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HEAVY METAL MOBILIZATION RESULTING FROM HYDROGEN PEROXIDE TREATMENT OF CONTAMINATED SOIL

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

William Jon Caime
May, 1993

DEDICATION

This thesis is dedicated to my wife Monica Tara who has sacrificed substantially so that I may have this opportunity. This work is also dedicated to my parents, Bill and Joyce who have been a positive influence on my life.

ACKNOWLEDGMENTS

I would like to thank my major professor, Dr. Kevin Robinson, for his guidance and my other committee members, Dr. M. Ghosh and Dr. Bob Siegrist, for their comments and assistance. I would also like to express my thanks to Monica, my wife, for her encouragement, patience and sacrifice.

ABSTRACT

Recently, destruction of organic contaminants using hydrogen peroxide (H_2O_2) has been investigated. Peroxidation, as the process is called, may mobilize metals bound to soil thereby increasing the potential of groundwater contamination and exposure to humans. Mobilization of soil-bound Lead (Pb), Zinc (Zn) and Uranium (U) upon peroxidation of soils was investigated in the present study. We evaluated the viability of soil peroxidation as a means of organic contaminant destruction and the concomitant release of soil-bound metals.

An alluvial soil with an organic matter (OM) content of ≈ 1.3% (dry weight basis) was used in this study. This soil was digested with H_2O_2 under controlled conditions to obtain an OM content of 0.4%. The digested soil was utilized to evaluate the effect of peroxidation upon metals bound to the soil mineral component and refractory OM.

Both soils were loaded with each metal (30 mg/kg) and treated with 0 to 32 mg H_2O_2/g soil (0-3% wt./wt.). Additional peroxide tests were conducted utilizing multiple peroxidation treatments and varying peroxide contact times.

Pb, Zn and U binding rates (kinetics) and equilibrium information (isotherms) were also investigated. These tests were conducted to gain an understanding of the metal binding system mechanics.

Soil peroxidation may change the pH of the system which may result in mobilized metals. The pH was monitored during soil peroxidation and observed pH changes were modeled in subsequent testing with an acid and base. Additional testing with substantial pH changes induced by an acid and base were evaluated for comparison purposes.

Zn mobilization was detected in the natural soil at an H_2O_2 loading $\geq$10 mg H_2O_2/g soil. Zn in the digested soil did not mobilize under the peroxide loadings tested indicating that Zn binding to this soil was to unoxidizable soil mineral components or refractory soil OM. Minimal mobilization of Pb and U was observed in either soil upon single H_2O_2 treatments with concentrations $\leq$32 mg H_2O_2/g soil which may denote a similar binding as observed with Zn in the digested soil.

Metal mobilization was observed upon multiple peroxidation treatments at H_2O_2 loadings of 32 mg H_2O_2/g soil. Upon repeated treatments, decreasing Zn mobilization and continuous Pb mobilization occurred. Additionally, longer H_2O_2 contact times resulted in increased metal mobilization. The extended contact times may have resulted in increased oxidation of metal binding sites.

A slight pH change in the soil was observed upon peroxidation, however this pH change resulted in no mobilized metal indicating that a mechanism other than pH change resulted in the mobilized metal observed during soil peroxidation. A pH change of one and two units below the natural pH of 6.5, resulted

in significant Zn mobilization but no Pb mobilization. A change of one and two pH units above the natural pH, resulted in a slight decrease in Zn mobilization and no change in Pb mobilization.

In summary, H_2O_2 treatment of soils for the oxidation of organic contaminants does have the potential to release metals from the soil possibly due to the oxidation of OM/metal binding sites. Metal mobility appears to be a function of soil OM quantity, oxidant concentration, H_2O_2 contact time, number of repeated peroxide treatments and the specific metal sorbed.

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CHAPTER I. INTRODUCTION

Hydrogen peroxide (H_2O_2) oxidation was investigated as an in-situ method to destroy Trichloroethylene (TCE) at the Department of Energy's (DOE) Portsmouth Gaseous Diffusion Plant unit X-231b in Piketon Ohio (Siegrist et al, 1993). This process, called peroxidation, may however mobilize metals bound to the soil thereby increasing the potential for human exposure.

One of the primary mechanisms of metal binding in soils is by adsorption to soil OM. An H_2O_2 treatment of soil may oxidize soil OM with the potential of releasing metals by destruction of OM/metal binding sites.

Three metals studied in this research, Lead (Pb), Zinc (Zn), and Uranium (U), are all heavy metals of environmental concern in high concentrations and found in significant concentrations at DOE sites. Past research on Zn mobility in soils found this metal to be one of the most mobile metals in soils (Brown et al, 1983). Any mobilization of Zn from soil peroxidation may be representative of the worst case scenario for metals mobilization (i.e. maximum mobilization). Pb, however, has been found to be one of the least mobile metals in soils, (Scokart et al, 1983), therefor Pb mobilization from peroxidation may be representative of the opposite end of the metal mobilization spectrum. Limited information is available on U mobility in soils.

A change in soil pH may occur upon soil peroxidation which may impact the behavior of metals in a soil. The solubility of cationic metals increases as pH decreases due to increased competition for binding sites with H^+.

Soil peroxidation may also result in formation of organic ligands. These ligands may affect metal mobility by chelation or creation of a disequilibrium between sorbed and free metal.

Although Pb and Zn mobility has been evaluated in the past under other circumstances such as sewage sludge disposal, this research expanded on the limited work conducted on Pb and Zn mobility from soil peroxidation. This research differentiates metal mobility due to a pH change induced upon peroxidation which has not been extensively examined before.

No work on U mobilization as a result of soil peroxidation has been conducted. Additionally, limited work has been performed in the past on U mobilization under other conditions and on U binding to soils.

This research also evaluated the yet unstudied changes on rate and equilibrium of metal binding from H_2O_2 digested soils. A lower OM digested (using H_2O_2) soil was examined in this work for metal binding and mobilization.

The experiments conducted evaluated the viability of soil peroxidation as a means of organic contaminant destruction in regards to potential metal mobilization side effects. Isolating metal mobility from a pH change induced during peroxidation, coupled with the investigation of metal mobility in the digested

soil, allowed a determination of the causes of metal mobility during soil peroxidation, primarily from the oxidation of metal/OM binding sites.

CHAPTER II. LITERATURE REVIEW

II.1 INTRODUCTION

The physical and chemical aspects of metal binding to soils are important parameters for a comprehensive estimate of what is occurring in the matrix upon peroxidation. Among the important physical parameters are the extent of metal binding at equilibrium (isotherm). Metal mobilization is also dependent on pH, binding strength and chemical factors such as soil OM and soil composition.

Work on soil peroxidation and metal mobilization has been conducted in the past. The effects of physical and chemical soil properties upon soil peroxidation has been documented as well as a limited evaluation of metal mobilization. Prior to evaluating metal mobilization upon soil peroxidation, the mechanics of the system should be understood.

II.2 HEAVY METAL BINDING IN SOILS

II.2.1 Introduction

Heavy metals primarily bind to soils through interaction with soil surfaces or through the formation of precipitates within the matrix. These soil surfaces can be divided into two main

categories, soil mineral surfaces (such as clay minerals and hydrous oxides of Fe and Mn), and soil OM.

II.2.2 Mineral Surfaces

Mineral surfaces are important in metal binding to soils. Mineral surfaces include clays, oxides of Fe and Mn and exchangeable carbonates. In soils with digested contents, these constituents may be important in metal binding.

Nriagu (1980) reports that lime particles strongly adsorb to Zn. Another important mechanism of Zn fixation in soils is the precipitation of Zn as $Zn(OH)_2$ in alkaline soils (Alloway, 1990). Under acidic conditions, the mechanism of Zn adsorption to clays is by cation exchange, however, in alkaline conditions Zn penetrates clay lattice patterns which fixes Zn irreversibly (Nriagu, 1980).

Oxides of iron, aluminum and manganese interact in the amount of Zn adsorbed to soils. A decrease in these oxides may result in increased Zn adsorption (Nriagu, 1980). Shuman (1988) found that removal of Fe oxides raised the adsorption maximum of Zn. Although Zn was bound to Fe oxide coatings, more binding sites were available upon Fe oxide removal.

Removal of Mn oxides from these soils created the opposite result with a significantly reduced Zn adsorption capacity (Shuman, 1988). Shuman also observed that removal of Mn oxides from a soil with a high sand content did not significantly affect

the adsorption capacity. He determined that this was due to the small amount of Mn oxides in this sandy soil prior to Mn removal.

Shuman (1988) concluded that Zn adsorption decreased upon increasing sand content. He deduced that this phenomenon was a function of surface area with sandier soils having less adsorption surface available than clays.

Schintu et al (1991) found that organic matter is important in the binding of Pb to lake sediments, however, they found exchangeable carbonates and Fe-Mn oxides contained higher fractions of Pb. The researchers concluded that these fractions are most susceptible to chemical changes and may consequently result in the release of bound Pb. Sheppard et al, (1989) found that upon extraction of a soil with 1M NaOH, Pb was present in inorganic forms and a lesser amount was associated with organic materials.

Most cationic metals are readily sorbed by clays in soils due to a net negative charge normally associated with clays. Berthelin et al (1987), however, found that clays in natural soils are not sinks for U. These researchers also found that the clay type may influence the amount of U fixation with small amounts fixed to montmorillonite and kaolinite clays. A kaolinite-geothite clay mixture however, fixed almost 5 times the amount of U, possibly due to U binding with the ferric oxide in this clay mixture.

Ivanovich and Harmon (1982) determined that trace amounts of phosphate will complex most of the U in a soil. Carbonate complexes are very important in a slightly acidic to alkaline pH

but in the presence of phosphate, all the U will complex with the phosphate. In many situations, small quantities of phosphates will dominate U sorption.

II.2.3 Organic Surfaces

The primary inorganic ligands, Cl^- and SO_4^{2-}, effect on metal speciation in soil is minor in comparison to organic ligands (Bergkvist et al, 1989). Organic ligands can be divided into two groups: 1.biochemicals found in living organisms such as simple aliphatic acids, amino acids and sugar acids and 2.humic substances which are primarily humic acids (HA) and fulvic acids (FA) (Bergkvist et al, 1989). Bergkvist et al (1989) determined that humic materials complex metals in soil very efficiently. As the concentration of humic materials increased, they found that the quantity of metals bound to those materials also increased.

Scokart et al (1983) determined that Zn in polluted soils near Zn smelters was bound to the soil OM. These workers also found a correlation between Cd and Zn mobility and soil OM but did not find the same correlation for Cu and Pb. Other workers found that Cd and Zn behaved similarly in soil and that soil OM was the most important soil fraction adsorbing Zn (Miller et al, 1983). Mangaroo (1965) concluded that the amount of Zn adsorbed in soil was directly proportional to the soil OM content except in very acidic soils.

Soil OM is also important in Pb binding to soils. In acidic soils Pb combines with organic compounds of the soil (Alloway,

1990). Shuman (1988) determined that Pb adsorption in soil is controlled by OM and Fe/Mn oxide surfaces. Scokart et al (1983) and Miller et al (1983) also found a strong fixation of Pb with soil OM.

Berthelin et al (1987) determined that microorganisms may have an affect on U fixation in soils. They determined that small amounts of U were bound by cellulose but in conditions that allowed better development of microbial populations approximately 10 times the amount of U were fixed to the soil. Berthelin concluded that increased U fixation from microbial activity may have been the result of a transformation of the cellulose to a form that more readily binds U. They also suggested that some other microbial induced mechanism, that enhanced U fixation, may have occurred. Functional groups that permit U fixation are present in the degradation products of plant materials (cellulose, lignin) and also in microbial constituents. Sheppard et al (1989) reports that one study found up to 90% of the U in dilute solutions can be adsorbed onto microbial biomass.

Berthelin et al (1987) found that organic decomposition may create organic chelating agents that desorb U bound to soils. They observed that U mobilization depends on the humus type which is determined by factors such as vegetation and microbial activity. They found that U mobilization increases when organic acids that weather U bearing minerals are formed from the slow decomposition of soil organic matter (Berthelin et al, 1987).

Ivanovich and Harmon (1982) determined that following U adsorption by OM, the uranyl ion may be reduced to U^{4+}.

Soil OM is made of complex chemicals, the exact structure of which is not well defined. The two most important constituents of soil OM are HA and FA. Himes (1957) studied Zn adsorption to soil OM and determined that the humic fraction retained 59% and the fulvic fraction 12% of the total Zn adsorbed by the soil. Petruzelli (1981) determined that soil OM type was more important in metal binding than the amount of soil OM due to findings that soils with similar quantities of OM sorbed varying concentrations of Pb.

Schnitzer and Skinner (1966) mixed FA with Zn and determined that one mole of FA reacted with two moles of Zn. They discovered a low reactivity of Zn and FA. In comparison to other studies the reactivity was much lower than Zn reactivity with HA (Schnitzer and Skinner, 1966).

Kerndorff and Schnitzer (1980) studied the sorption of metals to HA and determined that Hg and Fe had a strong adsorption, Cu, Pb and Al had an intermediate sorption and Ni, Cr, Zn, Mn, & Co were weakly adsorbed to HA. They also determined that as Pb concentrations were lowered, the sorption of Pb to HA increased.

FA is completely water soluble and possesses a large number of oxygen containing functional groups which are important in metal-OM interactions in soils (Petruzelli et al, 1981). Sheppard et al (1989) found extraction of peat with 1M

NaOH yielded a solid HA product and a liquid FA product. From these extractions they detected little Pb in the HA fraction and less than 9% of the original Pb in the FA fraction.

U in soils can also be bound to soil OM by adsorption to HA (Gueniot, 1988). Sheppard et al (1989) found substantial U was recovered in the HA fraction especially at low concentrations. When combined with the FA fraction, they found 65 to 89% of the U was extracted by the base.

Humic materials such as peat and lignite will adsorb U from ground water efficiently (Ivanovich and Harmon, 1982). These workers found that peat with HA removed, adsorbed more U than peat that contained HA.

Kerndorff and Schnitzer (1980) reported that humic substances contain many oxygen-containing functional groups (CO_2H, phenolic and alcoholic OH) which interact with inorganic constituents. Metals interact with these functional groups especially with the primary functional groups of HA which are CO_2H and phenolic OH groups (Kerndorff and Schnitzer, 1980). Guy et al (1978) reported that the primary mechanism of metals binding to humic materials was by phenolic and benzene carboxylic acid groups. Alberts and Giesy (1983) and Beckwith (1959) identified the binding sites of metals with OM was with carboxyl and phenolic or hydroxylic groups.

Schnitzer and Skinner (1965) discovered that OM and Zn had two reactions. The major reaction involved both acidic carboxyl

and phenolic hydroxyl groups. A secondary minor reaction of Zn and OM was with less acidic carboxyls.

Guy et al (1978) found that binding of heavy metals to the phenolic and benzene carboxylic sites of HA was by complexation and ion exchange. Tan et al (1971) studied the organic fraction of sewage sludge upon extraction with 0.1N NaOH and determined that binding was via covalent bonds between OH groups of FA, and electrovalent bonds between COO^-. The carboxylic and phenolic binding sites may disassociate below pH 7 (Buffle et al, 1977). Buffle also found that the ratio of phenolic to carboxylic sites was 1:2 .

II.3 MOBILITY OF METALS IN SOILS

II.3.1 Introduction

The occurrence of heavy metals in soils is not the primary concern in many environmental situations. When these metals mobilize, however, potential problems may arise, in particular the possibility of groundwater contamination and exposure to humans may increase.

The mobility of metals in soils is often dependent on the stability of binding within the soil matrix. The metals evaluated in this research where chosen due to their varied mobility in soil.

II.3.2 Metal Mobility Comparisons

Metals may mobilize within a soil matrix from two sources. The first is when soil OM in top soil, containing metals, mineralizes releasing bound metals (Bergkvist et al, 1989). These metals may then be transported in percolating soil water. This is especially true with Pb that tends to remain in the upper layers of soils when deposited. Bergkvist et al (1989) reported that Pb forms stable complexes with dissolved organic acids and is transported through soil in a complexed form. As these organic acids percolate through the soil, they become saturated with Al and Fe and precipitate (Bergkvist et al, 1989).

The second source of metal mobilization is from soils becoming acidic (Bergkvist et al, 1989). Zn is very sensitive to changes in soil acidity (Bergkvist et al, 1989). Zn is one of the most mobile metals in soils. An analysis of trenched sewage sludge found Zn to be the only metal of those analyzed that migrated into the soil (Sikora et al, 1980). An additional study found the mobility of Zn to be 10 times the mobility of Cu (Brown et al, 1983). Some reports found Ni to be the most mobile metal in sludges (Kotuby-Amacher and Gambrell, 1988), however, other researchers (Brown et al, 1983) have found Ni mobility to be similar to that of Zn.

Kotuby-Amacher (1988) determined that the formation of Pb complexes with anions such as Cl^-, F^-, CO_3^{2-}, HCO_3^{2-} and OH^-, increased the solubility. These complexes prevented the sorption of Pb on soil surfaces. Pb is strongly adsorbed in soil under high

pH, CEC and available phosphorous conditions but under reduced or acidic conditions it has the potential to become mobile (Brown et al, 1983). Pb deposited on soils however, does not tend to migrate far into soil subsurfaces.

The oxidation state of U can determine the magnitude of U mobilization in soil. U^{4+} has a lower solubility and binds more tightly to soils than U^{6+}, however, weathering causes the oxidation of U^{4+} to U^{6+} (Clarkson, 1991; Bondietti and Tamura, 1980).

Important mechanisms of U immobilization in soils are ion exchange, adsorption and precipitation (Polzer et al, 1981). Essington et al (1981) found that U associated with $CaCO_3$ precipitates had reduced mobility. Tetravalent U can replace Ca^{2+} in soils (Alloway, 1990).

Brown et al (1983) established the mobility of metals from land applied sewage effluent to be in the order of Cd =Zn =Ni>Pb>Cu. Scokart et al (1983) found similar results with the available fraction of metals in decreasing order to be Cd>Zn>Pb>Cu. Sheppard and Thibault (1991) studied leaching over a four year period and established the mobility of these metals in the order: I>>Tc>>Cr>Np>Mo>Cs≥U>Th.

Kerndorff and Schnitzer (1980) studied the competition of 10 metals for sorption on HA. As the concentration of metals were increased only Hg, Fe and Cr and to a lesser extent Al, Pb and Cu remained complexed to the HA. Zn, Ni and Mn became displaced by the other metals. Upon further increases in metal concentrations,

Hg, Fe and Cr displaced the Al, Pb and Cu. Hg was retained most firmly and could not be displaced by the other 10 metals (Kerndorff and Schnitzer, 1980).

II.3.3 Binding Strength

The stability constant (log K) of a metal is a measure of the strength of association between complex ions and ion pairs (Bohn, 1979). Stability constants help predict the behavior of metals in soils. The fate of a metal ion in soil will often depend on the stability of complexes with OM (Schnitzer and Skinner, 1967).

Fulvic acid is a constituent of soil OM that possesses a large number of oxygen containing functional groups that are important in metal-OM interactions in soils. Schnitzer and Skinner (1966) have established FA metal ion stability constants reported in table 1. Other stability constants for important functional groups of soil OM are also reported in this table.

Schnitzer and Skinner (1966) mixed FA with metals to study binding and determined that the number of bonds to FA was not as important as the strength of those bonds in the determination of stability constants. They found that Zn reacted with more functional groups of the FA than Cu and Fe but the stability constant was much lower.

Schnitzer and Skinner (1967) determined the stability constants for several fulvic acid and metal ion complexes. They established the log K at pH 3.5 in the order of Cu >Fe >Ni >Pb >Co

>Ca >Zn >Mn >Mg and at pH 5.0 in the order of Cu >Pb >Fe >Ni >Mn =Co >Ca >Zn >Mg.

TABLE 1
Selected Stability Constants (Log K)

Metal	Complexing Agent	pH	Log K	Reference
Zn	FA	3.5	1.73	Schnitzer & Skinner(1966)
Zn	FA	5	2.34	Schnitzer & Skinner(1966)
Zn	High mol. wt. FA	5.5	0.72	Tan et al (1971)
Zn	Low mol. wt. FA	5.5	1.75	Tan et al (1971)
Zn	Low mol. wt. FA	7.0	6.76	Tan et al (1971)
Pb	FA	3.5	3.09	Schnitzer & Skinner(1967)
Pb	FA	5	6.13	Schnitzer & Skinner(1967)
Zn	HA	3.5	4.42	Schnitzer & Skinner(1966)
Zn	HA	5.6	6.18	Schnitzer & Skinner(1966)
Pb	NOM	4.6	5.09(+/- 0.46)	Alberts and Giesy (1983)

FA = Fulvic Acid

HA = Humic Acid

NOM = Natural Organic Matter

II.4 ISOTHERM

II.4.1 Introduction

The adsorption of metals on soils can be described by isotherm models that have been developed. Two such models that are most widely accepted for the explanation of metal binding are the Langmuir and Fruendlich models. Prior to a discussion on these models it is necessary to investigate the physical properties of metal binding.

II.4.2 Adsorption of Metals

The physical binding of metals to a soil can be explained by adsorption (binding of metal to the soil surface), or absorption (penetration of metal into soil surfaces)(Weber, 1972). The term sorption is used to describe both mechanisms in which a metal moves from the aqueous phase and is accumulated on the soil.

Weber describes the magnitude of adsorption dependent on the solubility of a substance in solution and/or the preference of a substance for the solid surface. Weber explains that sorption is usually a combination of three forces; electrical attraction, van der Waals forces and chemical binding.

Ion exchange is a form of electrical attraction in which ions are drawn towards charged sites on a solid surface displacing other ions already present. An ion with a higher valence may be more strongly attracted to that surface than one of lower valence (Weber, 1972). When ions contain equal charge, a smaller hydrated

radius of the ion may be the determining factor of adsorption with smaller ions drawing nearer to adsorption sites. At higher concentrations, the charge of an ion is not as important with ions of varying charge exchanging to similar magnitudes (Weber, 1972).

In general the preference of an ion for a surface will increase with an increase in atomic number in a given series, due to an increasing ionic radius (Weber, 1972). The ionic radius is inversely proportional to the hydrated radius.

With van der Waals attraction adsorbed ions are not fixed to a particular site and can undergo movement on the surface. Ions that are chemically adsorbed, however, are fixed and do not move on the solid surface.

II.4.3 Langmuir Isotherm

The equilibrium between a substance in solution and adsorbed by solids can be represented as a plotted diagram called an adsorption isotherm. The Langmuir isotherm was originally developed to describe the adsorption of gases on solids and has since been used to describe the relationship between the adsorption of ions by solids (bound) with the concentration of ions remaining in solution (free). The langmuir isotherm can be used to estimate the total adsorption capacity of a soil for metals.

The Langmuir isotherm follows the equation (Weber, 1972):

$$q_e = \frac{Q^0 bC}{(1 + bC)} \qquad \text{(Equation II.4.a)}$$

where:

b=a constant related to the energy or net enthalpy, ΔH, of adsorption ($b \propto e^{\Delta H/RT}$) commonly referred to as the "Langmuir bonding energy coefficient"

C= concentration of metal remaining in solution at equilibrium

Q^o= maximum amount of metal that can be adsorbed for monolayer

q_e= amount of metal adsorbed per unit weight of soil

Equation II.4.a can be rearranged to the linear form of equation II.4.b which is illustrated in figure 2.1 (Weber, 1972):

$$\frac{1}{q_e} = \frac{1}{Q^o} + \left(\frac{1}{bQ^o}\right)\left(\frac{1}{C}\right) \qquad \text{(Equation II.4.b)}$$

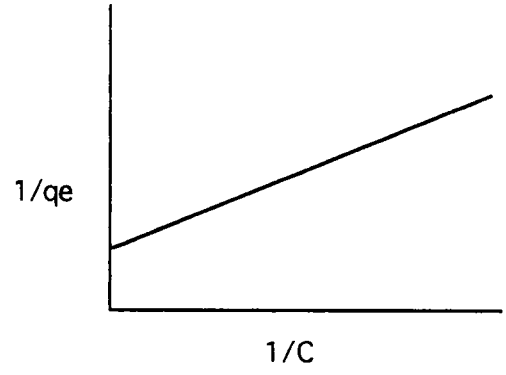


Figure 2.1 Illustration of Linear Langmuir Isotherm

Many researchers choose to use the terms "K" and "b" to describe the langmuir isotherm parameters. The term "K" is often used to describe the langmuir bonding energy coefficient which is the same as the term "b" in equation II.4.b. The commonly used

term "b" in the literature is the maximum amount of metal that can be adsorbed by the solid surface which is the same as the term Weber uses of "Q^o" in equation II.4.b.

Veith and Sposito (1977) caution that to use the langmuir model one must be certain that adsorbed ions are bound in monolayer on uniform localized sites. In addition they warn that the energy of adsorption must be the same for each ion so that there are non competing ions.

Shuman (1975) studied the adsorption of 8 different Zn concentrations in equilibrium with soil and found that the adsorption profile fit the Langmuir isotherm. Gerritse (1984) also found that Zn and Pb adsorption fit a Langmuir isotherm.

Shuman (1975) determined that there were two linear portions for plotted Zn adsorption data, one for lower Zn concentrations and another for higher concentrations. He found that the Langmuir isotherm profile was a better fit for the lower Zn concentrations curve than the higher concentrations curve. Shuman reported the adsorption capacity (Q^o) and bonding energy (b) were higher for soils high in clay or OM indicating that OM is involved in a high bonding energy.

Upon removal of Fe from soils, Shuman (1976) determined that the adsorption capacity (Q^o) for Zn increased. He also observed that the Zn adsorption isotherm fit the Langmuir model better upon Fe removal and did not have two separate linear parts. Shuman (1988) also found that the adsorption maximum (Q^o) was higher for finer textured soils than whole soils.

Shuman (1976) observed that bonding energies (b) were inversely related to adsorption capacity. He found that when the capacity of a soil to adsorb Zn is high, the energy with which the Zn is held is low.

Upon destruction of soil OM by H_2O_2, Petruzelli et al (1981) found a decrease in the maximum adsorption capacity (Q^o) of all the soils they studied and an increase in bonding energy (b) for some of the soils he studied. He concluded that humic substances are very important to Pb adsorption since the bonding energy (b) decreased after peroxidation.

II.4.4 Fruendlich Equation

A second isotherm equation is the Fruendlich equation in which the energy term (b) varies as a result of surface coverage (q_e). In this equation, the energy of adsorption decreases logarithmically as the surface becomes covered (Bohn, 1979).

The general form of the Fruendlich equation is :

$$q_e = K_f C^{1/n} \qquad \text{(Equation II.4.c)}$$

where:

K_F and n are constants and the other factors are the same as described above.

The data are usually fitted into the logarithmic form (Weber, 1972):

$$\log q_e = \log K_f + \frac{1}{n} \log C \qquad \text{(Equation II.4.d)}$$

This equation gives a straight line as illustrated in figure 2.2, with slope $^1/_n$ and an intercept where the log K_F is equal to 1 (log C=0) (Weber, 1972). This intercept is a rough gauge of sorption capacity and the slope ($^1/_n$) of adsorption intensity (Weber, 1972).

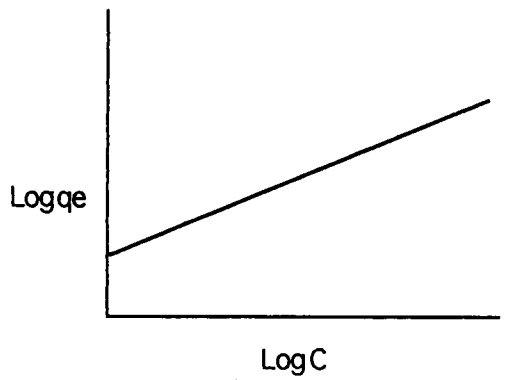


Figure 2.2 Illustration of Linear Fruendlich Isotherm

II.4.5 Comparison of Isotherms

In comparison of the two isotherm equations, the Langmuir equation is based on the assumption that the maximum adsorption occurs upon the saturation of a monolayer (Weber, 1972). Figure 2.3 is an illustration of this concept. This equation also assumes that adsorption energy remains constant and that bound metals do not migrate on the solid surface (Weber, 1972).

The Fruendlich equation however, assumes that the adsorption energy decreases as the extent of surface coverage

increases (Bohn, 1979). The Fruendlich equation does not predict an adsorption maximum. Figure 2.4 is an illustration of adsorption using the Fruendlich model. The two models do not match well at high concentrations (C) or at low concentrations (Weber, 1972).

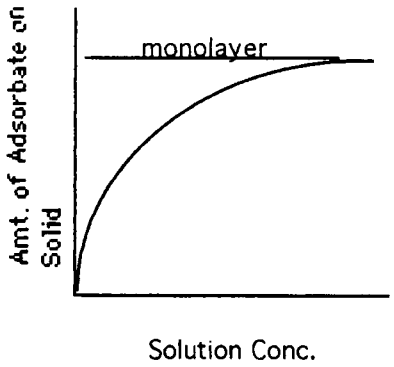


Figure 2.3. Monolayer Saturation of Langmuir Model

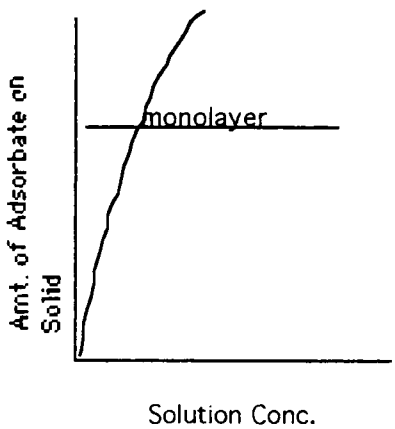


Figure 2.4 Illustration of Adsorption With the Fruendlich Model

II.5 pH EFFECTS ON METAL MOBILITY

II.5.1 Introduction

pH is an important parameter in metal mobilization from soils. Heavy metals will desorb below pH 3 due to the H^+ ions competing with cationic metals for adsorption sites (Dumontet et al, 1990). Hydrogen and hydroxyl ions are adsorbed strongly to soils (Weber, 1972). Upon soil peroxidation, a change in soil pH may occur which may impact the behavior of metals in a soil.

II.5.2 Metal Mobilization upon a pH Change

Zn is significantly affected by a change in pH. The solubility of Zn increases as pH decreases. Scokart et al (1983) and Alloway (1990), found Zn to be mobile below pH 5. At a pH of 4.2-6.6 Zn is readily mobile and at a pH 6.7-8.8 Zn is moderately mobile (Clarkson and Marian, 1991). Bergkvist et al, (1989) also found that the mobility of Zn increased with soil acidity with the critical pH at 4.0-4.5. Lindsay (1980) developed the relationship of pH to Zn concentration as $[Zn^{2+}] = 10^6[H^+]^2$.

Shuman (1975) also observed that pH is important in Zn adsorption to soils, especially on sandy soils. Above a pH of 8 he determined that all the soils studied removed similar amounts of Zn which he concluded was due to chemical precipitation of the Zn. Mangaroo (1965) found higher Zn adsorption in soils formed under a slightly acid or neutral conditions than soils formed under very acidic conditions.

Pb is usually tightly bound to soils and very immobile, however, extreme pH changes can mobilize Pb. Soil pH was found to be the property that most influenced metal mobility in a soil contaminated with Pb from a Pb battery acid facility (Kotuby-Amacher and Gambrell, 1988). Alloway (1990) found that a reduction in soil pH to 2.5-3 mobilized Pb however Gerritse (1984) found Pb much less affected by pH than Zn.

Bergkvist et al (1989) found that Pb was unaffected by added acidity to a soil. They determined that Pb was affected more by the release of OM. However, they also observed that complexation of Pb with OM significantly increased with an increase in pH and OM concentration.

Sheppard et al (1989) discovered that only 24% of the Pb in a soil was extractable with heated H_2SO_4 acid hydrolysis. This indicated that the Pb was very strongly bound to the soil due to the small extraction obtained with this severe process.

pH is an important factor in the mobilization of U in soils. Below pH 7.5, U may adsorb to soil but above pH 7.5 uranyl carbonate complexes can form which are soluble (Bondietti and Tamura, 1980).

Polzer et al, (1981) added a low level radioactive waste containing U to soils and observed that pH decreased which caused a decrease of carbonate. Polzer determined that this reduced the amount of U-carbonate complexation and generated new U species such as UO_2^{2+} or $UO_2(OH)_2$, that may have sorbed due to ion exchange or precipitation. An acidic pH, however, is known to

mobilize cationic metals in soils due to the competition of H^+ ions with cationic metals for soil sorption sites.

Distinct chemical species of U minerals are affected to different degrees upon a soil pH change. Berthelin et al (1987) studied the solubilization of U from 3 types of U-bearing rocks and minerals, phosphorite or natural rock phosphate, syenite, and natural uranium oxide. He found that the mobilization of U from these parent materials increased in acidic soil conditions. Syenite was influenced the most with 72-93% of the U mobilized when exposed to acidic soils. Uranium oxide was affected to a lesser degree with 32-45% of the U mobilized. The phosphorite had less U mobilization primarily due to phosphorite being less sensitive to acid soil conditions.

The charge of U in soils, which can be determined by pH, is an important parameter in U mobilization. Soils tend to be negatively charged and can adsorb U by cation exchange (Fowler et al, 1981) but the addition of a waste may change the pH. This pH change may affect the charge of the U and create an anionic U complex which will not bind to soils and be mobile. Fowler et al (1981) found that at a pH of 4.3 to 11.8 the charge on $^{233,234}U$ species in a particular waste were negative. Uranyl humates are insoluble in the pH range 2.2 to 6 with maximum U adsorption occurring at pH 4-5. Uranyl fulvates are insoluble in the pH range of 6 to 6.6 (Ivanovich and Harmon, 1982).

II.5.3 pH Effects on Stability Constants

A change in soil pH may affect the stability of a metal bound to a soil. Schnitzer and Skinner (1967) determined that stability constants were affected by a change in soil pH. These researchers found that log K values for FA and metal ions increased upon an increase in pH.

Tan et al (1971) examined the organic fraction of a sewage sludge extracted with 0.1 N NaOH. They found that when the pH increased from 5.5 to 7.0, a 10 fold increase in Zn complexation with low molecular weight FA occurred. In addition they observed an increase in the stability constant of this complex from 1.8 to 6.8.

