The Influence of Residence Time and Organic Acids on the Desorption of Trace Metals from Goethite

by

Leslie James Glover II

Thesis submitted to the faculty of the

Virginia Polytechnic Institute and State University

in partial fulfillment of the requirements for the degree of

Master of Science

in

Crop and Soil Environmental Sciences

APPROVED:

_____
Matthew J. Eick, chair

_____
Lucian Zelazny

_____
Mark Alley

June 2000
Blacksburg, Virginia

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Leslie James Glover II
Committee Chair: M.J. Eick
Crop and Soil Environmental Sciences

(ABSTRACT)

Trace metal concentrations in soil solution, and hence trace metal bioavailability and toxicity, are primarily controlled by sorption/desorption reactions at the mineral-water interface. While numerous studies have been conducted to understand the initial adsorption of these metals to soil minerals, less in known about long-term adsorption/ desorption processes. The objective of this study was to examine the influence of residence time and organic acids on the desorption of Pb^{2+} and Cd^{2+} from goethite. Adsorption experiments were conducted at pH 6.0. Lead adsorption was nearly completed after 4 hours, with very little additional sorption during a 20-week period. In contrast cadmium showed a continuous slight increase in the amount of adsorption over the 20-week period. Desorption experiments were conducted at pH 4.5 and similar to previous studies examining trace metal desorption from oxide surfaces, the desorption kinetics for Pb^{2+} and Cd^{2+} were slow compared to the sorption reaction. None of the experiments were completely reversible after an eight-hour desorption period. For all experiments except long-term Pb^{2+} desorption, the quantity of metal desorbed from goethite followed the order salicylate $>NaNO_3 >$ oxalate. Based on differences in cation affinity for the iron oxide surface one would expect a greater quantity of Cd^{2+} to be removed compared to Pb^{2+}, for each of the extracting solutions. However at a pH of 4.5 we did not find a statistically significant trend. We observed a difference between the amount of metal removed for short and long-term experiments in five of six experiments, but these differences were only significant for Pb^{2+} experiments in the presence of salicylate. Two first order rate equations best fit the kinetics of trace metals desorption, with R^2 values greater than 0.910 in all cases. Although our results show a decrease in rate coefficients (expect k_1 for oxalate) with increased residence time, statistical analysis indicates that these results were only significant for Pb^{2+} experiments in the presence of salicylate. However raw and transformed data both suggest that desorption values are diverging as a function of aging time. Similar to other researchers we believe that Pb^{2+} and Cd^{2+} are sequestered by the goethite surface with an increase in residence time. These results suggest that residence time effects observed by many researchers are much less prevalent at low pH values. Therefore a reduction in soil pH created by natural anthropogenic processes may reduce the ability of soils to naturally sequester metals over time.

Key words: Trace metals, organic acids, goethite, residence time, desorption, kinetics

Acknowledgements

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Chapter 1. Introduction and objectives

Trace elements can be defined as chemical elements whose indigenous concentrations are <100-mg metal kg^{-1} soil. Many of these elements are essential for proper plant, animal and human growth. Those trace elements that are necessary for proper plant and animal health are termed micronutrients, however at high concentrations these elements may become toxic to both plants and animals. Point sources are widely accepted as major contributors to the increase in trace metal pollution since World War II. However, in recent years non-point sources including return flow from irrigated agriculture, atmospheric deposition, urban runoff, and stream sediment deposition are known to contribute significantly to trace metal pollution (Novotny and Olem, 1994). Studies conducted by Marsalek and the National Urban Runoff Project indicated that trace metals were the most prevalent toxic contaminant detected in runoff and stream sediments in urban areas and adjacent vicinities (Novotny and Olem, 1994). In fact it is currently estimated that the toxicity of inorganic trace elements released into the environment exceeds that from organics and radioactive sources combined (Brady and Weil, 1999). Two of the more toxic and universal trace metals in the environment are lead and cadmium. Lead contamination of the environment is primarily due to anthropogenic activities, making lead the most ubiquitous toxic metal in the environment (Amdur et al., 1991). Because there is no known biological use for lead, and because it is toxic to most living things, research on lead has become a dominant topic for environmental and medical scientists (Amdur et al., 1991). Lead exists in soils principally in the 2+ oxidation state. It is strongly chalcophilic, occurring primarily as PbS in rocks and in reduced soils. Under oxidizing conditions, the Pb^{2+} ion becomes less soluble as soil pH is raised. Complexation with organic matter, chemisorption on metal oxides and silicate clays, and precipitation as carbonates, hydroxides, or phosphates are all favored at higher pH. In alkaline soils, solubility may increase by formation of soluble Pb-organic and Pb-hydroxyl complexes (McBride, 1994). Lead has a tendency to bioaccumulate in the humus-rich surface layer of soils, because of its strong complexation by organic matter, and it is the least mobile heavy metal in soils, especially under reducing or nonacid conditions (McBride, 1994).

All humans have lead in their bodies, primarily as a result of exposure to manmade sources. Today, the major accumulation of lead in the environment is due to paint, dust or particulates of lead dioxide, storage batteries, smelting and burning of coal, metal plating, fertilizers, pesticides, and as an additive in gasoline. For children, the most important pathways are ingestion of chips from lead-painted surfaces, inhalation of lead from automobile emissions, drinking water from lead- soldered plumbing, and medications in the form of folk remedies. Lead in vapor forms, particularly alkyl lead from automobile emissions, is a prominent source of lead exposure for urban residents in areas with congested traffic (Lum et al., 1994). Once lead is ingested into the body it is primarily located in the red blood cells, but can also be found in soft tissue (kidney, bone marrow, liver, and brain), and mineralizing tissue (bones and teeth) (Lum et al., 1994). Depending on the location and concentration of lead in the body different organ systems and biochemical activities can be seriously impaired (Amdur et al., 1991). There are

several highly contaminated lead sites in the United States including: the Gould Superfund site, Portland, Oregon, the California Gulch site, Leadville, Colorado; the Remington Arms site Bridgeport, Connecticut; and the Sandy Smelter site in Sandy, Utah (EPA, 1999). Furthermore, lead is one of the more common trace metal contaminants in urban soils due to atmospheric deposition from industry and automobile emissions.

Cadmium, a soft, silvery white, ductile metal, is usually found in the environment as aqueous Cd $(H_2O)_6 ^{-2}$ or as ion pairs, complexes, and co-precipitation in solid phases, and sorbed to soil constituents. Cadmium has a medium to high mobility in well drained acidic oxidizing solutions, because it adsorbs rather weakly on organic matter, silicate clays, and oxides unless the pH is higher than six (McBride, 1994). The mobility and bioavailability of Cd in neutral to alkaline soils is low. Natural geochemical processes, such as precipitation of Cd from sulfide minerals in peaty soils, have been known to concentrate Cd in surface soils (McBride, 1994). This high accumulation has created problems in regions where the climate is too dry for leaching to deplete naturally high levels of Cd in the soil. This combination of generally high bioavailability in soils and very high toxicity to animals and humans has made Cd the element of greatest concern in considering the value of sewage sludge as a soil amendment (McBride, 1994).

Most cadmium used in this country is extracted during the production of other metals such as zinc, lead, or copper. Cadmium has many uses in industry and consumer products; mainly batteries, pigments, metal coatings, plastics, and amalgam in dentistry (Merck Index, 1976). Ingestion (food) and inhalation (smoke) are the largest potential sources of cadmium exposure for members of the general public (Nriagu, 1980). As with lead, cadmium has no known positive effect on human health (EcoIndiana, 1998). Additionally, the International Agency for Research on Cancer and the Environmental Protection Agency have determined that cadmium is a potential human carcinogen. Toxicological effects of Cd include severe abdominal pain, vertigo, kidney damage, and lung damage (Nriagu, 1980).

There are two general remediation strategies that can be used on soils contaminated with trace metals. The first strategy involves ex-situ treatment, which physically removes soil and processes it in ways that reduce trace metal bioavailability (i.e. soil washing and physical separation). The second strategy involves on-site (in-situ) remediation where the soil is managed or treated in place (i.e. solidification and vitrification) (Pierzynski et al., 1994). Ex-situ treatment technologies have two major disadvantages: disposal of the removed trace metal and the removal of enormous quantities of soil (Pierzynski et al., 1994). Similarly, in-situ remediation processes require specialized equipment and may be cost prohibitive. Due to the toxicity and ubiquitous occurrence of lead and cadmium in soils, proper remediation of soils contaminated by these elements is necessary.

Monitored Natural Attenuation (MNA) has recently been examined as a remediation alternative to conventional in-situ and ex-situ techniques. Monitored Natural Attenuation, as defined by the EPA OSWER Directive 9200.4-17 are naturally occurring processes in soil and groundwater that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in those media. MNA has recently been considered as an alternative method used to achieve site-specific remedial cleanup objectives within a reasonable time frame as compared to more active methods

(EPA, 1997). These in situ processes include biodegradation, dispersion, dilution, sorption, precipitation, volatilization, and/or chemical and biochemical stabilization of contaminants (EPA, 1997). Research examining natural attenuation processes in soils has focused primarily on organic compounds and has demonstrated that many organic compounds are naturally attenuated over time (Stienberg et al., 1987; and Alexander, 1995). Numerous states have used MNA as a feasible remedial alternative for petroleum spills as microorganisms have demonstrated the capability to biodegrade almost all organic contaminants given the proper conditions (NRC, 1993). Unfortunately, metals cannot be degraded in a similar manner. Therefore, substantial scientific data demonstrating processes that will reduce metal bioavailability are necessary (NRC, 1993).

