cu among the eight fractions was similar for all samples (Table 8). Only about 1% of Cu was measured in the water and exchangeable steps, indicating that under normal conditions (neutral pH and low ionic strength) Cu is not expected to desorb from the sediment (Table 8). In cell 4B, in most cases, less than 10% of the Cu was in the Mn and Fe oxide fractions combined. The situation was generally similar in cell 4A except that the Cu concentration in the amorphous Fe oxide fraction was higher (5.1% compared with 1.9% for cell 4B) (Table 8). The low concentration of Cu in the oxide fractions is expected because, although Fe and Mn are generally excellent scavengers for metals, they become very unstable under the anoxic conditions that exist in this wetland (Tessier et al., 1979). Copper has a high affinity for organic matter. The organic fraction for the samples was less than 5%, very likely due to very low organic matter content (note that the samples represent an inorganic layer only). The acid soluble and residual fractions made up the largest fraction; an average of 10 and 72% respectively for acid soluble and residual fraction for cell 4A. The average residual fraction for Cu in cell 4B was 78%; i.e., even higher than in cell 4A.

**Table 8. Copper (in %) in various sediment phases.**

<b>Samples</b>	<b>Water %</b>	<b>Exch. %</b>	<b>Acid Soluble %</b>	<b>MnO<sub>2</sub> Occluded %</b>	<b>Organic %</b>	<b>Am. FeO %</b>	<b>Cry. FeO %</b>	<b>Residual %</b>
4AA-1	1.0	1.1	12.7	6.5	4.6	3.2	1.8	69.1
4AB-2	0.8	0.9	7.9	5.9	4.7	2.9	2.0	75.0
4AC-3	1.2	0.7	12.4	5.7	4.0	7.7	1.6	66.7
4AD-4	1.2	0.8	4.8	5.4	3.2	6.5	2.0	76.1
<b>Avg 4A</b>	<b>1.0</b>	<b>0.9</b>	<b>9.5</b>	<b>5.9</b>	<b>4.1</b>	<b>5.1</b>	<b>1.9</b>	<b>71.7</b>
<b>Stdev 4A</b>	<b>0.2</b>	<b>0.2</b>	<b>3.8</b>	<b>0.4</b>	<b>0.7</b>	<b>2.4</b>	<b>0.2</b>	<b>4.5</b>
4BA-5	2.2	0.6	4.9	4.0	3.3	2.4	2.4	80.2
4BB-1	0.8	0.8	4.6	5.2	2.4	1.8	1.8	82.8
4BC-2	0.7	0.6	3.2	2.5	1.8	1.7	1.7	87.8
4BD-3	2.9	1.5	13.5	8.6	7.2	1.7	1.7	62.9
<b>Avg 4B</b>	<b>1.6</b>	<b>0.9</b>	<b>6.5</b>	<b>5.1</b>	<b>3.7</b>	<b>1.9</b>	<b>1.9</b>	<b>78.4</b>
<b>Stdev 4B</b>	<b>1.1</b>	<b>0.4</b>	<b>4.7</b>	<b>2.6</b>	<b>2.5</b>	<b>0.4</b>	<b>0.4</b>	<b>10.8</b>
<b>Avg of 4A &amp; 4B</b>	<b>1.3</b>	<b>0.9</b>	<b>8.0</b>	<b>5.5</b>	<b>3.9</b>	<b>3.5</b>	<b>1.9</b>	<b>75.1</b>
<b>Stdev 4A &amp; 4B</b>	<b>0.8</b>	<b>0.3</b>	<b>4.2</b>	<b>1.8</b>	<b>1.7</b>	<b>2.3</b>	<b>0.3</b>	<b>8.5</b>

Table 9. Zinc (in %) in various sediment phases.

Samples	Water %	Exch. %	Acid Soluble %	MnO <sub>2</sub> Occluded %	Organic %	Am FeO %	Cry. FeO %	Residual %
4AA-1	1.5	2.9	7.5	4.1	9.2	0.6	2.8	71.4
4AB-2	2.4	2.8	4.9	0.9	0.4	1.5	2.7	84.3
4AC-3	1.2	1.6	4.6	0.8	0.5	1.7	2.0	87.5
4AD-4	2.8	2.4	2.1	1.6	1.1	0.9	3.1	86.0
<b>Avg 4A</b>	<b>2.0</b>	<b>2.4</b>	<b>4.8</b>	<b>1.9</b>	<b>2.8</b>	<b>1.2</b>	<b>2.7</b>	<b>82.3</b>
<b>Stdev 4A</b>	<b>0.8</b>	<b>0.6</b>	<b>2.2</b>	<b>1.5</b>	<b>4.3</b>	<b>0.5</b>	<b>0.5</b>	<b>7.4</b>
4BA-5	2.9	2.7	1.9	1.2	0.0	0.3	3.2	87.8
4BB-1	1.0	1.5	1.7	1.5	1.5	0.5	2.1	90.2
4BC-2	1.7	1.8	0.6	0.7	0.9	3.2	2.4	88.8
4BD-3	1.7	3.3	2.6	3.4	4.7	1.0	3.1	80.0
<b>Avg 4B</b>	<b>1.8</b>	<b>2.3</b>	<b>1.7</b>	<b>1.7</b>	<b>1.8</b>	<b>1.2</b>	<b>2.7</b>	<b>86.7</b>
<b>Stdev 4B</b>	<b>0.8</b>	<b>0.9</b>	<b>0.9</b>	<b>1.2</b>	<b>2.1</b>	<b>1.3</b>	<b>0.6</b>	<b>4.6</b>
<b>Avg of 4A &amp;4B</b>	<b>1.9</b>	<b>2.4</b>	<b>3.2</b>	<b>1.8</b>	<b>2.3</b>	<b>1.2</b>	<b>2.7</b>	<b>84.5</b>
<b>Stdev 4A &amp; 4B</b>	<b>0.7</b>	<b>0.7</b>	<b>2.2</b>	<b>1.3</b>	<b>3.2</b>	<b>0.9</b>	<b>0.5</b>	<b>6.2</b>

Table 10. Lead (in %) in various sediment phases.

Samples	Water %	Exch. %	Acid Soluble %	MnO <sub>2</sub> Occluded %	Organic %	Am FeO %	Cry. FeO %	Residual %
4AA-1	0.2	0.6	10.9	6.6	2.5	1.6	0.0	77.7
4AB-2	0.2	3.1	14.5	5.1	2.2	1.1	0.0	73.8
4AC-3	0.2	0.2	14.4	4.9	2.1	1.4	0.0	76.8
4AD-4	0.2	8.4	14.8	6.8	2.1	1.2	0.0	66.5
<b>Avg 4A</b>	<b>0.2</b>	<b>3.1</b>	<b>13.6</b>	<b>5.9</b>	<b>2.2</b>	<b>1.3</b>	<b>0.0</b>	<b>73.7</b>
<b>Stdev 4A</b>	<b>0.0</b>	<b>3.8</b>	<b>1.9</b>	<b>1.0</b>	<b>0.2</b>	<b>0.2</b>	<b>0.0</b>	<b>5.1</b>
4BA-5	1.1	7.9	16.2	4.8	2.5	1.1	0.0	66.3
4BB-1	0.1	3.7	10.7	3.2	1.3	0.6	0.0	80.3
4BC-2	0.1	4.0	11.8	3.8	1.6	0.7	0.0	78.1
4BD-3	0.2	7.5	18.8	4.8	1.9	0.8	0.0	65.9
<b>Avg 4B</b>	<b>0.4</b>	<b>5.8</b>	<b>14.4</b>	<b>4.1</b>	<b>1.8</b>	<b>0.8</b>	<b>0.0</b>	<b>72.7</b>
<b>Stdev 4B</b>	<b>0.5</b>	<b>2.2</b>	<b>3.8</b>	<b>0.8</b>	<b>0.5</b>	<b>0.2</b>	<b>0.0</b>	<b>7.6</b>
<b>Avg of 4A &amp;4B</b>	<b>0.3</b>	<b>4.4</b>	<b>14.0</b>	<b>5.0</b>	<b>2.0</b>	<b>1.1</b>	<b>0.0</b>	<b>73.2</b>
<b>Stdev 4A &amp; 4B</b>	<b>0.3</b>	<b>3.2</b>	<b>2.8</b>	<b>1.2</b>	<b>0.4</b>	<b>0.3</b>	<b>0.0</b>	<b>6.0</b>

Zinc concentrations in water and exchangeable fractions were similar throughout 4A and 4B, with an average value of about 2.5% (Table 9). A clear spatial distribution of Zn was observed in cell 4A; i.e., the highest percentage of acid soluble, organic and MnO<sub>2</sub> occluded fractions were found in quarter A which is proximal to the influent (Figure 2). In cell 4B, Zn associated with acid soluble, organic and MnO<sub>2</sub> occluded fractions was distributed evenly throughout all four quarters (Table 9). The distribution of Zn in cells 4A and 4B indicates that the major process that contributed to Zn removal was sorption of Zn on oxide and organic fractions and sulfide binding. Although the sequential extraction procedure used in this study is informative, it is necessary to specifically account for metals bound to sulfides. Because the goal of this wetland is to precipitate metals from the water column and bind them as sulfide minerals in the sediment, the fraction of metals bound to sulfides is important to this research.

**Table 11. Iron (in %) in various sediment phases, potentially mobile fraction (PMF), and recalcitrant factor (RF).**

Samples	Water %	Exch. %	Acid Soluble %	MnO <sub>2</sub> %	Organic %	Am FeO %	Cry. FeO %	Residual %	PMF %	RF %
4AA-1	0.2	42.9	4.2	6.3	9.1	6.1	0.0	31.1	68.8	31.2
4AB-2	0.1	34.7	12.5	6.3	7.7	5.2	0.0	33.5	66.4	33.6
4AC-3	0.2	42.5	5.4	7.3	7.9	5.1	0.0	31.5	68.5	31.5
4AD-4	0.1	49.1	4.3	8.0	7.2	4.7	0.0	26.6	73.4	26.6
<b>Avg 4A</b>	<b>0.2</b>	<b>42.3</b>	<b>6.6</b>	<b>7.0</b>	<b>8.0</b>	<b>5.3</b>	<b>0.0</b>	<b>30.7</b>	<b>69.3</b>	<b>30.7</b>
<b>Stdev 4A</b>	<b>0.0</b>	<b>5.9</b>	<b>3.9</b>	<b>0.8</b>	<b>0.8</b>	<b>0.6</b>	<b>0.0</b>	<b>2.9</b>	<b>2.9</b>	<b>2.9</b>
4BA-5	0.1	53.3	2.3	6.2	7.1	5.6	0.0	25.3	74.7	25.3
4BB-1	0.1	48.6	1.2	4.4	5.3	4.2	0.0	36.2	63.8	36.2
4BC-2	0.0	51.4	3.3	3.9	4.4	2.9	0.0	34.0	66.0	34.0
4BD-3	0.1	59.5	6.7	4.2	3.5	2.3	0.0	23.6	76.4	23.6
<b>Avg 4B</b>	<b>0.1</b>	<b>53.2</b>	<b>3.4</b>	<b>4.7</b>	<b>5.1</b>	<b>3.8</b>	<b>0.0</b>	<b>29.8</b>	<b>70.2</b>	<b>29.8</b>
<b>Stdev 4B</b>	<b>0.0</b>	<b>4.6</b>	<b>2.4</b>	<b>1.1</b>	<b>1.5</b>	<b>1.4</b>	<b>0.0</b>	<b>6.2</b>	<b>6.2</b>	<b>6.2</b>
<b>Avg of all</b>	<b>0.1</b>	<b>47.8</b>	<b>5.0</b>	<b>5.8</b>	<b>6.5</b>	<b>4.5</b>	<b>0.0</b>	<b>30.2</b>	<b>69.7</b>	<b>30.3</b>
<b>Stdev</b>	<b>0.1</b>	<b>7.6</b>	<b>3.5</b>	<b>1.5</b>	<b>1.9</b>	<b>1.3</b>	<b>0.0</b>	<b>4.5</b>	<b>4.5</b>	<b>4.5</b>

**Table 12. Manganese (in %) in various sediment phases, potentially mobile fraction (PMF), and recalcitrant factor (RF).**