Kerndorff and Schnitzer (1980) studied the sorption of metals to HA and concluded that raising the pH from 2.4 to 5.8 increased metal sorption to HA. They found that metal sorption was in the following decreasing orders at the pH values shown:

At pH 2.4: Hg >Fe >Pb >Cu =Al >Ni >Cr =Zn =Cd =Co =Mn,

At pH 3.7: Hg =Fe >Al >Pb >Cu >Cr >Cd =Zn =Ni >Co =Mn,

At pH 4.7: Hg =Fe =Pb =Cu =Al =Cr >Cd >Ni =Zn >Co >Mn,

At pH 5.8: Hg =Fe =Pb =Al =Cr =Cu >Cd >Zn >Ni >Co >Mn.

II.5.4 pH Effects on Soil Peroxidation

pH may also affect soil peroxidation. Bermond and Benzineb (1991) studied the extent of readsorption following extraction of heavy metals with H_2O_2. They observed that a high pH may reduce readsorption and may also reduce the kinetics of readsorption.

Douglas (1971) found that the addition of H_2O_2 to a soil caused the soil pH to become acidic, however, H_2O_2 added to an OM free clay resulted in a negligible pH change.

Hosking (1932) found complete oxidation of soil OM only occurring with a soil pH more acid than 5.8. He was able to develop the following equation on the effect of pH on OM oxidation by H_2O_2:

$$\text{Log}\left(\frac{x}{100 - x}\right) = K(pH - pH_1) \qquad \text{(Equation II.5.a)}$$

where:

x = portion of oxidizable OM destroyed at a pH being studied

pH_1 = pH where loss of OM from peroxide treatment is 50%

K= empirical constant

II.6 SOIL PEROXIDATION

II.6.1 Introduction

Robinson and Jones (1925) used H_2O_2 to study the decomposition of OM. Tessier et al (1979) suggested the use of soil peroxidation for the measurement of metals sorbed to the OM fraction of soils during sequential extraction procedures.

During soil peroxidation, however, the physical and chemical aspects of the soil and of metal binding may be altered. Metal may mobilize from a single H_2O_2 treatment, however the possibility exists that multiple treatments may mobilize additional metals.

The H_2O_2 contact time may also be an important factor in metal mobilization.

II.6.2 Effects on Chemical Properties of Soil

In addition to mobilizing metals, the peroxidation of a soil may result in chemical changes to the soil. Griffith and Schnitzer (1977), identified several products in the peroxidation of soil OM. Water-soluble organic compounds produced from peroxidation were primarily humic and fulvic acid degradation products such as n-alkanes, aliphatic acids, phenols and phenolic acids, benzenecarboxylic acids and N- and S- containing compounds. The most abundant group were the phenolics. The functional groups of the aromatic rings following peroxidation were OH and CO_2H. In addition, OM was also transformed to typical byproducts of CO_2 and H_2O. Organics that resisted peroxidation were primarily n-alkanes and n-fatty acids that were held strongly to the inorganic soil constituents such as clays and hydrous metal oxides (Griffith and Schnitzer, 1977).

Jordao and Nickless (1989) discovered that mobilized copper following soil peroxidation readsorbed over time onto unoxidizable OM. They determined that this unoxidizable OM consisted of paraffin-like materials and resistant structural residues.

Griffith and Schnitzer (1977) observed that $^2/_3$ to $^4/_5$ of the total N resisted oxidation possibly due to the low C:N ratios of the soils studied. The oxidation of soils containing large quantities of

OM under acidic conditions will produce NH_4^+ which is then fixed to clay minerals, however they did not find this to be true with their experiments.

McLean (1931) found that H_2O_2 addition to a soil oxidized organic compounds containing both carbon and nitrogen. Subsequent H_2O_2 treatments however, resulted only in the oxidation of nitrogen free organic compounds. McLean surmised that oxidizable nitrogen free residual OM compounds were of a cellulose quality while nitrogen containing OM compounds were unoxidizable.

An additional study found nitrogen losses were much smaller than carbon losses upon soil peroxidation (Hosking, 1932). Hosking also concluded that in some instances only compounds containing no nitrogen were attacked while in others all compounds were attacked to the same extent. Hosking noted that the carbon-nitrogen ratio of residual OM had a similar ratio as proteins and amino acids.

II.6.3 Effects on Physical Soil Properties

The peroxidation of soil may result in physical changes to the soil. In one study, the peroxidation of clays without organic matter resulted in a small degradation of clays as determined by X-ray diffraction, however, the addition of H_2O_2 to clay with sucrose caused significant clay alteration (Douglas and Fiessinger, 1971). Douglas and Fiessinger also determined that using a 1N sodium acetate buffer (pH 5) during peroxidation

minimized the degradation of clays with sucrose by preventing strongly acidic conditions.

Farmer and Mitchell (1963) also concluded that the properties of clays were altered significantly during the oxidation of OM with H_2O_2. These workers determined that water soluble chelated oxalates formed and possibly combined with aluminum and iron on clay surfaces.

Martin (1954) discovered that calcium oxalate was formed during soil peroxidation which may have resulted in an incomplete oxidation of soil OM. The calcium ions were supplied by $CaCO_3$ in the soil. Martin determined, however, that calcium oxalate formation in soils should not be a significant consideration due to the fact that this formation was found in only 5% of soils he sampled.

Farmer and Mitchell (1963) studied the decomposition of calcium oxalate during peroxidation and determined that the following changes occurred:

$$CaC_2O_4 \cdot 3H_2O \rightarrow CaC_2O_4 \rightarrow CaCO_3 + CO(g) \rightarrow CaO + CO_2$$

Tessier et al (1979) found a partial alteration of silicate material and mica upon soil peroxidation as did Burford et al (1964) who discovered that soil peroxidation lead to the exfoliation of mica crystal's edges.

Burford also found that the external surface area, as determined by low-temperature nitrogen adsorption, increased after soil peroxidation, especially for fine materials. A

determination of surface area by adsorption of cetylpyridinium bromide (CPB) to soils also showed an increase in surface area following soil peroxidation (Burford et al, 1964). This was explained as the removal of organic coatings of clays which may have prevented adsorption of CP^+ ions by blocking adsorption sites. In addition, the organic materials may have bound soil particles into aggregates blocking access to internal surface areas. From these findings Burford stressed the importance of the removal of organic matter prior to seeking the surface area of soil clays.

II.6.4 Effects on Metal Binding and Chemistry

Guy et al (1978) found that upon soil peroxidation, Copper (Cu) and Pb bound to soil organics mobilized but when bound to clays or hydrous oxides did not mobilize. These researchers also determined that metals bound to solid humic acid chemical mobilized upon H_2O_2 treatment but in the presence of clays did not mobilize as readily. This was explained by the mobilized metals readsorbing to the soil by exchanging with ions on clays (equilibrium between fixed metal and solution metal shifted). However, Hosking (1932) concluded that with lower amounts of clay more OM was completely oxidized during peroxidation which may result in increased metal mobilization.

Hosking (1932) also found less OM oxidation in alkaline soils containing free MnO_2 when treated with H_2O_2. Guy et al (1978) discovered that metals bound to humic acid in the presence of

MnO_2 did not mobilize as readily upon soil peroxidation. They concluded that this may have been due to two things. First the released metals may have readsorbed by the MnO_2. Secondly this may have been due to MnO_2 hindering the oxidation of humic acid by catalyzing the decomposition of H_2O_2 through the following reactions:

$$H_2O_2 + MnO_2 \rightarrow Mn(OH)_2 + O_2$$

$$H_2O_2 + Mn(OH)_2 \rightarrow MnO_2 + 2H_2O$$

Following soil peroxidation the capacity for metal sorption may change due to an alteration of soil characteristics. Bartlett (1936) found a loss of exchange capacity upon soil peroxidation. Petruzelli et al (1981) observed a significant decrease in the maximum adsorption capacity ("Q^o" value of equation II.5.b) for Pb following the destruction of OM by H_2O_2. Although the maximum adsorption capacity of the soils decreased, Petruzelli observed a significantly increased bonding energy coefficient ("b" value of equation II.5.b) and saturation of exchange capacity. He determined that new adsorption surfaces were created especially on clay surfaces.

II.6.5 Multiple H_2O_2 Applications

Multiple H_2O_2 applications may result in additional metal mobilization. In one report, the repeated H_2O_2 treatments of a Pb contaminated sediment resulted in Pb mobilization in the first treatment due to a strong oxidation of OM and the release of Pb

sorbed to OM (Rauret et al, 1989). In 3 subsequent treatments however, there was a decrease in Pb mobilization of approximately 50% with each successive treatment.

Rauret et al (1989) found a decrease in redox potential (Eh) upon repeated H_2O_2 treatments. They used Eh as an indicator of oxidant consumed to destroy OM. They observed sharp changes in Eh in the first extraction which indicated a strong oxidation of OM. Successive extractions had small Eh variations which suggested that no OM remained in solution.

II.6.6 Effects of H_2O_2 Contact Time on Metal Mobilization

The H_2O_2 contact time may also be an important factor in metal mobilization. Bermond and Benzineb (1991) studied the amount of mobilized Zn in sewage amended soils treated with H_2O_2 and determined that the magnitude of mobilized metal was dependent on time. The amount of Zn in solution reached a maximum and then decreased over time. This may have been due to mobilized metals readsorbing to the treated soil.

Rendell et al (1980) established that metal readsorption occurred during H_2O_2 treatment with a portion of the released metal readsorbing on the soil. They found that readsorption of mobilized metals increased with shorter extraction times. The decrease in readsorption over time may have been due to the release of organic ligands that are capable of competing with the soil for adsorbed metal or may have been due to the destruction of soil adsorption sites. Trace metals released during H_2O_2

treatment may also be competing with each other for available adsorption sites and with other metals such as Fe and Mn which were present in much higher concentrations.

II.7 LITERATURE GAPS

This research will expand on the limited knowledge of Pb and Zn mobilization upon soil peroxidation. The influence of a pH change during peroxidation has not been differentiated extensively which will be evaluated in this work. Additionally, this research will assess U mobilization from soil peroxidation which has not been conducted in the past.

The effects on metal binding mechanics such as kinetics and equilibrium information following soil digestion using H_2O_2 has not been evaluated. This research will also study this area.

CHAPTER III. MATERIALS AND METHODS

III.1 EXPERIMENTAL PLAN

The experimental plan flow chart is illustrated in figure III.1. Initial testing was conducted to determine the equilibrium contact time and isotherm information. Peroxidation tests were performed using single and multiple H_2O_2 treatments. Peroxidation side effect of pH change induced was also evaluated.

The primary purpose of this research was to evaluate the mobilization of Pb, Zn and U upon H_2O_2 addition to metal contaminated soil. The metals evaluated were chosen due to their varied mobility histories under other circumstances. Zn is fairly mobile in soils and Pb is relatively immobile. In order to estimate what is occurring during soil peroxidation, the rates of metal binding and equilibrium information was also sought.

Soil peroxidation may oxidize soil OM releasing bound metals. A digested soil that contained lower OM was therefor created to study the effects of metal mobilization due to soil peroxidation at binding sites on refractory OM and mineral surfaces.

The rate and equilibrium information was also necessary to produce a soil that was contaminated with Pb, Zn and U.

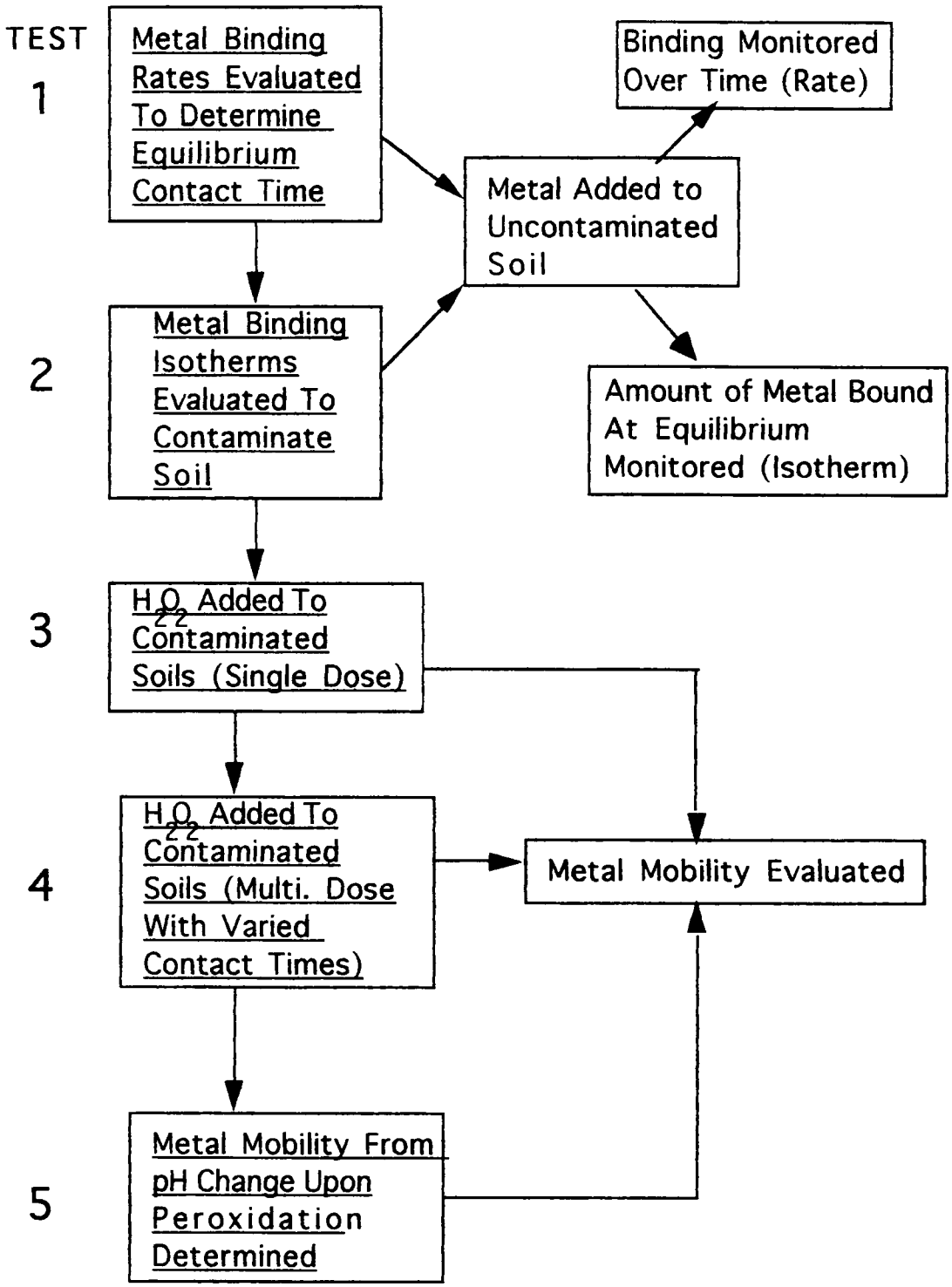


Figure 3.1 Experimental Plan Flow Chart

Additionally, this information gives insight into potential fates of these metals if mobilization occurred.

The peroxide tests were conducted initially with a single dose using varying concentrations of H_2O_2 to study the effects of dosage on metal mobilization. Additional tests were performed to evaluate the effects of multiple H_2O_2 treatments and varied H_2O_2 contact times.

The pH of the system may drop during soil peroxidation and result in mobilized metals. The pH change occurring during the addition of H_2O_2 was monitored and evaluated to differentiate this potential source of metal mobilization from mobilization due to oxidation of soil OM.

Soil peroxidation may also create organic ligands which mobilize metals. This was also monitored and assessed to separate this potential source of metal mobilization.

III.2 SOIL COLLECTION AND TREATMENT

The soil used in these experiments was collected approximately 100 meters east of lake Louden on the University of Tennessee Agricultural Experimental Farm located 15 kilometers south of Knoxville Tennessee. Ten centimeters of topsoil and organic litter was removed and discarded. The next 30 cm of soil was collected and placed in a cooler for transportation to the lab.

The moisture content of the soil was determined to be 1.93% (24 hour air dry) with a pH of 5.9. It was classified as sandy loam texture (55% sand, 29.7% silt, 14.8% clay) as determined by pipette method and sieve analysis for the sand fraction (Kilmer and Alexander, 1949). The soil had an organic carbon content of 1.23% as determined by TOC moderate temperature dry combustion (Nelson and Summers, 1982). The soil at the Portsmouth site was classified as a sandy clay loam texture (60% silt, 10% sand, 20-25% clay) with a lower organic carbon content (0.4%) than that of the soil collected. To closer represent field conditions, the collected soil was digested as described below to remove OM. After digestion, the soil OM content was 0.42%.

The method used to digest soil was developed by L.W. Zelazny at Virginia Tech. One hundred grams of undigested soil (sieved in a #4 sieve) was placed in a 2000 ml beaker which was partially immersed in a water bath. One hundred ml of 1N NaOAc (sodium acetate) buffer (pH= 5.0) and 50 ml of 30% H_2O_2 was added to the soil, the slurry stirred for 10 minutes, and then allowed to stand for 24 hours. The NaOAc buffer was prepared by adding approximately 17 ml of 10N reagent grade HCl to 700 ml of NaOAc.

After 24 hours, the soil solution was heated (30°C)while stirring for 10 minutes followed by heating at 65-70°C without stirring for 30 minutes. The volume of the soil slurry was then decreased from 2:1 to 1:1 (soil:liquid) by boiling (200-300 ml total final volume). While heating and stirring, ten ml of 30% H_2O_2

was added and allowed to react. This last step was then repeated once.

The resulting solution was then boiled to reduce the volume to <300 ml. The pH of the solution was adjusted to 8.0 with 24 mls of 1N Na_2CO_3. The solution was boiled 10 minutes to remove any remaining H_2O_2 , placed in 250 centrifuge bottles and centrifuged at 10,000 rpm for ten minutes.

The liquid portion was decanted and discarded and the soil was washed with 160 ml of 1N NaCl solution. The NaCl solution was added, soil was suspended by vigorous hand shaking and centrifuged. This washing was then repeated twice with distilled water rather than the NaCl solution by the same method. The soil finally was dried in an oven (180^0C) for approximately 2 hours, ground with a mortise and pestle and homogenized by mixing with a glass rod.

The available Fe content of the natural soil was determined by the DTPA digestion method set forth in the Methods of Soil Analysis (1982).

III.3 SAMPLE PRESERVATION AND ANALYSIS

All glassware, plastic, and laboratory equipment in contact with samples was acid washed to eliminate possible metal contamination of samples. All materials were soaked in Baxter SP Micro Laboratory Cleaning Solution for 24 hours, rinsed with tap

water and placed in a 6N nitric acid bath for an additional 24 hours. The materials were then triple rinsed in distilled water followed by triple rinsing with deionized (DI) water.

All experiments were performed using a solution of DI water adjusted to pH 7. The pH 7 was obtained by titrating approximately 1 ml of 0.2N NaOH into 2 L of DI water. This was done so that the DI water, with an initial pH of approximately 5, would minimize metal mobility. This pH 7 solution was used to dilute all stock metal solutions and as a wash water in the H_2O_2 experiments.

Metal standards were prepared by dilution of a stock atomic adsorption standard solution, purchased by Baxter Laboratory Supply Co., with the pH 7 DI water. The stock standard solutions consisted of 1 mg of metal per ml of solution in the following matrix:

Zn- Zn metal in HCl

Pb- $Pb(NO_3)$ in dilute HNO_3

U- $UO_2(NO_3)_2*6H_2O$

The standards and all samples were preserved by the addition of 0.05 ml concentrated double distilled HNO_3 per 30 ml of sample to a resulting pH of < 2. All standards and samples were stored at 4^oC to prevent volume loss per EPA method 3005 (EPA, 1986).

The sampling methods were per EPA method 7420 for Pb and 7950 for Zn (EPA, 1986). The samples were analyzed by atomic adsorption spectroscopy using an Aa/ae Spectrophotometer Video 12 (Instrument Laboratory). The Pb samples below 0.2 mg/L were

analyzed using a Thermo Jarell Ash Furnace Atomizer 188 graphite furnace per EPA method 7421 (EPA, 1986). The U was analyzed at the Oak Ridge National Laboratory by EPA method 200.8 (EPA, 1991).

III.4 EQUILIBRIUM EXPERIMENTS

III.4.1 Binding Rate Experiments

Experiments were initially conducted using both natural and digested soil to determine the amount of time required for equilibrium to be achieved between the sorbed and aqueous metal phases. Experiments were conducted in a single metal matrix by the addition of 100 ml of a stock metal solution and 10 g of soil (dry weight). The stock solution was added to the soil in a 250 ml Erlenmeyer flask and mixed, over time, on a Burrell Wrist Action shaker at 150 shakes per minute (1/3 revolution per shake). The stock metal concentration for the natural soil was 20 mg/L of either Zn, Pb or U. The second and third experiments for Pb were conducted using a higher initial metal concentration (50 mg/L) due to the extensive binding of the metal to this soil. For comparison purposes, an additional Zn experiment was conducted with the natural soil at an initial concentration of 50 mg Zn/L. The digested soil initial metal concentration was 20 mg/L for the Zn experiments and 100 mg/L for the Pb and U with an additional Pb experiment conducted at 50 mg/L for comparison purposes.

After addition of the stock metal solution to each soil, samples were mixed then centrifuged at 10,000 rpm for ten minutes at various time intervals. The supernatant was decanted and analyzed for each metal by flame atomic adsorption spectroscopy. The U was analyzed at the Oak Ridge National Laboratory by EPA method 200.8 (EPA, 1991).

The amount of metal adsorbed to the soil was determined by subtracting the mass of metal in solution from the initial mass of metal added to each sample. A blank solution containing the metal solution and no soil was also analyzed to determine the amount of sorption to the containers.

III.4.2 Isotherm Experiments (Single metal matrix)

Isotherm experiments were initially conducted on a single metal matrix to determine the capacity of the soil for each metal. This information was necessary to determine the amount of metal solution to add to an uncontaminated soil to achieve a sorbed metal concentration desired for future testing. These experiments were conducted using 100 ml of varying concentrations of metal solutions and 10 g of soil shaken in flasks until equilibrium was achieved. Equilibrium contact times of 24 hours for the natural soil and 72 hours for the digested soil were determined from kinetic experiments.

The first Pb matrix experiment for the natural soil was conducted using an initial concentration of 20 mg Pb/L with four additional lower concentrations of 15, 10, 5 and 2 mg Pb/L.

Maximum sorption capacity was determined to be higher than 20 mg Pb/L so experiments #2,3 & 4 for the Pb matrix on the natural soil were conducted an initial Pb concentration of 50 mg/L. The digested soil experiments for Pb were performed with an initial concentration of 100 mg Pb/L due to the higher sorption capacity of the digested soil vs. the natural soil.

The Zn isotherm experiments for the natural soil were conducted using an initial concentration of 20 mg Zn/L for the natural soil and 50 mg Zn/L for the digested soil. The U experiments were conducted at initial concentrations of 50 mg U/L and 100 mg U/L for the high and digested soils respectively.

After equilibrium was achieved (24 hours for the natural soil and 72 hours for the digested soil), the soil slurries were centrifuged at 10,000 rpm for 10 minutes. The supernatant was decanted and analyzed for each metal. The amount of sorbed metal was determined by subtracting the mass of metal in solution at equilibrium from the initial mass of metal added to each sample.

III.4.3 Isotherm Experiments (Multiple Metal Matrix)

The isotherm experiments were repeated with a multiple metal solution to determine competitive effects of each metal on adsorption in the natural soil. The effect of additional metals on Pb sorption was investigated by adding 4 mls of 100 mg/L Zn and 3 mls of 100 mg/L U (to achieve an initial concentration of 0.4 mg Zn/L and 0.3 mg U/L) to 10 g uncontaminated soil in 250 ml flasks. In addition, 93 mls of varying Pb concentrations were added to

achieve initial Pb concentrations of 53, 42, 32, 21 and 0 mg Pb/L. The experiments were then conducted as described with the single metal matrix.

The effect of additional metals on Zn sorption was studied by the addition of 3 mls of 100 mg/L Pb and 3 mls of 100 mg/L U (to achieve initial concentrations of 0.3 mg metal/L) added to 10 g uncontaminated soil in 250 ml flasks. In addition 94 mls of varying Zn concentrations were added to achieve initial Zn concentrations of 17, 12.5, 8, 4 and 0 mg Zn/L. The experiments were then conducted as described with the single metal matrix.

Due to the costs involved in U analysis, the effect of a multiple metal matrix on U sorption was not investigated.

III.5 METAL MOBILIZATION UPON H_2O_2 ADDITION

Mobilization of metals (Zn, Pb and U) upon peroxidation of both high and digested soils was evaluated. The soils were contaminated with metals (Zn, Pb and U) by placing 110 grams of uncontaminated air dried, sifted soil (#4 mesh) in a 250 ml centrifuge bottle with screw cap. Two hundred mls of a metals solution containing the concentrations of metals noted in table 4 of the Results and Discussion section were added to the soil. Metals loadings were chosen to model the concentrations found at the DOE site. The mixture was placed on a Burrell Wrist Action

shaker at 300 shakes per minute (1/3 revolution per shake), for 24 hours for the natural soil and 72 hours for the digested soil.

After equilibrium was achieved, the soil and metal mixture was centrifuged at 10,000 rpm for 10 minutes, the supernatant decanted and each metal measured. The contaminated soil was then washed with 160 mls of the pH 7 DI water to remove unbound metal in the soil pore water and any loosely associated metal. This washing was performed by suspending the soil using a vortex mixer, centrifuging the mixture at 10,000 rpm for 10 minutes and decanting the supernatant. The washing was done in triplicate and all three washings were combined and analyzed for each metal.

The washed contaminated soil was oven dried (103^{o}C) for approximately 4 hours. The dried soil was ground and homogenized in a mortise. Ten grams of dry contaminated soil was then placed in screw-capped centrifuge tubes (50 ml capacity) for peroxide addition.

Following the addition of H_2O_2 and reaction period, the soils were washed 3 times with 20 mls of pH 7 DI water to remove any metal in the pore water and metal loosely associated with the soil. This procedure was used to model soils which have been washed by years of rain. These experiments are the most representative of conditions that are likely to be seen at a weathered site.

III.5.1 Metal Mobilization Upon A Single Treatment Of Varying Doses Of H_2O_2

Two mls of H_2O_2 at varying concentrations from 0 to 32.2 mg H_2O_2/ g soil (0-0.32 % wt./wt.) were added to 10g of contaminated soil (both high and digested soils) in 50 ml screw-capped centrifuge tubes. These doses were chosen due to their optimal oxidation of contaminant organics. To evaluate background metal mobility, 2 mls of H_2O_2 at a concentration of 1 mg H_2O_2/ g soil, was added to 10 g of uncontaminated natural soil and analyzed. All tubes were placed on a Burrell Wrist Action shaker at 300 shakes per minute (1/3 revolution per shake), for 24 hours.

After equilibrium, each sample was washed to remove any mobilized metal. The washing method described above was utilized to evaluate metal mobility upon peroxidation treatment with the exception of each wash having 20 ml of pH 7 DI water for a total wash volume of 60 mls for each sample. The washings were combined and analyzed for metals.

Zn and Pb were analyzed by flame atomic adsorption spectroscopy. Due to the very low concentrations of Pb mobilized, analysis was performed utilizing a graphite furnace. U was analyzed at Oak Ridge National Laboratory by using EPA method 200.8.

The adsorption of the metals to the tubes and bottles was determined by placing 200 mls of each metal concentration in the bottles, shaking for 24 hours and analyzing for metals. Adsorption

was determined by subtracting the metal concentration at 24 hours from the initial metal concentration.

III.5.2 Metal Mobilization Upon A Multiple Treatment Of H_2O_2 With Varying Contact Times

The peroxidation treatment of a soil may have several significant factors that must be considered for metal mobilization. Among these is the effect of multiple peroxidation treatments of a soil zone. In addition, the contact time for the H_2O_2 and soil may be a significant factor to consider for either the treatment of a soil contaminant and/or for metal mobilization.

Batch experiments were conducted to study the effects of multiple treatments in conjunction with varying H_2O_2 contact times. Ten grams of contaminated natural soil was placed in 50 ml centrifuge tubes. Ten mls of H_2O_2 (final concentration = 32 mg H_2O_2/g soil) was added to the soil and allowed to react for 5 minutes, 1 hour or 12 hours. After these contact times the soil solution was centrifuged at 10,000 rpm for ten minutes, the supernatant decanted and measured for metals. The soil was then washed by the addition of 10 mls of pH 7 DI water, suspension of the soil seed with a vortex mixer and centrifugation as described above.

The treatment and washing process was repeated until a decrease in the amount of mobilized Zn was observed. Zn was used as an indicator of metal mobility due to the high mobility of this metal observed in the single H_2O_2 dose experiments. Controls

containing pH 7 DI water and soil but no H_2O_2 were also evaluated as a control to determine the extent of metal mobilization due to the water alone.

III.5.3 Metal Readsorption Following Mobilization From A Single Peroxidation Treatment Of A Contaminated Soil

The peroxidation of a soil may result in mobilized metals which then migrate to a lower zone and readsorb to the soil. An experiment was conducted to study the effects of mobilized metals readsorbing to a H_2O_2 pretreated soil zone by the method described below.

Ten grams of contaminated natural soil was placed in 50 ml centrifuge tubes. Ten mls of H_2O_2 (final concentration = 32 mg H_2O_2/g soil) was added to the soil and allowed to react for 12 hours. This time increment was shown to result in maximum metal mobilization. After 12 hours of H_2O_2 contact, the soil solution was centrifuged at 10,000 rpm for ten minutes and the supernatant decanted and measured for metals.

The supernatant was then reapplied to the treated soil, mixed with a vortex mixer and allowed 12 hours of additional contact time. The reapplied supernatant/soil solution was centrifuged and the new supernatant tested as described above.

The soil was then washed with 10 mls of pH 7 DI water as described above. The wash water supernatant was then measured for metals, reapplied to the treated soil and mixed with a vortex mixer. After 12 hours of contact time with the treated soil, the

reapplied wash water solution was centrifuged and the new supernatant tested for metals.

III.6 pH EFFECTS ON METALS MOBILIZATION

pH is an important factor in metals mobilization. The addition of H_2O_2 to a soil may result in a decrease of pH which may increase cationic metal mobilization. Experiments were performed to determine the effect on metal mobilization due to a pH change. These experiments were conducted by inducing a pH change of one and two units above and below the natural soil pH.

Ten grams of contaminated soil were placed in 50 ml beakers, 6 mls of pH 7 DI water was added and the pH measured per method set forth in Methods of Soil Analysis (1982). Acid or base (0.1N reagent grade HCl and 0.1N NaOH) was titrated to determine the amount needed to achieve a one and two pH unit change above and below the pH observed with pH 7 DI water alone. The amount of acid or base recorded was then added to new contaminated soil samples (10 g) in screw-capped centrifuge tubes, vortex mixed and allowed 0.5 hour contact time. The soils were then washed three times with 20 mls pH 7 DI water and measured for mobilized metals.

Additional experiments were performed to determine the metal mobilization of a pH change resulting from peroxidation of soil. Acid or base was used to model the pH change observed from

the various H_2O_2 loadings. The soil was contaminated with the metals as described in the H_2O_2 experiments. Ten grams of contaminated soil was placed in 40 ml beakers with six mls of pH 7 DI water and the pH measured. Two mls of H_2O_2 at the concentrations tested in the peroxidation experiments was added and the pH was monitored over a 24 hour period.

The pH change observed was then modeled with the acid and base by titration of the acid or base into 10 g of contaminated soil, (plus 6 mls of pH 7 DI water), to determine the amount of acid or base needed to model the pH change observed upon peroxidation.

The amount of acid or base thus recorded was then added to a new 10 grams of contaminated soil, stirred and allowed to react for 24 hours. The soil was then washed three times with 20 ml pH 7 DI water as indicated in the peroxide experiments, with the washings being combined and analyzed to determine the amount of metals mobilized.

III.7 INTERACTION OF OM AND MOBILIZED METAL

The peroxidation of soils may result in the subsequent release of soluble organic ligands which may then affect metal mobility. Experiments were conducted to study the effects on metal mobility of soluble organic ligands released during soil peroxidation.

III.7.1 Metal Mobilization due to Potential Organic Ligands Created During Soil Peroxidation

The first experiment was conducted to determine the effects on metal mobilization of organic ligands generated from soil peroxidation. Ten grams of uncontaminated soil was placed in 50 ml screw capped centrifuge tubes and 10 mls of H_2O_2 was added to achieve a loading of 32 mg H_2O_2/ g soil. The solution was mixed by vortex mixing and allowed 24 hours of contact. The solution was then centrifuged and washed with 10 mls of pH 7 DI water once as described in previous experiments. The supernatant from the peroxidation was combined with the supernatant from the washing and analyzed for metals and residual H_2O_2.

The method used to measure residual H_2O_2 was reported by a hydrogen peroxide manufacturer (Interox Inc., 1991). After the determination that no residual H_2O_2 was present in the combined supernatant, ten mls of the combined supernatant was applied to 10 g of metals contaminated soil, mixed with a vortex mixer and allowed 24 hours of contact time. The solutions were then centrifuged and the new supernatant (hereafter referred to as the "reapplied supernatant"), decanted. The contaminated soils were washed with 10 mls of pH 7 DI water once, as described previously, centrifuged and the new wash supernatant combined with the reapplied supernatant and analyzed for metals.

III.7.2 Metal Mobilization from the Application of Humic Acid (HA) to a Contaminated Soil

An additional experiment was conducted to determine metal mobilization upon the addition of a known concentration of soluble organic matter (humic acid) to a contaminated soil. Twenty mls of 100 mg/L humic acid sodium salt (HA) from Aldrich Chemical Inc., was added to 10 g of metals contaminated soil, mixed with a vortex mixer and shaken on a Burrell Wrist Action shaker at 300 shakes per minute (1/3 revolution per shake). After 24 hours of contact time, the soil solution was centrifuged and the supernatant decanted and measured for total Pb and Zn in solution. The pH of the soil solution was also analyzed to determine if the addition of the HA would alter the pH and consequently affect metal mobilization from a change in pH.

CHAPTER IV. RESULTS AND DISCUSSION

IV.1 SOIL COLLECTION AND TREATMENT

Digestion of the natural soil using H_2O_2 resulted in a final soil OM of 0.42%. This quantity of OM was $^1/_3$ of the OM in the original soil, which contained 1.23% organic carbon. The inability to completely oxidize the soil OM was also observed by several other workers. Griffith and Schnitzer (1977) found that soil OM did not completely oxidize by H_2O_2 with $^1/_5$ to $^1/_3$ of the initial soil OM resisting peroxidation. Others found peroxidation was not effective in as much as half of the soil OM (Sequi and Aringhieri, 1977).

