IRON AND MANGANESE DYNAMICS IN LABORATORY WETLAND MESOCOSMS: IMPLICATIONS FOR COAL MINE DRAINAGE TREATMENT[1]

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Abstract: The interstitial water dynamics of iron, manganese, and sulfide in wetland mesocosms exposed to different synthetic acidic mine waters were characterized to determine if the presence of iron, manganese, or sulfate influenced the anoxic removal of these metals. Twelve wetland mesocosms (PVC columns) were constructed in the laboratory employing spent mushroom compost as the organic substrate. Control columns received semiweekly additions of NaCl or Na_2SO_4 solutions (adjusted to pH 3 with HCl) for a period of 13 weeks. Treatment columns consisted of semiweekly additions of pH 3 solutions of (1) Fe(III) + Mn(II), (2) Fe(III) + SO_4, (3) Mn(II) + SO_4, or (4) Fe(III) + Mn(II) + SO_4 (added as metal chlorides or Na_2SO_4). After 8 and 13 weeks of exposure, interstitial water samples were collected and analyzed for pH, redox potential, sulfide, and metals, using standard procedures. Substantial acidification had occurred between 8 and 13 weeks of exposure. Iron and manganese acted synergistically with respect to metal removal, although iron had no influence (p=0.7) on manganese removal after 13 weeks. The inclusion of sulfate in synthetic mine water caused a slightly greater, but statistically significant (p<0.05), iron removal in mesocosms relative to mesocosms not receiving sulfate. Sulfate had no effect (p=0.5) on manganese removal. The results of this study suggest that the generation of sulfide by bacterial sulfate reduction can effectively retain iron, but not manganese, within anoxic soils. However, long-term removal of iron by this mechanism may be limited by an eventual decline in sulfate reduction owing to insufficient decomposable organic substrates or soil acidification.

Additional Key Words: coal mine drainage, wetlands, anoxic treatment, acidification.

Introduction

The mechanisms responsible for the removal and retention of iron, manganese, and sulfate in constructed wetlands receiving acidic mine drainage (AMD) include the formation of metal oxides (Wieder et al. 1990) and metal sulfides (Machemer and Wildeman 1992). The diagenetic remobilization of iron and manganese during suboxic diagenesis results in the diffusion of soluble metals from the subsurface into the overlying water, where they may ultimately arrive at the wetland effluent and be discharged. It has been suggested (Tarutis et al. 1992) that long-term metal retention in AMD wetlands would be enhanced by active sulfate reduction and the subsequent formation of metal sulfides. The purpose of this paper is to characterize the interstitial water dynamics of iron, manganese, and sulfide in wetland

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mesocosms exposed to synthetic mine drainages and to test whether or not the presence of iron, manganese, or sulfate in the synthetic mine waters influenced the anoxic removal of these metals.

Materials and Methods

Twelve simulated wetlands were constructed in the laboratory using PVC columns (75 cm x 15 cm i.d.) with PVC caps cemented to their base. Each column was completely filled with air-dried spent mushroom compost (SMC) obtained from the Mushroom Research Center, The Pennsylvania State University, University Park, PA. The dried SMC was used as received from the facility. Distilled water was added, and each column was covered with a loose-fitting PVC cap to prevent evaporation during a 6-month stabilization period. The columns were maintained in a temperature-controlled room at 22° C. At semiweekly intervals, 1 L of solution was aspirated from the water surface and replaced with distilled water. The stabilization period allowed the SMC to settle and create ambient conditions conducive to sulfate reduction. After the stabilization period, 1 L of different synthetic mine waters was added twice per week over a 13-week period in the same fashion as described above. The experiments, performed using duplicate columns, consisted of four treatments and two controls as described in table 1.

Table 1. Chemical composition of synthetic mine waters[1] to which the wetland mesocosms were exposed.