Samples	Water %	Exch. %	Acid Soluble %	MnO <sub>2</sub> %	Organic %	Am FeO %	Cry. FeO %	Residual %	PMF %	RF %
4AA-1	1.3	15.6	29.5	2.0	2.6	0.8	0.9	47.1	52.0	48.0
4AB-2	5.2	31.4	1.9	0.9	2.6	0.8	1.1	56.1	42.8	57.2
4AC-3	0.2	3.7	42.2	1.3	4.2	1.3	1.0	46.2	52.8	47.2
4AD-4	10.9	66.3	1.0	0.5	2.3	0.7	0.3	17.9	81.8	18.2
<b>Avg 4A</b>	<b>4.4</b>	<b>29.3</b>	<b>18.7</b>	<b>1.2</b>	<b>2.9</b>	<b>0.9</b>	<b>0.8</b>	<b>41.8</b>	<b>57.3</b>	<b>42.7</b>
<b>Stdev 4A</b>	<b>4.8</b>	<b>27.2</b>	<b>20.5</b>	<b>0.6</b>	<b>0.9</b>	<b>0.3</b>	<b>0.4</b>	<b>16.5</b>	<b>16.9</b>	<b>16.9</b>
4BA-5	5.5	66.8	9.5	0.3	1.7	0.5	0.3	15.4	84.3	15.7
4BB-1	5.1	47.0	1.0	1.2	3.0	1.2	0.5	41.0	58.6	41.4
4BC-2	5.3	36.0	17.7	1.0	2.7	0.8	0.3	36.3	63.4	36.6
4BD-3	4.8	47.0	1.6	0.9	2.2	0.7	0.5	42.4	57.1	42.9
<b>Avg 4B</b>	<b>5.2</b>	<b>49.2</b>	<b>7.5</b>	<b>0.8</b>	<b>2.4</b>	<b>0.8</b>	<b>0.4</b>	<b>33.8</b>	<b>65.9</b>	<b>34.1</b>
<b>Stdev 4B</b>	<b>0.3</b>	<b>12.8</b>	<b>7.8</b>	<b>0.4</b>	<b>0.6</b>	<b>0.3</b>	<b>0.1</b>	<b>12.5</b>	<b>12.6</b>	<b>12.6</b>
<b>Avg of all</b>	<b>4.8</b>	<b>39.2</b>	<b>13.1</b>	<b>1.0</b>	<b>2.7</b>	<b>0.8</b>	<b>0.6</b>	<b>37.8</b>	<b>61.6</b>	<b>38.4</b>
<b>Stdev</b>	<b>3.2</b>	<b>22.4</b>	<b>15.6</b>	<b>0.5</b>	<b>0.8</b>	<b>0.3</b>	<b>0.4</b>	<b>14.2</b>	<b>14.5</b>	<b>14.5</b>

Lead was associated mostly with the acid soluble and residual fractions; about 14% was found in the acid soluble fraction and about 73% in the residual fraction (Table 10). Lead has a stronger affinity for sulfide species than Zn; therefore, the Pb concentration in the acid soluble fraction was higher than the Zn concentration.

The Potentially Mobile Fraction (PMF) is an indicator of the contaminant fraction that has the potential to enter into the mobile aqueous phase under changeable environmental conditions, such as pH, Eh, temperature and others. Metals associated with the PMF are metals found in water, exchangeable, acid soluble, organic, and amorphous Mn and Fe oxide fractions. However, generally only water and exchangeable fractions are very easily mobile and available to plants or organisms. Under reduced wetland conditions, very likely only water, exchangeable and perhaps oxides fractions could be easily remobilized. The PMF was estimated using Equation 1:

$$\text{Potentially Mobile Fraction} = 100 - (F_{\text{Cry. oxides}} + F_{\text{Residual}}) \quad (1)$$

where:

$F_{\text{Cry. oxides}}$  = crystalline Fe oxide sequential extraction fraction (wt-%),  
 and  
 $F_{\text{Residual}}$  = residual sequential extraction fraction (wt-%).

The idea behind this construct is that the entire contaminant pool may not be accessible to the mobile aqueous phase. Some fractions of the contaminant pool are very strongly bound by the sediment, for example, crystalline oxides, sulfides or silicates and aluminosilicates. In this equation, the sulfide fraction is omitted because this fraction was not extracted in the sequential extraction; therefore, PMF values could be overestimated.

Generally, the PMF values for Cu, Zn, and Pb were about 20%. These PMF values for these three elements are rather low for the A-01 WTS sediment indicating that most of the removed metals (Cu, Zn, and Pb) were in very strongly bound phases and not easily extractable.

The PMF values were higher than the pool of Cu, Pb and Zn associated with easily mobile fractions (i.e., water and exchangeable fractions) for these elements (Tables 8, 9, and 10 and Figures 18, 19, and 20) indicating that remobilization and bioavailability of Cu, Pb and Zn were extremely low, 1% to 5%. The distribution of the PMF values for Cu was rather similar for all four transects in cell 4A (Figure 18). Generally, the PMF values were higher in cell 4A than cell 4B (Figure 18). Only for transect D was the PMF value higher for cell 4B, very like due to low recovery from the sequential extraction (Appendix 1, Table 1-1 and 1-2). Spatial distribution of the PMF values for Zn was similar to the Cu distribution in both cells with only one exception, the PMF value for Zn in cell 4A, transect A was highest (Figure 19).

The PMF values for Fe and Mn were the opposite of those shown by Cu Pb, and Zn. The PMF values were very high for both elements; i.e., about 70% or more for Fe (Table 11) and 57 to 66 % for Mn (Table 12). These high values of PMF for Fe and Mn indicate high potential desorption of these elements from the sediment and high solubility.

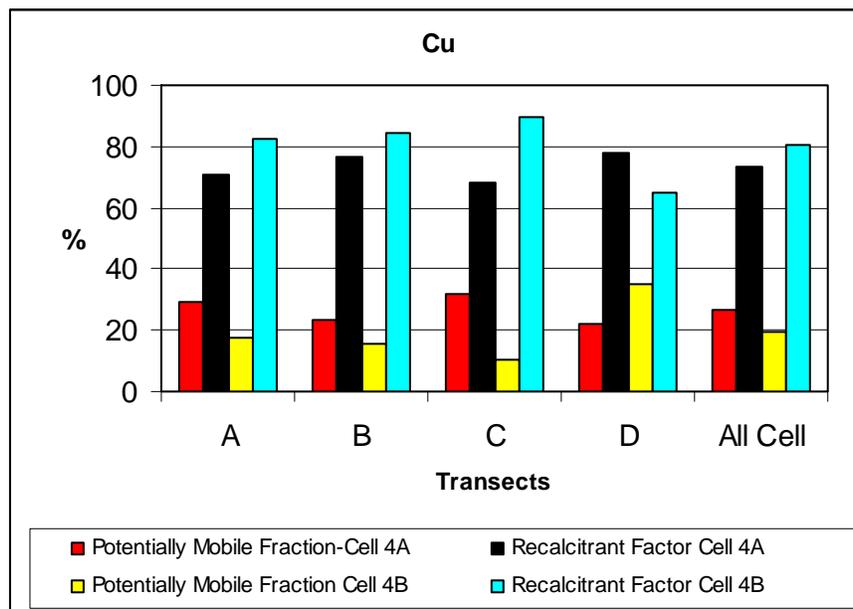
The sequential extraction data were also used to calculate the Recalcitrant Factor (RF). The RF is a ratio of strongly bound fractions to the total concentration of the element in the sediment (or the sum of all fractions). The meaning of the RF is opposite to PMF; i.e., the RF indicates the virtually irreversible retention of metals by solid phase.

For this study the RF was calculated using Equation 2:

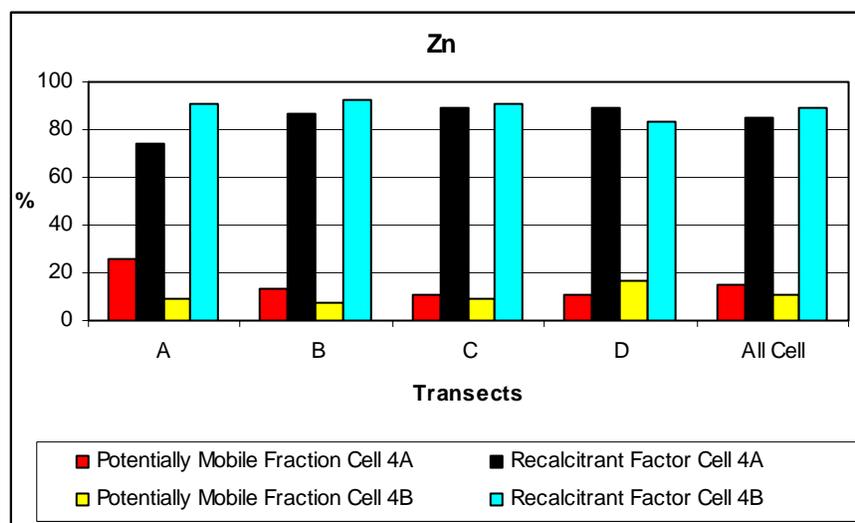
$$\text{recalcitrant factor} = \left[ \frac{C_{\text{cry.oxides}} + C_{\text{residual}}}{C_{\text{exch}} + C_{\text{AS}} + C_{\text{org}} + C_{\text{oxides}} + C_{\text{residual}}} \right] \times 100 \quad (2)$$

where: *C* represents concentration, and the subscripts *crystalline oxides* and *residual*, represent the two final fractions of the sequential extractions. The subscripts *exch*, *AS*, *org*, and *oxides* stand for water soluble and exchangeable pull of metals, acid soluble metals, organically bound metals and bound to amorphous and crystalline. This construct provides an estimate of the percentage of a contaminant in the sediment that was resistant to remobilization; i.e., retention of contaminants in wetland sediments.

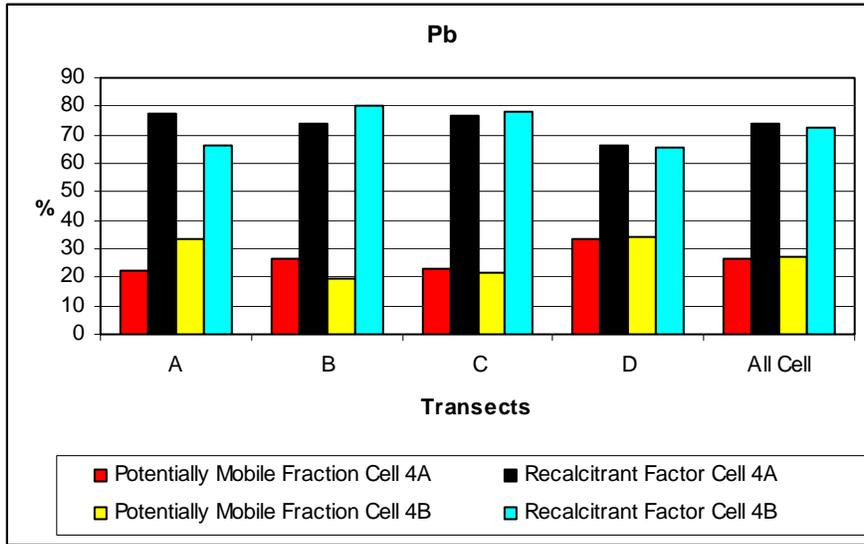
The RF values are about 80% for Cu, Zn and Pb in cells 4A and 4B, indicating high retention of these contaminants in the sediment (Figures 18, 19, and 20). The RF values for the Fe and Mn in cell 4A and 4B were much lower than for Cu, Zn, and Pb. They ranged from 30 to above 40, respectively, for Fe and Mn (Table 11 and 12).



**Figure 18. Potentially mobile fraction (PMF; in %) and Recalcitrant factor (RF; in %) for Cu in sediment samples from cell 4A and 4B.**



**Figure 19. Potentially mobile fraction (PMF; in %) and Recalcitrant Factor (RF; in %) for Zn in sediment samples from cell 4A and 4B.**



**Figure 20. Potentially mobile fraction (PMF; in %) and Recalcitrant Factor (RF; in %) for Pb in sediment samples from cell 4A and 4B.**

## 5.0 SUMMARY

Constructed wetlands have the ability to remove pollutants from water that is directed through them and retain them in sediment. The A-01 wetland treatment system (WTS) was designed to remove metals (primarily copper) from the A-01 effluent at the Savannah River Site, Aiken, SC. The A-01 effluent flows from a retention basin to a splitter box, where it is distributed to the four A-cells. The effluent flows through the A-cells into the B-cells, through the B-cells to the wetland outfall (a new A-01 outfall), and into Tim's Branch. Routine monitoring samples have been collected at the compliance point for monthly reporting since the treatment system began receiving A-01 effluent in July 2000.

Additionally, water and sediment samples were collected from numerous locations from the inflow to the system through the discharge to the receiving stream. The main purpose of research conducted during 2003 was to evaluate 1) the ability of the A-01 wetland treatment system to remediate waste water, 2) retention of the removed contaminants in wetland sediment, and 3) the potential remobilization of these contaminants from the sediment into the water column.