Griffith and Schnitzer (1977) identified that organics resisting peroxidation were primarily n-alkanes and n-fatty acids that were held strongly to the inorganic soil constituents such as clays and hydrous metal oxides. Jordao and Nickless (1989) determined that unoxidizable OM consisted of paraffin-like materials and resistant structural residues.

The original soil also contained 29.7% silt, 55% sand, and 14.8% clay. The proportions of these soil constituents should remain the same in the digested soil since soil peroxidation does not decompose these inorganic constituents. The peroxidation of soil may however result in physical changes to soil constituents.

Douglas and Fiessinger (1971) found a significant clay alteration as determined by X-ray diffraction but they determined that using a 1N sodium acetate buffer (pH 5) during peroxidation minimized the degradation of clays by preventing strongly acidic conditions. The clays in the digested digested soil of this thesis should have minimum clay alteration due to the use of the sodium acetate buffer in the digestion procedure for establishing this soil.

The possibility of degradation of other soil constituents does exist. Tessier et al (1979) found a partial alteration of silicate material and mica upon soil peroxidation. Burford et al (1964) also discovered mica degradation when they observed that soil peroxidation lead to the exfoliation of mica crystal's edges.

The digested soil may also have a larger surface area than the undigested natural soil. Burford et al (1964) found that the external surface area of a soil increased following soil peroxidation which they attributed to the removal of organic coatings on clays.

The digested soil should have a higher CEC than the undigested soil. The digestion procedure may have stripped a quantity of bound cations such as Fe and Mn from the original soil. This would have freed binding sites on the Digested soil and would consequently result in a higher CEC.

IV.2 EQUILIBRIUM EXPERIMENTS

IV.2.1 Binding Rate Experiments

Data plotted in figure 4.1 indicates that equilibrium was achieved within the first 6 hours for the lower initial Pb loadings of 500 and 1050 mg/kg soil. The lines on this and following figures were drawn by interpolation and may not be statistically accurate. The higher initial concentration added of 1120 mg/kg soil appears to have taken longer to reach equilibrium, possibly taking 8-12 hours. To assure equilibrium has been achieved in the digested soil, 72 hours of contact time was used for subsequent experiments with the digested soil.

Figure 4.2 compares the adsorption of Pb over time at an initial loading of 500 mg Pb/kg soil in both soils. Higher binding capacity was observed in the digested soil upon equal initial metal added to both soils.

Adsorption of Zn in both soils was rapid as plotted in figure 4.3. Ninety eight percent of the Zn in the original solution sorbed within the first sampling time of 2 hours.

Figure 4.4 illustrates the rate of binding for U in both soils. The limited number of samples that were analyzed do not show the complete picture of the amount of time needed to reach equilibrium in the digested soil. From the data plotted however, the 72 hour contact time used in subsequent experiments appears to be very close to the equilibrium contact time for U in the digested soil due to the change in the rate slope. The initial rate

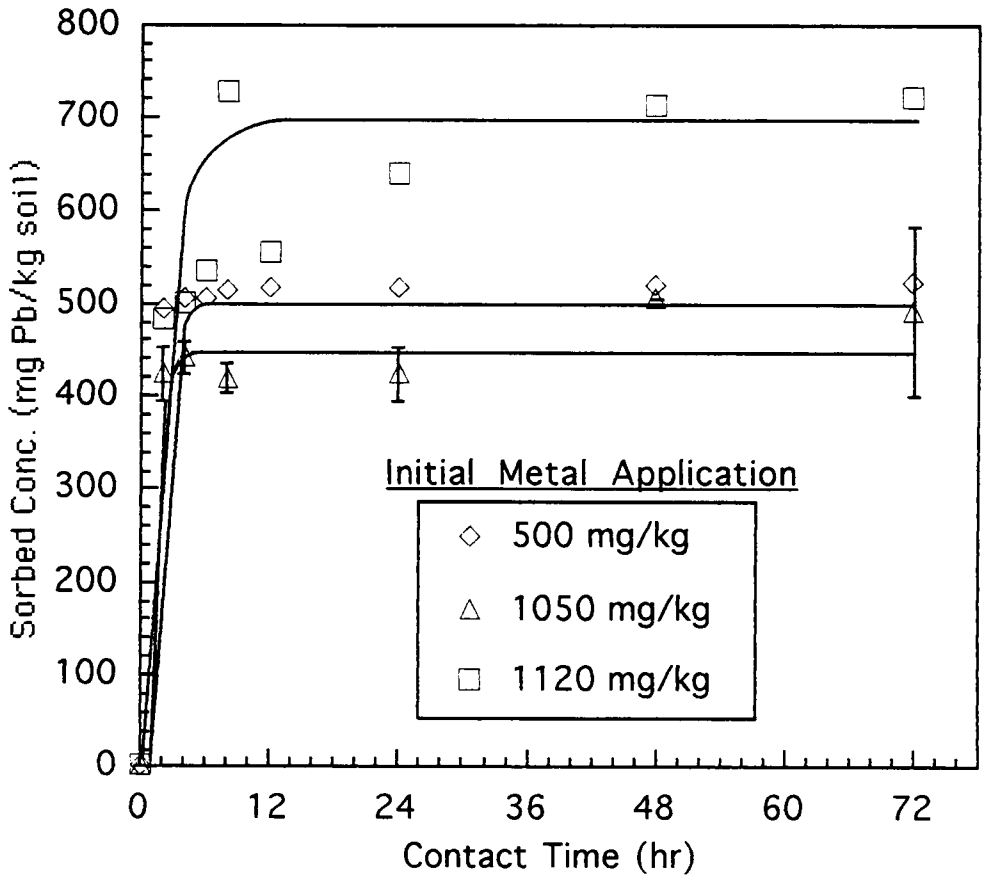


Figure 4.1. Pb adsorption to 10 g of digested soil over time.

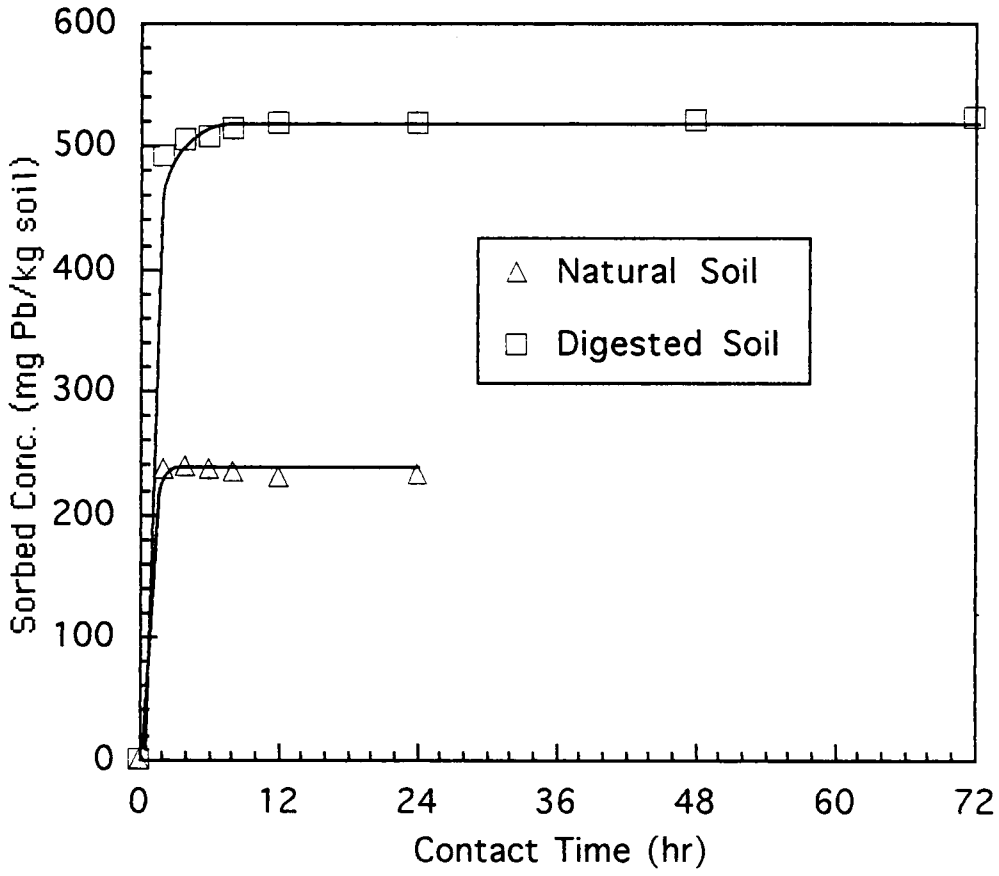


Figure 4.2 Comparison of Pb adsorption to 10 g of both natural and digested soils over time (initial metal application = 500 mg Pb/kg soil).

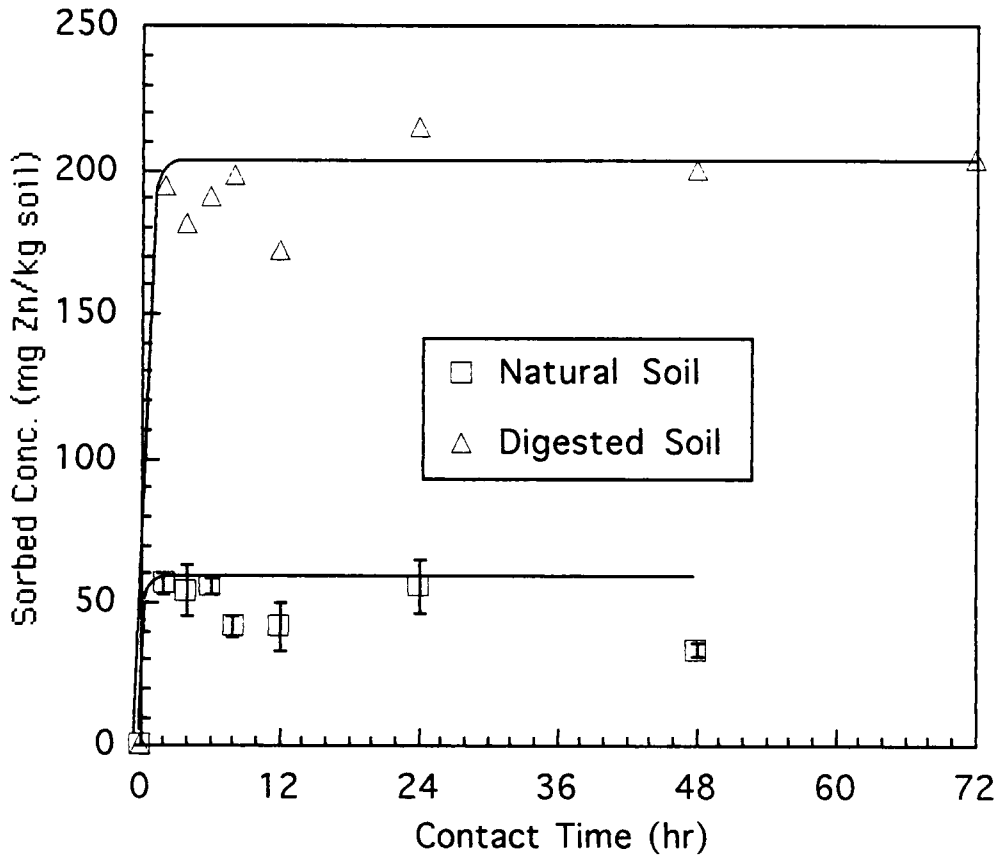


Figure 4.3 Comparison of Zn adsorption to 10 g of both natural and digested soils over time (initial metal application = 200 mg Zn/kg soil). (Each data point is the mean of three samples and their standard errors.)

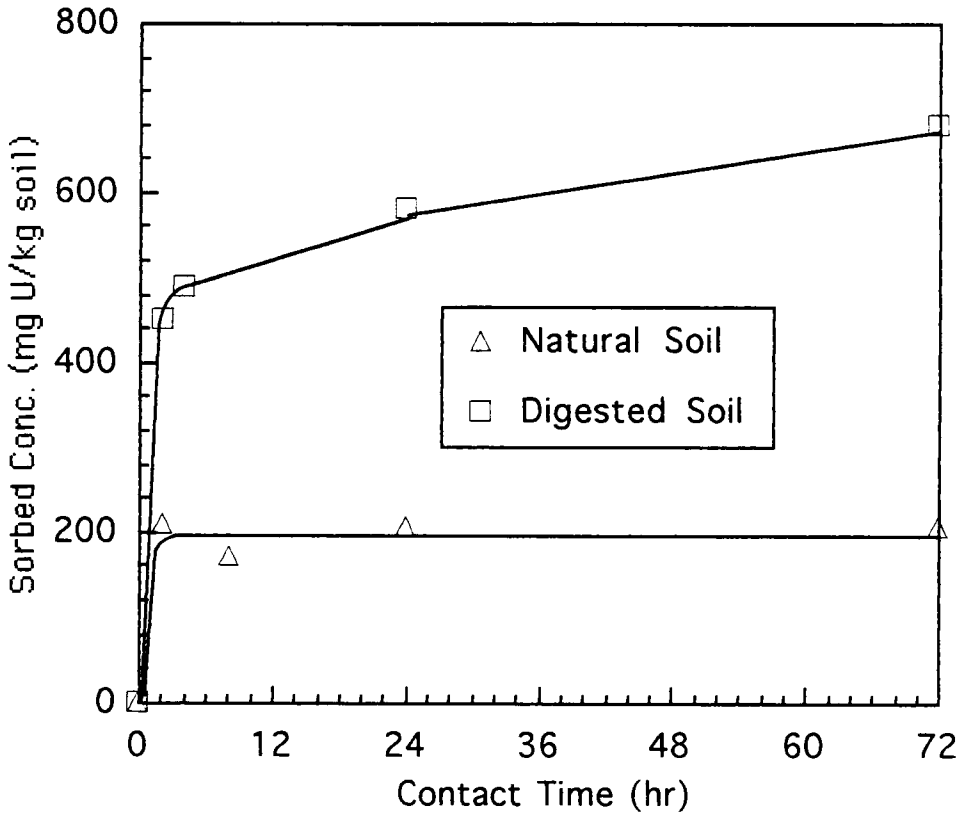


Figure 4.4 U adsorption to 10 g of both soils over time. (Initial metal application = 1000 mg U/kg soil to the digested soil and 200 mg U/kg soil to the natural soil).

slope was very steep indicating that binding was occurring very rapidly. The slope changes between 2 and 4 hours to a lesser slope which signals a slowing of U adsorption rate and an approach to a horizontal slope that would indicate equilibrium has been achieved.

Figure 4.1 is the first indication that higher initial metal loadings may take longer to achieve equilibrium in a digested soil. The highest initial metal loading of 1120 mg/kg soil may have taken up to twice as long as the lower initial metal loadings. This may be the result of two factors: 1.With lower initial metal loadings, more binding sites were available upon reaching equilibrium. This may have allowed for a faster rate of binding due to the ample number of easily accessible binding sites. At the highest loading of 1120 mg/kg soil the binding sites that were available may have taken longer to access due to a saturation of easily accessible binding sites. At this higher loading additional binding sites may have been available within the soil grain pores that may have taken longer to access. 2.Binding may be a rate limiting process. At lower initial concentrations, the binding may have been to the soil surface where the rate limiting step would be the hypothetical film barrier that exists between the liquid and soil. At the higher concentration binding may have also occurred in the individual soil pores. Had this occurred, the rate limiting step may be pore diffusion which may have taken longer to achieve equilibrium.

At an initial loading of 500 mg/kg soil, all of the Pb sorbed to the digested soil for a sorbed concentration of 500 mgPb/ kg soil. At this lower concentration, more binding sites may be available upon reaching equilibrium resulting in all of the Pb in the initial solution binding to the soil.

An interesting outcome illustrated in this figure is that more metal adsorbed at an initial loading of 500 mg Pb/kg soil than at 1050 mg Pb/kg soil. This may be the result of the higher loading not reaching equilibrium within the time studied. The 72 hour sample for the 1050 mg/kg loading had a wide range of error the upper limit of which is higher than the equilibrium of the 500 mg/kg initial loading. Therefor equilibrium may not have been achieved for the 1050 mg/kg soil loading. This may also be the result of experimental error or some other phenomena resulting from the digestion of this soil.

Figure 4.2 which compares the adsorption rates for Pb at an initial loading of 500 mg Pb/kg soil in both soils, reinforces this theory with higher binding in the digested soil. This higher binding capacity in the digested soil upon equal initial loadings to both soils indicates that more binding sites were available in the digested soil.

These additional binding sites may have been in the soil grain pores. This is supported by the work of Burford et al (1964) who found an increase in external surface area following soil peroxidation through an increased cetylpyridinium (CP^+) ion adsorption. They determined that organic coatings of clays may

have blocked adsorption sites. Reaching these soil grain pores may have taken longer as illustrated in figure A.2 of the appendix where the natural soil reached equilibrium within two hours however the digested soil took up to 6 hours. In addition, Burford suggested that the organic materials may have bound soil particles into aggregates blocking access to internal surface areas.

The natural soil sorbed 48% of the original Pb in solution for 230 mgPb/ kg soil compared to 100% sorption in the digested soil for 500 mgPb/ kg soil. This is approximately 2.2 times more Pb sorbed to the digested soil indicating that more binding sites are available in the digested soil.

These results are contradictory to results obtained by Petruzelli et al, 1981) who found a reduction of Pb adsorption capacity with the destruction of soil OM by H_2O_2. Other researchers found OM destruction by H_2O_2 liberated new soil sorption sites by the destruction of organic coatings on clays (Sequi and Aringhieri, 1977). This destruction of organic coatings created new binding sites that were blocked by the organic coatings prior to peroxidation.

The increased binding may have been the result of additional surface binding sites available in the digested soil from stripping of bound metals found in natural soil. In addition, during soil digestion to produce the digested soil, adsorption sites may have been stripped of bound metals in the natural soil such as Fe and Mn. This would also expose additional unoccupied binding sites and

possibly account for the increased sorption observed with the digested soil. Shuman (1976) found that removal of Fe from a soil increased the adsorption capacity (Q^o) for Zn. The available Fe content alone of the natural soil was determined to be 66.1 mg/kg soil. Release of just these binding sites would account for 20% of the additional binding sites found in the digested soil.

Adsorption of Zn in the digested soil as plotted in figure 4.3. also illustrates the phenomenon of increased adsorption in the digested soil, however, binding in both soils was rapid. The digested soil 3.5 times more Zn sorption to the digested soil than to the natural soil indicating once again that more binding sites are available in the digested soil. This similarity in binding rates may indicate a surface binding event with Zn and not pore diffusion. These easily accessible surface binding sites may have been sufficient in number to bind the Zn as was evident in the efficiency of Zn binding to the digested soil (98%) and consequently may have resulted in rapid binding.

Figure 4.4, which illustrates the rate of binding for U in both soils shows that adsorption of U to the natural soil is much more rapid than U adsorption to the digested soil. This may be the result of a higher initial loading to the digested soil or further evidence of a rate limiting binding event taking place.

This may also be due to the U having a higher affinity for binding sites on OM in the natural soil than clay in the digested soil. Berthelin et al (1987) found that clays in natural soils are

not sinks for U although the reason for this has not been determined.

Figure 4.5 illustrates that different metals do adsorb at different rates in a treated soil. The Pb reached equilibrium within 6 hours, however, the U took much longer to approach equilibrium and had still not achieved equilibrium after at least 24 hours.

The rate information may be helpful in estimating the rate of potential readsorption following H_2O_2 treatments. The digested soil may be a good indicator of the potential speed of readsorption following soil peroxidation due to that soil being an H_2O_2 treated soil.

IV.2.2 Single Metal Matrix Isotherm Experiments

Figure 4.6 is the comparison of Pb adsorption isotherms for both soils. This plot indicates a diminishing capacity for Pb adsorption to the natural soil at ≈ 150 mg Pb/ kg soil. This diminishing adsorption capacity suggests that binding sites are becoming filled at this point.

The linear plots of the data of figure 4.6, to determine the Langmuir coefficients are illustrated in figures 4.7 & 4.8. From figure 4.7 the natural soil has a maximum adsorption capacity of 236 mg Pb/kg soil and a bonding energy (b) of 2.49 as reported in table 2.

The digested soil plotted in figure 4.6 shows that binding sites are becoming filled upon a diminishing capacity for Pb

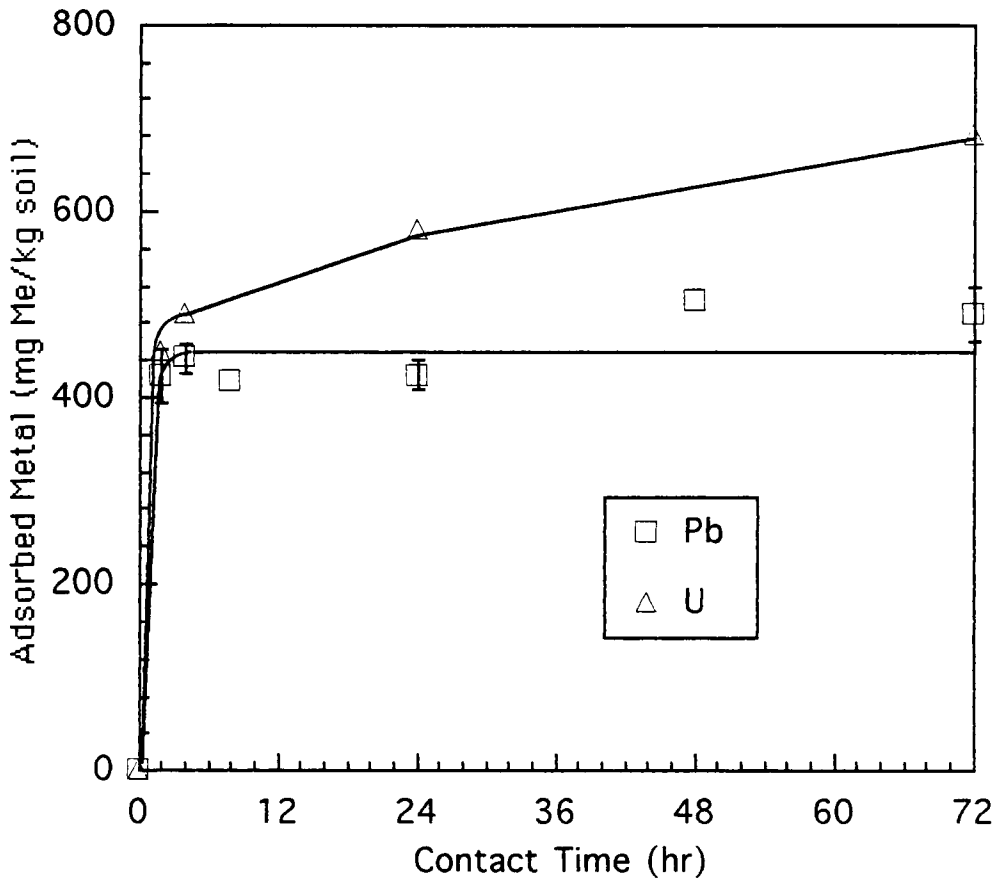


Figure 4.5 Comparison of Pb and U adsorption to 10 g of digested soil over time. (Initial metal application= 1000 mg metal/kg soil.)

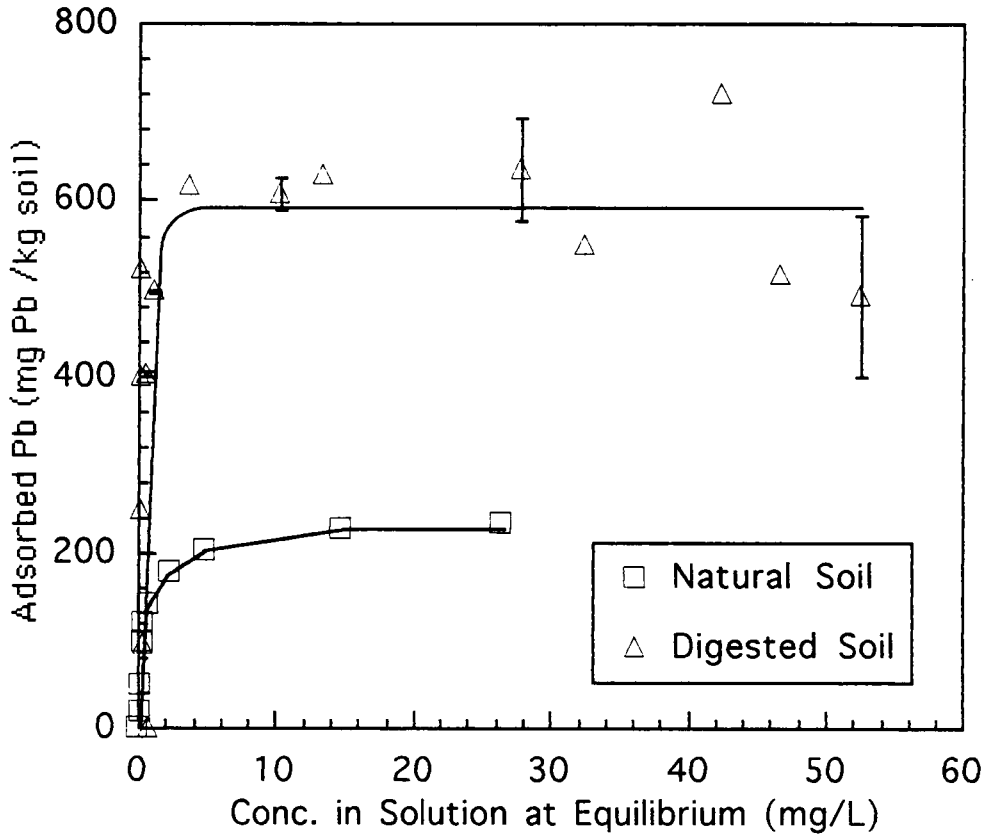


Figure 4.6 Pb adsorption isotherms for 10 g of both natural and digested soils with the addition of 100 ml of varying concentrations of Pb.

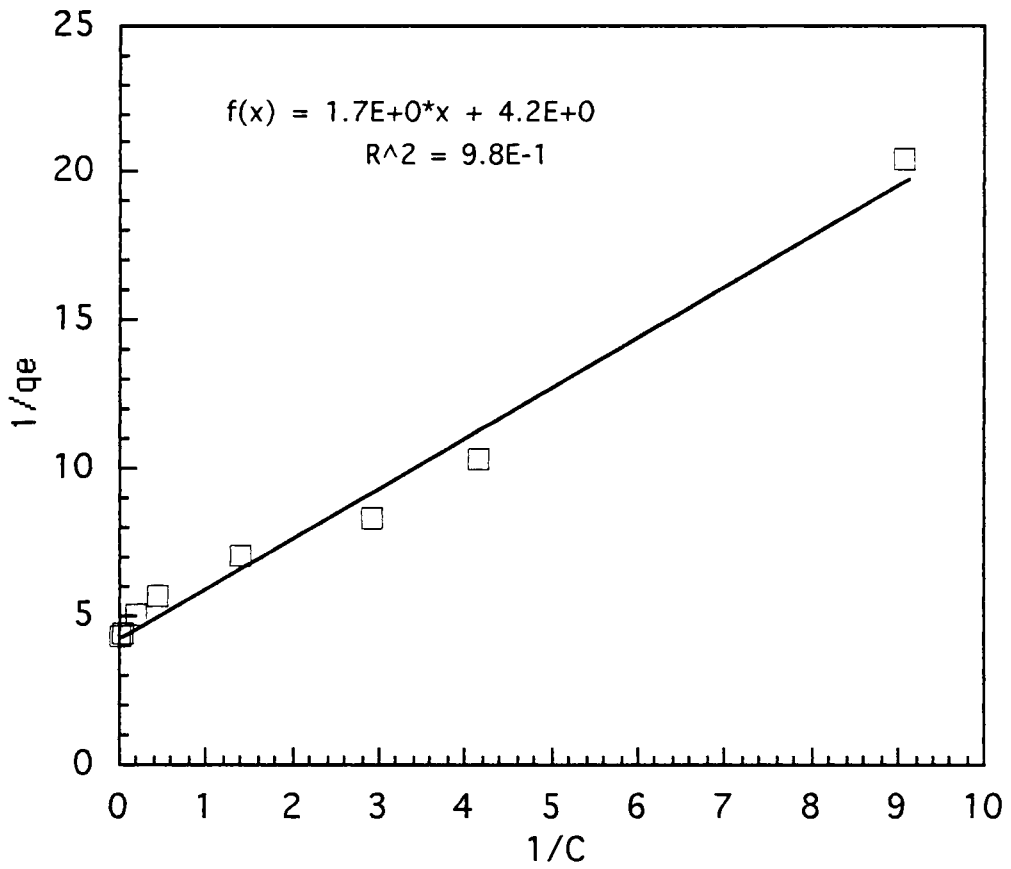


Figure 4.7 Linear plot of Pb adsorption to natural soil to determine adsorption parameters.

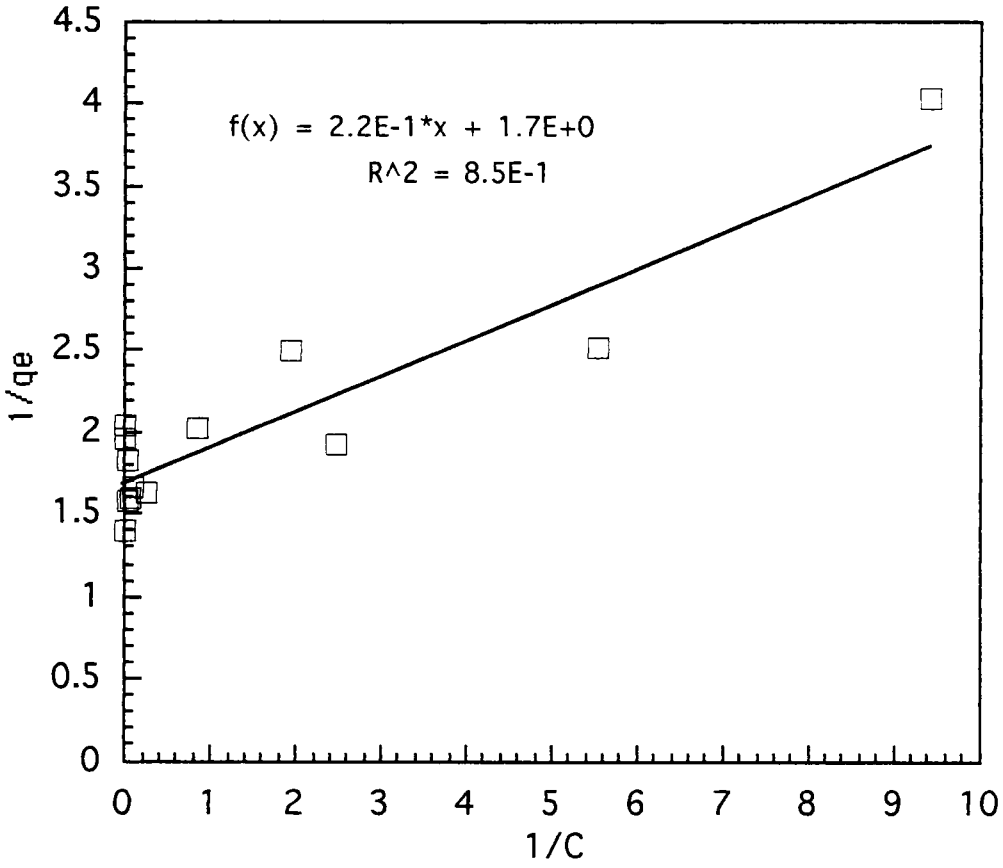


Figure 4.8 Linear plot of Pb adsorption to digested soil to determine adsorption parameters.

adsorption occurring ≈ 500 mg Pb/kg soil. The linear plot of this data in figure 4.8 resulted in the determination of a maximum adsorption capacity of 592 mg Pb/kg soil and a bonding energy of 7.68 as reported in table 2.

TABLE 2
Langmuir Bonding Energy Coefficients (b) and Maximum Sorption Coefficients (Q^0)

Soil	OM	Metal	Q^0	b
Clay (24% OM)*	Present	Pb	0.5636	0.4147
Clay (24% OM)*	Absent	Pb	0.2154	0.2871
Clay (0.81% OM)*	Present	Pb	0.5725	0.4252
Clay (0.81% OM)*	Absent	Pb	0.2637	2.0675
Clayloam(2.1%OM)*	Present	Pb	3.4698	0.0881
Clayloam(2.1%OM)*	Absent	Pb	1.2962	1.2854
Natural Soil		Pb	0.236	2.49
Digested Soil		Pb	0.592	7.68
Natural Soil		Zn	0.0595	3.22
Digested Soil		Zn	0.0336	1.13
Natural Soil	See note 1	U	2.35	0.06
Digested Soil	See note 1	U	1.56	0.02

*= From Petruzelli et al (1981)

1- values are obtained from an incomplete isotherm

The data plotted in figure 4.9 is a comparison of the adsorption isotherms for Zn in both soils. This figure indicates a diminishing capacity for Zn adsorption occurring at ≈ 20 mg Zn/ kg soil in the natural soil.