	Concentration, mg/L					
Treatment	Fe	Mn	SO_4	Na	Cl	pH[2]
Control . .	0	0	0	200	310	3.0
SO_4 only .	0	0	500	240	0	3.0
Fe(III) + Mn(II) .	200	100	0	0	510	3.0
Fe(III) + SO_4 . . .	200	0	500	240	380	3.0
Mn(II) + SO_4 . . .	0	100	500	240	130	3.0
Fe(III) + Mn(II) + SO_4 . . .	200	100	500	240	510	3.0

[1] Fe and Mn were added as chlorides and SO_4 was added as sodium salt.

[2] pH adjusted with HCl.

Differences among treatment means were analyzed by Student's *t*-test for paired data. After 8 and 13 weeks of exposure to the synthetic mine waters, interstitial water samples (10 mL) were obtained by hypodermic syringe at 5-cm depth intervals through prefitted septa cemented along the PVC column wall. Samples were immediately analyzed for redox potential (epoxy-body platinum electrode calibrated with ZoBell's solution [ZoBell 1946]), pH (plastic-body pH combination electrode), and sulfide (specific-ion electrode). Samples were then acidified to pH<2 with HNO_3, and organic matter was removed by the addition of 0.08M $AlCl_3$, followed by centrifugation (Robbins 1989), and analyzed for iron and manganese by flame atomic absorption spectrophotometry (AAS).

Results

Concentration-depth profiles of redox potential, pH, iron, manganese, and sulfide measured in the columns after 8 and 13 weeks of exposure to the synthetic mine waters are shown in figures 1-5. All mesocosms were entirely anoxic with redox potentials ranging from -250 to -350 mV during the initial weeks of the experiment (figs. 1-5); a pungent sulfide odor characteristic of active sulfate reduction was noticeable throughout the entire 13-week study period. There was essentially no difference in the concentration of dissolved constituents between the two control columns (with and without sulfate in the absence of

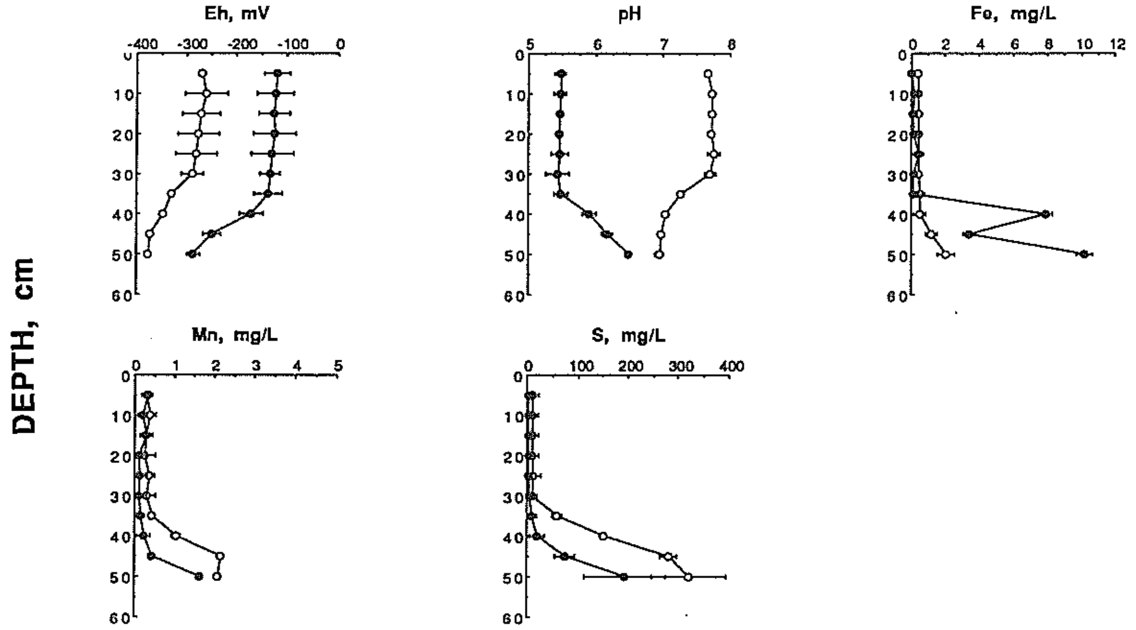

Figure 1. Interstitial water depth profiles of control (SO4 only) columns after 8 (○) and 13 (●) weeks of exposure. Points are means of duplicate samples, and error bars equal one standard deviation.

