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METALS RETENTION IN CONSTRUCTED WETLAND SEDIMENT

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ABSTRACT: The A-01 wetland treatment system (WTS) was designed to remove metals from the effluent at the A-01 NPDES outfall at the Savannah River Site, Aiken, SC. Sequential extraction data was used to evaluate remobilization and retention of Cu, Pb, Zn, Mn, and Fe in the wetland sediment. Remobilization of metals was determined by the Potentially Mobile Fraction (PMF) and metal retention by the Recalcitrant Factor (RF). The PMF, which includes water soluble, exchangeable, and oxides fractions, is the contaminant fraction that has the potential to enter into the mobile aqueous phase under changeable environmental conditions. PMF values were low for Cu, Zn and Pb (about 20%) and high for Fe and Mn (about 60 to 70%). The RF, which includes crystalline oxides, sulfides or silicates and aluminosilicates, is the ratio of strongly bound fractions to the total concentration of elements in sediment. RF values were about 80% for Cu, Zn and Pb, indicating high retention in the sediment and 30% to above 40% for Fe and Mn indicating low retention.

INTRODUCTION

Constructed wetlands have the ability to remove pollutants from water and retain them in sediment. Removal mechanisms can act uniquely, sequentially, or simultaneously on each contaminant group or species. Contaminant retention processes in constructed wetland sediments may be abiotic (physical/chemical) or biotic (microbial/phytological). The primary abiotic processes include 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. Biotic processes like biodegradation and plant uptake can also influence contaminant levels in wetland sediments. Some microbial/phytological processes occurring in wetlands include aerobic/anaerobic biodegradation, phytoaccumulation/ phytostabilization, and phytodegradation/rhizodegradation. A variety of microbial metabolic processes play a significant role in the removal of organic compounds, metals, and radionuclides in the aerobic/anaerobic wetland environment, and the products of these reactions are diverse.

The A-01 wetland treatment system was designed to remove metals, especially copper, from the A-01 effluent discharge. The treatment system consists of a stormwater retention basin, a splitter box, and four 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. The flow path of the A-01 effluent is from the retention basin to the splitter box, through the four A-cells, through the four B-cells, to the wetland outfall, and into the receiving stream.

The treatment system was constructed during the winter/spring of 2000 and began receiving A-01 effluent in July 2000. Specht and Nelson (2002) described sediment samples collected and analyzed in September, 2001 to provide baseline data on metal concentrations and general sediment chemistry early in the operational life of the treatment system. This paper describes the results of a second sampling program conducted in July-August, 2003 to evaluate retention of contaminants in the wetland sediment and their potential remobilization from the sediment into the water column.

MATERIALS AND METHODS

Sediment Sampling. Sediment sampling was conducted in cells 4A and 4B, with each cell being spatially divided into quarters along its long axis (Figure 1). Five cores were collected from each quarter using Plexiglas core tubes with plastic caps on each end. Samples were assigned a letter designating sampling location: "a" locations were near the influent progressing to "d" locations near the discharge point of each treatment cell. A 5 cm inorganic layer from below the highly organic surface detritus was analyzed from each sediment core.

