



Evaluation of a constructed wetland : sediment characterization and laboratory simulation of wetland chemical processes
by Dale Weller Lyons

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Land Rehabilitation
Montana State University
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Abstract:

Hard rock mining frequently results in acid mine drainage (AMD) or metal contamination of surface/groundwater resources. Constructed wetlands have been used as a method to remove metals from AMD and subsequently minimize environmental impact. This study was conducted to evaluate the geochemical processes responsible for removal of Cu, Fe, and Zn in a constructed wetland built to treat metal contaminated groundwater underlying the old Colorado Tailings impoundment (Butte, MT). A field study, which focused on the characterization of wetland sediments using chemical sequential extractions and scanning electron microscopy with energy dispersive analysis (SEM/EDAX), was coupled with thermodynamic geochemical modeling (MINTEQA2) of the wetland influent waste stream to predict possible solid phase formation. In concert with the field study, laboratory simulations of Cu and Zn sulfide formation in the presence and absence of Fe oxide were conducted in order to determine the fate of sorbed metals upon exposure to sulfide. The formation of sulfide phases in the presence of Fe oxide with sorbed Cu and Zn at 0.01 atm H₂S (g) was observed using sequential extraction, SEM/EDAX, and x-ray photoelectron spectroscopy (XPS). Geochemical modeling and direct analysis of wetland sediment phases suggest that sedimentation of oxides, carbonates, and sorbed phases occurred primarily in the upstream settling pond, of the constructed wetland, with possible formation of sulfide phases in the two downstream ponds. These processes resulted in significant removal of Cu and Fe, and to a lesser extent, Zn. Results from laboratory simulations of Cu and Zn sulfide formation indicate that the presence of Fe oxides do not inhibit the formation of Cu sulfide.

. However the rapid precipitation of Cu sulfide on the surface of Fe oxides may limit the interaction between dissolved sulfide and sorbed Zn. This has implications in the constructed wetland system where low concentrations of dissolved organic carbon may limit sulfide production, thereby precluding the formation Zn sulfide phases.

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CHEMICAL PROCESSES

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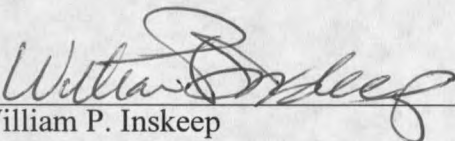
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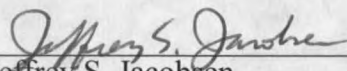
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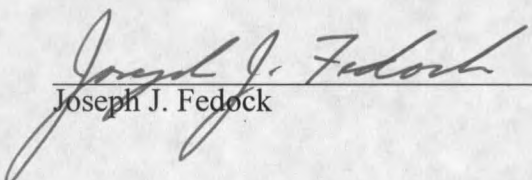
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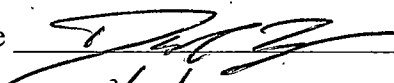

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ABSTRACT

Hard rock mining frequently results in acid mine drainage (AMD) or metal contamination of surface/groundwater resources. Constructed wetlands have been used as a method to remove metals from AMD and subsequently minimize environmental impact. This study was conducted to evaluate the geochemical processes responsible for removal of Cu, Fe, and Zn in a constructed wetland built to treat metal contaminated groundwater underlying the old Colorado Tailings impoundment (Butte, MT). A field study, which focused on the characterization of wetland sediments using chemical sequential extractions and scanning electron microscopy with energy dispersive analysis (SEM/EDAX), was coupled with thermodynamic geochemical modeling (MINTQA2) of the wetland influent waste stream to predict possible solid phase formation. In concert with the field study, laboratory simulations of Cu and Zn sulfide formation in the presence and absence of Fe oxide were conducted in order to determine the fate of sorbed metals upon exposure to sulfide. The formation of sulfide phases in the presence of Fe oxide with sorbed Cu and Zn at 0.01 atm H_2S (g) was observed using sequential extraction, SEM/EDAX, and x-ray photoelectron spectroscopy (XPS). Geochemical modeling and direct analysis of wetland sediment phases suggest that sedimentation of oxides, carbonates, and sorbed phases occurred primarily in the upstream settling pond, of the constructed wetland, with possible formation of sulfide phases in the two downstream ponds. These processes resulted in significant removal of Cu and Fe, and to a lesser extent, Zn. Results from laboratory simulations of Cu and Zn sulfide formation indicate that the presence of Fe oxides do not inhibit the formation of Cu sulfide. However the rapid precipitation of Cu sulfide on the surface of Fe oxides may limit the interaction between dissolved sulfide and sorbed Zn. This has implications in the constructed wetland system where low concentrations of dissolved organic carbon may limit sulfide production, thereby precluding the formation Zn sulfide phases.

CHAPTER 1

INTRODUCTION

Many factors affect trace metal mobilization in wetland environments. To a large degree, the mobility and cycling of trace metals depends on the properties of the trace metals themselves (i.e. solubility, reactivity for complexation or adsorption) (Tessier, 1989). Physical properties of wetland soils and sediments influencing metal speciation include texture, and type of clay mineralogy. Chemical properties that influence trace metal phase partitioning in wetlands include: oxidation-reduction status (pe), pH, organic matter content, salinity, and the presence of inorganic chemical components such as carbonates, sulfides, and oxide mineral phases. Oxidation-reduction status decreases as oxygen is consumed as a terminal electron acceptor in the microbially mediated process of carbon oxidation. As free oxygen is depleted from a system, the microbial community then turns to alternate electron acceptors such as NO_3^- , Fe^{3+} , Mn^{4+} , SO_4^{2-} , and other oxidized species. Hydrogen sulfide gas produced from the de-oxygenation (reduction) of SO_4^{2-} , then combines with reduced metal ions to form sulfide solid phases; this process being the primary pathway for metal removal in anoxic environments (Elder, 1988). Conversely, in oxidized waters with high concentrations of dissolved metals (i.e. acid mine drainages), the formation of Fe and Mn oxide solid phases is prevalent at near neutral pH. Oxide solid phases are important in acid mine drainages because they have

the potential to adsorb an abundance of contaminant metals, and subsequently remove these metals from solution (Gambrell, 1994). The control of metal activities in solution by the sorption to oxide phases has been well documented (Benjamin and Leckie, 1981; Bleam and McBride, 1985; Catts and Langmuir, 1986; Hatrer and Naidu, 1995; Zasoski and Burau, 1988).

The thesis research has attempted to elucidate geochemical processes responsible for metal removal in wetlands by combining field and laboratory based studies. In Chapter 2, I discuss the characterization of sediments collected from a pilot scale constructed wetland built in Butte, MT for the purposes of treating metal contaminated groundwater. The primary objectives of this research were to: 1) perform geochemical modeling of influent and wetland bulk water to determine potential of sorption reactions and precipitation reactions to remove Cu, Fe, and Zn; 2) characterize recently deposited wetland sediments to identify solid phase reactions controlling fate and distribution of Cu, Fe, and Zn; and 3) compare geochemical modeling results with direct characterization of aqueous and sediment samples to evaluate the potential for long-term treatment of Cu, Fe, and Zn. Given that Fe oxides solid phases serve as a potential sink for contaminant metals in wetlands, the research discussed in Chapter 3 focused on the fate of sorbed metals upon exposure to reducing environments where sulfide production occurs. The objective of this research was to determine whether the formation of Cu and Zn sulfide phases occur in the presence of Fe oxides, under conditions where aqueous sulfide species were controlled by fixing the partial pressure of H_2S (g) in a stirred reaction chamber.

CHAPTER 2

EVALUATION OF Cu, Fe, Zn, and S GEOCHEMICAL PROCESSES IN A CONSTRUCTED WETLAND: SEDIMENT CHARACTERIZATION

Introduction

In recent years, constructed wetlands have been used for the treatment of metal contaminated waters (Hammer and Bastien, 1989; Kleinmann, 1985). Studies of constructed wetlands built for the treatment of acid mine drainage (AMD) have documented their ability to remove As, Cu, Fe, Pb, Zn and other metals, as well as raise pH (Brodie et al., 1988; Karathanasis and Thompson, 1990; Eger, 1992; Machemer and Wildeman, 1992). Field studies of constructed wetlands have also shown that the primary mechanisms responsible for metal removal in oxidized environments involve precipitation of metal hydroxides and carbonates, and sorption reactions of metals by oxides (Fe, Al, Mn) and natural organic matter (NOM) (Karathanasis and Thompson, 1995; and Machemer and Wildeman, 1992). In reduced environments, it has been demonstrated that the respiratory products of sulfate reducing bacteria (H_2S) can precipitate dissolved divalent metals as metal sulfides and subsequently reduce aqueous phase trace metal concentrations (Jenne, 1968; Elder, 1988; Eger, 1992; Gambrell, 1994). While metal removal in wetlands is mediated by aerobic and anaerobic processes, the relative importance of specific mechanisms is dependent on pH, redox status (pe), and

concentrations of SO_4^{2-} necessary to produce S^{2-} for metal sulfide precipitation (Jenne, 1968).

In efforts to control the many chemical, biological, and physical variables that are important in constructed wetlands, many researchers have simulated constructed wetland treatment of acid mine drainage in bench scale experiments, which have been found to correlate with geochemical processes in actual wetlands constructed for the treatment of AMD (Bolis et al., 1991). Iron retention was found to be predominantly controlled by Fe oxide precipitation, and secondarily by Fe binding to organics in oxidized sphagnum peat moss substrates. The formation of Fe oxide was found to be inhibited by antiseptics (formaldehyde), suggesting Fe oxide formation is microbially mediated (Henrot and Wieder, 1990). Using a bench-scale biogenic sulfide and limestone treatment system, Hammock et al. (1994) found that 99% of Fe, Cu, Zn, and Al were removed from contaminated water. It was also found that Cu and Zn concentrates could be selectively recovered from the wastewater based on pH-dependent dissociation of H_2S (g). Christensen et al. (1996) found that sulfide production was initially boosted by inoculation of sulfate reducing bacteria in bench scale treatment chambers. However, over an extended period, sulfide production and subsequent precipitation of Cu, Fe, and Zn sulfides was not enhanced by inoculation. Dvorak et al. (1992) found that Cd, Fe, Ni, and some Zn were retained as sulfides in bench-scale chambers using spent mushroom compost, while Al, Mn, and some Zn were retained as insoluble hydroxides and carbonates. Ozawa et al. (1995) established that the primary mechanism for the removal of As, Cr, Cd, Cu, Fe, Pb, and Zn in an manure filled bioreactor was sulfide precipitation resulting from biogenic SO_4^{2-} reduction. In summary, studies of aerobic and anaerobic

wetland geochemical processes have been useful in assessing wetland treatment efficiency, and long term fate of metals sequestered in wetland systems.

The current study involves a pilot scale constructed wetland built for the purposes of treating metal contaminated groundwater underlying the old Colorado Tailings, in Butte, Montana. The Colorado Tailings depository (sometimes referred to as Lower Area One) covers an area of approximately 12 ha in the historic flood plain of Silver Bow Creek, bordered by I-90 and the Burlington Northern Railroad on the south and by Silver Bow Creek on the North.

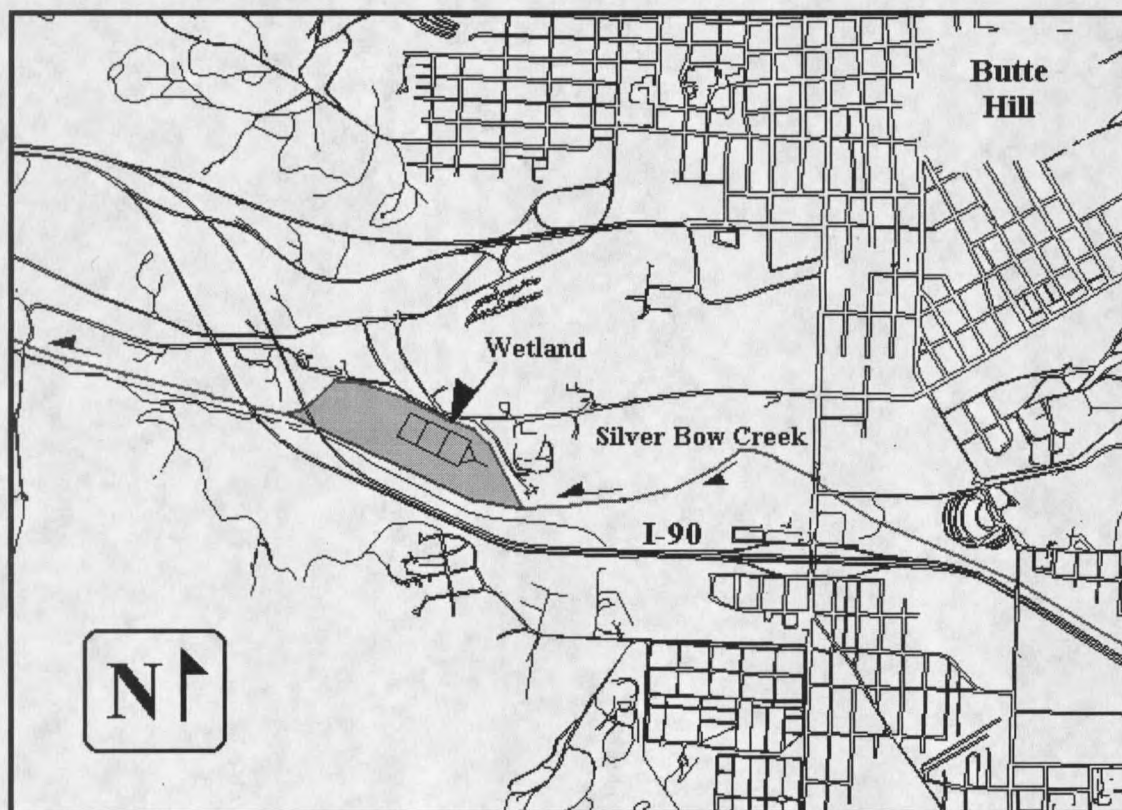


Figure 1. Overhead map of Lower Area One (shaded region) and Colorado Tailings wetland project site, Butte, MT.

The impoundment served as the waste depository of the Colorado and Montana Smelting Company's smelter and concentrator activities from 1879 to 1917. Originally, this site was a natural wetland primarily composed of an organic rich "peat" layer. This material, as well as the associated groundwater, which discharges into Silver Bow Creek, is now contaminated with numerous metals including Cd, Cl, Cu, Fe, Pb, and Zn. At present, the Atlantic Richfield Company (ARCO) has nearly completed the removal of contaminated materials from the flood plain of Silver Bow Creek, a process which began in 1994. A pilot scale constructed wetland was built within the old impoundment to treat groundwater prior to discharging into Silver Bow Creek. Groundwater has been pumped from down gradient positions within Lower Area 1 to the influent of the constructed wetland since January, 1997, with an average flow of 470 L/min. The pH of the unammended waste stream ranges from 6 - 7.5; although not particularly acidic, the influent is periodically treated with calcium hydroxide ($\text{Ca}(\text{OH})_2$) depending on the influent flow rate. The constructed wetland design consists of three settling ponds separated by two berms composed of cobbles and organic substrate. (Figure 2). The berms, as well as the sides of the ponds were initially planted with cattail (*Typha latifolia* L.). Hereafter, the three settling ponds will be referred to as Free Water 1-3 (FW1-3), and the two berms will be referred to as Treatment Wall 1 & 2 (TW1 and TW2).

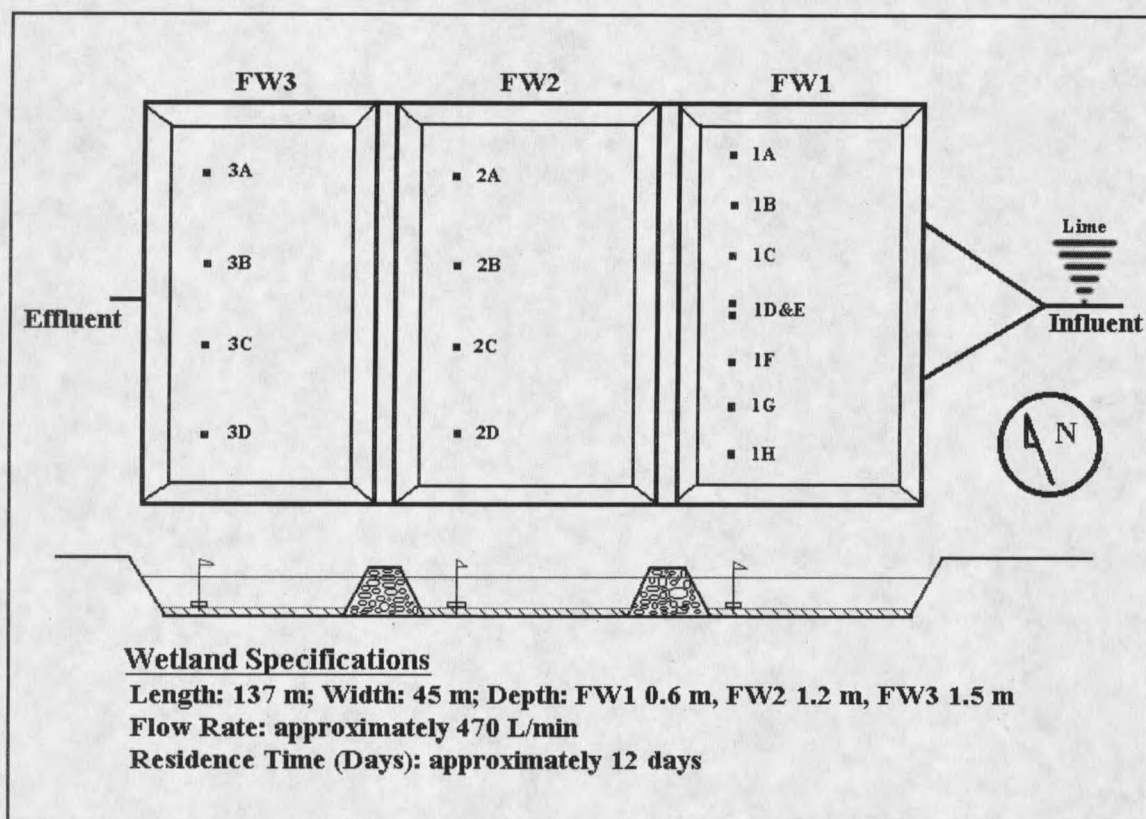


Figure 2. Colorado Tailings constructed wetland: specifications and location of sediment samplers.

The constructed wetland design was expected to facilitate precipitation of metal (Cu, Fe, Zn) hydroxides and sorption reactions in the aerated ponds, while encouraging metal sulfide precipitation in reduced environments of the treatment walls and pond sediments. The objectives of this research were to: 1) perform geochemical modeling of influent and wetland bulk water to determine potential of sorption and precipitation reactions to remove Cu, Fe, and Zn; 2) characterize recently deposited wetland sediments to identify solid phase reactions controlling fate and distribution of Cu, Fe, and Zn; and 3) compare geochemical modeling results with direct characterization of aqueous and sediment samples to evaluate the potential for long-term treatment of Cu, Fe, and Zn.

Geochemical modeling and direct analysis of sediment phases suggest that the present geochemical processes result in sedimentation of oxides, carbonates and sorbed phases primarily in FW1, with possible formation of sulfide phases in FW2 and FW3. These processes result in significant removal of Cu and Fe, and to a lesser extent, Zn.

Materials and Methods

Water Analysis

Influent, surface water, and effluent samples from the constructed wetland site were collected weekly and analyzed for a suite of constituents in collaboration with ARCO and the Dept. of Chemistry and Geochemistry (University of Montana - Montana Tech). Water samples were filtered with 0.2 μm nylon filters, and analyzed using inductively coupled plasma spectrometry (ICP-AES) and ion chromatography (IC). Average concentrations of dissolved (i.e. $<0.2 \mu\text{m}$) constituents compiled over the life of the project were used for geochemical modeling of the influent wastewater. The influent wastewater stream, and water within the wetland ponds, was also monitored for pH, redox potential (pe), electrical conductivity (EC), and dissolved oxygen (DO) with a Datasonde 3 Multiprobe (Hydrolab, Inc. Austin TX.) at the time of sample collection. Unfiltered aqueous samples were titrated with 0.01 M HCl to a pH 4.7 end-point to estimate total alkalinity.

Geochemical Modeling

Dissolved metal and ligand concentrations of influent wastewater (Table 1), compiled since construction of the wetland (1/97 to 4/98), were used as input data to the aqueous geochemical model MINTEQA2 (Allison et al., 1991). This model was used to predict saturation states (saturation index = $\log [\text{ion activity product} / \text{solubility product}]$) of potential solid phases over a range in redox potentials (pe). Because MINTEQA2 has no implicit kinetic considerations, it is more useful to interpret the results on the basis of evaluating thermodynamically favorable solids that are also kinetically favorable within the limited residence time of the constructed wetland. MINTEQA2 was also used to evaluate the potential role of sorption reactions on Fe oxide surfaces within the influent wastewater. The water chemistry of the influent waste stream has varied considerably over the course of the project as a result of tailings removal activities and subsequent hydrologic alterations. The influent water chemistry data used for geochemical modeling represented average values from several months of water monitoring; consequently, modeling results for influent water chemistry were interpreted as an approximation to the types of solid phases that may form in the constructed wetland. Additional modeling was conducted using water chemistry data of FW1, FW2, and FW3 on multiple sample dates to evaluate possible solid phases controlling the solubility of Fe, Cu, and Zn within the settling ponds.

Sediment Collection

In early July, 1997, 16 sediment collection traps were installed in the constructed wetland. The sediment collection traps consisted of a 20 x 20 x 8 cm deep polyethylene pan bolted to a 2 m long epoxy-coated threaded rod (0.5 cm diameter). The trap was perforated on the bottom and lined with 100-mesh polypropylene screen to prevent disruption of downward flow. Eight samplers were submerged, equally spaced, along the length of TW1 (treatment wall 1) in the deepest section of FW1 (pond 1), approximately 5 meters from TW1. Four sediment samplers were installed in each of the downstream ponds (FW2 and FW3) in the same fashion (Figure 2). At the time of sample collection, a weighted plastic disc (approximately 20 cm diameter) with a hole drilled in the center was placed on the sampler rod and allowed to submerge. This disc came to rest on top of the sediment collection traps and minimized disruption of sediment during removal.

Wetland sediments were collected once in September, and again in November, 1997. In September, sediments were collected from three samplers located within FW1: 1A, 1D, and 1G (Figure 2). In November, FW1 sediments were collected from three samplers: 1B, 1G, and 1H. Several of the FW1 sediment samples were separated into upper and lower fractions for analysis, while other samples (including those from FW2 and FW3) were composite samples (Appendix A). A total of four sediment samples were collected from FW2: 2A and 2D sampled in September; and 2A and 2B sampled in November. In addition to the sediments collected from FW2, a portion of an algal mat was also collected from this pond. A total of five sediment samples were collected from FW3: 3A, 3B, and 3D sampled in September; and 3B and 3C sampled in November.

Three soil samples were also collected from the site to serve as reference samples for comparison to sediments collected from the constructed wetland. One soil sample was taken from the northern wall of the wetland which was reportedly composed of uncontaminated fill material brought in from off site, and two samples of "peat" material which reportedly represents the bottom of the constructed wetland (John Pantano - ARCO, personal communication, 1997).

Suspended solids from the bulk water column of FW1 were collected in September, 1997 by submerging 1.0 L Nalgene bottles to three depths: 1.7 m, 0.75 m, and 0.1 m, followed by filtration using 0.2 μ m nylon filters. Suspended solids were also collected from the influent waste stream upstream from the lime amendment.

Sediments Analysis

Sediment samples were analyzed for a number of physical and chemical parameters including gravimetric water content, bulk density, particle size fraction, % organic matter (OM), total organic carbon (TOC), total organic nitrogen (TON), total organic sulfur (TOS), and calcium carbonate equivalent (CCE).

Total organic C (TOC) was determined by a modified Walkley-Black procedure; organic matter (OM) was determined using an assumed relationship between OM and TOC ($\text{TOC} \times 1.7 = \text{OM}$) (Nelson and Sommers, 1982). Total organic N was determined using a LECO furnace. Total organic S was determined by digestion of OM (whole sample) with nitric-perchloric acid, followed by S analysis using ICP-AES (Tabatabai, 1982). The calcium carbonate equivalent (CCE) was determined by measuring weight loss of a 2 g sample upon addition to 10 mL of 3M HCl (Nelson, 1982).

Sequential Extraction of Wetland Sediments

A sequential extraction procedure, adapted from the methods outlined by Tessier et al. (1979, 1984, and 1989), Chao (1984), and Belzile and Tessier (1990), was used to partition metals into operationally defined chemical fractions using a series of extraction steps. Sediment samples of 1 g (duplicate or triplicate) were weighed into 40 mL centrifuge tubes and subjected to the following:

- 1) Exchangeable metals – sediment samples were extracted under continuous agitation for 30 min with 8 mL of 1M MgCl initially at pH 7.0. Final reagent was deaerated with N₂ gas.
- 2) Metals bound to carbonates – sediment samples were extracted 5 h under continuous agitation with 8 mL of 1M Na acetate (CH₃COONa) buffered at pH 5.0 with 17.4 N CH₃COOH (acetic acid).
- 3) Metals bound to Mn oxides – sediment samples were extracted for 30 min under continuous agitation with 8 mL 0.1 M NH₂OH * HCl (hydroxylamine hydrochloride) in 0.1 M HNO₃.
- 4) Metals bound to Mn-Fe oxides – sediment samples were extracted for 6 h under continuous agitation at 96 °C with 8 mL of 0.04 M NH₂OH * HCl in 4.4 M CH₃COOH. Final reagent was deaerated with N₂ gas.
- 5) Metals bound to organic matter and sulfides – sediment samples were extracted for 5 h under occasional agitation at 85 °C with 8 mL 30% hydrogen peroxide (H₂O₂) initially adjusted to pH 2 with HNO₃. Care was taken to leave lids of the centrifuge

tubes cracked. After cooling, the sediment was extracted for 30 min at room temperature under occasional agitation with 8 mL of 3.2 M NH_4OAc in 3.2 M HNO_3 .

- 6) Residual metals – total digestion of remaining material with 5 parts 15.8 M HNO_3 and 1 part 11.6 M HClO_4 for 30 min. at 120 °C, 30 min. at 150 °C, and 30 min at 170 °C.

Between each extraction step, the suspensions were centrifuged at 15,000 rpm (17,540 g) for 30 min. The supernatant was then decanted into test tubes, diluted (1:10) with 2% 12.4 N HCl in a 0.01M KCl background solution, and analyzed for the following elements: As, Al, Fe, Cu, Mn, Mg, Zn and S using ICP-AES. Between each extraction step, the sediment samples were washed with 8 mL of DI water to remove previous reagent. Following centrifugation, supernatants were decanted before the next extraction step.

Commercially available ZnS and CuS (Aldrich Chemical Company) and laboratory prepared samples of 2-line ferrihydrite, with and without known amounts of sorbed Cu and Zn, were also analyzed using sequential extraction. These control samples were only subjected to the Mn-Fe oxide and sulfide-OM extractions (steps 4 and 5 listed above). Results from extraction of 2-line ferrihydrite containing sorbed Cu and Zn and pure CuS or ZnS indicated that the Mn-Fe oxide and sulfide-OM extraction steps were an accurate measure of the metals bound in two fractions. Of the extractable Cu and Zn from ferrihydrite with sorbed Cu and Zn subjected to sequential extraction, >99% was

extracted in the Mn-Fe oxide extraction step. Likewise, >98% of the extractable Cu, Zn and S present as CuS and/or ZnS was recovered in the sulfide-OM extraction step.

The averaged sequential extraction data shown in Figures 4-7 (with Mn and Mn-Fe oxide fractions combined) is compiled in Table 7 (Appendix A). All of the data for the sequential extractions of the wetland sediments and soil samples are compiled in Table 8 (Appendix A). Although they will not be discussed here, graphs of sequential extraction results for Al, As, Mn, P, and Pb are found in Figures 31-35 (Appendix A).

