HEAVY METAL REMOVAL FROM WATERS BY MOUNTAIN MEADOW BOGS

by

E.W. Brennan and W. L. Lindsay

Colorado Water

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ABSTRACT

Reduction had a direct effect on Fe minerals and an indirect effect on minerals containing Zn, Cd, and Pb. Transfer of electrons to Fe(III) oxides was examined throughout the pe + pH range of most soils subjected to anaerobic conditions. Reduction of Fe occurred regardless of the type of Fe(III) oxide used. The existence of numerous Fe mineral precipitates confirmed that Fe solubility was controlled by the most soluble Fe mineral present. Slow additions of small amounts of $O_2(g)$ from air resulted in the precipitation of Fe_3O_4(magnetite) when Fe^{2+} was present. Precipitation of magnetite was confirmed by XRD analysis. Rapid additions of large amounts of $O_2(g)$ resulted in a more soluble Fe mineral, $Fe_3O_4 \cdot xH_2O$. Because of its amorphous nature, this mineral was not detected by XRD analysis. The dissociation constant for this mineral is 40.65, and it is stable in the pe + pH range of soils of 4.5 to 11.2. Soluble Fe was controlled by $Fe(OH)_3$(amorp) for pe + pH measurements greater than 11.2.

Output from the chemical speciation model MINTEQA2 suggests that $ZnCO_3$(smithsonite), $CdCO_3$(octavite) and $PbCO_3$(cerrusite) precipitated as pe + pH decreased. As the soil suspensions were further reduced, FeS_2(pyrite),

ZnS(sphalerite), CdS(greennokite), and PbS(galena)
precipitation was shown to occur.

The results of this study indicate that transfer of
electrons to Fe(III) oxides results in the precipitation of
$Fe_3O_4 \cdot xH_2O$. This mineral was found to be 10 times less
soluble than the previously reported $Fe_3(OH)_8$(ferrosic
hyroxide). Prior to the precipitation of $Fe_3O_4 \cdot xH_2O$,
dissolution of Fe(III) was the principal factor causing pH
to increase. As a result of increased pH, precipitation of
Zn, Cd, and Pb as carbonate minerals was shown to occur.
Continual addition of electrons resulted in the
precipitation of Fe, Zn, Cd, and Pb sulfides.

Using Zn, Cd, and Pb carbonates along with $Fe_3O_4 \cdot xH_2O$ as
controlling minerals for these elements, the pe + pH at
which Fe, Zn, Cd, and Pb sulfides precipitate was
determined. With reduction, S^{2-} activity increased the
order of precipitation of the metal sulfides and the pe + pH
at which the precipitations occurred was 1) CdS(greennokite)
(pe + pH = 4.82), 2) ZnS(sphalerite) (pe + pH = 4.74), 3)
PbS(galena) (pe + pH = 4.69) and 4) FeS_2(pyrite) (pe + pH =
4.48).

The pe + pH values in these soils did not drop below
4.5. Likewise, the pe + pH of most soils seldomly goes
below pe + pH 4. Upon reduction, $Fe_3O_4 \cdot xH_2O$ transforms
FeS_2(pyrite) which fixes the equilibrium pe + pH near 4.5
when SO_4^{2-} is present at approximately 10^{-3} $\underline{M}$ as occurred in
this study. Only after all SO_4^{2-} reserves are reduced can

the pe + pH drop lower. Thus, Fe reduction plays a dominant role on the redox chemistry of submerged soils.

INTRODUCTION

High altitude wetlands in mining districts provide an
ideal situation in which to examine the effects of reduction
on metal solubility. Mining activities in Colorado in the
late 1800's and early 1900's had a considerable impact on
the concentrations of heavy metals in rivers and streams.
Many ores that were mined for silver and gold contained
sulfides of lead, cadmium, zinc, and copper. The heavy
metals are important because they are often toxic to human
and animal life. The solubilities of these metal sulfides
are extremely low, provided they are maintained under low
redox conditions. However, when these mining wastes are
exposed to oxygen and water, the sulfides oxidize and
release protons. This increased acidity increases the
solubility of metals and facilitates their transport into
streams and rivers. Waters contaminated with heavy metals
are often used downstream for irrigation purposes. In some
cases, spent mine tailings from processing sites were
transported to distant locations. Although at some sites
more than 90 years has passed since soils were impacted by
contaminated irrigation waters and tailings, high
concentrations of many of these heavy metals still persist
in these waters and soils.

An important consequence of decreased redox is increased pH due to the dissolution of Fe(III) oxide. When sufficient Fe(III) oxides are present, the addition of electrons solubilizes these minerals and releases OH- ions. The rate at which pH increases is dependent on the solubility of the Fe(III) oxide mineral. The resulting increase in pH decreases the concentrations of Zn, Cd, and Pb. These decreases are attributed to solubility controls imposed by mineral combinations (Lindsay, 1979), organic adsorption (Stevenson, 1982) or metal oxide adsorption (Barrow, 1987).

Carbonate and oxide minerals of Zn, Cd, and Pb will control the activity of these metal cations if they are present. The solubility of Zn, Cd, and Pb oxides and carbonates decrease with increasing pH. Because Fe(III)oxides accept electrons and release OH^- ions during the reduction process, these reactions were given key considerations in this study.

The reduction of sulfate increases the activity of S^{2-} in solution. When S^{2-} activities are increased sufficiently, precipitation of metal sulfides occur. Because metal sulfides at low pH are more stable that carbonates or oxides of Zn, Cd, and Pb, they will control the activities of these metals. Once precipitated, metal sulfides will depress the concentrations of Zn, Cd, and Pb as redox is lowered further.

The objectives of this study were to: 1) determine the

effect of redox on the solubility and transformation of iron oxide minerals, 2) explore the formation and solubility of $Fe_3O_4 \cdot xH_2O$ in soils, 3) examine the solubility of Zn, Cd, Pb , and Fe during the oxidation and reduction cycle of a mountain bog near Leadville, Colorado, and 4) determine the sequence of metal sulfides that precipitate as oxidized bogs undergo reduction.

CONTROL OF SOLUBLE Fe IN SOILS
BY $Fe_3O_4 \cdot xH_2O$ (edlinite)

Under carefully controlled laboratory conditions, the precipitation of $Fe_3O_4 \cdot xH_2O$ was found to control Fe solubility. Regardless of the Fe(III) oxide that was used to supply Fe, $Fe_3O_4 \cdot xH_2O$ precipitated under reducing conditions as $O_2(g)$ was added. Since soils contain Fe(III) oxides like those used in the previous study, it is possible that the mixed-valency $Fe_3O_4 \cdot xH_2O$ oxide can control Fe solubility in soils. Pt and other catalysts used in the laboratory to transfer electrons to Fe are generally ineffective in soils. Because soils contain numerous electron acceptors, the capacity of soils to accept electrons is much greater than a single electron sink such as Fe(III) oxides. Possibly a combination of decomposing organic matter and $H_2(g)$ may provide an affective means of reducing soils. In soils a similar transfer of electrons between $H_2(g)$ and Fe occurs by enzymes supplied by microbes.

The purpose of this study was to determine if $Fe_3O_4 \cdot xH_2O$ (edlinite) controls the solubility of Fe in soils reduced with $H_2(g)$ and organic matter.

METHODS AND MATERIALS

A surface Histic Cyroaquall described by Levy et al. (1992) was chosen because of its high organic matter and Fe content. Five grams of soil was placed in 125-mL erlenmeyer flasks with 30 mL of distilled-deionized H_2O. To insure the platinum electrodes were free of surface contaminants, 2 g of SiO_2 was placed in each flask as an abrasive agent. The flasks were placed on an orbital shaker at 60 revolutions min^{-1} and left open to the atmosphere. Water lost by evaporation was replaced daily. After 10 d, a small stirring bar was placed in the flask to insure sufficient mixing for pe and pH measurements. Holes were bored through a Nalgene stopper to accommodate a combination pH electrode (Ross semi-micro 81-15) and 1.0 mm x 60 mm platinum wire for pe measurements. The reference solution for the combination electrode was kept free of Ag to avoid precipitation with S^{2-} which would constitute an interference. The reference electrode from the combination electrode was also used as the reference electrode for pe measurements. A 10-mL aliquot was then removed from the flask and centrifuged at 12,000 rpm for 10 min followed by filtration through a 0.2 μm filter. The filtrate was analyzed for cations by ICP and important anions by ion chromatography.

For the reduction segment of the study, an aliquot was removed for analysis and the head space within the flask was purged with a gas mixture consisting of 1% $H_2(g)$, 5% $CO_2(g)$ and 94% Ar gas for 10 min. A small stirring bar was added to insure adequate stirring during redox measurements. This concentration of $CO_2(g)$ was used as it simulates conditions present in flooded soils. The argon hastened anaerobic microbial processes by lowering the partial pressure of oxygen. Flasks were purged with the reducing gas mixture every 24 h to insure a continual supply of $H_2(g)$. The flasks were stoppered and again placed on the orbital shaker. Redox measurements were monitored every 4 d. Gas inlet and outlet ports were included and were fabricated from 16-gauge syringes by inserting them into a nalgene stopper. During pe measurements $O_2(g)$ free Ar(g) was passed through the flask. Purging the flasks with Ar insured that $H_2(g)$ did not interfere with pe measurements. Measurements were recorded after steady state readings were obtained, which requires approximately 15 min. A 10-mL aliquot of the suspension was then removed by means of a syringe through the gas outlet and placed into a 50-mL centrifuge tube purged with argon. The suspension was then centrifuged for 10 min at 12,000 rpm in an Ar(g) purged 50-mL centrifuge tube. A 2-mL aliquot was removed through a septum in the centrifuge cap. For ICP analysis, 4 mL of the supernatant was transferred to a vial containing 15 μL of concentrated HCl to preclude metal oxide precipitation, and the remaining

portion was used to measure electrical conductivity. The
latter solution was then transferred to a vial open to the
atmosphere for 24 h to permit oxidation of S^{2-} to SO_4^{2-} and
were used subsequently for anion analysis. For the re-
oxidizing segment of the experiment, air was injected into
the flasks at 0.20 mL increments and stirring was continued.
Samples were taken until pe + pH reached approximately 13.5.
All concentration measurements were chemically speciated
using the chemical program, MINTEQA2.

RESULTS AND DISCUSSION

Hydrogen gas and organic matter was much less effective
in lowering pe + pH of soil than was the Pt-H_2(g) for
reducing Fe(III)oxide systems. Unlike the Fe(III) oxide
studies, the data points for soils moved up the
Fe(OH)$_3$(amorp) line (Fig. 1). Two explanations are
possible: First, the rate limiting step for the soil-H_2(g)
system was the rate of release of electrons from H_2(g) or
organic matter. Apparently the catalysis was limited by the
size of the microbial population and their ability to
synthesize enzymes. Secondly, soils contain numerous
electron acceptors which remove electrons and keep them from
accumulating above the equilibrium pe + pH level.

With continued reduction, the data points (Fig.1)
followed the Fe(OH)$_3$(amorp) isotherm to near pe + pH 9.0 and
then 6.5. At pe + pH 6.5, Fe(OH)$_3$(amorp) continued to
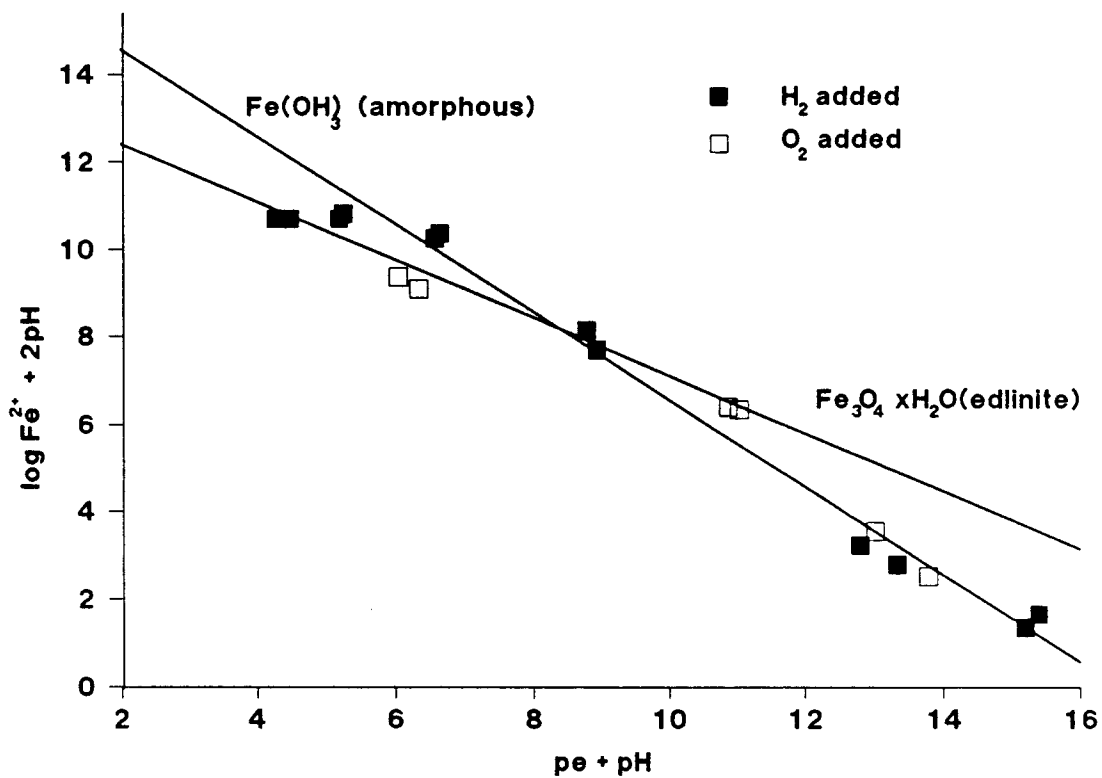
Fig. 1 The effect of redox on the solubility of Fe for two soils. Reduction with 1% $H_2(g)$ is indicated by the closed squares. Oxidation with air is shown by the open squares.

control Fe solubility even though $Fe_3O_4 \cdot xH_2O$ was more stable
at this redox. At this pe + pH, the rate of dissolution of
$Fe(OH)_3$(amorp) was greater than the rate of precipitation
for $Fe_3O_4 \cdot xH_2O$. Additional electrons moved the data points
between the two mineral isotherms at pe + pH 5.0 indicating
the rate of dissolution of $Fe(OH)_3$(amorp) was equal to the
rate of precipitation for $Fe_3O_4 \cdot xH_2O$. Additional electrons
moved the data points to the $Fe_3O_4 \cdot xH_2O$ line near pe + pH
4.2. The saturation indexes of the two soils were almost
identical and on the solubility partly fell on $Fe_3O_4 \cdot xH_2O$
isotherm. Saturation indexes were calculated in MINTEQA2 by
subtracting the log of the IAP (ion activity product) from
the log of the formation constant, K°. A negative
saturation index indicates the solution is undersaturated
with respect to the mineral, a positive saturation index
denotes supersaturation and a zero saturation index
indicates equilibrium with the mineral.