The A-01 WTS generally operates at circumneutral pH. Average dissolved organic carbon (DOC) concentrations in surface water were 7.8 ppm and 10.1 ppm for cells A and B, respectively. The lowest DOC concentrations were observed at the old A-01 outfall and the splitter box due to the small amount of organic detrital materials in this part of the system. Sulfate concentrations were steady throughout the entire system (from 0.6 to 0.9 ppm or 5.73 to 8.96  $\mu\text{M}$ ) and could be effective in removing metals from the water column. Copper, Zn, and Pb concentrations in water were reduced as the water passed through each phase of the treatment system. Copper and Pb levels were typically reduced by 70% and 80%, respectively, after passing through the first cell. The removal of Cu, Zn, and Pb from water occurs very rapidly in the wetland system, with most removal already completed prior to exiting the first cell of the series. However, Fe and Mn showed an opposite pattern: the lowest concentrations of Fe and Mn were observed in the old A-01 outfall and the highest concentrations in the stream (~250 ppb and 120 ppb, respectively, for Fe and Mn). High Fe and Mn concentrations in the stream water indicate dissolution of the solid mineral phases of these two elements, which very likely was due to higher content of dissolved organic carbon and reducing conditions in the wetland cells.

Generally, the highest concentration of Cu and Zn were found in the sediment from the first cells of the A-01 WTS. These results suggest that the most of the Cu and Zn present in the A-01 effluent is being bound to the sediment quickly as the effluent flows into the first cell. Retention of metals by the wetland sediment was evaluated by comparison of two data sets from 2001 and 2003. The spatial distribution of metals in the sediment was similar in both data sets; however, the metal concentrations were higher in 2003 sediment samples than in 2001 sediment samples.

Sequential extraction data were used to evaluate remobilization and retention of Cu, Pb, Zn, Mn, and Fe in the wetland sediment from the A-01 WTS. Remobilization of metals was determined by the Potentially Mobile Fraction (PMF) and metal retention by the Recalcitrant Factor (RF). PMF is an indicator of the contaminant fraction that has the potential to enter into the mobile aqueous phase under changeable environmental conditions, such as pH, Eh, temperature, and others. Metals associated with the PMF are metals found in water, exchangeable, acid soluble, organic, and amorphous Mn and Fe oxide fractions. Generally, the PMF values for Cu, Zn and Pb were about 20%. The low PMF values for Cu, Zn, and Pb in the A-01 WTS sediment indicate that most of the removed metals were in very strongly bound phases and not easily extractable. The PMF values for Fe and Mn show an opposite trend: for both elements the PMF values were very high; i.e., about 70% or more for Fe and 57 to 66 % for Mn. High PMF values for Fe and Mn indicate high desorption of these elements from the sediment and high solubility of their solid phases.

The RF is a ratio of strongly bound fractions to the total concentration of elements in sediment (or the sum of all fractions). The meaning of the RF is opposite to PMF; i.e., the RF indicates the virtually irreversible retention of metals by the solid phase. This construct provides an estimate of the percentage of a contaminant resistant to remobilization that is retained in the contaminated sediment. The RF values were about 80% for Cu, Zn and Pb, indicating high retention of these elements in the sediment. The RF values for Fe and Mn ranged from 30 to above 40 which was much lower than for Cu, Zn, and Pb.

The A-01 WTS removes metals from the effluent to concentrations that are below regulatory limits. However, it is important to continue research on contaminant retention, remobilization and bioavailability because the biogeochemical complexity of the system raises the possibility that some contaminants could be remobilized. As the treatment system matures, its ability to remove metals from the A-01 effluent is expected to increase due to organic matter produced by the wetland vegetation. Therefore, future research should also focus on the evaluation of metal binding by organic matter in the floc and organic layer.

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## 7.0 APPENDICES

## Appendix 1 Additional Data

Table 1-1. Concentration of Fe (ppm) in various fractions; the sediment samples from phase II, middle layer.

Samples	Water ppm	Exch. ppm	Acid Soluble ppm	MnO <sub>2</sub> ppm	Organic ppm	Am FeO ppm	Cry. FeO ppm	Residual ppm	Sum of 8 Steps ppm	Total Digestion ppm	Recovery %
4AA-1	3.4	796.0	78.1	116.5	168.4	113.9	0.5	577.6	1854.4	4166.8	44.5
4AB-2	3.1	791.5	284.5	144.2	175.7	117.7	0.5	765.6	2282.9	3815.1	59.8
4AC-3	3.8	835.1	105.4	144.2	155.9	100.4	0.5	617.7	1962.9	3991.0	49.2
4AD-4	2.0	906.4	80.2	148.3	133.2	86.2	0.4	490.8	1847.5	2764.3	66.8
<b>Avg 4A</b>	<b>3.1</b>	<b>832.3</b>	<b>137.1</b>	<b>138.3</b>	<b>158.3</b>	<b>104.5</b>	<b>0.5</b>	<b>612.9</b>	<b>1986.9</b>	<b>3684.3</b>	<b>55.1</b>
<b>Stdev 4A</b>	<b>0.8</b>	<b>53.2</b>	<b>99.1</b>	<b>14.7</b>	<b>18.6</b>	<b>14.3</b>	<b>0.1</b>	<b>114.7</b>	<b>204.3</b>	<b>629.9</b>	<b>10.1</b>
4BA-5	1.9	1103.1	48.3	128.8	147.6	115.2	0.5	523.9	2069.4	2595.8	79.7
4BB-1	1.7	1200.2	29.8	108.8	130.5	103.6	0.6	894.3	2469.4	3512.8	70.3
4BC-2	1.4	1481.7	93.7	111.5	128.1	84.7	0.5	978.3	2880.0	3131.4	92.0
4BD-3	2.2	1683.4	189.5	119.0	100.3	65.0	0.4	668.2	2827.9	4430.9	63.8
<b>Avg 4B</b>	<b>1.8</b>	<b>1367.1</b>	<b>90.3</b>	<b>117.0</b>	<b>126.6</b>	<b>92.1</b>	<b>0.5</b>	<b>766.2</b>	<b>2561.7</b>	<b>3417.7</b>	<b>76.5</b>
<b>Stdev 4B</b>	<b>0.3</b>	<b>265.0</b>	<b>71.3</b>	<b>9.0</b>	<b>19.6</b>	<b>22.0</b>	<b>0.1</b>	<b>207.9</b>	<b>375.5</b>	<b>773.1</b>	<b>12.2</b>
<b>Avg of all</b>	<b>2.4</b>	<b>1099.7</b>	<b>113.7</b>	<b>127.7</b>	<b>142.5</b>	<b>98.3</b>	<b>0.5</b>	<b>689.5</b>	<b>2274.3</b>	<b>3551.0</b>	<b>65.8</b>
<b>Stdev</b>	<b>0.9</b>	<b>336.2</b>	<b>83.7</b>	<b>16.0</b>	<b>24.5</b>	<b>18.4</b>	<b>0.1</b>	<b>175.7</b>	<b>415.6</b>	<b>668.2</b>	<b>15.4</b>

**Table 1-2 Concentration of Mn (ppm) in various fractions; the sediment samples from phase II, middle layer.**

Samples	Water ppm	Exch. ppm	Acid Soluble ppm	MnO <sub>2</sub> ppm	Organic ppm	Am FeO ppm	Cry. FeO ppm	Residual ppm	Sum of 8 Steps ppm	Total Digestion ppm	Recovery %
4AA-1	0.4	4.8	9.0	0.6	0.8	0.3	0.3	14.4	30.5	54.9	55.6
4AB-2	1.4	8.6	0.5	0.2	0.7	0.2	0.3	15.3	27.4	21.1	129.8
4AC-3	0.0	1.0	11.7	0.4	1.2	0.4	0.3	12.8	27.8	28.7	96.9
4AD-4	7.2	43.5	0.7	0.3	1.5	0.4	0.2	11.8	65.6	50.2	130.8
<b>Avg 4A</b>	<b>2.3</b>	<b>14.5</b>	<b>5.5</b>	<b>0.4</b>	<b>1.1</b>	<b>0.3</b>	<b>0.3</b>	<b>13.6</b>	<b>37.8</b>	<b>38.7</b>	<b>103.3</b>
<b>Stdev 4A</b>	<b>3.3</b>	<b>19.6</b>	<b>5.8</b>	<b>0.2</b>	<b>0.4</b>	<b>0.1</b>	<b>0.1</b>	<b>1.6</b>	<b>18.6</b>	<b>16.4</b>	<b>35.5</b>
4BA-5	5.2	63.2	9.0	0.3	1.6	0.5	0.3	14.6	94.7	54.3	174.5
4BB-1	2.7	24.8	0.5	0.6	1.6	0.6	0.2	21.6	52.7	33.6	157.0
4BC-2	3.5	23.9	11.7	0.7	1.8	0.5	0.2	24.1	66.4	55.8	118.8
4BD-3	1.9	18.9	0.7	0.3	0.9	0.3	0.2	17.1	40.2	24.4	165.2
<b>Avg 4B</b>	<b>3.3</b>	<b>32.7</b>	<b>5.5</b>	<b>0.5</b>	<b>1.5</b>	<b>0.5</b>	<b>0.2</b>	<b>19.3</b>	<b>63.5</b>	<b>42.0</b>	<b>153.9</b>
<b>Stdev 4B</b>	<b>1.4</b>	<b>20.5</b>	<b>5.8</b>	<b>0.2</b>	<b>0.4</b>	<b>0.1</b>	<b>0.0</b>	<b>4.3</b>	<b>23.4</b>	<b>15.5</b>	<b>24.4</b>
<b>Avg of 4A &amp;4B</b>	2.8	23.6	5.5	0.4	1.3	0.4	0.2	16.5	50.7	40.4	128.6
<b>Stdev 4A &amp; 4B</b>	2.4	21.0	5.3	0.2	0.4	0.1	0.0	4.3	23.9	14.9	39.1

**Appendix 2.**  
**The Original Report from Dr. John Seaman,**  
**Savannah River Ecology Laboratory**

**1.0 Introduction**

The A01 constructed wetland is a passive treatment system designed to remove metals from wastewater and storm water prior to discharge into a tributary of Tim's Branch. The wetland was constructed during the summer of 2000 and consists of eight one-acre cells containing *Scirpus californicus* (giant bulrush). Each cell consists of a hydro soil base amended with organic matter (primarily wood chips), fertilizer, and gypsum. The wetland began receiving effluent in July 2000.

Influent to the wetland originates at the Old A-01 outfall and flows to a storm water retention basin. It discharges from the basin via a pipe to a rip-rap channel and flows to a splitter box where it is directed to one of four pairs of treatment cells. Pretreated water enters the "A" cell of each treatment cell pair, flows across the cell, and discharges into the "B" cell. Effluent from the B cells coalesces in an underground pipe which flows to a new A-01 outfall, into the Tim's Branch system. Approximate retention time in each cell is 24 hours.

Primary effluents to the A-01 outfall are storm water, non-contact cooling water, steam condensate, laboratory waste, cooling tower overflow, well flush water, steam cleaning rack wastewater, and air stripper effluent generation from the operation of the A-01 outfall. Storm water runoff includes water from several sprinkler alarm valve houses, storage areas, various office buildings, vent areas, and labs.

**2.0 Materials and Methods***Sampling*

Samples were collected in four phases starting in July and continuing until August 2003. Two phases of water samples were collected (phases I and IV), as well as two phases of intact wetland cell cores, including surface water and soil (phases II and III). Each phase has differing analytes of interest.

*Chemical Analyses*

Upon arrival at the lab, all samples were cataloged and refrigerated. Aliquots from the original sample were taken, for metal analysis, pH, EC, dissolved organic carbon (DOC), and anion analyses (depending on phase), and preserved as appropriate. All samples were maintained at 4°C until analysis. Metal analysis was performed using an ICP-MS (Perkin Elmer), according to EPA Method 6020. Anions were determined using ion chromatography (Dionex) according to EPA Method 300.1. Dissolved organic carbon was determined using a TOC-5000A (Shimadzu).

## 2.1 Phase I Samples

For Phase I sampling, five rounds of surface water samples were collected from three locations. Grab samples were collected on 7/16/03, 7/17/03, 7/18/03, 7/21/03, and 7/22/03 at the compliance point of the old A-01 outfall, the splitter box, and just below the new A-01 outfall, for a total of 15 samples. These locations were selected to evaluate the removal efficiency of the retention basin and the treatment cells.

Prior to analysis, surface water samples were split into two sub-samples. One sub-sample was filtered through a 0.22  $\mu\text{m}$  nylon syringe filter; the second sample was not filtered. Both were acidified to a  $\text{pH} < 2$  and were analyzed for metals.

## 2.2 Phase II Samples

Samples for Phase II were collected in cells 1A, 1B, 3A and 3B, using Plexiglas core tubes with plastic caps on each end. Fifteen core tubes were received on 8/06/03; samples were refrigerated and stored upright/vertically. On 8/08/03, samples were grouped based on cell location. For each core, the top layer, or the organic layer, was identified and marked. A second layer was marked approximately 5 cm below the organic layer; this is designated as middle layer. The bottom layer is the remaining sediment below middle layer. The thickness of each layer was recorded and the marked cores were photographed.