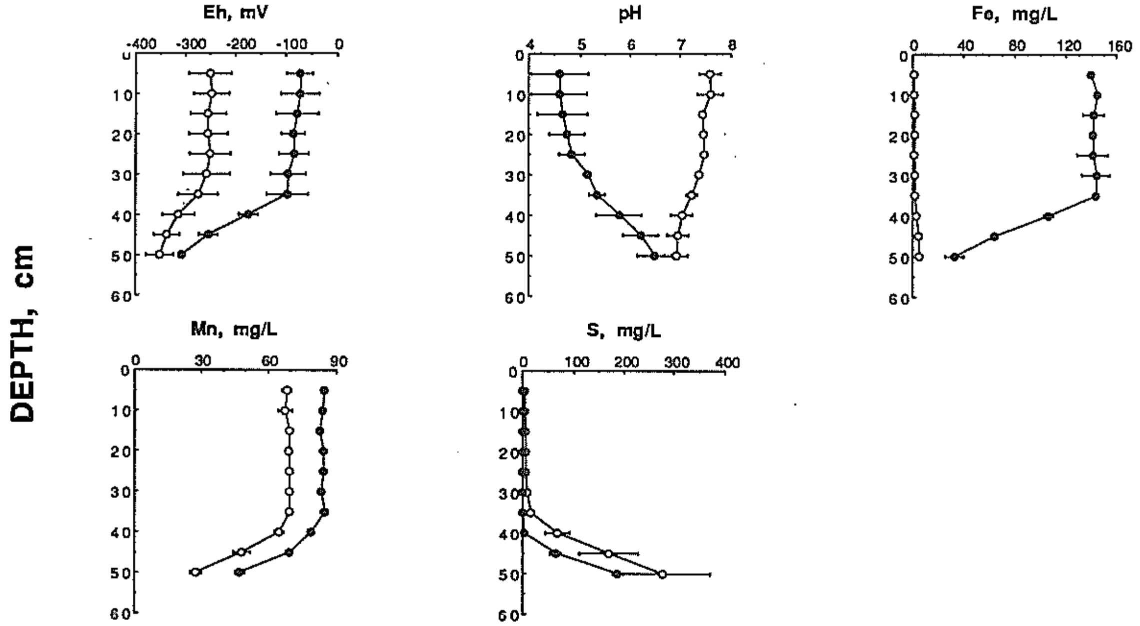

Figure 2. Interstitial water depth profiles of [Fe(III) + Mn(II)] treatment columns after 8 (○) and 13 (●) weeks of exposure. Points are means of duplicate samples, and error bars equal one standard deviation.