Surface Analysis of Wetland Sediments

Sediment collected from FW1, FW2, and FW3, as well as suspended solid from the influent and FW1 bulk pond water were analyzed using scanning electron microscopy (SEM), coupled with energy dispersive analysis of x-rays (EDAX) [Imaging and Chemical Analysis Laboratory (ICAL), Montana State University]. Particles containing heavy metals (e.g. aluminosilicates, Fe oxides, and sulfide solid phases) were located among aggregate samples using backscattered electron detection (BSE) and analyzed using EDAX in order to determine elemental composition. Observational and chemical analysis (SEM/EDAX) was used to confirm the existence of discrete mineral phases within the sediments.

Results

Influent Water Chemistry

The dominant cations and anions in the influent waste stream were Ca, Mg, Na, and SO_4^{2-} (Table 1). Dissolved Cu and Zn were significantly higher than aquatic standards (Circular WQB-7) and were the primary focus of wetland treatment. Although high levels of trace elements are often associated with low pH in acid mine drainages, the influent wastewater was near neutral (ranging from 7.0 to 8.5 from 1/97 - 4/98). Electrical conductivity (EC) in the influent wastewater ranged from 8.5 to 9.5 dS/m (mS/cm) from 1/97 - 4/98. Monitoring data for the wetland system shows reduction especially in Cu (one order of magnitude), Fe (two orders of magnitude), and to a lesser extent Zn (2 fold). Reductions in Cu, Fe, and Zn result in calculated treatment efficiencies of 93%, 99%, and 61%, respectively (Table 1). The removal of Cu, Fe, and Zn during wetland treatment suggests that the majority of solid phase formation was occurring in FW1, with smaller reductions in metal concentration occurring in FW2 and FW3.

Table 1. Averaged dissolved† water chemistry data of influent waste stream, FW1, FW2, FW3, and effluent stream from 1/97 to 4/98

Constituent	Influent	FW1	FW2	FW3‡	Effluent	% Removal
pH	6.9	7.7	7.4	8.5	8.5	
pe§	6.5	5.9	5.9	6.0	5.8	
DO, mM¶	0.2	0.2	0.3	0.3	0.3	
EC, dS/m	9.5	8.5	9.1	8.5	9.2	
Cations						
Ca, mM	3.3	3.3	3.2	3.3	3.3	0#
Na, mM	2	2	2	2	2	5
Mg, mM	1.2	1.1	1.1	1.1	1.1	6
K, µM	200	200	200	200	200	1
Zn, µM	200	100	85	92	77	61
Mn, µM	140	120	110	70	70	49
Fe, µM	70	0.5	0.1	0.1	0.7	99
Cu, µM	42	5.5	3.5	2.4	2.6	94
Cd, µM	0.4	0.3	0.2	0.2	0.2	57
Al, µM	0.4	0.4	0.3	0.4	0.3	18
Anions/ Neutrals						
SO ₄ ²⁻ , mM	3.9	3.8	3.7	3.9	3.8	3
Cl ⁻ , mM	0.96	0.97	0.95	0.96	0.96	0
NO ₃ ⁻ , µM	60	60	60	50	50	14
As, µM	0.7	0.1	0.08	0.1	0.1	85
Si, mM	1.7	0.47	0.45	0.45	0.44	74
Alk., mM	1.3	1.3	1.2	1.0	1.1	0
Charge Balance						
Sum of cations, mM	12.15	11.58	11.41	11.12	12.71	
Sum of anions, mM	8.86	8.65	8.36	8.77	8.61	
% Difference	16.0	14.4	15.4	17.7	13.4	

† dissolved concentrations (i.e. <0.2 µm) as defined by Clesceri et al. (1989)

‡ FW3 surface water analyzed beginning in 7/97

§ pe = E_H (mV)/59.2

¶ dissolved oxygen

% removals calculated prior to rounding

Geochemical Modeling of Influent Waste Stream

Dissolved metal and ligand concentrations of the influent water were used as input data to the geochemical model MINTEQA2 to predict the possible fate of metals and potential solid phase reactions in the wetland environment. Modeling runs were conducted at pH 7.0 over a range of redox potentials (pe 6.0 [355.2 mV] to pe -4 [-236.8 mV]), at a fixed CO₂ (g) partial pressure of 0.003 atm. Based on calculated ion activity products (IAP) and saturation indices (log[IAP/K_{SP}]) for known solid phases, the influent wastewater was oversaturated with respect to numerous solid phases of Cu, Fe, and Zn (Table 2). Under oxidized environments (pe >4), the influent water is oversaturated with respect to cupric ferrite (CuFe₂O₄), cuprous ferrite (α -Cu₂Fe₂O), and Cu(OH)₂. Iron was oversaturated with respect to all of the common Fe oxide minerals (e.g. Fe₃(OH)₈ and ferrihydrite [Fe₅O₈H • 4H₂O]) as well as mixed solids containing Cu mentioned above. In contrast to Cu and Fe, Zn was undersaturated with respect to Zn hydroxides, but near equilibrium with respect to amorphous ZnCO₃ and smithsonite (ZnCO₃). Under highly reduced environments (pe <4), S²⁻ begins to become an important S species, and as a result, the influent water becomes oversaturated with respect to sulfide solid phases of Cu, Fe, and Zn (Table 2).

Table 2. Saturation indices[†] computed from MINTEQA2 using average water chemistry data of the influent waste stream (pH 7.0)

Solid Phase	Redox Potential (pe) [‡]					
	6	4	2	0	-2	-4
Cu(OH) ₂	0.2	0.2	-0.1	-1.9	-3.9	-16.6
α-CuFe ₂ O ₄ (cupric ferrite)	19.8	17.9	13.7	7.9	1.9	-20.9
α-Cu ₂ Fe ₂ O ₄ (cuprous ferrite)	15.9	16.9	16.7	14.9	12.9	-2.9
CuS (covellite)	-55.2	-39.2	-23.5	-9.3	4.7	5.3
CuFeS ₂ (chalcopyrite)	-121	-88.5	-56.8	-26.6	3.4	14.2
Fe ₃ (OH) ₈ (am)	4.9	40.2	0.4	-3.6	-7.6	-20.9
Fe ₅ O ₈ H • 4H ₂ O (ferrihydrite)	3.5	2.6	0.6	-1.4	-3.4	-8.5
Fe ₂ O ₃ (hematite)	20.8	18.9	15.0	11.0	7.1	-3.2
α-FeO ₂ H (goethite)	7.9	6.9	5.0	3.0	1.0	-4.1
1/2γ-Fe ₂ O ₃ (maghematite)	10.4	8.6	4.6	0.6	-3.34	-13.6
Fe ₃ O ₄ (magnetite)	21.5	20.7	16.8	12.9	8.9	-4.5
FeS (am)	-74.7	-57.7	-41.6	-25.6	-9.6	0.6
Fe ₃ S ₄ (greigite)	-278	-214	-154	-94.7	-34.7	5.1
FeS ₂ (pyrite)	-121	-92.2	-64.1	-36.1	-8.1	11.3
ZnCO ₃ • 1H ₂ O	-0.5	-0.5	-0.5	-0.5	-0.5	-9.5
ZnCO ₃ (smithsonite)	-0.7	-0.7	-0.7	-0.7	-0.7	-9.7
ZnS (am)	-68.1	-52.1	-36.1	-20.1	-4.1	0.2
ZnS (sphalerite)	-65.5	-49.5	-33.5	-17.5	-1.5	2.8
ZnS (wurtzite)	-67.5	-51.5	-35.5	-19.5	-3.5	0.8

[†] Saturation index = log [IAP (ion activity product)/ K_{sp} (solubility product)]

[‡] pe = E_H (mV)/59.2

Given the importance of Fe oxides in aquatic systems as a potential sink for Cu and Zn, MINTEQA2 calculations were also performed to evaluate the potential role of sorption reactions on Fe oxides either precipitated or introduced into the wetland as suspended solid. Input parameters necessary to perform sorption calculations were estimated for Fe(OH)₃ (am) based on literature values (Davis and Leckie, 1978a;

Dzombak and Morel, 1990) and included: surface area = $600 \text{ m}^2/\text{g}$, site density = 0.00985 moles/g , and concentration of adsorbing surface = 0.004 g/L . Model predictions of sorption (in conjunction with solid phase precipitation) showed that approximately 68% of Cu^{2+} was sorbed in oxidized environments. As the redox potential decreases ($\text{pe} -4.0$), sorption of Cu was less important in favor of formation of Cu sulfide phases. Conversely, predicted sorption of Zn onto Fe oxides was limited in oxidized conditions (13% of dissolved Zn). As redox potential was decreased ($\text{pe} -4.0$), there was no predicted sorption of Zn, in favor of formation of Zn sulfide solid phases.

In summary, geochemical modeling of the influent wastewater suggests that in oxidized environments both Cu and Fe activities were controlled by hydroxide solid phase precipitation. Sorption of Cu, and to a lesser extent Zn, onto Fe oxides is also predicted to play an important role in oxidized environments. In reduced environments, Cu, Fe, and Zn were all predicted to precipitate as sulfide solid phases.

Water Chemistry of Treatment Ponds

Water monitoring data of FW1, FW2, and FW3 suggests the absence of significant anaerobic zones within the water column of the constructed wetland. During the study period (1/97 to 4/98), concentrations of dissolved organic carbon (DOC) within FW1, FW2, and FW3 remained relatively constant at approximately 2 mg/L . In addition, there wasn't a significant decrease in dissolved oxygen (DO) or redox potential (pe) in FW2 and FW3 relative to FW1, which have remained at approximately 0.2 mM and 350 mV , respectively.

In order to evaluate potential solid phase control of Cu, Fe, and Zn concentrations within FW1, FW2, and FW3, dissolved metal and ligand concentrations and associated pH values from representative sampling days between 1/97 and 11/97 were used as input to MINTEQA2. Calculated activities of free Cu^{2+} , Fe^{3+} , and Zn^{2+} were plotted vs. pH along with solubility relationships for several possible solid phases (Figure 3). Activities of Cu^{2+} , Fe^{3+} , and Zn^{2+} exhibited a similar pH dependence expected for equilibrium with hydroxide and/or carbonate solid phases. In fact, variations in metal activity among FW1, FW2, and FW3 were correlated with changes in pH rather than sample location. Calculated Cu^{2+} activities coincided with solubility lines for $\text{Cu}(\text{OH})_2$ (am) and malachite at pH values <8.5 . In all cases, Cu^{2+} activities were oversaturated with respect to cupric ferrite; however, the formation of this phase may be kinetically limited within the residence time of the constructed wetland (12 d). Calculated Fe^{3+} activities were oversaturated with respect to all typical Fe oxide phases (i.e. goethite, ferrihydrite) as well as $\text{Fe}(\text{OH})_3$ (am) and indicated the potential formation of Fe oxide phases in all FW ponds. Variations in Fe^{3+} activity among FW1, FW2, and FW3 were also inversely correlated with pH, rather than with sample location. As observed with Cu and Fe, there were no significant differences in Zn^{2+} activities among FW1, FW2, and FW3. At pH <8.5 , Zn^{2+} activities were near equilibrium with smithsonite. At pH >8.5 , calculated Zn^{2+} activities drop below the smithsonite (ZnCO_3) solubility line, suggesting possible formation of willemite (Zn_2SiO_4) or franklinite (ZnFe_2O_4) or sorption to oxide minerals.

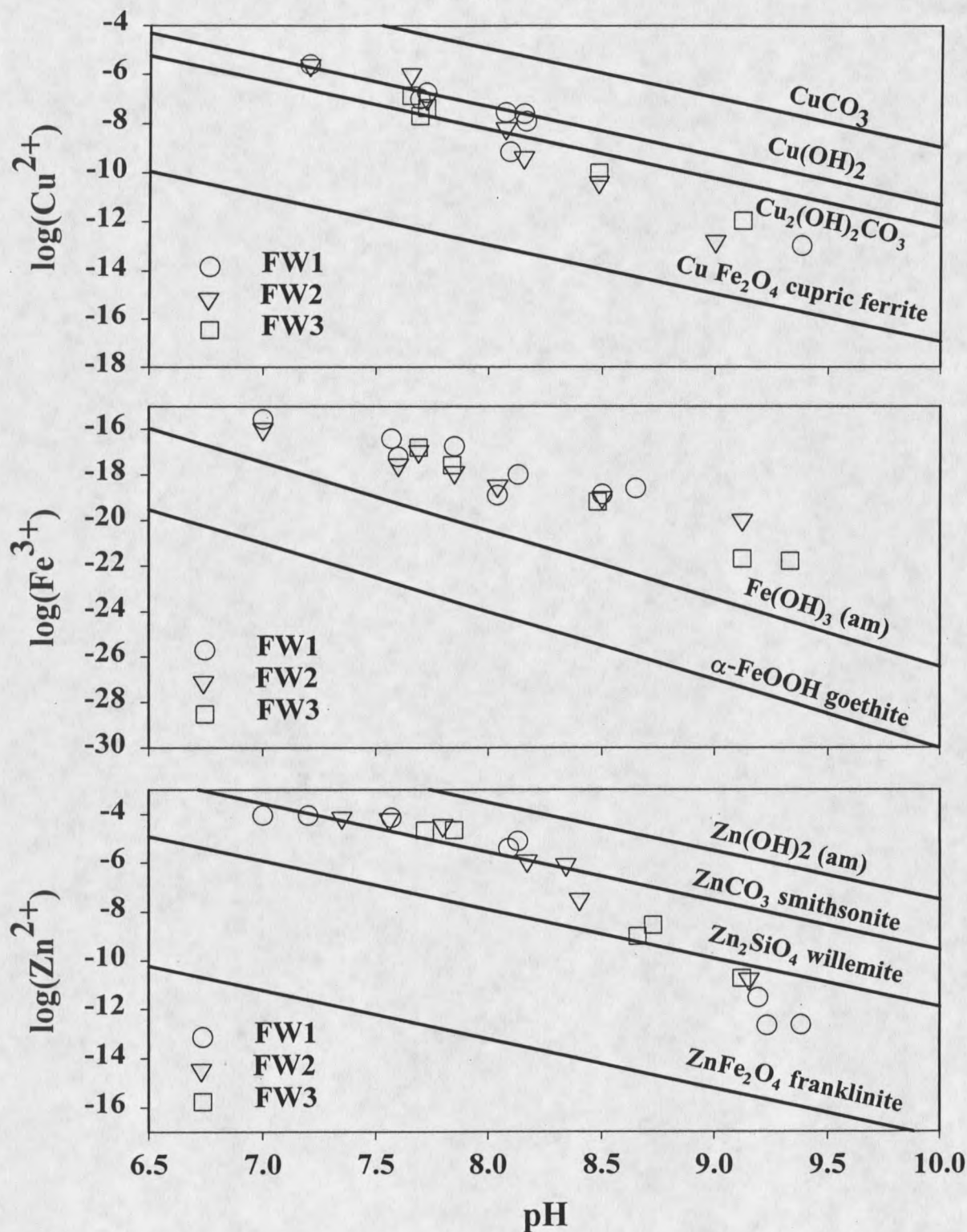


Figure 3. Computed (MINTEQA2) Cu^{2+} , Fe^{3+} , and Zn^{2+} activities plotted as a function of pH for representative water samples from FW1, FW2, and FW3 during the period 1/97 - 11/97. Partial pressure of CO_2 (g) was fixed at 0.003 atm.

Physical and Chemical Sediment Characterization

Sediments collected from FW1 were poorly consolidated and had a high water content. The lower fraction of FW1 sediment tended to be denser than the upper fraction, as clay sized particles accumulated in the bottom of the sediment samplers. Sediment deposition in FW1 was substantial, and in most cases buried the top rim of the collection tray by several centimeters. In contrast, sediments collected from FW2 and FW3 were relatively thin (<1.0 cm) and were composed largely of algae. Of the sediment accumulated within the constructed wetland, it is clear that the majority was deposited within FW1 as opposed to FW2 and FW3. Calculations of sediment mass accumulation within the entire wetland system, based on wetland removal of dissolved constituents as well as on the difference between dissolved constituents (Table 1) and suspended solids in the influent wastewater (1/97 – 11/97), indicated that approximately 5,000 kg sediment/month was retained within the constructed wetland. Estimates of sedimentation rates, derived from accumulated sediment depths, indicated that FW1 received approximately eight times more sediment (vol.) than FW2 and FW3 (40 mm/mo vs. 5 mm/mo). This suggests that of the 5,000 kg/mo total sediment accumulation, approximately 4,375 kg/mo was deposited in FW1. An estimate of accumulated mass within FW1, based on sedimentation rates (per unit area) and bulk density of FW1 sediment, was approximately 3 times larger than the value calculated above (approximately 18,000 kg/mo in FW1). The discrepancy between the two calculations may be accounted for by the overestimation of bulk density of FW1 sediment as a result of sample disturbance and subsequent de-watering at the time of collection.

Table 3. Summary of average physical and chemical parameters of collected wetland sediments

	Water Content %	Bulk Density g/cm ³	OM % by wt.	TOC % by wt.	TON % by wt.	TOS % by wt.	Carbonate Equivalence CaCO ₃ % by wt.
FW1	91	0.36 (3)†	1.9 (9)	0.17 (9)	0.14 (9)	0.27	2.07
FW2	94	--	32.0 (5)	18.9 (5)	1.60 (5)	--	12.98
FW3	95	--	28.1 (4)	16.6 (4)	1.41 (4)	--	10.2

† Numbers in parentheses represent the number of samples analyzed.

Sediment Characterization: Sequential Extraction

Total concentrations of Cu and Fe (Figures 4-5) were greater in sediments from FW1 than in FW2 and FW3. These data are consistent with observed changes in dissolved Cu and Fe across FW1-FW3 (Table 1) and estimated sediment accumulation rates, indicating the majority of Cu and Fe removal occurred as solid phase formation in FW1. The majority of the total Cu in FW1 was found in the carbonate (42%) and oxide bound (35%) fractions. Percents of Cu in carbonate and oxide bound fractions decreased in FW2 and FW3, as percent Cu bound in the sulfide-OM fraction increased in FW2 and FW3 sediments. The increase in percent Cu bound in the sulfide-OM fraction is consistent with higher OM contents that may have enhanced SO_4^{2-} reduction in sediments of FW2 and FW3, with subsequent formation of CuS phases. The percent of Fe bound in the Mn-Fe oxide fraction was also much higher in FW1 as compared to FW2 and FW3 (Figure 5). However, unlike Cu, the amount of Fe bound in the sulfide fraction did not increase in FW2 or FW3. Cu and Fe extractable in the residual fraction were likely part of the crystal lattice of primary and secondary minerals.

There were no measurable differences in total Zn concentrations among FW1, FW2, and FW3 (Figure 6). The majority of Zn within the FW1-FW3 sediments was bound to the carbonate fraction, while the remainder was bound to Mn-Fe oxides. It is possible that influent Zn formed carbonate mineral phases, consistent with the thermodynamic predictions of Zn carbonate solid phase formation within the constructed wetland system (Figure 3). As with Cu and Fe, Zn extractable in the residual fraction was likely part of the crystal lattice of primary and secondary minerals.

Sulfur concentrations within the wetland sediments were divided fairly evenly among the five fractions (Figure 7). Compared to FW1 there was an increase in the percent of S bound to the sulfide fraction in FW2 and FW3. Because the total S concentrations did not decrease in FW2 and FW3 relative to FW1, the downstream increase in S bound in the sulfide-OM fraction indicate that sulfide minerals may have formed in the accumulated sediments of FW2 and FW3.

The sequential extraction results for the soil sample collected from the northern retaining wall of FW1 and the peat samples revealed elemental compositions distinct from the wetland sediments (Table A2). Unlike the sediments, soil and peat samples did not show elevated levels of Cu and Zn. These results confirmed that the source of the Cu and Zn in the sediments from FW1-FW3 was not from the underlying peat material or from the retaining walls; rather, the primary source of the Cu and Zn in the sediments was from the influent wastewater stream.

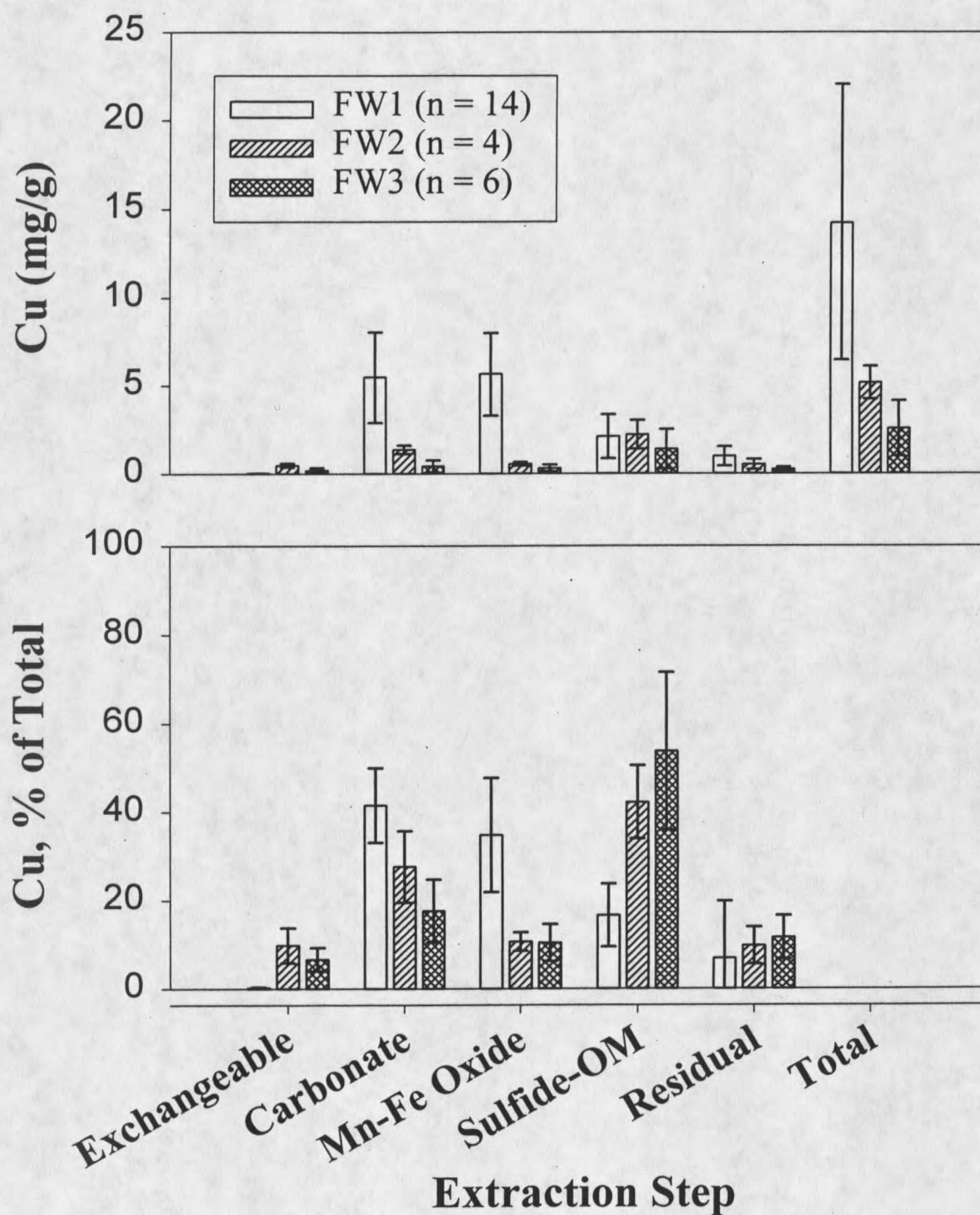


Figure 4. Concentrations and percentages of Cu in wetland sediments (FW1-FW3) among operationally defined chemical fractions, as determined by sequential extraction. Data represents averages from a number (n) of wetland sediment samples collected from each pond within the constructed wetland. Error bars represent standard deviations.

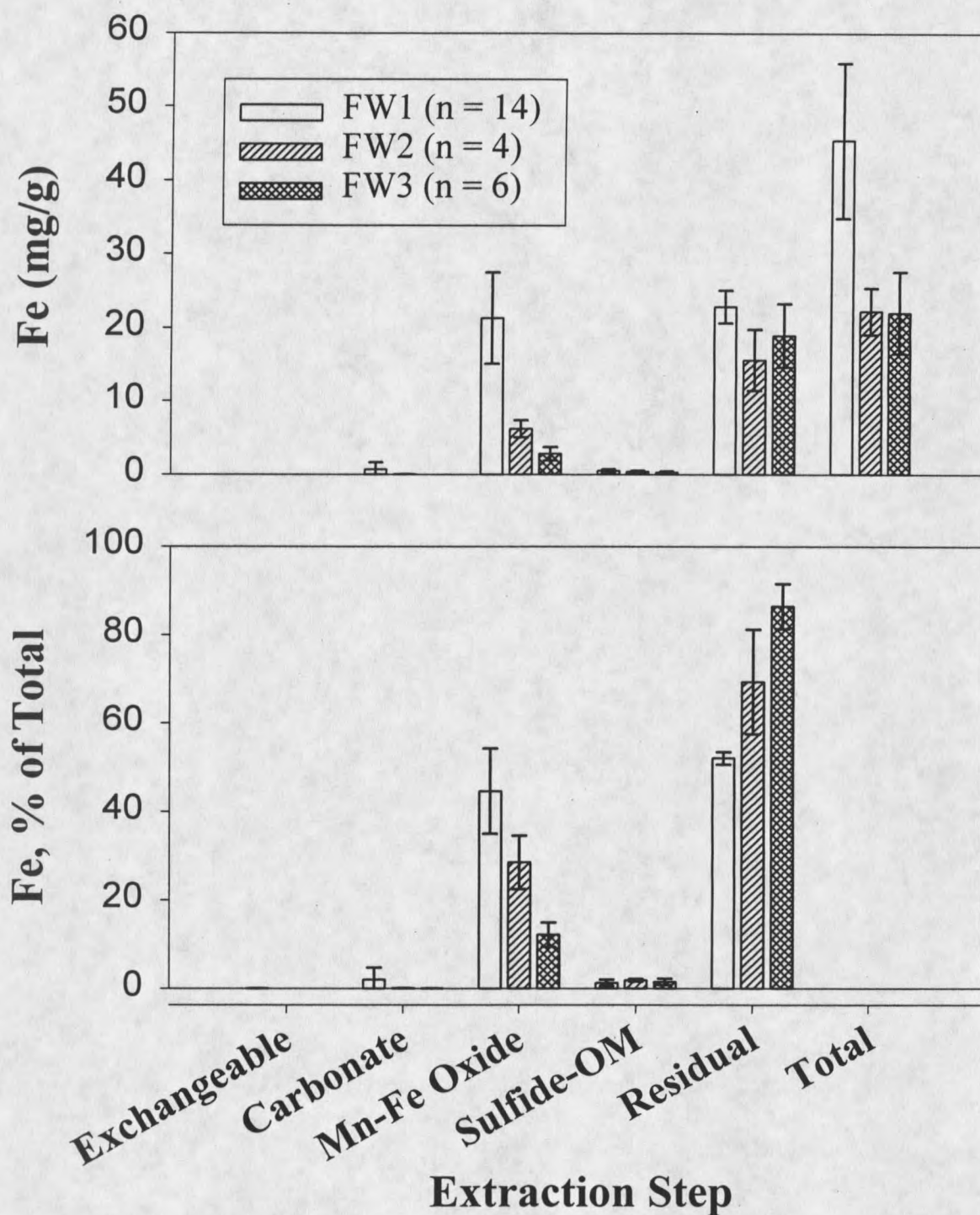


Figure 5. Concentrations and percentages of Fe in wetland sediments (FW1-FW3) among operationally defined chemical fractions, as determined by sequential extraction. Data represents averages from a number (n) of wetland sediment samples collected from each pond within the constructed wetland. Error bars represent standard deviations.

