AN ANALYSIS OF MANGANESE AS AN INDICATOR FOR HEAVY METAL REMOVAL IN PASSIVE TREATMENT USING LABORATORY SPENT MUSHROOM COMPOST COLUMNS[1]

by

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Abstract: The National Pollution Discharge Elimination System (NPDES) dictates removal of manganese in mine drainage to less than 4 mg/l daily or less than 2 mg/l on a monthly average. Owing to its high solubility at low and circumneutral pH, removal of manganese is often the most difficult of the NPDES discharge standards. This has lead to the use of Mn (II) as a surrogate for metal removal. However, recent studies concluded that zinc or nickel may be more appropriate indicators for removal of other metals. Our previous field studies showed zinc removal to be highly correlated to the removal of copper, cobalt, and nickel in a sulfate reducing subsurface loaded wetland, whereas manganese removal was poorly correlated. The objective of this study was to evaluate zinc and manganese retention under sulfate reducing conditions in bench scale columns containing fresh spent mushroom compost. Column effluent data were analyzed using an EPA geochemical computer model (MINTEQ) over the pH range of 6.0 to 6.8. Under these conditions, zinc and manganese displayed distinctly reactivities. $Zn(II)$ was supersaturated with respect to $ZnS_{(s)}$ and the $Zn(HS)_2^0$ and $Zn(HS)_3^-$ complexes dominated solubility. Soluble zinc concentrations were inversely correlated to sulfide. $Mn(II)$ remained as soluble Mn^{+2}. During early column operation at pH>7, $MnCO_{3(s)}$ was supersaturated. Manganese concentrations did not correlate with pH or sulfide. Given these fundamental differences in removal mechanisms between Zn and Mn under sulfate reducing conditions, the use of manganese removal as a surrogate for heavy metal removal in passive treatment of mine drainage seems unjustified.

Additional Key Words: acid mine drainage, manganese, zinc, sulfate reduction

Introduction

Considerable research has been conducted on the use of wetlands for removal of heavy metals in acidic coal mine drainage treatment (Brodie et al., 1988; Kleinmann, 1985; Wieder, 1989; Hedin and Nairn,1990; Stark et al., 1990). Effluent standards

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to be applied to mine drainage treatment systems were established by the Federal Clean Water Act (1972) and include pH (between 6 and 9), total iron (< 7 mg/l daily and < 3.5 mg/l on a monthly average), and total manganese (< 4 mg/l daily and < 2 mg/l on a monthly average; Hedin et. al, 1994). Manganese was intended to serve as a surrogate for typical heavy metals (arsenic, chromium, copper, lead, mercury, nickel, selenium and zinc) thereby providing an indication of the efficiency of mine water remediation by conventional chemical neutralization/oxidation processes. At elevated pH (~ pH 11), it was anticipated that the effective removal of manganese from the mine water would provide ample evidence of heavy metal removal (Weidman, 1982; Kleinmann and Watzlaf, 1988).

The geochemistry of the wetland environment differs markedly from the excessive alkaline conditions generated in the chemical treatment of acidic mine water and brings into question the appropriateness of Mn as an effluent quality parameter for mine water passive treatment systems (Kleinmann and Watzlaf, 1988; Royer et

al. 1998). Royer et al. (1998) reported that Mn removal was a poor indicator for heavy metal removal in constructed wetlands receiving subsurface influent loading regardless of the oxygen profile of the wetland. Removal of Zn correlated well with removal of copper, cobalt, and nickel in a subsurface loaded wetland, but there was either no correlation or negative correlation between Mn removal and removal of Zn, Ni, Cu, Al, Fe, and Co (Royer, et al. 1998).

Oxidation of Mn in a wetland primarily aerobic is promoted by chemical and microbiological action. In a system relying primarily on anaerobic processes, oxidation is minimal and removal of Mn is through adsorption onto metal precipitates and organic matter. According to Arakaki and Morse (1993) and Wildeman et al. (1994), adsorption of Mn has been shown to be more important than either Mn sulfide formation or coprecipitation with FeS. However, relying on Mn adsorption for removal is difficult due to the low affinity for organic binding sites of Mn(II) compared with other cations found in mine waters (Wieder and Lang 1986). Experiments conducted with fresh mushroom compost showed that Mn was poorly sorbed especially when iron and copper were present (Machemer and Wildeman 1992). If competition exists for adsorption sites, Mn will be one of the first trace metals to desorb. Mn may also be released due to the degradation of organic molecules that are responsible for binding of manganese.