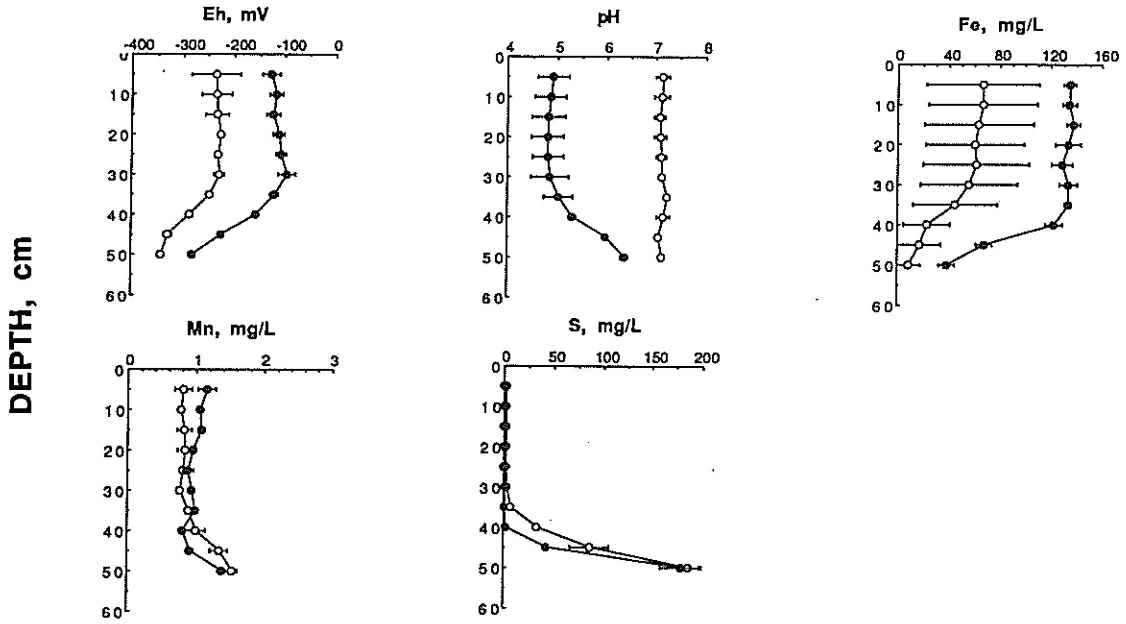

Figure 3. Interstitial water depth profiles of [Fe(III) + SO4] treatment columns after 8 (○) and 13 (●) weeks of exposure. Points are means of duplicate samples, and error bars equal one standard deviation.

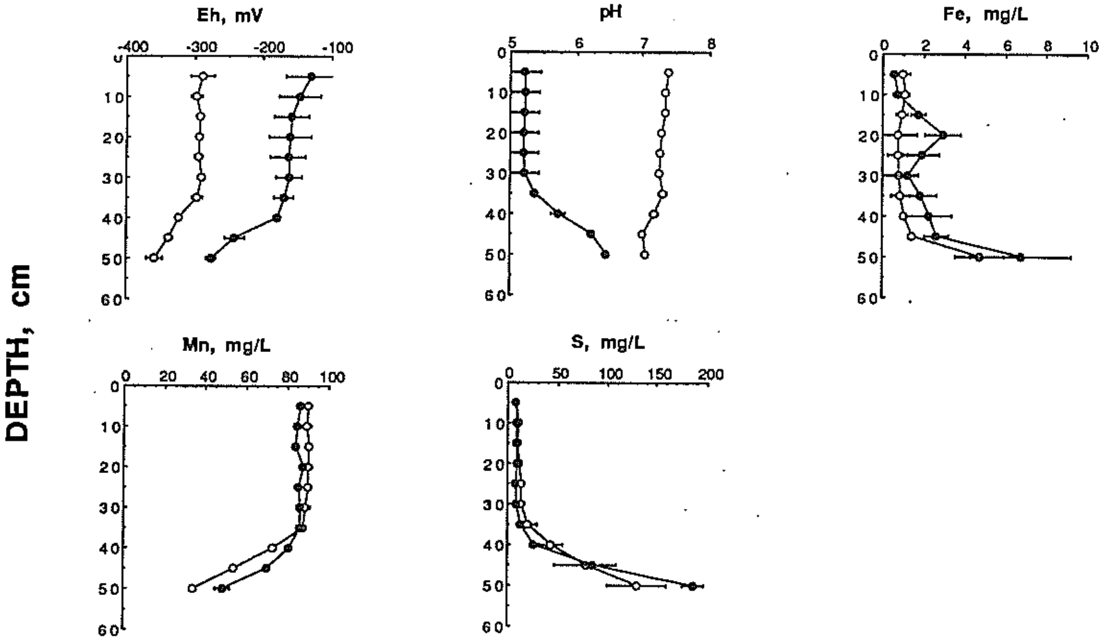

Figure 4. Interstitial water depth profiles of [Mn(II) + SO4] treatment columns after 8 (○) and 13 (●) weeks of exposure. Points are means of duplicate samples, and error bars equal one standard deviation.