Surface water was siphoned off the top of each core and water was filtered using a 0.22  $\mu\text{m}$  nylon syringe filter. An aliquot of each surface water sample was acidified to a  $\text{pH} < 2$  for metals analysis. Top, middle and bottom layers were separated when removing from tube, placed in pre-weighed and labeled plastic bags and weighed. Excess debris (organic detritus, fertilizer pellets, and rocks) was removed from middle and bottom layers. Percent moisture was determined for both middle and bottom layers. Middle sediment samples were acid digested according to EPA 3052; digested sediment was analyzed for metals.

An eight-step sequential extraction was performed using one sediment sample from each cell, using the middle layer. Approximately 1 g of soil was added to an Oak-Ridge tube for extraction. Each step used 30 mL of reagent (with the exception of crystalline Fe oxide extraction which used 15 mL); between each step the weight of total reagent used was recorded for more precise calculations. Water soluble metals were extracted for 16 hours using nanopure water, followed by a 16 hour extraction of exchangeable metals using 0.50 M  $\text{Ca}(\text{NO}_3)_2$ . Acid soluble metals were extracted for 8 hours using 0.44 M acetic acid/ 0.1 M  $\text{Ca}(\text{NO}_3)_2$ .  $\text{MnO}_2$  occluded metals were extracted for 30 minutes with 0.01M  $\text{NH}_2\text{OH}\cdot\text{HCl}$ / 0.1 M nitric acid. Organically bound metals were extracted for 24 hours with 0.1 M  $\text{Na}_4\text{P}_2\text{O}_7$ . Two types of Fe oxides were extracted: amorphous, using 0.175 M ammonium oxalate/ 0.1 M oxalic acid for four hours, and crystalline, using 0.175 M sodium citrate/ 0.05 M citric acid/  $\text{Na}_2\text{S}_2\text{O}_4$  for 30 minutes. After these extractions had been performed, the leftover soil pellets were air dried and acid digested according to EPA 3052. The extracts from each step of the sequential extraction and digested soil pellets were used for metals analysis.

### **2.3 Phase III**

Cells 4A and 4B were subdivided into four equal sections for collection. Five cores were collected, as described above, from each section. Samples were assigned a letter designating sampling location: "A" locations were proximal to influent progressing to "D" locations, which were distal, or at discharge point of treatment cell. Forty cores were received 8/18/03 and 8/19/03. Cores were identified, marked, and measured as described above.

Surface water was siphoned off the top of each core. An aliquot was filtered through a 0.22  $\mu\text{m}$  nylon syringe filter, and acidified to a  $\text{pH} < 2$  for metals analysis. The remaining unfiltered surface water was used for pH and anion analysis. Top, middle and bottom layers were separated and cleaned of debris as described above. Percent moisture was determined for middle layers. Pore water was extracted from the middle layers using Vectaspin tubes (10  $\mu\text{m}$ ). After separating the pore water at 10  $\mu\text{m}$ , it was further filtered using a 0.22  $\mu\text{m}$  nylon syringe filter. The pH and EC was immediately measured after extraction. An aliquot of the pore water was acidified to a  $\text{pH} < 2$  for metals analysis. The remaining pore water sample was used for anion analysis. Middle and top layer sediment samples were acid digested according to EPA 3052 and analyzed for metals. A sequential extraction, as described above, was performed for a sediment sample in each section of both cells.

### **2.4 Phase IV Samples**

Eleven surface water samples were collected on 8/28/03 from the outflow of each cell, both the new and old A-01 outfalls and the splitter box.

Immediately after receiving samples, pH and EC were measured. An aliquot was removed and filtered using a 0.22  $\mu\text{m}$  nylon syringe filter. The filtered sample was used for dissolved organic carbon and anion analyses. The remaining solution was acidified to a  $\text{pH} < 2$  and used for metals analysis.

## **3.0 RESULTS**

### **3.1 Phase I Samples**

Metal analysis was performed on phase I water samples, both filtered and unfiltered, from the old A-01 outfall, the splitter box, and the new A-01 outfall; these results are located in Table I-1 and I-2.

### **3.2 Phase II Samples**

Phase II samples had three phases of analysis: surface water, soil digestion of middle layer, and sequential extraction of middle soil layer. Surface water metal analysis for each individual soil core is included in Table II-1. Metal results from the middle layer sediment digests are included in Table II-2. Middle layer sequential extraction metal results are included in Table II-3.

### **3.3 Phase III Samples**

Phase III analysis consist of surface water, pore water, and soil digestion and sequential extraction from middle soil layer. Surface water pH and anion analyses are included in Table III-1. Surface water metal analysis is seen in Table III-2. Pore water was extracted from the middle layer of sediment; pH, EC, and anion results are included in Table III-3. Metal results for pore water is included in Table III-4. Middle layer sediment digest results are included in Table III-5; sequential extraction metal results are seen in Table III-6. Top layer sediment digest results are included in Table III-7.

### **3.4 Phase IV Samples**

Phase IV samples were analyzed to determine metal, DOC and anion concentrations. The pH, EC, DOC, and anion values for phase IV samples are included in Table IV-1. Metal results are summarized in Table IV-2.

Table I-1. Phase I Filtered Water Sample Metal Summary\*

Sample ID	Date	Al	Cr	Ni	Cu	Zn	Se	As	Ag	Sb	Pb	Fe	Mn	Hg
A01-CLD-001	7-16-03	21.505	0.598	0.358	27.755	49.965	0.162	0.556	5.169	0.204	1.128	26.975	1.786	0.055
A01-SPL-001	7-16-03	25.755	0.709	0.317	15.135	30.706	0.185	0.770	0.618	0.178	0.583	43.407	6.042	<0.05
A01-NEW-001	7-16-03	9.744	0.626	0.300	3.234	84.373	0.094	0.721	<0.096	0.092	0.081	249.838	118.118	<0.05
A01-CLD-001	7-17-03	10.956	0.753	0.260	21.860	50.616	0.168	0.369	<0.096	0.088	1.083	8.111	1.343	<0.05
A01-SPL-001	7-17-03	37.544	1.006	0.232	15.258	27.702	0.157	0.733	<0.096	0.111	0.549	47.849	5.296	<0.05
A01-NEW-001	7-17-03	9.806	0.711	0.284	3.068	21.378	<0.096	0.748	<0.096	<0.075	0.055	199.880	120.852	<0.05
A01-CLD-001	7-18-03	14.196	0.892	0.237	22.254	51.422	0.114	0.451	<0.096	0.082	0.951	7.894	1.314	<0.05
A01-SPL-001	7-18-03	46.289	1.059	0.307	15.325	23.917	0.111	0.630	<0.096	0.124	0.610	50.903	5.102	<0.05
A01-NEW-001	7-18-03	13.406	0.778	0.367	3.024	235.034	0.051	0.792	<0.096	<0.075	0.126	218.878	105.666	<0.05
A01-CLD-002	7-21-03	16.436	0.569	0.391	24.285	54.363	0.217	0.902	<0.096	0.135	0.333	30.942	1.866	<0.05
A01-SPL-002	7-21-03	46.663	0.587	0.385	17.025	40.561	0.136	0.713	<0.096	0.182	0.694	62.655	4.446	<0.05
A01-NEW-002	7-21-03	6.201	0.236	0.588	3.926	20.539	0.116	0.752	<0.096	<0.075	0.143	146.475	96.445	<0.05
A01-CLD-002	7-22-03	9.978	0.266	0.286	20.382	44.915	0.091	0.408	<0.096	<0.075	0.957	14.363	1.249	<0.05
A01-SPL-002	7-22-03	86.290	0.439	0.286	10.958	29.654	0.236	0.782	<0.096	0.137	0.374	43.946	1.172	<0.05
A01-NEW-002	7-22-03	8.016	0.148	7.067	3.436	19.098	0.058	0.659	<0.096	<0.075	0.081	136.690	90.910	<0.05

\*All units are in ppb

Table I-2. Phase I Unfiltered Water Sample Metal Summary\*

Sample ID	Date	Al	Cr	Ni	Cu	Zn	As	Se	Ag	Sb	Pb	Fe	Mn	Hg
A01-OLD-001	7-16-03	30.711	0.678	0.439	27.295	67.348	0.571	0.234	1.009	0.091	2.055	20.816	1.685	<0.05
A01-SPL-001	7-16-03	55.100	0.813	0.439	25.630	50.647	0.942	0.310	0.236	0.077	1.271	103.484	17.666	<0.05
A01-NEW-001	7-16-03	25.445	0.617	0.343	5.333	25.404	0.940	0.212	<0.096	<0.075	0.476	868.880	157.701	<0.05
A01-OLD-001	7-17-03	13.126	0.360	0.372	24.854	58.817	0.387	0.125	0.123	<0.075	1.536	21.346	1.467	<0.05
A01-SPL-001	7-17-03	54.458	0.660	0.397	24.115	45.303	0.820	0.236	<0.096	<0.075	1.299	100.055	13.937	<0.05
A01-NEW-001	7-17-03	23.531	0.481	0.327	5.485	24.959	0.884	0.119	<0.096	<0.075	0.264	740.560	141.700	<0.05
A01-OLD-001	7-18-03	16.418	0.624	0.393	27.305	68.630	0.570	0.177	<0.096	<0.075	1.764	24.372	1.651	<0.05
A01-SPL-001	7-18-03	60.939	0.634	0.497	23.875	52.515	0.734	0.121	<0.096	0.090	1.151	103.492	13.263	<0.05
A01-NEW-001	7-18-03	19.879	0.420	0.453	6.096	22.081	0.911	0.130	<0.096	<0.075	0.300	741.107	137.493	<0.05
A01-OLD-002	7-21-03	55.943	0.869	0.553	29.992	57.092	0.914	0.145	<0.096	<0.075	1.311	213.271	4.176	<0.05
A01-SPL-002	7-21-03	68.512	0.625	0.439	22.541	57.780	0.738	0.128	0.571	0.126	0.920	84.506	11.846	<0.05
A01-NEW-002	7-21-03	47.883	0.473	0.310	5.234	21.091	0.811	0.139	0.362	<0.075	0.173	679.264	130.640	<0.05
A01-OLD-002	7-22-03	17.533	0.453	0.527	27.585	48.017	0.505	0.129	<0.096	<0.075	1.343	24.389	2.045	<0.05
A01-SPL-002	7-22-03	180.678	0.547	0.542	24.656	45.569	0.806	0.130	<0.096	<0.075	1.323	128.855	15.637	<0.05
A01-NEW-002	7-22-03	29.504	0.322	0.345	5.981	22.019	0.734	0.066	<0.096	<0.075	0.233	549.102	122.158	<0.05

\*All units are in ppb

Table II-1. Phase II Surface Water Metal Summary\*

<u>Sample ID</u>	<u>Al</u>	<u>Cr</u>	<u>Ni</u>	<u>Cu</u>	<u>Zn</u>	<u>As</u>	<u>Se</u>	<u>Ag</u>	<u>Sb</u>	<u>Pb</u>	<u>Fe</u>	<u>Mn</u>	<u>Hg</u>
A01-1A1-001	204.669	1.391	0.902	2.915	53.840	5.430	< 0.130	1.167	0.870	0.177	219.244	519.051	< 0.05
A01-1A2-001	239.080	2.193	2.042	13.064	75.035	3.217	0.691	2.248	1.635	1.071	282.913	91.782	0.065
A01-1A3-001	264.254	1.452	1.877	17.664	83.338	2.251	< 0.130	0.313	0.960	0.599	353.717	75.327	0.059
A01-1A4-001	192.071	1.214	0.887	20.039	90.668	2.679	< 0.130	< 0.160	1.027	0.658	354.583	100.821	< 0.05
A01-1B1-001	103.936	0.903	0.624	4.315	146.718	2.601	< 0.130	< 0.160	0.847	0.091	95.678	167.140	< 0.05
A01-1B2-001	255.577	1.307	0.842	11.054	201.766	2.731	< 0.130	< 0.160	1.326	0.562	426.411	132.479	< 0.05
A01-1B3-001	161.058	1.148	1.048	11.789	90.349	2.059	< 0.130	< 0.160	0.735	0.611	384.659	163.404	< 0.05
A01-1B4-001	142.522	1.077	1.095	13.983	94.275	1.810	< 0.130	< 0.160	1.087	0.516	388.001	119.248	< 0.05
A01-3A1-001	80.550	0.813	0.434	9.026	55.242	2.246	< 0.130	< 0.160	0.511	0.109	99.521	201.594	< 0.05
A01-3A2-001	48.999	0.788	0.702	12.593	54.514	2.229	< 0.130	< 0.160	0.419	0.164	78.434	279.430	< 0.05
A01-3A3-001	63.044	0.879	0.664	11.016	37.104	3.147	< 0.130	< 0.160	0.576	0.214	96.655	422.928	< 0.05
A01-3A4-001	64.432	0.890	1.321	11.902	51.174	1.544	< 0.130	< 0.160	0.417	0.192	112.738	140.481	< 0.05
A01-3B1-001	35.739	0.573	1.380	4.246	35.796	1.147	< 0.130	< 0.160	0.408	< 0.040	60.897	289.331	< 0.05
A01-3B2-001	57.936	1.581	1.817	6.420	86.014	1.098	< 0.130	< 0.160	0.433	0.171	131.386	233.604	< 0.05
A01-3B3-001	110.231	1.021	1.214	13.364	81.013	1.235	< 0.130	< 0.160	0.689	< 0.040	180.299	138.147	< 0.05
A01-3B4-001	48.718	0.651	0.692	3.651	47.010	2.225	< 0.130	< 0.160	0.277	< 0.040	82.374	390.209	< 0.05