The main objective of this study was to evaluate Zn and Mn retention under sulfate reducing conditions in bench scale columns containing fresh spent mushroom compost. The working hypotheses were that Mn removal would be poor surrogate for removal of other metals, but that Zn would be removed via sulfide precipitation.

Materials and Methods

The bench-scale reactors consisted of eight vertically mounted independent 91.4x7.6cm polyvinylchloride (PVC) columns. Columns were packed with 3.8cm of inert pea gravel (approximately 1 cm i.d.) at the base followed by 87.6cm (approximately 1250g) of spent mushroom compost (SMC) above. Preparation of SMC included a 3-day drying period followed by screening (4.76mm). Plastic screens with 2mm mesh were placed below and above the gravel. Feed solution (described below) was pumped from storage reservoirs to the base of each column at a

flow rate of 0.20 ml/min using Harvard peristaltic pumps. This flow rate was selected to mimic the mean flow rate in a demonstration constructed mine water wetland located at the Bark Camp Run field site in Pennfield, Clearfield County, Pennsylvania. The columns were operated at 20 C in a constant temperature, walk-in incubator.

Water samples were obtained by syringe along a vertical transect in the column. Sampling points were accessed through four rubber septa cemented evenly spaced over depth of the column wall and at the effluent tubing. Alkalinity (method 2310 B, hot peroxide treatment), acidity (method 2320 B, potentiometric titration to a specific pH), pH (method 4500-H+), sulfide (Ag/S-2 electrode), and oxidation-reduction potential were measured. Sulfate reducing bacteria (SRB) were estimated using an MPN (Postgate's Medium E for sulfate reducing bacteria) (Atlas, 1995). Duplicate samples taken for metal analyses were filtered using 20μm filter paper and acidified to pH of <2 with high purity concentrated nitric acid (Fisher's Optima®). Acidified samples were analyzed for manganese and zinc using flame atomic absorption spectroscopy (method 31111, Standard Methods for the Examination of Water and Wastewater, 1995). Sulfate determinations were made using ion chromatography (Dionex DX 100 Ion Chromatograph).

The feed solutions were based on the nutritional requirements needed to support SRB. The chemical composition of the basal feed solution consisted of $NaNO_3$ (1.37mg/l), $MgSO_4$ (42.93 mg/l), $NaSO_4$ (374.2 mg/l), $CaSO_4$ (3.0 mg/l), $NH_4H_2PO_4$ (1.25 mg/l), K_2SO_4 (22.0 mg/l), H_2SO_4 (7.4E-4 M/l), and lactate (25 mg/l) in distilled deionized water was adjusted with HCl to pH 3.0. Varied Mn and Zn concentrations were charged to the columns as given in Table 1. Iron was intentionally omitted from the feed solution to avoid complicated iron/manganese interactions. At start up, columns received 100-ml of settled primary wastewater as an SRB inoculum.

Initially, columns received the basal feed solution without Mn and Zn for 100 days in order to adjust effluent pH, redox, acidity, and alkalinity to imitate values determined at the Bark Camp Run field site and to acclimate the system and establish an SRB population. Manipulation of the feed solution, in the first 100 days, to maintain the effluent pH at less than pH 7.0 proved difficult owing to the presence of limestone in the SMC.

Metals addition to the columns via basal

feed solutions was begun on day-100 and continued through to the conclusion of the experiment.

An EPA geochemical computer model, MINTEQ, was used to model the chemical speciation of Cu, Zn, Ni, Fe and Mn under equilibrium conditions in a sulfate reducing environment over a pH range of 3.5 to 6.0. Further analysis of Zn and Mn precipitation was conducted using column results as model input variables in MINTEQ to determine metal speciation and saturation in the experimental columns over the pH range 6 to 6.8. The saturation state for a mineral or amorphous material in solution is expressed as

$$SI = \log (IAP/K_{sp}) \qquad (1)$$

where

IAP = ion activity product determined by speciation model; and
K_{sp} = mineral equilibrium solubility product constant.