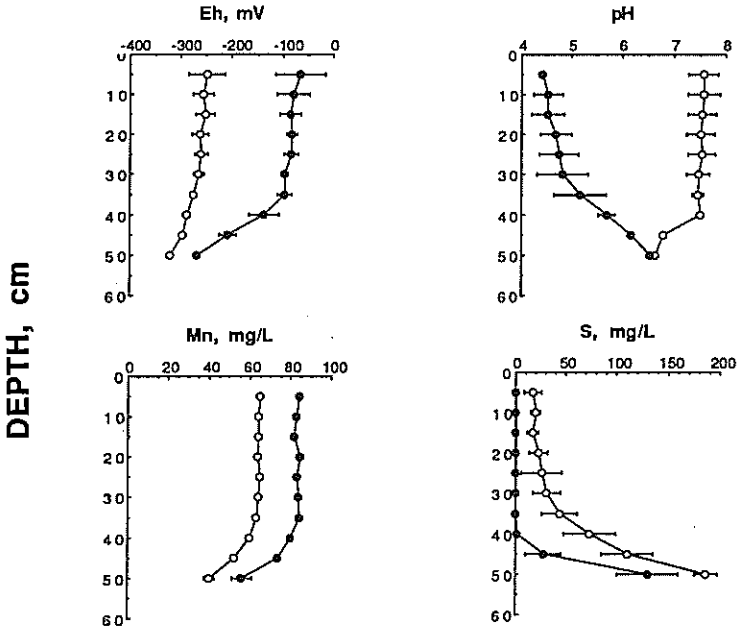

Figure 5. Interstitial water depth profiles of [Fe(III) + Mn(II) + SO_4] treatment columns after 8 (○) and 13 (●) weeks of exposure. Points are means of duplicate samples, and error bars equal one standard deviation.

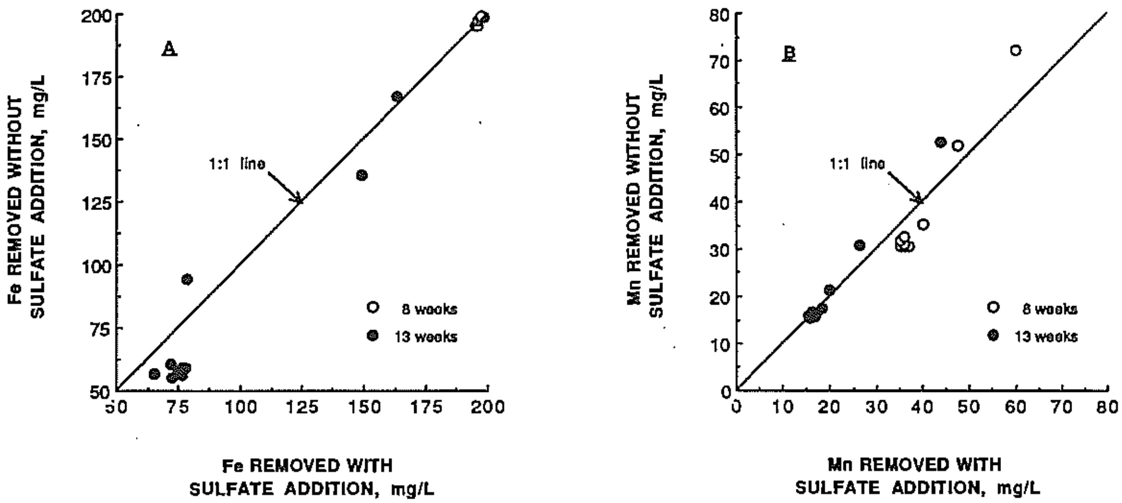

Figure 6. Comparison of removal of (A) iron and (B) manganese with and without sulfate addition for samples taken at various depths.