\*All Units are in ppb

Table II-2. Phase II Mid-Layer Soil Digest Metal Summary\*

<u>True ID</u>	<u>Al</u>	<u>Cr</u>	<u>Ni</u>	<u>Cu</u>	<u>Zn</u>	<u>As</u>	<u>Ag</u>	<u>Sb</u>	<u>Pb</u>	<u>Fe</u>	<u>Mn</u>	<u>Hg</u>
1A1	4433.153	13.886	3.700	10.069	14.298	1.470	0.081	0.210	4.939	3054.329	33.075	< 0.05
1A2	3439.824	8.934	2.881	3.692	7.664	1.219	< 0.096	0.171	4.739	2313.939	29.523	< 0.05
1A3	4226.305	8.740	2.851	3.337	7.275	1.142	< 0.096	0.174	4.261	2236.633	27.490	< 0.05
1A4	4972.440	7.771	3.115	7.734	12.155	0.973	< 0.096	0.161	4.149	2263.642	27.623	< 0.05
1B1	5557.317	7.939	3.158	3.357	7.359	1.130	< 0.096	0.157	4.380	2313.452	34.852	< 0.05
1B2	9442.210	181.687	5.166	4.581	7.824	9.354	< 0.096	1.138	12.382	16094.179	24.213	< 0.05
1B3	5165.229	9.067	3.167	3.923	7.923	1.195	2.433	0.165	4.526	2519.699	20.037	< 0.05
1B4	4962.740	10.228	3.966	3.857	8.017	1.320	0.683	0.209	5.503	2922.737	21.371	< 0.05
3A1	4590.268	8.283	3.297	3.892	8.580	1.059	0.765	0.168	4.207	2360.431	38.571	< 0.05
3A2	3437.161	8.302	3.161	3.818	7.716	1.022	0.449	0.150	4.133	2417.198	46.801	< 0.05
3A3	5274.335	9.377	3.556	4.039	8.492	1.361	0.403	0.174	5.178	2810.987	67.173	< 0.05
3A4	1386.103	3.918	0.866	2.883	9.540	1.418	< 0.096	< 0.035	3.597	1111.757	38.211	< 0.05
3B1	6297.822	10.145	4.966	4.960	9.882	1.395	0.175	0.206	4.844	3467.758	30.435	< 0.05
3B2	3752.532	11.408	5.334	4.772	10.220	1.453	0.824	0.222	4.864	3427.539	26.671	< 0.05
3B3	4089.677	9.251	4.232	4.264	9.301	1.156	0.480	0.206	4.193	3125.853	23.450	< 0.05
3B4	4588.622	10.852	6.849	4.947	10.242	1.376	0.313	0.210	4.635	3488.679	31.222	< 0.05

\*All units are mg/kg soil

Table II-3. Phase II Mid-Layer Sequential Extraction Summary\*

<u>Sample ID</u>	<u>Al</u>	<u>Cr</u>	<u>Ni</u>	<u>Cu</u>	<u>Zn</u>	<u>As</u>	<u>Se</u>	<u>Ag</u>	<u>Sb</u>	<u>Pb</u>	<u>Fe</u>	<u>Mn</u>	<u>Hg</u>
<u>Water:</u>													
1A4	6.026	<0.067	<0.049	0.071	0.129	<0.073	<0.130	<0.160	<0.075	0.011	2.527	0.029	<0.05
3A1	5.208	<0.067	<0.049	0.045	66.724	<0.073	<0.130	<0.160	<0.075	0.017	2.110	0.658	<0.05
1B2	3.242	<0.067	<0.049	0.062	0.168	<0.073	<0.130	<0.160	<0.075	0.063	2.364	0.198	<0.05
3B3	3.280	<0.067	<0.049	0.067	0.088	<0.073	<0.130	<0.160	<0.075	0.008	1.192	0.902	<0.05
<u>Exchangeable:</u>													
1A4	1.510	<0.067	0.830	0.162	1.312	0.086	1.118	0.331	<0.075	0.011	2263.285	0.450	<0.05
3A1	21.212	<0.067	0.957	0.055	0.246	<0.073	1.275	<0.160	<0.075	0.103	2642.035	12.519	<0.05
1B2	27.775	<0.067	1.200	0.106	1.340	<0.073	1.523	<0.160	<0.075	0.351	3234.395	3.736	<0.05
3B3	17.743	0.053	1.446	0.078	0.327	0.081	1.849	<0.160	<0.075	0.177	3931.741	13.359	<0.05
<u>Acid Soluble:</u>													
1A4	103.255	<0.067	<0.049	1.641	2.308	<0.073	<0.130	<0.160	<0.075	0.719	124.121	4.786	<0.05
3A1	112.148	<0.067	<0.049	0.252	0.457	<0.073	<0.130	<0.160	<0.075	0.880	158.189	6.393	<0.05
1B2	117.574	<0.067	<0.049	0.176	0.455	<0.073	<0.130	<0.160	<0.075	0.808	217.022	0.411	<0.05
3B3	89.746	<0.067	<0.049	0.194	0.187	<0.073	<0.130	<0.160	<0.075	0.480	216.788	0.628	<0.05
<u>MnO2 Occluded:</u>													
1A4	37.311	<0.067	<0.049	0.890	0.572	<0.073	0.027	<0.160	0.172	0.242	97.537	0.613	<0.05
3A1	34.596	<0.067	<0.049	0.177	0.096	<0.073	0.015	<0.160	0.108	0.217	100.809	2.482	<0.05
1B2	37.080	<0.067	<0.049	0.170	0.115	<0.073	0.021	<0.160	0.127	0.205	116.837	0.075	<0.05
3B3	29.883	<0.067	<0.049	0.102	0.118	<0.073	0.031	<0.160	0.128	0.157	84.536	0.180	<0.05
<u>Organically Bound:</u>													
1A4	159.489	0.414	<0.049	0.568	0.649	0.189	<0.130	<0.160	<0.075	0.076	69.620	0.709	<0.05
3A1	195.209	0.335	0.065	0.140	0.272	0.281	<0.130	<0.160	0.100	0.081	85.977	1.241	<0.05
1B2	234.217	0.474	0.097	0.109	<0.069	0.247	<0.130	<0.160	0.128	0.093	83.828	0.527	<0.05
3B3	174.021	0.203	<0.049	0.082	<0.069	0.252	<0.130	<0.160	<0.075	0.053	75.190	0.680	<0.05
<u>Amorphous Fe Oxides:</u>													
1A4	83.583	<0.067	<0.049	0.364	0.160	<0.073	<0.130	<0.160	0.078	0.031	51.841	0.160	<0.05
3A1	110.687	<0.067	<0.049	0.108	0.058	<0.073	<0.130	<0.160	0.093	0.038	54.928	0.302	<0.05
1B2	92.511	<0.067	<0.049	0.080	0.052	<0.073	<0.130	<0.160	0.108	0.043	50.729	0.111	<0.05
3B3	136.166	<0.067	<0.049	0.069	0.021	<0.073	<0.130	<0.160	0.079	0.027	101.050	0.249	<0.05
<u>Crystalline Fe Oxides:</u>													
1A4	27.280	0.181	0.074	0.507	0.105	<0.073	0.095	<0.160	<0.075	0.008	143.680	0.312	<0.05
3A1	34.711	0.189	0.072	0.367	0.064	<0.073	0.099	<0.160	<0.075	0.005	170.753	0.424	<0.05
1B2	31.798	0.199	0.073	0.381	0.057	0.168	0.071	<0.160	<0.075	0.006	154.742	0.299	<0.05
3B3	41.445	0.221	0.076	0.389	0.092	<0.073	0.080	<0.160	<0.075	0.009	235.948	0.591	<0.05
<u>Pellet HF Digests:</u>													
1A4	1125.562	0.126	0.472	0.110	0.728	<0.073	<0.130	<0.160	<0.075	0.332	20.673	1.000	<0.05
3A1	5094.918	4.136	2.329	2.438	6.571	<0.073	<0.130	<0.160	<0.075	1.737	438.524	15.426	<0.05
1B2	108.043	1.144	0.219	0.056	1.384	<0.073	<0.130	<0.160	<0.075	0.476	95.922	5.833	<0.05
3B3	1658.794	0.361	0.453	0.286	2.323	<0.073	<0.130	<0.160	<0.075	0.421	125.778	2.760	<0.05

\*All units are mg/kg soil

**Table III-1. Phase III Surface Water pH and Anion Summary\***

<u>Sample ID</u>	<u>pH</u>	<u>Chloride</u>	<u>Bromide</u>	<u>Nitrate</u>	<u>Sulfate</u>
A01-4AA-001	6.70	6.63	29.45	< 0.03	1.96
A01-4AA-002	6.87	5.31	< 0.05	0.55	3.32
A01-4AA-003	6.91	5.63	< 0.05	0.62	3.72
A01-4AA-005	6.77	4.83	29.72	< 0.03	2.26
A01-4AB-001	6.75	4.65	< 0.05	0.84	3.48
A01-4AB-002	6.69	4.44	< 0.05	0.25	1.12
A01-4AB-003	6.71	5.04	< 0.05	0.11	1.01
A01-4AB-004	6.58	4.91	< 0.05	0.21	1.04
A01-4AB-005	7.30	3.72	< 0.05	< 0.03	1.36
A01-4AC-001	6.52	4.36	< 0.05	0.32	1.68
A01-4AC-002	6.72	5.69	< 0.05	0.05	1.29
A01-4AC-003	6.44	7.53	< 0.05	0.07	1.22
A01-4AC-004	6.35	5.51	< 0.05	0.20	1.43
A01-4AC-005	6.62	5.39	< 0.05	0.17	1.41
A01-4AD-001	6.58	4.60	< 0.05	0.13	1.55
A01-4AD-002	6.49	5.17	< 0.05	0.19	2.46
A01-4AD-003	7.16	5.18	< 0.05	0.10	3.10
A01-4AD-004	6.75	4.98	< 0.05	0.08	1.55
A01-4AD-005	7.22	5.37	< 0.05	0.07	1.45
A01-4BA-001	6.43	7.66	< 0.05	0.27	1.43
A01-4BA-002	6.71	8.41	< 0.05	0.07	4.26
A01-4BA-005	6.74	5.11	< 0.05	< 0.03	1.12
A01-4BB-004	7.54	5.01	< 0.05	0.29	1.61
A01-4BB-005	7.23	4.89	< 0.05	0.07	2.25
A01-4BC-003	6.35	3.22	< 0.05	< 0.03	1.39
A01-4BD-001	6.89	5.57	< 0.05	0.06	3.21
A01-4BD-002	6.96	4.82	< 0.05	0.10	2.13
A01-4BD-004	6.85	4.70	< 0.05	< 0.03	4.70