Recent studies have demonstrated that trace metals can be naturally sequestered by soils over time (Bruemmer et al., 1988; Ainsworth et al., 1994; McLaren et al., 1998; Backes et al., 1995; Farley et al., 1985; and Eick et al., 1998). However, the sequestering mechanism is still the subject of debate. Several mechanisms have been proposed including: solid state diffusion within oxide particles (Bruemmer, et al., 1988), diffusion into micropore and intraparticles spaces (Eick et al., 1999), incorporation into the mineral structure via recrystallization (Ainsworth et al., 1994), and surface catalyzed hydrolysis and precipitation (Farley et al., 1985). The majority of these studies have focused on the ability of inorganic cations (i.e. Na^+ and Ca^{2+}) to desorb the metals from soil constituent surfaces. Limited information has examined the impact of low molecular weight organic acids on trace metals desorption in soils (Naidu and Harter, 1998). Several low and variable molecular weight organic acids (aromatic and aliphatic) have been identified in soils systems, and they have been described as natural complexing and dissolution agents. The distinctive character of organic substances is based on the fact that they contain a large number of complexing sites per molecule. In an aqueous system the total molar concentration of these sites can be comparable to simple ligands, but they can differ appreciably in their reactivity characteristics (Adriano, 1992). The ability of organic acids to complex trace elements and solubilize mineral surfaces may result in an increase in the bioavailability of trace elements sequestered by mineral surfaces. This would be especially important in environments dominated by high microbial activity. In order to justify the use of processes such as MNA as viable for remedial cleanup more research is necessary to understand how residence time and organic acids will affect the kinetics and mechanisms of trace metal desorption from mineral surfaces. Furthermore, most of the studies examining the influence of residence time on trace metal desorption have been conducted at near neutral pH values. Natural soil environments may experience a reduction in pH over time due to both natural and anthropogenic processes.

Accordingly the objectives of this study are to investigate the influence of residence time and organic acids on the adsorption/desorption of Cd^{2+} and Pb^{2+} from goethite.

Our first hypothesis considers the strength of adsorbent-adsorbate bonds and whether a metal adsorbs as a hydrolysis species [i.e. Pb $(OH)^+$]. This may influence the magnitude of the observed residence time effect. Using two cations with very different hydrolysis constants and affinities for mineral surfaces this hypothesis was tested (Table 1.1). The second hypothesis is that soil solutions are a complex mixture of cations, anions, and ligands, and these adsorptives can influence the desorption behavior of trace

elements and the magnitude of any observed residence time effect. This was tested by conducting desorption experiments in the presence of oxalate, salicylate, and Na^+. The third hypothesis is that natural attenuation processes will be less effective at low pH. This was tested by conducting desorption studies at a pH of 4.5.

TABLE 1.1 PROPERTIES OF TRACE ELEMENTS

TRACE ELEMENT	HYDRATED RADII (O)*	LOG HYDROLYSIS CONSTANT (MOH$^+$) **	ELECTRONNEG (KCAL/G ATOM)*	IONIC RADII (NM)*
Cd 2+	----	-10.08	---	.097
Pb 2+	4.5	-7.71	1.8	.120

* Kabata-Pendias and Pendias, 1984
** Baes and Mesmer, 1976

Chapter 2. Literature Review

METHODOLOGY FOR ADSORPTION/DESORPTION EXPERIMENTS WITH TRACE METALS

In general it is accepted that trace metal concentrations in soil solution, and hence trace metal bioavailability and toxicity, are controlled by adsorption/desorption reactions at the surfaces of soil colloids (McLaren et al., 1998). It has also been observed that hydrous metallic oxides, as homogeneous phases or more commonly as coatings on other solid particles, are dominant sorbents of trace metals and can therefore be important in controlling trace metal concentrations in soil solutions (Backes et al., 1995). Synthetically prepared oxides are often used as models for naturally occurring oxides, and by extension, as models for surface properties of whole soils (McLaren et al., 1998). While a great deal of research has been conducted examining trace metal and metal oxide interactions this research has focused primarily on the adsorption of trace elements on soil constituents surfaces with relatively little information on desorption (Eick et al., 1999). Since soils are seldom if ever at a state of equilibrium, understanding rates and mechanisms of desorption is paramount to assessing the bioavailability and potential toxicity of trace elements in natural environments.

Numerous kinetic methods have been used for studying adsorption/desorption reactions on soils and soil constituents surfaces including batch techniques, filter-flow techniques, stirred-flow techniques, stopped-flow techniques, and relaxation methods (Sparks, 1989). Each method has advantages and disadvantages and one must choose a method that works best for the system of interest and the objectives of the research. Batch methods and filter flow methods have been the most widely used techniques for measuring adsorption/desorption reactions on soil surfaces (Sparks, 1989). Batch methods involve placing an adsorbent and adsorptive in a vessel such as a centrifuge tube or a jacketed flask. The vessel is agitated using a shaker or stirrer for a certain time interval and the suspension is usually centrifuged or filtered to obtain a clear supernatant for subsequent analysis (Sparks, 1989). Several problems are associated with batch reactors. The first problem is a result of centrifugation of the suspension which can create electrokinetic effects close to soil constituents surfaces that may alter the ion distribution (Sparks, 1989). Additionally, centrifugation may require up to 5 minutes to separate the solid from the liquid phases, yet many reactions on soil constituents are complete by that time (Sparks, 1989). Finally, unless the suspension is thoroughly mixed, sampling may alter the reactant concentration, which may influence the kinetics. Many of the disadvantages of batch techniques can be eliminated with the batch technique developed by Zasoski and Burau (1978). This technique keeps the suspension well mixed and at a constant pH using a combination glass electrode along with an automatic titrator, or a pH-stat. Another important attribute of this technique is that it does not employ the use of centrifugation to obtain a clear supernatant solution. Furthermore, excellent mixing occurs within the reaction vessel, and one can maintain a constant solid –to – solution ratio throughout an experiment (Sparks, 1989).

Filter flow methods or miscible displacement techniques involve placing the adsorbent in a column, tube, or filter holder, and leaching it with a reacting solution

(Sparks, 1989). For adsorption/desorption studies samples can be injected as suspensions or spread as dry samples on a membrane filter. The filter holder is capped securely and then is attached to a fraction collector and a peristaltic pump, which maintains a constant flow rate. Monitoring the increasing concentration of the leachate with time enables one to follow the adsorption reaction. (Sparks, 1989). At apparent equilibrium, the effluent concentration equals that of the initial adsorptive solution. The desorption reaction is studied in a similar way, the reaction being followed by monitoring the decreasing concentration of the previously sorbed ion or other sorbate (Sparks, 1989). Though filter flow methods show some advantage to batch methods they still have potential problems. In continuous filter flow methods often the colloidal particles are not dispersed – for example, the time required for an adsorptive to travel through a thin layer of colloidal particles is not equivalent at all locations of the layer, consequently, mass transfer can be significant (Sparks, 1989). One advantage of using flow techniques is that soil constituents particles will be exposed to a greater mass of adsorptive than in a static batch system (Sparks, 1989). Also in a flow system ion exchange can be complete, since the replaced adsorbate ions are always removed from the system as more of the introduced adsorptive is added (Sparks, 1989). Finally, flow techniques may be more representative of reactions occurring in natural soil environments (Sparks, 1989). The miscible displacement technique has been used extensively to measure ion-exchange reactions as well as trace metal desorption from oxides and clays (Sparks and Jardine, 1984; Ogwada and Sparks, 1986; Backes et al., 1995; McLaren et al., 1998; Eick et al., 1999).

Many of the disadvantages of the continuous flow technique were eliminated with the stirred-flow technique (Sparks, 1989). This method creates perfect mixing so that the chamber and effluent concentrations are equal and the transport phenomena is minimized significantly (Sparks, 1989). The stirred flow technique also retains the attractive features of removing desorbed species at each step of the reaction process which simplifies the study of desorption kinetics (Sparks, 1989). The stirred flow technique was used by Eick et al., (1990) to measure adsorption kinetics of K^+ - Ca^{2+} exchange on clay minerals and by Bar-tal et al., (1995) to measure K^+ - Ca^{2+} exchange on clay minerals.