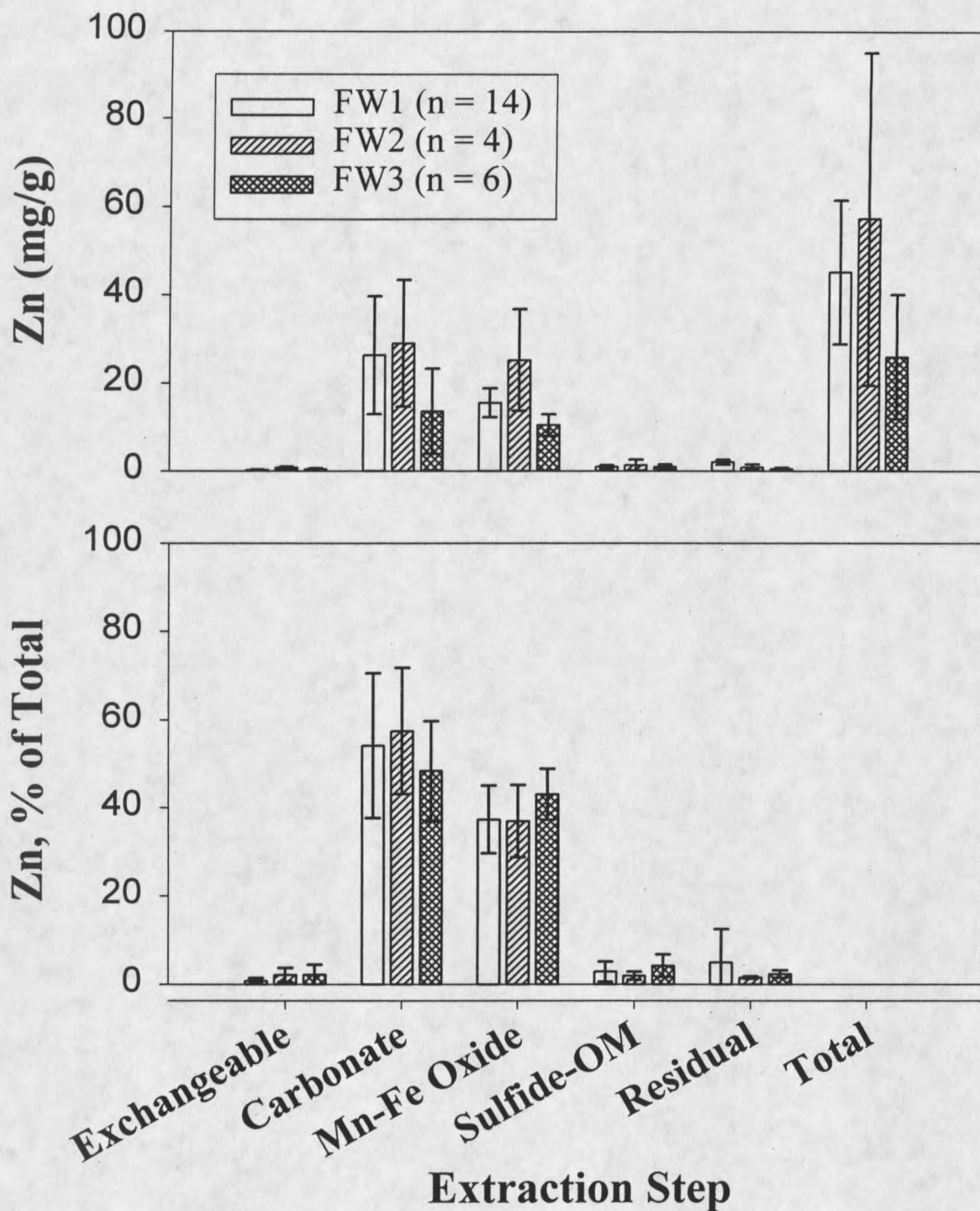


Figure 6. Concentrations and percentages of Zn in wetland sediments (FW1-FW3) among operationally defined chemical fractions, as determined by sequential extraction. Data represents averages from a number (n) of wetland sediment samples collected from each pond within the constructed wetland. Error bars represent standard deviations.

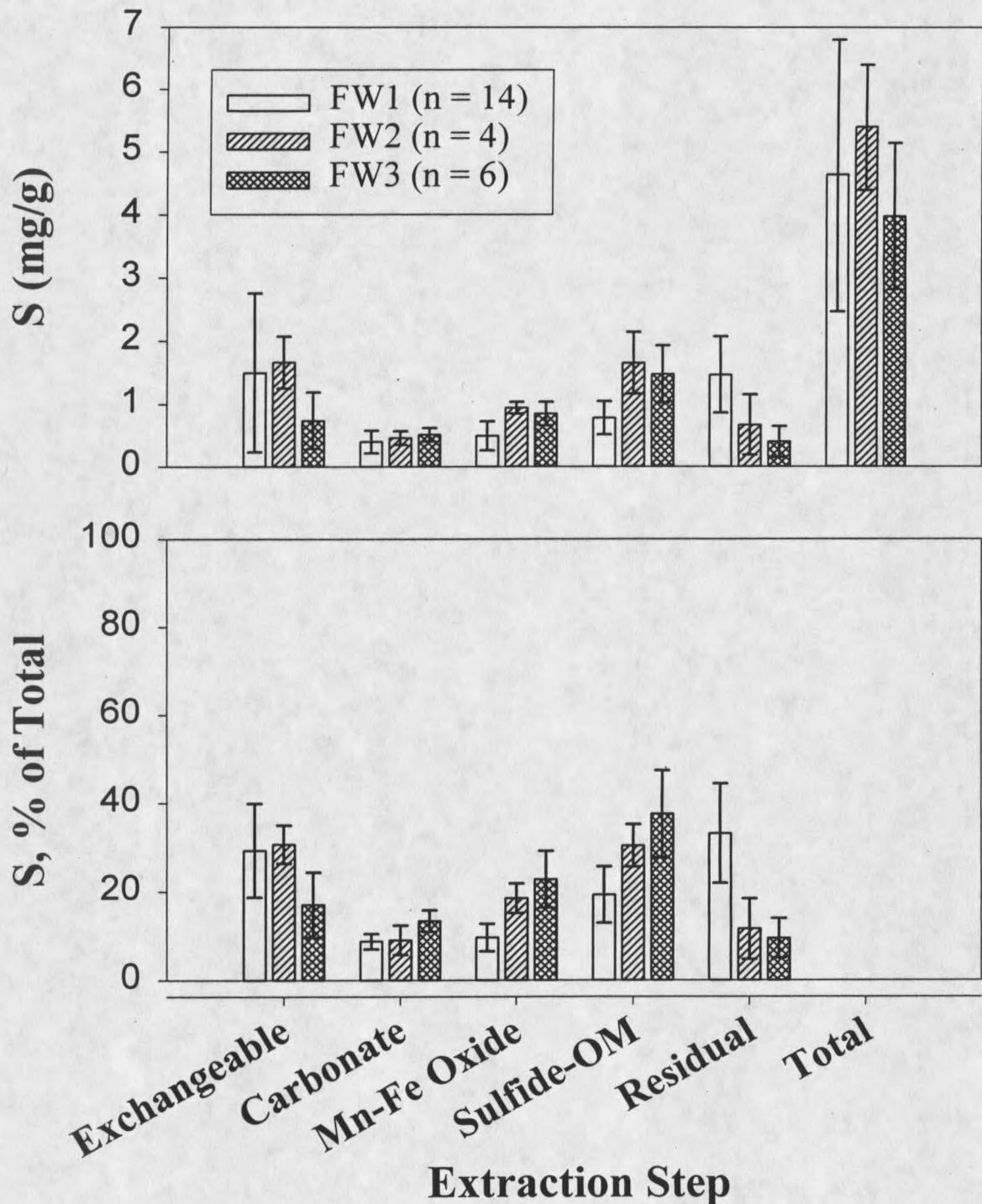


Figure 7. Concentrations and percentages of S in wetland sediments (FW1-FW3) among operationally defined chemical fractions, as determined by sequential extraction. Data represents averages from a number (n) of wetland sediment samples collected from each pond within the constructed wetland. Error bars represent standard deviations.

Sediment Characterization: SEM/EDAX Analysis

The existence of Cu, Fe, and Zn solid phases such as oxides and sulfides within the wetland sediments was confirmed using SEM/EDAX. In each of the three settling ponds, sediments contained substantial amounts of silicate minerals, Fe oxides, and Cu, Zn, and Fe sulfides of varying crystallinity. Observations using SEM showed many of the inorganic solids were aggregated with natural organic matter (NOM). Figure 8 shows a Zn solid phase (willemite or Zn coprecipitated on quartz) aggregated with organic matter. Diatoms were evident only in FW2 and FW3; Figure 9 of sediment sample from FW3 shows an example of numerous diatoms and organic matter comingled with an aluminosilicate mineral. While there were not an abundance of discrete Fe, Cu or Zn oxide phases found using SEM/EDAX, one example from FW1 shows an Fe oxide bound to organic matter (Figure 10). Cu, Zn, and Fe sulfide minerals were identified in sediments from FW1, FW2, and FW3. The majority of sulfides observed using SEM (Table 4) exhibited well defined crystal habit and were discrete particles ranging from 1 – 40 μm (e.g. Figure 11). Elemental mole % for the solid phase in Figure 11 suggests that both Cu ($\text{Cu/S} = 0.67$) and Fe ($\text{Fe/S} = 0.23$) are coprecipitated with S to form a sulfide solid phase, as evidenced by a total metal:S ratio of nearly 1:1 (Table 4). With the exception of one Cu sulfide particle found in FW1 (Figure 12), only FW3 contained sulfide minerals that displayed microcrystal habit, which in some cases may be indicative of recent sulfide formation (Wilkins and Barnes, 1997) (Figure 13 [note octahedral microcrystals], and Zn sulfide – Figure 14 [note small crystalline structures on surface]). The elemental mole % of the solid phase shown in Figure 13 ($\text{Fe/S} = 0.55$) is consistent with the stoichiometry of pyrite (FeS_2), while the Zn/S ratio of the solid phase shown in

Figure 14 ($\text{Zn/S} = 1.17$) is consistent with a discrete ZnS phase (Table 4). Analysis of suspended solids within the water column of FW1 contained numerous sulfide minerals interspersed with NOM, as depicted by the Zn sulfide in Figure 15 (possibly ZnS as indicated by Zn/S ratio of 0.87 [Table 4]). Suspended solids in the influent wastewater also contained numerous sulfide phases, as exemplified by the Cu/Zn sulfide in Figure 16. The $\Sigma\text{Me/S}$ ratio (nearly 1:1) of the solid phase shown in Figure 16 suggests the coprecipitation of CuS ($\text{Cu/S} = 0.45$) and ZnS ($\text{Zn/S} = 0.52$) (Table 4).

Table 4. Mole ratios of Cu, Fe, and Zn relative to S determined for specific particles using energy dispersive analysis of x-rays (EDAX)

	Cu/S	Fe/S	Zn/S	$\Sigma\text{Me/S}$
Figure 11	0.67	0.23	BD	0.91
Figure 12	1.21	0.09	0.17	1.48
Figure 13	BD	0.55	0.01	0.56
Figure 14	BD	0.11	1.17	1.27
Figure 15	BD	BD	0.87	0.87
Figure 16	0.45	BD	0.52	0.98

† BD indicates that the elemental mole percent for that particular element was below detection limits, and was not included in the analysis.



Figure 8. SEM photograph of Zn solid phase from FW2 sediment. The ratio of Zn and Si (Zn:Si = 8.5:5.3 elemental %) suggests that Zn is either coprecipitated with quartz, or that the solid is the Zn silicate mineral willemite (Zn_2SiO_4).



Figure 9. Diatoms (●) and organic matter (◆) affixed to aluminosilicate mineral phase from FW3 sediment.

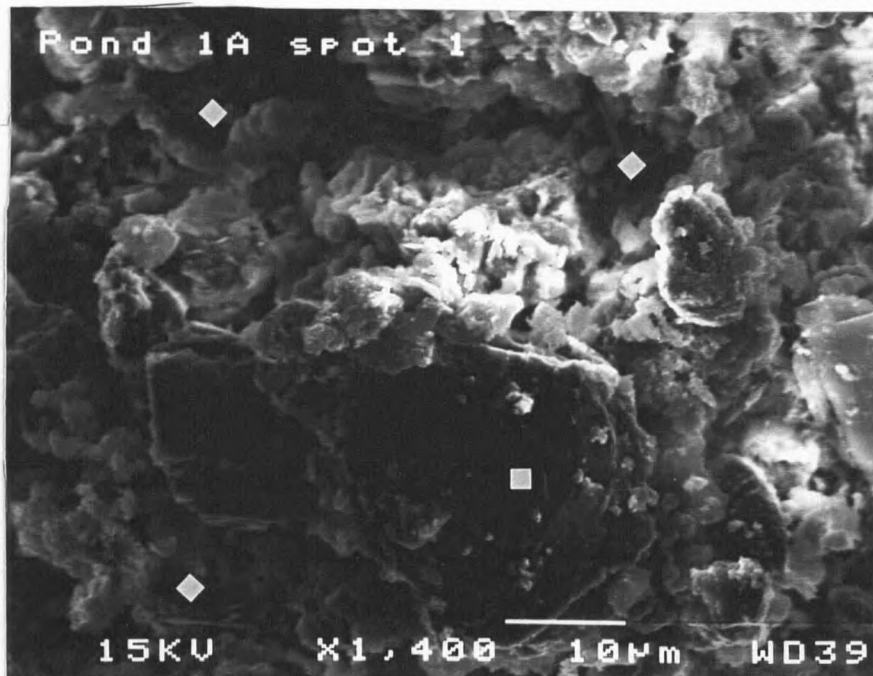


Figure 10. Iron oxide solid phase (■) affixed to organic matter (◆) from FW1 sediment.

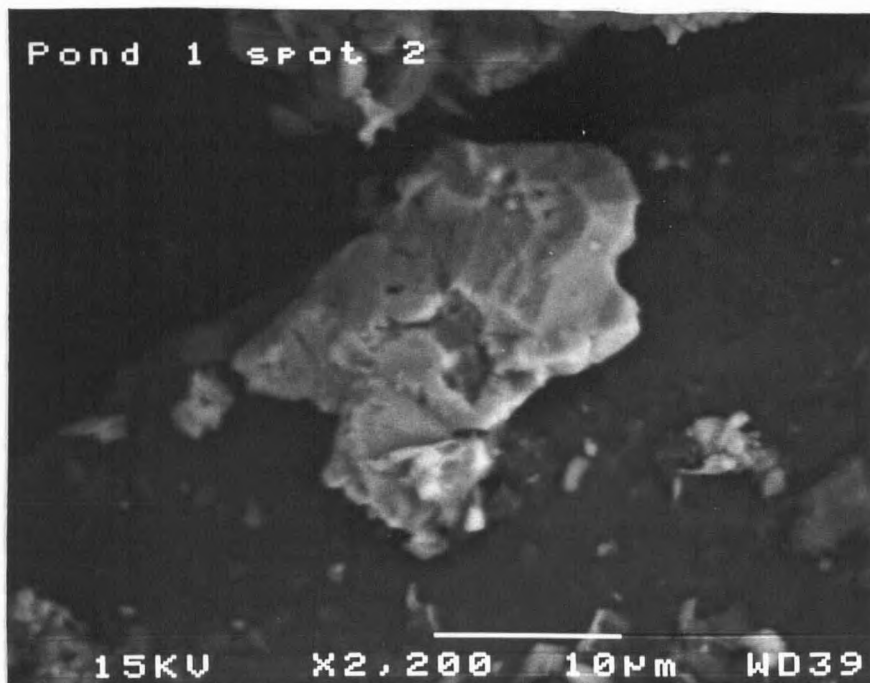


Figure 11. Cu sulfide solid phase from FW1 sediment.



Figure 12. Cu sulfide particle from FW1 sediment. Larger particle is composed of many small Cu sulfide precipitates.

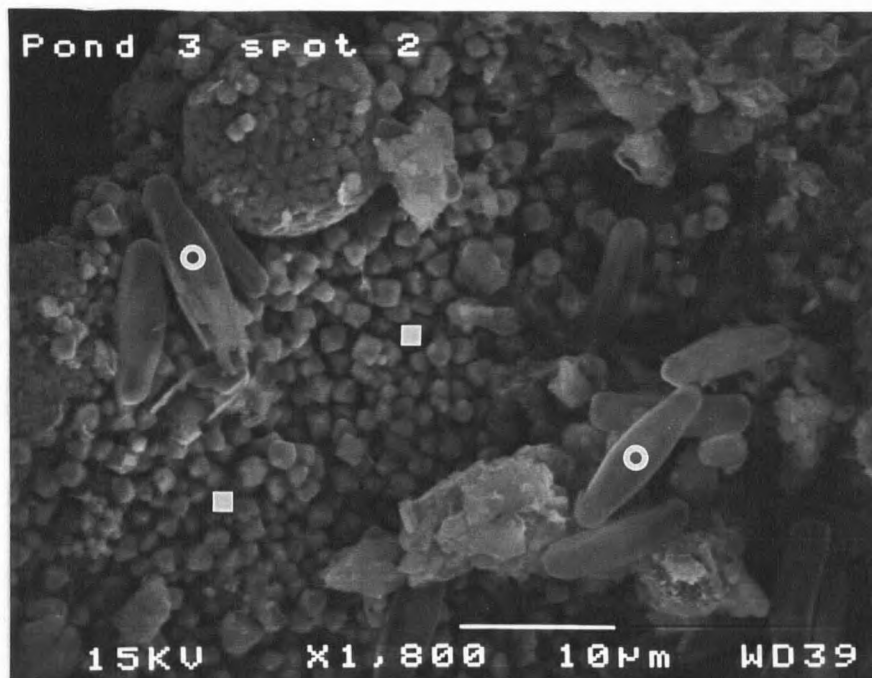


Figure 13. Fe sulfide framboid with associated diatoms (●) from FW3 sediment. The larger framboid mass is composed of many smaller octahedral Fe sulfide microcrystals (e.g. in the vicinity of ■).

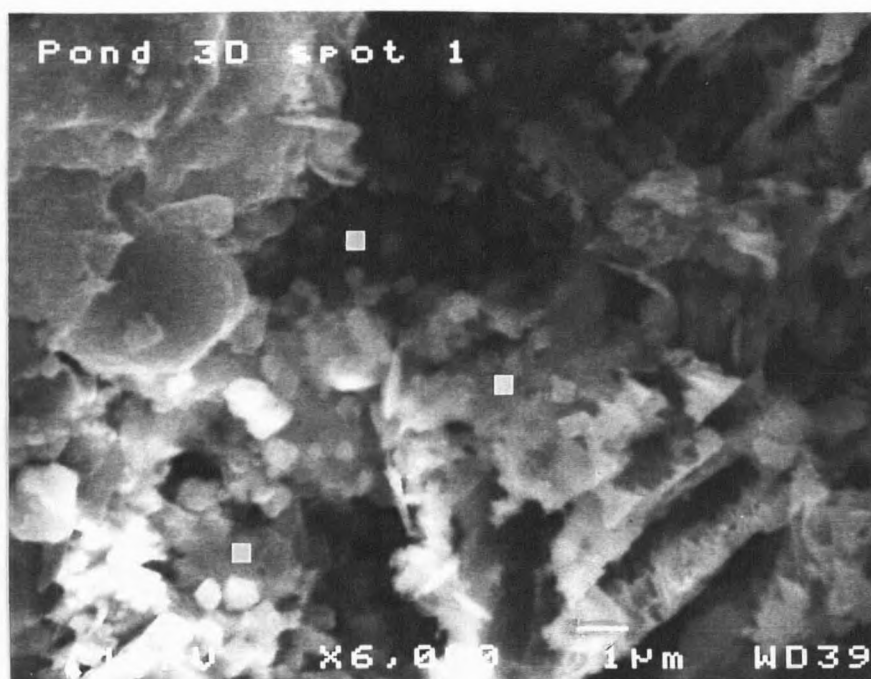


Figure 14. Zn sulfide particle with attached Zn sulfide microcrystals (e.g. in the vicinity of ■) from FW3 sediment.

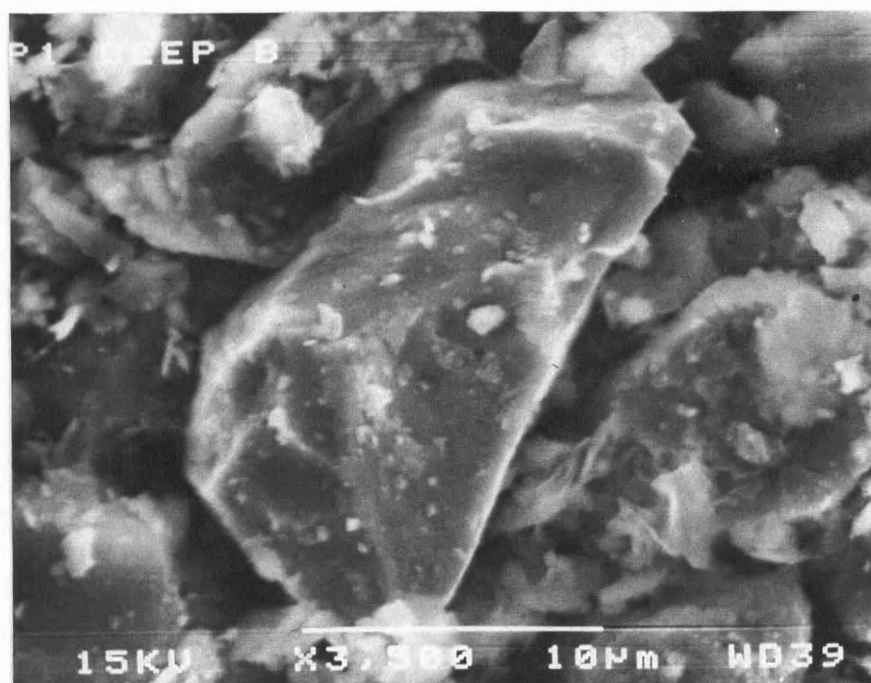


Figure 15. Zn sulfide particle suspended in the water column of FW1.

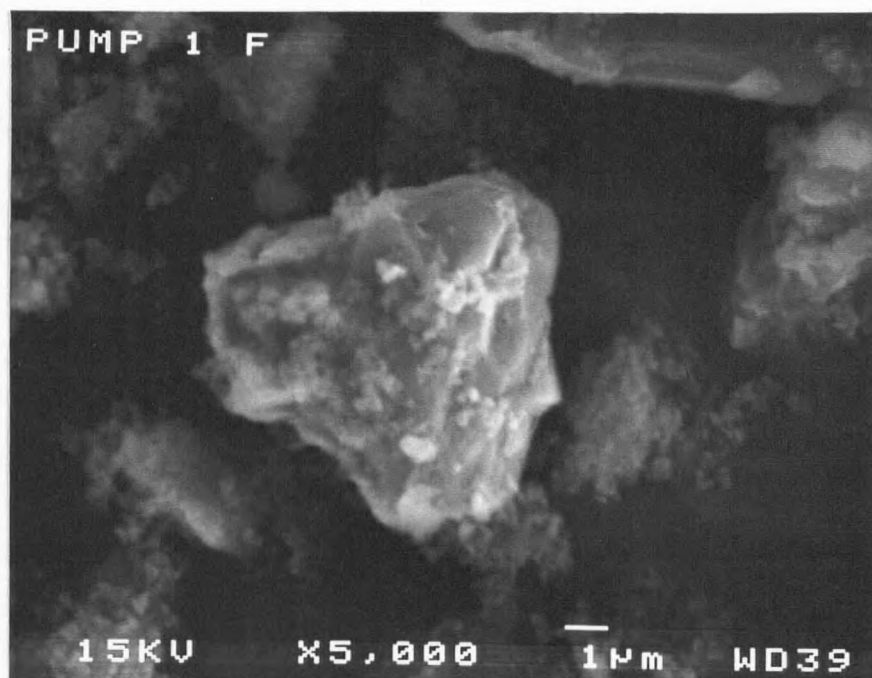


Figure 16. Zn/Cu sulfide particle suspended in the constructed wetland influent waste stream.

Discussion

The Fe oxides found in the sediments, especially in FW1, were likely contributed from dissolved Fe as well suspended Fe solid phases in the influent waste stream. Given that 99% of dissolved Fe removal occurred between the influent and FW1, approximately 2.7 kg/d of dissolved Fe was precipitated within FW1. In comparison, the influent supplied approximately 1.5 kg of suspended Fe solid phase/day, 90% of which was also removed between the influent and FW1. Frequent observations of a red precipitate within the influent waste stream suggest that Fe oxide formation occurs rapidly in the wastewater en route to the wetland, and subsequently deposits in FW1. The reduction of dissolved Cu and Zn from the influent to FW2 was likely due to (i) sorption reactions on Fe oxide minerals, and (ii) formation of metal hydroxides and/or carbonates.

Dissolved Zn concentrations were not reduced in the wetland system as much as concentrations of Cu and Fe (Table 1). MINTEQA2 predictions of solid phase formation within the wetland (Table 2) were consistent with observed differences in treatment efficiencies between Cu and Zn. These observations are a reflection of the higher solubilities of Zn vs. Cu solid phases (CuS and ZnS, log K -36.1 and -24.7, respectively [Lindsay, 1979]). As predicted from geochemical modeling of the influent wastewater, a significant amount of the dissolved Zn was expected to adsorb to Fe oxides as well as precipitate as Zn carbonate phases. This was consistent with results of sequential extraction analysis of wetland sediments, and with geochemical modeling of the bulk water within the wetland which suggests solution Zn^{2+} activities near equilibrium with Zn carbonate phases. Although Zn carbonate formation and sorption of Zn to Mn-Fe oxide

phases controlled solution Zn concentrations within the wetland, it is clear that these processes were not sufficient to meet treatment objectives for Zn. This was reflected in the limited removal of total dissolved Zn within the constructed wetland (62%).

Copper was the only primary metal that showed a significant portion bound to either organic matter or sulfide fractions in all of the ponds. The increase in Cu bound in the sulfide-OM fraction in FW2 and FW3 relative to FW1, accompanied by increases in percent S bound within the sulfide fraction, suggests the presence of Cu sulfides as opposed to OM-bound Cu. However, mole ratios of Cu/S extracted during the sulfide-OM step decline from 1.3 in FW1 to 0.5 in FW3. Furthermore, the substantial increase in % OM in FW2 and FW3 (approximately 42% and 34% by wt., respectively) relative to FW1 (2.25% by wt.), may have resulted in greater Cu-organic matter complexation in FW2 and FW3.

Scanning electron microscopy (SEM) revealed several different forms of Cu, Fe, and Zn sulfide minerals within the sediments. The majority of sulfide phases displayed well defined crystalline habit, and were likely of autogenic origin (e.g. Figure 11). Solid phases exhibiting identifiable crystal habit resembled suspended solid phases found in the interception ditch (e.g. Figure 16). This suggests that some or all of the sulfide phases found in the sediments were derived from the influent wastewater stream, and were not necessarily formed or precipitated as a result of sediment diagenesis. This hypothesis was also substantiated by the observation that crystalline sulfide phases were found suspended within the water column of FW1 (Figure 15). Assuming that sulfide mineral formation is largely dependent on organic rich anaerobic zones below the water/sediment interface,

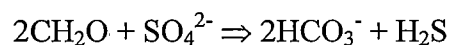
the existence of well crystalline sulfide particles in the bulk water would preclude the possibility that suspended sulfide minerals were formed within the sediment.

Though the majority of the sulfide minerals encountered in the wetland sediments resembled the macrocrystal habit of sulfide minerals suspended in the influent wastewater, we did find evidence of sulfide phases which either lacked well defined crystal habit (possibly of pedogenic origin) or displayed microcrystal habit, which may be indicative of more recent sulfide formation aggregation (Wilkins and Barnes, 1997). For example, Cu/Zn sulfide minerals were observed in FW2 with poorly defined crystal habit (Figure 12). It is possible that this particle represents an aggregation of many smaller Cu and Zn sulfide particles. The Zn sulfide phase shown in Figure 14 displayed varying morphology: the main particle in the background appears to be somewhat etched, while the surface is covered with several small Zn sulfide microcrystals. An example of well defined microcrystal habit was found in a Fe sulfide from FW3 (Figure 13), which exhibited physical characteristics of what is known as a greigite/pyrite framboid. The process of growth for this type of mineral form begins with: 1) nucleation and growth of initial FeS microcrystals; 2) reaction of microcrystals to greigite (Fe_3S_4); 3) aggregation of uniformly sized microcrystals (framboid growth); and finally 4) replacement of greigite framboids by pyrite. The octahedral microcrystals aggregate due to their high surface area/volume ratio. Therefore, the total free energy of a suspension of microcrystal colloids can be lowered by reducing the surface area (interfacial area) through the process of aggregation (Wilkins and Barnes, 1997). Though the Fe/S ratio of this solid (0.55) suggests the presence of FeS_2 (pyrite) as opposed to Fe_3S_4 (greigite) (which is thought to

be the precursor to pyrite formation), rapid pyrite formation (48 h) in reduced marine sediments has been documented (Howart, 1979).

