

MANGANESE AND TRACE METAL REMOVAL IN SUCCESSIVE ANAEROBIC AND AEROBIC WETLANDS

by

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Abstract. A microcosm study was conducted to evaluate the use of anaerobic wetlands preceding aerobic wetlands for removal of Mn, Cu, Ni, Zn, and Pb in wastewater. Initial concentrations for Mn, Cu, Ni, Pb, and Zn were 20, 2.0, 1.5, 2.1, and 2.0 mg/L, respectively. Each experimental unit consisted of three cattle-feeding troughs (cells) set in series. The first cell was anaerobic and the last two were aerobic. Water was delivered to the wetland cells at 20 mL/min for a period of 380 days starting August 24, 1994. The anaerobic wetlands consisted of three treatments replicated two times. The aerobic wetlands consisted of two treatments replicated three times. One anaerobic treatment contained organic matter and limestone (SP). Another anaerobic treatment contained organic matter, limestone, and canarygrass (SP&CG). The third anaerobic treatment consisted of canarygrass planted in river gravel (RG). Water flowed into the top and was discharged from the bottom of each anaerobic wetland. The aerobic treatments consisted of reciprocating or not reciprocating water between two cells containing river gravel. The anaerobic troughs with organic matter were effective in reducing sulfate to sulfide and producing alkalinity in the range from 80 to 300 mg/L. Manganese removal in the anaerobic systems decreased with time with the effluent anaerobic waters near equilibrium with respect to MnS and $MnCO_3$ toward the end of the experiment. Removal of Cu, Ni, Zn, and Pb was very effective in the anaerobic cells with organic matter due to precipitation of metal sulfides. Since Mn removal was ineffective in the long-term in the anaerobic system, aerobic wetlands would be necessary for further water treatment. Manganese removal in the reciprocating aerobic cells was quicker than in the nonreciprocating aerobic cells with removal due to precipitation of Mn oxides. Coupled anaerobic-aerobic wetlands appear to hold promise for removing trace metals via metal sulfide precipitation and Mn via Mn oxide precipitation.

Additional Key Words: alkalinity, compost, copper, lead, nickel, sulfate, sulfide, lead, zinc.

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INTRODUCTION

Due to federal limits placed on Fe and Mn concentrations in acid mine drainage effluent, considerable research has been conducted on the use of wetlands for removal of these metals. Monthly averages for Fe and Mn concentrations generally must be below 3 and 2 mg/L, respectively (Code of Federal Regulations, 1995). Both aerobic and anaerobic surface-flow wetlands have been used. Aerobic wetlands consist of a layer of water over soil with O₂ supplied via diffusion. Iron and Mn removal occurs via precipitation of metal oxides. Anaerobic wetlands consist of a layer of organic matter placed on top of soil. Anaerobic conditions are imposed with high C in the organic layer and rapid depletion of available O₂. Anaerobic conditions promote sulfate reduction to sulfide and subsequent precipitation of metal sulfides.

Removal rates for Fe and Mn in surface flow wetlands range from 10 to 20 and 0.5 to 1 g/m²/d, respectively (Hedin et al., 1994). The reason for less efficient removal of Mn is due to slower kinetic processes in the oxidation of Mn²⁺ (Stumm and Morgan, 1981). Ferrous Fe readily oxidizes to ferric Fe at pH above 3.5 with rapid precipitation of ferric Fe oxyhydroxides. Uncatalyzed Mn²⁺ oxidation does not occur readily until pH >10 (Brezonik, 1994). Manganese oxidation can occur quicker at lower pH from 6 to 9 with autocatalysis from Mn sorption onto Mn oxide precipitates (McBride, 1994), catalysis via microorganisms (Ghiorse, 1984; Bender et al., 1994), or Mn sorption onto other solids (Davies and Morgan, 1989). Another process that limits Mn removal is the reduction of oxidized Mn in the presence of ferrous Fe. Ferrous Fe will readily reduce oxidized Mn precipitated as oxides, keeping Mn in solution (Hedin et al., 1994; Burdige et al., 1992). Due to the

disadvantageous interaction between Fe and Mn, Mn removal in acid mine drainage does not occur significantly until Fe is reduced to low concentrations.

Passive Mn removal has been studied in a number of systems. Gordon (1989) and Gordon and Burr (1989) found Mn oxidation to be related to a black microbial coating found on rock surfaces. Adequate Mn removal occurred in rock bed filters with a similar black coating observed on rock surfaces (Thornton, 1995) and with gravel beds supporting a green algae-microbial mat consortium (Phillips et al., 1994). Manganese removal in both systems was purported to be biotically controlled. Biotic mediation in the algae mat may have been due to O₂ release and CO₂ uptake from the algae, maximizing Mn oxide precipitation in aerobic alkaline microenvironments (Bender et al., 1994). McMillen et al. (1994) studied the use of unsaturated vertical flow wetlands to provide conditions for Mn oxidation and precipitation and found effective Mn removal at initial Mn concentrations ranging from 0.5 to 60 mg/L. When a biocide was added, Mn removal remained high which indicated that abiotic catalysis of Mn oxidation and precipitation was the controlling factor for Mn removal. Contrary results were obtained in lake water samples with an initial Mn concentration of 2 mg/L where rate constants for Mn oxidation in poisoned samples were 10 to 100 times less than rate constants in unpoisoned samples (Johnson et al., 1995). Gordon and Burr (1989) also concluded microbial processes may play a vital role in Mn oxidation by studying Mn removal via microbial black slime on rock surfaces.

Iron and Mn have been the focus for metals removal in acid mine drainage. However, removal of trace metals in acid-mine drainage and other metal-laden wastewater will

receive more attention in the future due to impending limits on effluent concentrations via the Clean Water Act. Concentrations of Fe and Mn in acid mine drainage can range from 2 to greater than 150 mg/L, while concentrations of trace metals such as Cu, Ni, Pb, and Zn are usually less than 2 mg/L. An appropriate passive technology for trace metal removal is anaerobic wetlands since many of the trace metals of concern form metal sulfides with very low solubility. The disadvantage with surface-flow anaerobic wetlands is the anaerobic conditions are limited to the water-sediment interface with not all of the water being exposed to the reducing conditions. Improvement of treatment efficiency can occur by forcing water downward through an organic layer as done with successive alkalinity producing systems (SAPS) (Kepler and McCleary, 1994). A typical SAPS design consists of a surface layer of 1.6 to 1.9 m of water, 45 cm of compost below the water, and a 45 to 60 cm layer of limestone rock below the compost. The system provides reducing conditions and adds alkalinity to the water from sulfate reduction and limestone dissolution.

The objective of the current study was to ascertain mechanisms involved in the removal of Mn, Cu, Ni, Pb, and Zn in water treated by anaerobic and aerobic wetlands. The water used in the study was simulated acid mine drainage pretreated by an anoxic limestone drain and surface-flow aerobic wetlands where most of the Fe was removed. The anaerobic cells were hypothesized to remove the trace metals via sulfide precipitation. The aerobic cells were hypothesized to remove Mn via oxide formation.

MATERIALS AND METHODS

The study was conducted inside a greenhouse at the TVA Environmental Research Center in Muscle Shoals, AL. The cells used to simulate anaerobic and aerobic wetlands were insulated cattle feeding troughs that measured 1.1 x 0.6 x 0.6 m³. The troughs were lined with a 40 mil plastic liner to prevent metal leakage from the galvanized steel. Each experimental unit consisted of 3 troughs placed in series with the first trough being the anaerobic cell and the second two troughs being the aerobic cells (Fig. 1). The troughs were plumbed with PVC pipe so water entered the surface of the first cell, exited at the bottom of the first cell, entered the second cell at the bottom, exited the surface of the second cell, entered the surface of the third cell, and exited on the bottom of the third cell. Surface area of one trough and one experimental unit was 0.5 and 1.5 m², respectively. Volume of one trough and one experimental unit was 0.3 and 0.9 m³, respectively.