\*Anion units are ppm

Table III-2. Phase III Surface Water Metal Summary\*

Sample ID	Al	Cr	Ni	Cu	Zn	As	Se	Ag	Sb	Pb	Fe	Mn	Hg
A01-4AA-001	23.187	0.639	1.683	7.012	271.350	2.640	<0.130	<0.160	0.511	0.145	90.218	489.077	<0.05
A01-4AA-002	65.391	0.620	0.512	2.026	40.733	3.566	<0.130	<0.160	0.493	<0.040	72.108	359.293	<0.05
A01-4AA-003	35.986	0.570	2.929	6.744	148.041	1.347	<0.130	<0.160	0.281	0.049	94.931	688.631	<0.05
A01-4AA-005	23.067	1.102	2.431	3.516	107.720	1.430	<0.130	<0.160	<0.242	<0.040	71.826	720.871	<0.05
A01-4AB-001	45.376	0.769	0.583	8.689	74.422	2.827	<0.130	<0.160	0.546	0.139	100.513	143.486	<0.05
A01-4AB-002	42.354	0.501	1.571	7.569	75.337	1.294	<0.130	<0.160	0.402	0.088	73.912	277.628	<0.05
A01-4AB-003	45.250	1.079	0.629	8.210	79.414	1.636	<0.130	<0.160	0.577	0.147	70.692	245.518	<0.05
A01-4AB-004	51.845	0.873	1.034	6.442	81.269	1.257	<0.130	<0.160	0.425	0.193	106.373	205.879	<0.05
A01-4AB-005	71.734	0.648	0.360	3.552	46.876	1.319	<0.130	<0.160	0.384	<0.040	52.886	121.447	<0.05
A01-4AC-001	68.031	0.369	0.392	5.854	66.192	1.027	<0.130	0.989	0.677	0.184	127.127	39.633	<0.05
A01-4AC-002	54.895	0.319	0.345	27.071	77.162	0.696	<0.130	<0.160	0.464	1.457	73.445	105.677	<0.05
A01-4AC-003	37.453	0.494	1.004	10.439	114.670	1.221	<0.130	<0.160	0.536	0.165	99.896	312.822	<0.05
A01-4AC-004	52.752	0.397	0.908	10.470	64.869	1.858	<0.130	<0.160	0.490	0.315	137.301	178.011	<0.05
A01-4AC-005	65.517	0.330	0.670	2.187	109.112	0.976	<0.130	<0.160	0.287	0.073	124.327	2279.850	<0.05
A01-4AD-001	24.821	0.375	0.711	11.732	83.896	0.617	<0.130	<0.160	0.551	0.142	70.239	123.871	<0.05
A01-4AD-002	40.278	0.345	0.900	11.754	75.030	1.239	<0.130	<0.160	0.542	0.220	114.995	128.546	<0.05
A01-4AD-003	128.169	0.309	0.427	2.269	40.417	1.543	<0.130	<0.160	0.416	0.227	101.644	549.327	<0.05
A01-4AD-004	67.212	0.309	0.209	1.296	31.984	1.770	<0.130	<0.160	0.370	0.095	71.076	384.540	<0.05
A01-4AD-005	53.115	0.298	0.284	1.222	44.756	0.978	<0.130	<0.160	<0.242	0.059	57.386	548.852	<0.05
A01-4BA-001	82.513	2.176	1.433	10.732	142.829	2.039	<0.130	<0.160	0.794	0.322	293.070	117.800	<0.05
A01-4BA-002	31.057	0.476	1.256	3.291	35.897	0.943	<0.130	<0.160	0.299	0.102	90.739	1175.338	<0.05
A01-4BA-005	53.296	0.678	0.890	0.803	40.291	3.621	<0.130	<0.160	0.254	0.059	20018.325	10617.571	<0.05
A01-4BB-004	38.094	0.520	0.466	5.053	288.786	0.848	<0.130	0.294	0.412	0.073	128.046	65.948	<0.05
A01-4BB-005	19.879	0.357	0.357	5.131	64.585	0.896	<0.130	<0.160	0.552	0.147	247.205	70.374	<0.05
A01-4BC-003	29.775	0.364	0.941	2.823	50.463	0.853	<0.130	1.018	0.301	0.169	112.686	274.613	<0.05
A01-4BD-001	38.966	0.739	1.185	4.324	82.567	1.047	<0.130	<0.160	0.301	0.088	145.219	180.183	<0.05
A01-4BD-002	27.647	0.428	0.681	4.037	73.768	1.131	<0.130	<0.160	0.273	0.059	104.813	139.822	<0.05
A01-4BD-004	8.347	0.419	1.521	1.058	31.445	0.717	<0.130	<0.160	<0.242	<0.040	3958.767	2393.065	<0.05

\*All units are ppb

Table III-3. Phase III Mid-Layer Pore Water pH, EC, Anion Summary\*

<u>Sample ID</u>	<u>EC (uS/cm)</u>	<u>pH</u>	<u>Chloride</u>	<u>Bromide</u>	<u>Nitrate</u>	<u>Sulfate</u>
A01-4AA-001	149.7	6.74	12.06	< 0.05	< 0.03	71.38
A01-4AA-002	85.9	6.57	12.58	< 0.05	< 0.03	20.16
A01-4AA-003	149.8	7.25	18.48	< 0.05	< 0.03	98.64
A01-4AA-004	75.5	5.36	15.10	< 0.05	0.10	53.02
A01-4AA-005	193.4	5.39	17.78	< 0.05	< 0.03	115.02
A01-4AB-001	94.2	5.98	32.08	< 0.05	< 0.03	17.62
A01-4AB-002	131.8	6.20	20.74	< 0.05	0.14	142.22
A01-4AB-003	128.5	5.87	8.54	< 0.05	0.10	98.28
A01-4AB-004	129.8	5.95	7.70	< 0.05	< 0.03	9.80
A01-4AB-005	127.4	5.93	10.02	< 0.05	< 0.03	37.76
A01-4AC-001	122.1	6.74	13.74	< 0.05	< 0.03	138.56
A01-4AC-002	41.7	5.99	13.72	< 0.05	< 0.03	7.56
A01-4AC-003	80.4	7.03	11.62	< 0.05	< 0.03	17.24
A01-4AC-004	1031.0	6.55	9.22	< 0.05	0.14	0.00
A01-4AC-005	142.4	6.28	12.38	< 0.05	0.10	9.48
A01-4AD-001	56.5	6.45	31.06	< 0.05	0.10	9.48
A01-4AD-002	21.1	5.76	12.70	< 0.05	0.12	0.68
A01-4AD-003	201.9	6.79	6.96	< 0.05	0.10	125.16
A01-4AD-004	96.8	5.36	9.94	20.24	< 0.03	66.72
A01-4AD-005	113.7	6.68	13.26	< 0.05	< 0.03	12.02
A01-4BA-001	29.0	6.04	14.56	< 0.05	0.12	13.28
A01-4BA-002	52.3	6.81	9.48	< 0.05	0.16	113.08
A01-4BA-003	102.3	5.44	17.16	< 0.05	0.18	67.26
A01-4BA-004	62.1	4.96	13.28	< 0.05	0.14	108.18
A01-4BA-005	67.3	5.33	33.60	< 0.05	< 0.03	10.92
A01-4BB-001	77.6	5.85	13.44	< 0.05	< 0.03	87.96
A01-4BB-002	108.9	5.44	15.74	< 0.05	0.14	152.14
A01-4BB-003	159.7	6.13	25.36	< 0.05	0.12	32.58
A01-4BB-004	54.6	6.60	21.02	< 0.05	< 0.03	16.40
A01-4BB-005	144.4	7.44	19.58	< 0.05	0.14	40.3
A01-4BC-001	36.9	5.98	10.680	< 0.05	< 0.03	56.580
A01-4BC-002	65.1	5.99	14.70	< 0.05	< 0.03	8.10
A01-4BC-003	104.3	5.56	18.12	< 0.05	< 0.03	75.58
A01-4BC-004	149.4	5.78	13.02	< 0.05	< 0.03	23.4
A01-4BC-005	80.3	5.07	12.50	< 0.05	< 0.03	52.68
A01-4BD-001	30.0	5.96	12.880	< 0.05	< 0.03	12.860
A01-4BD-002	34.9	6.36	24.64	< 0.05	0.92	70.68
A01-4BD-003	40.7	6.01	12.98	< 0.05	0.12	165.86
A01-4BD-004	125.6	6.79	16.52	< 0.05	< 0.03	83.28
A01-4BD-005	93.9	5.66	11.88	< 0.05	0.12	32.86

\* Anion units are ppm

Table III-4. Phase III Mid-Layer Pore Water Metal Summary\*

<u>SampleID</u>	<u>Al</u>	<u>Cr</u>	<u>Ni</u>	<u>Cu</u>	<u>Zn</u>	<u>As</u>	<u>Se</u>	<u>Ag</u>	<u>Sb</u>	<u>Pb</u>	<u>Fe</u>	<u>Mn</u>	<u>Hg</u>
A01-4AA-001	2025.197	1.907	3.056	1.992	462.601	4.467	<0.130	15.351	<0.242	1.703	2985.891	1403.518	0.502
A01-4AA-002	4509.775	4.709	3.022	4.323	446.964	3.939	<0.130	7.563	<0.242	5.841	3281.073	589.601	<0.05
A01-4AA-003	264.635	<0.067	2.488	1.287	574.189	6.481	<0.130	25.543	<0.242	1.387	1992.789	1315.532	<0.05
A01-4AA-004	29.093	1.282	1.195	<0.038	306.003	6.994	<0.130	9.514	<0.242	<0.040	632.082	849.598	<0.05
A01-4AA-005	524.512	3.255	9.330	2.286	443.285	9.688	<0.130	11.262	<0.242	<0.040	7753.944	2651.743	<0.05
A01-4AB-001	882.306	2.726	0.987	<0.038	294.205	5.458	<0.130	BD	<0.242	0.412	5237.429	1774.264	<0.05
A01-4AB-002	923.773	2.884	2.581	1.023	241.883	6.953	<0.130	3.071	<0.242	2.078	11262.080	5171.792	<0.05
A01-4AB-003	42.452	1.286	2.167	1.188	365.499	5.008	<0.130	1.600	<0.242	<0.040	8965.461	1849.821	<0.05
A01-4AB-004	88.466	1.326	1.243	1.371	253.877	7.599	<0.130	<0.160	<0.242	<0.040	12453.603	3534.744	<0.05
A01-4AB-005	30.446	1.227	10.244	149.829	325.629	5.813	<0.130	<0.160	<0.242	8.255	13048.599	839.554	<0.05
A01-4AC-001	22.590	1.649	58.508	7.598	359.011	3.671	<0.130	<0.160	<0.242	<0.040	6433.640	1256.515	<0.05
A01-4AC-002	2690.434	3.839	1.613	1.401	241.974	4.478	<0.130	26.072	<0.242	1.381	3528.682	355.707	<0.05
A01-4AC-003	47.007	1.657	0.846	4.406	568.911	3.843	<0.130	<0.160	<0.242	<0.040	219.134	873.152	<0.05
A01-4AC-004	35.069	1.220	11.026	1.152	300.225	4.635	<0.130	<0.160	<0.242	<0.040	26629.665	3946.440	<0.05
A01-4AC-005	169.506	1.392	3.553	4.834	284.890	2.624	<0.130	<0.160	<0.242	<0.040	3598.060	3665.658	<0.05
A01-4AD-001	25.298	1.903	2.096	16.422	277.175	4.146	<0.130	62.076	<0.242	3.315	3490.335	868.199	<0.05
A01-4AD-002	159.212	1.572	<0.049	2.404	319.148	3.016	<0.130	6.922	<0.242	<0.040	311.034	57.893	<0.05
A01-4AD-003	389.553	1.973	3.814	4.815	254.044	11.891	<0.130	<0.160	<0.242	0.563	5689.419	2988.080	<0.05
A01-4AD-004	131.994	5.192	1.435	6.303	52.026	4.096	<0.130	5.021	<0.242	0.665	6504.043	5330.517	<0.05
A01-4AD-005	1304.556	2.274	1.974	5.743	320.778	6.655	<0.130	<0.160	<0.242	0.812	11952.853	2633.679	<0.05
A01-4BA-001	30662.369	23.809	14.102	23.537	97.965	7.427	<0.130	<0.160	<0.242	11.480	15426.684	128.377	<0.05
A01-4BA-002	37195.430	30.665	16.273	21.574	57.392	8.596	4.962	4.219	<0.242	14.031	20522.292	354.470	<0.05
A01-4BA-003	307.170	3.155	1.588	2.243	49.374	4.676	3.530	<0.160	<0.242	<0.040	148.620	2120.197	<0.05
A01-4BA-004	34.952	6.009	0.541	4.174	50.323	3.138	<0.130	23.895	<0.242	2.339	BD	1822.359	<0.05
A01-4BA-005	1118.204	5.579	2.125	7.285	49.013	3.783	3.626	<0.160	<0.242	1.381	988.489	2892.896	<0.05
A01-4BB-001	377.593	3.428	1.180	1.981	39.488	1.802	<0.130	<0.160	<0.242	<0.040	220.815	1652.447	<0.05
A01-4BB-002	25.538	11.976	3.039	28.036	49.301	2.302	6.584	63.683	<0.242	0.489	78.895	3045.641	0.678
A01-4BB-003	144.222	5.464	3.973	6.288	49.136	1.684	<0.130	<0.160	<0.242	0.571	58.071	3810.155	<0.05
A01-4BB-004	32407.825	17.957	13.366	16.763	118.465	5.439	5.439	7.704	<0.242	10.754	12383.421	455.335	<0.05
A01-4BB-005	337.131	5.178	2.349	2.201	30.366	BD	4.771	<0.160	<0.242	<0.040	201.866	1173.047	<0.05
A01-4BC-001	32699.982	16.838	13.800	12.235	86.889	9.205	3.530	<0.160	<0.242	9.980	10818.735	569.254	<0.05
A01-4BC-002	702.026	4.317	1.241	4.083	92.690	1.892	2.481	<0.160	<0.242	0.718	873.915	2398.831	<0.05
A01-4BC-003	245.502	4.762	1.389	2.442	38.549	5.470	3.626	<0.160	<0.242	0.864	38.320	2357.311	<0.05
A01-4BC-004	1481.806	5.120	3.585	6.515	55.019	2.198	3.053	4.797	<0.242	1.856	3288.781	5874.828	<0.05
A01-4BC-005	149.116	3.700	1.588	3.450	92.298	3.215	2.385	<0.160	<0.242	0.991	109.650	2753.917	<0.05
A01-4BD-001	13749.227	15.619	5.970	11.805	60.251	5.134	3.149	13.172	<0.242	3.961	5269.666	268.180	0.459
A01-4BD-002	75.602	1.506	3.614	0.975	264.427	4.509	<0.130	5.829	<0.242	0.708	916.283	559.512	<0.05
A01-4BD-003	4179.795	5.000	1.426	6.983	335.154	7.730	<0.130	<0.160	<0.242	11.499	3064.151	632.880	<0.05
A01-4BD-004	79.399	1.734	1.725	1.240	261.716	4.662	<0.130	<0.160	<0.242	<0.040	9000.791	866.142	<0.05
A01-4BD-005	986.359	2.153	1.605	2.752	302.105	9.716	<0.130	<0.160	<0.242	0.980	3755.861	1981.042	<0.05