A stopped-flow technique can be used to avoid the large volume of reactant solution necessary in flow methods. In the stopped-flow technique two solutions are mixed very rapidly by injecting them into a mixing chamber, designed to ensure that the flow is turbulent and complete mixing occurs very quickly. Behind the reaction chamber there is an observation cell fitted with a plunger that moves back as the liquids flood in, but which comes up against a stop after a certain volume has been admitted. The filling of that chamber corresponds to the sudden creation of an initial sample of the reaction mixture. The reaction then continues in the thoroughly mixed solution and is monitored spectrophotometrically (Atkins, 1996). Most of the major advances in stopped flow instruments since 1970 have been adapted in stopped-flow units with a variety of detection systems (Sparks, 1989). The stopped-flow technique was used by Ikeda et al., (1984) to measure cation exchange kinetics of Li^+, K^+, Rb^+, and Cs^+ for Na^+ on zeolites (Sparks, 1989).

Many adsorption/desorption reactions on soil constituent surfaces are extremely rapid and cannot be measured using the conventional techniques described above. Furthermore, many of these conventional techniques measure transport or diffusion

controlled reactions and therefore provides only apparent rate constants. These rapid reactions can be measured using relaxation techniques such as pressure-jump (p-jump), temperature-jump, and electrical field pulse. The p-jump technique has been used extensively to measure adsorption/desorption reactions of trace metals on oxide surfaces. With this method, the equilibrium of a reaction mixture is perturbed by a rapid alteration of the pressure. One obtains kinetic information by measuring the "relaxation time" as the reaction approaches a new equilibrium (Sparks, 1989). Advantages of p-jump are that measurements can be repeated at quicker intervals than other relaxation methods such as temperature jump, and adsorption/desorption rate constants can be determined in one experiment (Sparks, 1989). Pressure-jump studies on soil constituents include adsorption/desorption kinetics at the TiO_2-H_2O interface (Ashida et al., 1978), proton adsorption/desorption dynamics of acetic acid on silica-alumina particles (Ikeda et al., 1982), ion exchange kinetics of metals (Ikeda et al., 1984), and NH_4^+ on zeolites (Ikeda et al., 1984).   A number of studies have used p-jump to study fast catalytic and exchange reactions on soil constituent surfaces (Sparks, 1989). Recently, p-jump relaxation has been used to study trace metal and oxyanion adsorption on Fe oxides (Grossl et al., 1994, Grossl et al., 1997).

KINETICS OF ADSORPTION/DESORPTION REACTIONS

Many equations have been used for the analysis of adsorption/desorption kinetics on soil surfaces. Some of the most commonly used equations for the analysis of adsorption/desorption kinetics are first-order, second order, and zero order reactions (Sparks, 1989). The chemical kinetics of adsorption/desorption reactions on soil surfaces are concerned with three processes: (1) the rates of chemical reactions, (2) how the rate responds to changes in conditions or presence of a catalyst, and (3) the mechanism of the reaction (Atkins, 1996).

The first stage in investigating the rate and mechanism of a reaction is to determine the overall stoichiometry of the reaction, and to identify any side reactions. Once this is done, the next step is to determine how the concentrations of the reactants and products change with time after the reaction is initiated, which is done experimentally (Atkins, 1996). An empirical observation of the greatest importance is that the rate of reaction is often found to be proportional to the molar concentrations of the reactants raised to a simple power (Atkins, 1996). Chemical reactions are sensitive to changes in temperature, thus a constant temperature must be kept throughout the experiment in order to achieve reliable results (Atkins, 1996). Also conformity of kinetic data to a particular equation does not necessarily mean it is the best model, or that one can confirm reaction mechanisms based solely on this kinetic data (Sparks, 1989). Moreover, the sorbate/sorbent ratio may influence the kinetics of adsorption/desorption reactions (Dzombak and Morel 1985, Eick et al., 1999). Dzombak and Morel (1985) found at a fixed concentration the sorption of cadmium on a hydrous ferric oxide slowed considerably as the sorbate/ sorbent ratio increased. Eick et al., (1999) found that the desorption of Pb^{2+} from goethite decreased as the sorbate/sorbent ratio increased at a fixed concentration.

RATES OF ADSORPTION/DESORPTION REACTIONS

First order reactions have been used extensively to model both adsorption and desorption of trace metals from soil and soil constituent surfaces (Sparks, 1989). The first order reaction, can be written as

$$-\ln [A] + \ln [A]_0 = kt \tag{2.1}$$

where *[A]$_0$* is the concentration of species *A* at time zero, *k* being the first order rate constant, *t* being time, and *[A]* as the concentration of species A at a given time. The rate constant is important, as it is independent of the concentration of the species involved, and it can be used to predict the rate of reaction for any given composition of the reaction mixture (Atkins, 1996). In this linear form the rate constant, *k*, is equivalent to the slope calculated from a plot of the negative logarithm of the final concentration versus time (Sparks, 1989). Some of the investigations using first-order kinetics to describe adsorption/desorption include: potassium adsorption/desorption on clay minerals, (Mortland and Ellis, 1959; Burns and Barber, 1961; Huang et al., 1968; Sivasubramaniam and Talibudeen, 1972; Jardine and Sparks, 1984; Ogwada and Sparks, 1986), nitrate adsorption on clay minerals (Stanford *et al.,* 1975; Carski and Sparks, 1987), lead adsorption on river mud (Salim and Cooksy, 1980), and aluminum adsorption on clay minerals and peat (Jardine and Zelazny, 1986). Although first order equations have been the most widely used to model adsorption/desorption reactions on soil surfaces, second-order equations, zero-order equations, and fractional order equations have also been used (Sparks, 1989).

Mathematical models have also been used to analyze the kinetics of adsorption/desorption reactions (Backes et al., 1995; McLaren et al., 1998; Dzombak and Morel 1990). Currently available mathematical models of adsorption/desorption reactions from aqueous solution treat surfaces as consisting of a homogeneous solution of equivalent sites that follow mass law equations for equilibrium (Benjamin and Leckie, 1981). McLaren et al. (1998) and Backes et al. (1995) used two simultaneous first-order reactions and a lognormal distribution model for analyzing desorption kinetics of Cd^{2+} and Co^{2+} from Fe and Mn oxide surfaces. The mathematical expressions of these models are as follows:

$$C_M = C_1 \exp(-k_1 t) + C_2 \exp(-k_2 t) \tag{2.2}$$

$$\tag{2.3}$$
$$C_M = \frac{C_{des}}{\sigma\sqrt{2\pi}} \int_{-4\sigma}^{+4\sigma} \exp\left[\frac{-1}{2}\frac{(\kappa-\mu)^2}{\sigma}\right] \exp(-e^k t)d\kappa$$

Equation 2.2, two simultaneous first order equations, was optimized for concentrations and rate constants where C_M is the concentration of metal ion sorbed to the clay at time **t**, C_1 and C_2 are the initial concentrations (t=0) of metal ion bound to sites with first-order desorption rate constants k_1 and k_2 , respectively. These variables were optimized by computer using the assumption of discrete independent sites and that all sorbed metal ions would eventually desorb. Equation 2.3 is the lognormal distribution model, which assumed that these reactions resembled a continuous distribution of reaction sites, distributed lognormally with respect to a first order rate constant, and that all-metal ions would eventually desorb. Equation 2.3 was fitted to experimental data using a computer by optimizing μ, and the mean of the normal distribution in **ln k**, and σ, the corresponding standard deviation. Backes et al., (1995) and McLaren et al., (1998) used these equations to describe Co and Cd adsorption/desorption on oxides and clay minerals. Backes et al., (1995) found Equations (2.2) and (2.3), could be used to describe desorption of Cd^{2+} and Co^{2+} on two iron oxides (goethite and ferrihydrite), and two manganese oxides (hasumannite and cryptomelane). McLaren et al. (1998) also used both equations to describe desorption of Cd^{2+} and Co^{2+} from a Craigieburn silt loam and a Wakanui silt loam using similar experimental procedures.

The parabolic diffusion equation has been used to determine whether diffusion-controlled phenomena are rate limiting for adsorption/desorption of trace metals from soil constituent surfaces. The parabolic diffusion equation was originally derived based on radial diffusion in a cylinder where the ion concentration on the cylindrical surface is constant, and initially the ion concentration throughout the cylinder is uniform (Sparks, 1989). Equation 2.4 is the parabolic diffusion model from Hodges and Johnson (1987):

$$F_d = kt^{1/2} \tag{2.4}$$

Where F_d is the fraction of metal desorbed (1-P_{bt} / P_{b0}), $t^{1/2}$ is the square root of time in seconds, and k is the diffusion rate coefficient (s^{-1}). If the reaction is diffusion controlled then a graph of F_d versus $t^{1/2}$ should be linear with a slope of k.

Eick et al., (1999) used the parabolic diffusion equation to describe desorption of Pb^{2+} from goethite at different surface loading with a filter flow method. Eick et al. (1999) found at a sorbent concentration of 2.5 g/L the proportion of Pb^{2+} desorbed varied inversely with surface coverage. The parabolic diffusion equation best described the desorption of Pb^{2+} from goethite at all surface coverage investigated in contrast to a shell progressive particle diffusion equation, and single and two first order equations. This suggested that the reaction was transport or diffusion controlled (Eick et al., 1999). Other models used to describe adsorption/desorption reactions on soil constituent surfaces include a two-constant rate equation (Kuo and Lotse, 1973), and the Elovich equation (Sparks, 1989).