The experiment included 6 experimental units with 3 anaerobic treatments and 2 aerobic treatments. The anaerobic treatments consisted of canarygrass (CG) (*Phalaris arundinacea*), SAPS (SP) (12), and a SAPS+canarygrass combination (CG&SP). The SP treatment had a bottom 10 cm layer of crushed limestone gravel, a 30 cm mid-layer of composted chicken litter, and an 18 cm surface layer of water. The CG treatment consisted of canarygrass planted in 58 cm of river gravel. The CG&SP treatment consisted of river gravel on top of compost and limestone as set in the SP system and canarygrass planted in the gravel. Size distribution of the river gravel was 4% <6.7 mm, 66% 6.7 to 19 mm, 25% 19 to 25 mm, and 5% >25 mm. Size distribution of the limestone gravel was 4% <4.7 mm, 7% from 4.7 to 6.7 mm, 81% from 6.7 to 19 mm, and 8% from 19 to 25 mm. Size

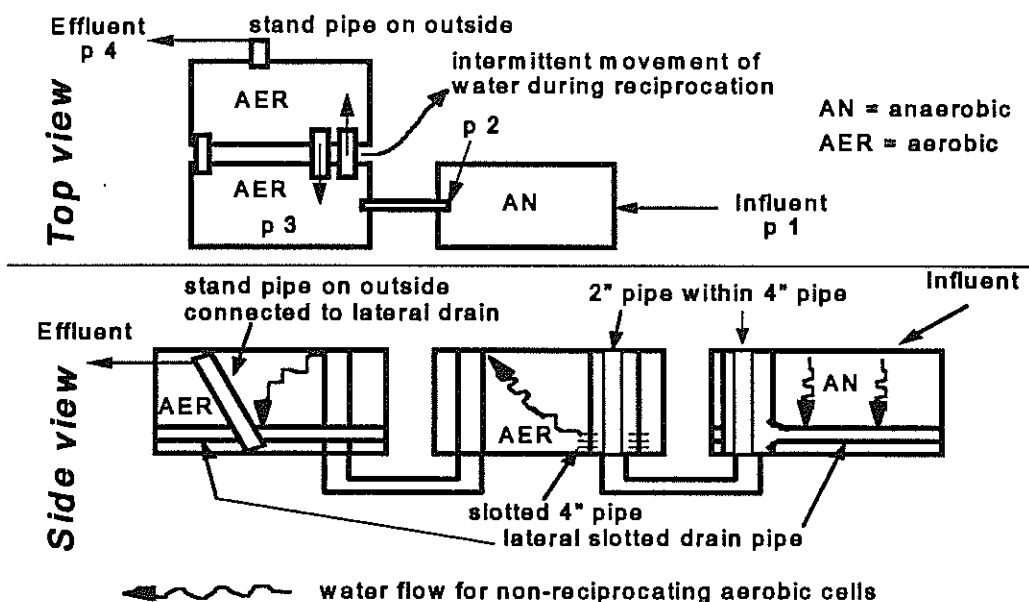


Figure 1. Diagram of one experimental unit used in the study. The four sampling positions are identified in Top view as p1, p2, p3, and p4.

distribution of the compost was 14% <0.4 mm, 3% from 0.4 to 0.6 mm, 8% from 0.6 to 1 mm, 3% from 1 to 1.2 mm, and 72% >1.2 mm.

The anaerobic treatments were replicated 2 times. Three replications of each of the two aerobic treatments were placed after a complete set of anaerobic treatments (Table 1). The two aerobic treatments consisted of reciprocating the top 20 cm of water from one cell to another (w/recip) or not reciprocating (wo/recip) (Behrends et al., 1993). The water was air-lifted by pumping air to the bottom of each of 2 paired aerobic cells through 5 cm diameter pipes. Air was intermittently pumped to each 5-cm pipe at 15 minute intervals. The pumped air moved the top 20 cm of water from one cell to another which exposed rock surface biofilms to air and provided aeration of the water.

After putting the appropriate media in the cells, 2 L of septic

tank effluent were added to the composted chicken litter and on the surface of the planted gravel in order to inoculate the system with sulfate reducing bacteria. Nutrient solution was flowed through the anaerobic cells at 20 mL/min for a period of 1 month to nourish the canarygrass and sulfate-reducing bacteria. The nutrient solution contained 112, 137, 55, 12, 46, 2.3, 3.6, and 186 mg/L NH₄-N, Ca, K, P, Mg, Na, Cl, and S, respectively. Micronutrients in the solution consisted of 11, 59, 55, 17, 13, 3.2 and 296 ug/L B, Co, Mn, Mo, Zn, Cu, and Fe, respectively.

Acid mine drainage that simulated water pretreated with an aerobic wetland was passed through the experimental cells beginning on August 24, 1994 after the cells were acclimated with nutrients. August 24 was considered the initial time of the experiment and represented as day 0 in the figures. The salts MnSO₄·H₂O, FeSO₄·7H₂O, NiSO₄, CuSO₄

Table 1. Outline of experimental treatments.

| Experi- mental unit | Anaerobic | | Aerobic | |
|---------------------------|-----------|-----|-----------|-----|
| | treatment | rep | treatment | rep |
| 1 | CG | 1 | w/recip | 1 |
| 2 | SP | 1 | w/recip | 2 |
| 3 | CG&SP | 1 | w/recip | 3 |
| 4 | CG | 2 | wo/recip | 1 |
| 5 | SP | 2 | wo/recip | 2 |
| 6 | CG&SP | 2 | wo/recip | 3 |

*5H₂O, PbSO₄, ZnSO₄*7H₂O, CaSO₄, and MgSO₄*7H₂O were added to 1135 L resulting in expected concentrations of 20, 1.5, 2, 2, 2, 2, 90, 90, and 209 mg/L of Mn, Fe(II), Ni, Cu, Pb, Zn, Ca, Mg, and S, respectively. The solution was delivered to the first trough in each experimental unit at a rate of 20 ml/min. This flow rate resulted in loading rates of 0.82 and 0.12 g/m²/d for Mn and Fe, respectively, and a loading rate of 0.08 g/m²/d for the trace metals Cu, Ni, Pb, and Zn. Assuming the effluent water from TVA aerobic wetlands (Brodie, 1993) were treated by an equivalently sized wetland system for Mn removal, the Mn loading rates would range from 0.03 to 1.73 g/m²/d with an average of 0.34 g/m²/d.

During May, 1995, the canary-grass was showing symptoms of N deficiency with very pale green leaves. Fertilizer was added on June 2, 1995 (day 282) to supply nutrients to canarygrass. To equalize effects of fertilizer addition on the anaerobic processes, fertilizer was added to all anaerobic treatments including the SP treatment that did not contain canarygrass. Fertilizer was added as N, P, and K as 34-0-0,

0-40-0, and reagent grade KCl at 60, 10, and 10 g, respectively, to each anaerobic cell. Fertilizer was mixed and added as a solid to the surface of each cell. In the gravel wetlands (CG and SP&CG), gravel was dug out to allow fertilizer to be added to the water. If the fertilizer was fully diluted with the water in the anaerobic wetlands, solution concentrations would be 154 mg/L N, 15 mg/L P, and 40 mg/L K.