Addition of air increased pe + pH to near 6.0 and the
data points were very near to the $Fe_3O_4 \cdot xH_2O$ isotherm (Fig.
1). Table 1 reveals that the saturation index for $Fe_3O_4 \cdot xH_2O$
was only slightly negative, indicating equilibrium with this
mineral. Additional depletion of electrons through the
addition of O_2(g) from air increased pe + pH to near 11,
with $Fe_3O_4 \cdot xH_2O$ continuing to control Fe. Even though
$Fe(OH)_3$(amorp) was more stable than $Fe_3O_4 \cdot xH_2O$ at this pe +
pH, the rate of dissolution for $Fe_3O_4 \cdot xH_2O$ was greater than
the rate of precipitation of $Fe(OH)_3$(amorp). Had redox been

Table 1. Data obtained from the chemical speciation MINTEQA2 used to determine saturation index for two soils reduced with 1% $H_2(g)$ and oxidized with air.

Time (d)	pH	pe + pH	(Fe^{2+})	(Fe^{3+})	$Fe(OH)_3$	$Fe_3O_4 \cdot xH_2O$
			----log $\underline{M}$-----		Saturation Index	
	Reduced with 10 ml L^{-1} $H_2(g)$					
0	4.87	15.19	-8.42	-11.14	-0.07	-6.31
	4.96	15.42	-8.39	-10.97	0.37	-5.22
5	4.16	12.74	-4.93	-9.39	-0.45	-5.00
	3.84	13.40	-4.92	-8.40	-0.42	-5.57
14	5.61	8.74	-2.95	-12.86	0.43	1.67
	5.33	8.91	-2.93	-12.39	0.06	0.36
32	6.45	6.60	-2.91	-15.80	0.01	2.52
	6.56	6.64	-2.91	-15.87	0.27	3.26
48	6.74	5.17	-2.81	-17.42	-0.74	1.70
	6.73	5.28	-2.76	-17.25	-0.60	2.01
62	6.66	4.51	-2.66	-17.85	-1.59	-0.13
	6.65	4.29	-2.67	-18.07	-1.66	-0.18
	Oxidized with air					
63	6.15	6.10	-2.87	-15.96	-1.05	-0.16
	6.18	6.03	-2.88	-16.07	-1.07	-0.15
65	4.70	11.10	-3.10	-9.74	0.82	0.45
	4.80	10.90	-3.19	-10.13	0.73	0.38
67	4.20	13.03	-4.83	-9.04	0.02	-3.88
	3.86	13.74	-5.13	-8.29	-0.25	-5.40

held at this point for an extended period, it is likely that $Fe(OH)_3$(amorp) would eventually control Fe solubility. With the final addition of air, the data points moved onto the $Fe(OH)_3$(amorp) line, indicating the rate of precipitation for $Fe(OH)_3$(amorp) was now greater than the rate of dissolution for $Fe_3O_4 \cdot xH_2O$, or edlinite may have completely dissolved.

A similar sequence of Fe mineral transformations is expected in soils subjected to fluctuating O_2(g) contents. Under flooded conditions when sufficient organic matter is present, $Fe_3O_4 \cdot xH_2O$ will form as pe + pH is lowered. Draining the soils will permit the entry of O_2(g), and result in the precipitation of $Fe(OH)_3$(amorp). If this flooding and draining is cyclic for relatively short periods of time, it is likely that only $Fe(OH)_3$(amorp) and $Fe_3O_4 \cdot xH_2O$ would be active in controlling Fe solubility. Extended periods of oxidation could precipitate more insoluble forms of Fe(III) oxides that could control Fe solubility. Flooding soils after the formation of an insoluble Fe(III) oxide would require longer periods of reduction to precipitate $Fe_3O_4 \cdot xH_2O$, as shown in the $Pt-H_2$(g)$-Fe$(III)oxide studies in. With very extensive reduction, it is possible for Fe sulfides to control Fe solubility.

SUMMARY

When oxidized soils with a pe + pH value of 15.5 were

slowly reduced with $H_2(g)$, Fe^{2+} solubility was controlled by $Fe(OH)_3$(amorp). After reaching pe + pH of 5.0, the solubility control shifted to $Fe_3O_4 \cdot xH_2O$. Release of electrons through microbial decomposition and enzymatic transfer of electrons from $H_2(g)$ resulted in the formation of $Fe_3O_4 \cdot xH_2O$(edlinite) at a pe + pH near 4.0. The formation of this mineral was further confirmed by movement of the solubility points down the isotherm of this mineral as the soil was re-oxidized. This mineral continued to be stable to approximately pe + pH 12, after which solubility shifted back to $Fe(OH)_3$(amorp).

Unlike the laboratory study in which Pt-catalyzed $Fe(OH)_3$(amorp) was reduced with of $H_2(g)$, soils were reduced much more slowly by $H_2(g)$. This is likely due to differences in catalytic efficiency of the two systems. In soils, the addition of electrons through microbial catalysis, $H_2(g)$ and organic matter decomposition was dependent upon the activity of the microbial community. In the laboratory study, the use of a Pt catalyst promoted the breakdown of $H_2(g)$ so the supply of electrons was not dependent on biological processes. In the presence of soil, Pt and other metal catalysts were poisoned and were not affective in the breakdown of $H_2(g)$.

SOLUBILITY OF Zn, Cd, Pb, AND Fe

IN MOUNTAIN BOGS

Many areas in Colorado are polluted by mine tailing wastes which contain heavy metals. These metals are affected by changes in redox, both directly and indirectly. The solubility relationships of heavy metals in reduced soils have not been thoroughly studied. The solubilities of most heavy metals are pH dependent and generally decrease with increasing pH. Such decreases are attributed to solubility controls from mineral formation (Lindsay, 1979), organic adsorption (Stevenson, 1982) and metal oxide adsorption (Barrow, 1987). When SO_4^{2-} is present and pe + pH is lowered, S^{2-} formation occurs and leads to the precipitation of heavy metal sulfides. Because of the very low solubility of metal sulfides, their precipitation may provide an important decontamination process for heavy-metal contaminated soils. Although the possibility was demonstrated (Perry and Kleinmang, 1991), solubility relationships of heavy metals in reduced soils are poorly understood.

To study the effect of redox on contaminated soils, a mountain bog was selected from Leadville, Colorado. The bog was contaminated 85 yr ago by the distribution of waste ores

containing addition of sulfides of Fe, Zn, Cd, and Pb onto the soil surface. Oxidation at the soil surface containing these metal sulfides resulted in decreased pH and downward movement of the solubilized metals into the soil profile.

The purpose of this study was to determine the effect of redox on the metal solubility relationships of these mountain bogs which had been contaminated with Zn, Cd, and Pb. It was hypothesized that increasing the amount of added organic matter to soil suspensions would decrease pe + pH sufficiently to precipitate metal sulfides. Changes in solution chemistry and heavy metal concentrations were monitored during the reduction process.

METHODS AND MATERIALS

A histic cyroaquall was chosen from near Leadville, Colorado, from a site one mile south of the Arkansas river and California gulch confluence and 30 m from the Arkansas river. The elevation was 3,000 m. An area of approximately 80 m in length and 50 m in width was previously irrigated between 1905 and 1910 with water from nearby California Gulch (personal communication, Edith Sepi). The water in California gulch at that time was untreated and contaminated with acid mine waters containing Zn, Cd, Pb, As, and Cu from mines and tailings in the Mosquito range mining area. This site showed a healthy plant population consisting of Carex spp. and Juncus spp. plant species. Finely ground mine

tailings were deposited on the bog area around 1915. These tailings included minerals such as ZnS (sphalerite), FeS_2(pyrite), PbS (galena) and CdS(greenakolite). The total area affected by the tailings was approximately 50 m in diameter. Vegetation within this area was dead due to the long term effects of metals and low pH.

A pit was excavated at this site with the dimensions of 3 m x 3m x 1 m. From the side of the pit, soil was removed starting at the surface and continuing in 5 cm increments to a depth of 60 cm. Approximately 1 kg of soil was removed at each depth and placed into a 1 L polypropylene container affixed with a sealable gas inlet and outlet. To inhibit oxidation by atmospheric oxygen, oxygen-free Ar(g) was passed through the container of each sample for 10 min before sealing. Containers were then placed into insulated coolers containing ice to retard microbial activity while the samples were being transported to the laboratory.

For the oxidizing segment of the study, 25 g of soil from the surface five depths of the contaminated bog and 40 mL of distilled-deionized H_2O were placed into 125-mL erlenmeyer flasks. To simulate a natural reduction process, organic matter from the surface of a nearby non-contaminated bog was added to the contaminated suspensions. It was added to the flasks at three levels: 5, 10, and 20 g. A control without added organic matter was also included. The control was not subjected to reduction. The flasks were placed on an orbital shaker and left open to the atmosphere for 36 h.

For the control without added organic matter, samples were placed on the shaker for 96 h.

For the reduction segment of the study, the head space within the flask was purged with a gas mixture consisting of 5% CO_2 and 95% argon gas for 10 min. Each flask was fitted with a Nalgene stopper, and a small stirring bar was placed in the suspension before it was placed on an orbital shaker. Flasks were purged with the gas mixture every five days to insure a renewed supply of $CO_2(g)$. Measurements of pe and pH were taken at 0, 14, 48 and 65 d. Holes were bored into the Nalgene stopper to accommodate a combination pH electrode (Ross semi-micro 81-15) and 1.0 mm x 60 mm platinum wire for pe measurements. Measurements were made when a steady state condition persisted, usually about 15 min. A 5-mL aliquot of the suspension was then removed by means of a syringe through the gas outlet and placed into a 50 mL centrifuged tube purged with argon. The suspension was then centrifuged for 10 min at 12,000 rpm in an Ar(g) purged 50-mL centrifugation tube. A 5-mL aliquot was removed through a septum in the centrifuge cap and filtered through a 0.2 μm porosity filtration disk. For ICP analysis, 2.5 mL of the supernatant was transferred to a vial containing 15 μL of concentrated HCl to avoid metal oxide precipitation while the remaining portion was used to measure electrical conductivity. The latter solution was then transferred to a vial open to the atmosphere for 24 h to permit oxidation of S^{2-} to SO_4^{2-}. These samples were also

used for subsequent anion analysis. For total analysis of soils, a nitric-perchloric acid digest (Soltanpour, 1982) was used. For total organic carbon, the method described by Nelson and Sommers (1982) was used.