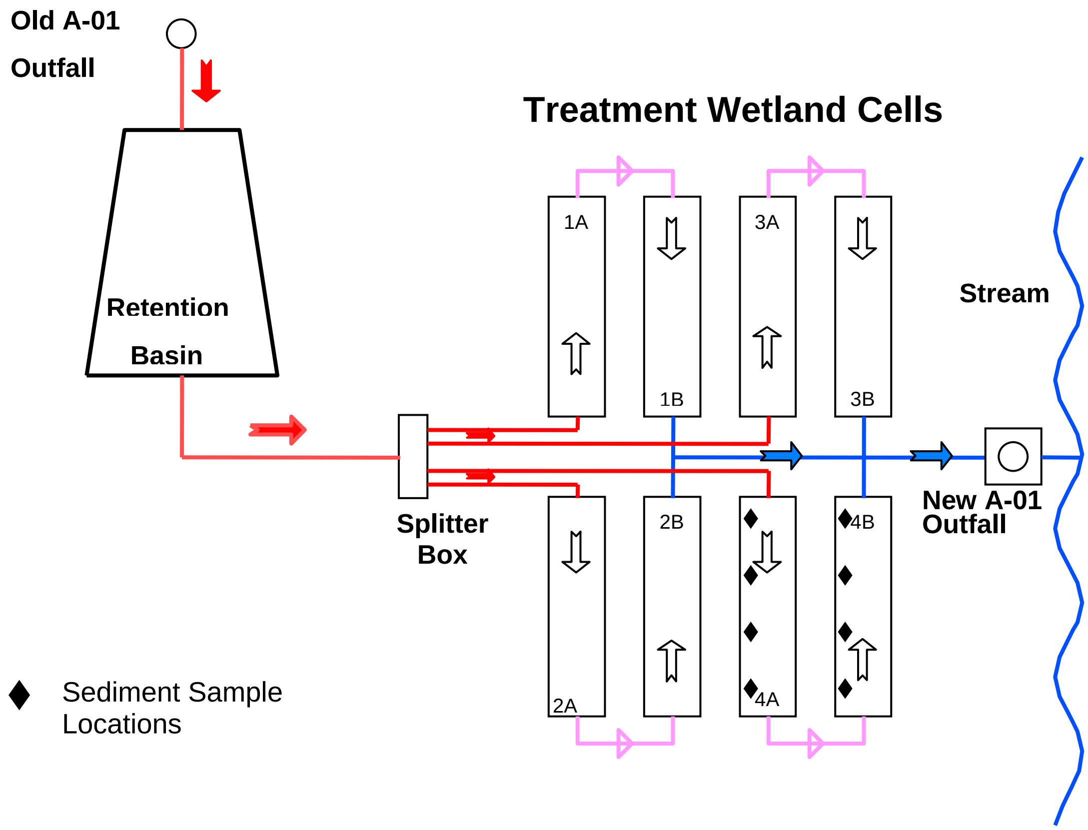

FIGURE 1. Schematic of the A-01 Wetland Treatment System and sampling locations.

Sediment sample analysis. The sediment samples were analyzed for total metal concentrations, with HNO_3 and HF acids according to EPA 3052 by inductively coupled plasma-mass spectroscopy (ICP-MS) using a Perkin Elmer Model Elan 6000. Additionally, an eight-step sequential extraction was performed on 1 g subsamples of selected sediment samples. 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). The following fractions were extracted: 1) water soluble, 2) exchangeable, 3) acid soluble metals/acid volatile sulfide (AVS), 4) MNO_2 occluded metals, 5) organically bound metals, 6) amorphous Fe oxides, 7) crystalline Fe oxides, and 8) residual (Knox et al., 2004). 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.

RESULTS AND DISCUSSION

Cu, Zn, and Pb concentrations in the A-01 effluent were reduced 70 to 80% by passage through the wetland treatment system (Knox et al. 2004, Nelson et al., 2002). However, Fe and Mn often increased after passage through the system. Sediment concentrations of Cu and Zn, two elements for which both 2001 and 2003 data were available, increased over time indicating that Cu and Zn accumulated in the sediment. Total sediment metal concentrations in the 4A and 4B treatment cells during 2003 averaged 5.5 ppm for Cu, 3506 ppm for Fe, 37 ppm for Mn, 10.1 ppm for Zn, and 5.6 ppm for Pb.