Based on rock and compost porosity, the average pore volume in the cells was 40%, the retention time through each cell was 4.2 days and the retention time through the experimental unit was 12.5 days. Retention time through the organic layer in the anaerobic cells was approx. 2.1 days. This retention time was less than the retention times of 5 to 10 d reported to be maximum required for adequate sulfate reduction (Eger, 1992). The retention time through the limestone layer in the SAPS was approx. 0.7 d which was greater than the retention time of 0.5 d required for maximum alkalinity production (Hedin et al., 1994). The hydraulic load for the whole experimental unit was 1.9 cm/d and was within the range of hydraulic loads of 0.9 to 27 cm/d reported for wetland systems treating acid mine drainage (Hedin et al., 1994; Brodie, 1993).

Approximately once a month for a total of 11 sampling periods, water samples were collected for chemical analyses. Samples were collected in 4 locations at the influent (p1), effluent of anaerobic cells (p2), a 10 cm diameter well in the first aerobic cell (p3), and final effluent from the aerobic cell (p4) (Fig. 1). Water samples for metal analyses were acidified with 0.5 mL HNO₃ per 50 mL and refrigerated until analysis. Samples were analyzed for Fe, Mn, Ni, Cu, Pb, Zn, Ca, and Mg by inductively coupled plasma spectrophotometer (ICP). Detection

limits were 0.003, 0.003, 0.005, 0.004, 0.03, and 0.003 mg/L for Fe, Mn, Ni, Cu, Pb, and Zn, respectively. Another set of water samples were frozen until analyses for SO₄-S, C, NH₄-N, NO₃-N, and PO₄-P. Sulfate was determined by ion chromatography. Nonpurgeable organic C was determined by a Dohrmann DC 190 TOC analyzer. Ammonium, NO₃-N, and PO₄-P were determined with LACHAT flow-injection analysis. Alkalinity, pH, and sulfide were determined in water immediately after sampling. After measuring pH with a glass electrode, total alkalinity was determined via titration to pH 4.5 with NaOH using the pH electrode to monitor the endpoint. Water was sampled directly into an Orion SAOB solution at a ratio of 10 mL sample to 10 mL SAOB solution and analyzed with a sulfide ion-selective electrode.

Probes were placed into access wells to monitor dissolved oxygen (DO), temperature, electrical conductivity (EC), and redox. Dissolved oxygen and temperature were monitored with a YSI probe and meter. Electrical conductivity was determined with an Orion probe and meter. Platinum-tipped copper wire electrodes were kept in place for redox measurements. Two redox electrodes were placed into the effluent sump of each anaerobic cell 7.5 cm from the bottom (p2, Fig. 1) and one redox probe was placed in a well in the first aerobic cell 15 cm from the bottom (p3, Fig. 1). Another redox probe was placed in a well in the second aerobic cell 15 cm from the bottom near the subsurface effluent header (see Fig. 1). The redox measured from this redox probe was assumed to be the redox of the effluent water (p4). The redox probes were checked every 3 months by placing the probes in a standardized redox solution (0.1 M Fe²⁺, 0.1 M Fe³⁺, and 1 M H₂SO₄) that should have yielded a 432 mV reading at 22 °C using a saturated calomel reference electrode. Greater than 90% of the

probes tested yielded values that were within ± 30 mV of the standard mV reading. If the probe tested fell outside of this range, it was replaced. The reference electrode used for redox determination was a saturated calomel electrode. The measured redox potentials were adjusted in reference to a standard H₂ reference electrode by adding 244 mV to the electrode readings (Stumm and Morgan, 1981).

There were six experimental units as outlined in Table 1 that were randomly laid out in the study. Data from the anaerobic and aerobic wetlands were analyzed separately to first discern differences among the three anaerobic treatments and then to discern differences among the two aerobic treatments. In an overview of the whole system (Table 2), data was averaged across the two replications for each anaerobic treatment and across the three replications for each aerobic treatment. Since the anaerobic effluent water from CG and the treatments with organic matter (SP and CG&SP) were very different, the effectiveness of the aerobic treatments was further evaluated (Table 3) for treating effluent only from anaerobic cells containing organic matter. The aerobic treatments were thus averaged across aerobic replications 2 and 3 as shown in Table 1.

Total alkalinity determined from titration also included HS⁻ and HPO₄²⁻ in the waters tested in addition to HCO₃⁻. Therefore,

$$A_T = A_C + [\text{HS}^-] + [\text{HPO}_4^{2-}]$$

where A_T is total alkalinity and A_C in carbonate alkalinity (Butler, 1991). The unit for alkalinity in the above equation is mole/L. Rearranging and solving for [HS⁻] and [HPO₄²⁻] to equal total sulfide and phosphorus concentrations yields:

$$A_C = [\text{HCO}_3^-] =$$

$$A_T - \frac{10^{-7.02} S_T}{10^{-7.02} + 10^{\text{pH}} a_{\text{HS}}} - \frac{10^{-7.2} P_T}{10^{-7.2} + 10^{\text{pH}} (a_{\text{HPO}_4}/a_{\text{H}_2\text{PO}_4})}$$

where S_T and P_T are total sulfide and phosphate concentrations, respectively, in mole/L and $10^{-7.02}$ and $10^{-7.2}$ are proton dissociation constants for H_2S and H_2PO_4^- , respectively. The activity coefficients (a_i) were calculated from Davies equation using electrical conductivity to estimate ionic strength (Lindsay, 1979). The carbonate alkalinity shown as mole/L HCO_3^- in the above equation was converted to CaCO_3 alkalinity with units of mg/L by:

$$A_C (100,000 \text{ mg CaCO}_3 / 2 \text{ mole HCO}_3^-)$$

Predicted carbonate alkalinity produced from calcite dissolution was calculated from the increase in Ca concentration observed from the influent to the effluent of the anaerobic wetlands. Assuming the Ca increase was due solely to calcite dissolution, 2 moles of alkalinity are produced for every mole of Ca dissolved:



The alkalinity was calculated in terms of CaCO_3 alkalinity in mg/L as:

$$\frac{(\text{Ca increase, mg/L})}{(40.1 \text{ mg Ca}^{2+}/\text{mmol})} \times (2 \text{ mmol HCO}_3^- / \text{mmol Ca}^{2+}) \times$$

$$(100 \text{ mg CaCO}_3 / 2 \text{ mmol HCO}_3^-)$$

For sulfate reduction, 2 moles of alkalinity are produced for every mole of sulfide produced:



Predicted alkalinity from sulfate reduction was calculated in terms of CaCO_3 alkalinity in mg/L as:

$$\frac{(\text{S conc., mg/L})}{(32.1 \text{ mg S}/\text{mmol})} \times (2 \text{ mmol HCO}_3^- / \text{mmol S}^{2-}) \times (100 \text{ mg CaCO}_3 / 2 \text{ mmol HCO}_3^-)$$

Activities of chemical components were calculated from solution concentrations using MINEQL⁺ (Schecher and McAvoy, 1991). The activities were used to determine the potential existence of various solid phases that would support determined metal activity levels assuming equilibrium conditions existed. For evaluation of potential Mn solid phases in the anaerobic wetlands, saturation indices were calculated for Mn solid phases as:

$$\text{Log (SI)} = \text{Log (IAP} / K_{sp})$$

where SI is the saturation index, IAP is the ion activity product in solution, and K_{sp} is the theoretical solubility product for the solid phase in question (Sposito, 1989). If Log (SI) were greater than 0, the solution was supersaturated with respect to the solid phase. If Log (SI) were less than 0, the solution was undersaturated with respect to the solid phase. In both these cases, the existence of the solid phase was not likely. If Log (SI) were equal to 0, the solution was in equilibrium with the solid phase and the existence of the solid phase in question was likely.