In general, a positive SI indicates the mineral is supersaturated, and precipitation is possible. When SI is zero, the mineral is exactly saturated. When SI is negative, the mineral is undersaturated and either dissolution is possible or there is no tendency to precipitate the solid phase.

The operational nature of the Zn and Mn in the treated SMC (0.1g dry weight sample) was determined on day 150 using four simultaneous metal extractions: 15ml of 0.5N HCl (15 minutes contact time) 5ml of 0.25N Hydroxylamine + 0.25N HCl (15 minutes contact time), 5ml of 0.2M CuSO4 (24 hours contact time), and 25ml of water (24 hours contact time). Following their respective contact times, samples were filtered (0.22um pore) and rinsed with distilled deionized water. Zn and Mn concentrations in all filtrates were determined by atomic adsorption spectrophotometry.

Results and Discussion

Metal removal

Profiles of effluent Mn and Zn concentrations for columns 1 through 8 over the course of the study period are presented in Figure 1. The mushroom compost contained initially substantial manganese and zinc compared to the mass added of each element accumulated from the feed solution (Figure 2). Consequently, almost no distinction in behavior of the metals in the columns

due to differences in the Zn and Mn concentrations of the feed solutions could be detected (Table 1). The feed solution contained no supplemented alkalinity; hence, alkalinity produced in the course of column operation was attributed to SRB activity and the dissolution of limestone in the mushroom compost.

The effluent Zn concentrations were nearly identical when the feed Zn was between 0 and 5mg/l. There was a large reservoir of Zn in the SMC (0.28 g per column). Less than one-tenth of the Zn (0.021 g) in the SMC was removed via column effluent in the period prior to metal addition. Approximately 0.14g Zn was added per column over days 100-200 for columns 4 and 5. Similarly, Mn discharge was independent of Mn column loading. Manganese initially in the SMC (0.38 g per column) was 2.6 times more than the total amount added over days 100-200 in columns loaded with 5 mg/l (total 0.144 g). Less Mn (0.009 g) was removed from the SMC prior to metal addition.

The insensitivity of discharged concentrations of Zn and Mn to the influent concentrations could be due to precipitation of a solid phase, or due to surface complexation with a sorbent that is concentrated relative to the Zn and Mn loading. Total sulfide and pH had the greatest effects on Zn in the column effluents. Increasing pH and total sulfide correlated with decreasing Zn. No consistent correlation was found between Mn and other measured parameters.

Manganese export from the SMC increased during days 110 through 145 (Figure 1). This export corresponded to an increase in Zn removal and increased biological sulfide production. SRB enumeration in all eight columns during this period resulted in populations between 10^4-10^5 cells/ml throughout the column. Bacterially produced sulfide and some organics, such as oxalate, pyruvate and some reducing sugars, which are produced during biological reactions, can rapidly reduce $MnO_{2(s)}$ to Mn^{+2} (Lovely, 1991). The observed increase in biological activity may have resulted in the reduction of Mn^{+4} bound in the SMC. After day 145, improvement in manganese removal was observed in each column. This increase in removal may reflect the availability of new binding sites on the compost through microbial fermentation of the mushroom compost and the formation of soluble substrates for SRB. Sulfate-sulfide mass balance in the column suggests that lactate utilization accounted for only

one-ninth the total carbon usage by the SRB. Organic binding has been implicated as a dominant mechanism of Mn removal in passive treatment (Weider, 1992).

In this study, Mn removal remained high in all columns. Early retention of Mn has been shown in other studies, however, sustained Mn retention has not been demonstrated using SMC in mesocosm wetlands, even under alkaline conditions (Stark et al., 1995; Tarutis and Unz, 1994). Inadequate weathering of the SMC in the columns has occurred justifying its Mn removal capability.

Computer modeling:

Initial MINTEQ model runs used to identify metal-sulfide affinity under sulfate reducing conditions at pH 6.0 indicated the reaction sequence: Cu>Zn>Ni=Fe>>>Mn, confirming previous studies suggesting a difference in precipitation chemistry between Mn and Zn (Wieder, 1992; McIntire and Edenborn, 1990; Hammack et al., 1994).