\*All units are in ppb

Table III-5. Phase III Mid-Layer Soil Digest Summary\*

Sample ID	Al	Cr	Ni	Cu	Zn	As	Se	Ag	Sb	Pb	Fe	Mn	Hg
A01-4AA-001	13528.355	23.145	5.314	5.803	13.422	2.678	0.249	3.571	0.182	6.438	4166.837	54.888	<0.05
A01-4AA-002	6108.750	19.030	4.559	4.217	11.722	1.982	0.258	1.926	0.176	5.005	3188.684	30.604	<0.05
A01-4AA-003	5504.558	14.478	4.463	4.191	10.536	1.736	0.153	1.330	0.168	5.129	3234.324	42.157	<0.05
A01-4AA-004	5595.697	17.013	4.373	5.773	11.118	2.042	0.133	1.183	0.192	5.324	3330.948	29.976	<0.05
A01-4AA-005	5225.858	11.409	4.271	5.271	9.673	1.848	<0.130	0.829	0.170	5.174	2985.315	37.615	<0.05
A01-4AB-001	4939.822	14.990	5.058	5.169	10.752	2.304	<0.130	0.734	0.210	6.324	4114.410	38.497	<0.05
A01-4AB-002	4624.419	14.963	6.797	5.049	9.777	2.286	<0.130	0.659	0.195	5.709	3815.134	21.072	<0.05
A01-4AB-003	4521.595	13.251	5.426	7.500	11.909	2.188	0.153	0.550	0.217	6.205	3923.058	21.409	<0.05
A01-4AB-004	5822.668	14.215	4.992	7.073	11.509	2.201	<0.130	0.417	0.211	6.203	3858.895	43.025	<0.05
A01-4AB-005	6451.656	13.874	5.306	8.416	12.388	2.040	<0.130	0.378	0.232	6.357	3830.132	22.230	<0.05
A01-4AC-001	5552.914	14.910	5.651	6.867	11.420	2.098	<0.130	0.942	0.280	7.068	4433.636	21.389	<0.05
A01-4AC-002	6603.419	12.730	4.941	17.151	16.960	1.852	<0.130	0.145	0.263	7.520	4100.826	23.611	<0.05
A01-4AC-003	4013.225	12.084	4.991	6.050	9.891	1.736	<0.130	0.121	0.251	6.360	3990.997	28.697	<0.05
A01-4AC-004	7248.738	15.506	5.185	6.350	11.224	1.904	<0.130	0.118	0.268	6.937	4439.403	27.179	<0.05
A01-4AC-005	4856.300	12.229	4.583	6.437	10.852	1.936	<0.130	0.113	0.248	6.924	4216.666	50.993	<0.05
A01-4AD-001	3952.334	11.877	4.781	5.381	9.298	1.481	<0.130	0.087	0.222	5.832	3564.624	27.328	<0.05
A01-4AD-002	4473.419	12.091	5.297	6.045	9.697	1.984	<0.130	0.770	0.259	6.027	3859.558	13.274	<0.05
A01-4AD-003	6796.716	14.606	5.841	7.573	11.984	1.783	<0.130	0.743	0.263	7.110	4191.973	61.158	<0.05
A01-4AD-004	3972.320	9.896	4.146	4.203	9.287	1.405	<0.130	0.422	0.212	5.971	2764.328	50.177	<0.05
A01-4AD-005	5826.211	12.169	5.134	4.868	9.635	1.835	<0.130	0.447	0.266	6.240	4118.256	34.897	<0.05
A01-4BA-001	4024.689	9.786	3.979	5.927	9.616	1.483	<0.130	0.297	0.220	5.493	3049.350	18.353	<0.05
A01-4BA-002	4593.642	11.401	4.385	5.512	8.741	1.450	<0.130	0.291	0.218	5.616	3303.804	25.530	<0.05
A01-4BA-003	5949.873	10.830	4.407	5.142	9.948	1.275	<0.130	0.307	0.217	5.575	3242.197	40.532	<0.05
A01-4BA-004	5285.264	8.567	3.300	3.794	8.755	1.048	<0.130	0.213	0.193	4.407	3076.808	36.492	<0.05
A01-4BA-005	4255.164	9.722	3.556	3.624	8.518	1.128	<0.130	0.390	0.212	4.835	2595.771	54.280	<0.05
A01-4BB-001	5497.853	11.333	4.538	4.953	9.743	1.577	<0.130	0.180	0.228	6.198	3512.797	33.552	<0.05
A01-4BB-002	4353.856	11.454	4.840	6.327	10.432	1.765	<0.130	<0.075	0.254	6.454	3952.800	24.664	<0.05
A01-4BB-003	4335.673	11.464	4.582	5.048	10.385	1.622	<0.130	<0.075	0.257	6.082	3436.971	40.006	<0.05
A01-4BB-004	11038.008	10.196	3.723	3.610	8.826	1.379	<0.130	<0.075	0.194	4.715	3433.000	45.484	<0.05
A01-4BB-005	5434.758	10.149	4.058	4.319	9.392	1.177	<0.130	0.202	0.223	5.949	3704.457	52.428	<0.05
A01-4AC-001	4561.733	7.543	2.741	2.955	7.039	0.886	<0.130	<0.075	0.173	4.016	2230.493	36.043	<0.05
A01-4AC-002	3806.204	9.475	4.314	3.950	9.632	1.443	<0.130	<0.075	0.222	5.247	3131.397	55.845	<0.05
A01-4AC-003	4687.446	8.882	2.896	3.136	7.225	0.991	<0.130	<0.075	0.194	4.996	2509.620	66.952	<0.05
A01-4AC-004	5600.528	11.395	4.084	4.662	9.611	1.304	<0.130	<0.075	0.220	5.267	3608.466	44.633	<0.05
A01-4AC-005	4873.759	9.810	3.636	3.490	8.102	1.143	<0.130	<0.075	0.201	5.082	2863.495	48.798	<0.05
A01-4BD-001	4560.146	9.756	3.383	3.469	8.202	1.078	<0.130	<0.075	0.194	4.623	2475.680	25.287	<0.05
A01-4BD-002	4117.389	11.160	4.454	4.288	9.288	1.637	<0.130	0.234	0.246	6.051	3561.504	31.750	<0.05
A01-4BD-003	5418.449	15.267	5.300	6.852	11.424	2.263	<0.130	0.182	0.293	7.131	4430.887	24.360	<0.05
A01-4BD-004	5019.752	9.629	3.772	3.832	8.432	1.095	<0.130	0.168	0.218	5.086	3032.457	60.672	<0.05
A01-4BD-005	4671.717	9.368	3.585	3.644	8.424	1.100	<0.130	0.110	0.206	5.067	2960.532	43.574	<0.05

\*All units are mg/kg soil

Table III-6. Phase III Mid-Layer Sequential Extraction Metal Summary\*

Sample ID	Al	Cr	Ni	Cu	Zn	As	Se	Ag	Sb	Pb	Fe	Mn	Hg
<u>Water:</u>													
4AA-1	6.206	<0.067	<0.049	0.043	0.220	<0.073	<0.130	<0.160	<0.075	0.008	3.391	0.401	<0.05
4AB-2	4.626	<0.067	<0.049	0.033	0.317	<0.073	<0.130	<0.160	<0.075	0.010	3.124	1.415	<0.05
4AC-3	7.344	<0.067	<0.049	0.056	0.205	<0.073	<0.130	<0.160	<0.075	0.011	3.831	0.049	<0.05
4AD-4	2.950	<0.067	<0.049	0.039	0.291	<0.073	<0.130	<0.160	<0.075	0.011	1.994	7.173	<0.05
4BA-5	2.960	<0.067	<0.049	0.073	0.291	<0.073	<0.130	<0.160	<0.075	0.048	1.948	5.229	<0.05
4BB-1	2.968	<0.067	<0.049	0.033	0.148	<0.073	<0.130	<0.160	<0.075	0.008	1.653	2.707	<0.05
4BC-2	2.228	<0.067	<0.049	0.032	0.233	<0.073	<0.130	<0.160	<0.075	0.005	1.401	3.492	<0.05
4BD-3	3.335	<0.067	<0.049	0.120	0.205	<0.073	<0.130	<0.160	<0.075	0.010	2.167	1.940	<0.05
<u>Exchangeable:</u>													
4AA-1	14.880	<0.067	0.385	0.048	0.421	0.103	0.607	<0.160	<0.075	0.028	795.998	4.773	<0.05
4AB-2	16.445	<0.067	0.399	0.039	0.366	0.130	0.664	<0.160	<0.075	0.159	791.546	8.584	<0.05
4AC-3	<0.215	<0.067	0.392	0.033	0.264	0.111	0.627	<0.160	<0.075	0.009	835.056	1.015	<0.05
4AD-4	30.558	<0.067	0.382	0.026	0.249	0.132	0.561	0.319	<0.075	0.370	906.422	43.544	<0.05
4BA-5	28.249	<0.067	0.410	0.019	0.268	0.140	0.736	<0.160	<0.075	0.338	1103.086	63.233	<0.05
4BB-1	19.150	<0.067	0.485	0.035	0.219	0.127	0.689	<0.160	<0.075	0.259	1200.225	24.775	<0.05
4BC-2	21.158	<0.067	0.530	0.028	0.248	0.159	0.822	<0.160	<0.075	0.215	1481.657	23.865	<0.05
4BD-3	15.182	<0.067	0.667	0.062	0.393	<0.073	1.036	<0.160	<0.075	0.353	1683.383	18.891	<0.05
<u>Acid Soluble:</u>													
4AA-1	138.353	0.278	<0.049	0.560	1.078	0.078	<0.130	<0.160	<0.075	0.533	78.104	9.009	<0.05
4AB-2	145.446	0.102	<0.049	0.341	0.638	<0.073	<0.130	<0.160	<0.075	0.734	284.535	0.526	<0.05
4AC-3	128.691	<0.067	<0.049	0.582	0.753	<0.073	<0.130	<0.160	<0.075	0.741	105.365	11.735	<0.05
4AD-4	95.784	<0.067	<0.049	0.155	0.219	<0.073	<0.130	<0.160	<0.075	0.650	80.196	0.653	<0.05
4BA-5	91.480	<0.067	<0.049	0.172	0.194	<0.073	<0.130	<0.160	<0.075	0.694	48.341	1.487	<0.05
4BB-1	100.164	<0.067	<0.049	0.226	0.257	<0.073	<0.130	<0.160	<0.075	0.744	29.795	1.218	<0.05
4BC-2	80.316	<0.067	<0.049	0.111	0.078	<0.073	<0.130	<0.160	<0.075	0.628	93.748	2.862	<0.05
4BD-3	115.774	<0.067	<0.049	0.194	0.310	<0.073	<0.130	<0.160	<0.075	0.879	189.461	0.648	<0.05
<u>MnO2 Occluded:</u>													
4AA-1	37.274	0.074	<0.049	0.285	0.590	<0.073	<0.130	<0.160	<0.075	0.325	116.511	0.619	<0.05
4AB-2	34.556	<0.067	<0.049	0.257	0.123	<0.073	<0.130	<0.160	<0.075	0.257	144.223	0.249	<0.05
4AC-3	34.324	<0.067	<0.049	0.267	0.131	<0.073	<0.130	<0.160	<0.075	0.251	144.232	0.351	<0.05
4AD-4	33.767	<0.067	<0.049	0.175	0.164	<0.073	<0.130	<0.160	<0.075	0.301	148.272	0.347	<0.05
4BA-5	32.727	<0.067	<0.049	0.163	0.120	<0.073	<0.130	<0.160	0.182	0.207	128.787	0.327	<0.05
4BB-1	35.340	<0.067	<0.049	0.200	0.225	<0.073	<0.130	<0.160	<0.075	0.222	108.768	0.630	<0.05
4BC-2	30.388	<0.067	<0.049	0.143	0.101	<0.073	<0.130	<0.160	<0.075	0.200	111.493	0.666	<0.05
4BD-3	35.757	<0.067	<0.049	0.566	0.404	<0.073	<0.130	<0.160	0.165	0.224	119.036	0.343	<0.05
<u>Organically Bound:</u>													
4AA-1	206.901	2.145	<0.049	0.203	1.326	0.331	<0.130	<0.160	0.084	0.124	168.353	0.804	<0.05
4AB-2	228.225	1.034	0.083	0.205	0.046	0.320	<0.130	<0.160	0.179	0.111	175.687	0.700	<0.05
4AC-3	204.276	0.586	0.062	0.187	0.087	0.287	<0.130	<0.160	<0.075	0.109	155.884	1.181	<0.05
4AD-4	209.536	0.443	0.062	0.102	0.110	0.301	<0.130	<0.160	0.153	0.091	133.247	1.542	<0.05
4BA-5	210.375	0.522	0.073	0.132	<0.069	0.342	<0.130	<0.160	0.093	0.108	147.606	1.573	<0.05
4BB-1	187.551	0.455	0.062	0.228	0.218	0.323	<0.130	<0.160	0.115	0.088	130.490	1.594	<0.05
4BC-2	181.095	0.353	<0.049	0.112	0.131	0.313	<0.130	<0.160	<0.075	0.084	128.122	1.805	<0.05
4BD-3	192.214	0.456	0.071	0.363	0.559	0.268	<0.130	<0.160	<0.075	0.089	100.348	0.873	<0.05