For evaluating the potential Cu, Ni, Pb, and Zn solid phases in the anaerobic wetlands and potential Mn solid phases in the aerobic wetlands, metal activities were plotted versus $\text{pe}+\text{pH}$ and compared to solubility lines for known solid phases. The pe was determined as redox (mV)/59.2 (Lindsay, 1979). The

pH was added to pe to obtain pe+pH. Since the reducing or oxidizing potential of an aquatic environment is affected by both pe and pH, the pe+pH is a useful parameter to define the oxidizing potential of the water. For comparison, another scale is presented for redox in mV at the average pH levels of the waters analyzed.

The $\text{Log}(\text{CO}_2, \text{atm})$ was calculated using the HCO_3^- activity calculated from MINEQL^+ and pH as:

$$\text{Log}(\text{CO}_2, \text{atm}) = 7.82 - \text{pH} + \text{log}(\text{HCO}_3^-)$$

Results and Discussion

Overview of Coupled Anaerobic and Aerobic Cells

Table 2 displays average water chemistry data across all sampling periods and replications for effluent waters from each anaerobic and aerobic treatment. In the anaerobic effluent waters, pH and alkalinity were greater in the SP and CG&SP treatments compared to the CG treatment (Table 1). The organic matter in the SP and CG&SP treatments was effective in producing highly anaerobic conditions as evidenced by redox less than -170 mV, DO less than 4% saturation, and sulfide concentrations from 19 to 21 mg/L in the effluent waters. The high alkalinity produced in these anaerobic waters resulted in CO_2 partial pressures that were supersaturated with respect to atmospheric CO_2 of $\text{log}(\text{CO}_2) = -3.52$ (Table 2). As the water was treated by the aerobic cells, the CO_2 degassed from the water more effectively in the reciprocating treatment compared to the non-reciprocating treatment which resulted in lower alkalinity, lower CO_2 partial pressures, and higher pH in the effluent from the

reciprocating treatment compared to the nonreciprocating treatment.

Calcium concentrations in the effluent of the anaerobic cells increased from the influent concentrations due to dissolution of calcite (Table 1). Calcite was added to the SP and CG&SP treatments as limestone. Since river gravel was the only medium used in the CG treatment, an increase in Ca concentration in this treatment is indicative of some calcite present in the river gravel. Batch titrations with HCl has shown the river gravel to have a calcium carbonate equivalence of 0.35%.

Manganese concentration was decreased approximately 50% in the anaerobic cells with further reduction to levels below 0.3 mg/L in the aerobic cells (Table 1). The SP and CG&SP treatments of the anaerobic cells were very effective in reducing concentrations of Cu, Ni, Pb, and Zn to levels near the detection limits of the ICP. The CG anaerobic treatment was less effective with concentrations ranging from 0.06 to 0.44 mg/L for Cu, Ni, and Zn.

The addition of compost in the SP and CG&SP anaerobic treatments resulted in greater $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ concentrations in the anaerobic effluent waters compared to the CG treatment (Table 1). The reciprocating aerobic wetland was very effective at reducing $\text{NH}_4\text{-N}$ levels below analytical detection. However, both reciprocating and nonreciprocating aerobic treatments only reduced $\text{PO}_4\text{-P}$ concentrations to 2.9 and 2.4 mg/L, respectively, with an average 3.6 mg/L aerobic influent concentration.

Table 2. Water chemistry of the influent and effluent of anaerobic cells and effluent of aerobic cells.

| <i>Parameter †</i> | <u>Anaerobic effluent</u> | | | | <u>Aerobic effluent</u> | |
|----------------------------|---------------------------|-------------|-------------|------------------|-------------------------|-----------------|
| | <i>Influent</i> | <i>CG</i> | <i>SP</i> | <i>CG&SP</i> | <i>w/recip</i> | <i>wo/recip</i> |
| pH | 4.9(0.5)‡ | 6.7(0.2) | 7.2(0.1) | 7.0(0.1) | 7.7(0.2) | 7.4(0.4) |
| Alkalinity | 0 | 81(33) | 142(44) | 193(59) | 57(18) | 118(41) |
| log(CO ₂ , atm) | | -1.73(0.13) | -1.96(0.26) | -1.64(0.21) | -2.88(0.19) | -2.12(0.37) |
| Redox | | 304(357) | -172(120) | -174(93) | 584(136) | 532(163) |
| DO | 98(14) | 11(11) | 3(3) | 1.8(1.8) | 92(18) | 30(19) |
| Ca | 90(5) | 120(15) | 122(10) | 133(17) | 127(14) | 142(14) |
| Mg | 93(5) | 96(3) | 99(3) | 98(4) | 89(14) | 92(18) |
| Mn | 20(1) | 11(8) | 10(5) | 10(6) | .04(.04) | .24(.24) |
| Cu | 2.0(0.2) | .06(.06) | .009(.009) | .005(.002) | .005(.003) | .03(.03) |
| Ni | 1.5(0.3) | 0.44(0.41) | .016(.016) | .008(.008) | .005(.004) | .006(.003) |
| Pb | 2.0(0.3) | .04(.03) | < .03 | .03(.01) | < .03 | < .03 |
| Zn | 2.1(0.1) | .30(.30) | .009(.009) | .01(.01) | .006(.005) | .007(.007) |
| Fe | 1.0(1.2) | 1.2(1.2) | .062(.062) | .073(.072) | .005(.005) | .009(.009) |
| S | < .02 | .10(.10) | 19(9) | 21(9) | < .02 | < .02 |
| SO ₄ -S | 207(36) | 211(31) | 193(36) | 182(33) | 209(42) | 198(31) |
| org-C | 1.7(1.0) | 2.2(1.6) | 5.3(1.8) | 5.2(2.1) | 3.5(1.8) | 3.7(2.1) |
| EC | 1.12(.04) | 1.23(.06) | 1.24(.04) | 1.27(.08) | 1.18(.17) | 1.26(.07) |
| NH ₄ -N | <.02 | .28(.28) | 2.2(2.2) | 1.6(1.6) | <.02 | .8(.8) |
| NO ₃ -N | .23(.06) | .04(.04) | <.02 | <.02 | 3.5(3.5) | 2.0(2.0) |
| PO ₄ -P | <.03 | .04(.04) | 4.8(3.9) | 6.0(5.0) | 2.9(2.9) | 2.4(2.4) |

† Units for all parameters are in mg/L except for pH and log (CO₂), which are unitless, redox is in mV, DO is % saturation, and EC is mS/cm.

‡ Data is averaged across sampling time and replications. Values in parenthesis represent standard deviations.