From the linear plot of the natural soil isotherm illustrated

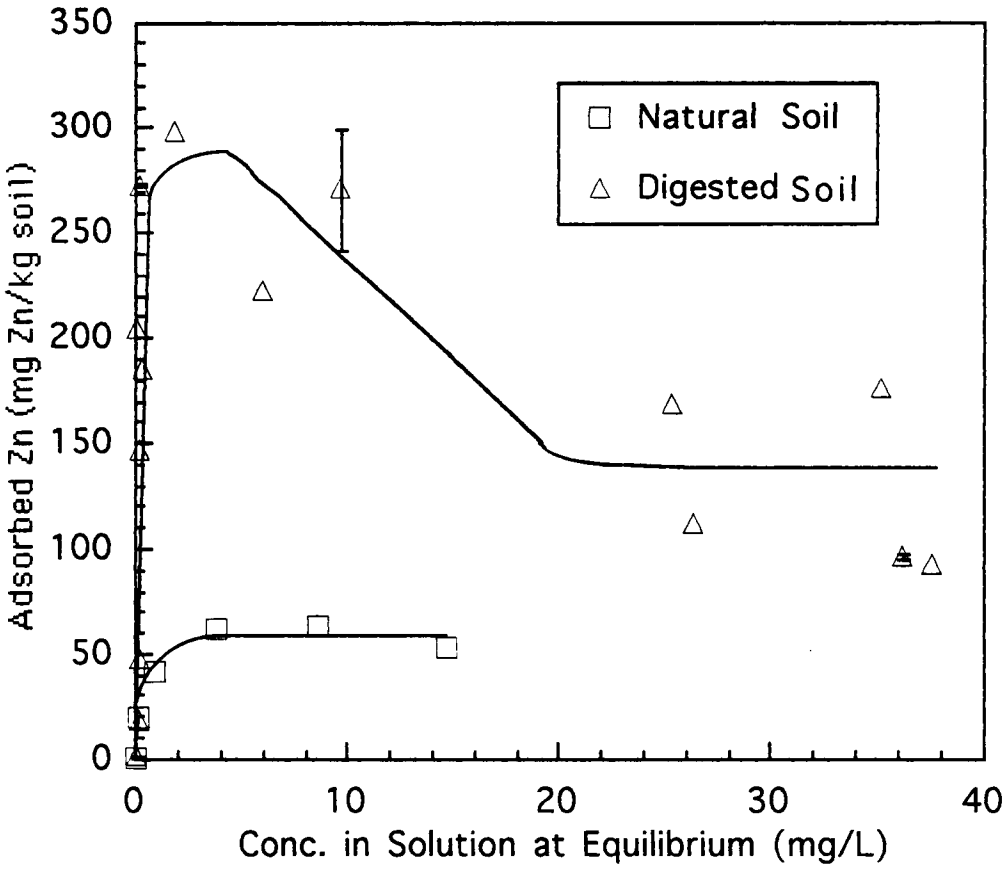


Figure 4.9 Comparison of Zn adsorption isotherms for 10 g of both natural and digested soils with the addition of 100 ml of varying concentrations of Zn.

in figure 4.10, the soil has a capacity to adsorb 60 mg Zn/kg soil and a binding energy term of 3.22. This plot uses all the data and had an excellent fit with a correlation coefficient of 0.986.

Figure 4.11 is the linear plot of Zn adsorption to the low OM soil. From this figure the soil has a maximum adsorption of 33.6 mg Zn/kg soil and a binding energy of 1.13.

Figure 4.12 illustrates U adsorption to both soils but is incomplete due to the limited number of samples analyzed. These plots indicate that the U adsorption is in the lower linear range of the typical Langmuir curve and has not reached the point of diminishing adsorption capacity.

Conversion of the plot to determine the maximum adsorption capacity and the bonding energy terms is shown in figures 4.13 & 4.14. From these two plots, the natural soil has a capacity to adsorb 2347 mg U/kg soil and the digested soil 1555 mg U/kg soil. This is opposite of the findings for Pb and Zn where binding capacity increased in the digested soil.

The binding energy was low in both soils. The binding energy in the digested soil was 0.02 which was lower than the natural soil of 0.06. This information and the binding capacity may be inaccurate, however, due to the information being derived from incomplete isotherms.

Figure 4.6 which is the comparison of Pb adsorption isotherms for both soils indicates that these figures follow the Langmuir adsorption isotherm model. Other researchers also found

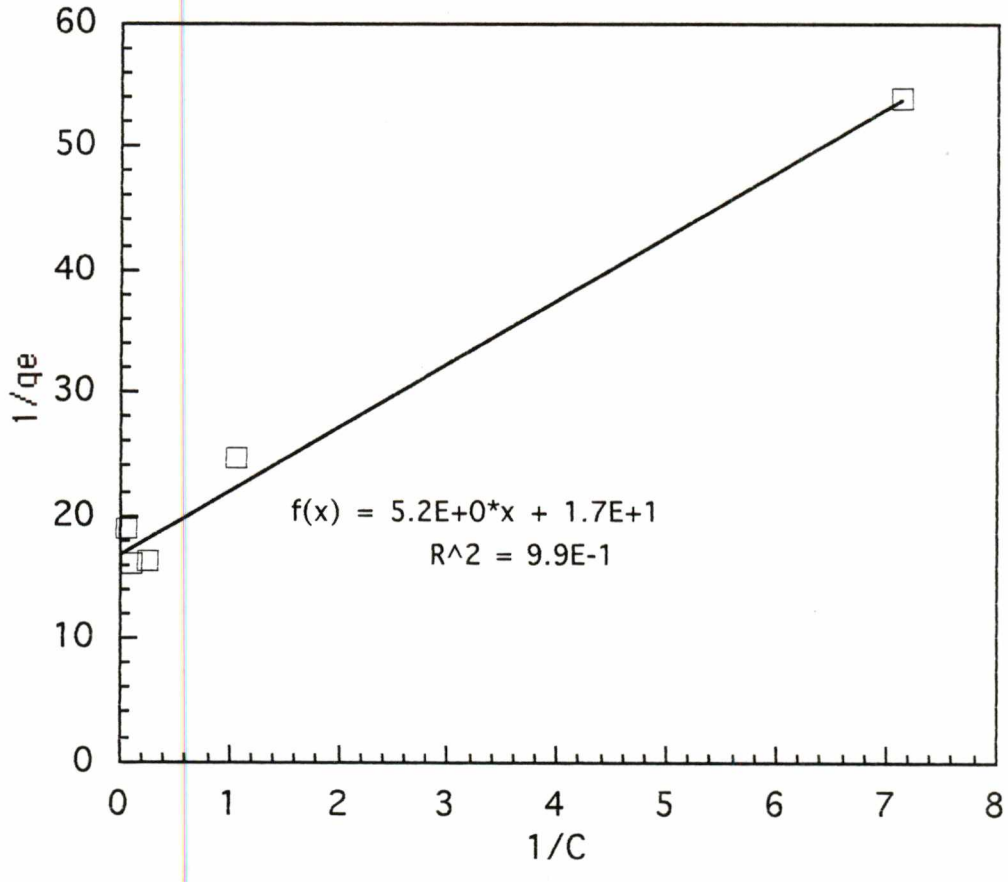


Figure 4.10 Linear plot of Zn adsorption to natural soil, using all data, to determine adsorption parameters.

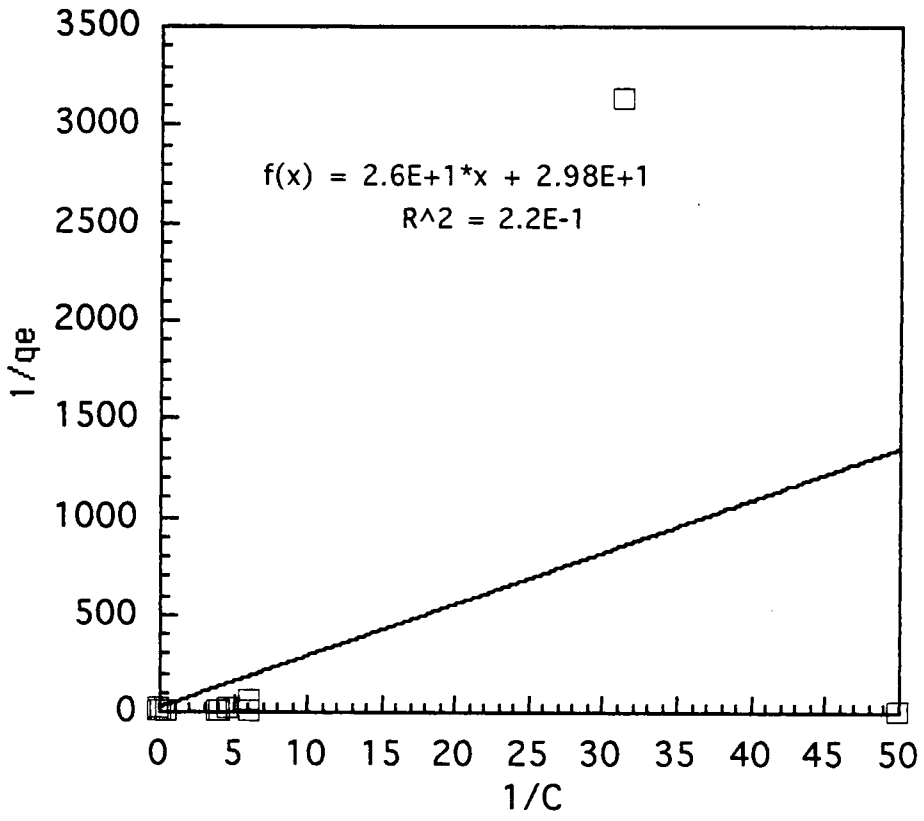


Figure 4.11 Linear plot of Zn adsorption to digested soil, using all data, to determine adsorption parameters.

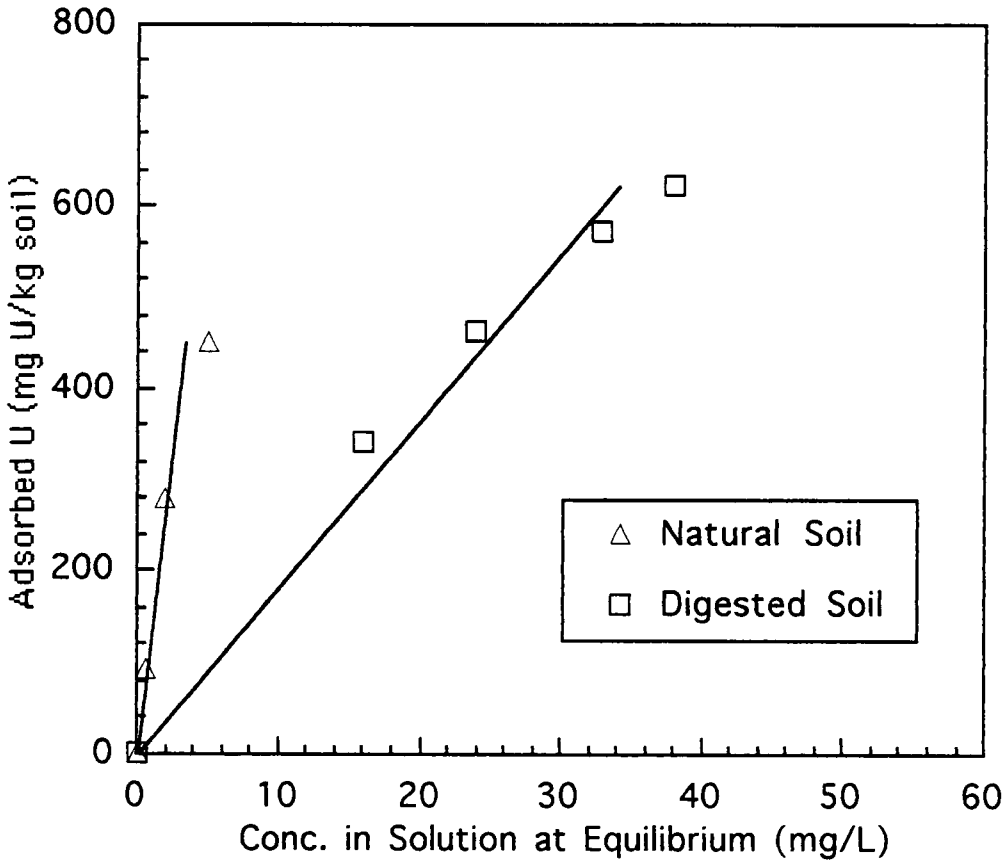


Figure 4.12 U adsorption to 10 g of both soils with the addition of 100 ml of varying concentrations of U.

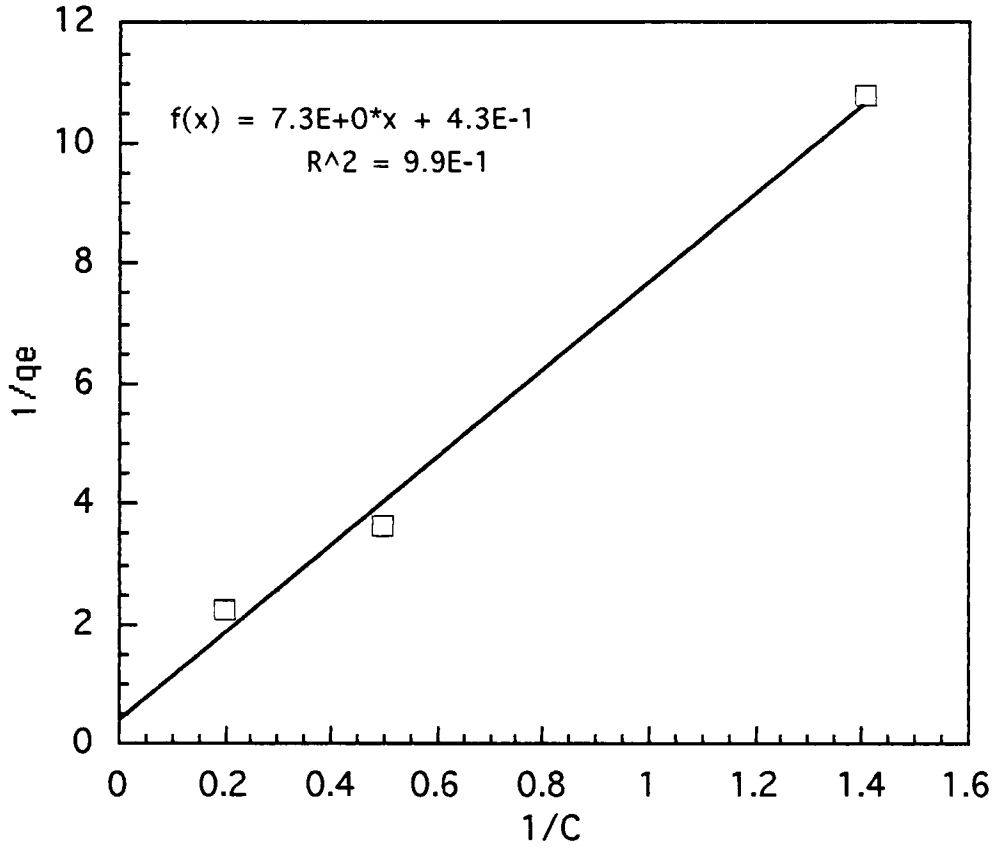


Figure 4.13 Linear plot of U adsorption to natural soil to determine adsorption parameters.

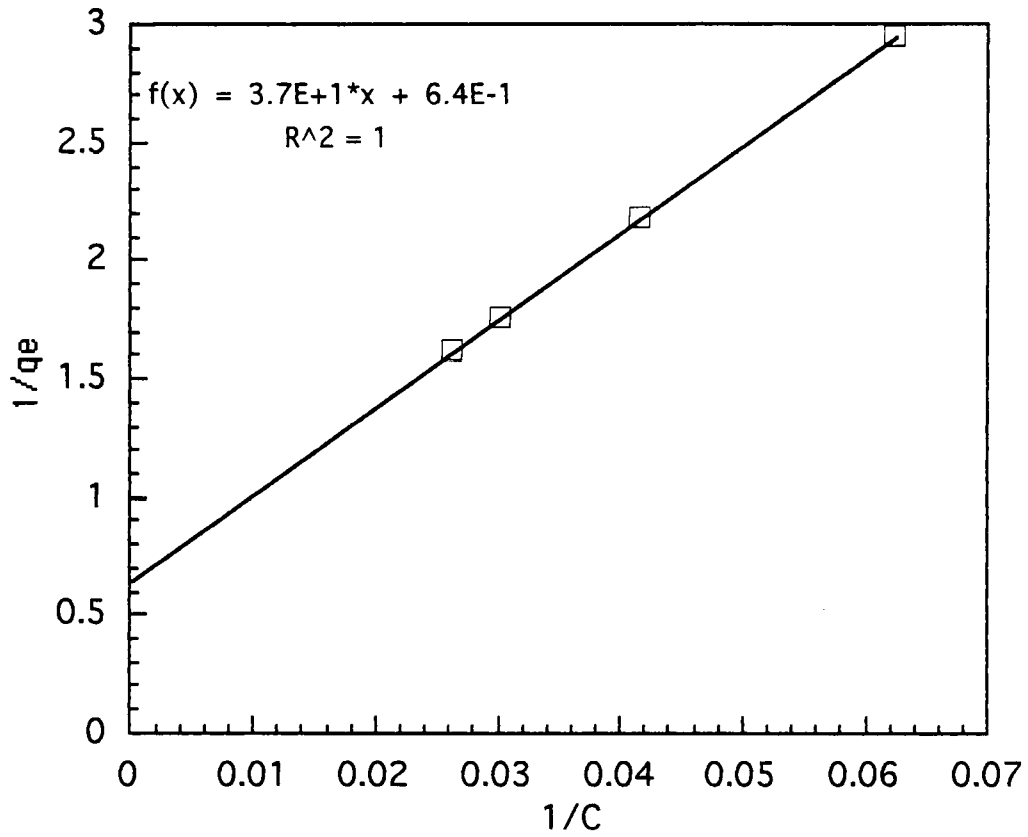


Figure 4.14 Linear plot of U adsorption to digested soil to determine adsorption parameters.

that Pb adsorption to soils fit the Langmuir isotherm (Gerritse and Van Driel, 1984).

In determining the best fit for figure 4.7, (linear plot of figure 4.6), it was observed that dropping the lowest concentration of bound metal at equilibrium gave a better linear fit. By dropping the lowest concentration the correlation coefficient (r^2) more than doubled from 0.45 to a near perfect fit of 0.98. The linear plot containing all the data is shown in the appendix as plot A.3. This indicates that the linear plot of the Langmuir isotherm may not fit well for lower sorbed concentrations.

In addition, the linear plots for the digested soil did not fit as well as the linear plots for the natural soil. From figure 4.6 this may be due to the wide scattering of data for the digested soil. The natural soil follows the typical Langmuir adsorption curve perfectly and the linear plot shows a good fit. The digested soil data, however is fairly scattered and the linear plot of this data did not give a good fit. The linear plots using all the data and dropping the lowest concentration are illustrated in figures A.4 & 5 of the appendix.

The natural soil was an undisturbed soil. The digested soil however was a treated soil which may have disrupted the soil properties so that the Langmuir model was no longer appropriate.

Even the more lenient Fruendlich model did not fit the data well. Plotting the data using the Fruendlich model uses a log-log plot which can be less sensitive to data variations. Plotting all

the Pb adsorption data gave a curve with a correlation coefficient of 0.32 as plotted in figure A.6 of the appendix. Dropping the two lowest adsorbed concentrations gave a better fit with an r^2 of 0.54 as plotted in figure A.7 of the appendix. This was still a poor fit especially in comparison to the r^2 of 0.85 achieved with the linear Langmuir plot upon dropping the two lowest adsorbed concentrations.

Figure 4.6 demonstrates once again that the digested digested soil has a higher capacity for Pb than the natural soil with 2.5 times more Pb binding to the digested soil than to the natural soil. The increased adsorption in the digested soil was discussed in the previous section.

The digested soil also had an increased bonding energy. The energy of adsorption to the digested soil was 3 times higher than the energy of adsorption to the natural soil. This indicates that binding to the digested soil was stronger than binding to the natural soil. This was also found by Petruzelli et al (1981) who found an increase in bonding energy of Pb in soils without OM as reported in table 2. Upon destruction of soil OM by H_2O_2, however, Petruzelli et al (1981) found a decrease in the maximum adsorption capacity (Q^o) which was not found in these Pb tests.

The data plotted in figure 4.9 shows that the natural soil isotherm follows the Langmuir adsorption model well. Several other workers found that Zn adsorption to soils fit the Langmuir model (Himes and Barber, 1957; Gerritse and Van Driel, 1984; Shuman, 1988).

The excellent fit of the linear Langmuir model using all the data as illustrated in figure 4.10 may be due to the low concentrations of adsorbed Zn. The spread of adsorbed Zn data was only 35 mg/kg soil from the lowest to the highest. The Pb natural soil had a 215 mg/kg spread of adsorbed data which is 6 times the Zn data spread. Because all the Zn data was at lower concentrations the need to eliminate lower adsorbed concentrations to obtain a better fit may have been eliminated. Had there been a wider range of adsorption data as was found in the Pb tests there may have been a need to eliminate the lower adsorbed concentration to obtain a better fit.

Figure 4.11 illustrates the results of a linear interpretation of Zn adsorption to the digested soil. The model was a poor fit with the best fit obtained using all the data. The Fruendlich model did not fit the data well for Zn adsorption in the digested soil either. The most significant fit was obtained using all the data as plotted in A.8 of the appendix. This plot only had an r^2 of 0.16 which indicates an extremely poor fit.

Bohn et al (1979) cautioned that the initial increase in apparent adsorption by a disappearance of metal from solution may be precipitation and not adsorption to soil. Had precipitation and not adsorption occurred at the lower concentrations, this probably would have been evident with the higher concentrations and may not account for the decreased adsorption found in this soil.

Figure 4.15 shows the digested soil also has the highest capacity for U sorption followed by Pb and then Zn as was found in the natural soil. Sheppard and Thibault (1991) found U much less mobile than Cr in natural soil cores indicating that U has a higher binding strength than Cr. Kerndorff and Schnitzer (1980) however found Cr and Pb sorption to HA extracted from a clay loam to be similar. This is similar to the findings of these tests in which Pb did not bind as readily as U in both the high and digested soil.

The strength of metal binding in these soils may be an important parameter in the magnitude of metal mobilization upon soil peroxidation. Additionally, the information pertaining to the digested soil (which was digested using H_2O_2) may be useful in understanding the mechanics of soil peroxidation.

IV.2.3 Multimetal Matrix Isotherm Experiments

Figure 4.16 shows the adsorption isotherm for Pb in a mixed metal matrix (Zn and U) in comparison to the adsorption isotherm for Pb alone in solution. The multimetal matrix resulted in more Pb adsorbed to the soil than the Pb in solution alone. A linear plot of the Pb multimetal matrix is illustrated in figure 4.17. From this plot the bonding energy term was 1.5 and the maximum adsorption capacity was 370 mg/kg soil as listed in table 3. This is an increase of 36% in Pb adsorption in a multimetal matrix in comparison to Pb in solution alone. Pb in competition with Zn for adsorption sites will be preferentially adsorbed as illustrated in

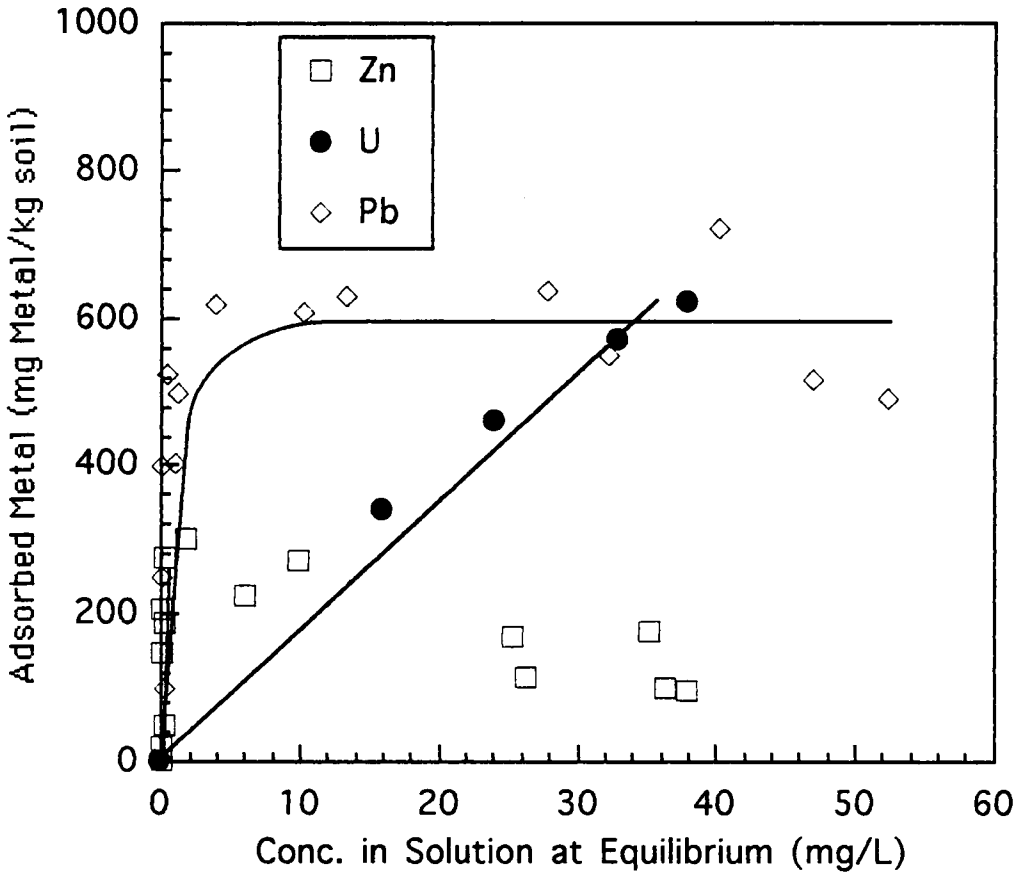


Figure 4.15 Comparison of Zn, Pb and U adsorption isotherms for 10 g of digested soil with the addition of 100 ml of varying concentrations of metal.

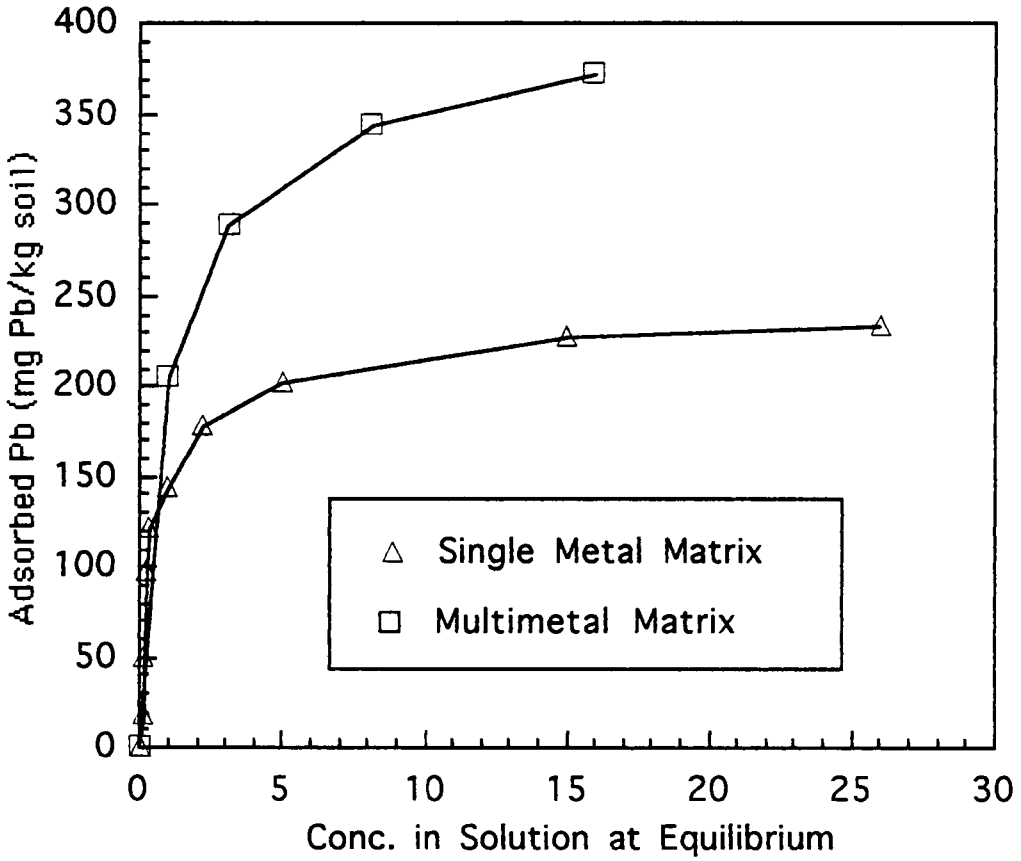


Figure 4.16 Multimetal matrix Pb adsorption to natural soil of varying concentrations of Pb in solution with 0.4 mg/L Zn and 0.3 mg/L U in comparison to Pb adsorption alone in solution. (Each data point is the mean of three samples and their standard errors.)

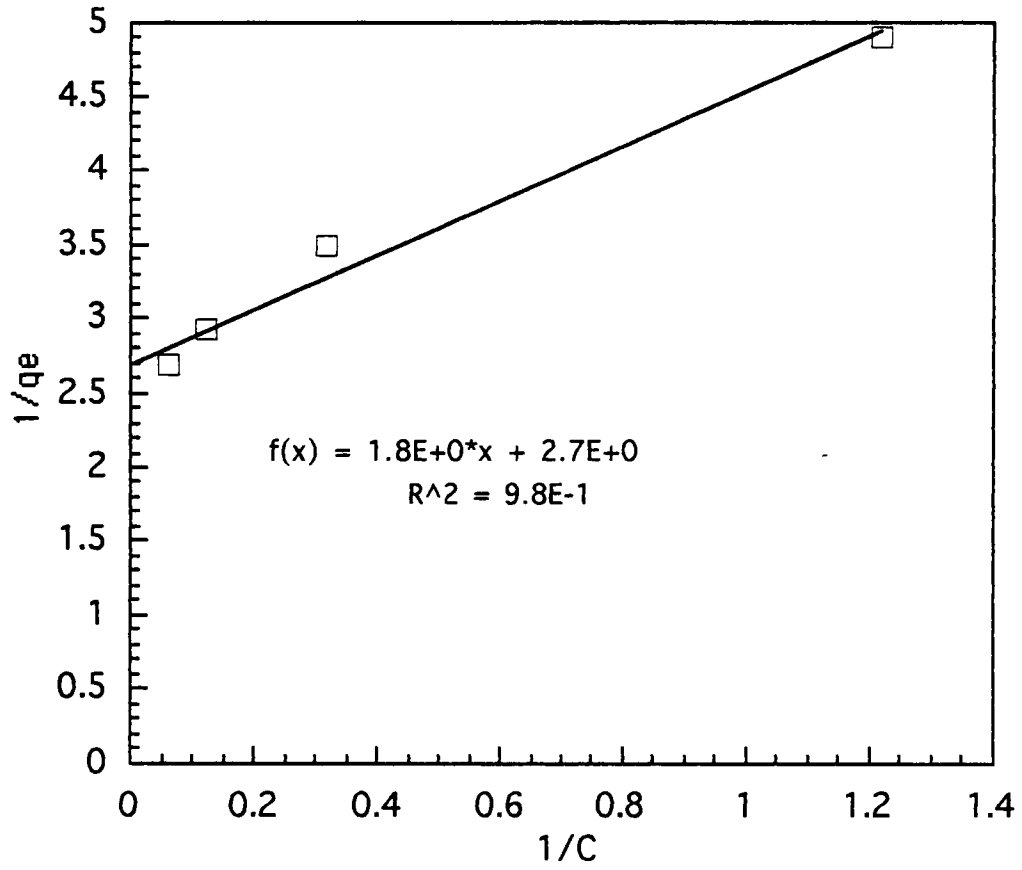


Figure 4.17 Linear plot to determine adsorption parameters of Pb adsorption to natural soil in a multimetal matrix of varying concentrations of Pb in solution with 0.4 mg/L Zn and 0.3 mg/L U.

figure 4.18 which shows the effect of Zn adsorption in the Pb multimetal matrix isotherm. As the concentration of Pb in solution increased, the amount of Zn sorbed to the soil decreased indicating that Pb is preferentially adsorbed over Zn.

TABLE 3

Langmuir Bonding Energy Coefficients (b) and Maximum Sorption Coefficients (Q^0) for Multimetal Isotherms in Comparison to Single Metal Isotherms

Matrix	Metal	Q^0	b
Single metal	Pb	0.236	2.49
Multimetal	Pb	0.37	1.5
Single metal	Zn	0.0595	3.22
Multimetal	Zn	0.051	2.78

Data plotted in figure 4.19 presents the adsorption isotherm for Zn with a constant Pb and U concentration in the initial metals solution in comparison with the adsorption isotherm for Zn in as reported in table 3. Therefore the decrease in Zn adsorption capacity was 14.5% in the multimetal matrix in comparison to the single metal matrix solution alone. Inspection of this figure shows that the multimetal matrix resulted in a lower Zn adsorption than the single metal matrix which is opposite of the findings for the Pb isotherms discussed above.

Figure 4.20 is a linear plot of the Zn multimetal matrix isotherm to determine the Langmuir coefficients. This figure was plotted dropping the lowest sorbed concentration. Using the lowest sorbed concentration gave a negative value of (-43.8) for the adsorption maximum and (-0.227) for the binding energy term which was felt to be in error. Dropping the lowest sorbed

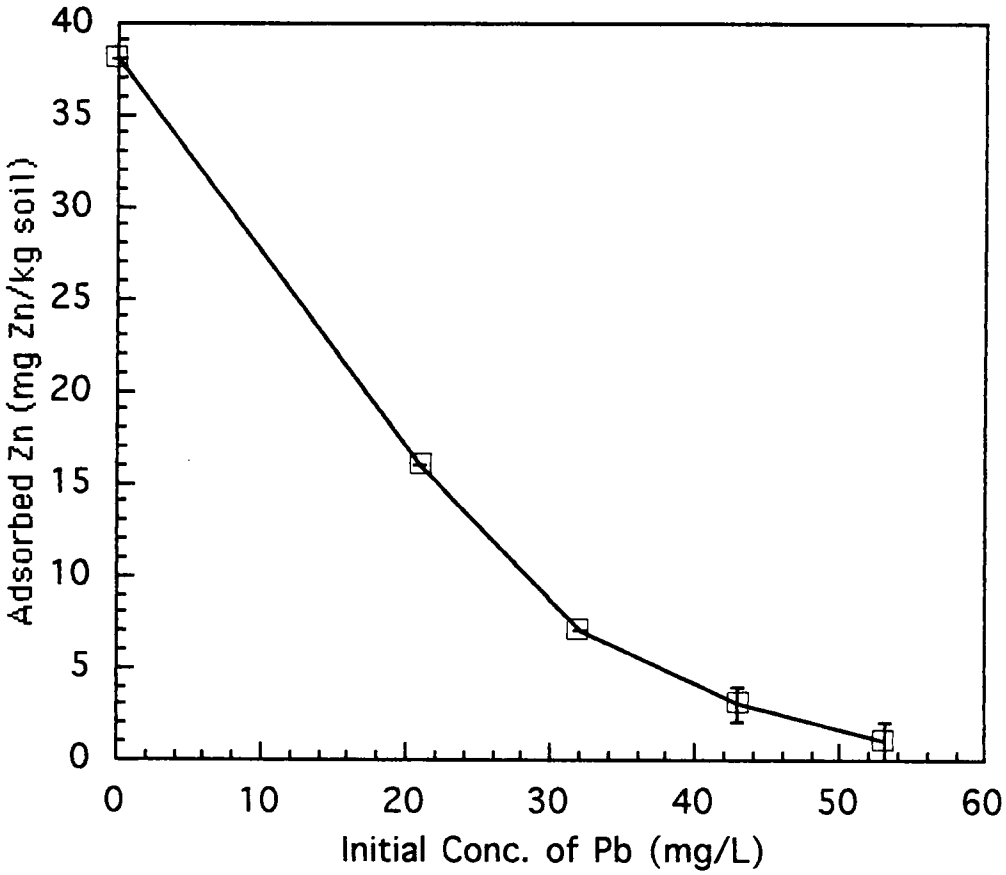


Figure 4.18 Effects on Zn adsorption to natural soil with varying concentrations of Pb in solution with 0.4 mg/L Zn and 0.3 mg/L U. (Each data point is the mean of three samples and their standard errors.)