RESULTS AND DISCUSSION

Bog Profile Analysis

Total concentrations of Zn, Cd, and Pb in the bog profile reveal that Zn, Cd, and Pb have moved downward into the soil profile during the past 85 y (Table 2). The concentrations of these metals had they completely dissolved from a 25 g sample in 40 mL of H_2O was calculated. This maximum concentration is compared to metal concentrations in solutions after being allowed to oxidize for 96 h (Fig. 2) with atmospheric $O_2(g)$. It is seen from this figure that oxidation for 96 h did not completely dissolve these metals. One exception is that the total Zn and Cd were completely dissolved from the surface 5 cm of soil. Apparently the original Zn and Cd sulfides had completely dissolved during the past 85 y. Apparently the release of protons from sulfide oxidation increased the solubility of these metals and allowed their downward movement. Due to the greater adsorption capacity of Pb compared to Zn and Cd (Kerndorff and Schnitzer, 1980), it is apparent that Pb was only slightly mobilized from the surface 5 cm. With depth, it is apparent that oxidation did not completely solubilize Zn,

Table 2. Selected chemical properties of a bog contaminated by metal sulfide mine tailings at different depths.

| depth (cm)	Fe	Mn	Cu	Zn	Cd	Pb	organic C %
				mg kg^{-1}			
0-5	571	1.55	0.81	8.57	0.10	3.62	5.81
5-10	566	0.38	0.45	3.47	0.42	4.58	7.56
10-15	385	0.57	1.34	6.09	0.93	9.94	24.0
15-20	673	1.69	0.81	13.20	0.13	16.30	5.50
20-25	404	1.19	0.24	7.98	0.15	11.10	4.55
25-30	259	0.68	0.15	5.56	0.11	4.35	4.14
30-35	174	0.72	0.05	3.70	0.06	0.21	4.11
35-40	172	0.45	0.05	1.78	0.01	0.12	3.28
40-45	158	0.47	0.04	1.00	0.01	0.13	2.65
45-50	217	0.65	0.04	0.42	0.01	0.12	3.05
50-55	208	0.47	0.03	0.30	0.01	0.06	1.76
55-60	206	0.30	0.01	0.50	0.01	0.05	0.44

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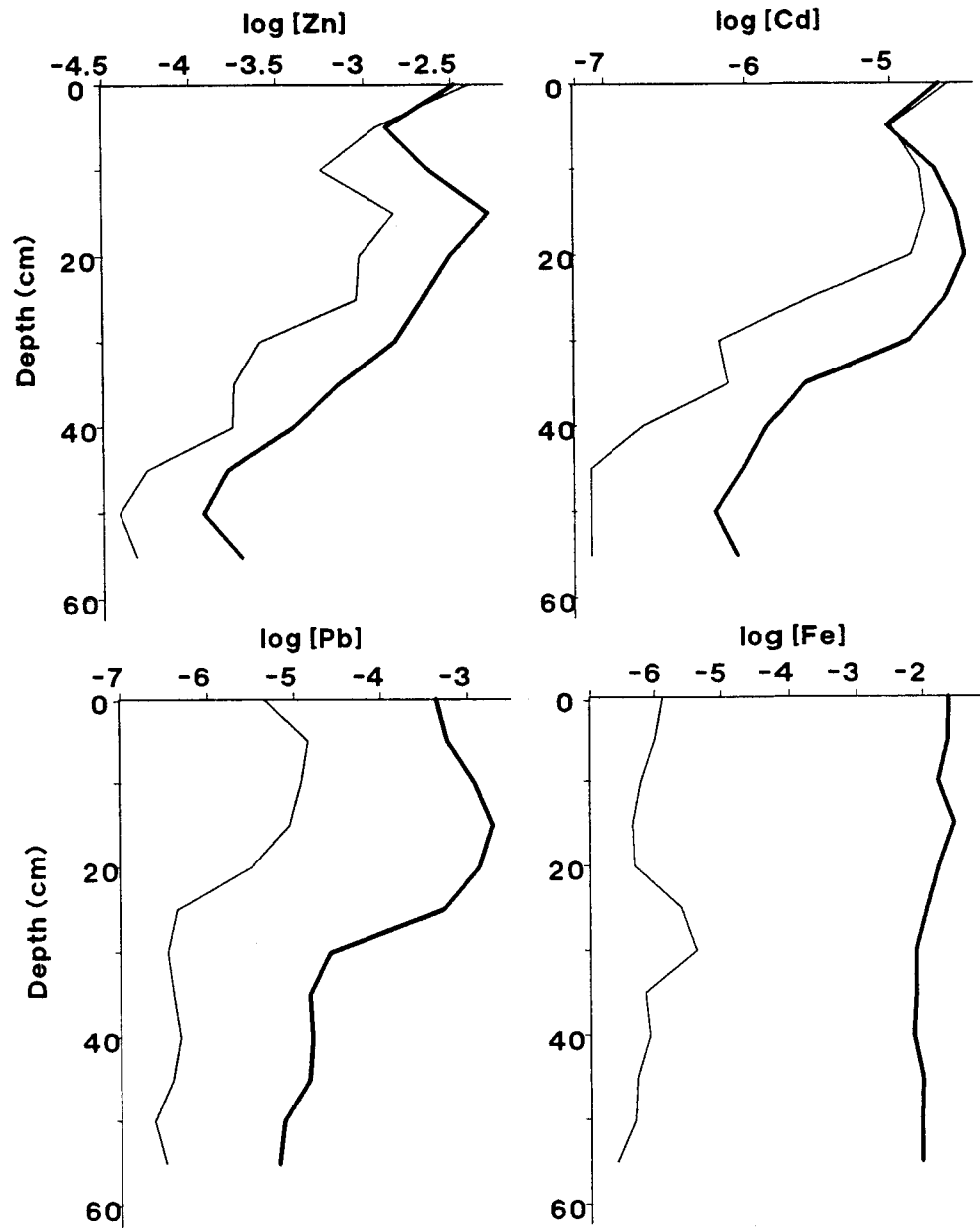
Fig. 2 Concentration of soluble Zn, Cd, Pb, and Fe in solution after 96 h of oxidation shown by thin line. The thick line represents concentration if 100 % dissolution of the metals had occurred.

Cd, and Pb. The metals were possibly held by organic
adsorption, metal oxide adsorption or mineral precipitation
(Levy et al, 1992).

Effect of Organic Matter on Reduction

From Fig. 3 it is seen that increasing organic matter
increased pH. For the surface depth, a 5-g organic matter
addition resulted in a 0.6 unit increase in pH, the 10-g
addition increased pH 1.75 units, and the 20-g addition
increased pH 2.0 units. A similar trend was seen
throughout the profile for all treatments, with the 20-g
treatment being most pronounced. The increase in pH was
dependent upon the amount of organic matter added. Figure
13 also shows that increasing the organic matter addition
lowered pe + pH. For the surface horizon, the 20-g organic
matter addition resulted in a pe + pH of 7.2. This is in
contrast to the 5-g addition which showed a pe + pH of 10.2.
These results clearly indicate that redox was influenced by
the amounts of organic matter added.

Changes in the concentration of Zn, Cd, and Pb were
seen throughout the soil profile (Fig. 4). For Zn, Cd, and
Pb, a decrease in pe + pH resulted in a decrease in the
their concentration, while the concentration of Fe
increased. The lowest redox treatment pushed Cd
concentration below the detection level in most of the
profile. Although Pb was substantially lowered by organic
matter treatments, little difference was seen between these

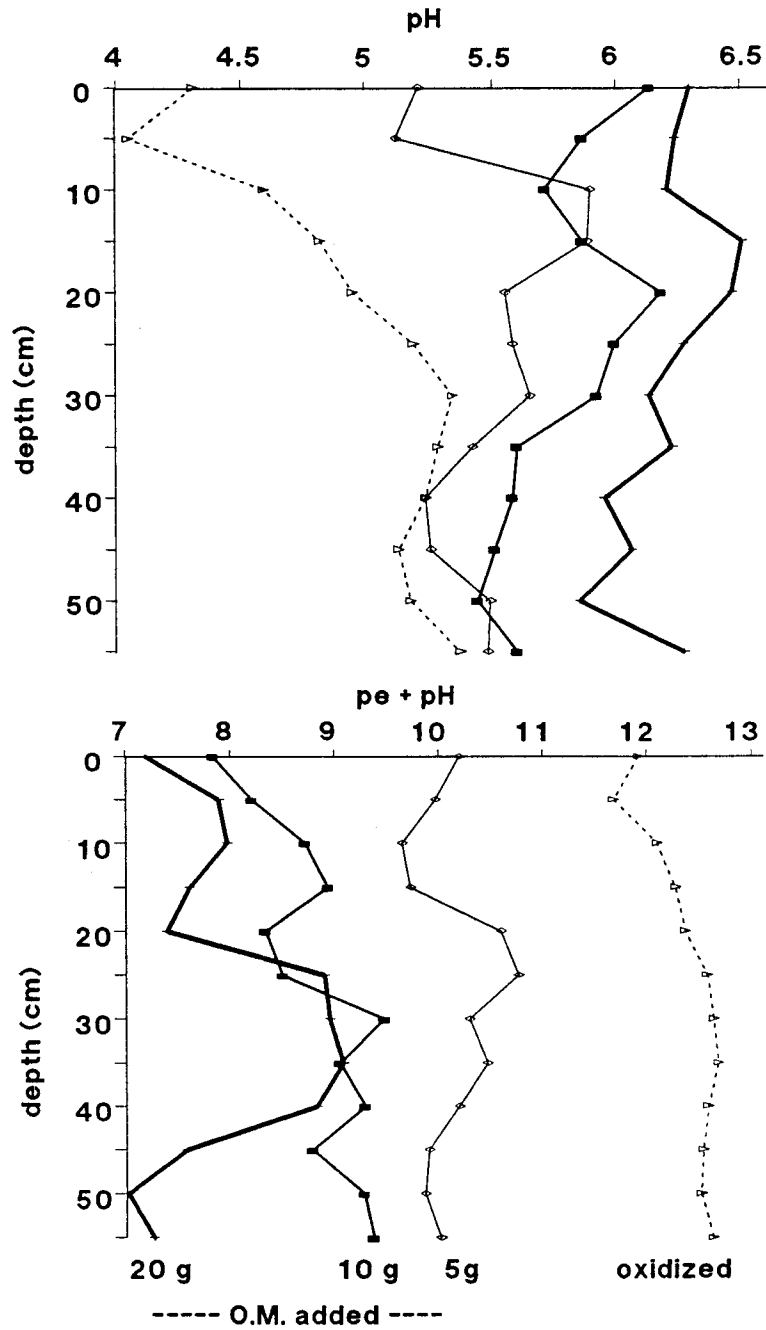Fig. 3 The effect of added organic matter on the pH and pe + pH 65 d of incubation with soil profile samples of a bog contaminated with mine tailings.
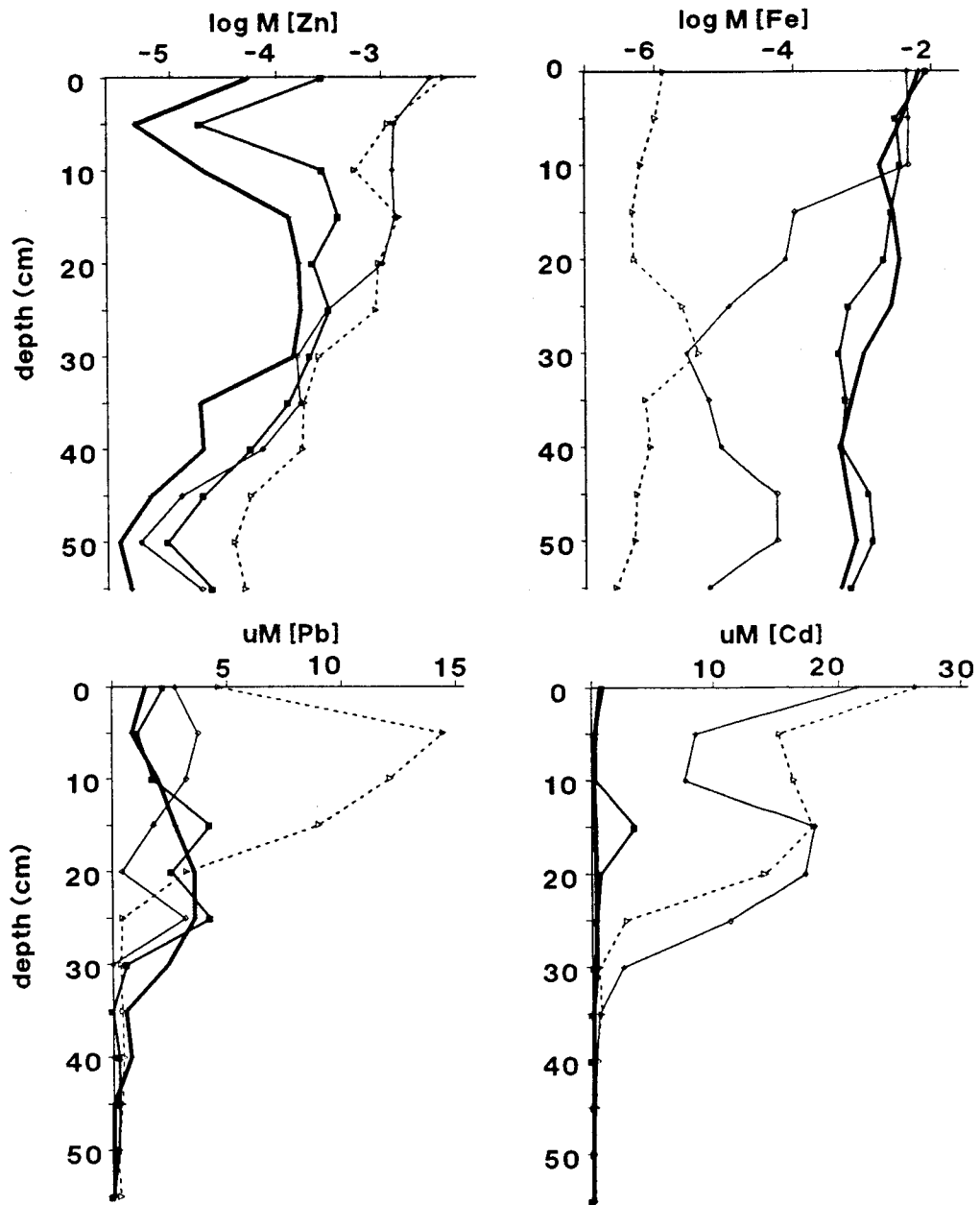
Fig. 4 The effect of reduction on the concentration of Zn, Cd, Pb and Fe throughout the profile of a contaminated bog. The dashed line represents the oxidized control, while increases in organic matter are represented by increased thickness of solid lines.

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treatments.

The concentration of Zn decreased in the presence of an increase of amount of organic matter. The concentrations of Zn throughout the profile were much greater than either Cd, or Pb. For Fe, a substantial increase in solubility accompanied decrease in pe + pH.

Fe Solubility

The total concentration of soluble Fe measured throughout the soil profile provides an indicator of the extent of contamination but does not predict the types of solubility controls that are present. The solution analysis for the surface 25 cm of soil was speciated by the chemical speciation program MINTEQA2. The results for Fe are plotted in Fig. 5 along with the solubility isotherms for $Fe(OH)_3$(amorp) and $Fe_3O_4 \cdot xH_2O$(edlinite). The graph reveals that the data points follow the solubility isotherm for $Fe(OH)_3$(amorp) throughout the pe + pH region encountered in this study. Because pe + pH did not go below 7.0, the formation of $Fe_3O_4 \cdot xH_2O$ could not form.