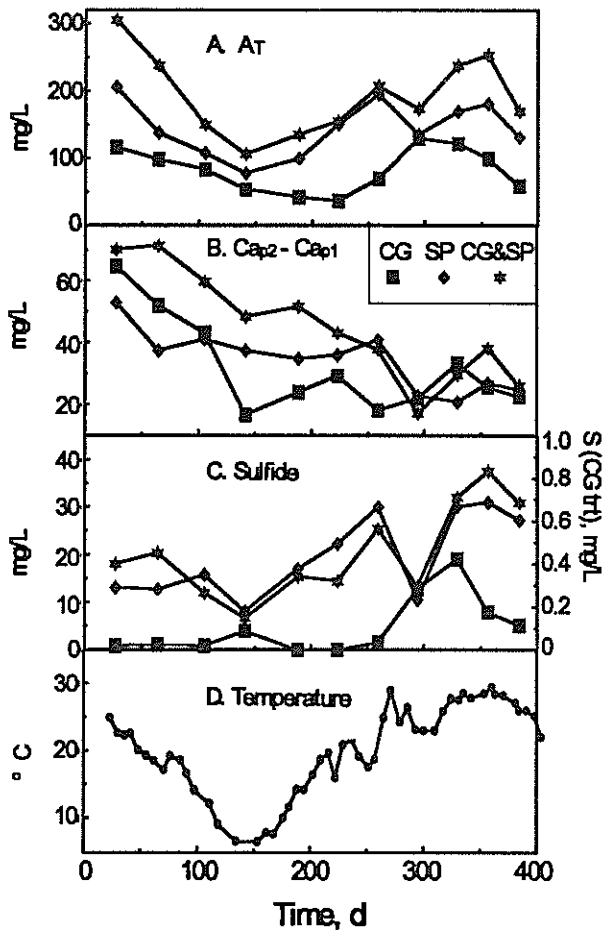


Figure 2. Total alkalinity, A_T (A), Ca increase (B), sulfide (C), and water temperature (D) changes with time in the effluent waters from the anaerobic wetland cells for the canarygrass (CG), SAPS (SP), and canarygrass+SAPS combination (CG&SP) treatments. Calcium increase is the difference in Ca concentrations in the effluent and influent waters of the anaerobic cells ($Ca_{\text{increase}} = Ca_{\text{out}} - Ca_{\text{in}}$).

Anaerobic Wetland Cells

Alkalinity in the effluent waters of the anaerobic cells was correlated fairly well with water temperature (Fig. 2A). Alkalinity was greater with higher water temperatures. Alkalinity generation was greater in the anaerobic treatments containing compost (SP and CG&SP) compared to CG. The alkalinity from CG&SP was greater

than SP alkalinity during the warmest times of the year at the initiation of the experiment (day 0 to day 60) and during the summer (day 320 to day 360).

A chemical parameter that has a relationship to alkalinity generation is Ca concentration difference between effluent and influent waters (Fig. 2B). If the Ca difference can be assumed to be due solely to calcite dissolution, some conclusions on calcite dissolution effectiveness can be made in these systems. Calcite dissolution was greatest at the initiation of the experiment and continually declined with time for all anaerobic treatments. Calcite dissolution declined more rapidly in the CG treatment probably due to a limited amount of calcite present in the river gravel. Calcite dissolution did not show seasonal trends. For example, the Ca difference continually declined during the warming time of the year from day 200 to day 400. The decline in calcite dissolution may have been due to calcite particles being continually coated by organic matter and inorganic precipitates.

Another chemical parameter related to alkalinity generation is sulfide concentrations as shown in Fig. 2C. Sulfide was much greater in the treatments containing compost (SP and CG&SP) compared to the treatment without compost (CG). The increase in sulfide concentrations was correlated well with increased water temperatures that must have increased productivity of sulfate reducing bacteria. At day 290 sampling, there was a drastic decline in sulfide concentration in SP and CG&SP. The systems were fertilized with N, P and K at day 282. The decline in S may have been due to sulfate-reducing bacteria unsuccessfully competing with other heterotrophic bacteria that may have flourished after adding supplemental nutrients.

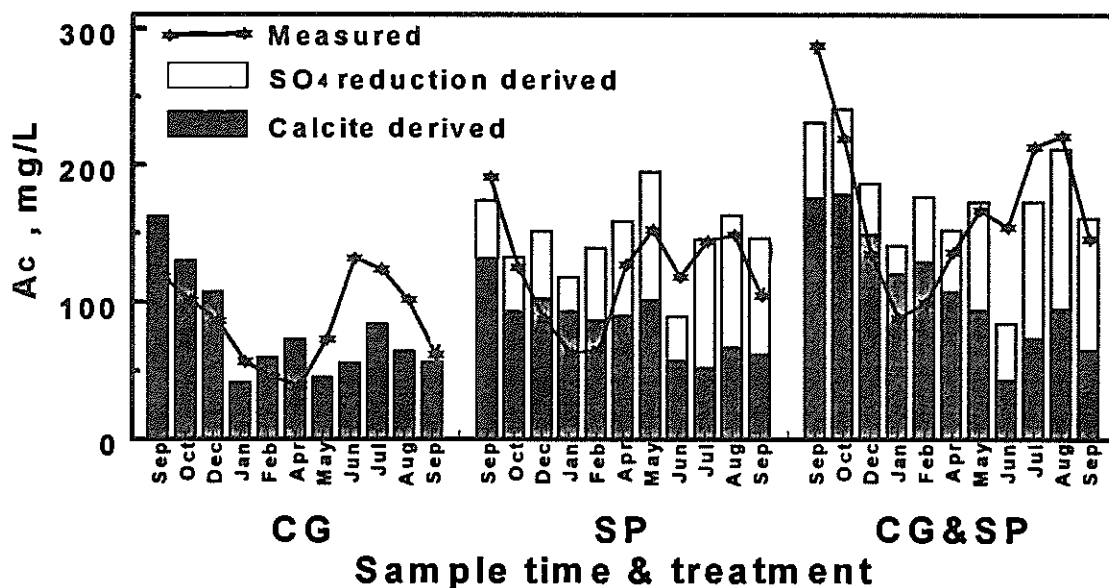


Figure 3. Calculated carbonate alkalinity (A_c) based on calcite dissolution and sulfate reduction compared to measured carbonate alkalinity in effluent waters from the anaerobic wetland cells for the canarygrass (CG), SAPS (SP), and canarygrass + SAPS combination (CG&SP) treatments.

The expected carbonate alkalinity produced from calcite dissolution and sulfate reduction was calculated and compared to carbonate alkalinity from measured total alkalinity (see Materials and Methods) (Fig. 3). Alkalinity calculated from calcite dissolution and sulfate reduction followed a trend similar to measured alkalinity with lower alkalinity during colder periods of the year and higher alkalinity during warmer periods. However, there were discrepancies between measured alkalinity and total alkalinity predicted from calcite dissolution and sulfate reduction. The overestimated alkalinity predicted from calcite dissolution and sulfate reduction can be due to an increase in Ca concentration related to chemical processes that do not release HCO_3^- into solution, such as exchangeable Ca or dissolution of non-carbonate Ca minerals such as gypsum. Another possible explanation is that pure calcite was not present

so the assumption that 2 moles of HCO_3^- was released for each mole of Ca dissolved may have overestimated alkalinity calculated from Ca dissolution. Yet another explanation is that HCO_3^- released from calcite dissolution precipitated with other metals, such as Mn, leaving Ca in solution while HCO_3^- was removed.