Understanding metal biogeochemistry in the A-01 wetland necessitates an investigation of solid phase chemical speciation because the particular distribution of metal compounds and their interaction with the native matrix under aqueous conditions determines their environmental mobility, bioavailability, and retention. The main intent of conducting sequential extractions was to determine how strongly metals were bound to the wetland sediment. Early extraction steps (water soluble, exchangeable, acid soluble [AVS] metal, amorphous Mn and Fe oxides, and organic fractions) tend to recover metal fractions that are less strongly bound than the fractions collected in the later extraction steps (crystalline oxides, sulfides, and residue fractions). These less strongly bound fractions can be termed the Potentially Mobile Fraction (PMF) because they constitute the contaminant fraction that has the potential to enter into the mobile aqueous phase under changeable environmental conditions, such as pH, Eh, temperature, etc.. Generally, only water and exchangeable fractions are very easily mobile and available to plants or organisms, although under reduced wetland conditions water, exchangeable, and perhaps oxides fractions could be easily remobilized. The PMF was estimated using Equation 1:

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

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

The sulfide fraction was omitted from this equation because it was not extracted in the sequential extraction; therefore, PMF values could be overestimated. The idea behind this construct is that the entire contaminant pool may not be accessible to the mobile aqueous phase.

The strongly bound fractions collected in the later extraction steps are likely to include metals that will be retained by the wetland sediments. Fractions of the contaminant pool that are very strongly bound by the sediment include crystalline oxides, sulfides or silicates, and aluminosilicates. These strongly bound fractions can be used to calculate the Recalcitrant Factor (RF). The RF is the ratio of strongly bound fractions to the total concentration of the element (i.e., sum of all fractions) in the sediment. 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. For this study the RF was calculated using Equation 2:

$$Recalcitrant\ \ Factor = \left[\frac{C_{cry.oxides} + C_{residual}}{C_{exch} + C_{AVS} + C_{org} + C_{oxides} + C_{residual}} \right] \times 100 \qquad (2)$$

where *C* represents concentration, and the subscripts *crystalline oxides* and *residual*, represent the two final fractions of the sequential extractions. 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 sequential extraction data showed that the distribution of Cu among the eight fractions was similar for all samples (Table 1). Only about 1% of the Cu was 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. 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 (average of 5.1% compared with 1.9% for cell 4B). 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 (Tessier et al., 1979, Stumm and Morgan, 1981). Copper has a high affinity for organic matter. However, the organic fraction for the samples was less than 5%, very likely due to the very low organic matter content of the sediment samples (which represented an inorganic layer only). The acid soluble (AVS) and residual fractions were the largest fractions, averaging 10% and 72%, respectively, in cell 4A and 7% and 78%, respectively, in cell 4B. These results are summarized by the PMF and RF values for Cu, which averaged 23% and 77%, respectively, indicating that most Cu was strongly retained by the sediments and not easily extractable (Figure 2).

To conserve space, only PMF and RF values are shown for the other metals of interest (Figure 2). PMF values for Zn and Pb averaged 13% and 27%, respectively, and RF values averaged 87% and 73%, respectively. As with Cu, these relatively low PMF and high RF values indicated that most of the Zn and Pb were strongly bound in the sediment and not easily extractable. In contrast to Cu, Zn, and Pb, the RF values for Fe and Mn were low (30% and 38%, respectively) and the PMF values were high (about 70% and 62%, respectively) indicating high potential desorption from the sediment and high solubility.

SUMMARY

The A-01 WTS removes metals from the A-01 effluent to concentrations that are below regulatory limits. Potentially detrimental elements including Cu, Pb, and Zn were strongly bound to the sediments suggesting they were in stable forms and unlikely to be

Table 1. Copper (in %) in various sediment phases.