Zn Solubility

Figure 6 shows that under low pH conditions, soluble Zn may be controlled by soil-Zn. With increases in pH, the Zn^{2+} activity moved horizontally and did not follow the soil-Zn isotherm. Most likely the time required for equilibrium with soil-Zn was not met. It further appears
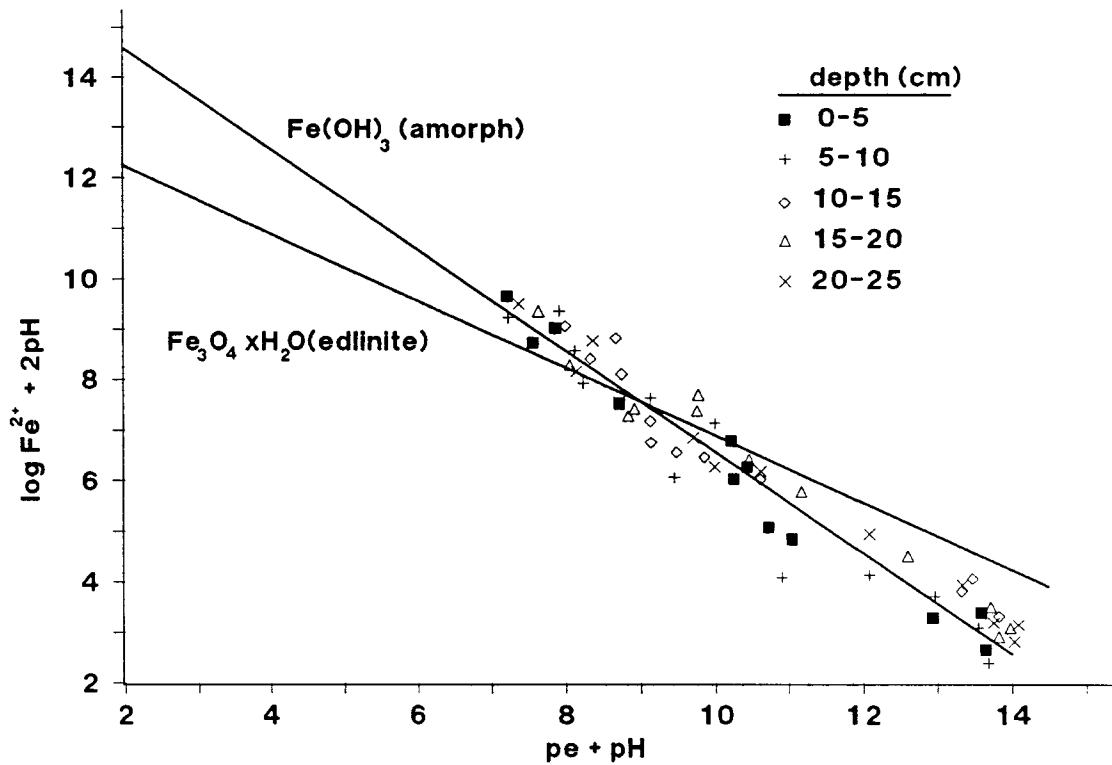
Fig. 5 The Fe^{2+} activities from the soil profile of a contaminated bog. Data includes three dates of sampling and three organic matter treatments.
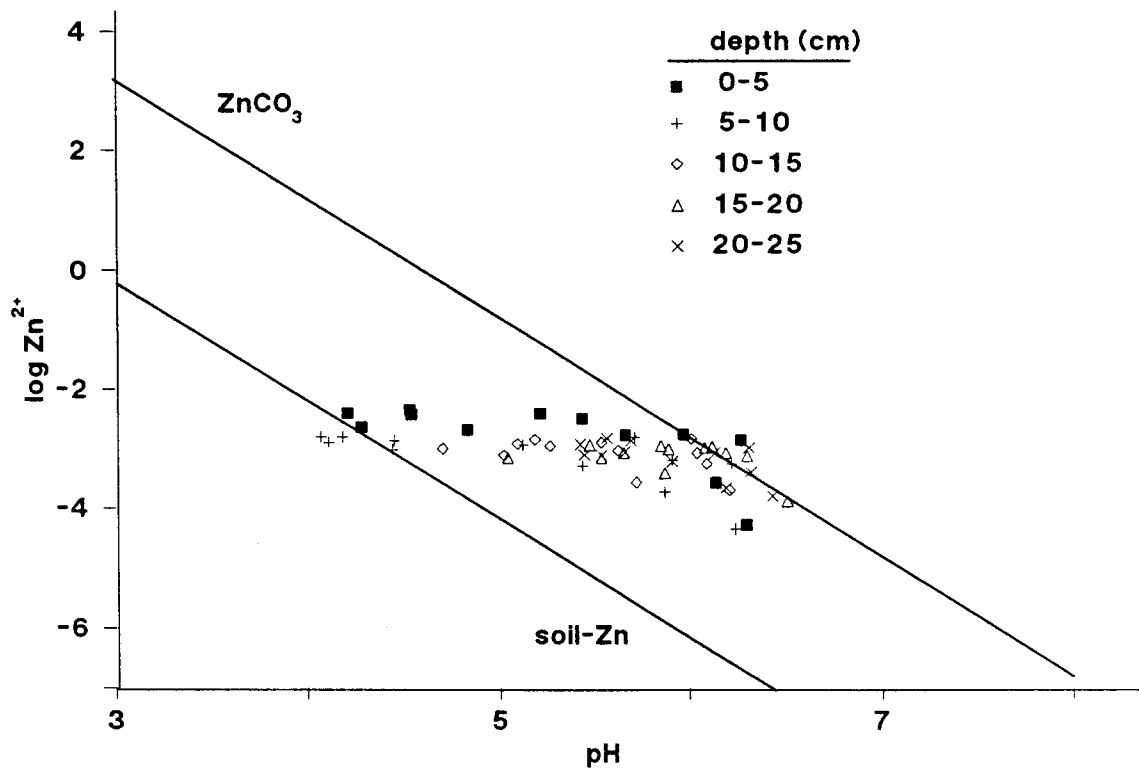
Fig. 6 The Zn^{2+} activities to the 25 cm depth of a
contaminated bog profile. The data include three dates of
sampling and three organic matter treatments.

that $ZnCO_3$(smithsonite) precipitated above pH 6.0 as demonstrated by the large number of data points clustered near this isotherm.

Cd Solubility

The measured Cd^{2+} activities are plotted in Fig. 7, along with soil-Cd and $CdCO_3$(octavite). When CO_2(g) is elevated to 0.05 atm, the solubility isotherm of $CdCO_3$(octavite) is near that of soil-Cd (Workman and Lindsay, 1991). The soil-suspensions in this study were undersaturated with respect to these Cd minerals except for the pH range above 6.0. Nearly half of the samples with pH values between 6 and 6.8 are near the $CdCO_3$(octavite) line, while the other half showed undersaturation with respect to this mineral. The activity of Cd^{2+} above this pH may very likely be controlled by $CdCO_3$(octavite).

Pb Solubility

The speciated Pb^{2+} activities are shown in Fig. 8. They show undersaturation to $PbCO_3$(cerrusite) in the pH range of 4 to 5.5. From pH 5.5 to 6.8, data points follow closely to the $PbCO_3$(cerrusite) isotherm. Although the precipitation of Pb is associated with more alkaline soil conditions (Santillan-Medrano and Jurinak, 1975), the elevated level of CO_2(g) used in this study allows Pb carbonate precipitation to occur at lower pH than occurs in normal alkaline soils.
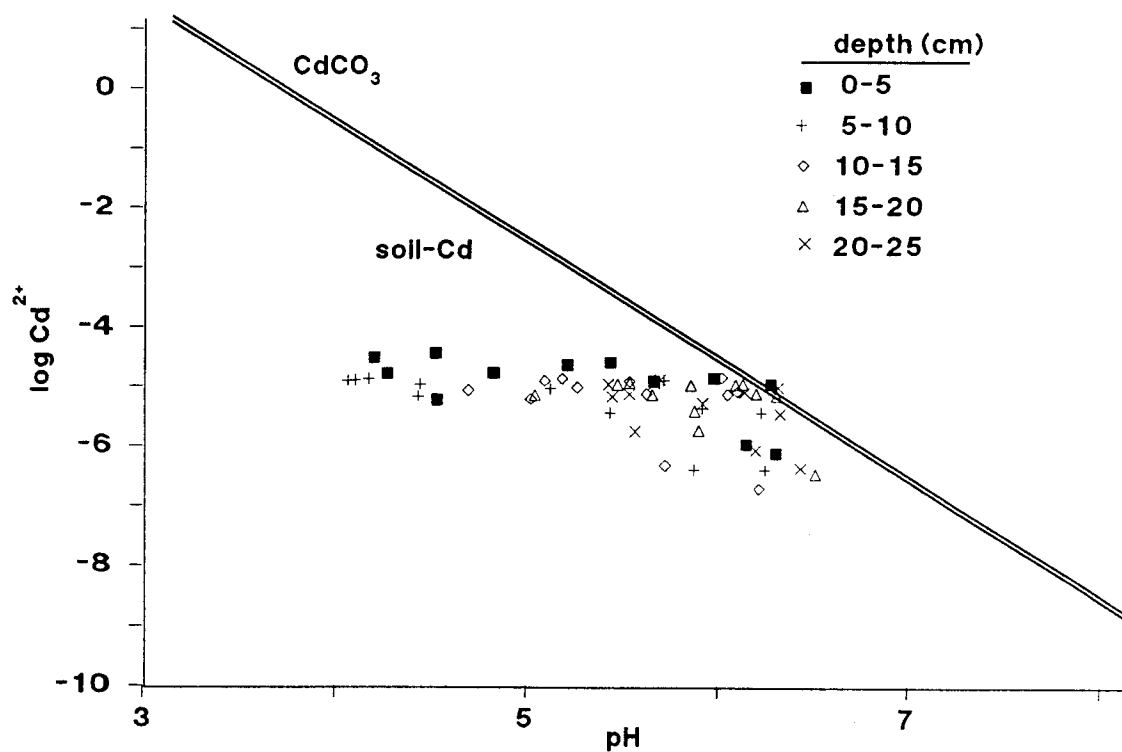
Fig. 7 The Cd^{2+} activities to the 25 cm depth of a contaminated bog. Data include three dates of sampling and three organic matter treatments.
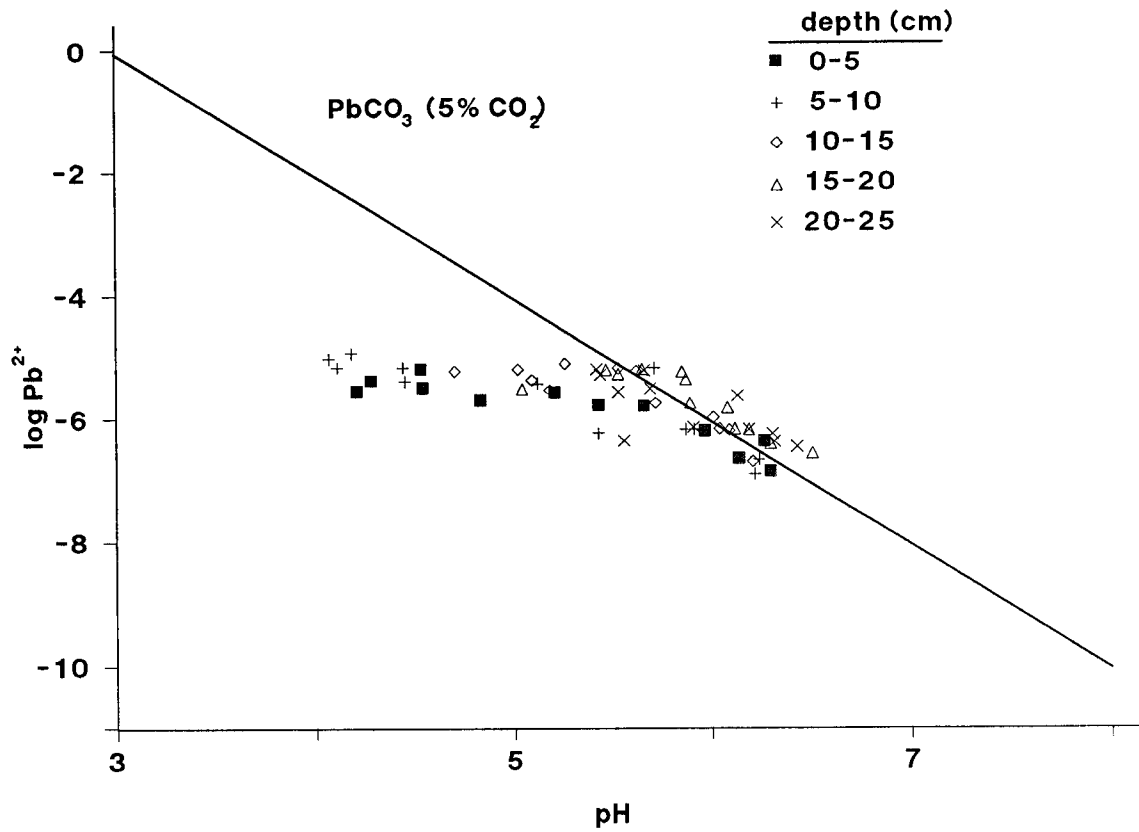
Fig. 8   The Pb^{2+} activities to the 25 cm depth of a contaminated bog.   Data include three dates of sampling and three organic matter treatments.