The underestimation of alkalinity during the months from May to August in CG and from June to July in CG&SP may have been due to active canarygrass roots releasing HCO_3^- during anion uptake (Mengel and Kirkby, 1982), which would be an unaccounted source of alkalinity. The SP treatment did not contain canarygrass, but did contain algae in the surface water. Lower CO_2 and higher pH were observed in the SP treatment compared to the CG and CG&SP treatments (Table 2). Algae absorbs CO_2 during photosynthesis which increases pH (Vymazal, 1995), but these processes counterbalance

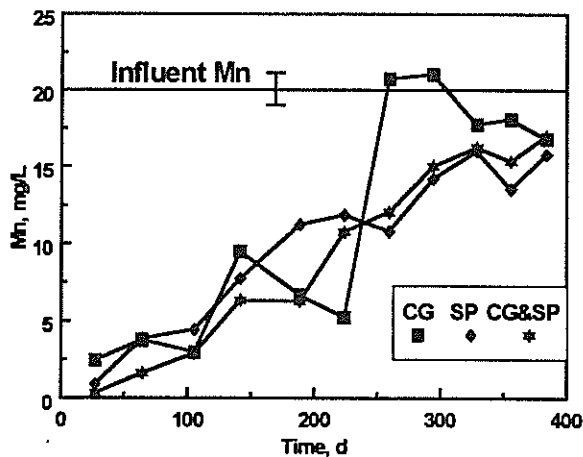


Figure 4. Manganese concentrations in effluent waters from the anaerobic wetland cells for the canarygrass (CG), SAPS (SP), and canarygrass+SAPS combination (CG&SP) treatments with time.

one another with no change in alkalinity (Butler, 1991). Therefore, large differences were not observed between measured and predicted alkalinity in SP during the summer months.

The anaerobic cells effectively removed Mn in influent waters with low effluent Mn concentrations observed at the beginning of the experiment (Fig. 4). However, as time progressed Mn removal efficiency declined as Mn concentrations approached influent concentration of 20 mg/L. Similar trends in Mn removal were observed by Wildeman et al. (1993) and Stark et al. (1995). In Wildeman et al. (1993), bench-scale studies of anaerobic systems have shown greater than 95% Mn removal from 24 to 71 days of operation. However, in a pilot-scale anaerobic wetland with influent Mn concentration of 31 mg/L, Mn removal efficiency was near 50% during the first 3 months with removal efficiencies declining to 10% from 6 to 24 months of the study. In Stark et al. (1996), results similar to Fig. 4 were obtained with Mn concentrations slowly increasing in

effluent of anaerobic wetlands with 50% removal efficiency occurring at approximately 120 day.

As anaerobic wetlands are initiated there may be plentiful sorption sites on organic matter and limestone for Mn to sorb onto. Although the affinity of organic functional groups for Mn is low (McBride, 1994; Wildeman et al., 1994), some sorption of Mn onto abundant carboxyl and hydroxyl functional groups in the compost should be expected. Manganese sorption onto limestone may occur via surface displacement of Ca^{2+} for Mn^{2+} to form a solid solution or precipitation of a $MnCO_3$ solid phase at the surface (Evangelou, 1995). Once Mn sorption capacities were reached on both compost and limestone media and no other important removal mechanism existed, Mn concentrations in effluent water from anaerobic wetlands would be expected to increase as observed in Fig. 4.

To determine what Mn solid phases were controlling Mn in the water of the anaerobic cells, saturation indices were calculated and are plotted in Fig. 5. Throughout the experiment, the water was very much undersaturated with respect to $MnOOH$. The Mn oxide solid phases contain Mn in an oxidized state. The reducing conditions of the anaerobic wetlands keep Mn in the reduced manganous state (Mn^{2+}), making formation of Mn oxides extremely unlikely.

The anaerobic waters were undersaturated with respect to $MnCO_3$ at the beginning of the experiment. From day 220 to day 400, water from the SP and CG&SP treatments was near equilibrium to supersaturated with respect to $MnCO_3$. From day 300 to day 400, water from CG was near equilibrium to undersaturated with respect to $MnCO_3$. Similar Log (SI) values were reported for $MnCO_3$ in effluent waters from anoxic limestone

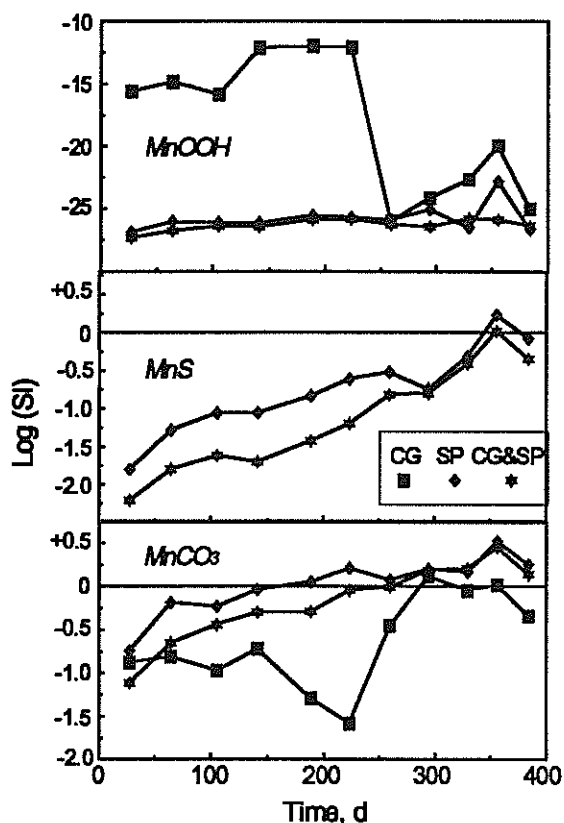


Figure 5. Logarithm of saturation indices (Log (SI)) for $MnOOH(s)$, $MnS(s)$, and $MnCO_3(s)$ in effluent waters from the anaerobic wetland cells for the canarygrass (CG), SAPS (SP), and canarygrass+SAPS combination (CG&SP) treatments with time.

drains (Hedin and Watzlaf, 1994) where limited Mn removal in the waters occurred. The Log (SI) values indicated conditions existed for $MnCO_3$ to form and may exert some control on Mn concentration in water toward the end of the experiment. The supersaturation levels that existed may have been due to kinetic limitations on $MnCO_3$ precipitation.

The waters from the treatments with organic matter (SP and CG&SP) were undersaturated with respect to MnS for most of the study until day 350 when the solutions were near equilibrium with this mineral. Saturation indices was not calculated for the CG treatment since sulfide

was not detected in most of the samples. The solubility of MnS is fairly high compared to other metal sulfides. Therefore, removal of Mn in anaerobic wetlands via MnS formation is not very effective.

The data in Fig. 5 further supports the hypothesis that Mn was being sorbed onto compost and limestone at the beginning of the experiment when the waters were undersaturated with respect to MnS and $MnCO_3$. As the sorption sites filled, Mn concentrations rose to a high enough level so MnS and $MnCO_3$ could begin to control Mn solubility. The advantage of removing Mn via precipitation as $MnCO_3$ or MnS is that the anion precipitating with Mn is in constant supply from the sulfate reduction process. This is contrary to Mn removal via sorption where the component removing Mn (sorption sites) has a finite availability. A disadvantage of Mn being removed as $MnCO_3$ or MnS is that the solubilities of the minerals are so high that they support Mn concentrations in water that are unacceptable for discharge (Fig. 4). Therefore, a subsequent oxidation of the Mn to form Mn oxides is required in an aerobic wetland.

The concentrations of Cu, Ni, Pb, and Zn in the effluent from the anaerobic cells containing organic matter (SP and SP&CG) were always near the detection limit for the ICP (Table 2). However, the Ni and Zn concentrations in the anaerobic effluents from the CG treatment increased to 1.1 to 1.2 mg/L after 120 days and subsequently decreased (Fig. 6).