Given that amorphous sulfides have a propensity to rapidly oxidize when sediment samples are dried (Moore et al., 1988; Wilkin and Barnes, 1996), it is possible that the sulfide mineral fraction of the accumulated sediments was significantly underestimated by sequential extraction procedures, as well by SEM/EDAX. Furthermore, based on the increase of Cu sulfides downstream within the wetland sediments, as determined by sequential extraction, and the absence of "amorphous" sulfide suspended in the influent and the water column, as determined by SEM/EDAX, it is possible that the accumulating sediment does provide a limited reducing environment for some sulfate reduction.

The relatively small amount of DOC in the wetland system (approximately 0.17 mM C) relative to dissolved SO_4^{2-} concentrations (approximately 3.6 mM S) suggests that sulfate reduction was significantly limited by the lack of available C. Dissimilatory reduction of SO_4^{2-} via microbial C oxidation can be approximated by the reaction:



where CH_2O is microbially available. This reaction suggests that approximately 7.2 mM of bioavailable C would be required to reduce the amount of SO_4^{2-} present in the wetland system; which is 40 times more than the total DOC present. The lack of bioavailable C is reflected in the constructed wetland system where on average only 3% of the total dissolved influent SO_4^{2-} was removed. Given the carbon limitation, the total amount of potential SO_4^{2-} reduction in the wetland system would be approximately 2.4% (i.e. 85 μM

of the total 3.6 mM SO_4^{2-}), which could account for small amounts of metal sulfide formation within the wetland (influent dissolved concentrations of Cu [42 μM], Fe [70 μM], and Zn [200 μM]). Again, this was perhaps reflected in the wetland sediments where a significant amount of the total Cu is bound as Cu sulfides.

Although the treatment walls were hoped to encourage the development of anaerobic zones by providing a high surface area for sulfate reducing bacterial growth, the relatively large settling ponds dictate that the primary means of wastewater treatment in the constructed wetland lay in the removal of metals by precipitation of hydroxides and carbonates as opposed to the formation of metal sulfides. Given that Zn remained elevated in the wetland effluent, the formation of Zn hydroxides and carbonates was not sufficient to remove all the dissolved Zn in the waste stream within the study period (1/97-4/98). Without major design modifications to the constructed wetland, it is doubtful that that system will foster significant SO_4^{2-} reduction given the existing carbon limitations. By expanding the treatment wall width, and perhaps by utilizing a smaller gravel substrate in addition to the use of an organic amendment within the treatment wall, it is possible to increase substrate surface area and contact time within the constructed wetland. Furthermore, the formation of anaerobic zones would also be encouraged by the establishment of a viable plant community, which would supply a renewable carbon source within the constructed wetland.

CHAPTER 3

PRECIPITATION OF Cu AND Zn SULFIDES IN THE PRESENCE OF Fe OXIDE

Introduction

High concentrations of dissolved Fe associated with acid mine drainage (AMD) often result in the formation of Fe oxides. Fe oxides are important because they have the potential to sorb contaminant metals, and subsequently remove these metals from solution (Gambrell, 1994). The control of metal activities in solution due to sorption on oxide phases has been well documented (Benjamin and Leckie, 1981; Bleam and McBride, 1985; Catts and Langmuir, 1986; Hatrer and Naidu, 1995; Zasoski and Burau, 1988). Transformation of Fe oxides to Fe sulfide phases may occur in reducing environments where sulfide is produced. Upon exposure of Fe oxides to H_2S (g) it is thought that sorbed metals are released in the process of Fe^{3+} reduction (Pyzik and Sommer, 1981). The desorbed metals then combine with dissolved sulfide to form sulfide solid phases that may nucleate at the Fe oxide surface. It has also been suggested that the formation of sulfide phases on the surface of Fe oxides may act as a protective layer preventing further dissolution of the oxide (Biber et al., 1994). Therefore, understanding the reaction mechanisms of sulfide phase formation at the Fe oxide surface is potentially important for determining the fate of sorbed metals in wetland systems used to treat AMD.

The stability of Fe oxides is influenced by changes in redox status largely driven by microbial mineralization and diagenesis of carbon. Under mildly reducing conditions ($E_h \approx -100$ mv), Fe^{3+} is often used as a terminal electron acceptor, resulting in the dissolution of Fe oxides (Elder, 1988). Under sulfate reducing conditions, Fe oxides are known to undergo the processes of pyritization (Howart, 1978; Canfield and Berner, 1987; Canfield, 1988; Canfield et al. 1992). Reactivity of Fe oxides in reducing environments is a function of mineralogy, crystallinity, and grain size (Canfield, et al., 1992; Lovley and Phillips, 1987). In general, Fe oxide dissolution is a surface controlled reaction that is strongly accelerated by organic ligands, reductants, or both (Postma, 1993). The rate of reductive dissolution of (hydr)oxides by H_2S is a function of the surface concentration of dissolution promoting species. Oxidized species on the surface of the oxide (for example: Fe^{3+} on the surface of ferrihydrite) are reduced by adsorbed reductants (i.e. FeS^- or $FeSH$); Fe^{2+} is then released to the solution faster than Fe^{3+} because the bonds between the reduced Fe and O_2^- ions of the crystalline lattice are weakened (Afonso and Stumm, 1992). Rickard (1974, 1995) proposed a two-stage mechanism for the reaction between Fe oxides and sulfide: diffusion of H_2S to the surface, and reaction of H_2S with dissolved Fe^{3+} . Pyzik and Sommer (1981) have described reactions of sulfide with $Fe(OH)_3$ and α - $FeOOH$ (goethite), proposing a model following these steps: (i) protonation of the surface layer, (ii) exchange of bisulfide species for hydroxide in the mobile layer, (iii) reduction of surface ferric ions of goethite by dissolved bisulfide species producing a ferrous hydroxide surface layer with elemental sulfur and thiosulfate, (iv) dissolution of surface layer ferrous hydroxide, and (v) precipitation of dissolved ferrous species and aqueous bisulfide ions. Pyzik and Sommer

(1981) postulated that in the process of sorption of aqueous sulfide to surface ferric iron, and subsequent dissolution of surface Fe^{2+} , other sorbed ions (Cu, Zn, etc.) may also be released into solution.

The microbial reduction of Fe oxides is significantly inhibited by the surface adsorption of Fe^{2+} (Roden and Zachara, 1996). Similar reductive inhibition as a result of Fe^{2+} accumulation on the surface of Fe oxides was noted by Postma (1993). In addition, the adsorption of oxoanions such as phosphate, arsenate, and borate, significantly inhibit reductive dissolution (via H_2S) of Fe oxides (Biber et al., 1994). Dissolution is thought to be a breaking, or depolymerization, of the extended cross-linked polymers on the crystal surface, which bear the surface functional groups of the Fe oxide. Adsorbates that reduce this cross-linking behavior favor the dissolution of the solid. Conversely, adsorbates which reinforce the lattice and cross-linking structure at the surface would retard the dissolution of the solid. In addition to adsorbed surface complexes, the formation of Fe sulfide on the Fe oxide surface may block surface sites from interaction with ligands or protons (Biber et al., 1994). This phenomenon has also been observed in natural sediments where pyrite coatings on magnetite have effectively shielded the inner oxide phase from further reduction in the presence of high concentrations of H_2S (Canfield and Brener, 1987).

While it is understood that sorption of metal ions may inhibit reduction and subsequent pyritization of Fe oxide, the fate of adsorbed metal ions such as Cu and Zn in reduced environments is uncertain. Consequently, the objective of the current study was to determine whether the formation of Cu and Zn sulfide phases occur in the presence of Fe oxides, under conditions where aqueous sulfide species were controlled by fixing the

partial pressure of H_2S (g) in a stirred reaction chamber. Our interest in Cu and Zn sulfide formation stems from efforts to characterize sediment samples from a constructed wetland used to treat metal contaminated water in Butte, MT. Sulfate reduction and formation of metal sulfide phases may be an important process during the diagenesis of wetland sediments. In the current study, the surface chemistry of Fe oxides containing sorbed Cu and Zn was examined before and during H_2S treatment using chemical sequential extraction, scanning electron microscopy (SEM), energy dispersive analysis (EDAX), and x-ray photoelectron microscopy (XPS). Results from our work show that sorbed Cu is converted to a sulfide phase within several days, while Zn remains sorbed to the Fe oxide phase.

Materials and Methods

Precipitation of Cu and Zn Sulfides

Laboratory batch experiments were conducted to determine rates of Cu and Zn sulfide precipitation from oversaturated solutions in the presence and absence of ferrihydrite. These experiments were conducted in a 2 L closed head space polycarbonate vessel containing multiple access ports for a pH probe and $\text{N}_2/\text{H}_2\text{S}$ (g) delivery. The chamber was stirred on a magnetic stir plate with an elevated stir bar mounted on a Teflon disk. The chamber solution (1.8 L of 0.01 M KCl) was manually kept constant at pH 6.5 using 0.05 M KOH. Experiments were conducted in a hood to avoid exposure to H_2S (g), and chamber exhaust gas was routed through a series of gas traps filled with strong base to encourage the conversion of residual H_2S (g) to SO_4^{2-} .

Sulfide activity in the stirred chamber was fixed by controlling pH and the partial pressure of H_2S (g); at a pH of 6.5, the dominant species of sulfide are H_2S (aq) and HS^- (Figure 17). The chamber solution was bubbled using peristaltic pumps with certified N_2 (g) (99% N_2 , 1% CO_2), and H_2S (g) at 20 mL/min and 0.25 mL/min, respectively. The partial pressure of H_2S (g) in the influent tubing, as well as in the chamber head space, was confirmed to be approximately 0.01 atm using gas chromatography (GC).

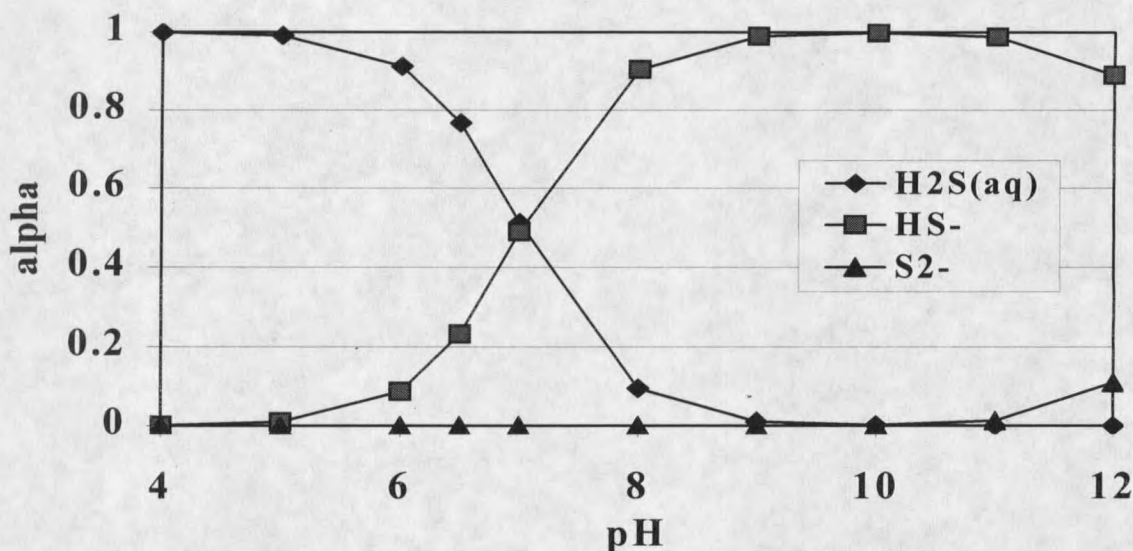


Figure 17. Distribution coefficients for H₂S (aq), HS⁻, and S²⁻ species over a range of pH.

Although we attempted to fix the partial pressure of H₂S (g) at 0.01 atm, measured total dissolved sulfide concentrations (S_{TS}) in the stirred chamber were less than thermodynamically predicted levels (approximately 1 mM). Total dissolved sulfide concentrations in the absence of metals equilibrated in roughly six hours at approximately 0.046 mM (1.5 mg/L), as determined from unacidified liquid samples using the colorimetric sulfide method (Clesceri et al. 1989). Total S analysis of the equilibrated chamber solution using ICP agreed with the total sulfide measurements. In addition, analysis using ion chromatography (IC), confirmed that SO_4^{2-} concentrations were negligible (2.6 μ M). The discrepancy between predicted and measured S_{TS} concentrations may partially be due to filtration, and subsequent oxidation of aqueous samples prior to sulfide analysis, as well as to pH fluctuations.

In order to study dissolved Cu and Zn precipitation as metal sulfide phases, experiments involved using dissolved metal concentrations similar to those found in the constructed wetland. The first experiment incorporated only dissolved Cu in the stirred chamber at a concentration of 32 μM (2 mg/L) prior to bubbling with H_2S and N_2 (g). In an identical experiment, only dissolved Zn was added at 31 μM (2 mg/L). During equilibration with 0.01 atm H_2S (g), liquid samples were extracted from the chamber at various times over the course of the experiment. Aqueous samples were extracted from the chamber with 100 mL syringes, filtered with 0.2 μm nylon filters, acidified with 2% HCl, and refrigerated until analyzed for dissolved Cu and Zn using atomic adsorption spectroscopy (AAS). In addition to studying the precipitation characteristics of Cu and Zn in separate experiments, competitive sulfide precipitation between Cu and Zn was studied in experiments where both metals were present. Once the metals were precipitated as sulfide phases to below detection using (AAS), the chamber was bubbled with air to facilitate resolubilization of Cu and Zn upon oxidation and subsequent dissolution of the sulfide phases.

Sulfide Treatment in the Presence of Ferrihydrite

The formation of Cu and Zn sulfides was also studied in systems containing Cu and Zn sorbed to ferrihydrite. An amorphous Fe oxide was prepared at pH 7.5 following methods for the preparation of 2-line ferrihydrite, as outlined by Schwertmann and Cornell (1991). The surface area was determined using a 3-point N_2 (g) – BET isotherm,

and found to be 425 m²/g. ICP analysis determined that the ferrihydrite was 56.2 % Fe by weight, after the solid was dissolved in 6 % HCl for 24 h.

Batch sorption isotherm experiments were conducted for Cu and Zn using a solid:solution ratio of 0.1 g ferrihydrite/L (1×10^{-3} mol Fe/L) in polypropylene centrifuge tubes using a total volume of 30 mL. The pH remained constant at 6.0 ± 0.3 in a background solution of 0.01 M KCl over the course of the isotherm experiments by: equilibrating the ferrihydrite in a pH 6.0 background solution prior to use in isotherm experiments, and equilibrating all solutions containing dissolved Cu and Zn at pH 6.0 prior to addition to centrifuge tubes. Experiments were conducted using initial Cu and Zn concentrations ranging from 1.5 to 470 μ M Cu and Zn (0.0, 0.3, 1.0, 3.0, 10.0, and 30.0 mg Cu and Zn /L), in separate experiments and in experiments containing both ions. After 4 d of equilibration, aqueous phase Cu and Zn were analyzed using AAS, and the amount of Cu and Zn sorbed was determined by difference between initial and equilibrium metal concentrations. Control vessels without ferrihydrite indicated insignificant sorption to containers and no precipitation of hydroxide or carbonate solids. Adsorption isotherm results are shown in Appendix B, Figure 36.

Sulfide precipitation experiments were conducted with ferrihydrite samples containing sorbed Cu and Zn using two approaches (Table 5): A.) addition of ferrihydrite into the stirred chamber, followed by equilibration with atmospheric air for 1 d prior to bubbling 0.01 atm H₂S (g); B.) addition of ferrihydrite simultaneously with initiation of 0.01 atm H₂S (g). The ferrihydrite used in A. had a higher loading of sorbed metals (especially Zn) than the ferrihydrite in B. The pH was maintained at 6.5 for duration of the experiment (approximately 4 days) by periodic addition of 0.05 M KOH. Aliquots of

the suspension were sampled roughly 15 times over 4 d, by withdrawing approximately 20 mL, and immediately filtering using 0.2 μm nylon filters. A portion of the filtrate was acidified and analyzed for dissolved Cu, Fe, and Zn using ICP, while the remaining unacidified filtrate was analyzed for total soluble sulfide using the colorimetric method. Several filters were analyzed using x-ray photoelectron spectroscopy (XPS) to determine elemental mole composition of the suspended solid phase. Based on total soluble concentrations of Cu, Fe, S, and Zn within the chamber over the course of the experiments, the geochemical model MINTEQA2 (Allison et al., 1991) was employed to calculate ion activity products (IAP) and respective saturation indices (IAP/ K_{SP}) with respect to the following solid phases: covellite, tenorite, $\text{Cu}(\text{OH})_2$, CuCO_3 , FeS amorp., pyrite, ferrihydrite, $\text{Fe}_3(\text{OH})_8$, ZnS amorp., sphalerite, ZnCO_3 , and smithsonite.

Table 5. Experimental conditions for sulfide precipitation experiments in the presence of ferrihydrite

Experiment	pH	Background sol. (1.8 L)	H_2S (g)	Ferrihydrite (g)	Sorbed Cu ($\mu\text{mol/g}$ solid)	Sorbed Zn ($\mu\text{mol/g}$ solid)
A.	6.5	0.01 M KCl	At 1 d	3.86	86	71
B.	6.5	0.01 M KCl	At 0 d	3.50	90	13

Approximately 0.2 g aliquots of solid phase from the bottom of the stirred chamber were collected on 0.45 μm nylon filters eight times during the experiment. Solid phase samples recovered after filtration were containerized, dried under N_2 (g), and

analyzed using sequential extraction analysis, scanning electron microscopy with energy dispersive analysis (SEM/EDAX), and XPS.

Two steps of a sequential extraction procedure (Tessier et al., 1989; Chao, 1984; Belzile and Tessier, 1990) were used to estimate the amount of Fe oxide bound and sulfide bound Cu, Fe, and Zn in solid phase samples collected during equilibration with 0.01 atm H_2S (g). Subsamples (0.1 g) of collected solids were extracted (i) for 6 hr under continuous agitation at 96 °C with 5.6 mL of deaerated 0.04 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ in 4.4 M acetic acid (CH_3COOH), and (ii) for 5 hr under occasional agitation at 85 °C with 5.6 mL 30% H_2O_2 initially adjusted to pH 2 with 15.8 M HNO_3 , after cooling, the sediment was extracted for 30 min at 25 °C under occasional agitation with 5.6 mL of 3.2 M NH_4 acetate in 3.2 M HNO_3 . Extractions were performed in 100 mL centrifuge tubes, and centrifuged at 15,000 rpm (17,540 g) for 30 min. Supernatants were decanted, diluted (1:10) with 2% HCl in a 0.01M KCl background solution, then analyzed for Cu, Fe, S, and Zn using ICP. Between extraction steps, the sample was washed with 8 mL of DI water, centrifuged, then decanted prior to addition of reagent (ii) given above. Well characterized solid phase phases including commercially available ZnS and CuS (Aldrich Chemical Company), and 2-line ferrihydrite (with and without sorbed Cu and Zn) were also subjected to sequential extraction as controls to establish confidence in partitioning Cu and Zn among oxide and sulfide bound fractions.

Solid phase samples were also analyzed using (i) scanning electron microscopy (SEM) coupled with energy dispersive analysis of x-rays (EDAX) using a JEOL model 6100 and (ii) x-ray photoelectron spectroscopy (XPS) using a PHI model 5600CI

(Imaging and Chemical Analysis Laboratory, Montana State University). The purpose of these analyses was to identify potential metal sulfide precipitation on Fe oxide surfaces during equilibration with 0.01 atm H_2S (g). Observations using SEM provided visual evidence of surface sulfide precipitation coupled with chemical information (EDAX) based on a probe depth of approximately $1\text{ }\mu\text{m}$ ($100\text{ }\text{\AA}$). For each time point, a minimum of six particles were selected at random for EDAX analysis. In addition, chemical analysis of the near surface environment (from 0 to $40\text{--}80\text{ }\text{\AA}$) was obtained using small-spot XPS (Vempati et al., 1996) using an Al K α x-ray source (1486.6 eV). Dried solids were analyzed directly on nylon filters, while control solids (CuS, ZnS, and ferrihydrite) were pressed on In foil. Mounted samples were then brought to 1×10^{-8} Torr and analyzed (area of analysis = $800\text{ }\mu\text{m}^2$) for Cu, Fe, O, S, and Zn using multiple scans for the following photoelectrons and their associated binding energies: Cu2p (933-953 eV), Fe3p (53 eV), O1s (531 eV), S2p (164 eV), and Zn2p3 (89 eV).

Results

Sulfide Precipitation in the Absence of Ferrihydrite

In experiments containing 32 μM Cu (2 mg/L) or 31 μM Zn (2 mg/L) prior to bubbling 0.01 atm H_2S (g), the nucleation and subsequent precipitation of Cu and Zn sulfides was rapid, and commenced prior to the detection of aqueous sulfide (detection limit ≈ 4.4 μM H_2S). At 32 μM initial Cu and equilibrium concentrations of approximately 44 μM (1.5 mg/L) dissolved sulfide, Cu was below detection by AAS (detection limit ≈ 0.16 μM Cu [0.01 mg/L]) within 12 h. When the same experiment was conducted with 31 μM Zn (2.0 mg/L), the precipitation rate was very similar, and dissolved Zn was nondetectable by AAS within 12 h. However, when 32 μM Cu and 31 μM Zn were combined, the precipitation of Zn was temporarily inhibited until the majority of Cu was precipitated as a sulfide phase; the Cu removal rate did not appear to be significantly slowed by the presence of dissolved Zn. After one day, 0.01 atm H_2S (g) was replaced with air (20 mL/min), and dissolved sulfide concentrations decreased below detection within approximately 12 h. At this time, Zn concentration increased to 7.64 μM Zn (0.5 mg/L), while Cu remained bound as a sulfide phase for the remainder of experiment (Figure 18.).

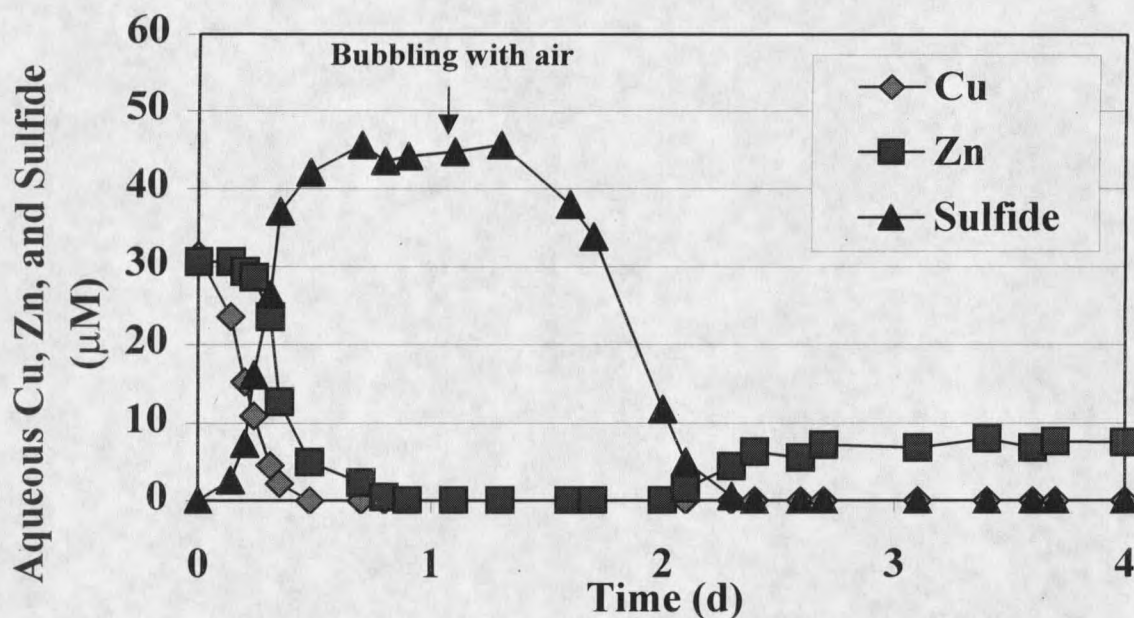


Figure 18. Precipitation of Cu and Zn sulfides during treatment with 0.01 atm H_2S (g) at pH 6.5. After approximately 1.5 d, the chamber was bubbled with atmospheric air. As dissolved sulfide concentrations decreased, ZnS partially dissolves.

Sulfide Precipitation in the Presence of Ferrihydrite

Concentrations of dissolved Cu and Zn increased within the first day following addition of ferrihydrite, but prior to bubbling with H_2S (g) (Figure 19). This increase in dissolved Cu and Zn was attributed to rapid desorption of Cu and Zn in 0.01 M KCl. Dissolved Cu and Zn concentrations were below detection within 0.15 d and 2.5 d after bubbling H_2S (g), respectively. Dissolved Fe was detected approximately 0.4 d after the introduction of 0.01 atm H_2S (g) and equilibrated by day 3 at approximately 36 μM Fe (2 mg/L).

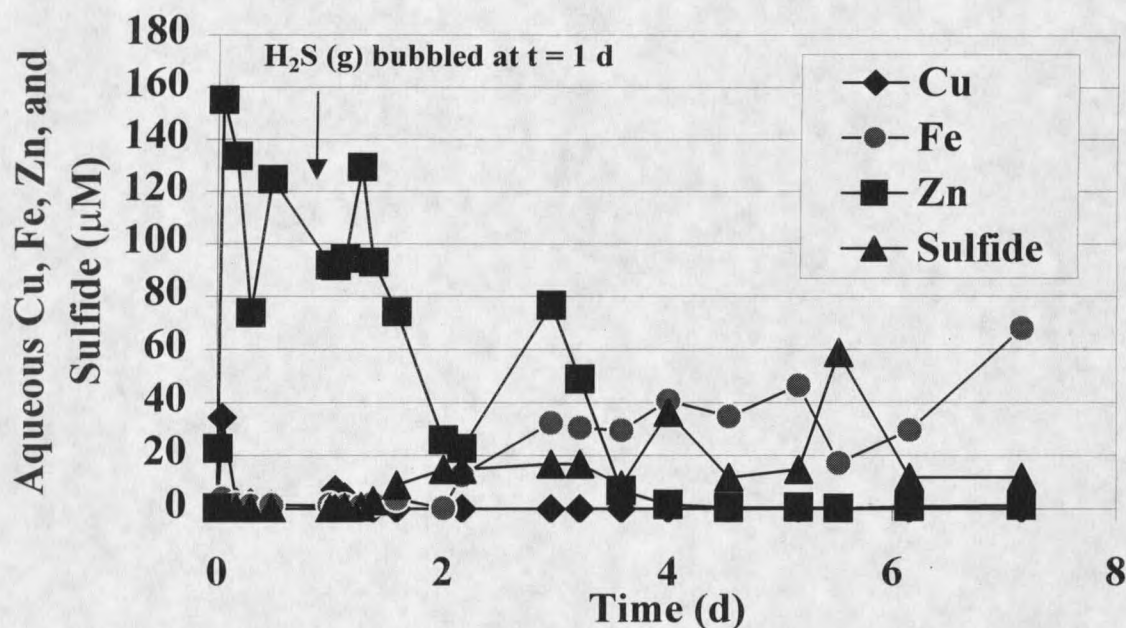


Figure 19. Dissolved concentrations of Cu, Fe, Zn, and sulfide in experiment (A) where H₂S (g) treatment was initiated at 1 d. Concentrations of Zn increase upon addition of ferrihydrite at 0 d, but decrease after introduction of H₂S (g); dissolved Fe increases to approximately 36 μM at 3.2 d.