SUMMARY

After 85 y of metal sulfide oxidation at the surface of
a contaminated bog, total metal analysis revealed that Zn,
Cd, and Pb had moved downward through 55 cm of soil.
Samples exposed to $O_2(g)$ from the atmosphere for 96 h did
not completely release these metals into solution. An
exception was seen at the surface 5 cm for Zn and Cd, in
which the remaining metals were completely dissolved.
Reduction of the soil profile following oxidation for 36 h
had a dramatic effect on the concentration of Fe, Zn, Cd,
and Pb. The magnitude of reduction throughout the
contaminated bog profile depended on the amount of organic
matter present. As organic matter content increased, pH
increased but pe + pH decreased. Soluble Fe increased with
reduction while soluble Zn, Cd, and Pb decreased. Chemical
speciation of the equilibrium extract from the first 25 cm
revealed that no known minerals controlled the solubility of
Zn, Cd, and Pb under oxidizing conditions. For Fe, it was
found that $Fe(OH)_3$(amorp) controlled Fe solubility
throughout the redox range of pe + pH 14 to 7 found in this
study. As reduction occurred, pH increased and pe + pH
decreased the metal solubilities approached closely to those
of $ZnCO_3$(smithsonite) and $CdCO_3$(octavite). Solubility control
of Pb approached very closely to the $PbCO_3$(cerrusite)

isotherm at pH values above 5.5. The addition of organic matter in these studies was not sufficient of form heavy metal sulfides. This point will be pursued in a subsequent study.

SEQUENCE OF METAL SULFIDE PRECIPITATION

IN MOUNTAIN BOGS

Metal sulfides are very insoluble, and their precipitation can potentially reduce the concentration of toxic heavy metals in contaminated soils. As previoulsy demenstrated, organic matter was successfully used to reduce soils, but it did not lower pe + pH sufficiently to precipitate metal sulfides. A pe + pH range of 4.2 to 4.7 is required for the precipitation of Zn, Fe, Cd, and Pb sulfides (Lindsay, 1979). In natural systems, this redox region is attained by heterotrophic respiration of organic substrates by numerous microbial genera (Alexander, 1980). The rate at which this decomposition proceeds is dependent upon the quantity and kinds of the organic substrates. With organic matter substrates such as those found in peat bogs, are difficult to decompose, so reduction is retarded. To expedite the reduction process, other electron sources such as $H_2(g)$ can also be used. It was hypothesized that the use of $H_2(g)$ would lower pe + pH sufficiently for Zn, Cd, and Pb sulfides to precipitate.

The objectives of this study were to: 1) determine if $H_2(g)$ could be used to lower the redox of soils; 2) examine the solubility relationships of metals in polluted soils

subjected to oxidation (in air) and subsequent reduction with $H_2(g)$; and 3) determine the conditions which are necessary for the precipitation of Zn, Cd, and Pb as sulfides.

THEORY

Equilibrium between a metal carbonate and its sulfide provides a unique pe + pH at which both solids can coexist. For example, if $PbCO_3$(cerrusite) controls Pb^{2+} activity in a reducing soil, a unique pe + pH will occur when the activity of S^{2-} is sufficient to precipitate a Pb sulfide. To calculate the unique pe + pH, pe, pH, the partial pressure of $CO_2(g)$ must be known. This relationship is shown by the following reaction:

$$\underline{\log K^\circ}$$

$$PbCO_3(cerr) + 2H^+ \iff Pb^{2+} + CO_2(g) + H_2O \quad 4.65 \qquad [1]$$
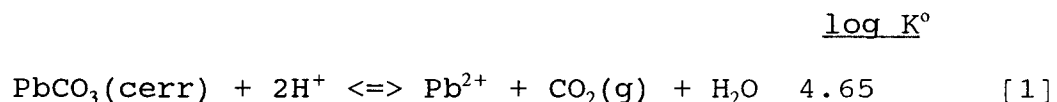
The equilibrium expression for the sulfide is shown as follows,

$$\underline{\log K^\circ}$$

$$PbS(galena) + H^+ \iff Pb^{2+} + HS^- \qquad\qquad -14.61 \qquad [2]$$
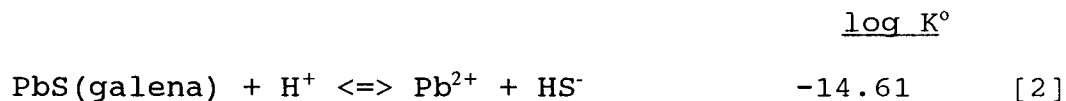
The S^{2-} activity can be determined by knowing the pe, pH and SO_4^{2-} activity in solution as expressed by the following reaction:

$$SO_4^{2-} + 8H^+ + 8e^- <=> S^{2-} \qquad 20.74 \qquad [3]$$

$$\underline{log\ K^\circ}$$

Combining Eq. [1], [2], and [3] gives the following equilibrium reaction:

$$\underline{log\ K^\circ}$$

$$PbCO_3(cerr) + 10H^+ + 8e^- + SO_4^{2-} <=> PbS$$
$$+ CO_2(g) + 5H2O \quad 52.9 \qquad [4]$$
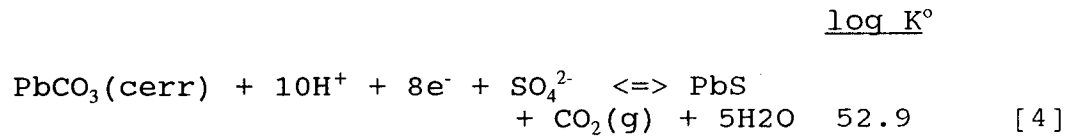
Rearranging this equation to solve for pe + pH, gives:

$$8(pe + pH) = 52.9 - 2pH - log\ CO_2(g) + log\ SO_4^{2-} \qquad [5]$$

Using a $CO_2(g)$ partial pressure of 0.05 atm, an average soil SO_4^{2-} activity of 10^{-3} $\underline{M}$ (Lindsay, 1979), and a pH of 7.0, the pe + pH at which these minerals co-exist is 4.65. As the soil is reduced pe + pH will be fixed until the mineral $PbCO_3$(cerrusite) is depleted. Upon depletion of $PbCO_3$, the activity of Pb^{2+} will be controlled by PbS(galena). As a result, any further decrease in redox will lower the activity of Pb^{2+}. This would be seen by a downward movement of Pb^{2+} activity as predicted by PbS solubility when pe + pH is plotted against Pb^{2+} activity.

A similar procedure can be used for $CdCO_3$(octavite) and $ZnCO_3$(smithsonite) for the corresponding minerals CdS and ZnS. Based on previous findings, the mineral $Fe_3O_4 \cdot xH_2O$(edlinite) was used as the iron solubility control

to give the $Fe_3O_4 \cdot xH_2O$(edlinite)-FeS_2(pyrite) mineral couple. The equilibrium constants used for this study are summarized in Table 3.

Using a SO_4^{2-} activity of $10^{-3.0}$ and pH of 7.0, the equilibrium pe + pH was calculated for each of the following mineral relationships.

		Controlling mineral	pe + pH
1)	CdS(greennokite)	$CdCO_3$(octavite)	4.78
2)	ZnS(sphalerite)	$ZnCO_3$(smithsonite)	4.70
3)	PbS(galena)	$PbCO_3$(cerrusite)	4.65
4)	FeS_2(pyrite)	$Fe_3O_4 \cdot xH_2O$	4.48

METHODS AND MATERIALS

Two surface samples (0-5 cm depth) were collected randomly within a 10 m^2 area from the contaminated bog previously described. The soils were labeled soil A and soil B. Both soils were reduced for periods of 0, 14, 42, 55 and 65 d. Twenty five grams g of soil and 40 mL of distilled-deionized H_2O were placed into a 125-mL erlenmeyer flask. Because possible exposure of the flasks to O_2(g) from the air during sampling can retard S^{2-} formation, a separate flask for each reaction period was prepared, giving a total of 10 flasks. Two grams of SiO_2 was placed in each flask to insure that the Pt electrodes were free of surface contaminants. To this soil-solution, 10 g of organic

Table 3. Dissociation constants used in this study.

mineral	log K°
$CdS(greennokite)[1] \iff Cd^{2+} + S^{2-}$	-27.26
$ZnS(sphalerite)[2] \iff Zn^{2+} + S^{2-}$	-24.27
$PbS(galena)[2] \iff Pb^{2+} + S^{2-}$	-27.51
$FeS_2(pyrite)[3] + 2e^- \iff Fe^{2+} + 2S^{2-}$	-44.27
$CdCO_3(octavite)[2] + 2H^+ \iff Cd^{2+} + CO_2(g) + H_2O$	9.74
$ZnCO_3(smithsonite)[2] + 2H^+ \iff Zn^{2+} + CO_2(g) + H_2O$	7.91
$PbCO_3(cerrusite)[2] + 2H^+ \iff Pb^{2+} + CO_2(g) + H_2O$	4.65
$Fe_3O_4 \cdot xH_2O(amorp)[3] + 8H+ + 2e^- \iff 3Fe^{2+} + xH_2O$	40.65
$soil\text{-}Cd[4] \iff Cd^{2+} + 2H^+$	7.60
$HS^- \iff 2H^+ + S^{2-}$	-12.9

[1] Daskalakis, K.D. and G.R. Helz (1992)

[2] Lindsay, W.L. (1979)

[3] Licht, S. (1988)

[4] Workman, S.M. and W.L. Lindsay (1990)

surface material from a nearby non-contaminated bog was added as an organic substrate. A small stirring bar was placed into each flask to provide adequate stirring during pe + pH measurements. The flasks were placed on an orbital shaker at 60 revolutions min^{-1} and left open to the atmosphere. Water lost by evaporation was replaced daily. Holes were bored into a nalgene stopper to accommodate a combination pH electrode (Ross semi-micro 81-15) and 1.0 mm x 60 mm platinum wire for pe measurements. The use of this type of combination electrode was important in the reduction segment of the initial study because its reference solution did not contain Ag which precipitates when S^{2-} is present. The reference electrode from the combination electrode was also used as the pe reference. For each sampling date, a 3-mL aliquot was removed from the flask and centrifuged at 12,000 rpm for 10 min followed by filtration through a 0.2 μm porosity filter. The first sampling was identified as time 0 for the study. The filtered solution was analyzed for important cations by ICP and important anions by ion chromatography.

For the reduction segment of the study, the head space within the flask was purged with a gas mixture consisting of 1% $H_2(g)$, 5% $CO_2(g)$ and 94% Ar for 10 min. The $CO_2(g)$ concentration simulated conditions present in flooded soils, and the argon hastened anaerobic microbial processes by lowering the partial pressure of oxygen. Flasks were rotated taken from the orbital shaker to a 28 °C constant

temperature bath every 24 h. Gas inlet and outlet
connectors placed in the stopper allowed a re-charge of the
reducing gas mixture every 2 d to insure a continual source
of electrons from $H_2(g)$. After 14 d, pe and pH measurements
were made and samples were taken for analysis. To insure
that $H_2(g)$ would not interfere with pe measurements, an
inlet and outlet fabricated from 16-gauge syringes were
inserted into the nalgene stopper while $O_2(g)$ free $Ar(g)$ was
passed through the flask at the time of sampling.
Measurements were made when a steady state for pe was
obtained, approximately 15 min. A 3-mL aliquot of the
suspension was then removed by means of a syringe through
the gas outlet and placed into a 50-mL centrifuged tube
purged with argon. The suspension was then centrifuged for
10 min at 12,000 rpm in an $Ar(g)$ purged 50-mL centrifuge
tube. A 3-mL aliquot was removed through a septum in the
centrifuge cap. For ICP analysis, 1.5 mL of the supernatant
was transferred to a vial containing 3 μL of concentrated
HCl to avoid metal oxide precipitation. The remaining
portion was used to measure electrical conductivity. The
latter solution was then transferred to a vial open to the
atmosphere for 24 h to permit oxidation of S^{2-} to SO_4^{2-}. This
solution was then analyzed for anions. Sampling was
repeated at 42, 55, and 65 d. Activities for important ions
were calculated using the chemical speciation model,
MINTEQA2.

RESULTS AND DISCUSSION

Changes in pe, pH and pe + pH that occurred during
reduction of soils from two sites are shown in Fig. 9, and
indicate that solutions became sufficiently reduced to
precipitate the metal sulfides of interest in this study.
Changes in the concentrations of Fe, Zn, Cd, and Pb with
time of reduction are shown in Fig. 10. A sharp increase in
the concentration of Fe occurred during the first 42 d of
reduction, with a slower rate of change for 45 to 65 d. The
concentrations of Zn, Cd, and Pb decreased with time.
Changes in pe, pH and the concentration of important anions
and cations are summarized in Table 4.

Activities for selected ions obtained from the chemical
speciation model MINTEQA2 are shown in Table 5 for both
replicates. The activities from this table were used to
determine the saturation indexes of selected Fe, Zn, Cd, and
Pb minerals. Only minerals showing possible equilibrium
were selected from the MINTEQA2 data base. Saturation
indexes were calculated in MINTEQA2 by subtracting the log
of the IAP (ion activity product) from the formation
constant, K°. The dissociation constants used in this study
are shown in Table 3. A negative saturation index indicates
the solution is undersaturated with respect to the mineral,
a positive saturation denotes supersaturation and a zero
saturation index indicates equilibrium with the mineral.