Data for days 100 to 200 for the eight columns were used with MINTEQ to predict chemical speciation. Soluble $ZnHS^-$ complexes dominated the Zn(II) speciation. Zn^{+2} ranged from 1.75×10^{-13} to 9.67×10^{-17} over the pH range 6.0 to 6.7. Ninety-nine percent to 94.7% of Zn (II) was as $Zn(HS)_2$ and 0.9% to 5.3% was as $Zn(HS)_3^-$. Sphalerite (ZnS) was supersaturated over the entire pH range (Figure 3). This affirms the similarity between zinc and other heavy metals in metal sulfide formation.

Most Mn (87.8% to 80.8) was predicted to be Mn^{+2}. The second largest Mn fraction (7.4% to 14.7%) occurred as $MnHCO_3^+$. Rhodochrosite ($MnCO_3$) was always supersaturated during some parts of the 0-100 day startup period, but was undersaturated during the 100-200 day period. Manganese did not become supersaturated with respect to $MnS_{(s)}$ in the observed pH range. This supports previous column studies indicating that manganese can be retained under sulfate reducing conditions in SMC, but retention is not related to sulfate reduction (Tarutis and Unz, 1994).

Manganese as a surrogate indicator for heavy metal removal from AMD is grounded in the application of alkaline chemicals to elevate pH and initiate oxidation/hydrolysis and precipitation of metals

(Kleinman and Watzlaf, 1988). The level alkalinity necessary to facilitate Mn removal is greater than that required for other commonly found metals in AMD. Metal removal processes inherent in passive treatment, particularly anoxic wetlands, do not achieve high pH values generated in chemical treatment.

Conclusion

Selection of a surrogate indicator for metal removal in passive AMD treatment should be based, in part, on metal removal processes for each metal targeted. Under sulfate reducing conditions, Zn and Mn displayed distinctly different mechanisms of removal from solution.

The discharge concentrations of Zn and Mn were nearly identical in columns 1-8 perhaps due to the initial large inventory of Zn and Mn in the SMC. The discharge concentrations of Zn and Mn showed significant temporal changes. Soluble Zn was inversely related to pH and soluble sulfide. The behavior of Mn was more complicated, with both increases and decreases occurring as pH and soluble sulfide increased. Chemical speciation modeling (MINTEQ) for Zn indicated supersaturation with respect to sphalerite (a $ZnS_{(s)}$ precipitate). Zn^{+2} was a minor constituent of soluble Zn(II). $Zn(HS)_2$ and $Zn(HS)_3^-$ dominated Zn(II) and were present at more than 10^7 times the Zn^{+2} concentration. Other metals in mine drainage (Cu(II), Ni(II), Co(II), Cr(II)) also are reactive with sulfide. These calculations clearly demonstrate the significant reactivates of sulfide and zinc. Chemical speciation modeling of Mn(II) showed no significant reaction with sulfide species. At higher pH values, $MnCO_{3(s)}$ became supersaturated. The experimental and computational results in this paper support the contention that Zn(II) is a better predictor than Mn(II) for likely removal of these metals.

Acknowledgements

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Table 1. Zinc and manganese concentrations (mg/l) present in solutions charged to the columns