The redox in the treatments with organic matter were always at very low values (approx. -200 mV) throughout the experiment, whereas the redox in the effluent stream from the CG treatment was >400 mV up to day 240 and then drastically dropped to maintain redox levels between -200 and 200 mV. The decrease in the

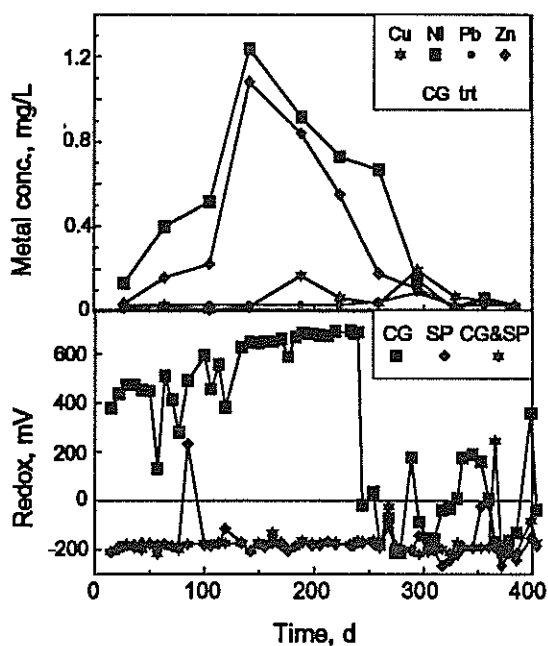


Figure 6. Concentrations of Cu, Ni, Pb, and Zn and redox in effluent waters from the anaerobic wetland cells for the canarygrass (CG), SAPS (SP), and canarygrass+SAPS combination (CG&SP) treatments with time.

redox in the CG treatment coincided with the spring growth of the canarygrass in late April 1995. As in this study, canarygrass growth has been observed to reduce redox levels to very low values in gravel bed wetlands (Zhu and Sikora, 1995; Steinberg and Coonrod, 1994). Because of this ability to reduce redox levels, canarygrass was chosen for this experiment to determine if sulfide could be produced in a plant-rock system without organic matter. Even though redox levels were low (<200 mV), there must still have been limitations to sulfate reduction due to the low sulfide concentrations observed (Fig. 2). The limitation was probably a lack of available C.

To determine what solid phases may have been controlling concentration of trace metals in the anaerobic wetland effluents, stability diagrams were constructed

with log of metal activities plotted versus $pe+pH$ (Fig. 7). The data represented in the figure is only from samples in which the metal was detected above analytical detection limits of the ICP. This represented 33, 30, 8, and 42 % of the samples collected for Cu, Ni, Pb, and Zn, respectively. The data for the treatments with organic matter (SP and CG&SP) were combined since there was very little difference between these treatments. The Cu activities were undersaturated with respect to $CuCO_3$. Except for some data from the CG treatment, there was an observable trend that Cu activities were drastically reduced with a decrease in $pe+pH$ due to precipitation of CuS . Most of the CG data at higher $pe+pH$ indicate Cu may be controlled by a Cu oxide solid phase. Nickel activity levels were undersaturated with respect to $NiCO_3$ and $Ni(OH)_2$ indicating some other solid phase or sorption was controlling this metal in solution. At low $pe+pH$, data clustered around the NiS solubility line. From the limited data available for Pb, $Pb(OH)_2$ appeared to control Pb activities at high $pe+pH$ and PbS controlled Pb activity at low $pe+pH$. For Zn, solubility appeared to be controlled by $ZnCO_3$ in the CG data at high $pe+pH$ and by ZnS at low $pe+pH$ for all treatments. Figure 7 is only useful as a qualitative predictor of what minerals may control metal activities in solution because indirect analysis of what solid phases may be present is made from solution chemistry. Other solid phases not considered or sorption of metals onto Fe and Mn oxides (McBride, 1989) may have also controlled metal solution activities.

The similarity in the solubility diagrams of Fig. 7 is that metal sulfides precipitate and reduce metal activities to very low levels in solution at low $pe+pH$. The $pe+pH$ value at which the metal sulfide solubility line begins to decline depends on the solubility of the

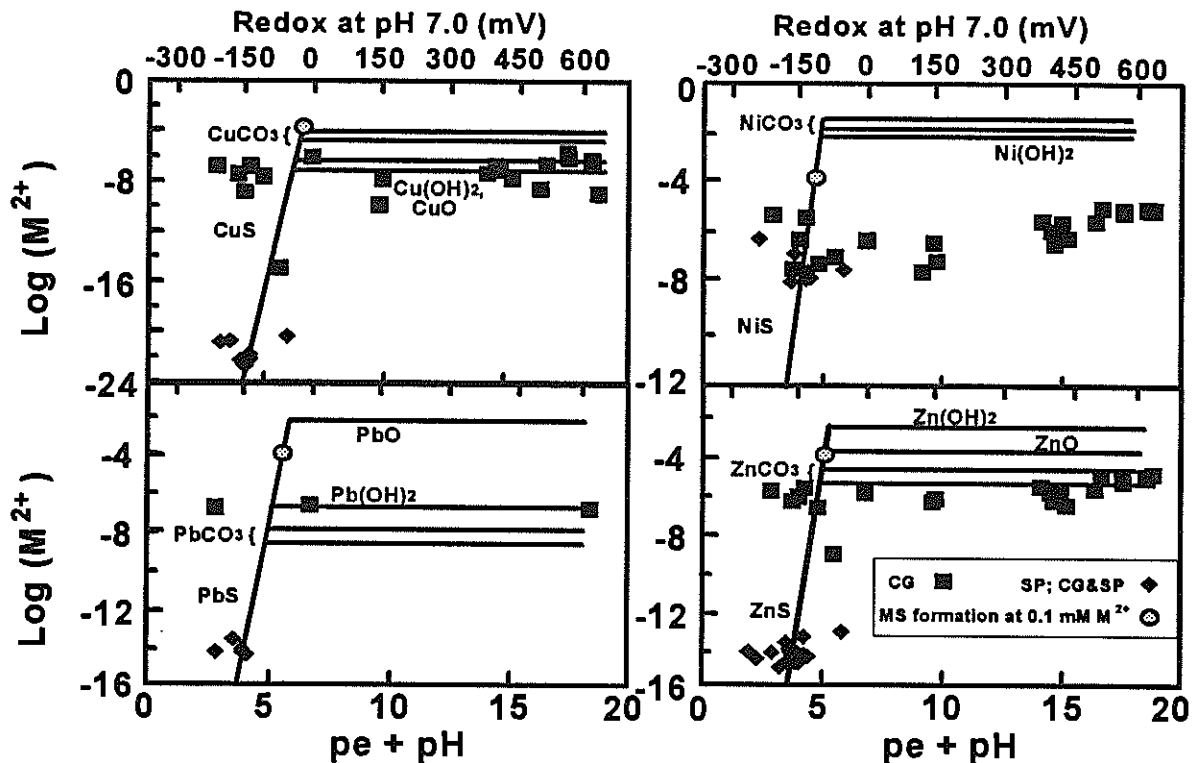


Figure 7. Metal activities as a function of $pe + pH$ for Cu, Ni, Pb, and Zn in effluent waters from the anaerobic wetland cells for the canarygrass (CG), SAPS (SP), and canarygrass+SAPS combination (CG&SP) treatments. Symbols represent experimental data. Lines represent solubility of known solids. The two lines for $MnCO_3$ represents the range of $MnCO_3$ solubility for low measured alkalinity (upper line) and high measured alkalinity (lower line). The upper x axis is the equivalent redox value for the average pH level of 7.0.

metal sulfide. The greater the solubility, the lower the $pe+pH$ has to be before precipitation of the metal sulfide begins. The redox levels at pH 7 required to reduce metal activities below 0.1 mM are -24, -62, -94, and -114 mV for Cu, Pb, Zn, and Ni, respectively (shown as shaded circles in Fig. 7). Although not shown in Fig. 7, the required redox at pH 7 to reduce Mn activities below 0.1 mM via MnS formation is -175 mV. Therefore, the affinity of metals to form metal sulfides decreases in the order $Cu > Pb > Zn > Ni > Mn$. The same trend for metal sulfide formation can be presented by comparing solubility products of the metal sulfides (Hedin et al., 1994). Both the anaerobic

treatments with organic matter (SP and CG&SP) produced very low redox levels, which were adequate in precipitating Cu, Ni, Pb, and Zn as metals sulfides and reducing solution concentrations of the metals to very low levels (Table 1).