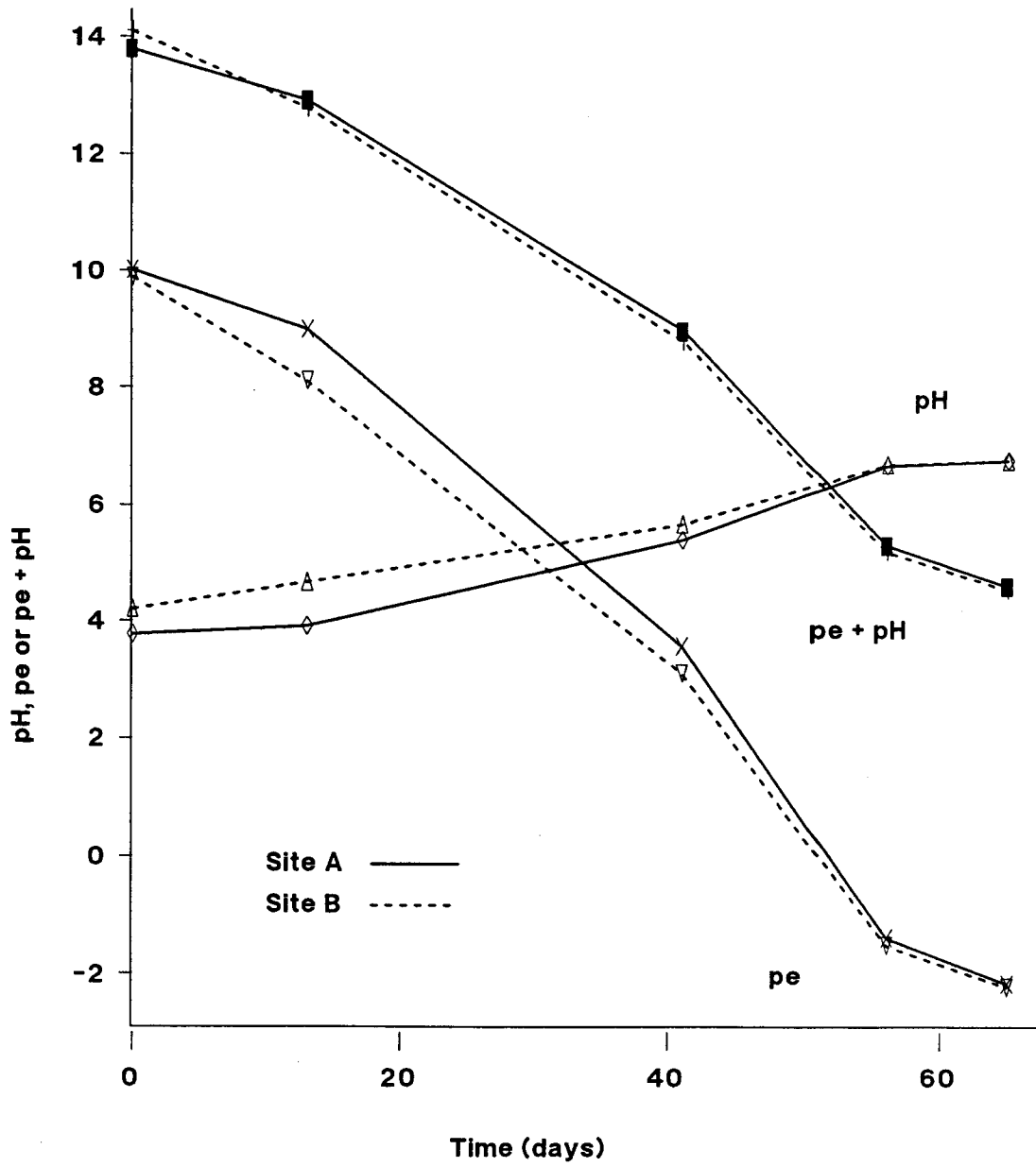Saturation indexes for both soils A and B are shown

Fig. 9 Changes in pe, pH and pe + pH for two surface soils of a contaminated bog. Hydrogen gas and organic matter were used as electron sources.
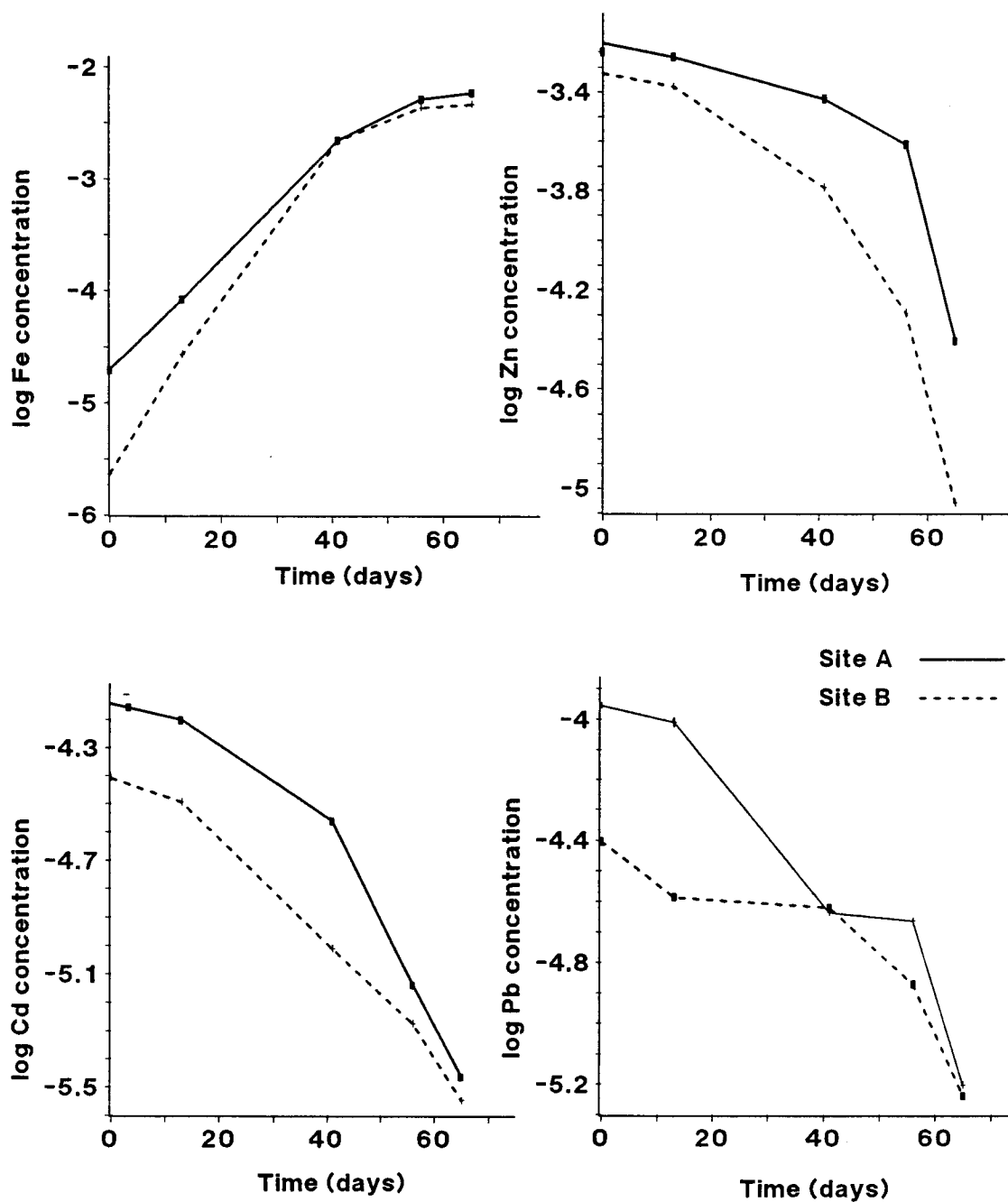
Fig. 10   Changes in the concentration Fe, Zn, Cd, and Pb from two surface samples of a contaminated bog.   Soils were reduced for 65 d with organic matter and 1% $H_2(g)$.

Table 4. Analytical data for two sites from the surface of a bog contaminated by metal sulfide mine tailings and reduced with 1% $H_2(g)$ over a 65 d period.

Time	pH	pe + pH	Zn	Fe	SO_4^{2-}	Cd	Pb
d				----------------	μM	----------------------	
Site A							
0	3.79	13.81	629	19.7	1,832	27.2	11.1
14	3.93	12.93	552	84.1	1,905	6.3	9.8
42	5.40	8.98	374	2,237	1,780	2.8	2.3
55	6.68	5.31	224	5,155	1,977	0.7	2.2
65	6.77	4.61	39	5,871	1,821	0.3	0.6
Site B							
0	4.22	14.12	477	2.3	1,530	3.9	4.0
14	4.69	12.80	418	27.0	1,426	3.2	2.4
42	5.68	8.80	163	2,198	1,499	1.0	0.5
55	6.70	5.20	51	4,333	1,717	0.5	2.6
65	6.76	4.55	8	4,657	1,738	0.3	0.6

Table 5. Activities of selected ions for two sites from the surface (0-25 cm) of a bog contaminated with metal sulfide mine tailings and reduced with 1% $H_2(g)$ over a 65 d period.

Time d	(Fe^{2+})	(Zn^{2+})	(Cd^{2+})	(Pb^{2+})	(S^{2-})	(SO_4^{2-})
				log activity		
Site A						
0	-5.04	-3.84	-5.47	-5.28	* *	-3.10
14	-4.33	-3.52	-5.50	-5.32	* *	-3.07
42	-2.93	-3.71	-5.88	-6.00	* *	-3.14
55	-2.74	-4.03	-6.55	-6.95	-24.27	-3.13
65	-2.97	-4.88	-6.91	-7.64	-19.31	-3.17
Site B						
0	-6.05	-3.56	-5.69	-5.69	* *	-3.15
14	-4.88	-3.62	-6.23	-5.91	* *	-3.21
42	-2.94	-4.07	-6.33	-6.27	* *	-3.22
55	-2.82	-4.73	-6.65	-7.18	-24.02	-3.16
65	-3.02	-5.53	-6.98	-7.67	-18.03	-3.17

* * less than 10^{-30} $\underline{M}$

respectively in Tables 6 and 7. Both soils attained near saturation with $Fe(OH)_3$(amorp) from pe + pH near 14 to 8.7. Decreasing redox showed undersaturation with this mineral, but slight supersaturation with $Fe_3O_4 \cdot xH_2O$(edlinite). At the lowest pe + pH measurements, equilibrium with edlinite mineral was shown. Under oxidizing conditions, mineral controls for Zn, Cd, and Pb were not identifiable. As pe + pH decreased, soil-suspensions approached equilibrium with carbonates of Zn, Cd, and Pb. Soil-Cd was also near saturation under reducing conditions, following closely the $CdCO_3$(octavite) isotherm. At the lowest pe + pH values, 4.61 for replicate A and 4.55 for replicate B, solutions were near equilibrium for $PbCO_3$(cerrusite). For both replicates, $ZnCO_3$(smithsonite) showed the greatest undersaturation while $CdCO_3$(octavite) was intermediate.

The precipitation of carbonates was promoted by two factors not found in the oxidized environments, elevated CO_2(g) and increased pH. The increased activity of CO_3^{2-} and increased pH were sufficient to precipitate carbonates.

Tables 6 and 7, suggest that sulfide precipitation occurred at the lowest pe + pH. At this redox, solutions for both soils were slightly supersaturated with respect to ZnS(sphalerite), CdS(greenakolite), and PbS(galena), while FeS_2(pyrite) was slightly undersaturated.

These results support the findings shown previously on the control of soluble Fe. In oxidizing environments, Fe solubility is controlled by $Fe(OH)_3$(amorp) while under

Table 6.   Saturation indexes[1] for site A.

pe + pH	ZnS	FeS$_2$	CdS	PbS	Fe$_3$O$_4 \cdot$xH$_2$O
13.81	*	*	*	*	-5.91
12.93	*	*	*	*	-4.69
8.98	*	*	*	*	0.53
5.31	-4.34	-10.92	-4.36	-4.29	1.34
4.61	0.32	-0.64	0.86	0.57	0.28

	CdCO$_3$	PbCO$_3$	ZnCO$_3$	Fe(OH)$_3$(amorp)	soil-Cd
13.81	-5.35	-3.65	-5.35	-0.23	-4.39
12.93	-5.10	-3.41	-5.11	-0.12	-4.14
8.93	-2.54	-1.15	-2.36	-0.26	-1.58
5.31	-0.68	0.45	-0.13	-0.65	0.30
4.61	-0.84	-0.05	-0.79	-1.17	0.12

Saturation index = log IAP/K^o

* less than -15

Table 7.   Saturation indexes[1] for site B.

pe + pH	ZnS	FeS$_2$	CdS	PbS	Fe$_3$O$_4$·xH$_2$O
14.12	*	*	*	*	-5.86
12.80	*	*	*	*	-2.03
8.80	*	*	*	*	1.74
5.20	-4.22	-9.57	-3.60	-3.68	0.97
4.55	0.34	-0.45	1.45	1.14	-0.05

	CdCO$_3$	PbCO$_3$	ZnCO$_3$	Fe(OH)$_3$(amorp)	soil-Cd
14.21	-4.71	-3.20	-4.07	-0.07	-3.75
12.80	-2.48	-2.48	-3.71	0.71	-3.35
8.80	-2.44	-0.86	-2.16	0.64	-1.49
5.20	-0.72	0.26	-0.78	-0.81	0.24
4.55	-0.91	-0.08	-1.44	-1.26	0.05

Saturation Index = log IAP/K°

* less than -15

reducing conditions, $Fe_3O_4 \cdot xH_2O$(edlinite) controls soluble Fe. It is seen that decreasing pe + pH increases the probability of Zn, Cd, and Pb carbonate formation and soil-Cd precipitation.