Concentrations of Cu and Zn also increased upon the addition of ferrihydrite in experiment (B) where the H₂S (g) treatment was initiated at $t = 0$ (Figure 20, 21). Concentrations of Cu and Zn increased to 27 μM , but were below detection within 0.25 d. Concentrations of dissolved Fe were detectable at 0.1 d; and increased to approximately 107 μM (6 mg/L) by 2 d. In experiments A and B, desorption of Cu and Zn resulted in the formation of CuS (s) and ZnS (s) upon exposure to dissolved sulfide; once these solid phases nucleated they appeared to stay in suspension. In both Experiments A and B, a black precipitate was observed in suspension 2 d after the chamber was initially bubbled with H₂S (g).

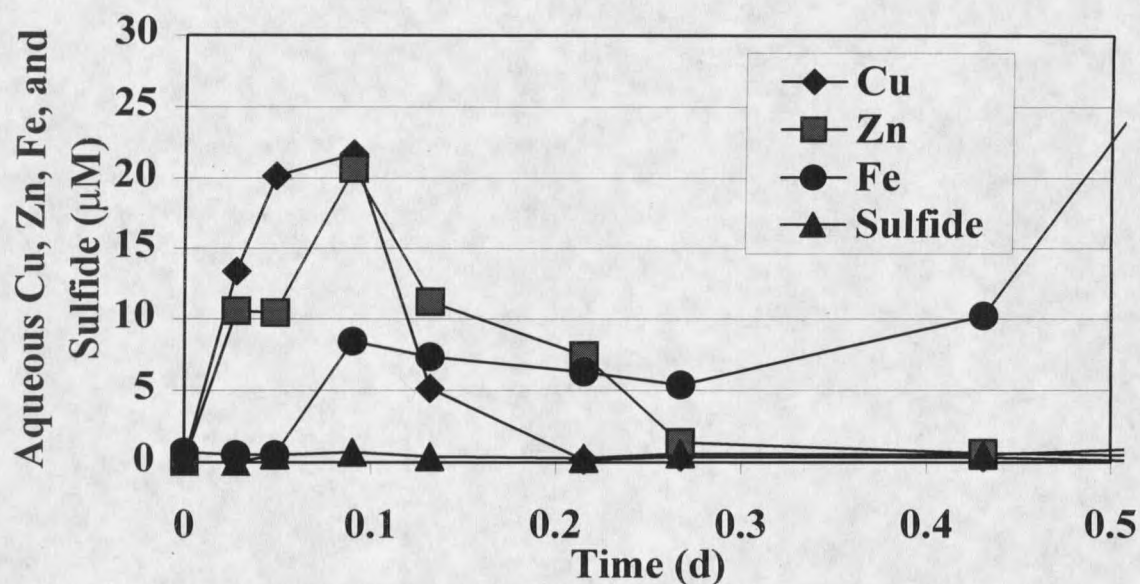


Figure 20. Dissolved Cu, Fe, Zn, and sulfide concentrations within the initial 12 hrs in experiment where H_2S (g) was initiated at $t = 0$ d (B). Concentrations of Cu and Zn increased to approximately $20 \mu\text{M}$ at 0.1 d, and were below detection limits within 0.27 d.

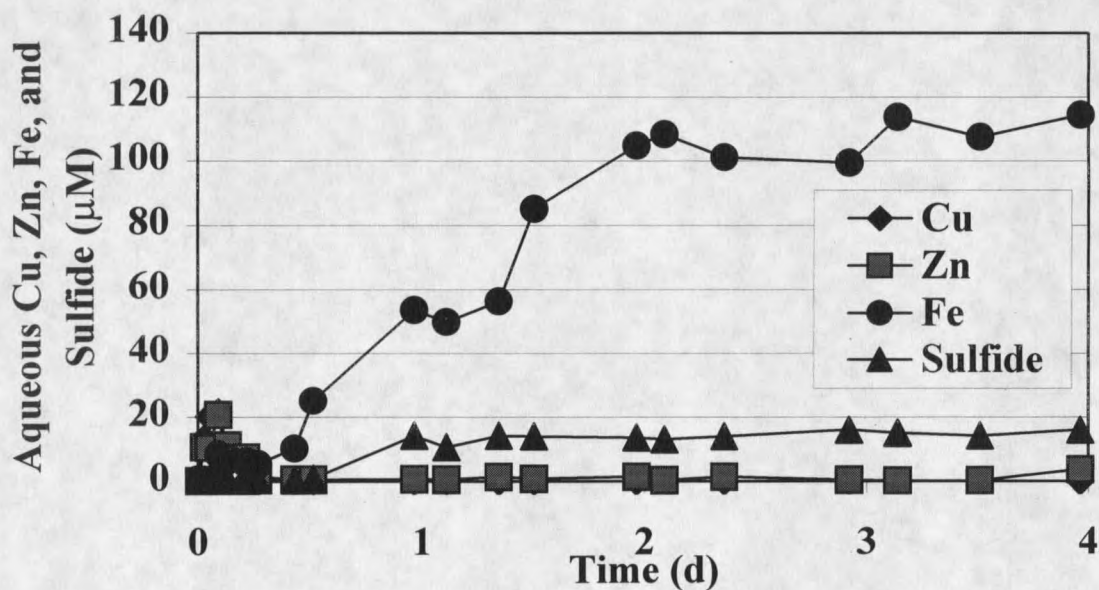


Figure 21. Dissolved metal concentrations in experiment where H_2S (g) was initiated at $t = 0$ d (B). Concentrations of dissolved Fe increased until 2 d, when Fe equilibrated at approximately $107 \mu\text{M}$.

Sequential extraction of solid phase samples collected from experiment A and B (Table 5) prior to exposure to H_2S (g) ($t = 0$ d) showed that Cu and Zn, initially sorbed to ferrihydrite, were completely extracted as Fe oxide bound metal (Figure 22, 23). However, after 2 d of H_2S (g) treatment, >99 % of total extractable Cu was extracted as sulfide bound metal. In contrast, >98 % of total extractable Zn in Experiments A and B remained within the Fe oxide fraction throughout the experiments. The amount of FeS formed, if any, was not detectable by sequential extraction during the course of experiments, and the majority of extractable Fe remained in the Fe oxide fraction. Based on an equilibrium value $107 \mu\text{M}$ Fe in experiment B after 2 d, it is estimated that only 0.55 % of the total Fe by weight is dissolved. Presuming this relatively small amount of Fe did form sulfide phases, it is unlikely that it would have been detectable using sequential extraction given the excess of Fe oxide.

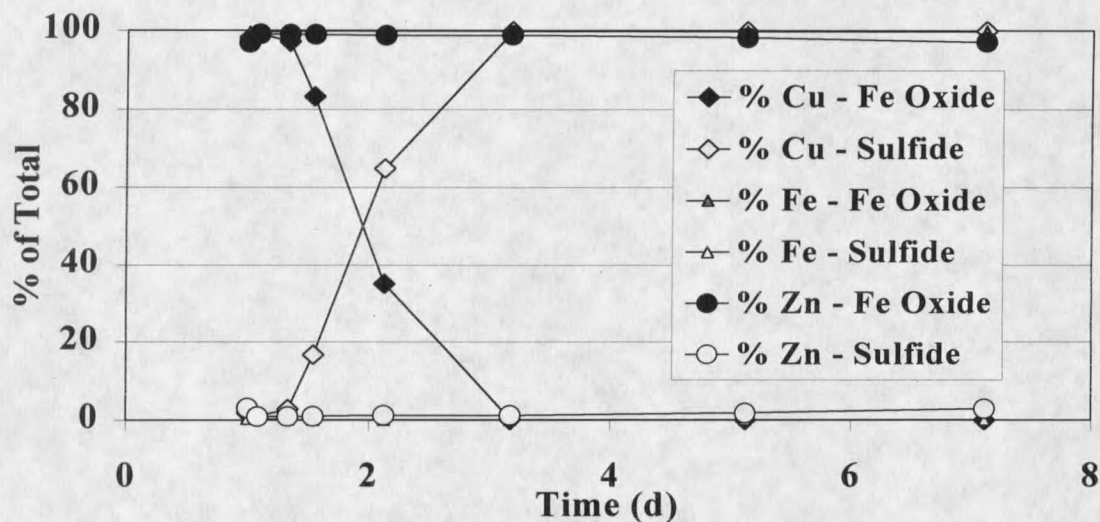


Figure 22. Results from sequential extraction of ferrihydrite samples treated with 0.01 atm H₂S (g) at t = 1d (A). Sequential extraction steps designed to extract Cu and Zn bound to Fe oxide or bound as a sulfide phase.

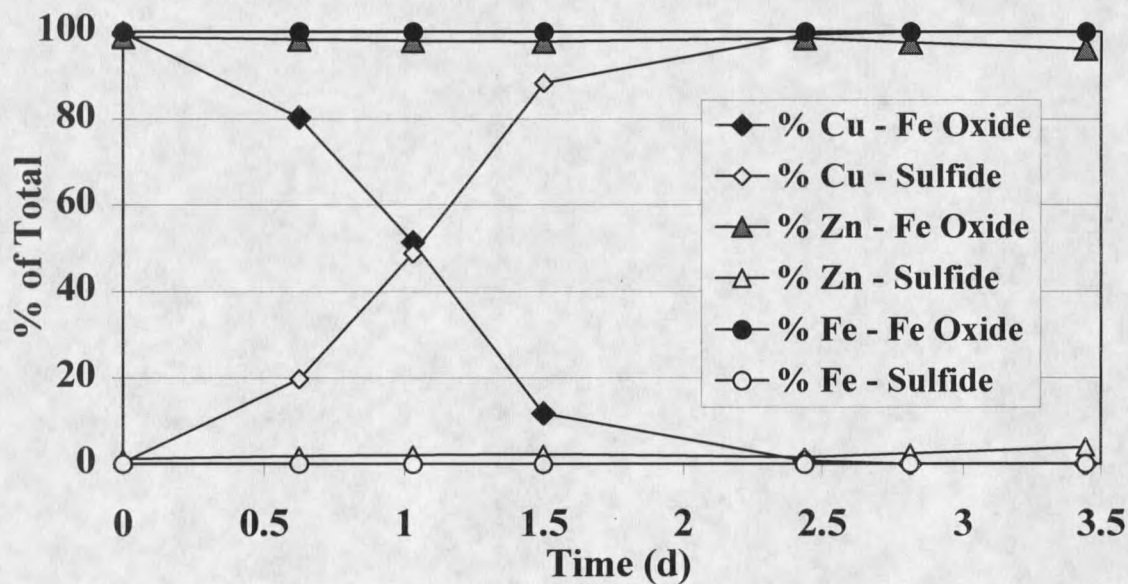


Figure 23. Results from sequential extraction of ferrihydrite samples treated with 0.01 atm H₂S at t = 0 d (B). Sequential extraction steps designed to extract Cu and Zn bound to Fe oxide or bound as a sulfide

Sequential extraction procedures applied to complex samples such as soils and sediments are often useful for only rough approximations of metal partitioning within various solid phase fractions (Tessier et al., 1989; Chao, 1984; Belzile and Tessier, 1990). In the current study, well characterized solids including CuS, ZnS, and ferrihydrite (with and without sorbed Cu and Zn) were also subjected to both steps of the sequential extraction procedure outlined above. Results for the known solid phases indicated that the sequential extraction procedure was able to extract approximately 80% (mass basis) of the total Cu and Zn from a given 0.1 g sample (CuS, ZnS, or Cu and Zn sorbed to ferrihydrite). In addition, the Fe oxide and sulfide-OM extraction steps were an accurate measure of the metals bound in the two fractions based on total extractable metal. Almost all of the total extractable Cu and Zn sorbed to the laboratory prepared 2-line ferrihydrite (99% - mole basis) was recovered in the Fe oxide extraction step. Likewise, 98% of the total extractable Cu, Zn, and S were recovered in the sulfide extraction from the CuS and ZnS control solids. Consequently, sequential extraction of the solid phases collected from our experiments provide strong evidence that all of the Cu originally sorbed to ferrihydrite was converted to a sulfide phase. Conversely, little or no sorbed Zn was converted to a Zn sulfide phase.

Visible sulfide precipitates were observed on the ferrihydrite surface after exposure to 0.01 atm H_2S (g) (Figure 24-26).

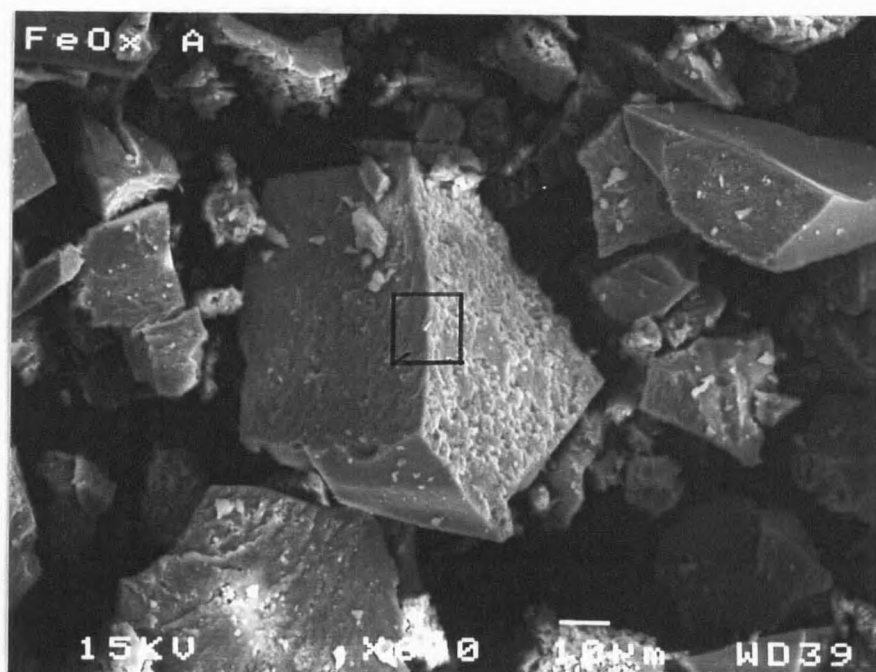


Figure 24. SEM photograph of 2-line ferrihydrite prior to the exposure to H_2S (g).

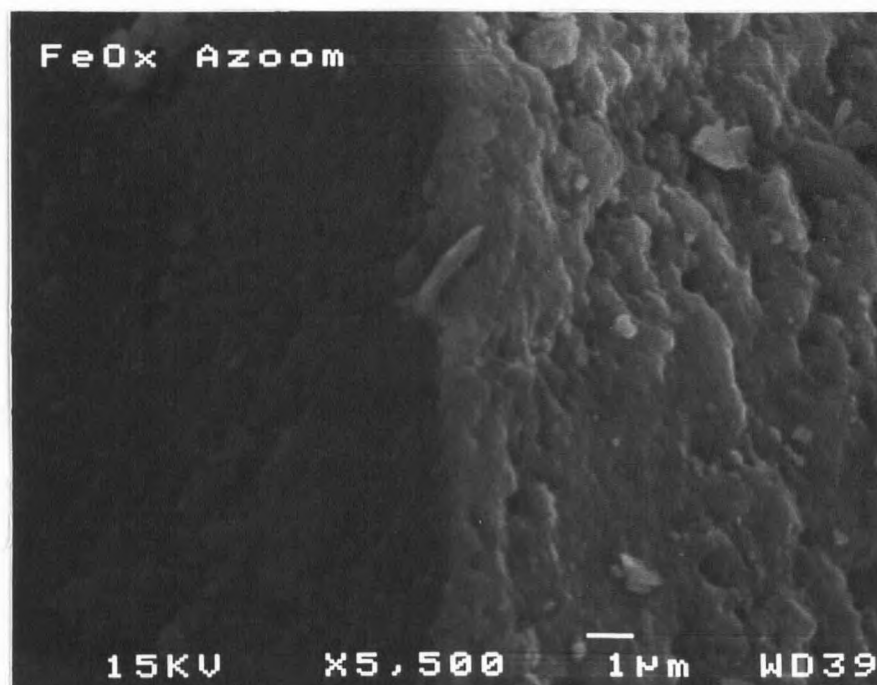


Figure 25. Enlargement of an area marked in Fig. 24, showing surface roughness of 2-line ferrihydrite prior to the exposure to H_2S (g).

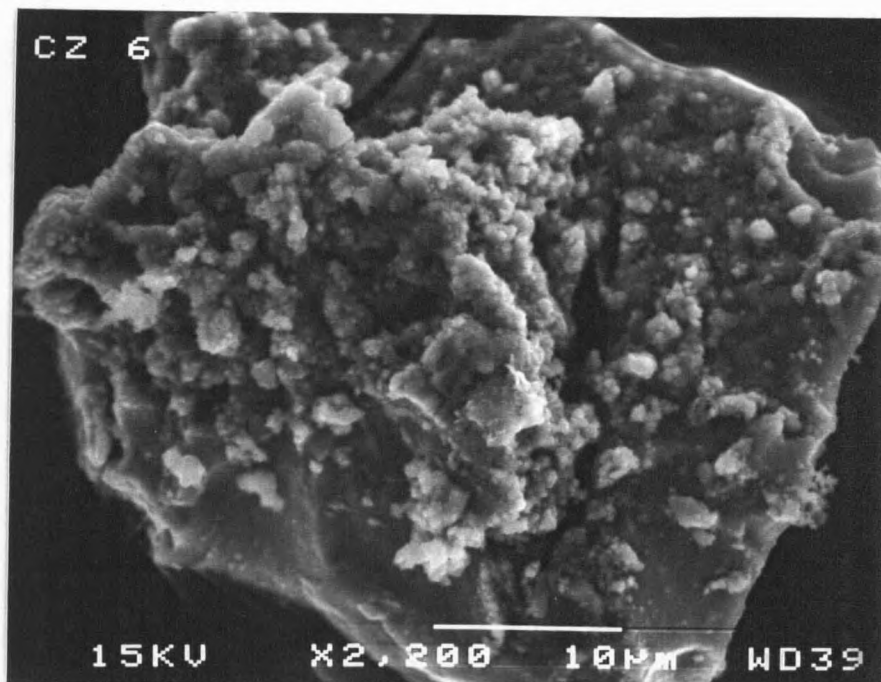


Figure 26. SEM photograph of 2-line ferrihydrite after exposure to H_2S (g) showing sulfide precipitate on the surface of the solid.

Results from the chemical analysis (EDAX) of solid phases collected from experiments A and B (Table 5) were nearly identical; therefore, results are shown for only experiment A (Figure 27). Average whole particle analysis ($n=6$) of samples throughout the H_2S (g) treatment showed that mole percents of Cu and S increased, Fe and O decreased, while Zn remained relatively constant. EDAX analyses were also obtained specifically for surface precipitates observed using SEM (such as shown in Figure 26) and compared to EDAX data obtained from portions of the Fe oxide which visually appeared to be unreacted. Results of this comparison showed that surface precipitates had higher Cu and S, and lower Fe percents as compared to fractions of the surface that appeared unreacted (Table 6.) However, because EDAX represents an

analysis depth of at least 1 μm , it may not accurately reflect the composition of surface precipitates having depths less than 1 μm .

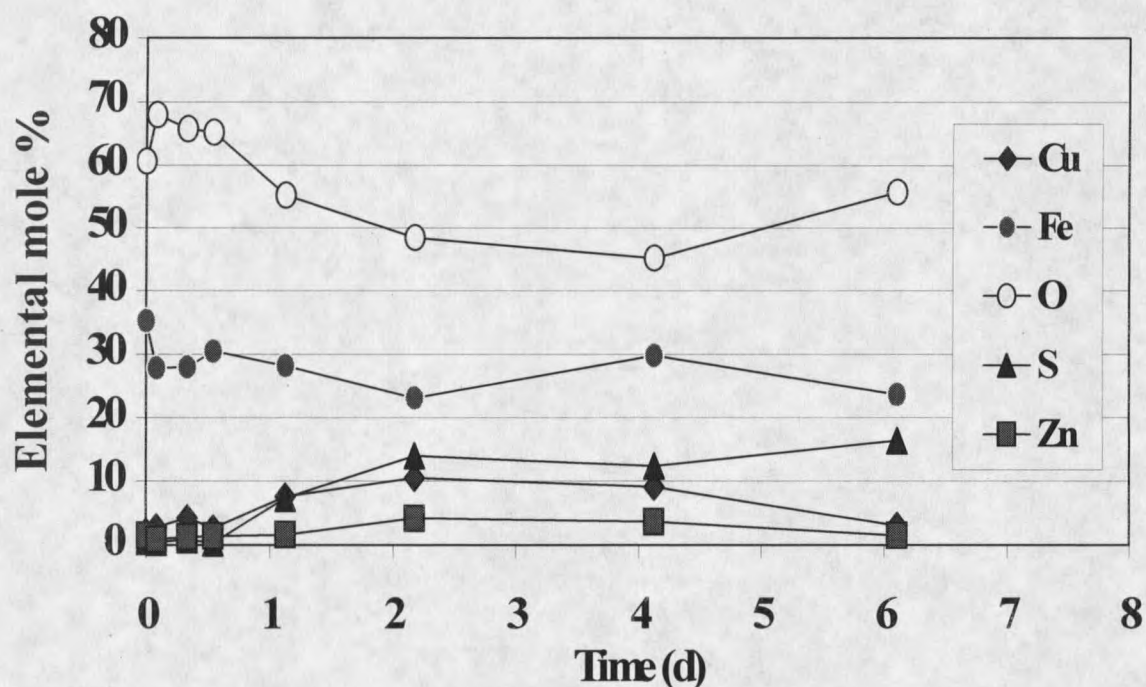


Figure 27. SEM/EDAX analysis of ferrihydrite during treatment with 0.01 atm H_2S (g) showing increases in Cu and S, and decreases in Fe and O.

Table 6. Mole percents of O, Fe, Cu, Zn, and S obtained using energy dispersive analysis of x-rays (EDAX) of portions of Fe oxide surface exhibiting no precipitates (unreacted) and those with numerous surface precipitates (reacted). Values are averages of 48 analyses over the 7 day experiment. Values in parentheses represent standard deviations

Surface	O	Fe	Cu	Zn	S
Mole %					
Unreacted	60.7 (5.4)	36.0 (4.6)	2.0 (0.7)	0.3 (0.7)	0.97 (1.0)
Reacted	58.4 (10.3)	28.2 (7.4)	8.5 (6.3)	0.1 (0.2)	4.8 (7.55)

Chemical analysis of ferrihydrite sampled throughout the experiment was also conducted using x-ray photoelectron spectroscopy (XPS) to obtain compositional information of the near surface environment (from 0 to 40-80 Å). XPS analysis of solids collected after bubbling with 0.01 atm H_2S (g) (at 1 d) in experiment A (Table 5) revealed an initial increase in Cu and S on the surface of the solids. The mole percent of Cu on the surface of the solids increased from 12 % at 1 d to 22 % at 1.15 d (0.15 d after H_2S (g) treatment began), while S increased from 0 % at 1 d to 3 % at 1.15 d. Although the mole percent of Zn remained relatively low during the initial 0.5 d after exposure to H_2S (g), Zn increased to 17 % by 3.2 d, accompanied by a decrease in Cu (Figure 28). As shown in Figure 19, solution Zn concentrations increased to approximately 153 μM Zn (10 mg/L) prior to H_2S (g) treatment as a result of desorption from ferrihydrite. It is possible that the increase in Zn on the surface of the ferrihydrite after 1.5 d (0.5 d after H_2S (g) treatment began), was a result of ZnS accumulation on the surface of the solid, which effectively masked CuS precipitate.

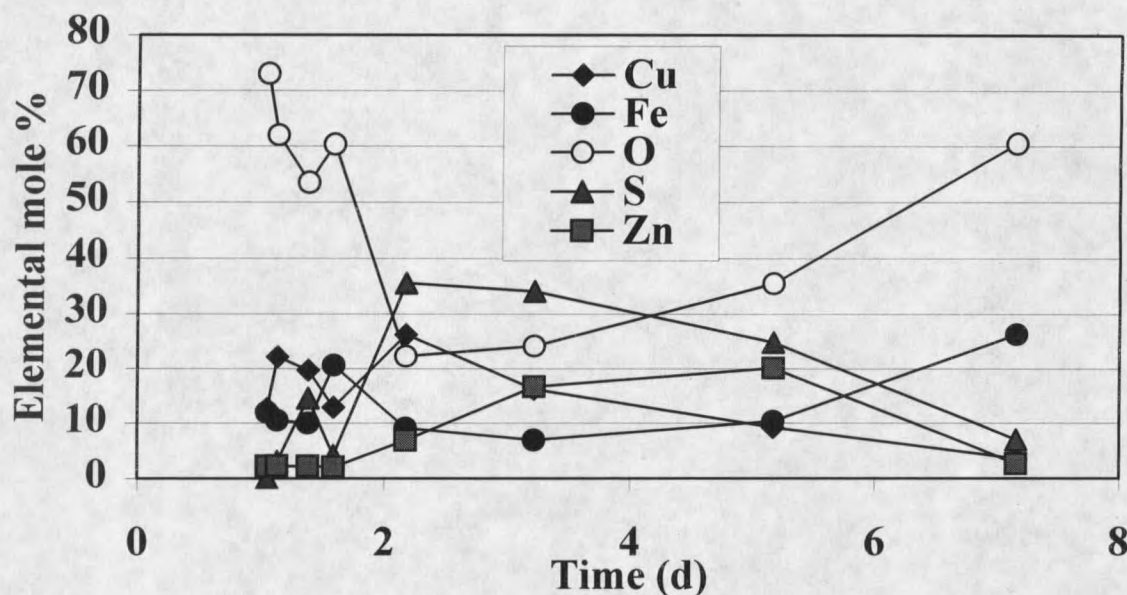


Figure 28. Analysis of ferrihydrite (with sorbed Cu and Zn) treated with 0.01 atm H_2S (g) (experiment A) using x-ray photoelectron spectroscopy (XPS). Results show an initial increase of Cu and S on the surface, which decrease after 2 d, while Zn increases after 1.5 d.

XPS analysis of solids collected from experiment B, where H_2S (g) was introduced at $t = 0$ (Table 5), revealed a similar initial increase in percent Cu on the surface from 3 to 25 % within 1 d (Figure 29). Over this same period, S increased from 0 to 20 %, indicating a Cu:S mole ratio of nearly 1:1. Mole percents of Fe and O decrease dramatically within 0.5-1 d indicating a rapid change from a ferrihydrite surface to one dominated by CuS. Interestingly, the mole percent of Zn on the surface remained relatively low throughout the experiment B (0.5-1.5 %), suggesting that ZnS was not formed upon treatment with 0.01 atm H_2S (g). After a peak in surface Cu at 1 d, Cu concentrations declined to approximately 10 % by 3.5 d. The decline in Cu was accompanied by an increase in Fe on the surface from approximately 8.4 % at 0.5 d, to 19.2 % at 3.5 d (Figure 29), suggesting the accumulation of FeS precipitate. This is

substantiated by the increase in dissolved Fe within the stirred solution after treatment with H_2S (g) (Figure 21), which likely resulted in the nucleation and subsequent precipitation of FeS within the chamber solution. This was confirmed by XPS analysis of suspended particles within the stirred solution (not solids at the bottom of the chamber) after the solution appeared to turn black (after 2 d), which revealed a mole composition suggesting FeS accumulation (54.5 % O, 28 % Fe, 16.6 % S, 0.6 % Cu, and 0.2 % Zn). Furthermore, calculations of ion activity products (MINTEQA2) based on concentrations of total soluble Fe at pH 6.5 (107 μM Fe) showed that the solution was oversaturated with respect to FeS PPT (amorphous Fe sulfide [Sadiq and Lindsay, 1979*]) ($\log \text{IAP}/K_{\text{SP}} = 0.717$ [$\log K -3.915^*$]) and pyrite ($\log \text{IAP}/K_{\text{SP}} = 6.095$ [$\log K -18.47$]), while the solution was undersaturated with respect to siderite (FeCO_3) ($\log \text{IAP}/K_{\text{SP}} = -0.766$ [$\log K -10.55$]) and wustite ($\text{Fe}_{0.95}\text{O}$) ($\log \text{IAP}/K_{\text{SP}} = -2.622$ [$\log K 11.687$]).