MECHANISMS OF TRACE METAL ADSORPTION/DESORPTION

Several researchers have demonstrated that adsorption occurs in two steps; a rapid adsorption stage, followed by a very slow continuous uptake. Metal concentration, pH, type of metal cation, and composition of sorbent material can affect these processes. The rapid stage characteristic of trace metal adsorption on variable charge surfaces has been ascribed to chemisorption (Ainsworth et al., 1994). Non crystalline aluminosilicates, oxides and hydroxides of Fe, Al, and Mn, and even the edges of layer silicates to a lesser extent, provide surfaces sites for the chemisorption of trace metals. All of these minerals present a similar type of adsorptive site: a valence unsatisfied OH^- or H_2O ligand bound to a metal ion (usually Fe^{3+}, Al^{3+}, and $Mn^{3+,+4}$). For example McBride (1994), suggests that iron oxides, can bind trace metals (M), according to the following reaction:

$$>Fe-OH]^{-1/2} + M(H_2O)_6{}^{n+} \rightarrow >Fe-O-M(H_2O)_5]^{(n-3/2)+} + H_3O^+$$
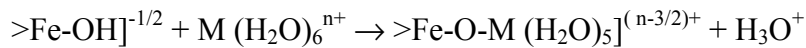
Generally, adsorption of metals seems to be more nearly reversible at low than at high pH. This may arise from the fact that the monodentate complexation reaction should give way to a bidentate reaction at higher pH. The latter reaction, involving two metal surface bonds, is expected to have a very slow rate in the reverse direction (desorption) (McBride, 1994). Also, as pH increases there is an increased tendency for metals to hydrolyze and bind as $M(OH)^{n-1}$ or $M(OH)_2{}^{n-2}$. Studies of trace metal bonding on pure oxides have indicated that the chemisorption reaction step is fast and probably diffusion controlled ($k_f \approx 10^5$ moles^{-1} liter sec^{-1}), whereas the desorption reaction step has a rate constant that may be as much as three orders of magnitude slower (McBride, 1994).

Thermodynamics also plays an important role in adsorption/desorption reactions. Adsorption may or may not require a significant activation energy E_a, depending on whether a strong bond must be broken to allow the metal ion to coordinate to the surface. In contrast, assuming that the adsorption reaction is energetically favorable, desorption always requires an activation energy to at least overcome the adsorption energy (McBride, 1994). As was discussed earlier desorption rates are often several magnitudes slower than adsorption rates (McBride, 1994; Bruemmer et al., 1988). Not all research is in agreement with this explanation. Elkhatib et al., (1993) found that energy of activation values for desorption were smaller than adsorption in a thermodynamic study of lead sorption and desorption from soils. Elkhatib et al., (1993) also found that energy of activation values of Pb^{2+} on three soil types ranged from 1.55 to 27.72 kJ mol^{-1} while energy of activation values for desorption ranged from 0.66 to 6.78 kJ mol^{-1}. Decreases in activation energies between adsorption and desorption were attributed to increases in surface coverage along with diffusion controlled reactions. Further research in both thermodynamics and kinetics is required to resolve these discrepancies.

RESIDENCE TIME EFFECTS

Recent studies have demonstrated that the desorption of trace metals from soil constituent surfaces is slower than adsorption and that desorption becomes more difficult with time (Ainsworth et al., 1994; Eick et al., 1999; McBride, 1994; Bakes et al., 1995; McLaren et al., 1998). The slow process has been related to mechanisms such as recrystallization of metals into the mineral structure, diffusion into micropores, surface precipitation, change in surface complex, and solid state diffusion into the crystal matrix.

Ainsworth et al., (1994) examined the residence time effect of Co^{2+}, Cd^{2+}, and Pb^{2+} adsorption to hydrous ferrous oxide (HFO). The researchers found that after 16 hours of aging 18% of the total Cd^{2+} and 30 % of the total Co^{2+} could not be desorbed as pH was decreased. Furthermore, the total quantity of both Cd^{2+} and Co^{2+} that could not be desorbed increased with an increase in residence time. In contrast essentially all of the Pb^{2+} was desorbed as pH decreased regardless of residence time (Ainsworth et al., 1994).

The magnitude of hysteresis followed the order Co>Cd>Pb, which is the inverse of the ionic radii of the metal sorbates (Ainsworth et al., 1994). It was suggested the residence time effect observed for Co^{2+} and Cd^{2+} was a result of the metals being incorporated into a recrystallizing solid though isomorphic substitution, rather than by micropore diffusion or a slow reversible adsorption process (Ainsworth, et al., 1994). However due to the large ionic radii of Pb^{2+} it was unable to isomorphically substitute for Fe^{3+} in the HFO, as it became more crystalline. Naturally occurring goethite has been observed to contain trace metal impurities such as Co^{2+}, Cu^{2+}, and Ni^{2+} (Ainsworth et al., 1994). The size of the ionic radii of the metal seemed to dictate whether the metal was incorporated into the crystal and at what rate the incorporation took place (Ainsworth et al., 1994).

Bruemmer et al. (1988) examined the influence of residence time on the adsorption of Ni^{2+}, Zn^{2+}, and Cd^{2+} on goethite. The researchers suggested that solid state diffusion was the mechanism for the slow continuous uptake of Ni^{2+}, Zn^{2+}, and Cd^{2+} on goethite. Bruemmer (1988) proposed this mechanism using information from unpublished results of Gerth which indicated that goethite particles contain domains, micropores, and defects of different size in relation to the synthesis conditions which presented possible pathways for diffusion. Bruemmer tested this hypothesis by using thermodynamic based diffusion coefficients and the Arrhenius equation to model maximum relative diffusion rates of each of the metals on goethite (Bruemmer et al., 1988). The researchers found that maximum relative diffusion rates of Ni^{2+}, Zn^{2+}, and Cd^{2+} can be related to the ionic radii and binding strength of the metals. Nickel showed the highest binding strength to goethite followed by Cd^{2+}, and Zn^{2+}, and that Ni^{2+} also had the greatest diffusion rate based on ionic radii followed by Zn^{2+}, and Cd^{2+} (Bruemmer et al., 1988).

Research conducted by Farley et al., (1985) suggested that surface precipitation was responsible for the slow adsorption of metal cations on amorphous iron hydroxide. This was accomplished by extending the surface complexation approach by considering precipitation on the solid to be described by the formation of a solid solution whose composition varies continuously between that of the original solid and a pure precipitate of the sorbing cation. Farley et al., (1985) used a surface precipitation model that exhibited Langmuir behavior at low metal concentrations, and Freundlich behavior at higher metal concentration to adequately predict pH-edge shifts for a single metal on an

oxide for different sorbate/sorbent ratios given three adjustable parameters (Farley et al., 1985). The predicted values corresponded well to laboratory data for variations in the concentrations of both total iron and total sorbate metal for Cu, Pb, and Cd on amorphous iron hydroxide (Farley et al., 1985).

Eick et al., (1999) examined the influence of residence time on the desorption of Pb^{2+} from goethite. Rate coefficients for desorption decreased as residence time increased at all sorption densities investigated. Although these results were not statistically significant, it was deemed unlikely that experimental error would consistently produce the observed trends. These researchers suggested that diffusion within micropores may be responsible for the observed trends.

Two important studies, which exhibit residence time effects for adsorption/desorption of Cd^{2+} and Co^{2+}, are Backes et al., (1995) and McLaren et al., (1998). Backes et al., (1995) examined the kinetics of cadmium and cobalt desorption from iron oxides (goethite and ferrihydrite) and manganese oxides (hausmannite and cryptomelane). In comparing adsorption/desorption between Mn oxides and Fe oxides, Mn oxides sorbed larger amounts of Cd^{2+} and Co^{2+} than Fe oxides. After one week of adsorption Mn oxides sorbed between 0.19–0.51 $\mu mol\ m^{-2}$ of Cd^{2+} while Fe oxides adsorbed between 0.06-0.21 $\mu mol\ m^{-2}$. Similar results where seen at one week for Co^{2+} adsorption. After 14 weeks of adsorption time Mn oxides sorbed between 0.20-0.50 $\mu mol\ m^{-2}$ of Cd^{2+} while Fe oxides adsorbed between 0.04-0.10 $\mu mol\ m^{-2}$. For iron oxides, goethite sorbed greater amounts of Cd^{2+} and Co^{2+} than did ferrihydrite on a surface-area basis (Backes et al., 1995). All adsorptives exhibited residence time effects, however, goethite exhibited a pronounced residence time effect where increasing the length of sorption substantially decreased the rate and quantity of desorbed Co^{2+} and Cd^{2+}. After one week of sorption 98% of Cd^{2+} was desorbed, while only 55% was desorbed after a 15-week sorption period. For Co^{2+} 48% was desorbed after one week of sorption, while 23% was desorbed after a 14-week sorption period.