Fe Solubility Controls

The solubility controls of Fe, Zn, Cd, and Pb can be identified by examining changes in metal ion activities when plotted against possible mineral controls. Changes in the activity of Fe as the soil-suspensions were reduced are shown in Fig. 11. Under the most oxidized pe + pH conditions (high pe + pH), $Fe(OH)_3$(amorp) controlled Fe solubility. This mineral continued to control Fe solubility down to pe + pH 8. Further additions of electrons resulted in undersaturation with respect to $Fe(OH)_3$(amorp) and supersaturation with respect to $Fe_3O_4 \cdot xH_2O$) at pe + pH near 5. Reduction at 30 d was near pe + pH near 4.5 for both soils and showed near equilibrium for $Fe_3O_4 \cdot xH_2O$(edlinite) and FeS_2(pyrite).

Zn Solubility Controls

Oxidized soil-suspensions were extremely undersaturated with respect to $ZnCO_3$(smithsonite) (Fig. 12). As pe + pH decreased and pH increased, the isotherm for $ZnCO_3$(smithsonite) and the data points converged. At pe + pH near 5, soil A showed near equilibrium with this mineral. Continual addition of electrons moved the data points for
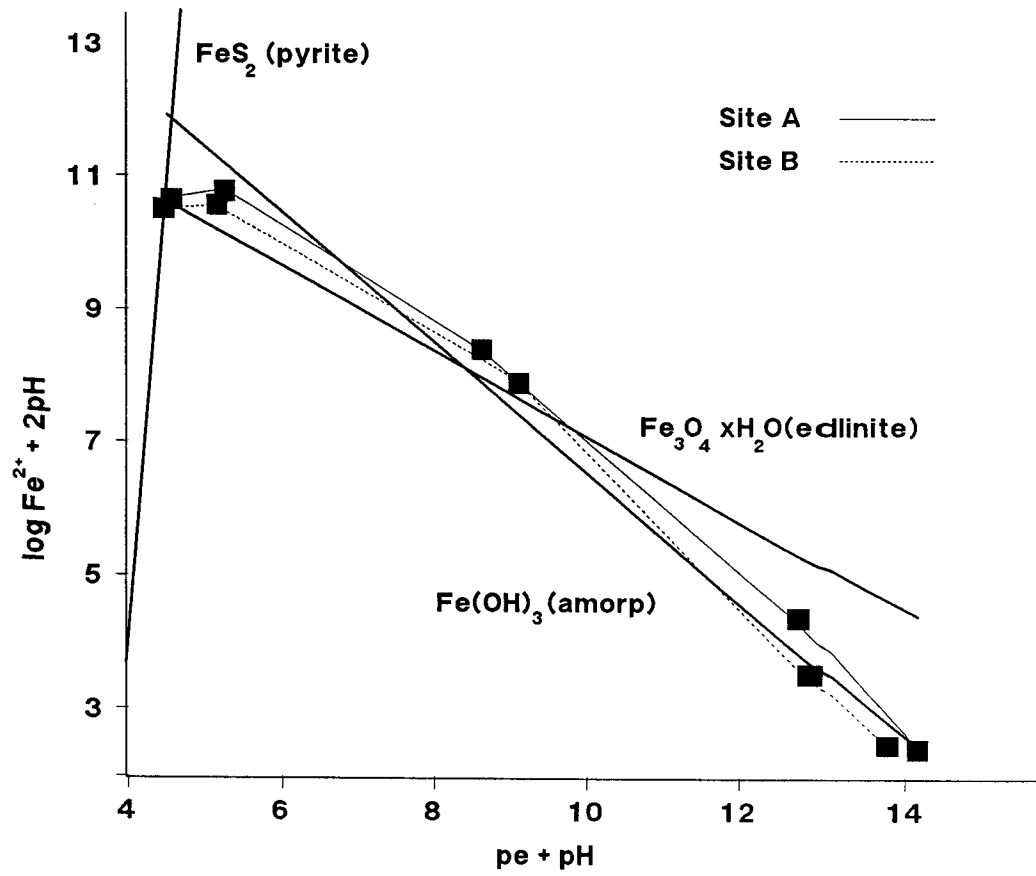
Fig. 11 The Fe^{2+} activities for two soils reduced with 1% $H_2(g)$ and organic matter after 65 d. Possible Fe mineral controls are included.
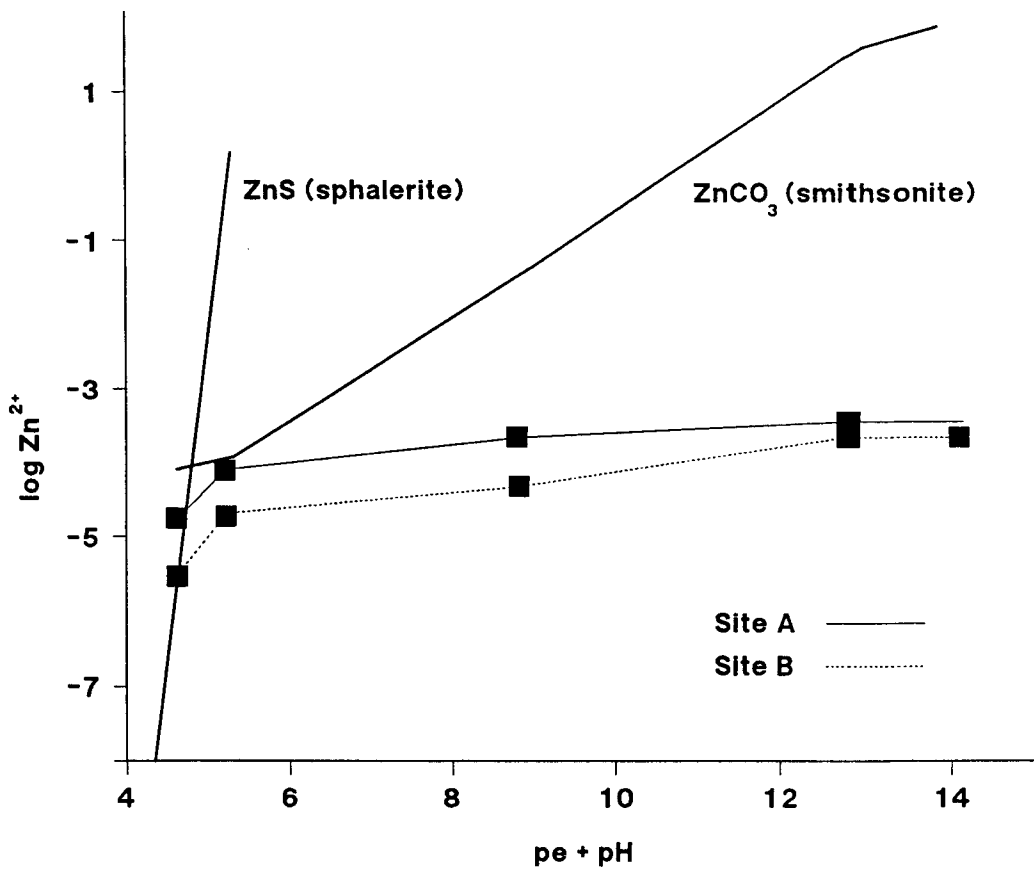
Fig. 12 The Zn^{2+} activities for two soils reduced with 1% $H_2(g)$ and organic matter after 65 d. Possible mineral controls are included for comparison to the solubility measurements.

both sampling sites sharply downward to the ZnS(sphalerite) isotherm, strongly suggesting equilibrium with this mineral.

Cd Solubility Controls

Experimental Cd activities are shown in Fig. 13 and are compared to two Cd minerals, soil-Cd and $CdCO_3$(octavite). The solutions remained undersaturated with respect to both minerals throughout the reduction process. Similar to Zn, a significant decrease in Cd^{2+} activity occurred from pe + pH 5 to 4.5, as the data points moved down the CdS(greennokite) isotherm.

Pb Solubility Controls

The oxidized soils were highly undersaturated with respect to $PbCO_3$(cerrusite). Unlike Zn and Cd, slight supersaturation of this mineral was seen at pe + pH near 5 (Fig. 14). Further decreases in pe + pH show the data points very near to both $PbCO_3$(cerrusite) and PbS(galena).

Sequence of Metal Sulfide Precipitation

The results of this study indicate that carbonates of for Zn, Cd, and Pb very likely form as redox is lowered. For Fe, it is shown that $Fe_3O_4 \cdot xH_2O$(edlinite) controls Fe at low redox. At the lowest pe + pH measurements, the solutions reached saturation with the sulfides of Fe, Zn, Cd, and Pb. Equilibrium expressions combining the carbonate and sulfide minerals of Zn, Cd, and Pb and
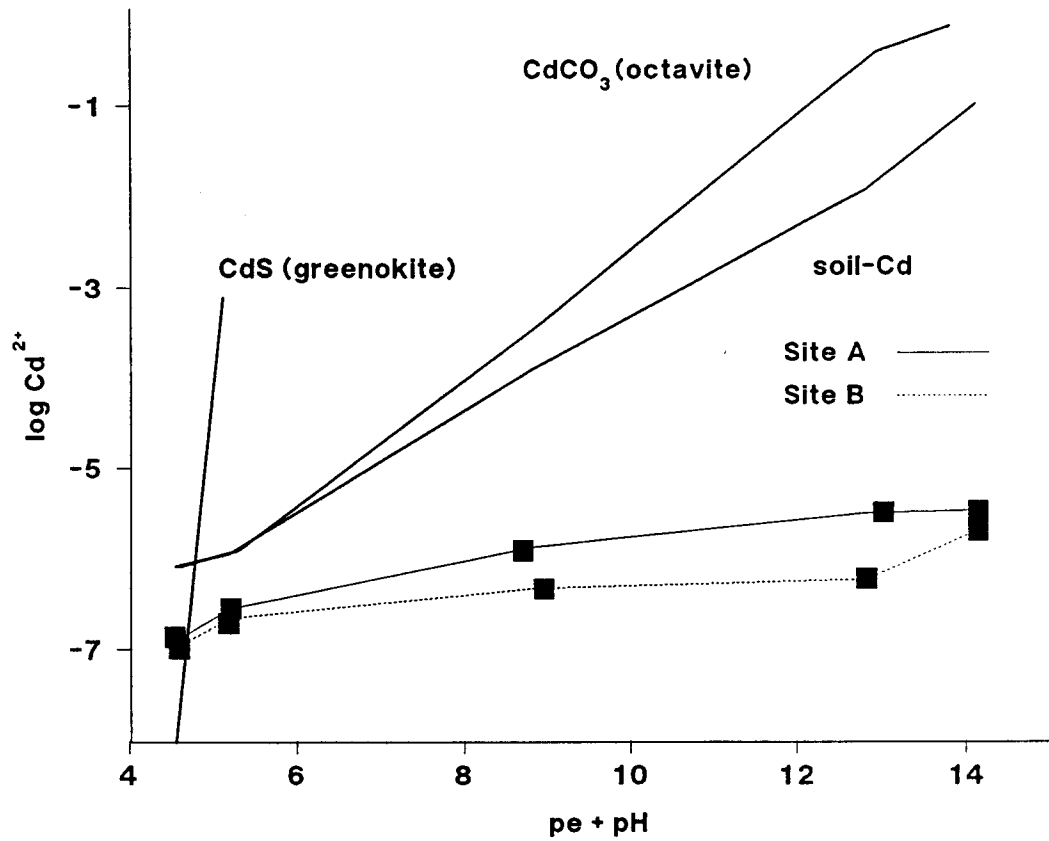
Fig. 13 The Cd^{2+} activities for two soils reduced with 1%
H$_2$(g) and organic matter after 65 d. Possible mineral
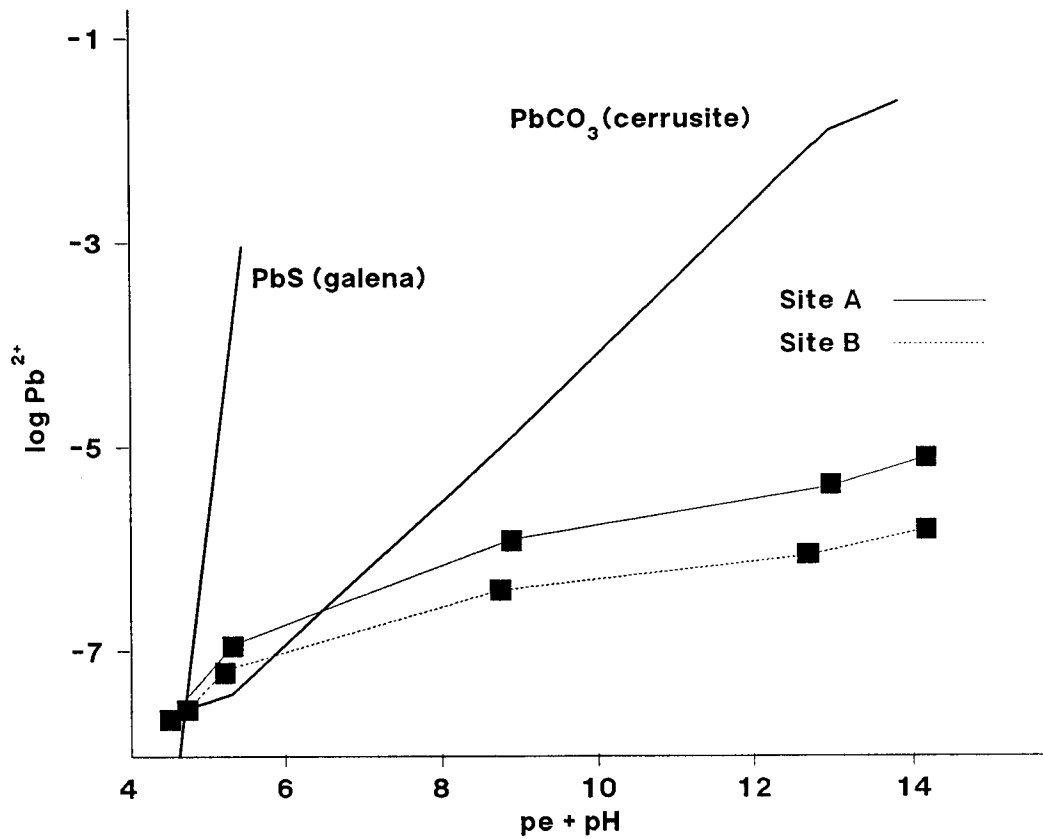controls are included for comparison to the solubility
measurements.