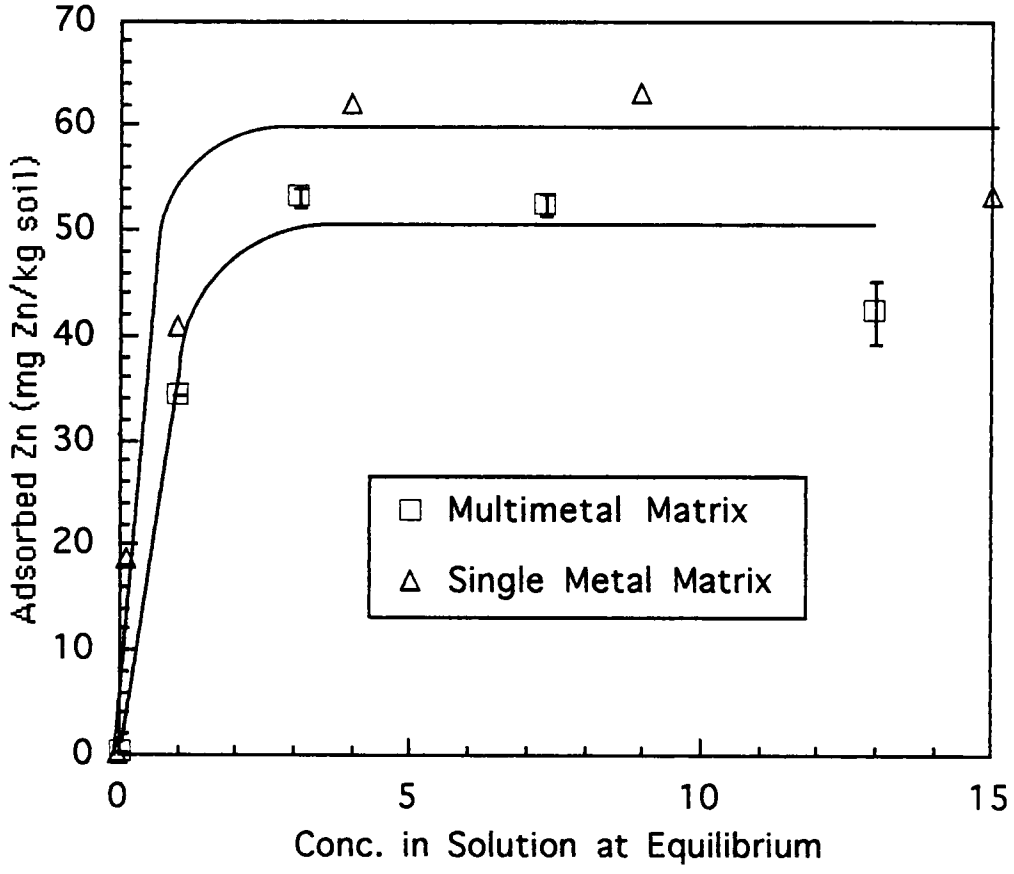


Figure 4.19 Multimetal matrix Zn adsorption to the natural soil of varying concentrations of Zn in solution with 0.3 mg/L Pb and U in comparison to Zn adsorption alone in solution. (Each data point is the mean of three samples and their standard errors.)

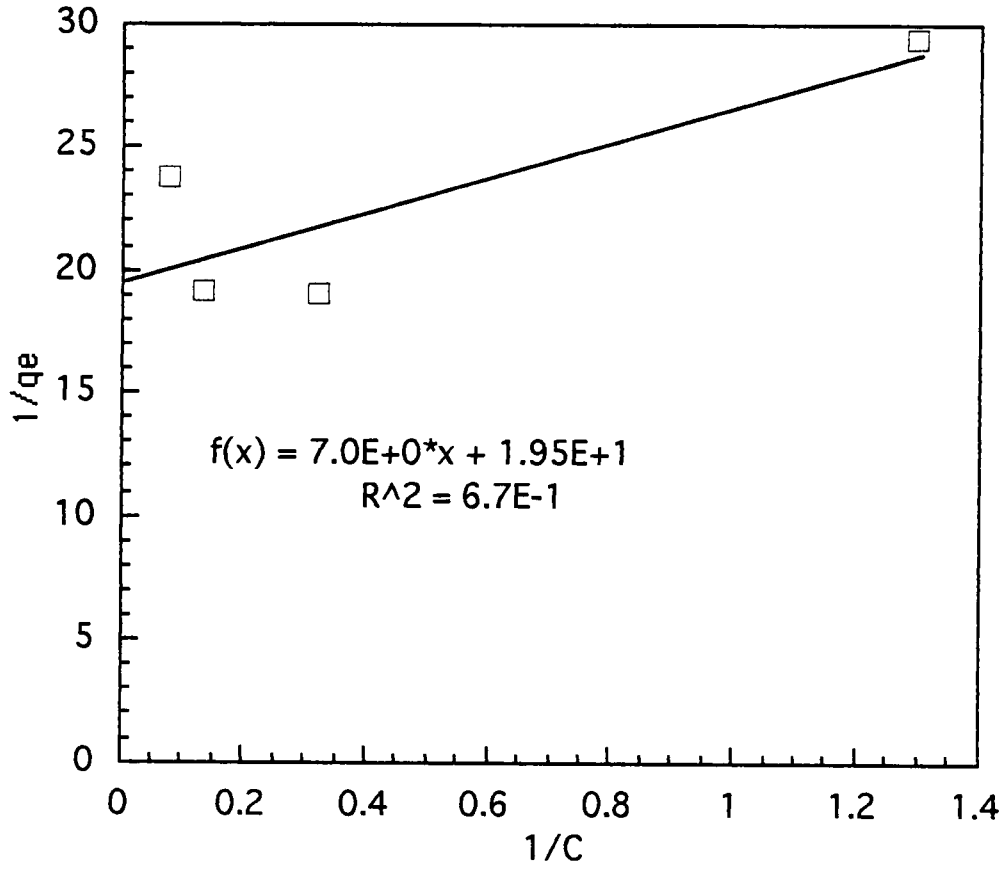


Figure 4.20 Linear plot of Zn adsorption to natural soil in a multimetal matrix of varying concentrations of Zn in solution with 0.3 mg/L Pb and U. to determine adsorption parameters.

concentration gave a more realistic value of 51.3 mg/kg soil as the adsorption maximum.

Figure 4.21 shows the effect of Zn concentration on Pb sorption in the multimetal matrix. This figure demonstrates that little if any effect on Pb adsorption was observed with increasing concentrations of Zn.

The bonding energy decreased in the multimetal matrix, as reported in table 3, by 40% upon an increase in initial Pb added indicating that the increased Pb adsorption in the multimetal matrix occurred at the expense of binding strength. The Pb in the single matrix was bound stronger than the multimetal matrix.

From the data plotted in figure 4.18, Pb is preferentially adsorbed over Zn which may be due to Pb having a higher stability constant than Zn for natural OM. Schnitzer and Skinner (1967) established the FA-metal stability constants (Log K) at pH 3.5 of Pb at 3.09 and at pH 5.0 of 6.13 compared to a Zn log K at pH 3.5 of 1.73 and at pH 5.0 a log K of 2.34. Miller et al (1983), also established that Pb has a higher stability constant and is preferentially adsorbed over Zn.

These results are also supported by the work of Kerndorff and Schnitzer (1980) who studied the competition of 10 metals for sorption on HA extracted from a clay loam. As the concentration of metals increased, Pb remained sorbed on the HA and Zn became displaced by the other metals.

Pb and U may also have been preferentially adsorbed over Zn in the multimetal Zn matrix upon increase in initial Zn added. The

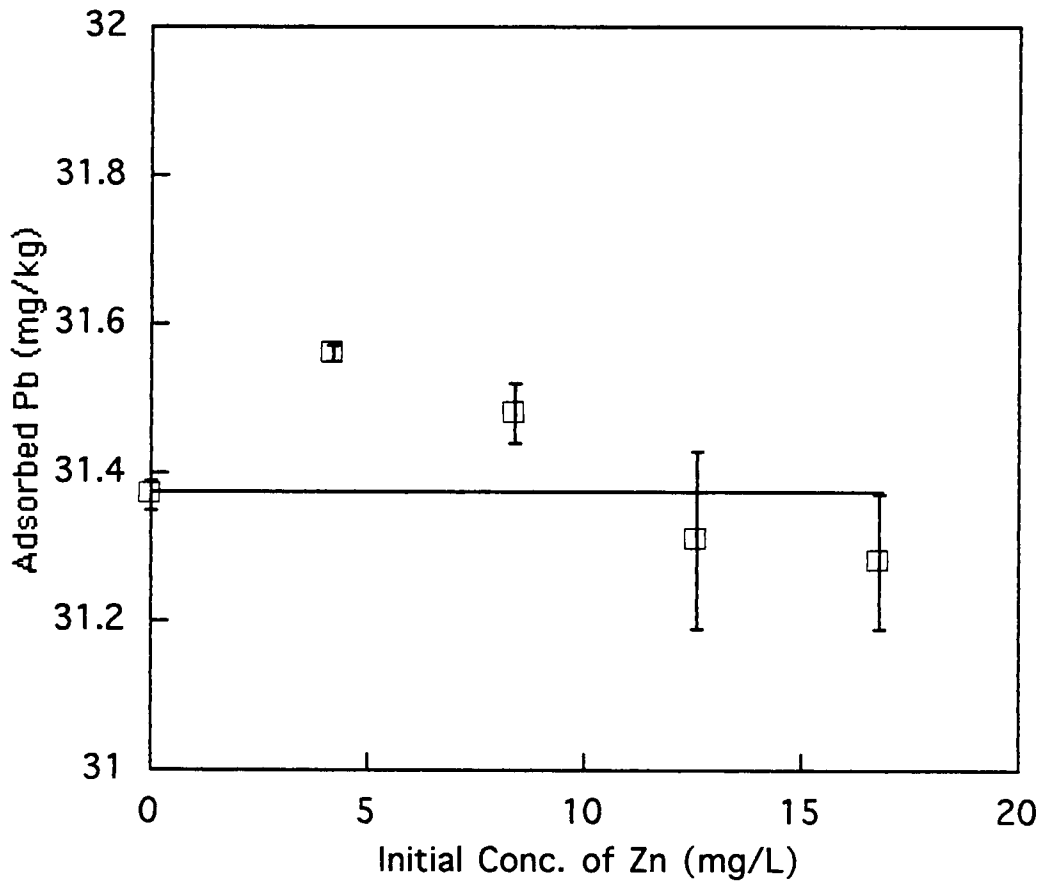


Figure 4.21 Effects on Pb adsorption in the natural soil with varying concentrations of Zn in solution with 0.3 mg/L Pb and U. (Each data point is the mean of three samples and their standard errors.)

increased Zn adsorption in the single metal matrix may be due to the finite number of adsorption sites not occupied by Pb and U as they are in the multimetal matrix. This would result in more Zn adsorption to the soil in the single metal matrix. From figure 4.21 the higher stability constant of Pb over Zn as discussed above may be why the Pb is unaffected by the increased Zn concentrations studied.

IV.3 METAL MOBILIZATION UPON H_2O_2 ADDITION

IV.3.1 Determination of Metal Loadings and Background Metal

From the data contained in table 4, the test tube adherence of Pb was negligible when 200 mls of a solution containing 3.37 mg Pb was shaken in the tubes. Adherence of 0.02 mg Zn was observed when 200 mls of a solution containing 4.33 mg Zn was shaken in the tubes. This adherence was 0.46% of the original Zn in solution and can probably be attributed to analytical error especially when consideration is given to the standard deviation of the results. No adherence was observed for the U. The soil metal loadings for the single H_2O_2 dose tests to the natural soil are also presented in table 4.

The metal loading to the natural soil was determined by using a mass balance from the data in the table 4. The amount of metal going into solution with the uncontaminated soil, labeled initial conc. (t=0), was determined. Then the concentration in

solution after equilibrium was achieved between metal and soil was obtained as listed in conc. at equilibrium (t=24).

TABLE 4

Data to Determine Test Tube Adsorption and Soil Metal Loadings for H_2O_2 Tests

Parameter (units)	Pb (n=3)		Zn (n=3)		Uranium
	Ave.	SD	Ave.	SD	
Initial Conc. {t=0}(mg/L)	16.86	0.65	21.67	0.006	1.6
Conc. at Equilibrium {t=24} (mg/L)	0.02	0.005	2.50	0.51	0.03
Wash Water Conc. {ww} (mg/L)	0.05	0.01	0.28	0.01	0.03
Test Tube Adherence (mg)	(-0.03)	0.07	0.02	0.03	0.0
Initial Metal Loading (mg Me/kg soil)	30.4	1.21	33.63	0.99	3.0

{ } = abbreviations used in calculations

n = number of samples

Ave.= average of samples

SD = standard deviation of error on averages

The soil was then washed to remove loosely bound metal and metal remaining in the macropores. This was done to better simulate a natural soil washed by years of rain. The quantity of metal thus obtained is listed under wash water (ww) and was subtracted from the conc. at equilibrium to account for this loss of metal from the original solution prior to addition to the soil. An additional loss was metal that adhered to the test tubes which was also subtracted from the original solution. The remaining difference in metal from the original solution was therefor assumed to be bound to the soil.

To evaluate the amount of background metal that mobilized in the natural uncontaminated soil upon soil peroxidation, the soil was treated with 1 mg H_2O_2 (0.01% wt/wt). This resulted in mobilization of an average 0.05 mg Pb, 0.18 mg Zn, and 0.01 mg U per g of soil.

These results suggest that Zn is more mobile than Pb and U in the native soil. This may also indicate that weathered soils have a strong binding of metals or that this soil does not contain large quantities of metals. An additional possibility is that the metals in the weathered soil are bound to unoxidizable mineral surfaces or to refractory OM.

The levels of Zn and Pb found at the Portsmouth, OH site were 30 mg/kg soil and the U levels were 1-150 mg/kg soil. These levels were modeled in the experiments of this research with the natural soil contaminated to the levels shown in table 4.

The H_2O_2 added to the soils reported in results of the following experiments were determined from equation IV.4.a.

$$H_2O_2 \text{ Added} = \frac{(\%(\text{wt./wt.})\ H_2O_2 / 100)(10 \text{ mls})(\text{density mg / ml})}{10 \text{ g soil}} \quad \text{(IV.4.a)}$$

IV.3.2 Metal Mobilization Upon a Single Treatment of Varying Doses of H_2O_2

Data plotted in figure 4.22 shows Pb mobilization upon peroxidation of the contaminated soils loaded with 31.8 and 27.5 mg Pb/kg soil to the natural and digested soils respectively. This figure suggests that little, if any, mobilization of Pb occurred even at the highest H_2O_2 loadings in both soils.

The data plotted in figure 4.23 illustrates the metal mobilization of Zn at initial loadings of 32.46 and 31.03 mg Zn/kg soil to the high and digested soils respectively. This figure indicates that below a loading of 10.0 mg H_2O_2 per g soil, no Zn mobilized from either soil. Mobilization of Zn in the natural soil does occur however, above approximately 10 mg H_2O_2 per g soil.

Figure 4.24 is the results of U mobilization from both natural and digested soils upon soil peroxidation. The U loading on the natural soil was 3.03 mgU/kg soil and the digested soil was contaminated to 24.1 mg/kg soil. From the data plotted in this figure, no U mobilized from either soil under the various H_2O_2 loadings.

The lack of Pb mobilization upon soil peroxidation

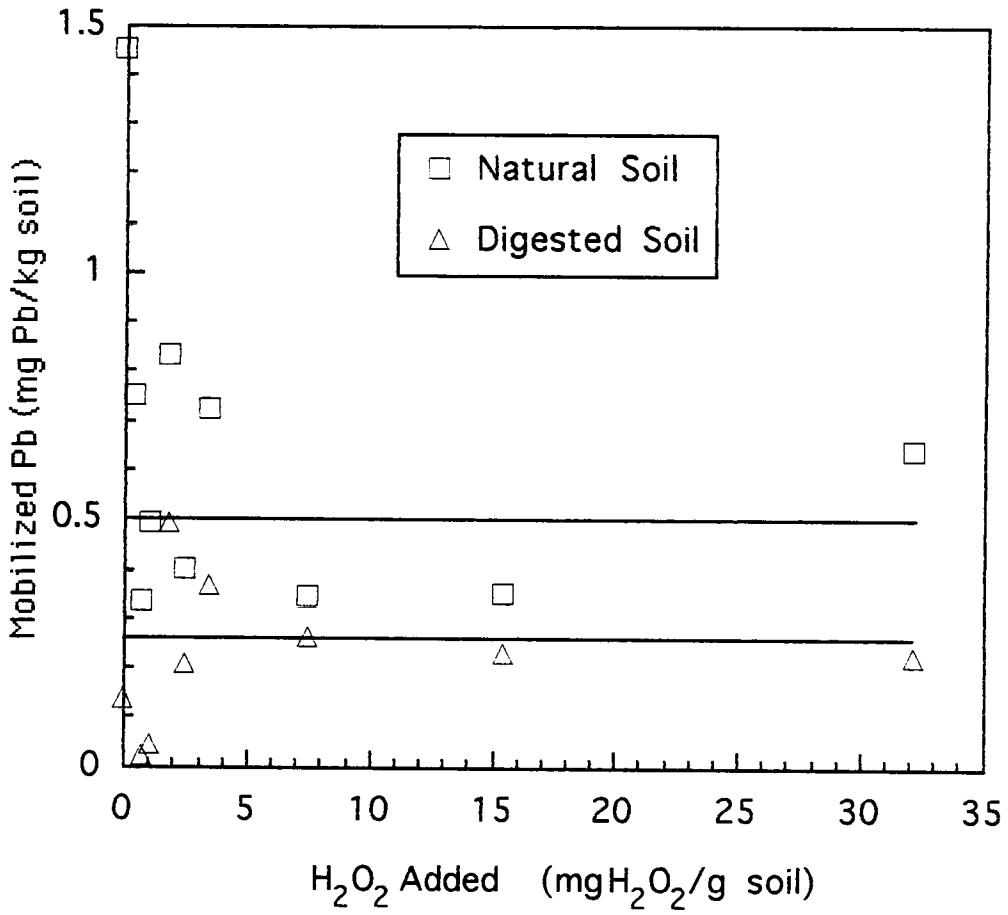


Figure 4.22 Pb mobilization after an H_2O_2 addition to 10 g of natural or digested soil followed by triple washing with 20 ml of pH 7 DI water.

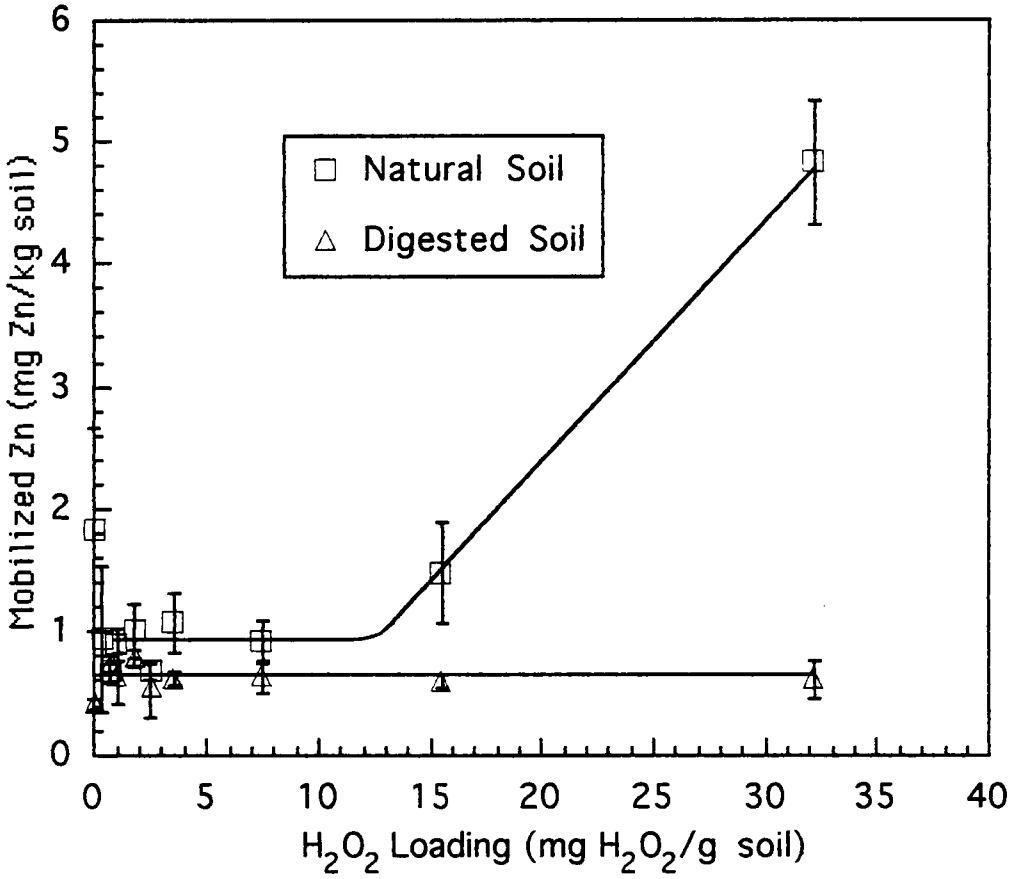


Figure 4.23 Zn mobilization after an H_2O_2 addition to 10 g of natural or digested soil followed by triple washing with 20 ml of pH 7 DI water. (Each data point is the mean of three samples and their standard errors.)

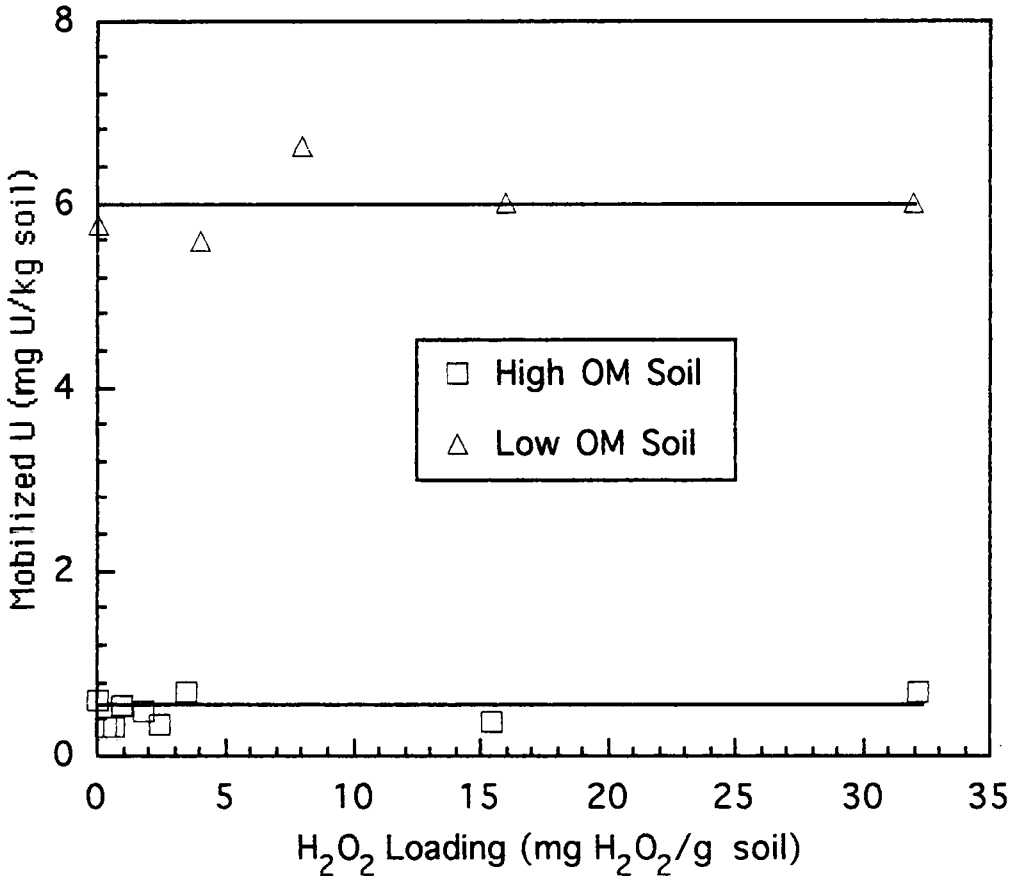


Figure 4.24 U mobilizations after an H_2O_2 addition to 10 g of high or digested soil followed by triple washing with 20 ml of pH 7 DI water.

illustrated in figure 4.22 may be the result of Pb being strongly bound to the soil. Sheppard et al (1989) found only 24% of the Pb in a soil was extracted with heated H_2SO_4 acid hydrolysis. This indicated that the Pb was very strongly bound to the soil due to the small extraction obtained with this severe process.

The minimal Pb mobility observed may also have been due to Pb binding to unoxidizable clay and mineral surfaces or to refractory OM sites. Schintu et al (1991) found that OM is important in the binding of Pb to lake sediments however he found exchangeable carbonates and Fe-Mn oxides contained higher fraction of Pb. These mineral binding sites may not be affected by soil peroxidation and consequently result in no mobilized Pb bound to these sites.

The binding of Pb to unoxidizable mineral surfaces was also found by Guy et al (1978). They observed that upon soil peroxidation, Pb bound to soil organics mobilized but when bound to clays or hydrous oxides, Pb did not mobilize.

Less Pb mobilized from the digested soil indicating that the Pb may have been more strongly bound than to the natural soil. This is reinforced by the Langmuir bonding energy coefficients (b) determined in the isotherm experiments which increased indicating a stronger adsorption to the digested soil. The bonding energy term increased from 2.49 in the natural soil to 7.68 in the digested soil. This 3 fold increase is a substantial increase in bonding energy.

The data presented in this figure is quite variable which may be due to the small scale used. This apparently noisy data may not be noticed as readily on a larger scale as illustrated in a later figure.

Figure 4.23 may indicate that mobility of Zn in the natural soil may not have occurred at lower H_2O_2 concentrations added due to these doses being insufficient in oxidation potential to oxidize metal/OM binding sites. At higher H_2O_2 loadings, however, the oxidation potential was adequate enough to oxidize OM binding sites releasing Zn. Upon further increases in H_2O_2 dose more Zn mobilization was observed due to the oxidation of additional Zn binding sites on soil OM.

Figure 4.23 also shows that no mobilization of Zn occurred in the digested soil. From this figure the conclusion can be drawn that Zn is less mobile in the digested soil than the natural soil up to 10 mg H_2O_2 per g soil loading. Above this H_2O_2 loading the Zn in the digested soil is much less mobile.

The oxidation of Zn OM binding sites may have been via the oxygen-containing functional groups on HA (CO_2H, phenolic and alcoholic OH). Kerndorff and Schnitzer (1980), Guy et al (1978) and Alberts and Giesy (1983) reported that these binding sites are the functional groups were metals will bind to soil OM. The release of the Zn upon soil peroxidation may have due to the destruction of these binding sites.

These findings may also indicate a stronger binding of the Zn in the digested soil. However, the Langmuir bonding energy

coefficient (b) decreased in the digested soil of the isotherm experiments in comparison to the natural soil. This would indicate a stronger Zn adsorption to the natural soil. However the fit of the digested soil to the Langmuir model was extremely poor so the binding energy term was most likely in error.

A more plausible explanation for the increased mobility in the natural soil may have be that the Zn was bound to oxidizable soil OM which released the metal upon the oxidation of OM/metal bindings sites. The Zn in the digested soil may have been bound to unoxidizable soil mineral components or to refractory soil OM. This is supported by the work of Guy et al (1978) who found that upon soil peroxidation, metals bound to soil organics mobilized but metals bound to clays or hydrous oxides did not mobilize. These researchers also determined that metals bound to humic acid mobilized upon an H_2O_2 treatment but in the presence of clays did not mobilize as readily.

Additionally, the digested soil was digested to remove OM. The residual OM on this soil was refractory and any Zn bound to these refractory sites would be unaffected by soil peroxidation as may have been evidenced by the lack of Zn mobilization in the digested soil.

No U mobilized from either soil under the various H_2O_2 loadings illustrated in figure 4.24, indicating that U was bound to unoxidizable soil mineral binding sites or to refractory soil OM as observed for Pb in both soils and Zn in the digested soil.

Although no mobilization due to H_2O_2 was observed, inspection figure 4.24 shows that more U was in solution in the digested soil experiments than the natural soil experiments. This may be the result of a higher U loading to the digested soil, however, this was probably due to the DI water used in the digested test which was obtained from a malfunctioning deionizing unit.

In previous tests the DI water found to be slightly acidic prior to adding base to formulate a pH 7 DI water. This water was used in the natural U experiments. The water used in the digested U experiments was found to be basic prior to the addition of an acid to create the pH 7 DI water.

Although the pH in both waters was neutral the water used in the digested tests was found to have mobilized metals. The multiple treatment tests discussed in a following section were first run with DI water obtained from the malfunctioning deionizing unit. When the determination was made that this water may be mobilizing metals the packing on the deionizing unit water columns was replaced and the tests were rerun.

Figure 4.25 compares the metal mobilization from repeated treatments using the problematic DI water in comparison to the rerun of these tests using DI water that was obtained after replacing the DI unit. From this figure it is obvious that the problematic DI water was mobilizing metals in comparison to the unflawed DI water. Unfortunately cost constraints did not allow the U digested test to be rerun.

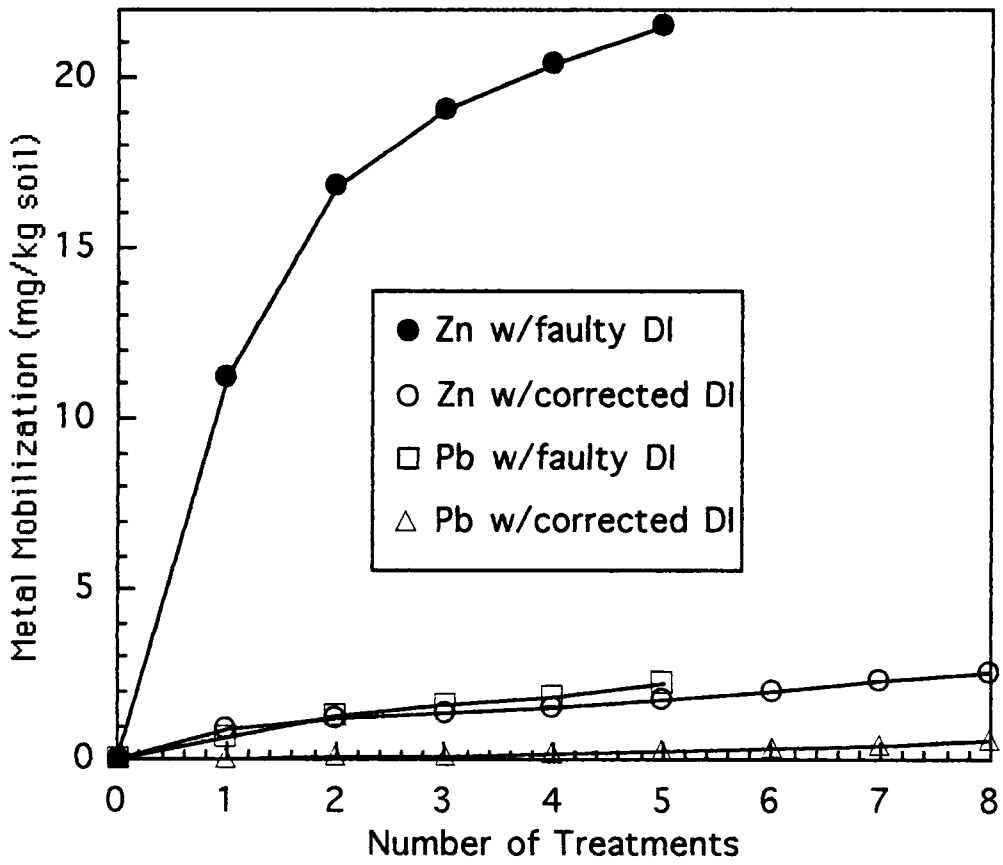


Figure 4.25 Comparison of metal mobilizations from the repeated treatments of a contaminated soil with water from faulty and repaired DI columns.

Figure 4.26 further illustrate that Zn is more mobile than Pb in soils which is similar to the findings discussed in the Literature Review indicating Zn is one of the most mobile metals in soils. These results are also similar to findings reported by Tessier et al (1979) who found more Zn extracted than Pb during soil peroxidation.

This may have been due to Pb having a stronger binding to the soil than Zn. Comparison of the U binding energy determined in the isotherm experiments with Pb and Zn is not reasonable due to the extremely small value of the U binding energy term. The bonding energy of Zn however was higher than Pb in the natural soil.

This seems contradictory to the results obtained in the H_2O_2 tests but the mobility of Zn was probably the result of Zn being bound to oxidizable binding sites as discussed above. The Pb and U may have been bound to binding sites such as mineral surfaces and refractory OM that were not as susceptible to oxidation.

Figures 4.26 also indicates that Pb and U behave similarly in the H_2O_2 tests. There also was a similarity in the behavior of sorption Pb and U in the equilibrium rate tests discussed in the appendix and illustrated in figure A.2. This may indicate that Pb and U are bound in similar fashions to the natural soil.