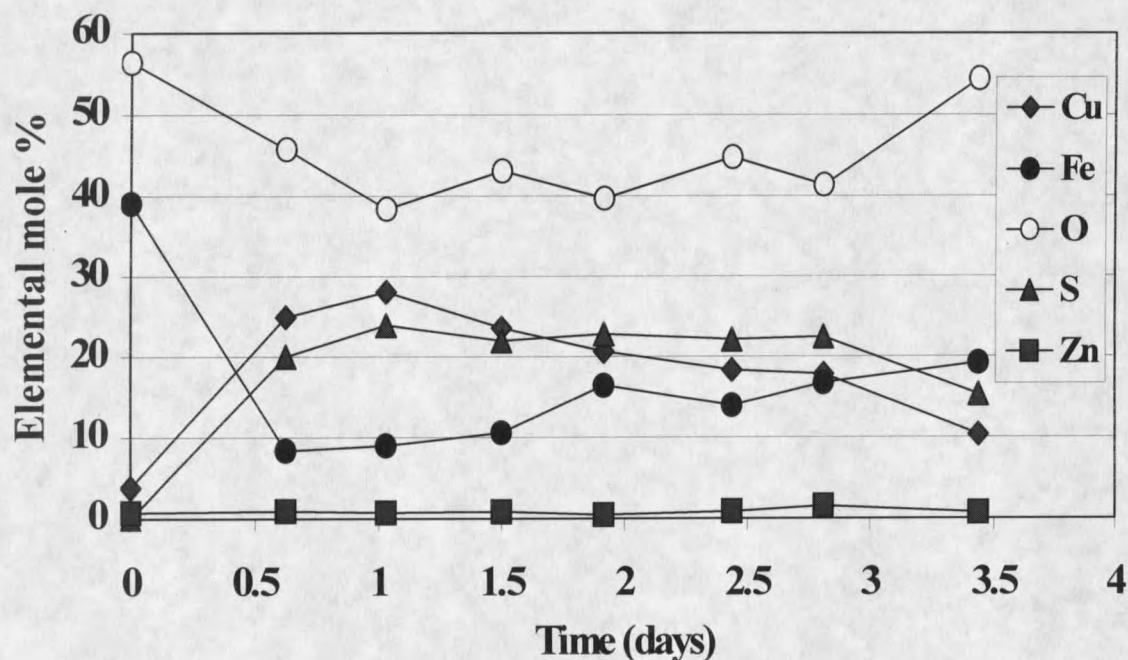


Figure 29. Analysis of ferrihydrite (with sorbed Cu and Zn) treated with 0.01 atm H_2S (g) (experiment B) using x-ray photoelectron spectroscopy (XPS). Results show an initial increase of Cu and S on the surface, which decrease after 1 d, while percent Zn remains relatively low on the surface.

Further evidence for the formation of CuS on the surface of ferrihydrite was found in the XPS spectra for $\text{Cu}2p$. When the Cu ion is in an excited chemical state, the kinetic energy of the photoelectron is reduced by the same amount as the difference between the ground state and excited state. This phenomenon results in the formation of satellite peaks (or shake-up lines) which are unique to each chemical state and/or bonding environment (Moulder, 1992). Shake-up lines are evident in the $\text{Cu}2p$ spectra of Cu sorbed to ferrihydrite prior to exposure to H_2S (g) (Figure 30-A), and are consistent with shake-up lines observed in a Cu-O bonding environment. The absence of shake-up lines,

as seen in XPS spectra of control solid Cu(II)S and Cu sulfide precipitate on ferrihydrite solids, may be indicative of the Cu-S bonding environment (Figure 30, B & C).

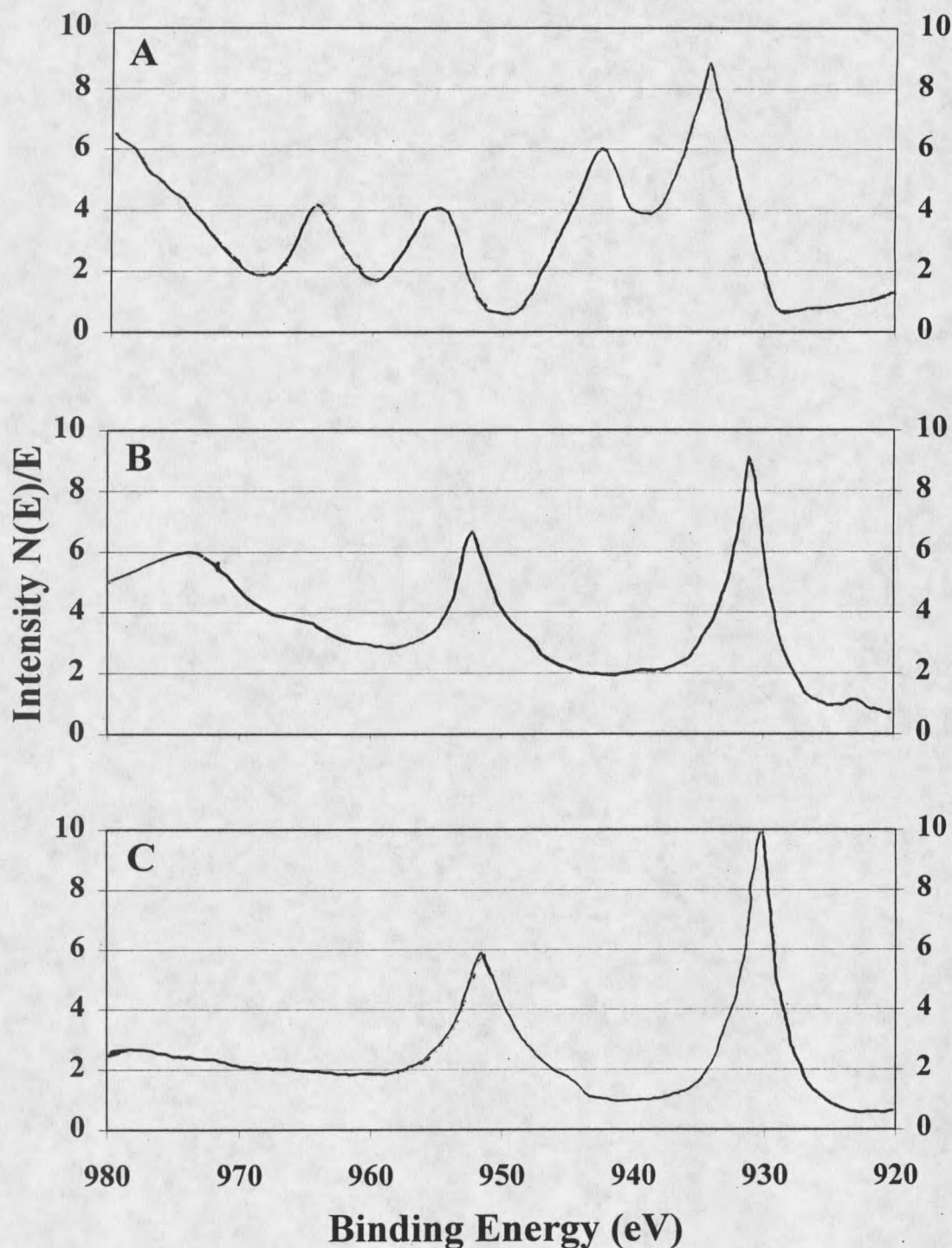


Figure 30. XPS spectra showing disappearance of Cu "shake-up" lines as sorbed Cu is converted to CuS during experiments where ferrihydrite was exposed to 0.01 atm H_2S (g). A. XPS spectra of ferrihydrite prior to exposure to H_2S (g) shows Cu shake-up lines typical of Cu-O bonding environments; B. spectra of ferrihydrite after several days exposure to H_2S (g); C. spectra of pure $Cu(II)S$.

Discussion

In the absence of ferrihydrite, precipitation of Cu and Zn sulfides occurred within approximately 0.5 d, while the conversion rate of Cu initially sorbed to ferrihydrite to CuS (s) was approximately 2.5 d (Experiment B.). In the context of time scales in natural aquatic systems, such as in wetlands, the difference in rates of CuS formation between experiments with and without ferrihydrite is relatively small. Furthermore, the observed difference in the rate of CuS (s) formation may be partially explained by higher initial Cu concentrations and higher equilibrium sulfide concentrations in experiments without ferrihydrite, resulting in greater oversaturation with respect to CuS phases. Because the conversion rate of sorbed Cu to CuS (s) was similar to the precipitation rate of CuS (s) in the absence of ferrihydrite, the presence of Fe oxides is not expected to significantly hinder the formation of CuS (s) in aquatic systems where Fe oxides are deposited and subsequently exposed to dissolved sulfide as a result of SO_4^{2-} reduction. However, as noted by Biber et al. (1994) and by Canfield and Brener (1987), the formation of CuS precipitate on the surface of Fe oxides serves to limit the diffusion of sulfide, subsequently inhibiting sulfide interaction with Fe and metals still sorbed to the Fe oxide.

Results from our experiments showed that CuS (s) formation precedes ZnS (s) formation in the presence and absence of ferrihydrite. This has implications in aquatic systems where the formation of CuS (s) may consume dissolved sulfide prior to formation of other metal sulfides such as Fe and Zn, or to reductive dissolution of Fe oxides. However, in batch experiments involving ferrihydrite, it was noted that increases

in sulfide concentration causing CuS formation on the ferrihydrite surface eventually resulted in increases in dissolved Fe, indicating Fe oxide dissolution. Although total soluble Fe concentrations increased to 107 μM after 2 d, sequential extraction of solid phases sampled after 3.5 d of exposure to H_2S (g) suggested that none of the Fe was converted to FeS (s) (experiment B). Analysis of these same solids using XPS indicated that there was a measurable amount of Fe (8.36-19.23%) within the upper 40-80 Å. These data suggest that CuS precipitation on the surface of the Fe oxide was either heterogeneous, and/or thinner than 40-80 Å. The hypothesis that the ferrihydrite surface was not completely encased in CuS precipitate was confirmed by direct observation using SEM. Furthermore, increases in dissolved Fe within the chamber indicated that ferrihydrite dissolution proceeded until at least 2 d, whereupon dissolved Fe concentrations appeared to equilibrate at 107 μM .

Though sequential extraction indicated that there was no Fe sulfide formation among the chamber solids, XPS analysis showed a slight increase in Fe mole % after approximately 0.6 days (from 8 to 19 %), accompanied by a decrease in Cu mole % on the surface of the solids after 1 d (from 28 % to 10 %) (experiment B). Calculations of saturation indices for Fe sulfide phases at 11.8 μM dissolved sulfide and 107 μM dissolved Fe^{2+} in the 0.01 M KCL background solution at pH 6.5 reveal that the solution was slightly oversaturated with respect to amorphous FeS (s) and supersaturated with respect to pyrite. It was noted by Doner and Lynn (1977) that amorphous FeS (and other intermediate solid phases) impart a distinct black color. Therefore, the precipitation of FeS (s) from dissolved Fe^{2+} is consistent with observations of a black precipitate in

suspension at approximately 2 d. The precipitation rate of FeS after 2 days is expected to be roughly equal to the dissolution rate of Fe oxide upon continued exposure to H_2S (g). Although the continued increase in surface Fe after 2 d could be due to FeS (s) accumulation, we believe the majority of freshly precipitated FeS (s) stayed in suspension within the stirred chamber solution. Our sampling protocol was biased towards solid phases accumulated at the bottom of the stirred chamber, as opposed to the those in suspension. This would explain why there was no measurable FeS in solids analyzed by sequential extraction. Further, analysis of suspended solid phases characteristic of black precipitates formed after 2 d suggested the formation of an FeS phase.

CHAPTER 4

SUMMARY

In efforts to remove Cu, Fe, Zn, and other metals from contaminated groundwater underlying the old Colorado Tailings impoundment, in Butte, MT., a surface/sub-surface flow constructed wetland was constructed. A field study was conducted which focused on the characterization of wetland sediments by means of chemical sequential extraction and scanning electron microscopy with energy dispersive analysis of x-rays (SEM/EDAX). These results were correlated with thermodynamic geochemical modeling of the influent waste stream which was used to predict possible solid phase formation. In concert with the field study, laboratory simulations of wetland reducing environments were conducted in a stirred chamber where a fixed partial pressure of H_2S (g) was used to study the formation of Cu and Zn sulfides in the absence and presence of Fe oxide solids. Solid phases formed in stirred batch reactions were analyzed using SEM/EDAX, x-ray photoelectron spectroscopy, and sequential extraction. By combining the field and laboratory studies, the thesis research has served to expand the sum of knowledge concerning the treatment of metal contaminated waters using constructed wetlands.

The constructed wetland research was useful for determining geochemical processes responsible for the removal of Cu, Fe, S, and Zn. The study indicates that a majority of the metal hydroxide and metal carbonate formation occurs within the upstream pond (FW1), while sulfide phases may have formed in the downstream ponds (FW2 and FW3). A majority of the Cu coming into the wetland system was removed from solution by sorption to Mn-Fe oxide phases, as well as by the formation of Cu sulfide solid phases. Fe was removed primarily by the precipitation of Fe oxide solid phases. While very little of the total SO_4^{2-} was removed from the influent waste stream; S retained within the constructed wetland system was primarily complexed with sulfide mineralogy. Roughly half of the influent Zn was removed within the wetland system; the retained Zn was primarily bound in carbonate phases and sorbed to Mn-Fe oxide phases. The carbon budget within the constructed wetland indicates that the system was carbon limited with respect to total SO_4^{2-} removal. The limited magnitude of microbial carbon oxidation, which results in low levels of SO_4^{2-} reduction, was manifested in a relatively small amount of total metal sulfide formation. Design changes to the existing pilot scale constructed wetland that would encourage the formation of anaerobic zones would aid in the removal of Zn and SO_4^{2-} .

Laboratory simulations of Cu and Zn sulfide formation were useful in determining relative rates of precipitation and the interaction with Fe oxides in reduced wetland environments. Cu sulfide formation occurred prior to Zn sulfide formation when both metals were sorbed to Fe oxides, as well as when both metals were dissolved in solution. This suggests that in sulfide limited aquatic systems, Cu sulfide formation will likely scavenge all available dissolved sulfide. The relative rate of Cu sulfide formation

in the presence and absence of Fe oxides is similar in comparison to the residence time in most constructed wetlands. Therefore, it is thought that the presence of Fe oxides in metal contaminated water will not significantly inhibit the conversion of sorbed Cu to Cu sulfide:

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APPENDIX A

ADDITIONAL SEQUENTIAL EXTRACTION DATA

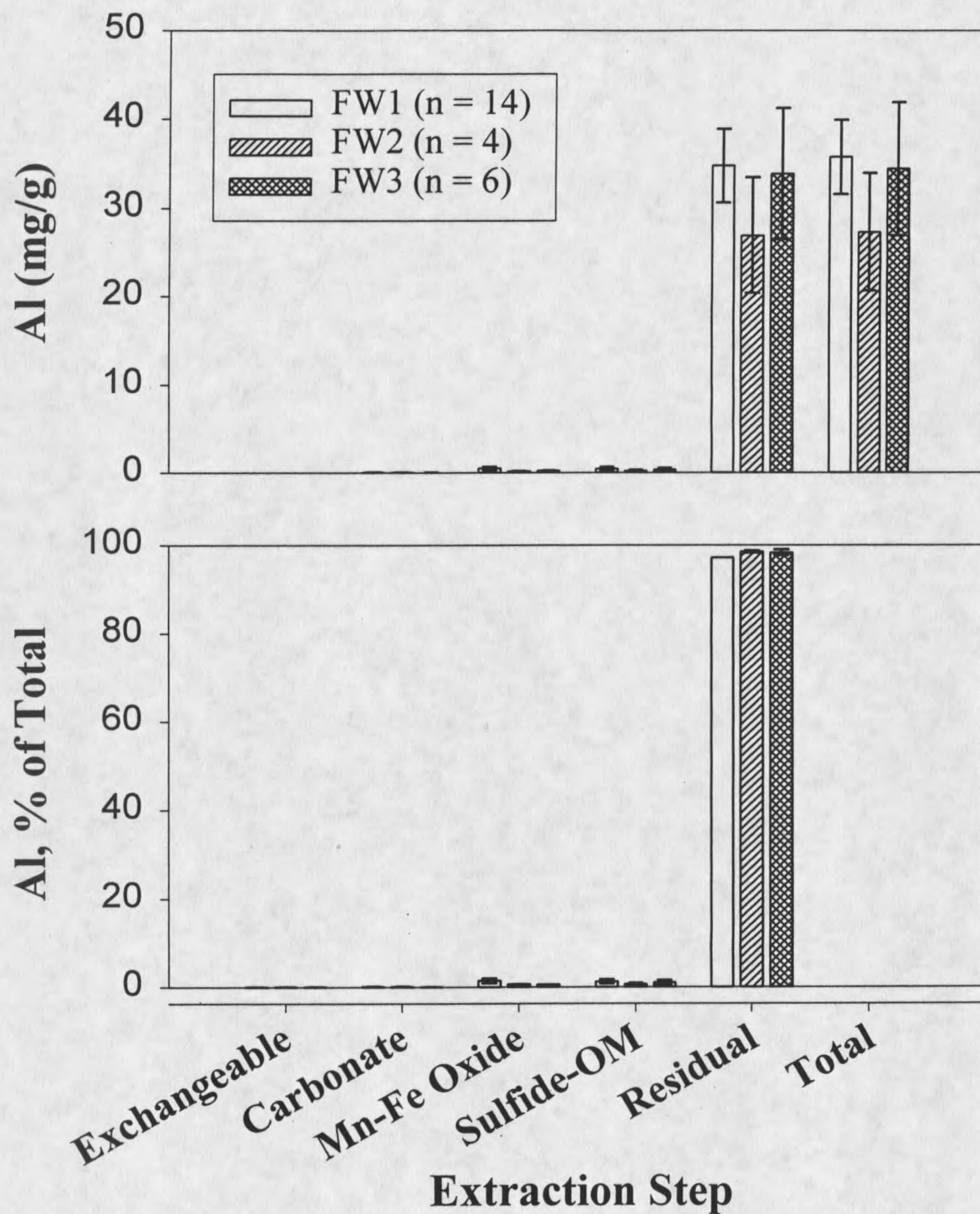


Figure 31. Concentrations and percentages of Al in wetland sediments (FW1-FW3) among operationally defined chemical fractions, as determined by sequential extraction. Data represents averages from a number (n) of wetland sediment samples collected from each pond within the constructed wetland. Error bars represent standard deviations.

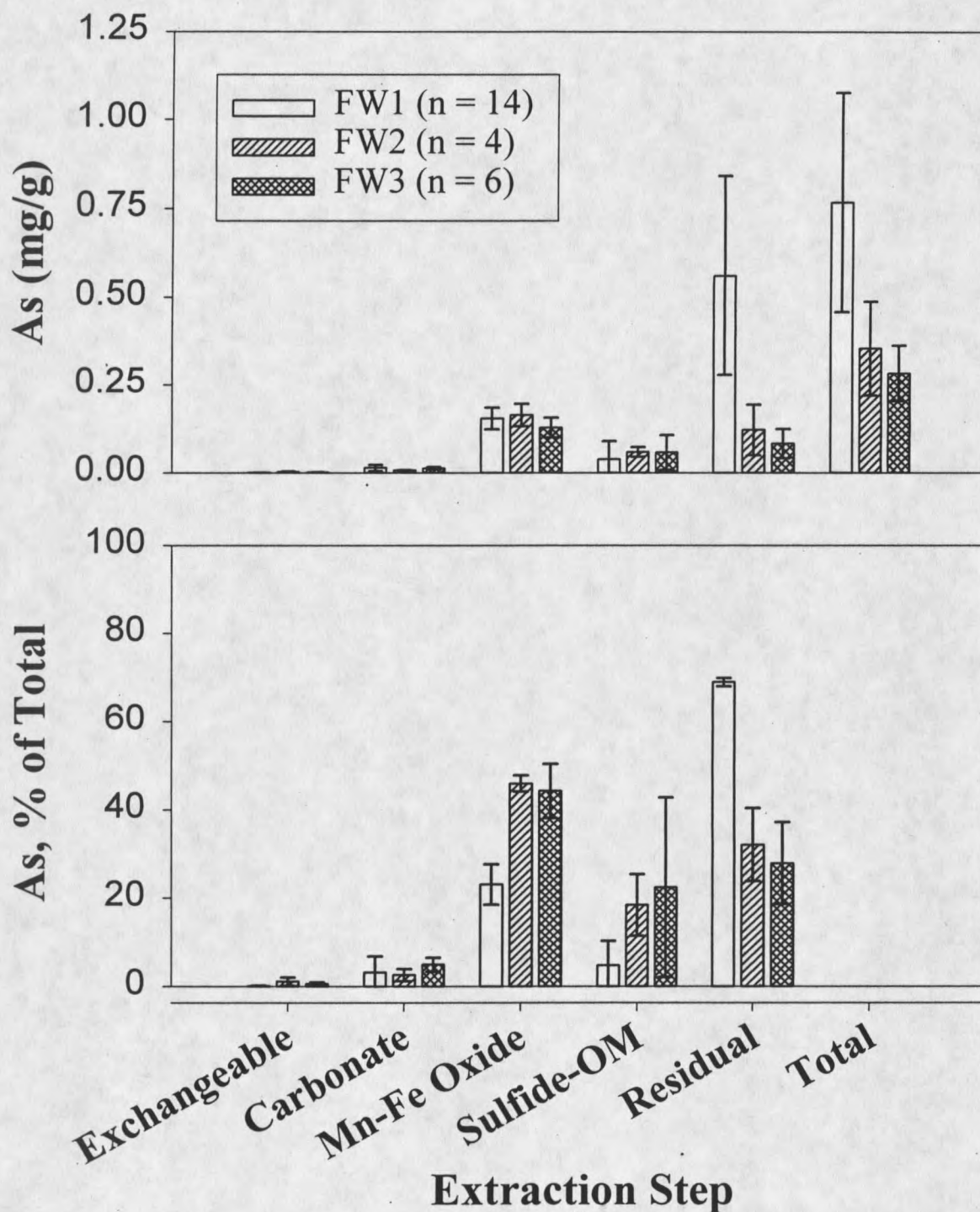


Figure 32. Concentrations and percentages of As in wetland sediments (FW1-FW3) among operationally defined chemical fractions, as determined by sequential extraction. Data represents averages from a number (n) of wetland sediment samples collected from each pond within the constructed wetland. Error bars represent standard deviations.

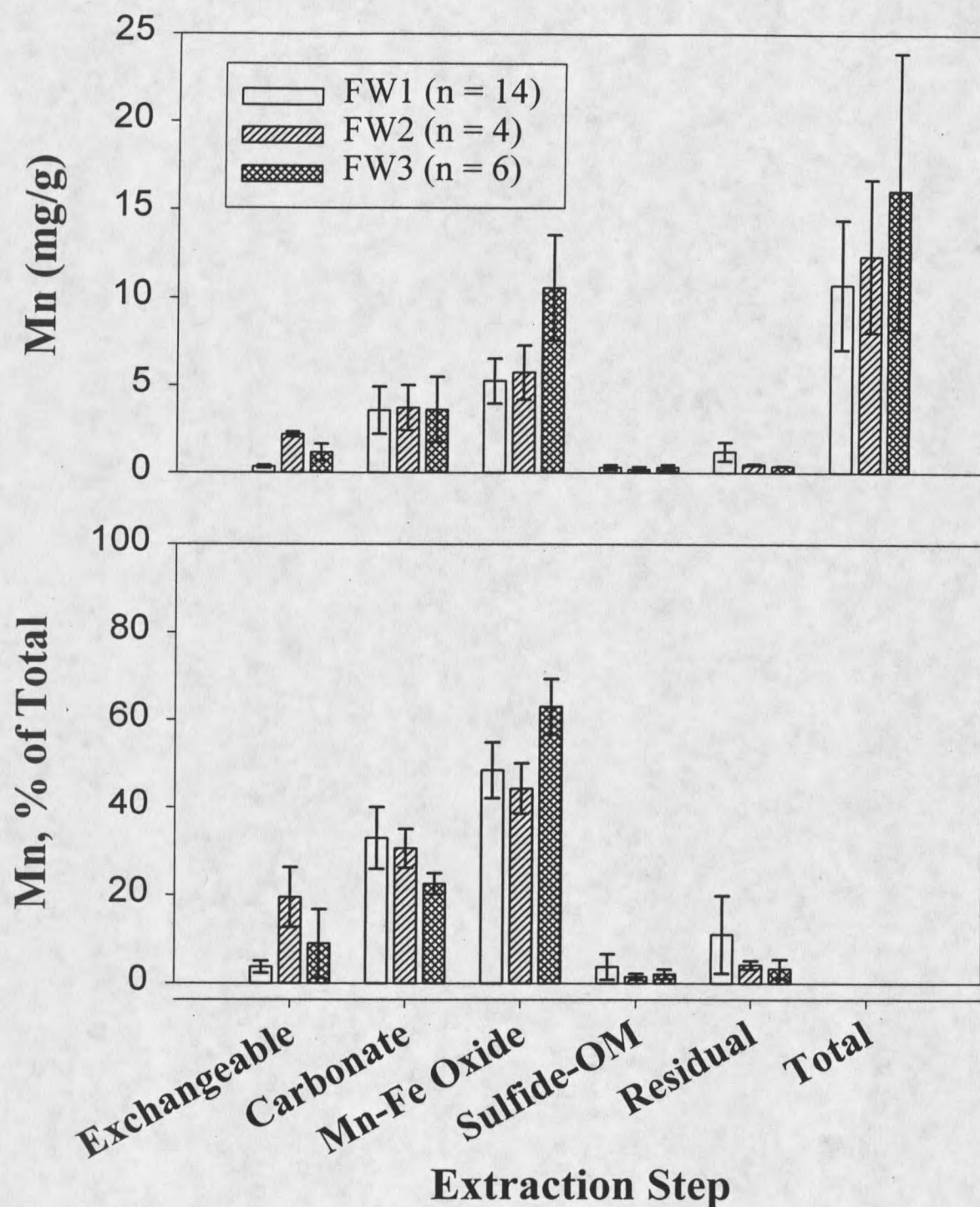


Figure 33. Concentrations and percentages of Mn in wetland sediments (FW1-FW3) among operationally defined chemical fractions, as determined by sequential extraction. Data represents averages from a number (n) of wetland sediment samples collected from each pond within the constructed wetland. Error bars represent standard deviations.

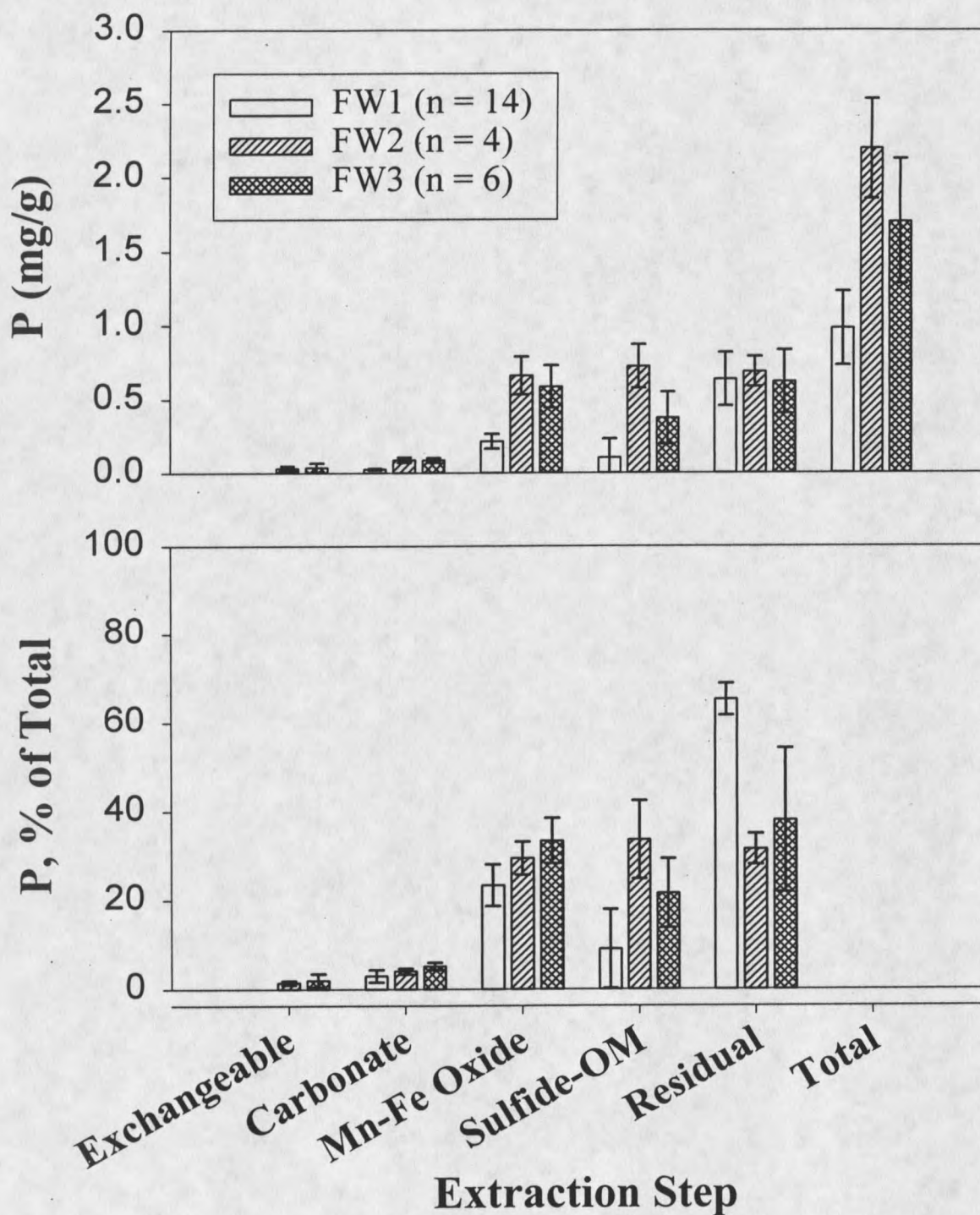


Figure 34. Concentrations and percentages of P in wetland sediments (FW1-FW3) among operationally defined chemical fractions, as determined by sequential extraction. Data represents averages from a number (n) of wetland sediment samples collected from each pond within the constructed wetland. Error bars represent standard deviations.