metals) after either 8 or 13 weeks of exposure (fig. 1). Without exception, the addition of acidic water caused a marked decrease in the pH of interstitial water in the upper portion of the columns, from circumneutrality to about 4.5 to 5.5 between the two sampling periods, which corresponded with a 100- to 200-mV increase in redox potential. In addition, after each sampling period the pH of interstitial water tended toward neutrality with increasing depth. Dissolved iron and manganese concentrations were low in the control columns, and dissolved sulfide increased dramatically in the lower 15 cm of all columns (figs. 1-5).

During the 13-week treatment period, the interior of all columns exposed to iron turned black almost immediately upon addition of synthetic mine water, but this seemed to decline throughout the course of the experiment. This was most pronounced in columns receiving both iron and manganese compared with columns receiving iron only. Columns not receiving iron showed no evidence of black color. The effect of iron and manganese on metal removal was statistically determined by comparison (paired *t*-test) of samples obtained from equal depths for selected treatments (table 2). The addition of manganese greatly enhanced iron removal during the first 8 weeks of exposure ($p<0.0005$); however, after 13 weeks of exposure manganese had little effect on iron removal, although it was statistically significant ($p=0.002$). Similarly, the addition of iron significantly enhanced manganese removal after 8 weeks ($p<0.0005$), but after 13 weeks no enhancement was observed ($p=0.686$). The addition of sulfate had a slight, but statistically significant, effect on the removal of iron after both 8 and 13 weeks ($p=0.019$; fig. 6A); sulfate had no effect on manganese removal over the same period ($p=0.472$; fig. 6B).

Discussion

The lack of an oxic zone in the wetland mesocosms afforded the opportunity to study the removal of iron and manganese from the synthetic mine waters in a totally anoxic environment. Such environments are common in the sediments of natural wetlands rich in organic carbon (Mitsch and Gosselink 1986). This was not a problem in the wetland mesocosms since carbon-rich SMC was used as the organic substrate.

The anoxic circumneutral conditions in the simulated wetlands are typical of waterlogged soils and sediments (Lindsay 1979). The addition of acidic solutions during the first 8 weeks did not appreciably affect the pH of the interstitial waters, but substantial acidification did occur during the following 5 weeks. Alkalinity generation by the decomposition of organic matter effectively buffers the pH of anoxic sediments exposed to acidified waters (Herlihy and Mills 1986). Herlihy et al. (1987) have shown alkalinity generation by sulfate reduction to be an important pH-buffering mechanism in lakes receiving AMD. In addition, the release of calcium from anoxic sediments provides another pH-buffering mechanism (Davison and Woof 1990). Gypsum ($CaSO_4 \bullet 2H_2O$) is a major component of SMC (Lohr et al. 1984) and is a potential source of calcium. Both sulfate reduction and calcium release probably contributed to the maintenance of circumneutral pH in the wetland mesocosms in this study, but these processes cannot go on indefinitely. For example, Carignan and Tessier (1988) found that acidic lake sediments eventually lose their capacity to generate alkalinity by sulfate reduction after prolonged exposure to acid rain.

A consequence of acidification is the potential for the rapid oxidation of iron sulfides by ferric iron (Moses et al. 1987). Acidification is brought about initially by the addition of acidic mine water to the columns. As the pH drops below 5, the rate of iron sulfide oxidation by free ferric iron increases dramatically, generating ferrous iron, sulfate, and hydrogen ions (Moses et al. 1987). This contributed to the observed decrease in pH and the increase in dissolved iron concentrations between the two sampling periods (figs. 1-5).