\*All units are mg/kg soil; Table continued on next page

Table III-6. Phase III Mid-Layer Sequential Extraction Metal Summary (continued)\*

Sample ID	Al	Cr	Ni	Cu	Zn	As	Se	Ag	Sb	Pb	Fe	Mn	Hg
<u>Amorphous Fe Oxides:</u>													
4AA-1	125.002	0.829	<0.049	0.143	0.088	0.074	<0.130	<0.160	0.089	0.079	113.900	0.252	<0.05
4AB-2	132.026	0.211	<0.049	0.124	0.193	<0.073	<0.130	<0.160	0.224	0.058	117.675	0.229	<0.05
4AC-3	124.143	0.070	<0.049	0.362	0.287	<0.073	<0.130	<0.160	<0.075	0.070	100.389	0.355	<0.05
4AD-4	112.538	0.154	<0.049	0.210	0.088	<0.073	<0.130	<0.160	<0.075	0.053	86.205	0.441	<0.05
4BA-5	125.866	<0.067	<0.049	0.110	<0.069	<0.073	<0.130	<0.160	<0.075	0.046	115.236	0.500	<0.05
4BB-1	134.195	<0.067	<0.049	0.104	<0.069	<0.073	<0.130	<0.160	0.134	0.044	103.616	0.617	<0.05
4BC-2	118.770	<0.067	<0.049	0.079	0.450	<0.073	<0.130	<0.160	0.085	0.036	84.718	0.534	<0.05
4BD-3	94.299	<0.067	<0.049	0.305	0.117	<0.073	<0.130	<0.160	0.080	0.039	65.015	0.273	<0.05
<u>Crystalline Fe Oxides:</u>													
4AA-1	44.988	0.519	<0.049	0.080	0.401	0.071	<0.130	<0.160	<0.075	0.002	0.474	0.276	<0.05
4AB-2	47.287	0.605	<0.049	0.086	0.353	0.075	<0.130	<0.160	<0.075	0.006	0.506	0.308	<0.05
4AC-3	46.331	0.572	<0.049	0.075	0.337	0.077	<0.130	<0.160	<0.075	0.007	0.504	0.287	0.096
4AD-4	31.379	0.305	<0.049	0.065	0.320	0.063	<0.130	<0.160	<0.075	0.005	0.356	0.183	<0.05
4BA-5	37.317	0.430	<0.049	0.081	0.322	0.067	<0.130	<0.160	<0.075	0.008	0.493	0.258	<0.05
4BB-1	38.972	0.438	<0.049	0.078	0.309	0.073	<0.130	<0.160	<0.075	0.008	0.570	0.243	<0.05
4BC-2	37.679	0.354	<0.049	0.074	0.331	0.070	<0.130	<0.160	<0.075	0.007	0.549	0.192	<0.05
4BD-3	30.387	0.304	<0.049	0.072	0.366	0.084	<0.130	<0.160	<0.075	0.005	0.350	0.191	<0.05
<u>Pellet HF Digests:</u>													
4AA-1	4560.006	5.502	2.089	3.045	10.293	0.256	<0.130	<0.160	0.139	3.816	577.621	14.377	0.206
4AB-2	6317.476	6.083	2.685	3.246	10.973	BD	<0.130	<0.160	0.127	3.744	765.617	15.338	0.100
4AC-3	5968.125	4.969	2.606	3.121	14.430	BD	<0.130	<0.160	0.125	3.951	617.654	12.834	0.059
4AD-4	4084.699	4.816	1.913	2.457	8.822	BD	<0.130	<0.160	0.109	2.929	490.798	11.767	<0.05
4BA-5	4216.899	5.488	2.030	2.666	8.818	BD	<0.130	<0.160	0.130	2.836	523.948	14.595	<0.05
4BB-1	7451.296	6.630	3.048	3.629	13.366	BD	<0.130	<0.160	0.153	5.575	894.263	21.574	<0.05
4BC-2	7802.079	7.409	3.461	3.904	12.476	BD	<0.130	<0.160	0.145	4.170	978.320	24.065	0.055
4BD-3	5733.979	5.968	2.728	2.647	9.423	BD	<0.130	<0.160	0.117	3.080	668.152	17.069	<0.05

\*All units are mg/kg soil

**Table III-7. Phase III Top-Layer Sediment Digest Summary\***

<b>Sample ID</b>	<b>Al</b>	<b>Cr</b>	<b>Ni</b>	<b>Cu</b>	<b>Zn</b>	<b>As</b>	<b>Se</b>	<b>Ag</b>	<b>Sb</b>	<b>Pb</b>	<b>Fe</b>	<b>Mn</b>	<b>Hg</b>
4AA-1	1898.453	10.257	3.482	27.228	26.593	4.539	0.423	< 0.160	0.258	8.606	3691.026	17.272	< 0.05
4AA-2	1324.497	8.506	1.930	19.719	23.561	2.332	< 0.130	< 0.160	< 0.075	6.099	1666.807	7.012	< 0.05
4AB-1	3322.607	12.430	4.214	49.281	45.259	3.779	0.192	< 0.160	0.094	9.470	3397.585	14.111	< 0.05
4AB-2	914.238	2.690	0.369	9.171	14.199	1.331	0.241	< 0.160	< 0.075	2.416	661.990	3.656	< 0.05
4AC-1	948.051	4.632	1.253	16.143	19.458	1.747	< 0.130	< 0.160	< 0.075	3.974	1086.257	6.218	< 0.05
4AC-2	3051.563	9.001	3.111	53.217	51.543	2.484	0.339	< 0.160	0.080	6.844	2046.469	9.338	< 0.05
4AD-1	3288.116	10.399	3.797	42.911	42.960	3.293	< 0.130	< 0.160	0.084	8.363	2344.531	9.724	< 0.05
4AD-2	1546.783	7.405	1.559	14.609	17.937	1.765	0.306	< 0.160	< 0.075	4.240	1515.738	7.517	< 0.05
4BA-1	2169.950	5.490	1.444	25.114	27.852	1.574	< 0.130	< 0.160	0.075	3.898	1301.861	5.494	< 0.05
4BA-2	1448.194	3.150	0.638	4.502	10.378	1.501	< 0.130	< 0.160	< 0.075	2.725	983.974	7.045	< 0.05
4BB-1	1515.447	12.803	4.460	12.773	26.804	2.538	0.349	< 0.160	0.087	6.816	2269.309	30.182	< 0.05
4BB-2	1519.451	6.910	2.333	6.866	13.358	2.407	0.132	< 0.160	< 0.075	5.855	2101.222	13.276	< 0.05
4BC-1	1358.595	3.582	0.821	4.913	11.095	1.138	< 0.130	< 0.160	< 0.075	3.162	937.429	32.921	< 0.05
4BC-2	1757.768	13.223	5.307	14.605	24.521	3.948	< 0.130	< 0.160	0.245	10.437	3540.045	36.430	< 0.05
4BD-1	1645.209	4.752	1.410	5.304	12.583	1.613	< 0.130	< 0.160	< 0.075	3.859	1416.104	9.516	< 0.05
4BD-2	2044.468	6.993	1.219	6.613	15.463	1.436	< 0.130	< 0.160	< 0.075	3.918	1451.130	10.825	< 0.05

\*All units are mg/kg soil

**Table IV-1. Phase IV pH, EC, DOC and Anion Summary\***

<b>Sample ID</b>	<b>pH</b>	<b>DOC</b>	<b>EC (uS/cm)</b>	<b>Chloride</b>	<b>Bromide</b>	<b>Nitrate</b>	<b>Sulfate</b>
A01-1A0-001	6.36	7.552	36.1	3.91	< 0.05	< 0.03	0.58
A01-2A0-001	6.44	6.733	37.7	5.11	< 0.05	0.08	0.85
A01-3A0-001	6.35	8.959	34.9	5.05	< 0.05	< 0.03	0.70
A01-4A0-001	6.35	8.074	35.9	4.25	< 0.05	< 0.03	0.67
A01-NEW-001	6.61	7.500	36.9	3.82	< 0.05	< 0.03	0.55
A01-OLD-001	7.72	3.112	38.0	4.35	< 0.05	0.70	0.85
A01-SPL-001	9.32	5.424	38.0	4.83	< 0.05	0.39	0.86
A01-1B0-001	6.21	10.000	37.1	4.20	< 0.05	< 0.03	0.54
A01-2B0-001	6.26	11.060	35.2	3.78	< 0.05	< 0.03	0.54
A01-3B0-001	6.07	10.710	35.8	5.14	< 0.05	< 0.03	1.53
A01-4B0-001	6.23	8.477	35.5	4.31	< 0.05	< 0.03	0.67

\*DOC and anion units are ppm

Table IV-2. Phase IV Metal Summary\*

<u>Sample ID</u>	<u>Al</u>	<u>Cr</u>	<u>Ni</u>	<u>Cu</u>	<u>Zn</u>	<u>As</u>	<u>Se</u>	<u>Ag</u>	<u>Sb</u>	<u>Pb</u>	<u>Fe</u>	<u>Mn</u>	<u>Hg</u>
A01-1A0-001	11.988	0.244	0.235	3.459	73.957	0.539	0.234	2.127	<0.242	0.099	137.313	40.559	0.051
A01-2A0-001	10.747	0.189	0.369	4.508	54.297	0.535	0.219	<0.160	<0.242	0.117	142.771	68.210	<0.05
A01-3A0-001	47.851	1.257	0.679	3.426	38.156	0.566	0.262	<0.160	<0.242	0.088	156.003	22.952	<0.05
A01-4A0-001	17.683	0.397	0.382	3.695	60.184	0.578	0.231	<0.160	<0.242	0.266	168.361	53.419	<0.05
A01-NEW-001	12.563	0.185	0.169	2.017	57.080	0.513	0.350	<0.160	<0.242	<0.04	129.025	63.039	<0.05
A01-CLD-001	18.802	0.435	0.194	23.834	79.751	0.408	0.329	<0.160	<0.242	0.539	23.279	1.483	<0.05
A01-SPL-001	44.289	0.435	0.141	12.134	51.480	0.499	0.289	<0.160	<0.242	0.521	59.652	1.561	<0.05
A01-1B0-001	12.146	0.422	0.210	2.626	84.641	0.595	0.225	<0.160	<0.242	<0.04	151.741	56.858	<0.05
A01-2B0-001	13.246	0.266	0.189	2.256	54.921	0.519	0.240	<0.160	<0.242	0.362	114.475	75.831	<0.05
A01-3B0-001	11.734	0.288	0.397	2.090	171.945	1.059	0.216	<0.160	<0.242	<0.04	99.965	42.134	<0.05
A01-4B0-001	8.190	0.163	0.662	2.333	60.654	0.483	<0.130	<0.160	<0.242	0.047	132.414	81.778	<0.05

\*All units are in ppb