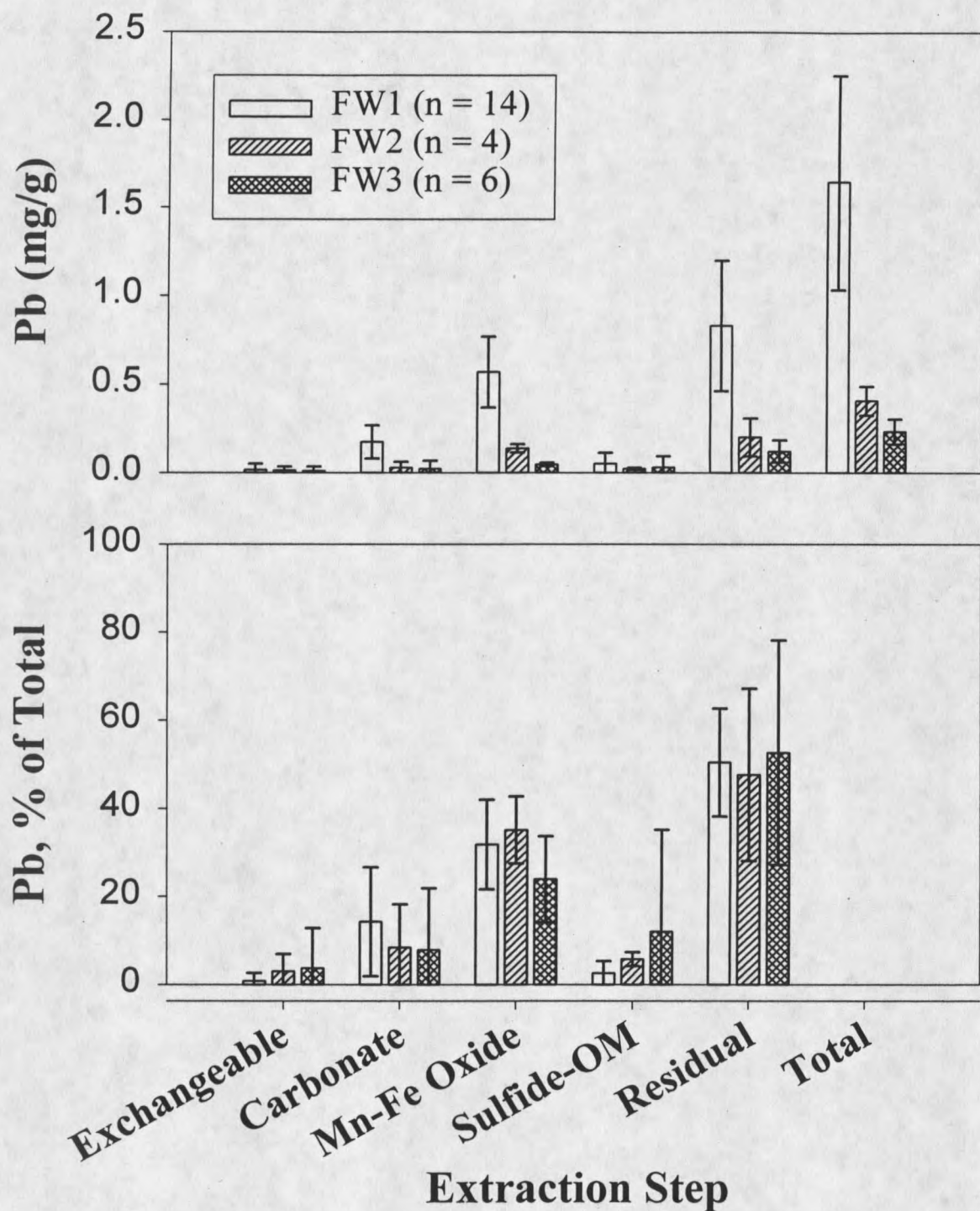


Figure 35. Concentrations and percentages of Pb in wetland sediments (FW1-FW3) among operationally defined chemical fractions, as determined by sequential extraction. Data represents averages from a number (n) of wetland sediment samples collected from each pond within the constructed wetland. Error bars represent standard deviations.

Table 7

Global Averaged Data from Sequential Extraction of Wetland Sediments and Soil Samples

- Data is shown as averages with associated standard deviations, as well as percents of totals with associated standard deviations.

- Mn/Fe oxide extraction steps are combined

FW01 (n=14)	Al	As	Cu	Fe	Mn	P	Pb	S	Zn
Extraction Step	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)
Exchangable	2.96	0.86	27.38	0.12	356.19	0.00	16.79	1495.46	258.57
Carbonate	35.15	14.17	5465.00	709.51	3578.66	26.17	174.35	398.29	26367.96
Mn-Fe Oxide	495.63	153.54	5645.51	21298.51	5256.78	215.80	569.44	493.95	15534.80
Sulfide-OM	444.08	38.08	2109.57	527.77	317.98	103.25	50.97	780.05	986.75
Residual	34785.71	560.07	986.36	22853.57	1222.46	633.93	830.71	1463.57	2046.79
Total	35763.54	766.72	14233.81	45389.49	10732.06	979.15	1642.27	4631.33	45194.87

FW01	Al	As	Cu	Fe	Mn	P	Pb	S	Zn
Extraction Step	(STDEV)	(STDEV)	(STDEV)	(STDEV)	(STDEV)	(STDEV)	(STDEV)	(STDEV)	(STDEV)
Exchangable	1.35	0.45	13.21	0.22	94.93	0.00	35.25	1260.56	110.12
Carbonate	22.72	8.82	2571.81	935.36	1345.11	6.47	93.98	179.85	13375.44
Mn-Fe Oxide	176.13	30.56	2350.85	6204.36	1281.44	50.41	198.99	232.39	3312.55
Sulfide-OM	198.09	50.80	1246.31	216.19	137.90	127.65	63.05	266.11	371.41
Residual	4097.35	281.69	550.59	2195.93	532.72	179.91	367.12	602.30	585.97
Total	4152.83	309.20	7810.17	10521.74	3684.50	248.54	612.03	2171.43	16293.95

FW01	Al	As	Cu	Fe	Mn	P	Pb	S	Zn
Extraction Step	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
Exchangable	0.01	0.13	0.25	0.00	3.72	0.00	0.84	29.32	0.77
Carbonate	0.09	3.15	41.51	1.97	32.96	2.94	14.28	8.70	54.17
Mn-Fe Oxide	1.42	23.07	34.76	44.69	48.52	23.40	31.82	9.58	37.32
Sulfide-OM	1.23	4.72	16.58	1.26	3.74	9.00	2.59	19.25	2.84
Residual	97.24	68.95	6.90	52.08	11.06	65.22	50.46	33.14	4.91

FW01	Al	As	Cu	Fe	Mn	P	Pb	S	Zn
Extraction Step	(% STDEV)	(% STDEV)	(% STDEV)	(% STDEV)	(% STDEV)	(% STDEV)	(% STDEV)	(% STDEV)	(% STDEV)
Exchangable	0.00	0.10	0.13	0.00	1.36	0.00	1.78	10.60	0.65
Carbonate	0.06	3.60	8.44	2.74	7.11	1.39	12.38	1.73	16.48
Mn-Fe Oxide	0.54	4.60	12.88	9.62	6.42	4.72	10.20	3.08	7.68
Sulfide-OM	0.48	5.49	7.12	0.70	2.92	8.85	2.81	6.43	2.23
Residual	0.00	0.92	12.91	1.45	8.76	3.60	12.26	11.20	7.46

FW02 (n=4)	Al	As	Cu	Fe	Mn	P	Pb	S	Zn
Extraction Step	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)
Exchangable	5.76	3.14	480.52	0.00	2200.20	32.54	14.02	1663.96	810.38
Carbonate	26.46	7.72	1368.36	28.00	3730.84	87.34	29.40	460.28	29044.60
Mn-Fe Oxide	168.68	162.84	546.24	6184.58	5748.48	660.88	138.83	943.88	25230.94
Sulfide-OM	195.68	58.56	2221.84	418.96	206.68	723.08	23.16	1651.12	1370.44
Residual	26937.50	121.13	519.50	15587.50	482.88	686.25	202.00	668.75	890.88
Total	27334.08	353.39	5136.46	22219.04	12369.08	2190.09	407.41	5387.99	57347.24

FW02	Al	As	Cu	Fe	Mn	P	Pb	S	Zn
Extraction Step	(STDEV)	(STDEV)	(STDEV)	(STDEV)	(STDEV)	(STDEV)	(STDEV)	(STDEV)	(STDEV)
Exchangable	1.37	1.77	110.92	0.00	154.16	14.98	20.60	409.78	221.97
Carbonate	9.52	1.31	247.45	6.27	1295.17	17.44	34.00	109.91	14387.13
Mn-Fe Oxide	27.70	31.82	109.50	1146.53	1550.99	127.35	23.99	94.25	11515.03
Sulfide-OM	100.27	13.28	815.69	130.20	147.93	145.98	5.65	488.26	1249.96
Residual	6544.38	71.15	284.85	4200.27	56.28	101.44	107.09	480.65	627.57
Total	6663.21	134.31	922.89	3140.92	4332.31	337.26	81.05	1003.73	37878.17

FW02	Al	As	Cu	Fe	Mn	P	Pb	S	Zn
Extraction Step	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
Exchangable	0.02	1.11	9.83	0.00	19.47	1.44	3.00	30.70	2.12
Carbonate	0.10	2.56	27.60	0.13	30.55	4.01	8.45	8.97	57.46
Mn-Fe Oxide	0.62	45.89	10.67	28.57	44.32	29.47	35.12	18.45	36.95
Sulfide-OM	0.68	18.40	42.17	1.85	1.51	33.60	5.79	30.39	1.95
Residual	98.57	32.07	9.73	69.47	4.15	31.47	47.67	11.49	1.52

FW02	Al	As	Cu	Fe	Mn	P	Pb	S	Zn
Extraction Step	(% STDEV)	(% STDEV)	(% STDEV)	(% STDEV)	(% STDEV)	(% STDEV)	(% STDEV)	(% STDEV)	(% STDEV)
Exchangable	0.01	0.95	3.95	0.00	6.75	0.47	3.91	4.33	1.53
Carbonate	0.05	1.38	8.09	0.01	4.44	0.67	9.80	3.31	14.38
Mn-Fe Oxide	0.06	1.84	2.06	6.07	5.79	3.75	7.63	3.37	8.18
Sulfide-OM	0.22	7.02	8.27	0.31	0.68	8.75	1.57	4.78	0.91
Residual	0.24	8.26	4.19	11.83	0.98	3.46	19.56	6.84	0.28

FW03 (n=6)	Al	As	Cu	Fe	Mn	P	Pb	S	Zn
Extraction Step	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)
Exchangable	2.80	1.63	184.89	0.00	1168.73	36.40	10.13	736.80	432.99
Carbonate	12.45	13.01	421.61	2.16	3625.89	85.40	22.73	512.57	13599.20
Mn-Fe Oxide	202.23	127.45	315.04	2801.49	10561.99	585.95	47.71	847.72	10446.35
Sulfide-OM	346.85	57.39	1393.31	314.91	323.49	373.25	31.07	1474.93	948.77
Residual	33891.67	82.50	241.83	18916.67	390.67	617.50	122.00	400.00	524.83
Total	34456.00	281.98	2556.69	22035.23	16070.77	1698.50	233.64	3972.03	25952.14

FW03	Al	As	Cu	Fe	Mn	P	Pb	S	Zn
Extraction Step	(STDEV)	(STDEV)	(STDEV)	(STDEV)	(STDEV)	(STDEV)	(STDEV)	(STDEV)	(STDEV)
Exchangable	1.33	1.01	148.41	0.00	482.55	31.57	24.82	452.51	291.80
Carbonate	6.00	3.38	335.89	3.51	1871.30	16.41	46.11	108.81	9737.31
Mn-Fe Oxide	43.66	27.74	189.05	915.19	3003.23	143.29	10.82	186.00	2498.95
Sulfide-OM	192.98	48.72	1121.24	148.84	149.12	176.98	63.19	450.42	565.45
Residual	7372.14	41.55	130.63	4327.09	21.08	213.58	62.76	248.96	262.88
Total	7465.18	79.49	1573.88	5558.69	7854.64	420.71	71.76	1158.04	14101.85

FW03	Al	As	Cu	Fe	Mn	P	Pb	S	Zn
Extraction Step	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
Exchangable	0.01	0.57	6.66	0.00	9.00	1.97	3.71	17.02	2.16
Carbonate	0.04	4.91	17.61	0.01	22.53	5.13	7.91	13.30	48.36

Mn-Fe Oxide	0.58	44.23	10.37	12.15	63.08	33.37	23.91	22.73	43.01
Sulfide-OM	1.02	22.41	53.76	1.51	2.12	21.55	12.04	37.55	4.17
Residual	98.35	27.89	11.60	86.49	3.28	37.97	52.67	9.40	2.30

FW03	Al	As	Cu	Fe	Mn	P	Pb	S	Zn
Extraction Step	(% STDEV)	(% STDEV)	(% STDEV)	(% STDEV)	(% STDEV)	(% STDEV)	(% STDEV)	(% STDEV)	(% STDEV)
Exchangable	0.01	0.39	2.65	0.00	7.79	1.47	9.10	7.42	2.26
Carbonate	0.03	1.58	7.09	0.01	2.36	0.85	13.97	2.45	11.42
Mn-Fe Oxide	0.00	6.11	4.18	2.75	6.37	5.09	9.80	6.47	5.77
Sulfide-OM	0.49	20.30	17.85	0.74	1.09	7.80	23.17	9.79	2.53
Residual	0.67	9.34	4.92	5.07	2.16	16.16	25.49	4.42	0.85

Algal Mat (n=1)	Al	As	Cu	Fe	Mn	P	Pb	S	Zn
Extraction Step	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)
Exchangable	2.92	4.28	369.76	0	2156.96	9.56	0.56	612.92	597.84
Carbonate	33.16	11.56	1709.32	24	7287.32	53.88	28.92	405.84	32878
Mn-Fe Oxide	191.6	179.36	990.96	5847.52	7444.88	283.92	101.44	497.28	13588.48
Sulfide-OM	249.84	39.36	640.96	565.92	193.28	167.12	25.6	933.84	691.44
Residual	36100	97.75	382.25	20150	462.25	617.5	120	245	488
Total	36577.52	332.31	4093.25	26581.08	17544.69	1131.98	274.56	2694.88	48243.76

Peat # 1 (n=1)	Al	As	Cu	Fe	Mn	P	Pb	S	Zn
Extraction Step	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)
Exchangable	0.8	0.48	2.08	0.48	7.2	0	0.92	731.84	47.24
Carbonate	322.56	10.08	808.56	297.72	18.32	15.76	16.92	101.84	402.68
Mn-Fe Oxide	1743.48	85.88	189.28	3819.12	84.72	157.96	35.4	74.84	309
Sulfide-OM	190.4	33.04	413.52	1106.16	1.12	91.12	2.96	1204.24	63.04
Residual	23175	64.75	265.25	28625	100.5	160	80.25	26852.5	360
Total	25432.24	194.23	1678.69	33848.48	211.86	414.52	136.45	28961.9	1181.96

Peat # 2 (n=1)	Al	As	Cu	Fe	Mn	P	Pb	S	Zn
Extraction Step	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)
Exchangable	0.56	1.64	3.28	0	123.08	0	1.12	96.56	119.76
Carbonate	108.52	69.88	1355	1445.36	328.2	33.56	107.84	32.2	2799.48
Mn-Fe Oxide	624.36	367.96	377.48	3474.32	377.68	241.12	86.04	128.92	824
Sulfide-OM	194	53.44	157.44	715.44	12.16	104.56	5.12	651.04	74.88
Residual	21125	70.25	152.75	7700	196	97.5	110.25	4692.5	989.75
Total	22052.44	563.17	2045.95	13334.88	1037.12	467.5	308.85	5594.14	4807.87

Wall (n=1)	Al	As	Cu	Fe	Mn	P	Pb	S	Zn
Extraction Step	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)
Exchangable	1.32	1.16	11.04	0	240.12	0	0	60.72	80.52
Carbonate	45.12	15.4	593.28	739.96	599	31.72	66.16	57.2	2096.76
Mn-Fe Oxide	609.96	45.68	151.76	2015	276.68	422.28	43.56	50.8	578.48
Sulfide-OM	568	22.64	87.12	324.64	15.12	86.64	0	419.52	61.44
Residual	34025	12.75	15	12600	164.5	100	23.25	125	68.25
Total	35249.4	97.63	858.2	15678.96	1295.42	631.28	129.81	706.24	2885.45

Table 8

Sequential Extraction Results of Wetland Sediments and Soil Samples

Note: duplicate samples are averaged

Extraction Step	1AL	1A U	1B	1D	1G	1G L	1G U	1H	2A	2B	2D	3A	3B	3C	3D	Algal Mat	Peat # 1	Peat # 2	Wall
Extraction Step	Al (µg/g)	Al (µg/g)	Al (µg/g)	Al (µg/g)	Al (µg/g)	Al (µg/g)	Al (µg/g)	Al (µg/g)	Al (µg/g)	Al (µg/g)	Al (µg/g)	Al (µg/g)	Al (µg/g)	Al (µg/g)	Al (µg/g)	Al (µg/g)	Al (µg/g)	Al (µg/g)	Al (µg/g)
Exchangeable	3.16	4.60	1.36	2.80	2.40	4.56	2.12	1.84	6.84	4.24	5.12	3.24	2.24	1.68	4.16	2.92	0.80	0.56	1.32
Carbonate	8.64	9.16	65.08	21.12	59.52	50.12	51.12	22.16	27.40	29.60	21.44	11.40	10.80	7.20	23.12	33.16	322.56	108.52	45.12
Mn Oxide	4.28	38.00	3.20	44.44	3.36	389.20	379.88	3.12	8.12	1.92	17.92	49.92	9.52	2.40	19.20	8.00	949.72	342.44	278.68
Mn-Fe Oxide	465.56	554.16	211.48	635.20	205.76	216.32	198.32	446.56	147.40	221.68	122.16	259.00	139.40	153.76	122.32	183.60	793.76	281.92	331.28
Sulfide-OM	293.12	460.24	184.88	435.04	285.28	704.16	708.64	359.68	177.68	317.44	109.92	579.84	162.80	270.24	325.60	249.84	190.40	194.00	568.00
Residual	30850.00	34150.00	36875.00	27700.00	37400.00	39150.00	38800.00	34550.00	27350.00	31750.00	21300.00	37800.00	31175.00	40900.00	24500.00	36100.00	23175.00	21125.00	34025.00
Total	31624.76	35216.16	37341.00	28838.60	37956.32	40514.36	40140.08	35383.36	27717.44	32324.88	21576.56	38703.40	31499.76	41335.28	24994.40	36577.52	25432.24	22052.44	35249.40
Digestion	31900.00	44100.00	38000.00	31400.00	72400.00	69800.00													
% Recovery	99.14	79.86	98.27	91.84		55.96	57.51												

Extraction Step	1AL	1A U	1B	1D	1G	1G L	1G U	1H	2A	2B	2D	3A	3B	3C	3D	Algal Mat	Peat # 1	Peat # 2	Wall
Extraction Step	Al (%)	Al (%)	Al (%)	Al (%)	Al (%)	Al (%)	Al (%)	Al (%)	Al (%)	Al (%)	Al (%)	Al (%)	Al (%)	Al (%)	Al (%)	Al (%)	Al (%)	Al (%)	Al (%)
Exchangeable	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.02	0.01	0.01	0.00	0.02	0.01	0.00	0.00	0.00
Carbonate	0.03	0.03	0.17	0.07	0.16	0.12	0.13	0.06	0.10	0.09	0.10	0.03	0.03	0.02	0.09	0.09	1.27	0.49	0.13
Mn Oxide	0.01	0.11	0.01	0.15	0.01	0.96	0.95	0.01	0.03	0.01	0.08	0.13	0.03	0.01	0.08	0.02	3.73	1.55	0.79
Mn-Fe Oxide	1.47	1.57	0.57	2.20	0.54	0.53	0.49	1.26	0.53	0.69	0.57	0.67	0.44	0.37	0.49	0.50	3.12	1.28	0.94
Sulfide-OM	0.93	1.31	0.50	1.51	0.75	1.74	1.77	1.02	0.64	0.98	0.51	1.50	0.52	0.65	1.30	0.68	0.75	0.88	1.61
Residual	97.55	96.97	98.75	96.05	98.53	96.63	96.66	97.64	98.67	98.22	98.72	97.67	98.97	98.95	98.02	98.69	91.12	95.79	96.53

Extraction Step	1AL	1A U	1B	1D	1G	1G L	1G U	1H	2A	2B	2D	3A	3B	3C	3D	Algal Mat	Peat # 1	Peat # 2	Wall
Extraction Step	As (µg/g)	As (µg/g)	As (µg/g)	As (µg/g)	As (µg/g)	As (µg/g)	As (µg/g)	As (µg/g)	As (µg/g)	As (µg/g)	As (µg/g)	As (µg/g)	As (µg/g)	As (µg/g)	As (µg/g)	As (µg/g)	As (µg/g)	As (µg/g)	As (µg/g)
Exchangeable	0.36	0.96	0.96	1.12	1.36	1.16	0.28	1.04	4.60	2.24	1.12	1.64	0.96	3.12	1.44	4.28	0.48	1.64	1.16
Carbonate	8.12	7.72	10.96	8.64	9.20	27.64	27.24	8.56	8.72	7.44	6.00	17.20	10.84	10.96	11.04	11.56	10.08	69.88	15.40
Mn Oxide	0.00	0.28	2.76	2.20	0.64	28.88	31.48	0.08	3.92	1.52	2.64	21.36	10.72	3.12	25.04	4.68	12.96	97.96	18.88
Mn-Fe Oxide	172.04	128.44	182.88	166.44	168.16	84.48	79.20	222.48	146.04	136.88	210.40	143.28	99.36	50.64	136.48	174.68	72.92	270.00	26.80
Sulfide-OM	16.88	16.16	93.68	11.44	144.32	9.28	9.76	74.40	48.08	63.20	74.88	24.32	43.68	152.96	55.36	39.36	33.04	53.44	22.64
Residual	843.50	766.50	476.25	775.50	637.50	174.50	163.00	805.00	117.25	67.50	182.50	106.00	71.50	27.50	112.50	97.75	64.75	70.25	12.75
Total	1040.90	920.06	767.49	965.34	961.18	325.94	310.96	1111.56	328.61	278.78	477.54	313.80	237.06	248.30	341.86	332.31	194.23	563.17	97.63
Digestion	1099.00	1125.00	1005.00	400.00															
% Recovery	94.59	81.78	69.02	96.05		81.49	81.40												

Extraction Step	1AL	1A U	1B	1D	1G	1G L	1G U	1H	2A	2B	2D	3A	3B	3C	3D	Algal Mat	Peat # 1	Peat # 2	Wall
Extraction Step	As (%)	As (%)	As (%)	As (%)	As (%)	As (%)	As (%)	As (%)	As (%)	As (%)	As (%)	As (%)	As (%)	As (%)	As (%)	As (%)	As (%)	As (%)	As (%)
Exchangeable	0.03	0.10	0.13	0.12	0.14	0.36	0.09	0.09	1.40	0.80	0.23	0.52	0.40	1.26	0.42	1.29	0.25	0.29	1.19
Carbonate	0.78	0.84	1.43	0.90	0.96	8.48	8.76	0.77	2.65	2.67	1.26	5.48	4.57	4.41	3.23	3.48	5.19	12.41	15.77
Mn Oxide	0.00	0.03	0.36	0.23	0.07	8.86	10.12	0.01	1.19	0.55	0.55	6.81	4.52	1.26	7.32	1.41	6.67	17.39	19.34
Mn-Fe Oxide	16.53	13.96	23.83	17.24	17.50	25.92	25.47	20.02	44.44	49.10	44.06	45.66	41.91	20.39	39.92	52.57	37.54	47.94	27.45
Sulfide-OM	1.62	1.76	12.21	1.19	15.01	2.85	3.14	6.69	14.63	22.67	15.68	7.75	18.43	61.60	16.19	11.84	17.01	9.49	23.19
Residual	81.04	83.31	62.05	80.33	66.32	53.54	52.42	72.42	35.68	24.21	38.22	33.78	30.16	11.08	32.91	29.42	33.34	12.47	13.06

Extraction Step	1AL	1A U	1B	1D	1G	1G L	1G U	1H	2A	2B	2D	3A	3B	3C	3D	Algal Mat	Peat # 1	Peat # 2	Wall
Extraction Step	Cu (µg/g)	Cu (µg/g)	Cu (µg/g)	Cu (µg/g)	Cu (µg/g)	Cu (µg/g)	Cu (µg/g)	Cu (µg/g)	Cu (µg/g)	Cu (µg/g)	Cu (µg/g)	Cu (µg/g)	Cu (µg/g)	Cu (µg/g)	Cu (µg/g)	Cu (µg/g)	Cu (µg/g)	Cu (µg/g)	Cu (µg/g)
Exchangeable	17.72	37.00	30.12	31.48	58.96	14.04	13.76	36.08	494.84	484.48	447.92	366.12	61.00	175.52	79.60	369.76	2.08	3.28	11.04
Carbonate	6634.36	6657.60	6238.84	7752.40	7576.96	1690.68	1593.28	7798.72	1341.40	1693.36	1097.28	854.80	214.20	182.72	208.96	1709.32	808.56	1355.00	593.28
Mn Oxide	680.48	2660.00	432.40	2814.16	378.88	919.44	832.60	2065.68	99.80	59.52	229.68	111.16	12.32	7.68	14.56	198.88	145.52	348.28	135.56
Mn-Fe Oxide	8489.20	6193.24	2188.24	7192.52	1928.16	24.84	19.08	9832.00	314.72	548.08	518.64	689.68	74.04	68.96	24.64	792.08	43.76	29.20	16.20
Sulfide-OM	2781.60	3063.60	1977.20	2320.16	4247.52	798.64	709.92	2021.20	1680.80	3164.16	1543.12	555.44	3469.60	693.12	640.96	413.52	157.44	87.12	
Residual	1656.50	1100.00	1073.50	1186.50	1239.00	216.50	213.50	1677.00	556.75	204.00	760.50	408.00	166.75	120.50	181.00	382.25	265.25	152.75	15.00
Total	20259.86	19711.44	11900.30	21297.22	15429.48	3664.14	3382.14	23413.64	4828.71	4670.24	6218.18	3972.88	1083.75	4024.98	1201.88	4093.25	1678.69	2045.95	858.20
Digestion	18743.00	18955.00	18849.00	19411.00		3417.00	3125.00												
% Recovery	108.09	103.99	63.13	109.72		107.23	108.23												