Figure 4.27 is a comparison of the metal mobilizations observed upon an addition of H_2O_2 to the digested soil. The high amount of U mobilized from the digested soil as plotted in this

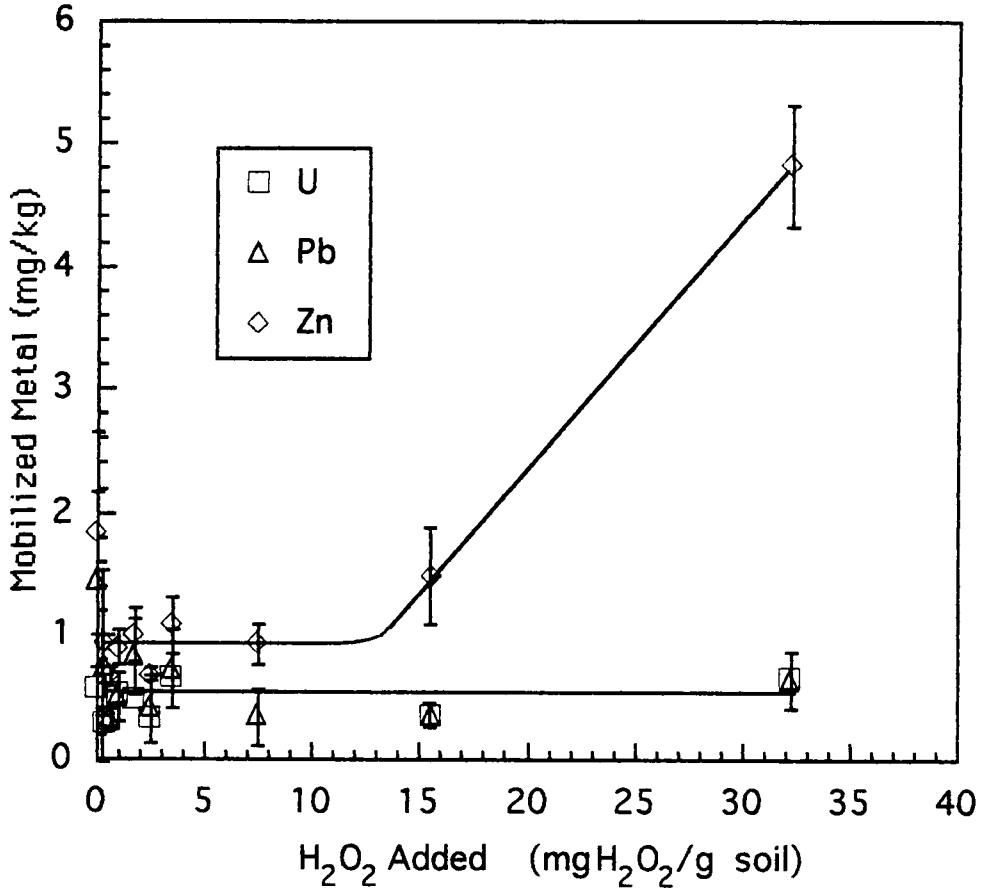


Figure 4.26 Comparison of metal mobilizations (Pb, Zn & U) after an H_2O_2 addition to 10 g of natural soil.

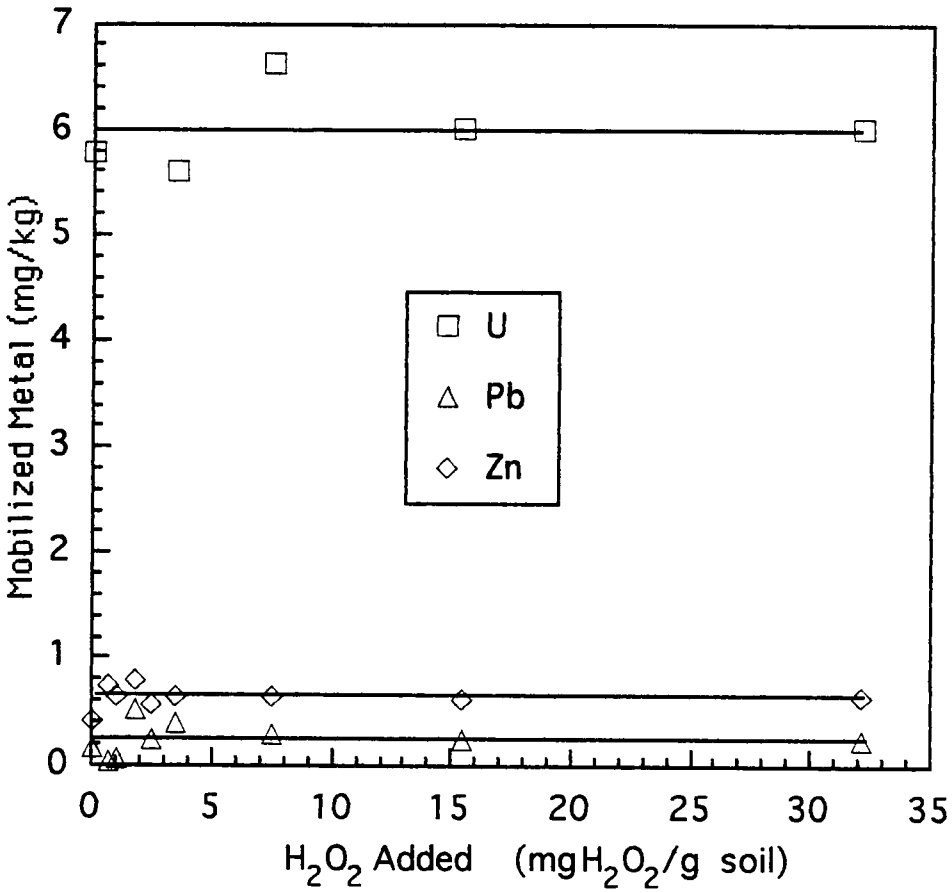


Figure 4.27 Comparison of metal mobilizations (Pb, Zn & U) after an H_2O_2 addition to 10 g of digested soil. (Soils contaminated to 30 mg metal/kg soil.)

figure was probably due to the faulty DI water used in the U digested tests as discussed above.

Comparison of the U bonding energy term is difficult due to the extremely small value obtained that may have been the result of an incomplete isotherm. The digested soil however had the opposite effect of the natural soil on the binding energy terms of Pb and Zn. The Pb value was 6.8 times higher than Zn which may indicate that the Pb is held stronger to the soil than Zn as observed in figure 4.27 where Pb is less mobile than Zn. Use of the Langmuir binding energy coefficients to describe Zn binding strength in the digested soil may not be accurate, however, due to the extremely poor fit of the Zn adsorption isotherm to the Langmuir model.

This figure illustrates that the H_2O_2 loadings studied in the digested soil had minimal impact on metal mobilization. This is probably the result of the metals being bound to mineral surfaces or to refractory OM. The digested soil was digested to remove OM so OM that may have remained would be unaffected by H_2O_2. Consequently metals binding sites on this refractory OM would also not be influenced by an H_2O_2 addition.

The digested soil probably had increased mineral binding sites which also may not have been subject to oxidation upon soil peroxidation. Sequi and Aringhieri (1977) found that soil peroxidation destroyed organic coatings on clays exposing clay binding sites which would not be susceptible to oxidation.

IV.3.3 Metal Mobilization Upon A Multiple Treatment of H_2O_2 With Varying Contact Times:

The results of Pb mobilization from consecutive peroxidation treatments with varying contact times between treatments is illustrated in figure 4.28. This figure indicates that 1 hour of contact time mobilized the most Pb per treatment after the fourth successive treatment. After the third treatment Pb mobilization continues to occur upon each repeated treatment except for the 12 hour contact time tests in which mobilization stabilized.

Data plotted in figure 4.29 illustrates Zn mobilization from repeated H_2O_2 treatments with varying contact times. A decrease in the amount of mobilized Zn was observed with each successive treatment for the times studied. Longer H_2O_2 contact times resulted in more mobilized Zn with 12 hour contact resulting in the highest Zn mobilization.

More Pb mobilized in the 1 hour test as illustrated in figure 4.28, than the 5 minute test which may indicate an initial increase in Pb mobilization with an increase in H_2O_2 contact time. However mobilization from the 12 hour contact time test stabilized after the third treatment and resulted in less mobilization than the 1 hour test possibly indicating that mobilized Pb was resorbing to the soil with longer H_2O_2 contact times.

This is supported by the work of Bermond and Benzineb (1991) who found an initial increase in mobilized Zn following

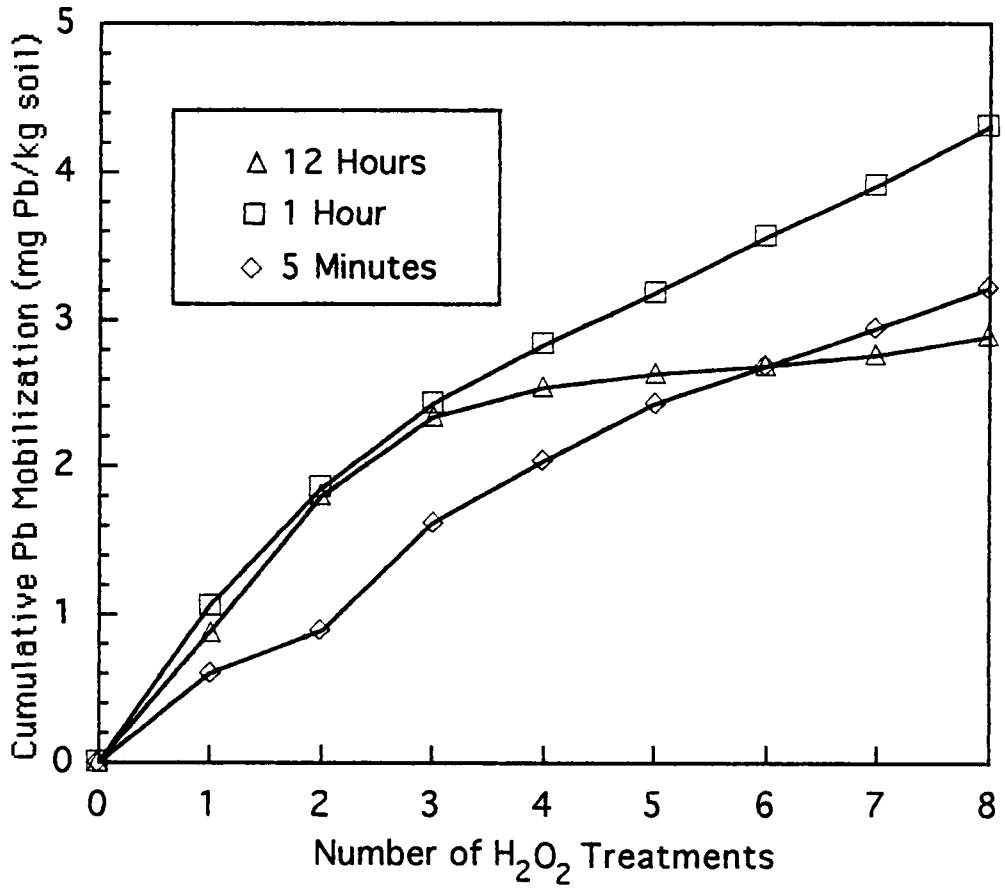


Figure 4.28 Cumulative Pb mobilization from repeated H_2O_2 treatments of natural soil at a loading of 32 mg H_2O_2/g soil with contact times of 5 min., 1 hr or 12 hrs. between each subsequent treatment. (Each data point is the mean of three samples and their standard errors. Initial metal loading = 30 mg metal/kg soil.)

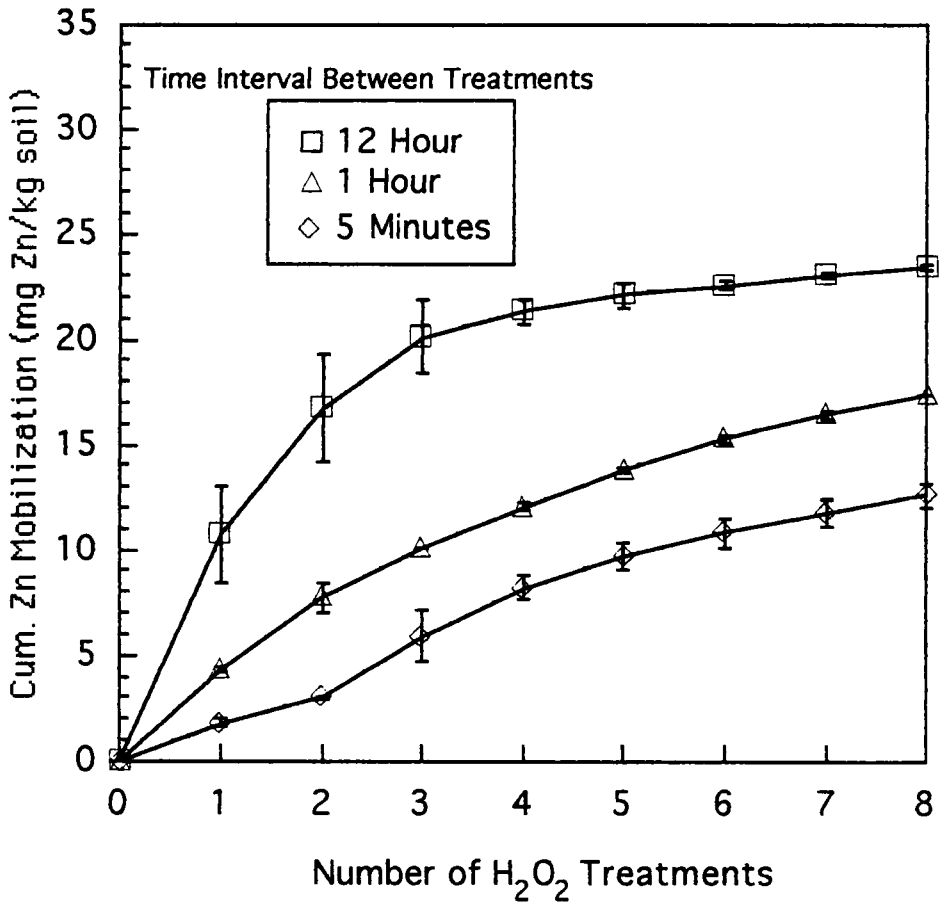


Figure 4.29 Cumulative Zn mobilization from repeated H_2O_2 treatments natural soil at a loading of 32 mg H_2O_2/g soil with contact times of 5 min., 1 hr or 12 hrs. between each subsequent treatment. (Each data point is the mean of three samples and their standard errors. Initial metal loading = 30 mg metal/ kg soil.)

soil peroxidation with a subsequent decrease of mobilized Zn over time which they explained as the destruction of OM releasing Zn and then readsorption of mobilized Zn on the soil mineral fraction.

Rendell et al (1980) also established that metal readsorption occurred during H_2O_2 treatment with a portion of the released metal readsorbing on the soil. They found, however, that readsorption of mobilized metals increased with shorter extraction times which was not observed with the contact times studied in these Pb tests.

In an additional study, Rauret et al (1989) observed that repeated H_2O_2 treatments of a Pb contaminated sediment resulted in Pb mobilization in the first treatment due to a strong oxidation of OM and the release of Pb sorbed to OM. They observed a decrease in Pb mobilization upon subsequent treatments which is similar to the findings of these experiments.

An additional researcher observed metal readsorption upon soil peroxidation. Guy et al (1978) found that mobilized metals readsorbed to the soil by exchanging with ions on clays and binding to MnO_2.

Rauret et al (1989) found a decrease in redox potential (Eh) upon repeated H_2O_2 treatments. They used Eh as an indicator of oxidant consumed to destroy OM. They observed sharp changes in Eh in the first extraction which they interpreted as a strong oxidation of OM. Successive extractions had smaller Eh variations which suggested that no OM remained in solution.

Soil peroxidation is an exothermic reaction. The addition of H2O to the soil may have raised the temperature which may have affected metal mobility. Temperature effects were not analyzed in this work.

Data plotted in figure 4.29 illustrates Zn mobilization from repeated H_2O_2 treatments with varying contact times. A decrease in the amount of mobilized Zn was observed with each successive treatment for the times studied. No readsorption of mobilized Zn was evident from these tests due to the fact that longer H_2O_2 contact times resulted in more mobilized Zn. This was not found to be true for the tests described above, however, Zn mobilization did stabilized after the third treatment for the 12 hour contact times as in the Pb tests.

As the oxidation of soil OM continues, the metal binding sites that remain will be unoxidizable mineral surfaces and refractory OM binding sites. This is evident in the 12 hour tests where Zn mobilization discontinues after the fourth treatment. At this point the soil begins to be similar to the digested soil with metal binding sites being unoxidizable.

These findings are not similar to the findings described above by Bermond and Benzineb (1991) where mobilized Zn in sewage amended soils treated with H_2O_2 reached a maximum and then decreased over time. The amount of Zn mobilized in these tests increased with longer contact times.

Metals released during peroxidation may also be competing with each other for available adsorption sites and with other

metals such as Fe and Mn which may be present in much higher concentrations. Zn in competition with other metals for binding sites, may not readsorb due to a preferential sorption of other metals over Zn. Pb however may have readsorbed to the soil due to a higher binding affinity for the soil in comparison to Zn and other metals.

The data plotted in figures A.10-A.12 show once again that Zn is more mobile than Pb as has been seen throughout this work. The Zn mobilization decrease observed upon subsequent treatments may have been due to decreasing oxidizable soil OM with each succeeding treatment. This is especially evident in figure A.12 which illustrates the results of 12 hours of H_2O_2 contact between treatments.

Figure A.12 indicates that no additional Pb and only a small quantity of Zn mobilized after the third treatment for the 12 hour tests. At this point the soil begins to behave as the digested soil with binding sites being less susceptible to oxidation.

Figure 4.30 compares the metal mobilization observed from the addition of H_2O_2 with the mobilization observed from the addition of pH 7 DI water alone. This figure illustrates that the mobilization observed upon peroxidation was due to the H_2O_2 treatment and not due to the testing procedure.

In summary the magnitude of metal mobilization from soil peroxidation is affected by H_2O_2 contact time and the number of repeated treatments. Longer H_2O_2 contact times result in more Zn mobilization. Pb mobilization increased with shorter H_2O_2 contact

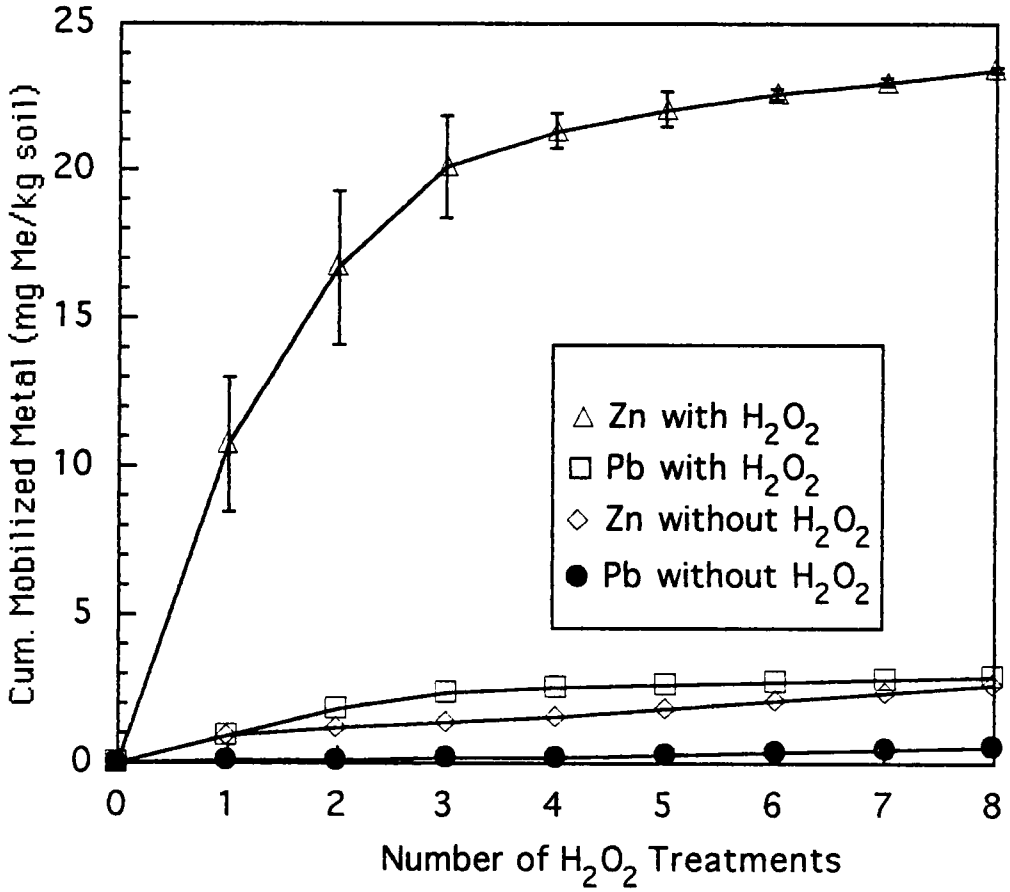


Figure 4.30 Mobilization of Pb & Zn from repeated treatments of pH 7 DI water in comparison with mobilization of Pb & Zn from repeated H_2O_2 treatments at a loading of 32 mg H_2O_2/g soil at 12 hrs. of contact time between each subsequent treatment. (Each data point is the mean of three samples and their standard errors.)

times possibly due to a readsorption of mobilized Pb to the soil over time.

Repeated H_2O_2 treatments result in continual mobilization of both Pb and Zn with shorter treatment times of 5 minutes and 1 hour. With 12 hours of contact between treatments however additional Zn and Pb mobilization did not occur after the third treatment possibly due to OM being fully oxidized to refractory materials or due to metals binding to mineral components.

IV.3.4 Metal Readsorption Following Mobilization From A Single Peroxidation Treatment Of A Contaminated Soil

The data reported in table 5 indicates that the reapplied treatment solution may mobilize an additional 10.6% Pb than was observed for the original treatment solution. This may indicate that the treatment solution is continuing to mobilize Pb. Therefor a mobilized Pb and H_2O_2 solution in an H_2O_2 treated soil zone may migrate to a lower H_2O_2 treated soil zone and mobilize additional Pb. Consideration of the standard deviation (SD) of the errors for this test however may lead to the conclusion that the treatment solution is not mobilizing additional Pb upon reapplication.

The wash water reported in this table did not show a significant decrease in mobilized Pb when reapplied to the treated soil. This may indicate that no readsorption of mobilized Pb was occurring with the wash water.

The mobilized Zn and H_2O_2 solution reported in table 6 did not show a significant change in mobilized Zn when reapplied and

TABLE 5

Effects on Pb from the Reapplication of an H_2O_2 Treatment Solution To a Treated Soil

	Test#1 mgPb/ kg soil mobil- ized	Test#2 mgPb/ kg soil mobil- ized	Test#3 mgPb/ kg soil mobil- ized	mg Pb/kg soil mobilized		% Change from origin- al
				Ave	SD.	
Treatment Solution	1.18	1.26	1.35	1.26	0.09	
Treatment Solution Reapplied	1.35	1.40	1.47	1.41	0.06	10.6
Wash	0.62	0.55	0.62	0.60	0.04	
Wash Sol. Reapplied	0.54	0.54	0.59	0.56	0.03	(-6.6)

TABLE 6

Effects on Zn from the Reapplication of an H_2O_2 Treatment Solution To a Treated Soil

	Test#1 mgPb/ kg soil mobil- ized	Test#2 mgPb/ kg soil mobil- ized	Test#3 mgPb/ kg soil mobil- ized	mg Pb/kg soil mobilized		% Change from origin- al
				Ave	SD.	
Treatment Solution	13.01	12.83	11.21	12.4	0.99	
Treatment Solution Reapplied	11.72	12.58	11.39	11.9	0.61	(-3.6)
Wash	4.09	3.31	2.94	3.45	0.59	
Wash Sol. Reapplied	4.31	4.18	3.74	4.08	0.3	15.4

allowed 12 hours of contact time. The wash water reported in this table resulted in a possible 15.4% increase in mobilized Zn when reapplied and allowed 12 hours of contact time which may indicate the wash water is mobilizing additional Zn when reapplied. This may also be a result of organic ligands in the wash water desorbing metals when reapplied. However, again the large standard deviation (SD) from this test may indicate that the additional metal mobilization observed was not significant.

IV.4 pH EFFECTS ON METALS MOBILIZATION

As reported from the literature, metal mobilization does occur with a change in pH due to H^+ ions competing with cationic metals for adsorption sites. Weber (1972) states that hydrogen and hydroxyl ions are strongly adsorbed to soils. The results of tests performed on metal mobilization from a significant pH change can be used to estimate metal mobility in this soil due to pH effects.

Figure 4.31 shows Zn mobilization from a change in pH of one and two units above and below the pH observed for the DI water alone (pH=6.5). The acidic pH changes resulted in significant Zn mobilization while the change in pH towards the basic end resulted in a very slight decrease in Zn mobilization. These tests further illustrate that Zn is more mobile than Pb. Observation of figure 4.32, however, indicates that a change in pH of one to two

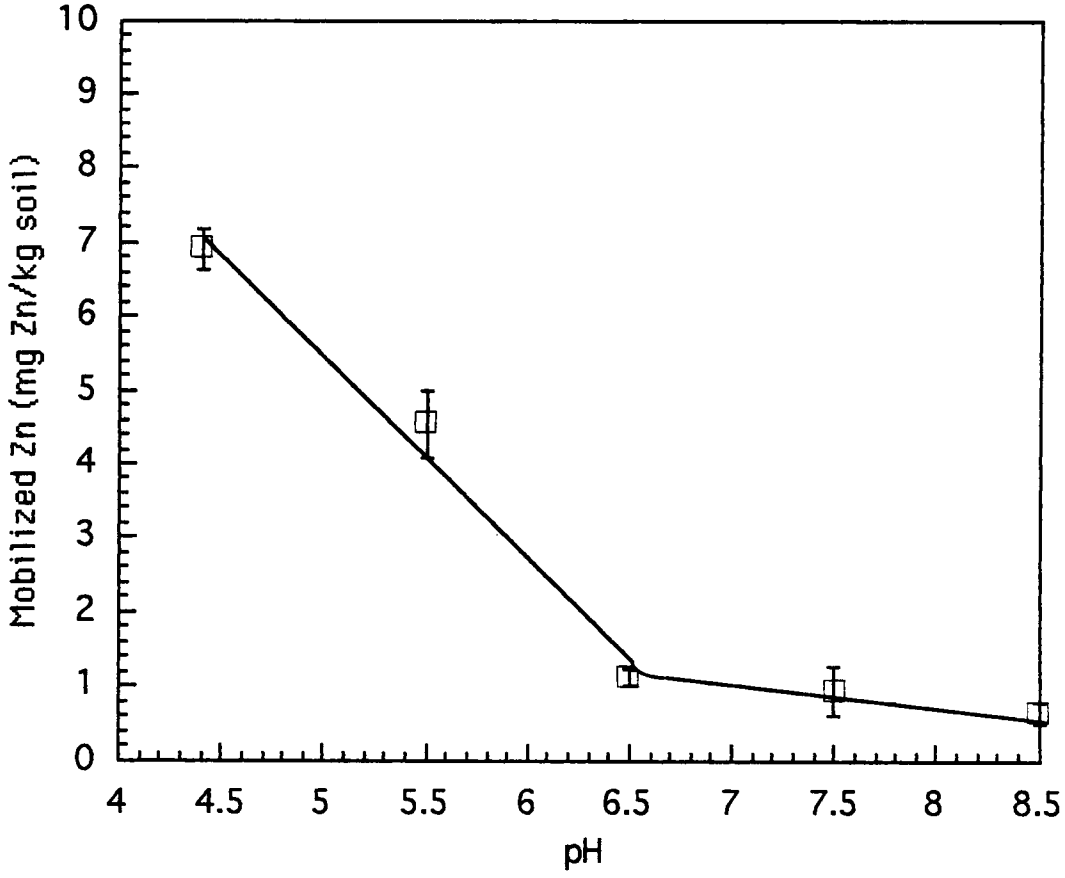


Figure 4.31 Zn mobilization after a pH change of one and two units above and below the natural pH of 6.5. (Each data point is the mean of three samples and their standard errors. Initial metal loading= 30 mg Zn/kg soil.)

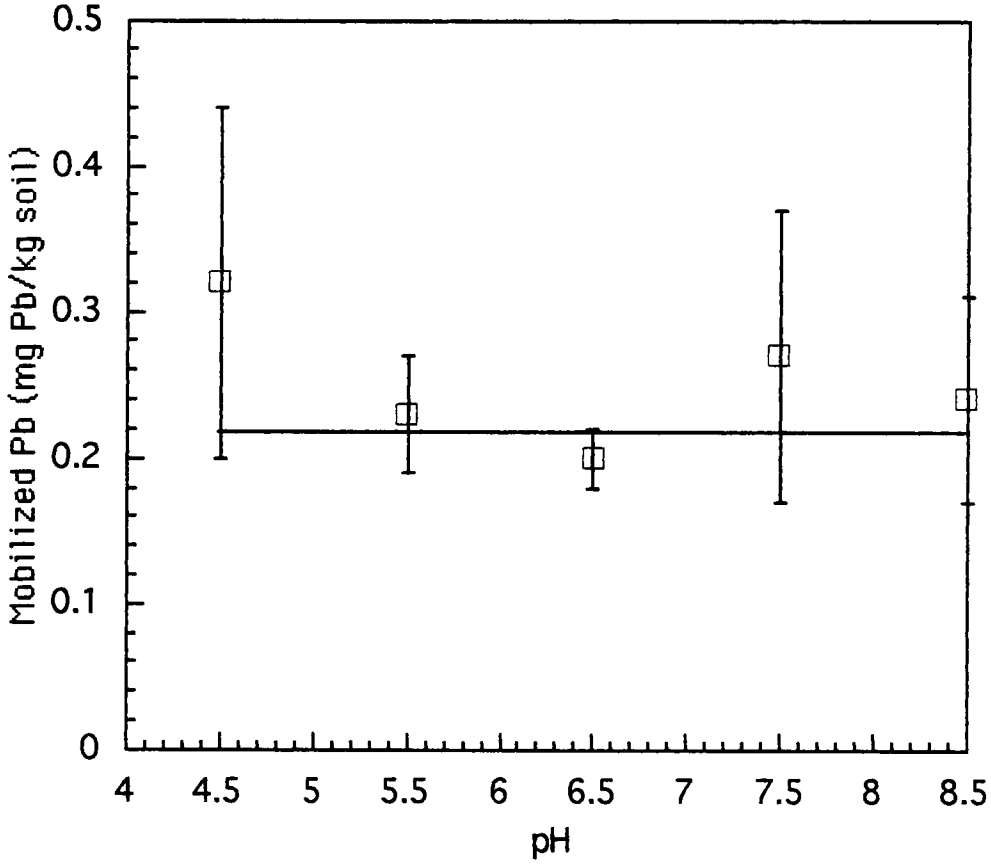


Figure 4.32 Pb mobilization after a pH change of one and two units above and below the natural pH of 6.5. (Each data point is the mean of three samples and their standard errors. Initial metal loading= 30 mg Pb/kg soil.)

units below and above pH 6.5 resulted in little change in Pb mobilization.

Additional experiments were performed to determine if a change in pH was occurring with the addition of H_2O_2 to the soils. pH was monitored as a function of H_2O_2 addition. From figure 4.33 it was determined that only the addition of 32 mg H_2O_2/g soil resulted in a significant pH change beyond the pH change observed for the water alone after an 8 hour contact time.

To determine the effects of these pH changes on metal mobilization, these pH changes were modeled using acids and bases and the resulting mobilized metals were recorded as shown in figure 4.34. This figure illustrates that no additional metal mobilization occurred from a pH change during peroxidation, above the amount of metal mobilized for the pH 7 DI water.

As the pH decreased in figure 4.31, the number of H^+ ions in solution increased, and an increase in competition for soil binding sites resulted in Zn mobilization. Scokart et al (1983) and Alloway (1990), also found Zn to be mobile below pH 5. Clarkson and Marian (1991) found that at a pH of 4.2-6.6 Zn is readily mobile as witnessed in this test.

From figure 4.32 Pb was unaffected by the pH changes studied which may have been due to the Pb being tightly bound to soils. Other researchers found similar results with Pb very immobile. Gerritse (1984) observed Pb to be much less affected by pH than Zn.

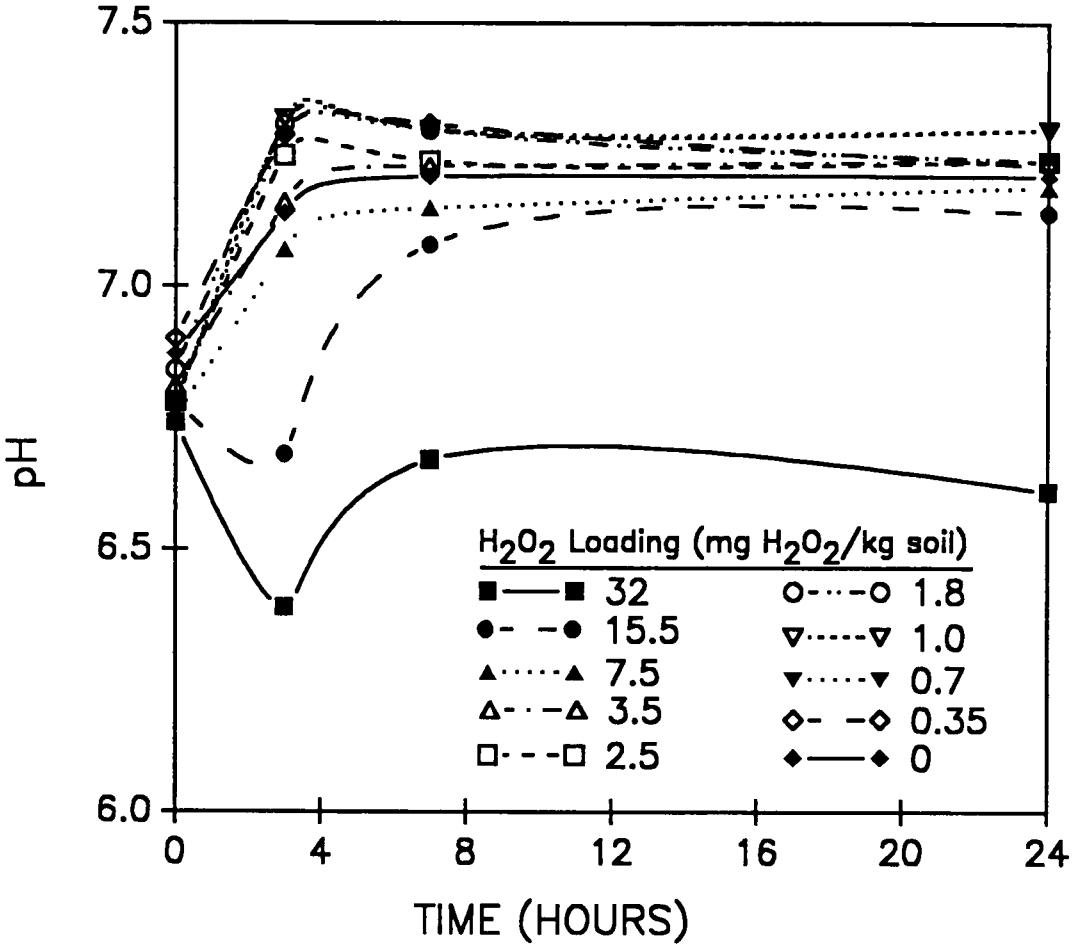


Figure 4.33 pH change observed with the addition of various H_2O_2 loadings to the natural soil. (Each data point is the mean of three samples and their standard errors.)