Fig. 14 The Pb^{2+} activities for two soils reduced with 1%
$H_2(g)$ and organic matter after 65 d. Possible mineral
controls are included for comparison of data measurements.

$Fe_3O_4 \cdot xH_2O$(edlinte) and FeS_2(pyrite) were then used to determine the order of metal sulfide precipitation. For this determination, pH, a partial pressure of CO_2(g) of 0.05 atm and the activity of SO_4^{2-} taken from the lowest redox measurements were used to determine the final pe + pH at which the minerals can co-exist. The results of this determination are as follows:

		controlling mineral	pe + pH
1)	CdS(greennokite)	$CdCO_3$(octavite)	4.82
2)	ZnS(sphalerite)	$ZnCO_3$(smithsonite)	4.74
3)	PbS(galena)	$PbCO_3$(cerrusite)	4.69
4)	FeS_2(pyrite)	$Fe_3O_4 \cdot xH_2O$(amorp)	4.48

The order of precipitation for these metal sulfides is shown in Fig. 15. The activity of S^{2-} is fixed by the pe + pH of the solution. This graph was constructed with pH fixed at 6.77, and SO_4^{2-} activity at $10^{-3.17}$ $\underline{M}$ corresponding to the pH and SO_4^{2-} activity measured to the two soil sites. As redox was lowered, the activity of S^{2-} increased as shown by the lower line. The activities of Fe, Zn, Cd, and Pb are fixed by the respective carbonates of Zn, Cd, and Pb. Soil-Cd was omitted because of its identical solubility to $CdCO_3$(cerrusite) at the partial pressure of CO_2(g) used in this study.
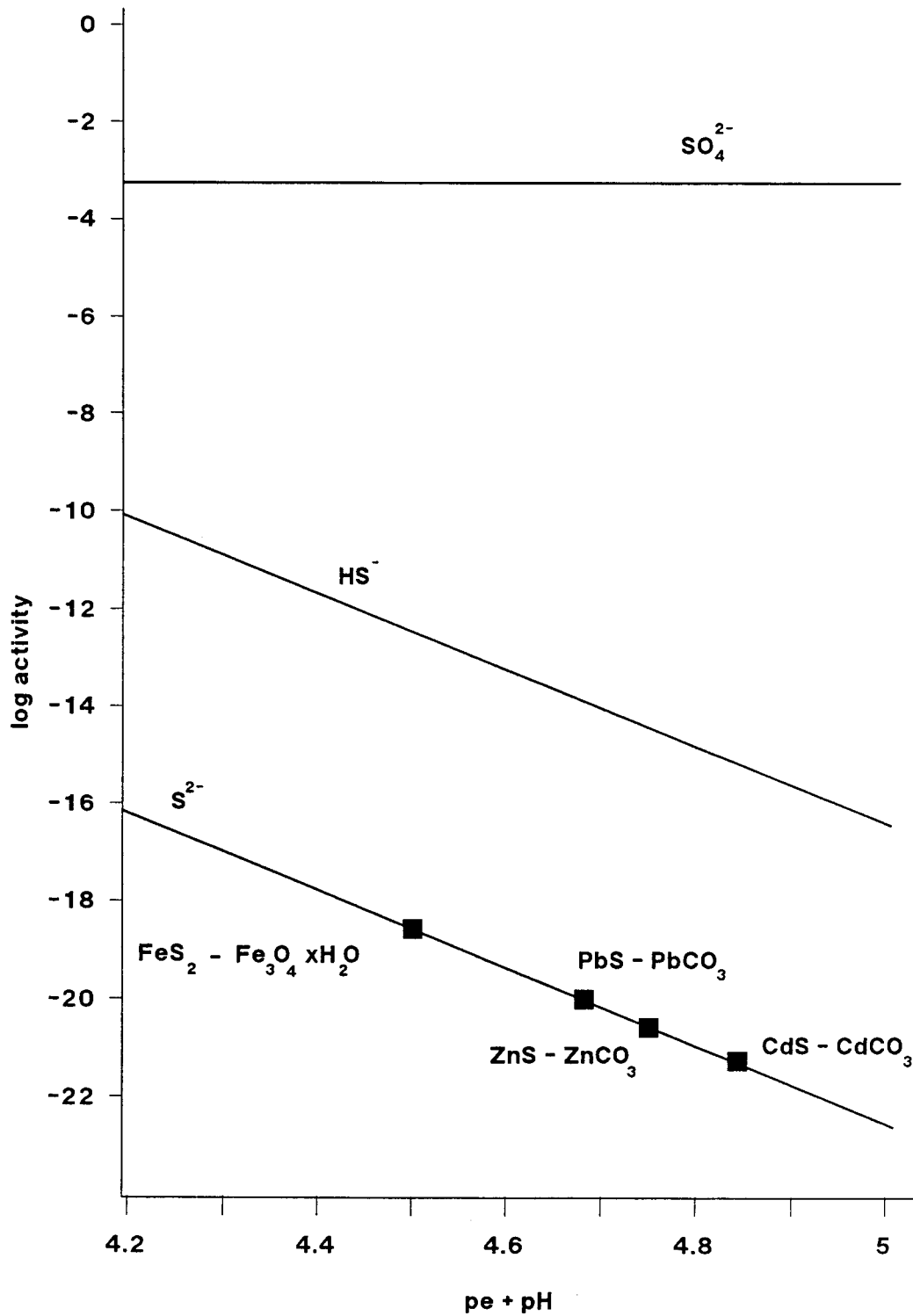
Fig. 15 Predicted order of metal sulfide precipitation based on data from study.

SUMMARY

The sequence of redox levels at which Fe, Zn, Cd, and Pb sulfides precipitate in a contaminated soil was determined. When soil-suspensions containing these metals were oxidized, the pH decreased, the concentrations of Zn, Cd, and Pb increased, and that of Fe decreased. The addition of electrons to these suspensions from decomposing organic matter and enzymatic degradation of $H_2(g)$ resulted in increases in pH and decreases in pe + pH. As a result, the concentration of Zn, Cd, and Pb decreased while Fe concentrations increased. For pe + pH values between 14 to 8, Fe was controlled by $Fe(OH)_3$(amorp). Further decreases in pe + pH showed that $Fe_3O_4 \cdot xH_2O$(edlinte) controlled Fe solubility. The dissolution of these Fe minerals was the primary driving force for increasing pH. At the lowest pe + pH, solutions were near saturation to FeS_2(pyrite).

For Zn, Cd, and Pb, the initial soil suspensions were extremely undersaturated with respect to carbonates of these metals. Increases in pH and lowering pe + pH to 5, brought the solutions close to equilibria with $ZnCO_3$(smithsonite) and $CdCO_3$(octavite) and slightly super saturated with respect to $PbCO_3$(cerrusite). When pe + pH was further reduced, Zn, Cd, and Pb showed near equilibrium with ZnS(sphalerite), CdS(greennokite) and PbS(galena).

Using $Fe_3O_4 \cdot xH_2O$(edlinite), $ZnCO_3$(smithsonite), $CdCO_3$(greennokite) and $PbCO_3$(cerrusite) as controlling

minerals, it is possible to predict the pe + pH at which
each sulfide precipitates. This simplified model indicates
the order of precipitation and the pe + pH at which each
occurs is 1) CdS(greennokite)(4.82), 2)
ZnS(sphalerite)(4.74), 3) PbS(galena)(4.69) and 4)
FeS_2(pyrite)(4.48).

As a result of the metal sulfide precipitations, the
solubility of Fe, Zn, Cd, and Pb are decreased. This is
especially significant for the toxic heavy metals, Zn, Cd,
and Pb. Continual additions of electrons will result in
movement of heavy metal activities down the metal sulfide
isotherms. Because of the steep slope for these isotherms,
a slight decrease in pe + pH results in a significant
decrease in the solubility of these metals. It is unlikely
that a substantial decrease in pe + pH would occur.

In this study, decreasing pe + pH from 14 to 5 required
25 d. For the solutions to decrease from 5 to 4.5, an
additional 35 d was required. The logical explanation for
this slow decrease in pe + pH is the buffering effect of co-
existing solid phase comprising $Fe_3O_4 \cdot xH_2O$(edlinte) and
FeS_2(pyrite). These minerals will co-exist until all of the
$Fe_3O_4 \cdot xH_2O$(edlinite) is dissolved and the Fe precipitates as
FeS_2(pyrite). Because of the large abundance of Fe in these
soils, this process requires long periods of time. The
presence of these two co-existing minerals will fix pe + pH
near 4.48. For this reason the pe + pH of submerged soils
seldom goes much below this level. Another possibility in

this reduction process is that SO_4^{2-} will be reduced to S^{2-} before all Fe^{3+} is reduced to Fe^{2+}.

RESEARCH SUMMARY

Research on this project lead to the discovery of a new iron oxide precipitate, $Fe_3O_4 \cdot xH_2O$. This mineral forms as an amorphous, mixed valency, iron oxide under strongly reducing conditions. It can form both as an oxidized environment becomes reduced and also as a highly reduced environment becomes oxidized. The measured value for the dissociation constant for this mineral is :

$$\underline{\log K^\circ}$$

$$Fe_3O_4 \cdot xH_2O + 8H^+ + 2e^- \longleftrightarrow Fe^{2+} + xH_2O \qquad 40.65$$
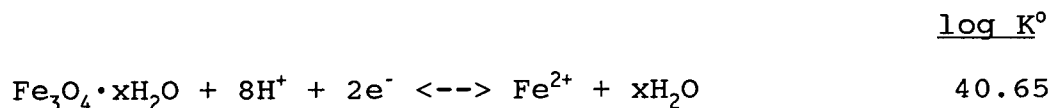
This mineral most likely controls the solubility of iron in many bog-like areas. Although the mineral is metastable to other known iron minerals, its formation and persisitance was demonstrated over the pe + pH range of 4 to 13. Under low redox conditions where oxygen is highly limiting, Fe_3O_4(magnetite) is favored while in redox environments above pe + pH 12, $Fe(OH)_3$(amorphous) is preferentially formed. The discovory of this mineral and the redox relationships that accompany its presence is an important contribution to environmental soil chemistry.

The heavy metal sulfides of polluted soils and sediments taken from the California Gulch area near Leadville, Colorado add considerably to our knowledge of how changing redox affects the formation and dissolution of

metal sulfides under bog conditions. Surface oxidation of sulfide ore wastes applied in 1910 to the bog used in this study showed considerable downward movement of the metals Zn, Cd, and Pb (approximately 55 cm). When soils samples removed from the reduced bog were oxidized, the sulfides transformed to sulfate with the release of high amounts of acidity causing the pH to drop to around 3 to 4. Under these conditions the metal concentrations in solution increased. When the soils were once again reduced, the pH rose to near 7 and the metals precipitated as predicted in the study research proposal. The solubility controls of these metals approached those of their carbonate minerals as redox was lowered to pe + pH near 5.0.

As redox was lowered even further, sulfides of Cd, Zn, Pb, and Fe precipitated in that order. The solid phase mineral combinations that controlled these metal solubilities when sulfides precipitated were: $CdS-CdCO_3$, $ZnS-ZnCO_3$, $PbS-PbCO_3$, and $FeS_2-Fe_3O_4 \cdot xH_2O$. Because of the abundance of Fe oxides, the latter pyrite-$Fe_3O_4 \cdot xH_2O$ mineral couple controlled the solubilities of all the precipitated heavy metals: Cd, Zn, Pb, and Fe through their sulfides.

This study has demonstrated in a very vivid way the effect of redox on the formation and dissolution of metal sulfides and the role that sulfides play in immobilizing heavy metals in reduced environments as occur in bogs. This knowledge can be used to develop guidelines for the management of bogs to avoid the dangers that can occur in

the future should the bogs be drained and oxidized

conditions return.

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REFERENCES CITED

Alexander, M. 1977. Introduction to soil microbiology. J. Wiley & Sons. New York

Barrow, N.J. 1987. Reactions with variable-charge soils. Martinus Nijhoff. Dordrecht.

Daskalakis, K.D. and G.R. Helz. 1992. Solubility of CdS(greenockite) in sulfidic waters at 25 °C. Environ. Sci. Technol. 26:2462-2468.

Levy, D.B., Barbarick, K.A., Siemer, E.G., and Sommers, L.E. Distribution and partitioning of trace metals in contaminated soils near Leadville, Colorado. J. Environ. Qual. 21:185-195.

Lindsay, W.L. 1979. Chemical Equilibria in Soils. Wiley-Interscience, New York.

Licht, S. 1988. Aqueous solubilities, solubility products and standard oxidation-reduction potentials of the metal sulfides. J. Electrochem. Soc. 135:2971-2975.

Santillan-Medrano, J. and J. Jurinak. 1975. The chemsitry of lead and cadmium in soil: Solid phase formation. Soil Sci.Soc. Proc. 39:851-856.

Stevenson, F.J. 1982. Humus Chemsitry. J. Wiley & Sons. New York.

Workman, S.M. and W.L. Lindsay. 1990. Estimating divalent cadmium activities measured in arid-zone soils using competive chelation. Soil Sci. Soc. Am. J. 54:987-993.