Extraction Step	1AL	1A U	1B	1D	1G	1G L	1G U	1H	2A	2B	2D	3A	3B	3C	3D	Algal Mat	Peat # 1	Peat # 2	Wall
Extraction Step	Cu (%)	Cu (%)	Cu (%)	Cu (%)	Cu (%)	Cu (%)	Cu (%)	Cu (%)	Cu (%)	Cu (%)	Cu (%)	Cu (%)	Cu (%)	Cu (%)	Cu (%)	Cu (%)	Cu (%)	Cu (%)	Cu (%)
Exchangeable	0.09	0.19	0.25	0.15	0.38	0.38	0.41	0.15	10.25	10.37	7.20	9.22	5.63	4.36	6.62	9.03	0.12	0.16	1.29
Carbonate	32.75	33.78	52.43	36.40	49.11	46.14	47.11	33.31	27.78	36.26	17.65	21.52	19.76	4.54	17.39	41.76	48.17	66.23	69.13
Mn Oxide	3.36	13.49	3.63	13.21	2.46	25.09	24.62	8.57	2.07	1.27	3.69	2.80	1.14	0.19	1.21	4.86	8.67	17.02	15.80
Mn-Fe Oxide	41.90	31.42	18.39	33.77	12.50	0.68	0.56	41.99	6.52	11.74	8.34	17.36	6.83	1.71	2.05	19.35	2.61	1.43	1.89

Sulfide-OM	13.73	15.54	16.28	10.89	27.53	21.80	20.99	8.82	41.86	35.99	50.89	38.84	51.25	86.20	57.67	15.66	24.63	7.70	10.15
Residual	8.18	5.58	9.02	5.57	8.03	5.91	6.31	7.16	11.53	4.37	12.23	10.27	15.39	2.99	15.06	9.34	15.80	7.47	1.75

Extraction Step	1AL Fe (µg/g)	1A U Fe (µg/g)	1B Fe (µg/g)	1D Fe (µg/g)	1G Fe (µg/g)	1G L Fe (µg/g)	1G U Fe (µg/g)	1H Fe (µg/g)	2A Fe (µg/g)	2B Fe (µg/g)	2D Fe (µg/g)	3A Fe (µg/g)	3B Fe (µg/g)	3C Fe (µg/g)	3D Fe (µg/g)	Algal Mat Fe (µg/g)	Peat # 1 Fe (µg/g)	Peat # 2 Fe (µg/g)	Wall Fe (µg/g)
Exchangable	0.24	0.00	0.00	0.32	0.00	0.28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.48	0.00	0.00
Carbonate	22.88	76.92	194.84	238.20	199.36	2150.36	2110.32	146.80	24.84	34.80	27.52	0.00	2.40	8.16	0.00	24.00	297.72	1445.36	739.96
Mn Oxide	252.72	8271.60	274.40	7951.68	349.28	5224.96	4614.60	1476.16	248.64	85.52	652.48	138.32	7.64	15.52	0.00	193.40	842.72	1090.76	583.32
Mn-Fe Oxide	25978.80	22546.80	11778.40	22860.80	13588.80	7507.60	6875.32	34489.60	4703.56	6417.04	7678.88	4998.60	1674.12	1481.36	1674.72	5654.12	2976.40	2383.56	1431.68
Sulfide-OM	220.56	481.36	364.00	462.56	551.20	740.00	783.84	732.96	379.36	593.60	323.52	263.04	215.52	597.12	335.20	565.92	1106.16	715.44	324.64
Residual	23450.00	25050.00	23325.00	23650.00	24700.00	20000.00	19400.00	25500.00	15575.00	19250.00	11950.00	21950.00	17175.00	21900.00	13350.00	20150.00	28625.00	7700.00	12600.00
Total	49925.20	56426.68	35936.64	55163.56	39388.64	35623.20	33784.08	62345.52	20931.40	26380.96	20632.40	27349.96	19074.68	24002.16	15359.92	26587.44	33848.48	13335.12	15679.60
Digestion	52900.00	61800.00	57350.00	54500.00			49100.00			48200.00									
% Recovery	94.38	91.30	62.66	101.22		72.55	70.09												

Extraction Step	1AL Fe (%)	1A U Fe (%)	1B Fe (%)	1D Fe (%)	1G Fe (%)	1G L Fe (%)	1G U Fe (%)	1H Fe (%)	2A Fe (%)	2B Fe (%)	2D Fe (%)	3A Fe (%)	3B Fe (%)	3C Fe (%)	3D Fe (%)	Algal Mat Fe (%)	Peat # 1 Fe (%)	Peat # 2 Fe (%)	Wall Fe (%)
Exchangable	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Carbonate	0.05	0.14	0.54	0.43	0.51	6.04	6.25	0.24	0.12	0.13	0.13	0.00	0.01	0.03	0.00	0.09	0.88	10.84	4.72
Mn Oxide	0.51	14.66	0.76	14.41	0.89	14.67	13.66	2.37	1.19	0.32	3.16	0.51	0.04	0.06	0.00	0.73	2.49	8.18	3.72
Mn-Fe Oxide	52.04	39.96	32.78	41.44	34.50	21.08	20.35	55.32	22.47	24.32	37.22	18.28	8.78	6.17	10.90	21.27	8.79	17.87	9.13
Sulfide-OM	0.44	0.85	1.01	0.84	1.40	2.08	2.32	1.18	1.81	2.25	1.57	0.96	1.13	2.49	2.18	2.13	3.27	5.37	2.07
Residual	46.97	44.39	64.91	42.87	62.71	56.14	57.42	40.90	74.41	72.97	57.92	80.26	90.04	91.24	86.91	75.79	84.57	57.74	80.36

Extraction Step	1AL Mn (µg/g)	1A U Mn (µg/g)	1B Mn (µg/g)	1D Mn (µg/g)	1G Mn (µg/g)	1G L Mn (µg/g)	1G U Mn (µg/g)	1H Mn (µg/g)	2A Mn (µg/g)	2B Mn (µg/g)	2D Mn (µg/g)	3A Mn (µg/g)	3B Mn (µg/g)	3C Mn (µg/g)	3D Mn (µg/g)	Algal Mat Mn (µg/g)	Peat # 1 Mn (µg/g)	Peat # 2 Mn (µg/g)	Wall Mn (µg/g)
Exchangable	182.80	393.32	419.20	371.72	502.64	336.00	302.68	472.56	2234.92	2347.36	1983.60	1255.32	871.16	1717.68	1041.76	2156.96	7.20	123.08	240.12
Carbonate	4538.76	4127.44	4339.16	4228.48	4906.56	1532.04	1585.00	4492.88	4188.16	3304.56	3242.48	3627.44	3798.40	1402.96	5500.72	7287.32	18.32	328.20	599.00
Mn Oxide	4185.12	2958.00	2497.96	1648.60	2079.44	1521.48	1375.08	2723.92	1952.40	1426.88	2690.00	8879.60	6618.76	1832.96	10291.20	5238.60	25.40	108.28	190.00
Mn-Fe Oxide	5165.40	1466.36	4815.96	1276.76	3928.32	1917.68	1788.36	3629.68	4339.88	1799.12	4493.36	2967.64	4077.64	1283.68	4876.40	2206.28	59.32	269.40	86.68
Sulfide-OM	345.68	230.40	152.16	218.48	259.84	488.56	497.20	326.88	231.60	84.96	278.56	412.88	251.68	276.16	335.68	193.28	1.12	12.16	15.12
Residual	1658.00	1452.00	1459.25	1639.50	1634.00	429.00	418.00	1369.00	495.00	413.00	528.50	390.50	377.75	431.50	376.00	462.25	100.50	196.00	164.50
Total	16075.76	10627.52	13683.69	9383.54	13310.80	6224.76	5966.32	13014.92	13441.96	9375.88	13216.50	17533.58	15995.39	6944.94	22421.76	17544.69	211.86	1037.12	1295.42
Digestion	15887.00	10075.00	12981.00	8741.00		6064.00	5880.00												
% Recovery	101.19	105.48	105.41	107.35		102.65	101.47												

Extraction Step	1AL Mn (%)	1A U Mn (%)	1B Mn (%)	1D Mn (%)	1G Mn (%)	1G L Mn (%)	1G U Mn (%)	1H Mn (%)	2A Mn (%)	2B Mn (%)	2D Mn (%)	3A Mn (%)	3B Mn (%)	3C Mn (%)	3D Mn (%)	Algal Mat Mn (%)	Peat # 1 Mn (%)	Peat # 2 Mn (%)	Wall Mn (%)
Exchangable	1.14	3.70	3.06	3.96	3.78	5.40	5.07	3.63	16.63	25.04	15.01	7.16	5.45	24.73	4.65	12.29	3.40	11.87	18.54
Carbonate	28.23	38.84	31.71	45.06	36.86	24.61	26.57	14.52	31.16	35.25	24.53	20.69	23.75	20.20	24.53	41.54	8.65	31.65	46.24
Mn Oxide	26.03	27.83	18.26	17.57	15.62	24.44	23.05	20.93	14.52	15.22	20.35	50.64	41.38	26.39	45.90	29.86	11.99	10.44	14.67
Mn-Fe Oxide	32.13	13.80	35.19	13.61	29.51	30.81	29.97	27.89	32.29	19.19	34.00	16.93	25.49	18.48	21.75	12.58	28.00	25.98	6.69
Sulfide-OM	2.15	2.17	1.11	2.33	1.95	7.85	8.33	2.51	1.72	0.91	2.11	2.35	1.57	3.98	1.50	1.10	0.53	1.17	1.17
Residual	10.31	13.66	10.66	17.47	12.28	6.89	7.01	10.52	3.68	4.40	4.00	2.23	2.36	6.21	1.68	2.63	47.44	18.90	12.70

Extraction Step	1AL P (µg/g)	1A U P (µg/g)	1B P (µg/g)	1D P (µg/g)	1G P (µg/g)	1G L P (µg/g)	1G U P (µg/g)	1H P (µg/g)	2A P (µg/g)	2B P (µg/g)	2D P (µg/g)	3A P (µg/g)	3B P (µg/g)	3C P (µg/g)	3D P (µg/g)	Algal Mat P (µg/g)	Peat # 1 P (µg/g)	Peat # 2 P (µg/g)	Wall P (µg/g)
Exchangable	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	36.40	21.92	35.44	9.68	46.92	58.40	9.56	0.00	0.00	0.00	0.00
Carbonate	21.20	17.28	30.76	20.80	25.60	33.04	33.96	26.72	98.76	85.12	66.72	69.92	100.44	81.28	90.40	53.88	15.76	33.56	31.72
Mn Oxide	4.52	5.12	8.32	4.68	5.76	87.48	101.64	4.24	18.72	4.64	10.16	63.32	46.88	15.68	104.48	10.24	29.76	104.40	319.20
Mn-Fe Oxide	188.64	134.76	281.44	161.52	241.04	138.68	134.76	267.04	665.48	554.32	706.00	293.64	691.32	434.24	770.96	273.68	128.20	136.72	103.08
Sulfide-OM	28.72	36.24	354.32	28.40	239.04	37.84	34.16	167.04	757.76	858.88	517.92	192.56	491.84	275.84	594.88	167.12	91.12	104.56	86.64
Residual	705.00	835.00	655.00	735.00	745.00	390.00	355.00	780.00	667.50	640.00	770.00	870.00	452.50	490.00	617.50	160.00	97.50	100.00	100.00
Total	948.08	1028.40	1329.84	950.40	1256.44	687.04	659.52	1245.04	2244.62	2164.88	2106.24	1499.12	1829.90	1343.84	2189.12	1131.98	424.84	476.74	640.64
Digestion	860.00	1120.00	990.00	870.00		870.00	890.00												
% Recovery	109.62	91.27	134.15	108.61		78.34	73.39												

Extraction Step	1AL P (%)	1A U P (%)	1B P (%)	1D P (%)	1G P (%)	1G L P (%)	1G U P (%)	1H P (%)	2A P (%)	2B P (%)	2D P (%)	3A P (%)	3B P (%)	3C P (%)	3D P (%)	Algal Mat P (%)	Peat # 1 P (%)	Peat # 2 P (%)	Wall P (%)
Exchangable	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.62	1.01	1.68	0.65	2.56	3.48	2.67	0.84	0.00	0.00	0.00
Carbonate	2.24	1.68	2.31	2.19	2.04	4.81	5.15	2.15	4.40	3.93	3.17	4.66	5.49	6.05	4.13	4.76	3.71	7.04	4.95
Mn Oxide	0.48	0.50	0.63	0.49	0.46	12.73	15.41	0.34	0.83	0.21	0.48	4.22	2.56	1.17	4.77	0.90	7.00	21.90	49.83
Mn-Fe Oxide	19.90	13.10	21.16	16.99	19.18	20.19	20.43	21.45	29.65	25.61	33.52	19.59	37.78	32.31	35.22	24.18	30.18	28.68	16.09
Sulfide-OM	3.03	3.52	26.64	2.99	19.03	5.51	5.18	13.42	33.76	39.67	24.59	12.84	26.88	20.53	27.17	14.76	21.45	21.93	13.52
Residual	74.36	81.19	49.25	77.34	59.29	56.77	53.83	62.65	29.74	29.56	36.56	58.03	24.73	36.46	26.04	54.55	37.66	20.45	15.61

Extraction Step	IAL Pb (µg/g)	1A U Pb (µg/g)	1B Pb (µg/g)	1D Pb (µg/g)	1G Pb (µg/g)	1G L Pb (µg/g)	1G U Pb (µg/g)	1H Pb (µg/g)	2A Pb (µg/g)	2B Pb (µg/g)	2D Pb (µg/g)	3A Pb (µg/g)	3B Pb (µg/g)	3C Pb (µg/g)	3D Pb (µg/g)	Algal Mat Pb (µg/g)	Peat # 1 Pb (µg/g)	Peat # 2 Pb (µg/g)	Wall Pb (µg/g)
Exchangable	61.40	21.48	3.52	27.96	2.08	0.00	0.00	4.32	2.44	6.56	44.64	30.40	0.00	0.00	0.00	0.56	0.92	1.12	0.00
Carbonate	84.00	91.32	221.00	107.72	338.64	200.88	281.52	129.36	28.28	61.04	0.00	0.00	4.76	10.56	116.32	28.92	16.92	107.84	66.16
Mn Oxide	0.00	50.12	6.12	41.82	10.24	88.39	86.66	7.92	7.75	0.00	31.73	8.00	5.20	0.00	9.87	2.24	12.60	46.40	23.52
Mn-Fe Oxide	439.96	608.74	850.60	663.93	996.88	64.32	51.19	1053.44	112.32	167.76	115.68	29.64	50.96	57.04	31.76	99.20	22.80	39.64	20.04
Sulfide-OM	5.52	61.04	81.92	38.48	197.76	5.36	6.48	118.24	19.04	30.88	23.68	6.32	3.92	160.00	5.92	25.60	2.96	5.12	0.00
Residual	1299.50	1027.50	661.50	1188.50	821.50	366.50	353.00	1015.50	197.25	119.00	294.50	163.00	100.25	43.50	162.00	120.00	80.25	110.25	23.25
Total	1890.38	1860.20	1824.66	2068.42	2367.10	725.45	778.85	2328.78	367.08	385.24	510.23	237.36	165.09	271.10	325.87	276.52	136.45	310.37	132.97
Digestion	2024.00	2349.00	2186.50	2215.00		962.00	904.00												
% Recovery	93.40	79.19	83.45	93.38		75.41	86.16												

Extraction Step	IAL Pb (%)	1A U Pb (%)	1B Pb (%)	1D Pb (%)	1G Pb (%)	1G L Pb (%)	1G U Pb (%)	1H Pb (%)	2A Pb (%)	2B Pb (%)	2D Pb (%)	3A Pb (%)	3B Pb (%)	3C Pb (%)	3D Pb (%)	Algal Mat Pb (%)	Peat # 1 Pb (%)	Peat # 2 Pb (%)	Wall Pb (%)
Exchangable	3.25	1.15	0.19	1.35	0.09	0.00	0.00	0.19	0.66	1.70	8.75	12.81	0.00	0.00	0.00	0.20	0.67	0.36	0.00
Carbonate	4.44	4.91	12.11	5.21	14.31	27.69	36.15	5.55	7.70	15.84	0.00	0.00	2.88	3.90	35.70	10.46	12.40	34.75	49.76
Mn Oxide	0.00	2.69	0.34	2.02	0.43	12.18	11.13	0.34	2.11	0.00	6.22	3.37	3.15	0.00	3.03	0.81	9.23	14.95	17.69
Mn-Fe Oxide	23.27	32.72	46.62	32.10	42.11	8.87	6.57	45.24	30.60	43.55	22.67	12.49	30.87	21.04	9.75	35.87	16.71	12.77	15.07
Sulfide-OM	0.29	3.28	4.49	1.86	8.35	0.74	0.83	5.08	5.19	8.02	4.64	2.66	2.37	59.02	1.82	9.26	2.17	1.65	0.00
Residual	68.74	55.24	36.25	57.46	34.70	50.52	45.32	43.61	53.74	30.89	57.72	68.67	60.72	16.05	49.71	43.40	58.81	35.52	17.49

Extraction Step	IAL S (µg/g)	1A U S (µg/g)	1B S (µg/g)	1D S (µg/g)	1G S (µg/g)	1G L S (µg/g)	1G U S (µg/g)	1H S (µg/g)	2A S (µg/g)	2B S (µg/g)	2D S (µg/g)	3A S (µg/g)	3B S (µg/g)	3C S (µg/g)	3D S (µg/g)	Algal Mat S (µg/g)	Peat # 1 S (µg/g)	Peat # 2 S (µg/g)	Wall S (µg/g)
Exchangable	1179.12	1187.16	1996.48	1467.20	2150.00	542.64	351.68	5337.92	1833.52	1077.28	1911.52	543.68	736.00	761.84	1099.60	612.92	731.84	96.56	60.72
Carbonate	517.96	457.20	459.32	493.52	700.88	141.88	141.96	451.52	502.68	537.76	298.00	431.20	571.76	469.84	599.68	405.84	101.84	32.20	57.20
Mn Oxide	187.56	44.32	225.76	109.28	245.92	15.16	14.68	209.44	154.84	223.68	118.80	97.24	186.04	173.20	190.72	196.24	0.00	0.00	0.00
Mn-Fe Oxide	372.28	136.68	1154.96	154.92	676.96	119.60	114.48	483.68	825.84	847.76	623.92	289.52	966.92	911.68	731.28	301.04	74.84	128.92	50.80
Sulfide-OM	877.60	938.32	888.64	743.28	1367.04	495.36	483.04	701.12	1460.96	1360.80	2321.76	1787.28	1233.68	1123.20	1684.48	933.84	1204.24	651.04	419.52
Residual	2135.00	2065.00	1692.50	1485.00	1675.00	590.00	630.00	1620.00	670.00	250.00	1085.00	425.00	387.50	110.00	665.00	245.00	2685.50	4692.50	125.00
Total	5269.52	4828.68	6417.66	4453.20	6815.80	1904.64	1735.84	8803.68	5447.84	4297.28	6359.00	3573.92	4081.90	3549.76	4970.76	2694.88	28965.26	5601.22	713.24
Digestion	5190.00	4840.00	5015.00	4410.00		2270.00	2290.00												
% Recovery	101.53	99.77	127.97	100.98		83.90	75.80												

Extraction Step	IAL S (%)	1A U S (%)	1B S (%)	1D S (%)	1G S (%)	1G L S (%)	1G U S (%)	1H S (%)	2A S (%)	2B S (%)	2D S (%)	3A S (%)	3B S (%)	3C S (%)	3D S (%)	Algal Mat S (%)	Peat # 1 S (%)	Peat # 2 S (%)	Wall S (%)
Exchangable	22.38	24.59	31.11	32.95	31.54	28.49	20.26	60.63	33.66	25.07	30.06	15.21	18.03	21.46	22.12	22.74	2.53	1.72	8.51
Carbonate	9.83	9.47	7.16	11.08	10.28	7.45	8.18	5.13	9.23	12.51	4.69	12.07	14.01	13.24	12.06	15.06	0.35	0.57	8.02
Mn Oxide	3.56	0.92	3.52	2.45	3.61	0.80	0.85	2.38	2.84	5.21	1.87	2.72	4.56	4.88	3.84	7.28	0.00	0.00	0.00
Mn-Fe Oxide	7.06	2.83	18.00	3.48	9.93	6.28	6.60	5.49	15.16	19.73	9.81	8.10	23.69	25.68	14.71	11.17	0.26	2.30	7.12
Sulfide-OM	16.65	19.43	13.85	16.69	20.06	26.01	27.83	7.96	26.82	31.67	36.51	50.01	30.22	31.64	33.89	34.65	4.16	11.62	58.82
Residual	40.52	42.77	26.37	33.35	24.58	30.98	36.29	18.40	12.30	5.82	17.06	11.89	9.49	3.10	13.38	9.09	92.71	83.78	17.53

Extraction Step	IAL Zn (µg/g)	1A U Zn (µg/g)	1B Zn (µg/g)	1D Zn (µg/g)	1G Zn (µg/g)	1G L Zn (µg/g)	1G U Zn (µg/g)	1H Zn (µg/g)	2A Zn (µg/g)	2B Zn (µg/g)	2D Zn (µg/g)	3A Zn (µg/g)	3B Zn (µg/g)	3C Zn (µg/g)	3D Zn (µg/g)	Algal Mat Zn (µg/g)	Peat # 1 Zn (µg/g)	Peat # 2 Zn (µg/g)	Wall Zn (µg/g)
Exchangable	153.00	242.24	128.12	329.20	213.92	410.72	370.52	138.48	732.80	1103.68	672.24	221.88	468.68	575.28	641.52	597.84	47.24	119.76	80.52
Carbonate	30892.00	29567.20	32277.60	37694.40	34856.80	6986.28	7047.04	45365.60	30323.60	19615.20	35916.00	11864.80	14137.00	3320.40	26271.20	32878.00	402.68	2799.48	2096.76
Mn Oxide	5208.28	11296.40	3547.76	7752.52	4108.40	7419.00	6722.32	8804.00	4141.24	1947.44	13739.20	5116.60	3429.72	885.28	5553.44	6662.48	117.76	595.64	480.76
Mn-Fe Oxide	16450.40	10153.20	6527.68	7361.08	6489.92	5222.04	4741.12	13280.80	19871.32	5008.00	32204.00	8840.40	6287.20	2949.68	5941.84	6926.00	191.24	228.36	97.72
Sulfide-OM	1157.60	1100.40	388.32	762.96	727.52	1370.56	1369.52	788.32	1340.24	334.40	2466.88	1606.96	557.60	673.92	689.60	691.44	63.04	74.88	61.44
Residual	3126.00	2484.00	1628.50	2248.00	1654.00	1509.00	1506.00	1998.00	905.00	319.50	1434.00	834.50	382.25	226.50	489.00	488.00	360.00	989.75	68.25
Total	56987.28	54843.44	44498.22	56148.16	48050.56	22917.60	21756.52	70375.20	57314.20	28328.22	86432.32	28485.14	25262.45	8631.06	39586.60	48243.76	1181.96	4807.87	2885.45
Digestion	57156.00	54804.00	55980.00	54969.00		21874.00	21352.00												
% Recovery	99.70	100.07	79.49	102.15		104.77	101.89												

Extraction Step	IAL Zn (%)	1A U Zn (%)	1B Zn (%)	1D Zn (%)	1G Zn (%)	1G L Zn (%)	1G U Zn (%)	1H Zn (%)	2A Zn (%)	2B Zn (%)	2D Zn (%)	3A Zn (%)	3B Zn (%)	3C Zn (%)	3D Zn (%)	Algal Mat Zn (%)	Peat # 1 Zn (%)	Peat # 2 Zn (%)	Wall Zn (%)
Exchangable	0.27	0.44	0.29	0.59	0.45	1.79	1.70	0.20	1.28	1.86	0.78	0.78	0.78	0.67	1.62	1.24	4.00	2.49	2.79
Carbonate	54.21	53.91	72.54	67.13	72.54	30.48	32.39	64.46	52.91	69.24	41.55	41.65	55.96	38.47	66.36	68.15	34.07	58.23	72.67
Mn Oxide	9.14	20.60	7.97	13.81	8.55	32.37	30.90	12.51	7.23	6.87	15.90	17.96	13.58	10.26	14.03	13.81	9.96	12.39	16.66
Mn-Fe Oxide	28.87	18.51	14.67	13.11	13.51	22.79	21.79	18.87	34.67	17.68	37.26	31.04	24.89	34.18	15.01	14.36	16.18	4.75	3.39
Sulfide-OM	2.03	2.01	0.87	1.36	1.51	5.98	6.29	1.12	2.34	1.18	2.85	5.64	2.21	7.81	1.74	5.33	1.56	2.13	2.13
Residual	5.49	4.53	3.66	4.00	3.44	6.58	6.92	2.84	1.58	1.13	1.66	2.93	1.51	2.62	1.24	1.01	30.46	20.59	2.37

APPENDIX B
ADSORPTION ISOTHERM RESULTS

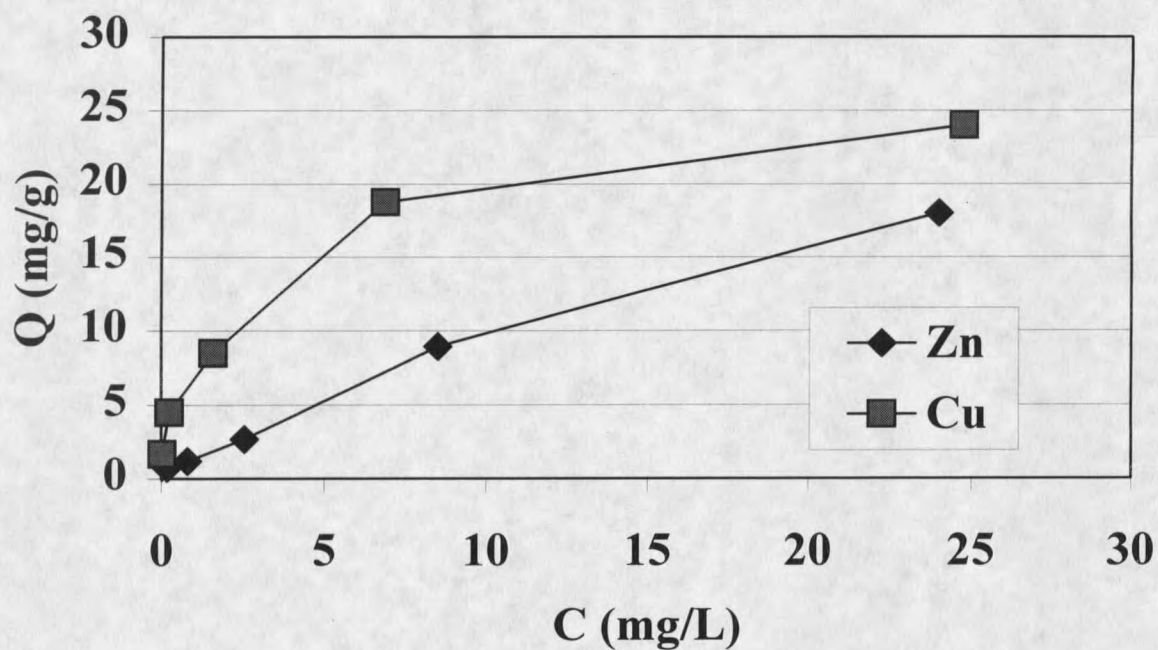


Figure 36. Adsorption isotherm results using 2-line ferrihydrite. Experiment was conducted at pH 6.0 with a solid to solution ratio of 0.056 g Fe/L, in 0.01M KCL. Aliquots of the solid were exposed to 0.0, 0.3, 1.0, 3.0, 10.0, and 30.0 mg/L dissolved Cu and Zn over 4 d equilibration time. Q = mg Cu and Zn sorbed/g; C = equilibrium concentration in mg/L.

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