The stability diagrams for Ni and Zn concentrations in the CG treatment in Fig. 7 can be used to explain observed changes in Ni and Zn concentrations (Fig. 6). At higher $pe+pH$, $ZnCO_3$ appeared to control Zn solubility (Fig. 7). At the beginning of the experiment, alkalinity was high which would be expected to lower Zn concentrations

Table 3. Water chemical parameters affected by reciprocation in aerobic treatments. Only the aerobic cells treating effluent from the SP and CG&SP anaerobic treatments are considered.

| Parameter † | Anaerobic effluent | First aerobic cell | | Aerobic effluent | |
|-----------------------|--------------------|--------------------|-------------|------------------|-------------|
| | | w/recip | wo/recip | w/recip | wo/recip |
| pH | 7.1 | 7.7(0.2)‡ | 7.2(0.1) | 7.7(0.2) | 7.3(0.4) |
| Alkalinity | 168 | 63(19) | 149(62) | 63(16) | 127(46) |
| Log(CO ₂) | -1.8 | -2.85(0.10) | -1.91(0.20) | -2.85(0.13) | -2.17(0.46) |
| Redox | -173 | 544(124) | -195(87) | 588(112) | 509(155) |
| DO | 2.4 | 94(14) | 2.3(2.3) | 93(14) | 11(11) |
| Mn | 10 | 0.31(0.88) | 6.2(3.4) | 0.05(0.08) | 0.35(0.35) |

† Units for pH and Log (CO₂,atm) are unitless, alkalinity is in mg/L, redox is in mV, DO is in % saturation, and Mn is in mg/L.

‡ Data is averaged across sampling time and replications. Values in parenthesis represent standard deviations.

due to ZnCO₃ precipitation. As time progressed, alkalinity declined (Fig. 1) resulting in subsequent increase in Zn concentrations (Fig. 6). The redox of the CG effluent water dramatically dropped at day 240 (Fig. 6) which resulted in a decrease in pe+pH to levels that predicted ZnS and NiS controlled (Fig. 7) and lowered Zn and Ni concentrations (Fig. 6).

Aerobic Wetland Cells

There were little differences in Mn concentrations in the effluent waters from the aerobic cells treating water from the anaerobic cells containing organic matter when comparing reciprocating and non-reciprocating treatments (Table 3). However, considerable differences were observed for these parameters in waters taken from the first aerobic cells (Table 3). The cells with reciprocation resulted in higher DO,

redox, and pH levels in the first aerobic cells compared to non-reciprocating cells. The high redox and pH levels most likely resulted in lower Mn concentrations in the first reciprocating aerobic cells compared to the first nonreciprocating cells (Table 3) due to greater likelihood for Mn oxide precipitation to occur. The long retention time of 9 days in the aerobic cells was ample for adequate removal of Mn in the final effluent whether the cells were reciprocating or not.

A plot of log Mn activity vs pe+pH was constructed (Fig. 8) for predicting what solid phases may have been controlling Mn concentrations in the aerobic wetlands. The lines are predictive solubility lines for MnS, MnCO₃, MnOOH, Mn₂O₃, and Mn₃O₄. Without reciprocation, most of the waters in the first aerobic cells had low pe+pH values and the Mn

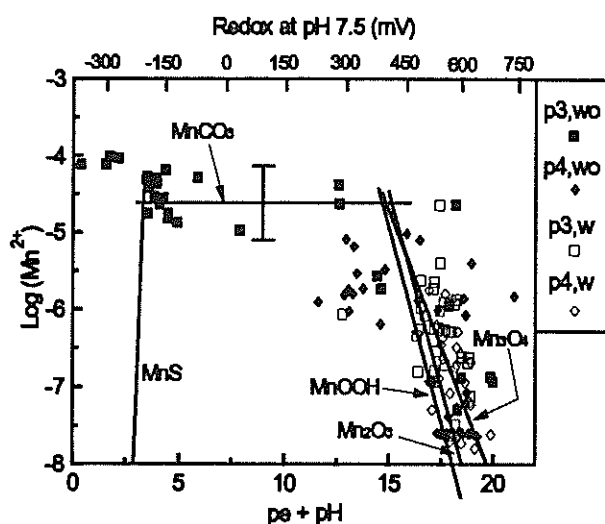


Figure 8. Manganese activities as a function of $pe + pH$ in water sampled from p3 and p4 (see Fig. 1) in the aerobic wetland cells for treatments without reciprocation (wo) and with reciprocation (w). Symbols represent experimental data. Lines represent solubility of known solids. The error bar for $MnCO_3$ represents the range of $MnCO_3$ solubility for low measured alkalinity (upper boundary) and high measured alkalinity (lower boundary). The upper x axis is the equivalent redox value for the average pH level of 7.5.

activities appeared to be controlled by a combination of MnS and $MnCO_3$. In the effluent waters of the nonreciprocating treatment, the $pe+pH$ levels increased and the Mn activities approached solubility with Mn oxides. The $pe+pH$ levels were high at both sampling positions in the reciprocating treatment with Mn activities clustered around the Mn oxide solubility lines.

It is difficult to ascertain whether the mechanism for Mn oxidation was biotic or abiotic since poisoned abiotic treatments were not included in the experiment. However, a conclusion can be made that producing an environment that thermodynamically favors Mn^{2+} oxidation and precipitation as Mn oxides is the first requirement for Mn removal from solution. Such an

environment is produced with $pe+pH$ above 15 or redox above 400 mV at pH 7.5. A second requirement may be that an appropriate type and quantity of bacteria needs to be present to increase the rate of Mn oxidation. The influent waters to the aerobic systems were highly anaerobic which may have exaggerated the utility of having a reciprocating aerobic wetland to rapidly increase $pe+pH$ to allow for rapid Mn oxidation and subsequent precipitation. For waters that already have higher $pe+pH$, aerating the water may not be that critical. Although aeration occurred via reciprocating water in a gravel bed in the current experiment, aeration by passing the water over a riprap may also suffice in increasing $pe+pH$ levels to allow for rapid Mn oxidation and precipitation.

CONCLUSIONS

The data collected the first year of this study has shown decreased calcite dissolution and Mn removal efficiencies with time in anaerobic wetlands. Alkalinity generation was observed to be seasonal with greater alkalinity in the warmer time of the year. Mn removal was very effective in aerobic wetlands following anaerobic wetlands. Aeration of effluent waters from anaerobic wetlands is required for raising $pe+pH$ to high enough levels to allow for rapid oxidation of Mn to form Mn oxide precipitates. Trace metal removal was very effective in the anaerobic treatments with organic matter due to precipitation of metal sulfides. The study is being conducted for another year to determine long term efficiencies of the wetland systems and to develop scaled-up design criteria.

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