



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.

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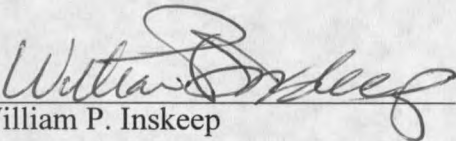
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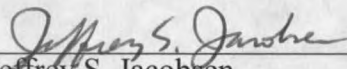
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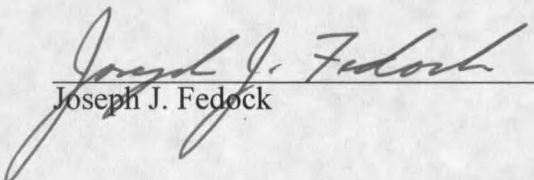
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ABSTRACT

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; Blean 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 CHARACTERIZATIONIntroduction

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; Macheimer 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 Macheimer 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.

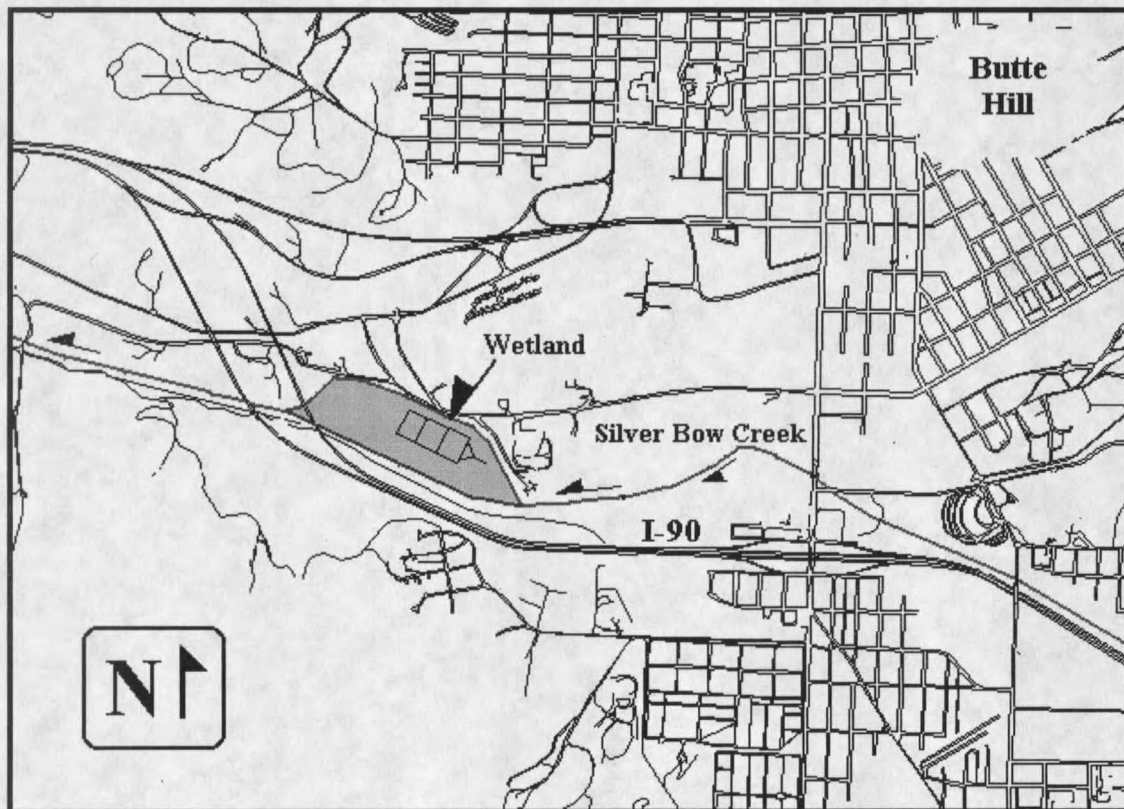


Figure 1. Overhead map of Lower Area One (shaded region) and Colorado Tailings wetland project site, Butte, MT.

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).

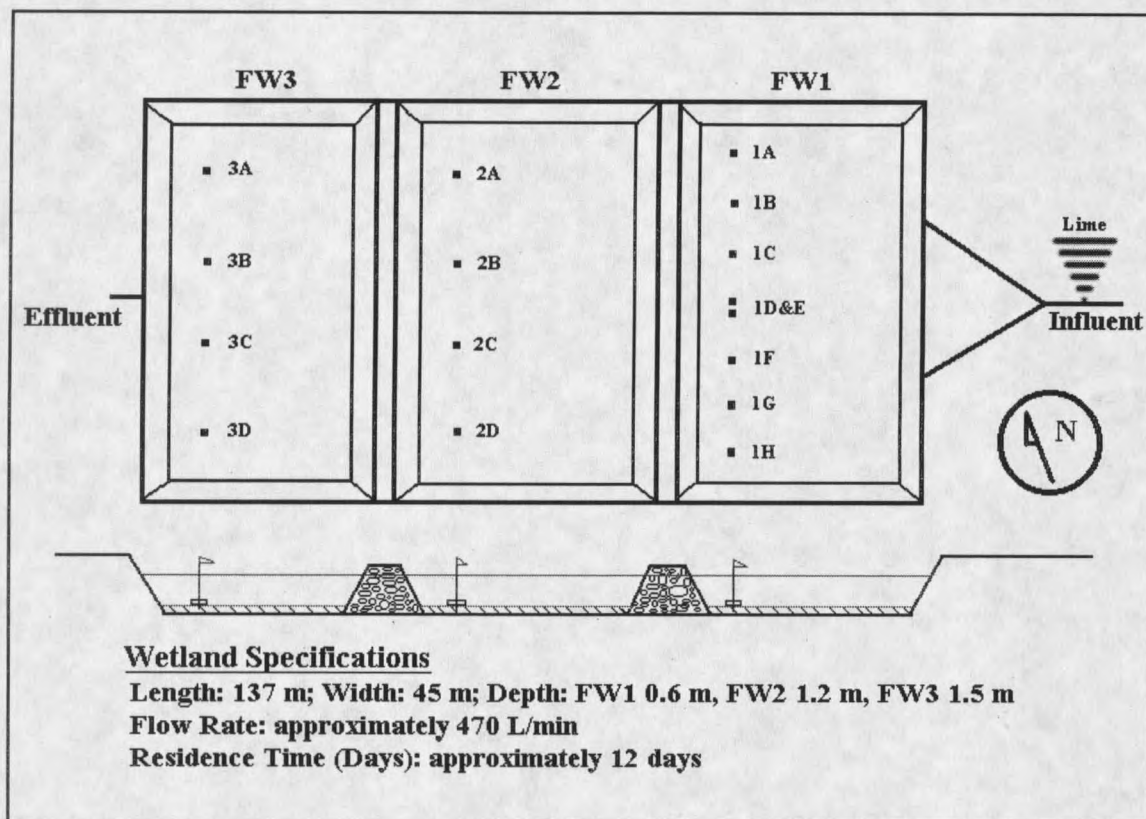


Figure 2. Colorado Tailings constructed wetland: specifications and location of sediment samplers.

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 (Alison 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.