The researchers evaluated the desorption kinetics of Co^{2+} and Cd^{2+} using two different kinetic models (Equation 2.2 and 2.3). In the first model (discrete site model) it was observed that two reaction rates could be described by assuming that desorption was controlled by two simultaneous first order reactions and that ultimately all the sorbed metals would be desorbed (Backes et al., 1995). For the discrete site model three fitted parameters where necessary: C_1 represented the concentration of metal associated with the faster of the two first-order reactions, k_1 represented the rate constant for the initial first order reaction (a relatively rapid desorption), and k_2 represented the rate constant for the much slower desorption reaction. There was little difference between the k_1 values for Cd^{2+} or Co^{2+}, for all oxides investigated. Furthermore there was little difference in k_1 values for the different sorption periods. However differences were observed for k_2 values for all oxides investigated. The difference was most pronounced for goethite where the rates of desorption (k_2) of Cd^{2+} decrease from -3.63 s^{-1} after 1 wk of sorption to -4.73 s^{-1} after 15 wk of sorption. For Co^{2+} k_2 decreased from -4.89 s^{-1} after 1 wk of sorption to -5.22 s^{-1} after 14 wk of sorption. In addition an increase in the proportion of sorbed Cd^{2+} and Co^{2+} associated with the slower reaction was observed with an increase in sorption period particularly for goethite. For goethite Cd^{2+} sorption increased from

48% (1wk) to 62% (15 wk) with the slower reaction, and from 65% (1 wk) to 85% (15 wk) for Co (Backes et al., 1995).

Because of some of the uncertainty of interpreting optimized k values for discrete site models, a separate model (lognormal model) was also chosen to interpret data. This model was based on a hypothesis that metal binding sites form a continuous lognormal distribution with respect to the first-order rate constant (Backes et al., 1995). The lognormal model required two fitted parameters μ, (the mean log k), and σ, the standard deviation of log k. Mean log k (μ) values obtained from the lognormal model were comparable with k values obtained from the two discrete site models. In cases where the two discrete site model predicted $> 80\%$ of sorbed Cd^{2+} or Co^{2+} associated with the slower reaction, μ values corresponded to k_2 values. In cases where the discrete site model predicted $< 80\%$ of sorbed Cd^{2+} or Co^{2+} associated with the slower reaction, μ values fell between k_1 and k_2 values.

The greatest amount of metal desorption was observed for Cd^{2+} and goethite where 98% was desorbed after one week. For the long-term sorption experiment Cd desorption from goethite was also highest at 55%. The lowest amount of metal desorption was observed for Co^{2+} from hausmannite at 2%. Increases in the proportions of sorbed metals, and differences in the k_2 values for metals, oxides, and sorption periods were used to explain the differences seen in the desorption percentages of Cd and Co. One interpretation of the observed trends was movement of trace metals from reaction sites associated with the fast desorption reaction to sites associated with the slower reaction. Another explanation suggests changes in the original binding sites which may or may not have to do with alterations in structure and crystallinity observed in oxides over long periods of equilibration in aqueous solutions (Backes et al., 1995).

McLaren et al. (1998) examined the kinetics of Cd^{2+} and Co^{2+} desorption from soil clay fractions using the same techniques and models of Backes et al. (1998). In particular they investigated how an increase in sorption period would influence the quantity and rate of desorption. The two clay fractions (Craigieburn and Wakanui) had similar organic C contents but differed in their dominant mineralogy with the Craigieburn clay containing a higher concentration of short range order and crystalline Fe materials, than the Wakanui clay. No substantial differences were seen in the concentrations of Cd^{2+} and Co^{2+} adsorbed between clay fractions, or at the different sorption periods used (1wk and 12-16 wk). This was attributed to the similarity in the organic C content of both clay fractions (McLaren et al., 1998). Although the amount of Cd^{2+} and Co^{2+} sorbed where similar the amount desorbed differed considerably. The quantity of cadmium desorbed was between 37-71% while the quantity of cobalt desorbed was between 12-37% for both clay fractions. There was also a dramatic difference in the amount desorbed after increased sorption period. Both Cd^{2+} and Co^{2+} exhibited decreased desorption after the initial sorption period was increased (McLaren et al., 1998). For Cd^{2+} the amount desorbed decreased from 50% to 36% on the Craigieburn soil from 1-12 weeks, and from 70%-44% on the Wakanui soil from 1-12 weeks. A similar decrease was seen in Co^{2+} for both soils investigated.

Both the discrete site model and the lognormal model revealed a consistent decrease in the desorption rate with increasing sorption period for trace metal and clay fraction. The changes associated with increased sorption period was hypothesized to be a

shifting of the trace metals to more slowly desorbing sites, or a result of slower intraparticle diffusion rates associated with the movement of ions to more inaccessible sites (McLaren et al., 1998).

Backes et al., (1995) and McLaren et al., (1998) both induced desorption of trace metals with an inorganic electrolyte solution ($CaCl_2$) at near neutral pH. In order to fully understand trace metal sorption/desorption behaviors in natural soil environments it is also important to investigate the influence of naturally occurring organic acids and lower soil pH on these processes. As indicated by the above studies the kinetics and mechanisms of observed residence time effects vary widely among different trace elements and soil constituent's surfaces. Since the capacity of the soil to sequester these metals over time is critical to the success of natural attenuation processes, more research must be done to understand the kinetics and mechanisms of these processes. By understanding these processes and the condition under which they occur, natural attenuation can be used as a viable remediation alternative for trace metals.

Chapter 3. Goethite synthesis and characterization

MATERIAL AND METHODS

Goethite synthesis

Goethites with two different surface areas were synthesized for our experiments. The first goethite (70 m^2/g) was synthesized according to a procedure developed by Schwertmann et al., (1985). The synthesis and crystallization process was initiated by filling a polypropylene container with 1800 ml of the 0.10 M KOH solution, and adding 200 ml of a 0.10 M Fe(NO$_3$)$_2$ solution in 10 ml aliquots using an EDP Plus Motorized Microfilter Pipette under constant stirring with a Caframo RZR-2000 stirrer. The solution was stored at 298 °K in an acid washed polypropylene container for 28 days until the α-FeOOH was completely crystallized and flocculated. The second goethite (103 m^2/g) was synthesized by reacting Fe(NO$_3$)$_3$ with 4M NaOH. The desired concentration of Fe(NO$_3$)$_3$ solution is prepared by dissolving 80.8 grams of non-hydrolyzed Fe(NO$_3$)$_3$ 9H2O into four liters of distilled doubly de-ionized water. A 4M NaOH solution was added dropwise using a burette under constant stirring until a pH of 12.0 was achieved. The red-brown precipitate (ferrihydrite) was allowed to stand at room temperature (298 °K) for fourteen days until ferrihydrite crystallized into goethite. To ensure a complete conversion of ferrihydrite into goethite the precipitate was placed into a 312 °K oven overnight (Schwertmann and Cornell, 1991).

Once the goethite crystallized and flocculated it was transferred into dialysis membranes. Prior to filling the dialysis membranes with goethite they were hydrated and boiled to remove excess contaminates such as chloride, nitrate, sulfate, or ammonium (Schwertmann and Cornell, 1991). The goethite filled membranes were placed into a covered polyethylene tub filled with distilled doubly de-ionized water. This insured that the pH of the goethite suspension decreased, excess salts were removed, and that excessive CO$_2$ did not dissolve into the distilled doubly de-ionized water. The distilled doubly de-ionized water was changed periodically (3-6 times daily) until the conductivity of the wash solution was approximately equal to distilled doubly de-ionized water. The conductivity was measured using a Barnstead Conductivity Bridge Model PM 70-CB.

After the conductivity of the wash solution was approximately equal to distilled doubly de-ionized water the goethite was transferred to 250 ml acid washed polyethylene centrifuge bottles, and gently mixed with a 0.4 M solution of HNO$_3$ for two hours using an Innova 4230 refrigerated incubator rotating shaker set at 100 rpm and 298 °K. The solution was gently mixed to reduce particle abrasion between the crystals, which may alter the goethite surface area. The 0.40 M solution of HNO$_3$ was used to dissolve any remaining amorphous Fe-oxide since it is very soluble at this pH while goethite is only slightly soluble (Schwertmann and Cornell, 1991). After two hours the suspension was centrifuged at 10,000 rpm using a Sorvall RC-5B Refrigerated Superspeed centrifuge. The goethite was re-suspended in distilled de-ionized water, poured into new dialysis membranes, and placed into a distilled doubly de-ionized water bath to remove excess HNO$_3$. When the conductivity of the wash solution was again near distilled doubly de-

ionized water the goethite in the membranes was transferred back into 250-ml acid washed polyethylene centrifuge bottles. The bottles were then dipped into liquid nitrogen (quick freeze) and subsequently freeze-dried using a Labconco freeze dryer at 3000 microns Hg and -173° K. "Quick freezing" with liquid nitrogen prevented the settling and aggregation of the goethite suspension before it was freeze dried. This allowed for easier hydration of goethite for adsorption/desorption experiments.