Examination of concentration-depth profiles revealed that iron was removed from solution far more easily and to a much greater extent than manganese. Dissolved sulfide preferentially complexes iron, forming the black iron monosulfide mineral mackinawite

(FeS; Morse et al. 1987). Iron was removed from solution more effectively in the presence of manganese (compare fig. 2 and fig. 5 with fig. 3; table 2). Manganese commonly forms mixed Ca-Mn-Mg carbonates or mixed Fe-Mn sulfides by coprecipitation (Middelburg et al. 1987). Columns in which both metals were added were much more black relative to columns receiving iron only. This suggests the formation of a mixed Fe-Mn sulfide mineral of lower solubility than "pure" iron monosulfide. Conversely, Arakaki and Morse (1993) found that adsorption of manganese to mackinawite to be quantitatively much more important (generally >90%) than coprecipitation; therefore, the rapid formation of black FeS likely enhanced manganese removal by adsorption (table 2).

The removal of iron and manganese was not affected to any appreciable extent by the addition of sulfate to the columns (figs. 6A and 6B; table 2). It was hypothesized that sulfate addition would stimulate bacterial sulfate reduction and provide additional sulfide to precipitate metals. Limited analysis of interstitial water sulfate revealed uniformly high sulfate levels (>500 mg/L) in all columns. It appears that gypsum in SMC provided sufficient sulfate for bacterial reduction, at least over the time frame of these experiments.

Higher metal removals were observed near the bottom of all columns treated with synthetic mine water, which corresponded spatially with increased dissolved sulfide concentrations (figs. 2-5). This was most likely due to a higher detention time near the column bottom. The mean detention time in the columns was about 40 days; however, the addition and removal of solutions from the top of the columns likely caused a decrease in detention time near the surface and an increase near the bottom. Thus, spatial

Table 2. Comparison (paired *t*-test) of iron and manganese removal for various treatment combinations.

Treatment[1]	*t*-statistic	d.f.[2]	*p*-value
Pooled data:			
Fe: SO4 vs Mn+SO4	5.285[3]	39	<.0005
Mn: SO4 vs Fe+SO4	4.791[3]	39	<.0005
Fe: Mn vs Mn+SO4	2.450[3]	39	.019
Mn: Fe vs Fe+SO4	0.726	39	.472
8 weeks:			
Fe: SO4 vs Mn+SO4	5.772[3]	19	<.0005
Mn: SO4 vs Fe+SO4	7.256[3]	19	<.0005
Fe: Mn vs Mn+SO4	2.188[3]	19	.041
Mn: Fe vs Fe+SO4	1.713	19	.103
13 weeks:			
Fe: SO4 vs Mn+SO4	3.549[3]	19	.002
Mn: SO4 vs Fe+SO4	0.410	19	.686
Fe: Mn vs Mn+SO4	3.181[3]	19	.005
Mn: Fe vs Fe+SO4	1.330	19	.199

[1] The variable appearing before the colon is the object of the treatment. The parameter immediately following the colon was tested for its effect on the variable relative to the additional treatment, indicated by "vs."

[2] d.f.=degrees of freedom.

[3] Significant at the 0.05 level.

The biogeochemical interactions of carbon and sulfur were found to influence the removal and release of iron and manganese under reducing conditions characteristic of AMD wetland soils. Iron and manganese appeared to act synergistically with respect to the net removal of these metals under anoxic conditions, probably due to manganese adsorption and coprecipitation reactions with iron sulfides. The results of this study suggest that the generation of sulfide by bacterial sulfate reduction can effectively retain iron, but not manganese, within the anoxic soil. However, long-term removal of iron by this mechanism may be limited by an eventual decline in sulfate reduction due potentially to insufficient decomposable organic substrates or soil acidification.

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