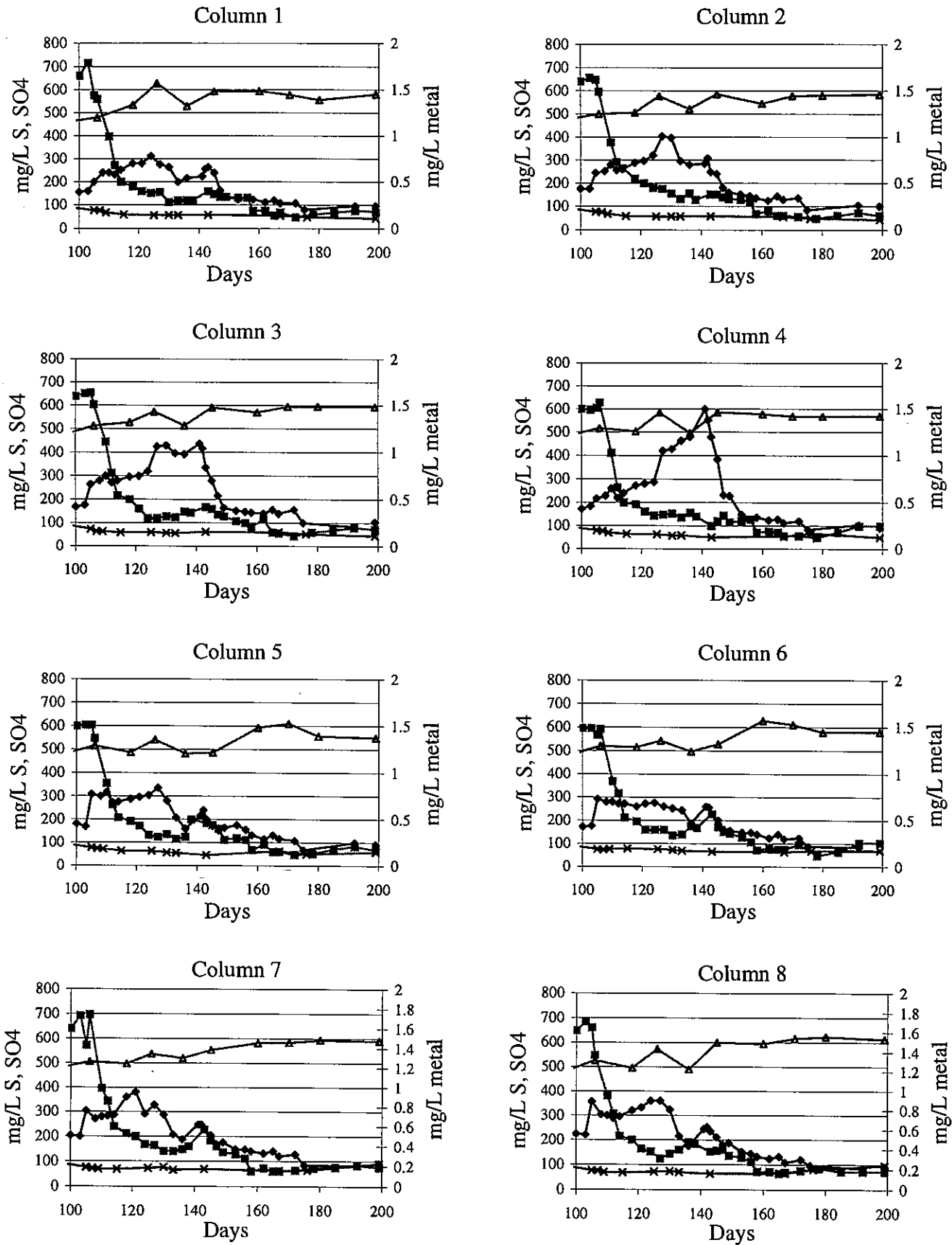| Column #	Metals	
	Mn	Zn
1	0.0	0.0
2	0.0	1.0
3	0.0	3.0
4	0.0	5.0
5	5.0	5.0
6	5.0	3.0
7	5.0	1.0
8	5.0	0.0