Characterization of goethite

The goethite was characterized using X-ray diffraction (XRD) analysis, Thermogravimetric Analysis (TGA), Transmission electron microscopy (TEM), and a ratio of oxalate extractable iron (Fe_o) to total soluble iron (Fe_t). The specific surface area was determined by a five point N_2 Brunauer-Emmett-Teller gas adsorption isotherm method (BET).

X-ray powder diffraction can be used as a diagnostic tool to provide information on crystal size, crystal disorder, structural parameters, surface area, and degree of isomorphic substitution (Schwertmann and Cornell, 1991). Random powder mounts of goethite were used for X-ray diffraction analysis according to the method of Jackson (1969). The sample was identified with a Scintag XDS 2000 X-ray Diffractometer with Cu-Kα radiation from 2 – 70° 2θ.

Thermogravimetric analysis (TGA) can be used to provide information about absorbed and structural water present in iron oxides and about phase-specific transformations. Thermogravimetric analysis was conducted by heating a 10 mg sample of goethite between 523 - 673°K continuously at a constant rate and measuring its weight loss on a mechanical balance with a HI-RES TGA 2950 Thermogravimetric Analyzer.

Transmission electron microscopy provided results on the morphology and size of the goethite crystals, the uniformity of the crystals, and the presence of amorphous phases. For TEM experiments grains were either deposited on a holey carbon film supported by a copper mesh grid or cut from Enbed 812 epoxy resin using a diamond knife and then mounted on the holey carbon film. The samples were subsequently coated with carbon and analyzed using a JEOL JEM 2000 FX TEM.

The ratio between the oxalate extractable iron and total soluble iron was used to determine the presence of amorphous oxides. Amorphous iron oxides are rapidly dissolved in the presence of oxalate. The acidified ammonium oxalate used in this experiment was made according to the procedure of Loeppert and Inskeep (1996) from solutions of 0.175-M ammonium oxalate and 0.10-M solution of oxalic acid. Ammonium oxalate and oxalic acid were made from certified analytical reagents and distilled doubly de-ionized water. The oxalate extraction solution was brought to a pH of approximately 3.0 using 0.10 M HCl and 0.10 M NH_4OH. Ten milliliters of oxalate solution were added to centrifuge tubes containing 0.1 g of goethite. The solution was gently mixed for two hours in dark conditions (wrapped in aluminum foil) in an environmentally controlled rotating shaker at 100 rpm and 298◇ K. After two hours the sample was filtered under vacuum using a fritted-glass filter equipped with a 0.10 μm cellulose ester membrane. Total soluble iron was determined by dissolving 0.10 g of goethite with 40 ml of concentrated (12.1 M) HCl for 48 hours. Extractable oxalate and

total soluble iron samples were analyzed using atomic adsorption spectroscopy. The ratio Fe_o/Fe_t was determined on a weight basis (Loeppert and Inskeep, 1996).

Surface area measurements were run in duplicate using a Micromeritics ASAP-2000. Samples were analyzed with N_2 using a 5 point BET isotherm. Calibrations were performed with two NIST standards of 10.9 m^2/g and 218 m^2/g. The samples were dried and degassed overnight under vacuum at 323 °K.

RESULTS AND DISCUSSION

An X-ray diffractogram of standard goethite (ASTM 17-536) exhibits a high intensity peak at 4.18Ⓞ (110) d-spacing, and moderate intensity peaks at 2.69Ⓞ (131) d-spacing and 2.45Ⓞ (111) d-spacing respectively (Joint Committee, 1974). An X-ray diffractogram from a random powder mount of synthesized 103 m^2/g goethite (Figure 3.1) exhibited a sharp high intensity peak at 4.20Ⓞ, and sharp moderate intensity peaks at 2.70Ⓞ and 2.45Ⓞ. An X-ray diffractogram of a random powder mount of synthesized 70 m^2/g goethite had similar peaks.

FIGURE 3.1 X-RAY DIFFRACTOGRAM OF 103 M^2/G GOETHITE (RANDOM POWDER MOUNT)
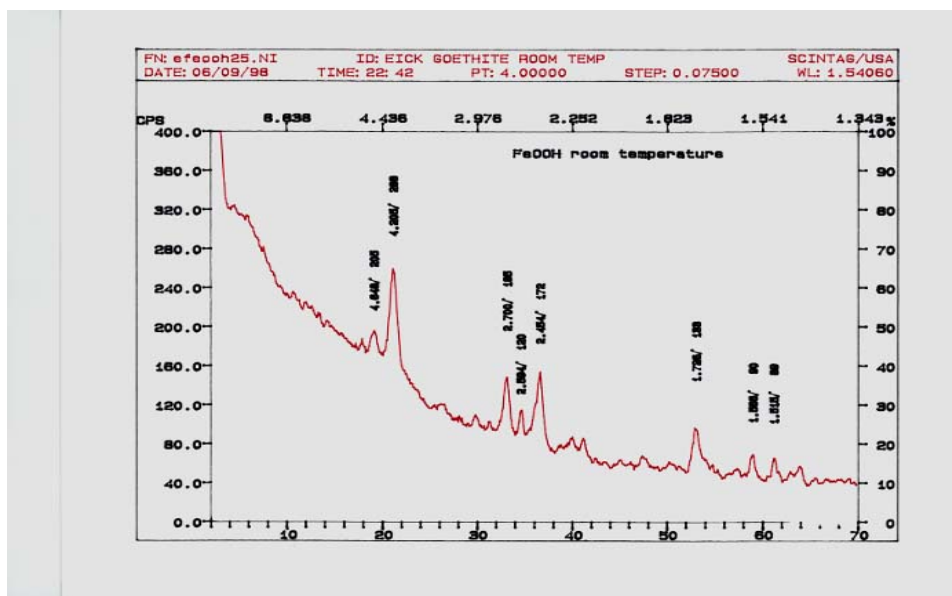
The intensity and d-spacing of the peaks verified that the sample was a well-crystallized goethite. A 10.58 % weight loss between 473-598 ◇K was observed for 103 m^2/g goethite using TGA (Figure 3.2). This number is slightly higher than the theoretical weight loss of 10.14%, but this difference may be a remnant of the goethite synthesis method used (Schwertmann et al., 1985; Todor, 1976). Also, the thermal analysis curves of iron oxides can vary appreciably with respect to peak temperature, and general shape (McKenzie, 1970). A TGA of the 70 m^2/g goethite had very similar peaks to the 103 m^2/g material.

FIGURE 3.2 THERMOGRAVIMETRIC ANALYSIS GRAPH OF 103 M^2/G GOETHITE
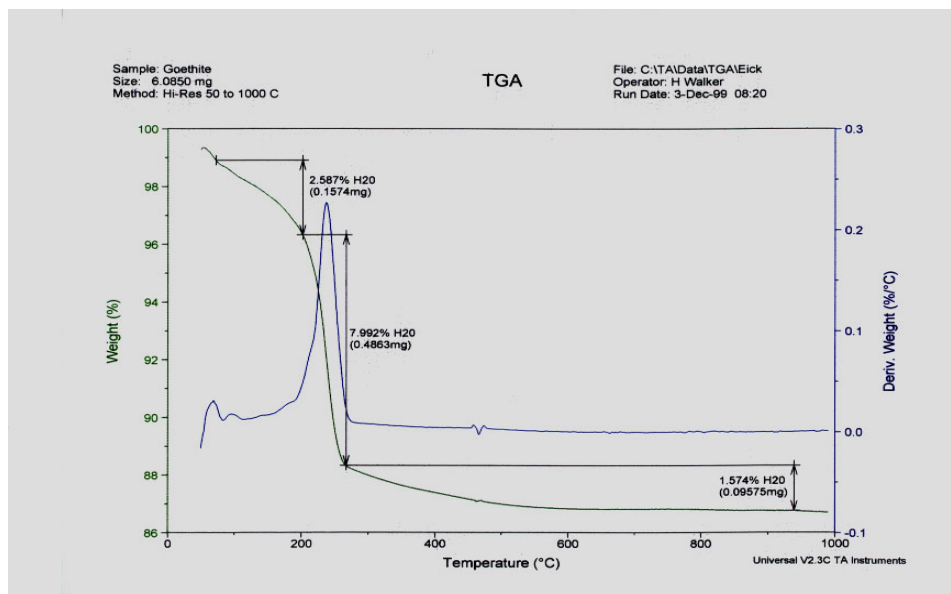
Well crystallized pure goethite exhibits acicular crystals where size depends upon synthesis method and crystallization temperature. Transmission electron micrographs of goethite samples indicated uniform crystals with no apparent amorphous phases present (Figure 3.3, 3.4).