Samples	Water	Exch.	Acid Soluble (AVS)	MnO_2 Occluded	Organic	Am. FeO	Cry. FeO	Residual
	%	%	%	%	%	%	%	%
4A-a	1.0	1.1	12.7	6.5	4.6	3.2	1.8	69.1
4A-b	0.8	0.9	7.9	5.9	4.7	2.9	2.0	75.0
4A-c	1.2	0.7	12.4	5.7	4.0	7.7	1.6	66.7
4A-d	1.2	0.8	4.8	5.4	3.2	6.5	2.0	76.1
Avg 4A	**1.0**	**0.9**	**9.5**	**5.9**	**4.1**	**5.1**	**1.9**	**71.7**
Stdev 4A	**0.2**	**0.2**	**3.8**	**0.4**	**0.7**	**2.4**	**0.2**	**4.5**
4B-a	2.2	0.6	4.9	4.0	3.3	2.4	2.4	80.2
4B-b	0.8	0.8	4.6	5.2	2.4	1.8	1.8	82.8
4B-c	0.7	0.6	3.2	2.5	1.8	1.7	1.7	87.8
4B-d	2.9	1.5	13.5	8.6	7.2	1.7	1.7	62.9
Avg 4B	**1.6**	**0.9**	**6.5**	**5.1**	**3.7**	**1.9**	**1.9**	**78.4**
Stdev 4B	**1.1**	**0.4**	**4.7**	**2.6**	**2.5**	**0.4**	**0.4**	**10.8**
Avg of 4A &4B	**1.3**	**0.9**	**8.0**	**5.5**	**3.9**	**3.5**	**1.9**	**75.1**
Stdev 4A & 4B	**0.8**	**0.3**	**4.2**	**1.8**	**1.7**	**2.3**	**0.3**	**8.5**

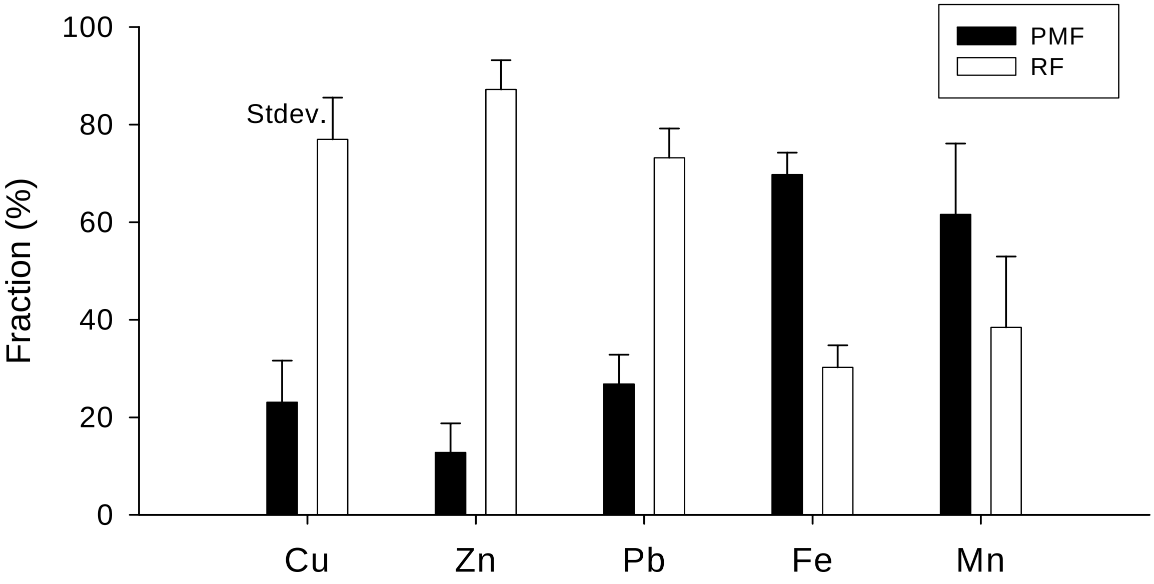

FIGURE 2. Mean potentially mobile fraction (PMF) and Recalcitrant factor (RF) for elements in sediment samples from cells 4A and 4B.

released. 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 and released to the water column or air. 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. Future research will focus on the evaluation of metal binding by organic matter in the floc and organic sediment layers.

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