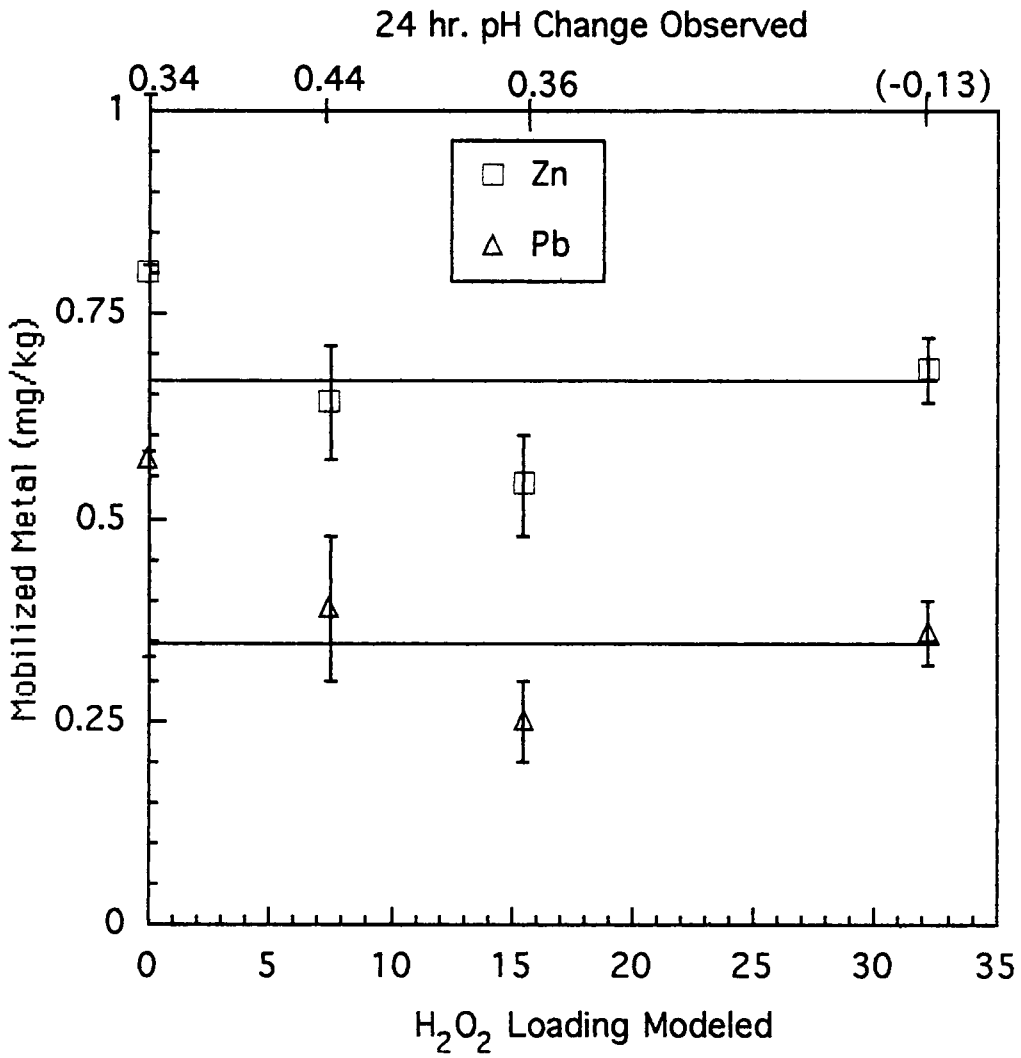


Figure 4.34 Metal mobilization after a pH change by 0.1N HCl and 0.1N NaOH to model the pH change observed with the addition of various H_2O_2 loadings to the natural soil. (Each data point is the mean of three samples and their standard errors.)

The addition of H_2O_2 to the soil illustrated in figure 4.33 resulted in an initial decrease in soil pH at 32 and 15.5 mg H_2O_2/g soil due to the release of H^+ ions into solution from the oxidation of soil OM. Over time the soil began to buffer the pH drop and the pH stabilized at slightly higher than neutral except for the highest H_2O_2 loading.

Figure 4.35 compares the metal mobilization observed from a pH change during peroxidation with metal mobilization from an H_2O_2 addition. The results illustrated in this figure indicate that the Zn mobilization in the single dose H_2O_2 tests was due to the peroxide addition and not due to a pH change that occurred during peroxidation.

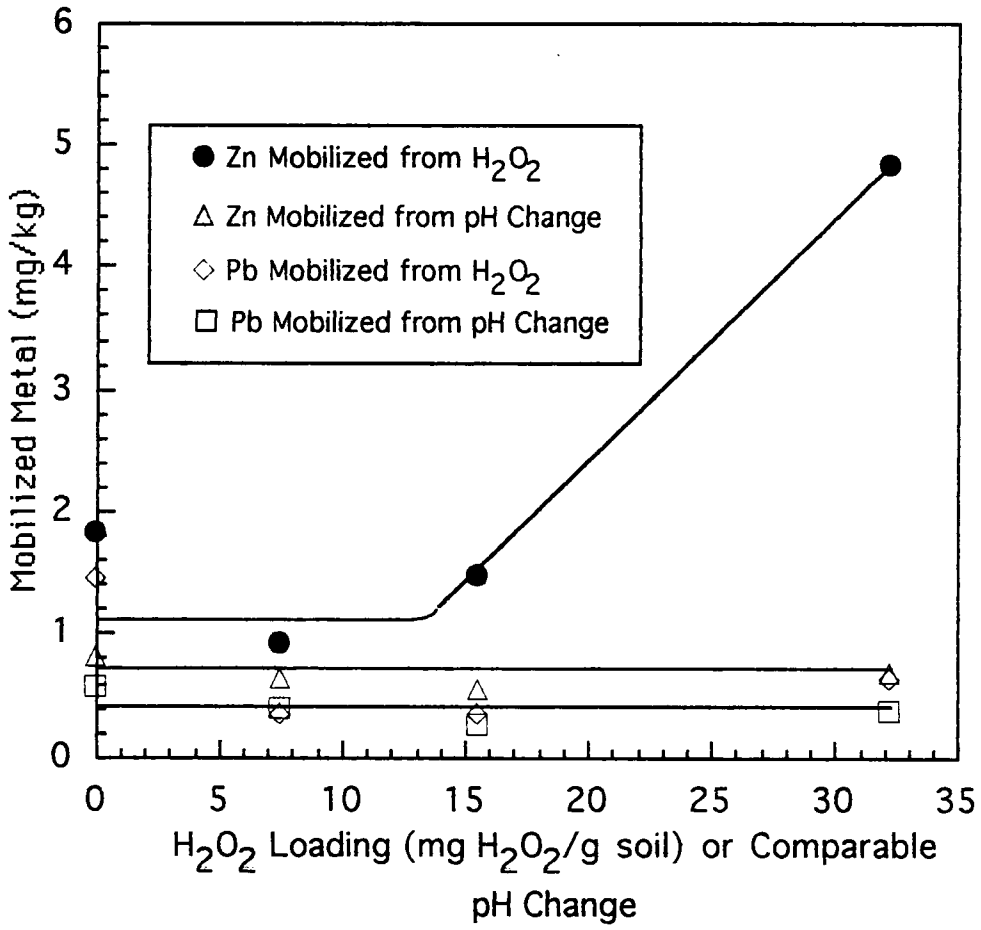


Figure 4.35 Metal mobilization after a pH change by 0.1N HCl and 0.1N NaOH to model the pH change observed with the addition of various H_2O_2 loadings to the natural soil in comparison with the mobilization observed from the H_2O_2 loadings. (Each data point is the mean of three samples and their standard errors.)

CHAPTER V. SUMMARY AND RECOMMENDATIONS

V.1 Summary

Adsorption to the natural soil was rapid (<2 hrs.) for Zn, Pb and U. Adsorption to the digested soil was rapid for Zn (<2 hrs.) and for lower concentrations of Pb (<6 hrs.). An initial solution containing 1120 mg Pb/kg soil took 8-12 hours to reach equilibrium. U adsorption to the digested soil at an initial concentration of 1000 mg U/kg soil had still not achieved equilibrium within the 72 hour time period analyzed.

The natural soil fit the Langmuir adsorption model well for Pb and Zn with an adsorption maximum of 236 mg Pb and 60 mg Zn sorbed per kg soil. The Langmuir binding energy coefficients for Pb and Zn in this soil were 2.49 and 3.22 respectively.

Adsorption of these two metals to the digested soil did not fit the Langmuir model as well especially for Zn. Even the more lenient Fruendlich model did not fit the Pb and Zn adsorption data in the digested soil. Binding increased in the digested soil with a capacity to adsorb 592 mg Pb and potentially 140 mg Zn per kg soil. The Pb Langmuir binding energy coefficient also increased in the digested soil to 7.68. The coefficients for Zn in the digested soil may be in error due to the extremely poor fit of this metal to the models.

U adsorption may have decreased in the digested soil with an adsorption maximum of 1560 mg U/kg soil in comparison to 2350 mg U/kg soil sorbed to the natural soil. These adsorption maximums and the Langmuir binding energy coefficients may be in error due to incomplete isotherm.

The effects on adsorption equilibrium due to multimetals in the initial solution were an increased Pb adsorption maximum and decreased Zn adsorption maximum. The Pb adsorption increased to 370 mg/kg soil with a concurrent drop in Langmuir bonding energy coefficient of 1.5 in comparison to the single metal matrix. Zn binding decreased in a multimetal matrix with an adsorption maximum of 51 mg/kg soil and a Langmuir bonding energy coefficient of 2.78.

Zn mobilization was observed in the natural soil upon a single H_2O_2 treatment with doses $\geq$10 mg H_2O_2 /g soil up to the maximum dose evaluated of 32 mg H_2O_2/g soil, but minimal Zn mobilization occurred in the digested soil. Minimal Pb and U mobilization was detected in either soil upon a single H_2O_2 treatment with the doses studied.

Repeated H_2O_2 treatments resulted in continual mobilization of both Pb and Zn with shorter treatment times of 5 minutes and 1 hour. With twelve hours of contact between treatments however additional Zn and Pb mobilization did not occur after the third treatment possibly due to OM being fully oxidized to refractory materials or due to metals binding to mineral components.

A slight pH change was observed upon soil peroxidation. This pH change, however, when modeled with an acid and base did not result in metal mobilization.

The results obtained in this work are specific to the soil used and the metals evaluated in these experiments. These results are also impacted by the conditions utilized to perform these tests. These experiments, however, can be used to extrapolate in the following conclusions which may be applicable to other conditions.

V.2 Conclusions

- The speed at which the metals adsorb may be an important factor when metals are released from the peroxidation of a contaminated soil. This rate may be dependent on factors such as metal species and concentration.

- Pb and U appear to have similar binding rates in natural soil. In addition, these two metals both had a lack of mobilization in the H_2O_2 natural tests. This may indicate that Pb and U are bound in a similar manner to the natural soil.

- The digested soil used in these tests has a higher capacity for metal adsorption than the natural soil possibly due to an increase in available binding sites following soil digestion to produce the digested soil. Adsorption to digested soil may have been higher due to an increased surface area or an increase in

the number of available binding sites. The increased available binding sites may be the result of a stripping of bound metals found naturally in the soil.

- The binding capacity of the metals in both soils was in the order of U, Pb and finally Zn which may indicate the order of binding strength to these soils.

- Soil peroxidation may result in metal mobilization especially with metals that have lower metal binding strengths to soils as was observed with the Zn in these experiments.

- Zn in soils can be mobilized upon soil peroxidation especially in soils with higher OM contents however Pb and U are less susceptible to mobilization upon soil peroxidation possibly due to binding to unoxidizable surfaces.

- Lower OM soils result in less metal mobilization than higher OM soils potentially due to the lack of oxidizable metal binding sites.

- Although a slight pH change was observed upon soil peroxidation, this pH change did not result in mobilized metal when modeled with an acid indicating that the metal mobilization observed upon soil peroxidation was not an effect of a pH change induced.

- Multiple peroxidation treatments result in continual Zn & Pb desorption although at a diminishing rate which may be caused by the decrease in oxidizable bindings sites (OM) upon repeated treatments.

- Longer H_2O_2 contact times result in more mobilized Zn. Pb, however, may readsorb to the soil over time.

- The magnitude of metal mobilization from soil peroxidation is a function of H_2O_2 contact time, number of repeated treatments, H_2O_2 dose, soil OM content and binding strength of specific metals sorbed.

The use of H_2O_2 to oxidize organic contaminants in soil has the potential to release some metals sorbed to the soil. However, if lower H_2O_2 doses are used, metal mobilization will be minimized. Mobilization of metals upon soil peroxidation may be beneficial. High concentrations of H_2O_2 may mobilize certain metals from soil. This may have potential in the remediation of metals contaminated soils and may warrant further investigation.

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APPENDIX

APPENDIX

A.1 EQUILIBRIUM EXPERIMENTS

A.1.1 BINDING RATE EXPERIMENTS

Data plotted in figure A.1 indicate that equilibrium was achieved very rapidly for Pb at the various concentrations of metal applied to the natural soil. Although equilibrium was achieved in the first two hours, 24 hours of contact time was used in subsequent experiments to ensure adequate contact. An increase in the initial metal added did not influence the rate of Pb adsorption within the contact times studied. All Pb loadings reached equilibrium within the first two hours.

An initial loading of 200 mg Pb/kg soil resulted in a sorbed mass of ≈ 175 mg Pb/kg soil. Higher initial loadings of 490 and 530 mgPb/kg soil resulted in ≈ 230 and 265 mg Pb/kg soil respectively.

Figure A.2 relates the adsorption of the three metals for the natural soil at an initial metal loading of 200 mg metal/kg soil. In this illustration it is apparent that metal species does not affect time of adsorption with all three metals reaching equilibrium by the first sampling time of two hours. Zn did not adsorb as readily as Pb or U in these experiments. These results were also observed by other researchers (Clarkson and Marian, 1991) who found Zn not as readily sorbed as Pb.

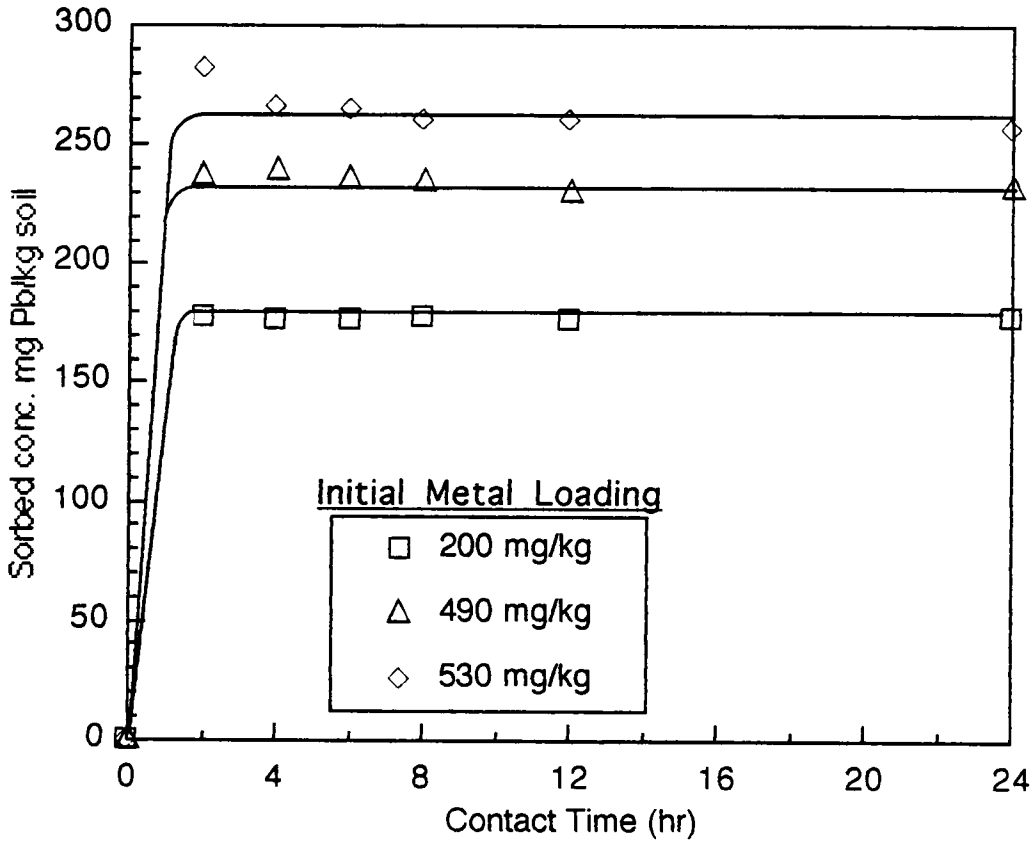


Figure A.1 Pb adsorption to 10 g of natural soil over time.

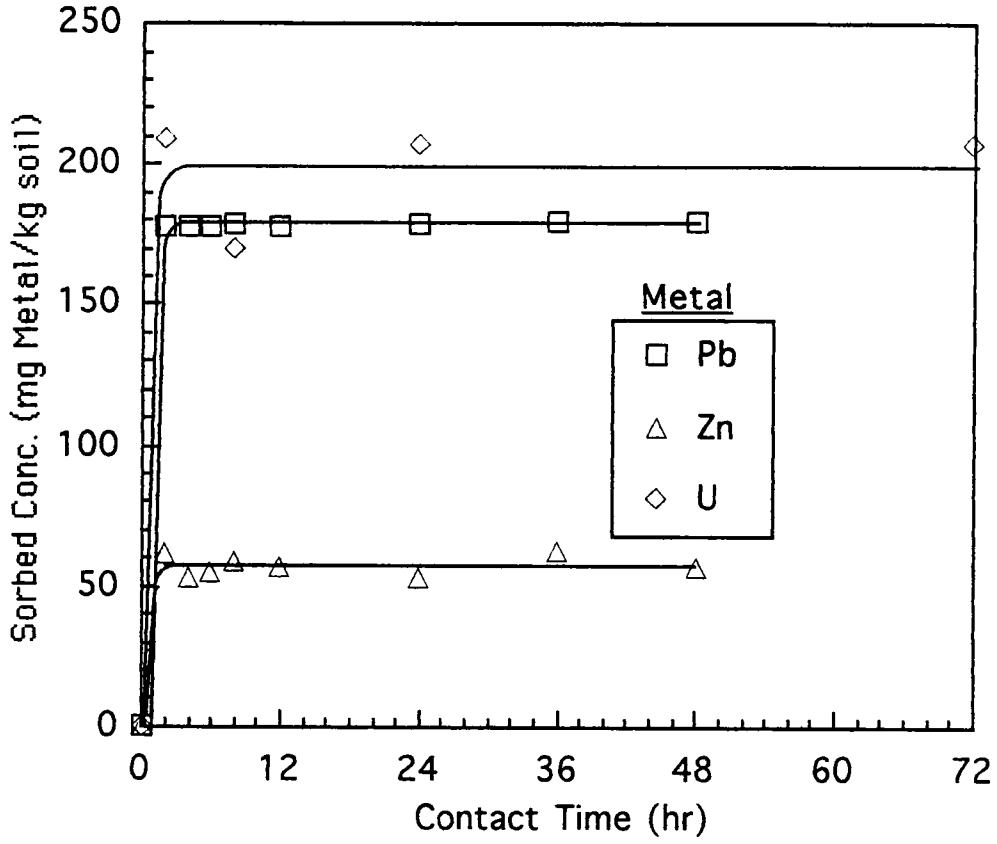


Figure A.2 Comparison of Pb, Zn and U adsorption to 10 g of natural soil over time with the initial loading of 200 mg metal/kg soil.

A.1.2 LANGMUIR AND FRUENDLICH PLOTS

Figures A.3- A.9 are iterations of plots used to determine isotherm parameter.

A.1.3 ISOTHERM COMPARISON FOR NATURAL SOIL

From the data plotted in figure A.10 it is apparent that the natural soil has the greatest capacity to adsorb U followed by Pb and finally Zn. These results are similar to findings of Kerndorff and Schnitzer (1980) who studied the sorption of metals to HA extracted from a clay loam and determined that Pb had an intermediate sorption and Zn was weakly adsorbed to HA.

In general the preference of an ion for a surface will increase with an increase in atomic number in a given series, due to an increasing ionic radius (Weber, 1972). The ionic radius of Pb is 1.2Å which is larger than Zn with an ionic radius of 0.74Å so the ionic radius of these two metal may have been a determining factor.

The adsorption capacity of the natural soil was higher for Pb than Zn but the energy to which the Pb was held was lower according to the bonding energy terms which were higher for Zn than Pb. Comparison of the bonding energy term of U is difficult due to the extremely small value obtained which may have been the result of an incomplete isotherm.

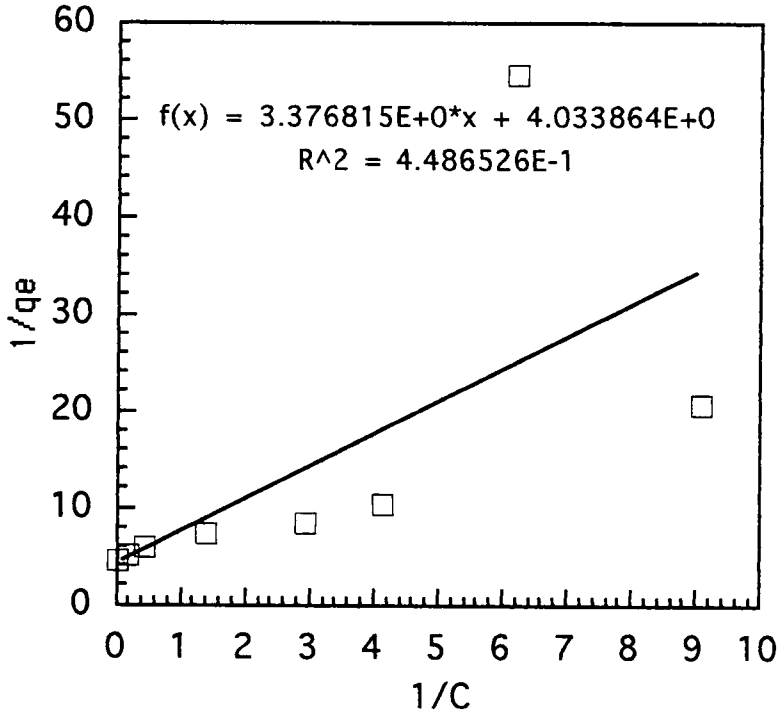


Figure A.3 Linear plot of Pb adsorption to natural soil, using all data, to determine adsorption parameters.

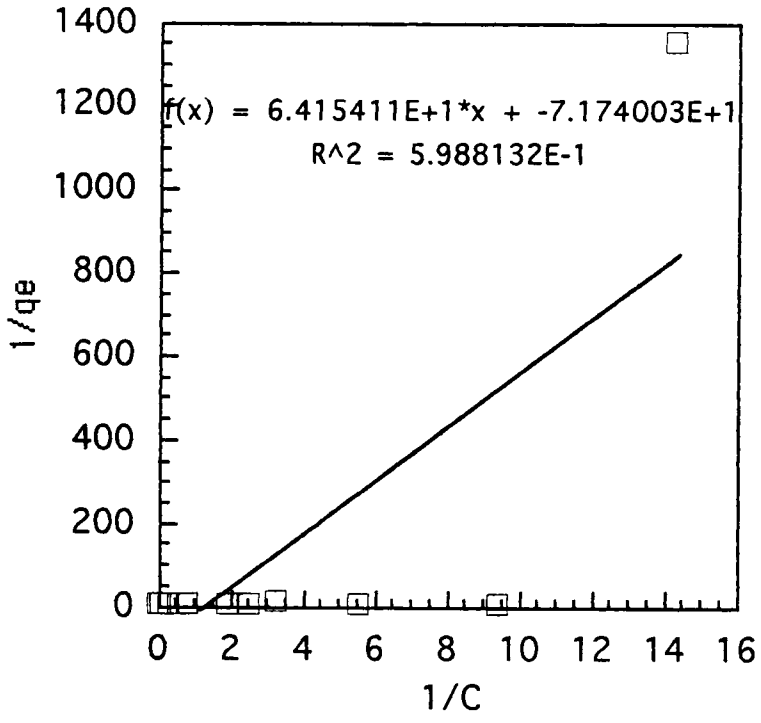


Figure A.4 Linear plot of Pb adsorption to digested soil, using all data, to determine adsorption parameters.

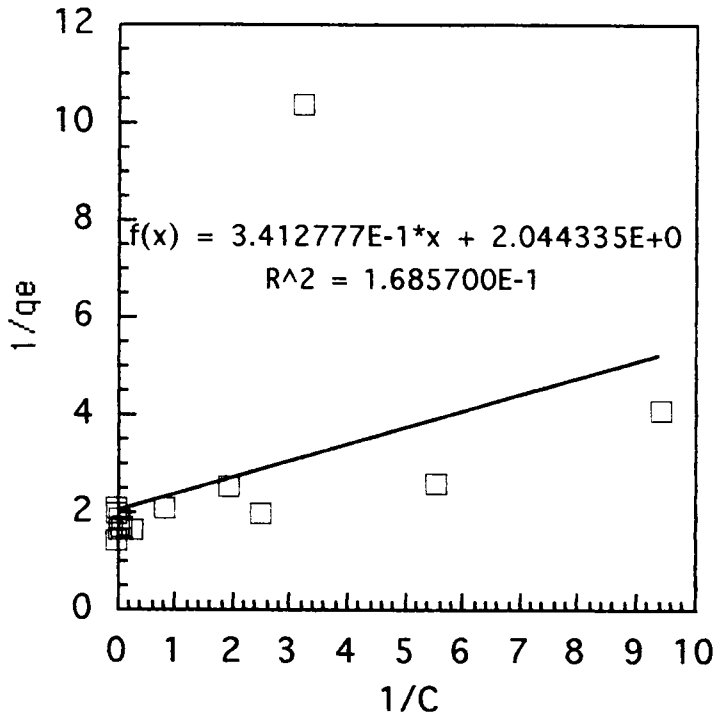


Figure A.5 Linear plot of Pb adsorption to digested soil to determine Langmuir adsorption parameters. (The lowest adsorbed concentration has been dropped to obtain a more significant fit.)

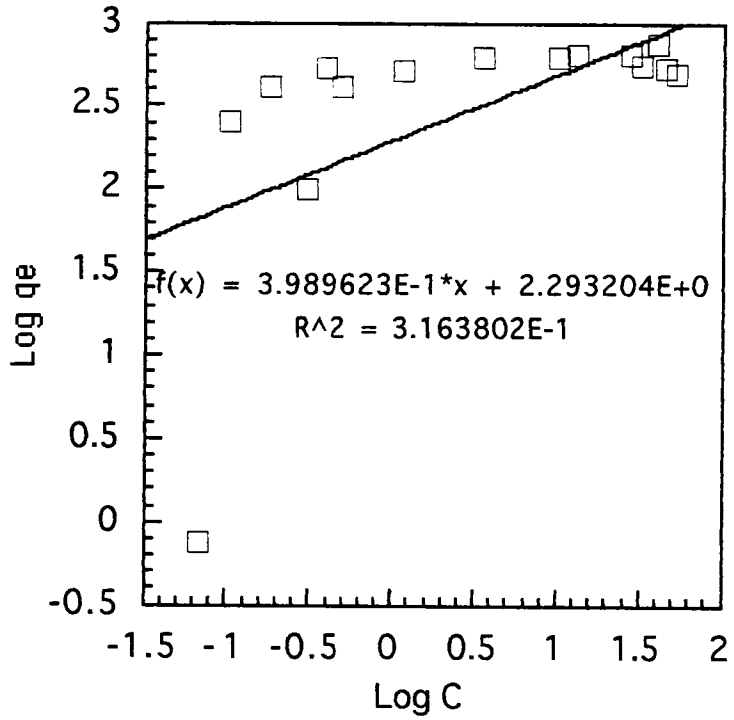


Figure A.6 Plot of Pb adsorption to digested soil using the Fruendlich model with all data.

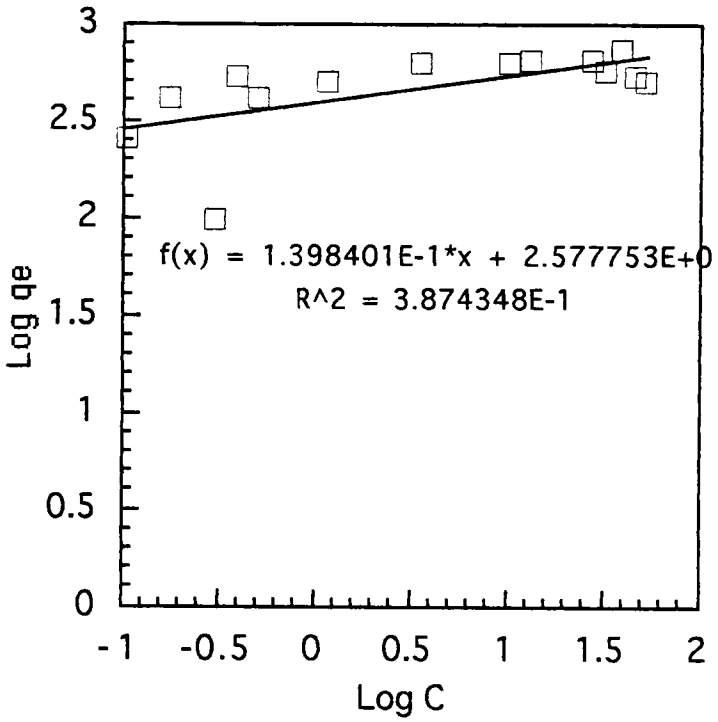


Figure A.7 Plot of Pb adsorption to digested soil using the Fruendlich model dropping the lowest adsorbed concentrations.

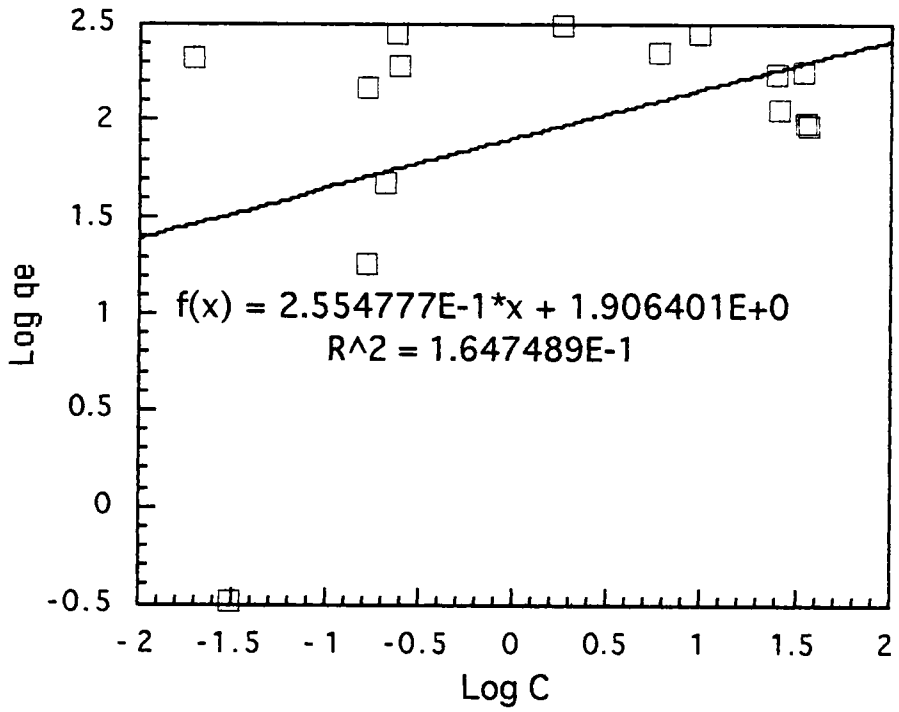


Figure A.8 Plot of Zn adsorption to digested soil using the Fruendlich model with all data.