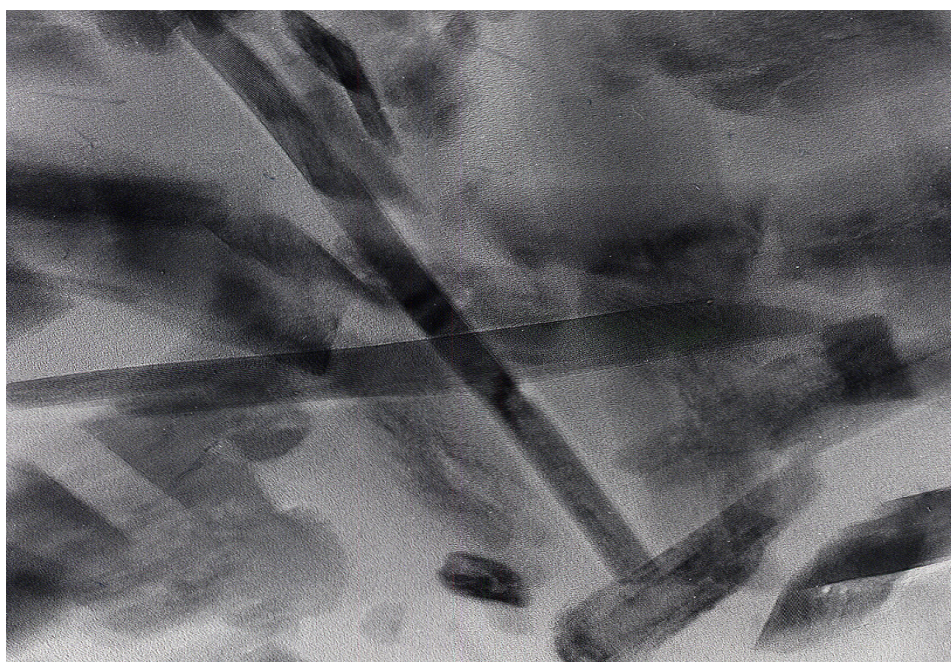FIGURE 3.3 HIGH RESOLUTION TRANSMISSION ELECTRON MICROGRAPH

FIGURE 3.4 LOW RESOLUTION TRANSMISSION ELECTRON MICROGRAPH
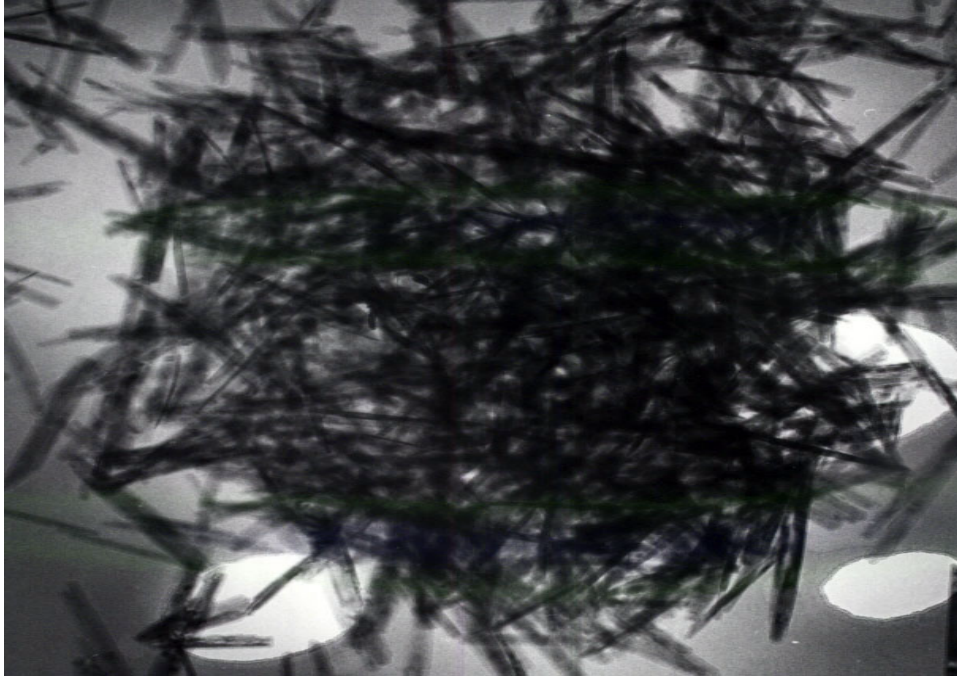
The ratio of oxalate soluble iron (Fe $_o$) to total soluble iron (Fe $_t$) was calculated by dividing Fe $_o$/Fe $_t$ multiplied by 100 (Table 3.1). The ratio 1.05% was less than 2% which indicates essentially a complete conversion of KOH and $Fe(NO_3)_2$ to goethite rather than ferrihydrite (Schwertmann et al.,1985). For the 103 m^2/g goethite the higher ratio of oxalate extractable to total extractable iron may be due to the higher surface area and hence smaller size of the goethite or lower crystallinity of the particles.

B.E.T. results yielded goethite with surface areas of 70 m^2/g and 103 m^2/g. The 70 m^2/g goethite was used for the Cd^{2+} studies while the 103 m^2/ g was used for the Pb^{2+} experiments. For both experiments adsorptive concentrations were low enough that surface coverage was well below theoretical monolayer coverage. Therefore, differences in surface area should not influence total trace metal adsorbed, which was verified by preliminary experiments.

TABLE 3.1 SURFACE PROPERTIES OF OXIDES

Oxides	Fe_o/Fe_t x 10^2	Specific Surface Area (m^2/g)
Goethite I	1.05	70
Goethite II	4.5	103

Chapter 4. Trace metal adsorption on goethite surfaces

MATERIAL AND METHODS

Adsorption edges

We conducted adsorption edges to examine the influence of pH during trace metal and organic acid adsorption on goethite. The four adsorption edges were conducted using a batch technique with 5 g/L suspensions of goethite, , a background electrolyte solution of 0.10 M $NaNO_3$, and 1 x 10^{-4} M Pb^{2+} , 1 x 10^{-4} M Cd^{2+}, 2 x 10^{-3} M oxalate, and 2 x 10^{-3} M salicylate respectively. Goethite was placed in 350 ml of 0.1 M $NaNO_3$ and sonicated using a Fisher Scientific 550 Sonic Dismembrator. The suspension was then placed in the jacketed reaction vessel (Figure 4.1) and hydrated for 24 hours. Each trace metal and organic acid was dispensed in stepwise quantities from a stock solution to minimize local supersaturation of the suspension. Stock solutions were made from analytical grade reagents and distilled doubly de-ionized water. The pH of trace metal adsorption edges was increased from pH 3-pH 8 with 0.10 M NaOH dispensed by an automatic titrator at two hour intervals. Organic acid adsorption edges where decreased from pH 9- pH 3 with 0.10 M HNO_3 dispensed by an automatic titrator at two hour intervals. Each adsorption edge was kept well stirred with the aid of a mechanical stirrer (Caframo RZR-2000). All experiments were conducted at 298 °K +/- 0.1 °K and 1 atm pressure under a N_2 environment to eliminate CO_2 influences.

Short and long term adsorption experiments

Adsorption experiments were conducted using a batch technique with 5 g/L suspensions of goethite, 1 x 10^{-4} M solutions of Pb^{2+} and Cd^{2+}, and a background electrolyte solution of 0.10 M $NaNO_3$. All suspensions were undersaturated with respect to $Pb(OH)_2$, and $Cd(OH)_2$ based on MINTEQ computer calculations and kept constant at a pH of 6.00 +/- 0.02 (EPA, 1998). Samples of goethite were weighed into a Teflon lined flat-bottomed, water-jacketed reaction vessel (500 ml) with a removable glass lid containing entry ports for a mechanical stirrer, pH electrode, N_2 gas, burette tip, and pipette (Figure 4.1).

FIGURE 4.1 EXPERIMENTAL SETUP FOR ADSORPTION STUDIES
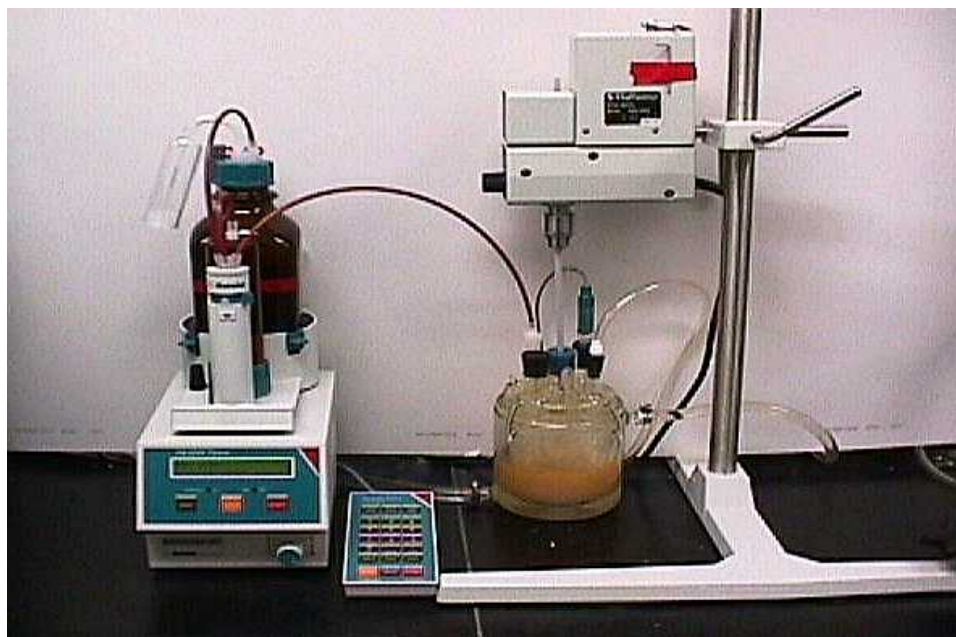
The goethite was placed in 350 ml of 0.10 M $NaNO_3$ and sonicated using a Fisher Scientific 550 Sonic Dismembrator. The suspension was then placed in the jacketed reaction vessel and hydrated for 24 hours. The suspension was adjusted to pH 6 using 0.10 M HNO_3. Each trace metal was dispensed in stepwise quantities from a stock solution to minimize local supersaturation of the suspension. Stock solutions of Pb^{2+} and Cd^{2+} were made from analytical grade reagents and distilled doubly de-ionized water. The suspension pH was kept constant and well stirred with the aid of an automatic titrator (Brinkman, Metrohm 718 Stat Titrino) and mechanical stirrer (Caframo RZR-2000), respectively. All experiments were conducted at 298 °K +/- 0.1 °K and 1 atm pressure under a N_2 environment to eliminate CO_2 influences.