Figure 1. Zinc, manganese, sulfate, and sulfide effluent concentrations (mg/L) in metal supplemented feed solutions charged to respective spent mushroom compost columns. Influent metal concentrations (Mn, Zn) are column 1 (0.0, 0.0), column 2 (0.0, 1.0), column 3 (0.0, 3.0), column 4 (0.0, 5.0), column 5 (5.0, 5.0), column 6 (5.0. 3.0), column 7 (5.0, 1.0), column (5.0, 0.0).
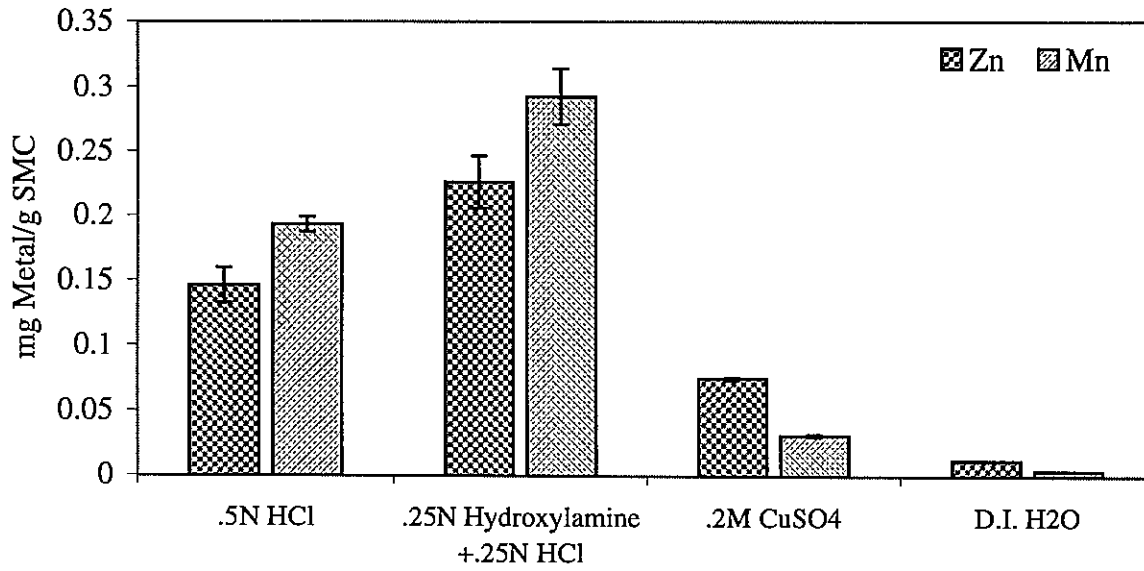
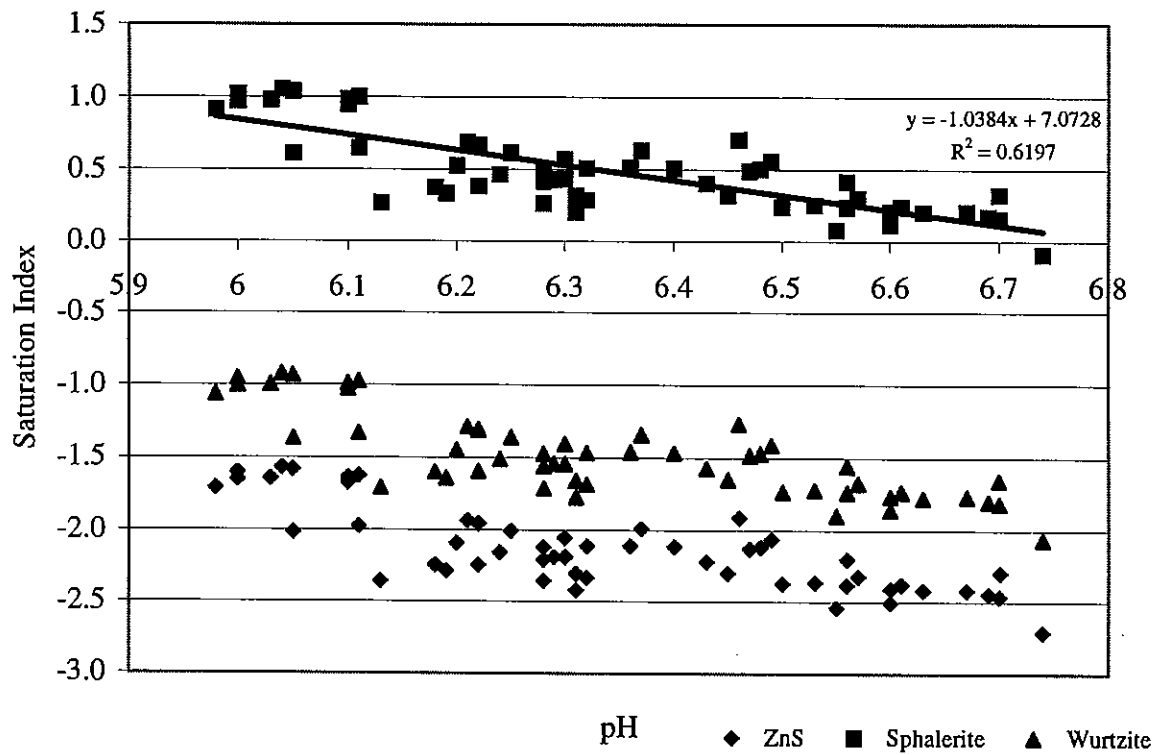Figure 2. Zinc and Manganese bound fractions (mg/l) per gram of spent mushroom compost.

Figure 3. MINTEQ Saturation indexes for three ZnS(s) with respect to pH.
Data for total soluble sulfide, zinc, alkalinity, and pH from all 8 columns were used.