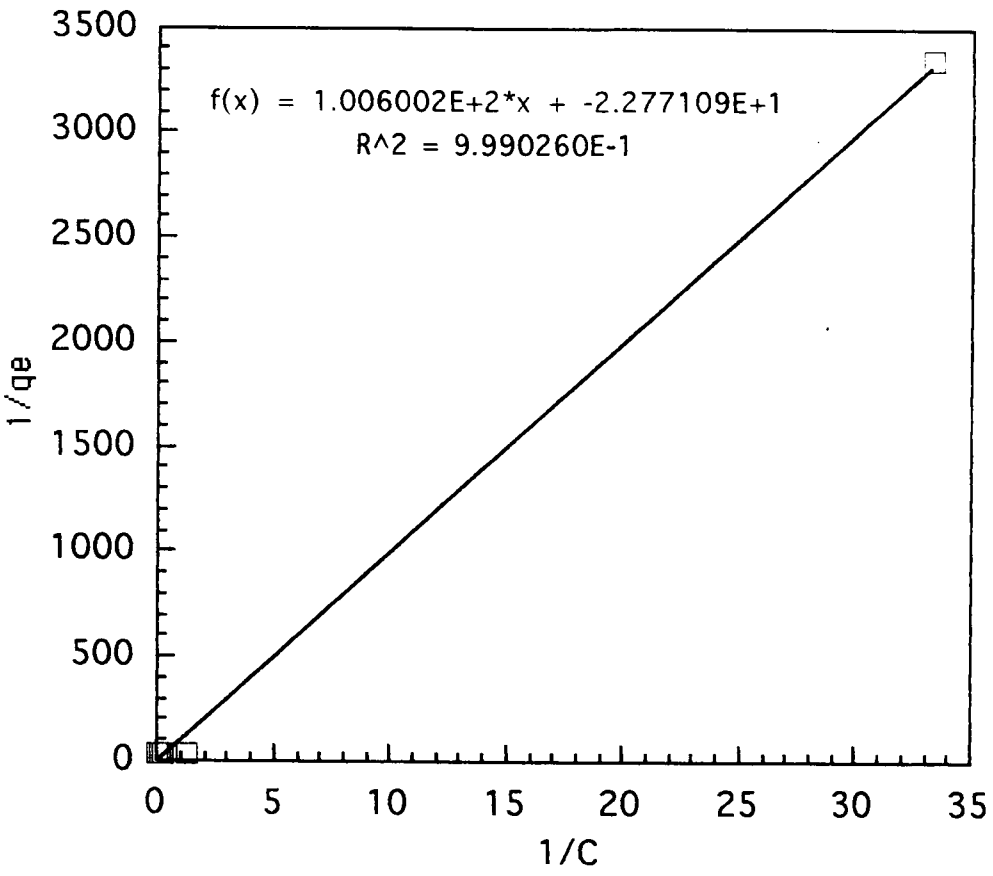


Figure A.9 Zn multimetal matrix using all data (creates negative adsorption parameters.)

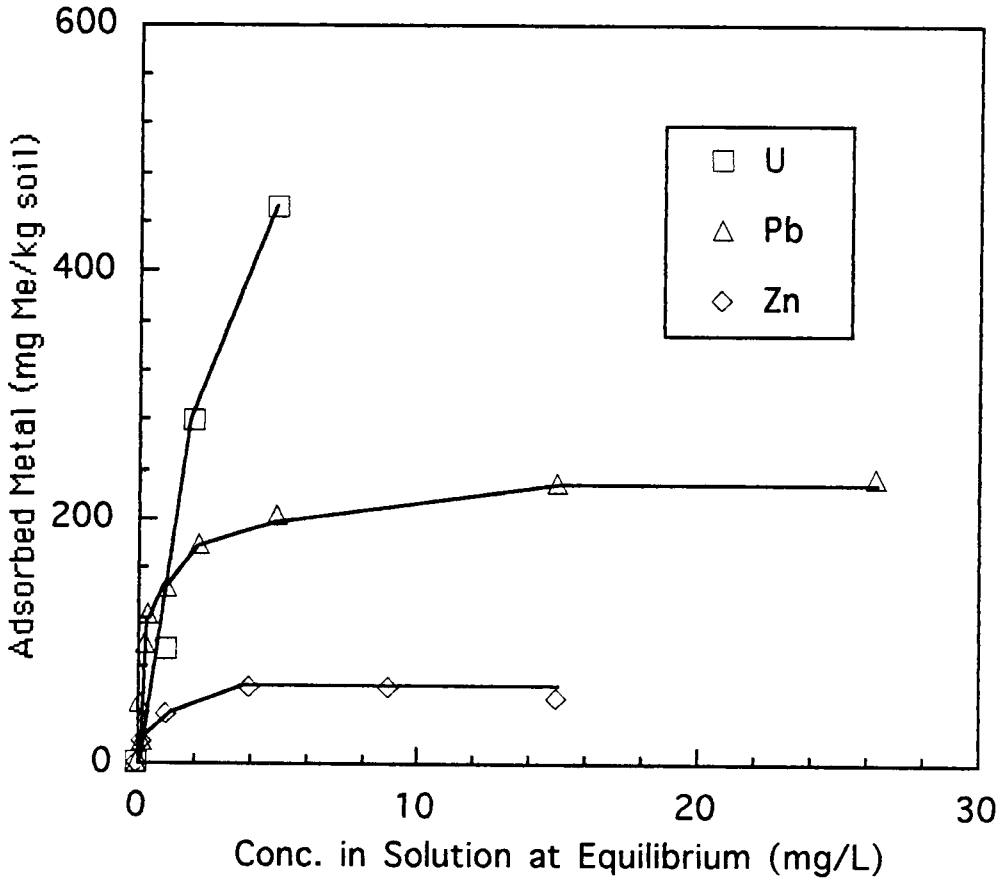


Figure A.10 Comparison of Zn, Pb and U adsorption isotherms for 10 g of natural soil with the addition of 100 ml of varying concentrations of Metal.

A.2 MULTIPLE PEROXIDATION EXPERIMENTS

Figures A.11-A.13 are comparison plots of Zn and Pb mobilization for each time period studied in the multiple peroxidation treatment tests.

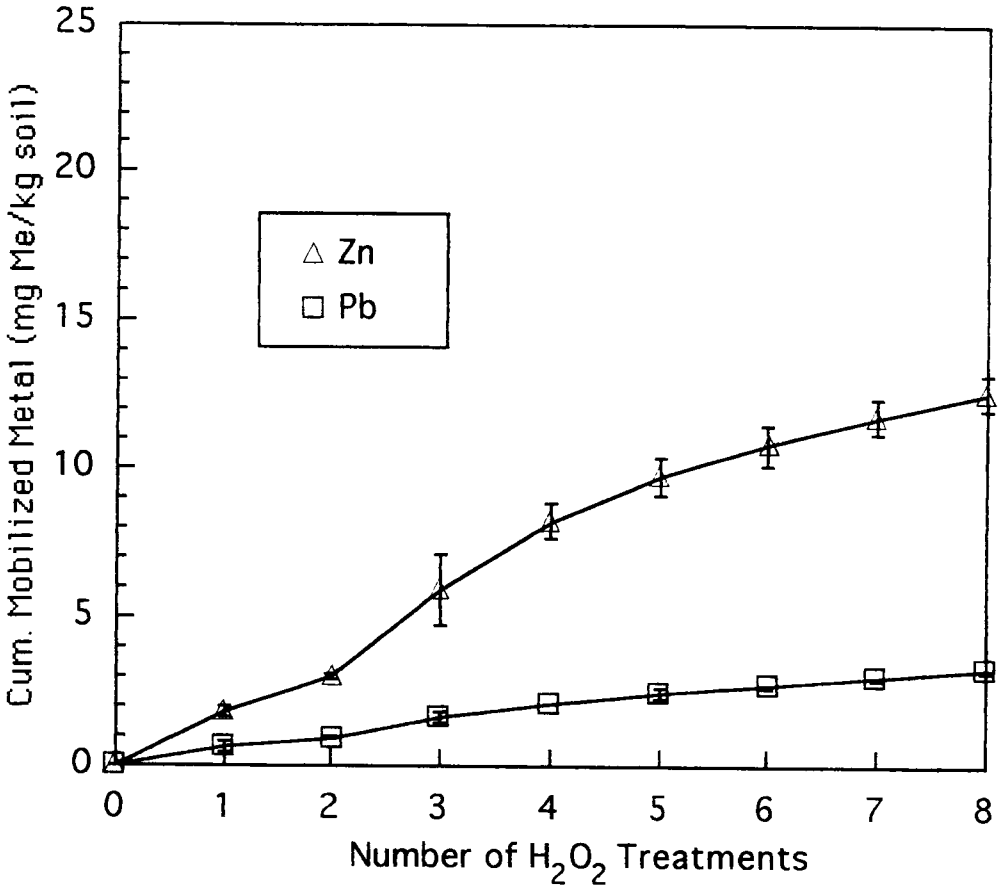


Figure A.11 Cumulative Pb & Zn mobilization from repeated H_2O_2 treatments of the natural soil at a loading of 32 mg H_2O_2/g soil with 5 min. of contact time between each subsequent treatment. (Each data point is the mean of three samples and their standard errors.)

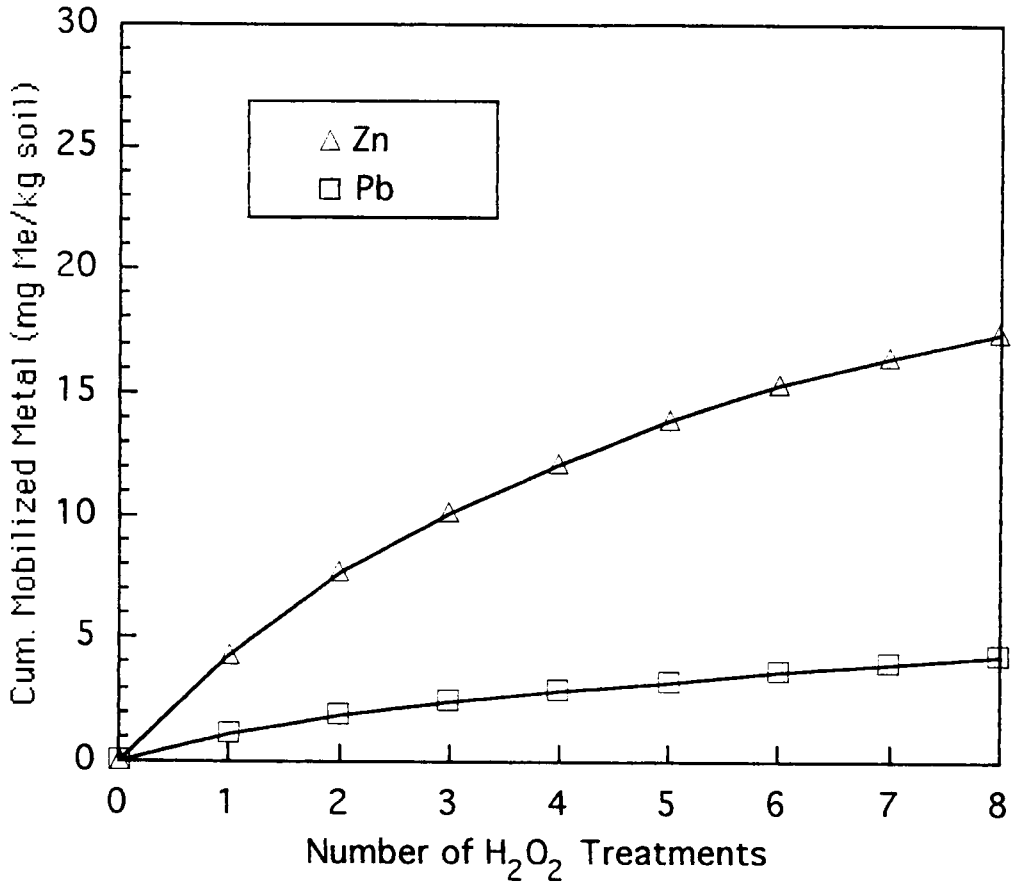


Figure A.12 Pb & Zn mobilization from repeated H_2O_2 treatments to the natural soil at a loading of 32 mg H_2O_2/g soil with 1 hr of contact time between each subsequent treatment. (Each data point is the mean of three samples and their standard errors.)

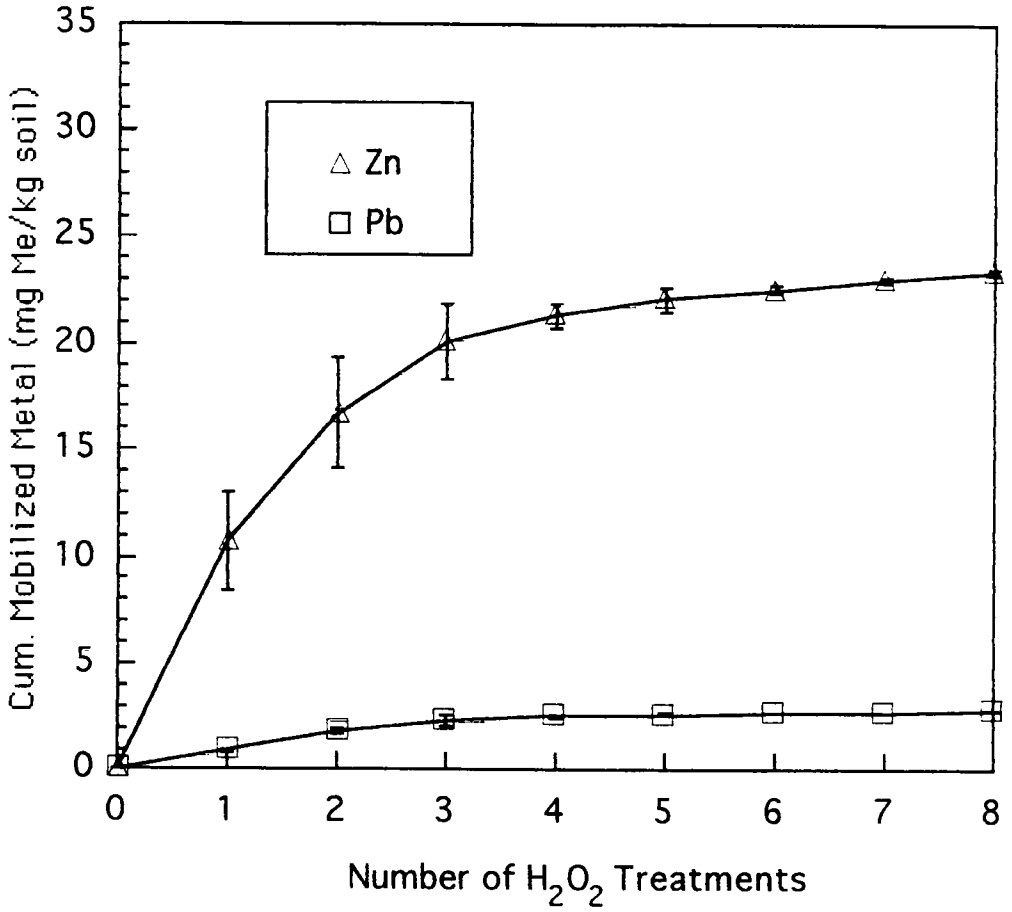


Figure A.13 Cumulative Pb & Zn mobilization from repeated H_2O_2 treatments of natural soil at a loading of 32 mg H_2O_2/g soil with 12 hrs. of contact time between each subsequent treatment. (Each data point is the mean of three samples and their standard errors.)

A.3 Metal Mobilization from the Application of Humic Acid (HA) to a Contaminated Soil

From the data presented in table A.1 the addition of 20 mls of a 100 mg/L HA solution to a contaminated soil had minimal impact on metal mobilization. No Pb mobilization was observed from the addition of the HA however 35% more Zn was observed in solution in comparison to Zn in solution after the addition of the pH 7 DI water alone. This may have been due to a preferential sorption of Zn for the HA and a subsequent desorption of soil sorbed Zn onto the HA.

An additional potential source for the increased Zn mobilization is that soluble HA adsorbed the more mobile Zn in solution and disrupted the equilibrium of sorbed and aqueous Zn. This disruption would allow more Zn to desorb into solution to maintain the equilibrium of sorbed and aqueous Zn. The less mobile Pb may have been more strongly attached to the soil and consequently less affected by the HA addition.

The decrease in pH of (-0.13) from the addition of HA was less than the decrease in pH observed from the addition of the pH 7 DI water alone (-0.28). Therefor the slight pH change occurring during HA addition probably did not have an effect on metal mobilization.

These tests show that organic ligands (HA) do affect Zn mobility. From these tests Pb does not appear to be affected by organic ligands as readily. This may indicate further that Pb has a stronger binding with the soil than Zn.

TABLE A.1

Results of the Application of 20 mls of a 100 mg/L HA Solution to a Contaminated Soil

	From the Addition of HA	From the Addition of pH 7 DI Water
Average Mobilized Pb (mg Pb/kg soil) n=3	0.0	0.05
Average Mobilized Zn (mg Zn/kg soil) n=3	1.22	0.9
Initial pH	5.07	5.0
pH After 24 Hours of contact	4.94	4.72

A.4 Metal Mobilization from Supernatant Reapplication of an H2O2 Addition to an Uncontaminated Soil

The peroxidation of a metals contaminated soil did result in mobilized metals as observed in the previous tests. The addition of H_2O_2 to the soil, however, may have produced organic ligands that affected metal mobilization, as was seen from the addition of HA to a contaminated soil, or may have been the result of OM/metal binding sites being oxidized. These tests studied the potential creation of organic ligands created during soil peroxidation.

The combined supernatant (treatment solution and wash water) from an H_2O_2 addition to an uncontaminated soil had no Pb and 0.063 mgZn/L as reported in table A.2. The H_2O_2 added to the contaminated soil completely decomposed as determined from the data presented in table A.3. From this data and equation A.4a it was determined that no residual H_2O_2 remained in the combined supernatant due to the fact that the "A" quantity of sodium thiosulfate was equal to the "B" quantity of sodium thiosulfate in the following equation (Interox Inc., 1991):

$$\text{residual } H_2O_2, \%\ (w/w) = \frac{(A-B)(N)(1.7007)}{(\text{sample wt.})} \qquad \text{(Equation A.4.a)}$$

The application of the combined supernatant to a contaminated soil resulted in the mobilization of Pb and Zn. From the data presented in table A.2 and plotted on figures A.15 & A.16, it can be seen that the application of the combined supernatant resulted in 80% more Pb and 50% additional Zn mobilization than observed from the addition of pH 7 DI water alone.

TABLE A.2

Effects on Metal Mobilization From the Application of Combined Supernatants (From an H_2O_2 Addition and Wash of an Uncontaminated Soil) to a Contaminated Soil

SOURCE	Average Pb Mobilized (n=3)		Average Zn Mobilized (n=3)	
	mg/L	mg/kg soil	mg/L	mg/kg soil
Combined Supernatants from Uncontaminated Soil	0.00	0.00	0.06	0.126
Reapplication of Combined Supernatant to a Metals Contaminated Soil	0.04	0.09	0.74	1.35
pH 7 DI Water Addition to a Contaminated Soil (From Previous Testing)		0.05		0.9
H_2O_2 Addition to A Contaminated Soil (From Previous Testing)		0.88		10.79

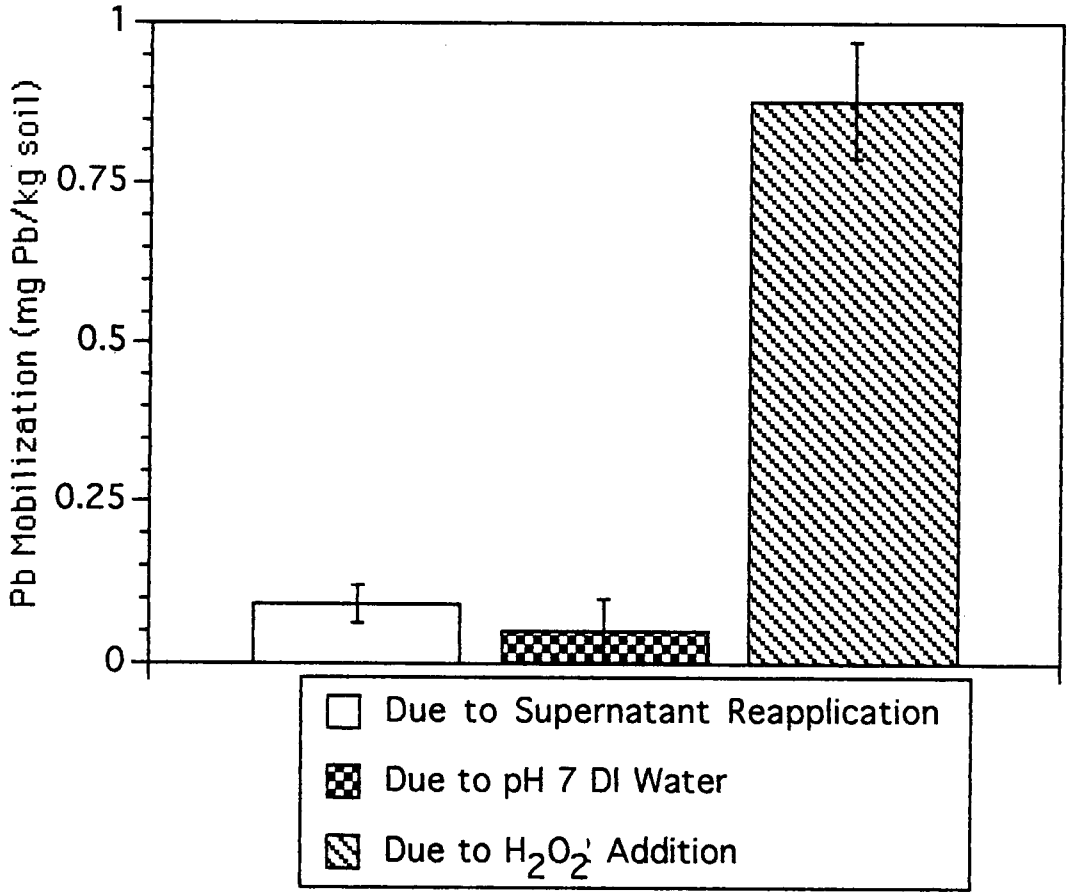


Figure A.15 Comparison of Pb Mobilizations From a Metals Contaminated Soil Due to; (1) the addition of H_2O_2, (2) the Addition of pH 7 DI Water and, (3) the Application of a Supernatant Resulting From the Addition of H_2O_2 to an Uncontaminated Soil.

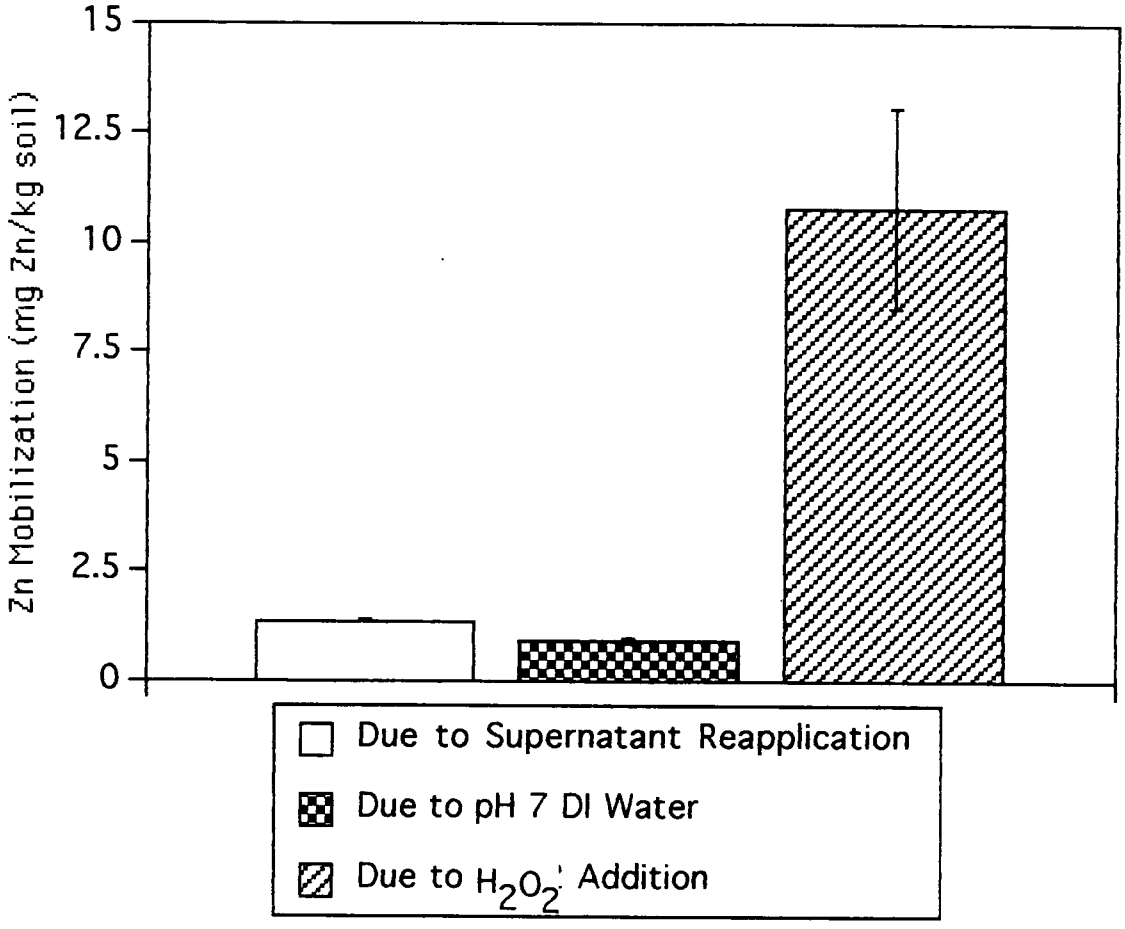


Figure A.16 Comparison of Zn Mobilizations From a Metals Contaminated Soil Due to; (1) the addition of H_2O_2, (2) the Addition of pH 7 DI Water and, (3) the Application of a Supernatant Resulting From the Addition of H_2O_2 to an Uncontaminated Soil.

A potential cause for the additional metal mobilization may have been from organic ligands produced from the oxidation of soil OM during peroxidation of the uncontaminated soil. These ligands may have desorbed metals from the soil by preferential sorption of the metals to the ligands as was observed by the previous tests with a HA addition resulting in mobilized Zn.

As stated earlier another possible cause for the additional mobilization from the soil is that organic ligands in solution may have bound metals in solution creating a disequilibrium between the soil-sorbed metal and metals in solution. This may have resulted in the desorption of soil-sorbed metal into solution to reestablish the equilibrium of soil-sorbed metal and solution metal.

TABLE A.3
Results of the Determination of residual H_2O_2 from the Addition H_2O_2 to an Uncontaminated Soil

SOURCE	Amount of Sodium Thiosulfate Titrated (ml)				
	Test #1	Test #2	Test #3	Ave.	Stan. Dev.
Sodium Thiosulfate Normality Determination	20.3	20.2	20.2	20.2	0.06
"A" Quantity (Sample)	19.8	19.8	19.8	19.8	0.00
"B" Quantity (Control)	19.8	19.8	19.8	19.8	0.00

The amount of Pb and Zn mobilized from the possible addition of soluble organic ligands produced during peroxidation (in the combined supernatant), however, does not account for the amount of metal mobilized during soil peroxidation. From figures A.15 & A.16 it is apparent that much more Pb and Zn mobilized due to soil peroxidation than due to possible organic ligands formed from soil peroxidation. The amount of Pb and Zn mobilized from the application of the combined supernatant (which may have contained organic ligands) to a contaminated soil, only accounts for 10% of the Pb and 13% of the Zn mobilized from the application of H_2O_2 to a contaminated soil.

Previous tests showed that U and Pb may behave similarly in the natural soil. Berthelin et al (1987) found that organic decomposition may create organic chelating agents that desorb U bound to soils. This may also occur with this soil to a similar magnitude as observed with the Pb in these tests.

From these results, the addition of H_2O_2 to a soil may have produced organic ligands that resulted in additional metal mobilization from the soil. These ligands, however, may only account for a small fraction of the metal mobilization observed from the H_2O_2 addition.

TABULAR RAW DATA

TABLE A.4
Mobilized Lead After H_2O_2 Addition to a Synthetically Contaminated Natural Soil

H_2O_2 Added (mgH_2O_2 /g soil)	TEST #1		TEST #2		TEST #3	
	% of original Pb on soil	mg/kg soil	% of original Pb on soil	mg/kg soil	% of original Pb on soil	mg/kg soil
0	2.3	0.725	7.3	2.16	4.9	1.47
0.35	0.7	0.234	5.52	1.64	1.2	0.37
0.7	1.03	0.402	6.77	0.23	1.2	0.35
1	2.2	0.69	1.6	0.48	0.98	0.29
1.8	2.9	0.918	3.7	1.09	1.6	0.48
2.5	2.2	0.698	1.2	0.35	0.5	0.16
3.5	3.4	1.085	1.8	0.52	1.8	0.54
7.5			0.57	0.17	1.68	0.5
15.5	0.8	0.26	1.1	0.33	1.5	0.46
32.2	1.2	0.38	2.8	0.83	2.4	0.7
1 uncont.	0.2	0.066	0.07	0.02	0.2	0.07

TABLE A.5

Mobilized Zinc After H_2O_2 Addition to a Synthetically Contaminated Natural Soil

H_2O_2 Loading (mg H_2O_2 /g soil)	TEST #1		TEST #2		TEST #3	
	% of original Zn on soil	mg/kg soil	% of original Zn on soil	mg/kg soil	% of original Zn on soil	mg/kg soil
0	3.9	1.27	8.1	2.78	4.3	1.45
0.35	1.8	0.58	4.7	1.62	1.8	0.62
0.7	2.3	0.76	1.9	0.66	1.8	0.6
1	3.0	0.98	2.9	0.98	2.1	0.73
1.8	2.9	0.94	3.6	1.25	2.4	0.82
2.5	2.1	0.67	2.2	0.75	1.8	0.63
3.5	4.0	1.34	3.0	1.02	2.6	0.88
7.5			2.4	0.82	3.0	1.04
15.5	6.0	1.94	3.7	1.26	3.7	1.25
32.2	16.7	5.42	13	4.5	13.3	4.53
1 uncont.	0.6	0.18	0.4	0.15	0.6	0.2

TABLE A.6

Mobilized Metal After H_2O_2 Addition to a Synthetically Contaminated Natural Soil

H_2O_2 Loading (mg H_2O_2 /g soil)	Average Mobilized Lead (N=3)		Average Mobilized Zinc (N=3)		Mobilized Uranium (N=1)
	mg/kg soil	stand. dev.	mg/kg soil	stand. dev.	mg/kg soil
0	1.45	0.72	1.83	0.82	0.57
0.35	0.75	0.78	0.94	0.59	0.28
0.7	0.33	0.09	0.67	0.08	0.29
1.0	0.49	0.2	0.9	0.14	0.52
1.8	0.83	0.31	1	0.22	0.47
2.5	0.4	0.27	0.68	0.06	0.32
3.5	0.72	0.32	1.08	0.24	0.66
7.5	0.34	0.23	0.93	0.16	
15.5	0.35	0.10	1.48	0.40	0.35
32.2	0.64	0.23	4.82	0.52	0.66
1 uncon.	0.05	0.03	0.18	0.03	0.01

LOWER OM SOIL TESTS:

TABLE A.7
Mobilized Lead After H_2O_2 Addition to a Synthetically Contaminated Digested Soil

H_2O_2 Loading (mgH_2O_2/ g soil)	TEST #1		TEST #2		TEST #3	
	mgPb/ L	mg/kg soil	mgPb/ L	mg/kg soil	mgPb/ L	mg/kg soil
t=0hr	15.6		15.6		15.64	
t=72hr	0.055	27.44	0.084	27.21	0.005	27.79
wash water	0.189		0.230		0.145	
0	0.025	0.15	0.016	0.096	0.026	0.156
0.7	0.024	0.144	0.035	0.21	0.041	0.246
1.0	0.006	0.036	0.012	0.072	0.004	0.024
1.8	0.077	0.462	0.08	0.48	0.087	0.522
2.5	0.01	0.06	0.048	0.288	0.046	0.276
3.5	0.056	0.366	0.072	0.432	0.054	0.324
7.5	0.059	0.354	0.036	0.216	0.036	0.216
15.5	0.036	0.216	0.039	0.234	0.040	0.240
32	0.049	0.294	0.024	0.144	0.037	0.222
1uncont.	0.016	0.094	0.013	0.078	0.008	0.048

TABLE A.8

Mobilized Zinc After H_2O_2 Addition to a Synthetically Contaminated Digested Soil

H_2O_2 Loading (mgH_2O_2/ g soil)	TEST #1		TEST #2		TEST #3	
	mgZn/ L	mg/kg soil	mgZn/ L	mg/kg soil	mgZn/ L	mg/kg soil
t=0hr	18.16		18.16		17.9	
t=72hr	0.323	31.14	0.371	31.03	0.207	30.93
wash water	0.295		0.301		0.285	
0	0.075	0.45	0.069	0.414	0.060	0.360
0.7	0.132	0.792	0.112	0.672	0.125	0.750
1.0	0.119	0.714	0.127	0.762	0.065	0.390
1.8	0.131	0.786	0.118	0.708	0.140	0.84
2.5	0.046	0.276	0.119	0.714	0.105	0.63
3.5	0.093	0.558	0.111	0.666	0.106	0.636
7.5	0.126	0.756	0.101	0.606	0.086	0.516
15.5	0.103	0.618	0.106	0.636	0.090	0.54
32	0.131	0.786	0.096	0.576	0.082	0.492
1uncont.	0.06	0.360	0.098	0.588	0.080	0.480

TABLE A.9

Mobilized Zinc After Repeated H_2O_2 Treatments to a Synthetically Contaminated soil with Varying Contact Times Between Treatments

Treat. Number	5 minutes		1 Hour		12 Hour	
	Cumul. Mobil. Metal	SD	Cumul. Mobil. Metal	SD	Cumul. Mobil. Metal	SD
1	1.8	0.2	4.3	0.16	10.8	2.3
2	3.01	0.1	7.72	0.66	16.8	2.6
3	5.89	1.2	10.06	0.01	20.1	1.8
4	8.2	0.6	12.06	0.17	21.4	0.6
5	9.74	0.7	13.82	0.11	22.1	0.3
6	10.81	0.7	15.29	0.18	22.6	0.2
7	11.75	0.6	16.44	0.18	23	0.1
8	12.59	0.6	17.43	0.01	23.5	0.1

TABLE A.10

Mobilized Lead After Repeated H_2O_2 Treatments to a Synthetically Contaminated soil with Varying Contact Times Between Treatments

Treat. Number	5 minutes		1 Hour		12 Hour	
	Cumul. Mobil. Metal	SD	Cumul. Mobil. Metal	SD	Cumul. Mobil. Metal	SD
1	0.6	0.22	1.07	0.08	0.88	0.09
2	0.9	0.07	1.87	0.1	1.8	0.16
3	1.62	0.2	2.43	0.1	2.34	0.25
4	2.05	0.01	2.83	0.07	2.54	0.09
5	2.43	0.2	3.18	0.02	2.62	0.05
6	2.64	0.05	3.56	0.13	2.68	0
7	2.93	0.08	3.9	0.03	2.75	0.02
8	3.21	0.05	4.31	0.02	2.88	0

VITA

The author was born in Syracuse, NY and graduated from Clemson University with a BS in Civil Engineering (1987). The author is dedicated to a sound Environmental vision for ours and future generations. We must never forget that the Earth can live without Man however Man cannot live without the Earth.