The adsorption experiments consisted of short and long term adsorption reactions. Short-term experiments were performed for 7 days on the pH-Stat apparatus according to the above procedure. Long-term experiments were conducted for 7 days according to the above procedure and then were removed from the pH-Stat apparatus, placed in acid washed high density polyethylene centrifuge bottles sealed with Teflon tape, and placed in an environmentally controlled rotating shaker. The pH was maintained constant at 6.00 +/- 0.02 throughout the studies with the manual addition of 0.10 M HNO_3 or 0.10 M NaOH. Samples were taken throughout the duration of the long-term reactions for a comparison of adsorption between trace metals. Sampling consisted of removing a 6-ml aliquot from the well-stirred batch reaction and filtering it through a 0.01 μm Gelman metrical membrane into an acid washed polypropylene test tube. All suspension aliquots were carefully removed from the batch reactor using a Rainin electronic pipette in order to avoid changes in the total surface area to background solution ratio. The filtered samples were acidified to a pH < 2 with 8 M HNO_3, sealed with parafilm, and stored in a refrigerator prior to analysis. Each sample was analyzed using an Inductively Coupled

Plasma Atomic Emission Spectrometer (ICP-AES) or a Perkin Elmer HGA 600 Graphite Furnace (Table 4.1).

TABLE 4.1 TRACE METAL DETECTION LIMIT

Element	Inductively Coupled Plasma Atomic Emission (ppm)	Atomic Absorption Graphite Furnace (ppb)
Pb	0.020	0.050
Cd	0.002	0.003

RESULTS AND DISCUSSION

Adsorption edges

Adsorption edges are often used to characterize the affinity of trace metal cations and anions for mineral surfaces as a function of pH. Lead and cadmium exhibited typical S-shaped adsorption edges where sorption increased with increases in pH (Fig. 4.2). From figure 4.2 it is clear that Pb^{2+} has a higher affinity for the goethite surface compared to Cd^{2+}. The Pb^{2+} adsorption edge is shifted to a lower pH and 100% of the added Pb^{2+} is adsorbed at a pH of 6.0. In contrast 100% adsorption of Cd^{2+} is not reached until pH 8. Other investigators (Ainsworth et al.,1994) have observed similar results. Furthermore a much greater percentage of Pb^{2+} is adsorbed at pH 4.5 compared to Cd^{2+}. Recent spectroscopic evidence has indicated that easily hydrolyzable cations adsorb to oxide surfaces depending upon their affinity as hydrolysis species. This may explain the higher affinity of Pb^{2+} for the goethite as a function of pH (Barger et al., 1997).

Salicylate and oxalate exhibit adsorption edges that are opposite to the trace metal cations. Adsorption of the organic acids increases with a decrease in pH. The adsorption of oxalate is less effected by pH compared to salicylate. A greater percentage of oxalate was adsorbed at all pH values. The affinity of organic acids for oxide surfaces has been related to the type of surface complex formed, functional group composition, and the stability of the functional group for the metal composing the oxide (Stumm 1992). Oxalate has a higher stability constant for Fe^{3+} and may form more stable multidentate complexes with goethite compared to salicylate, which may explain its higher affinity.

FIGURE 4.2 ADSORPTION EDGE OF Cd^{2+} AND Pb^{2+} ON GOETHITE

FIGURE 4.2 ADSORPTION EDGE OF Cd^{2+} AND Pb^{2+} ON GOETHITE
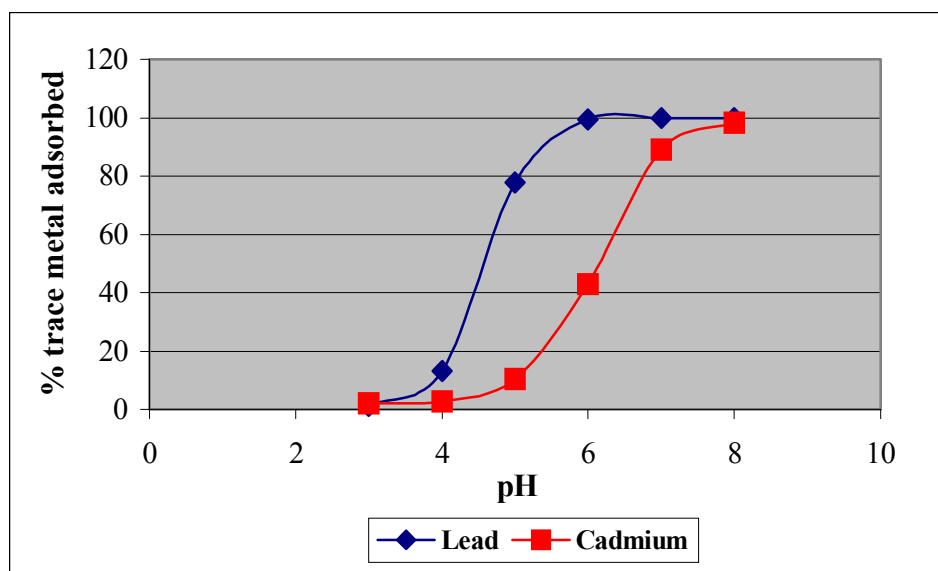
FIGURE 4.3 ADSORPTION EDGE OF OXALATE AND SALICYLATE ON GOETHTIE
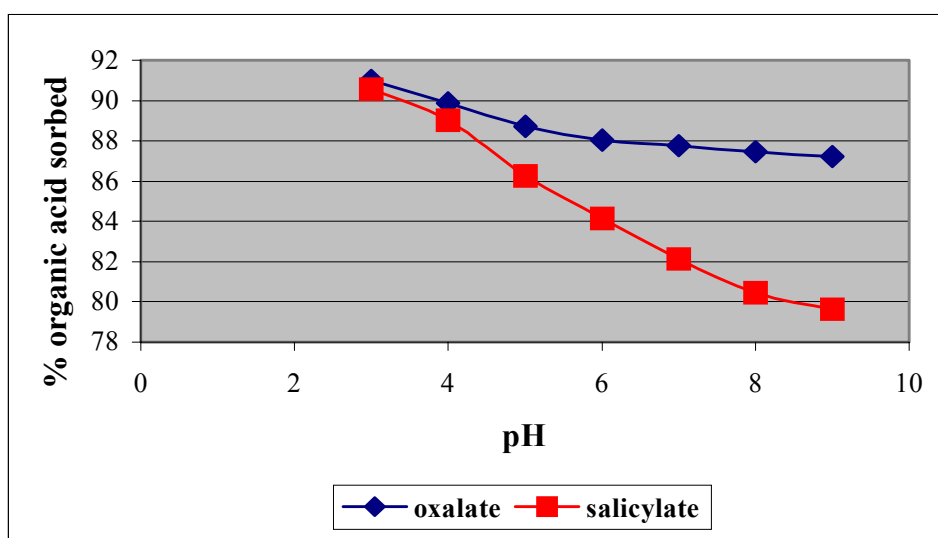
Short and long term adsorption experiments

Trace metal sorption on oxide surfaces is often characterized by an initial rapid step (<1-5 hr) follow by a slow continuous adsorption (McKenzie 1970, Bruemmer et al., 1988). The rapid reaction has been attributed to adsorption on high affinity surface sites. However the slow reaction mechanism is not as well understood and has been attributed to diffusion into crystal defects or dead-end pores, surface precipitation, and change in the type of surface complex (Ainsworth et al., 1994; Farley et al.,1985). However in this study the adsorption behavior of Pb^{2+} and Cd^{2+} were markedly different. Lead adsorption

was nearly completed after 4 hours, with very little additional sorption occurring during the 20-week period (Fig 4.4).

FIGURE 4.4 LONG TERM CADMIUM AND LEAD ADSORPTION
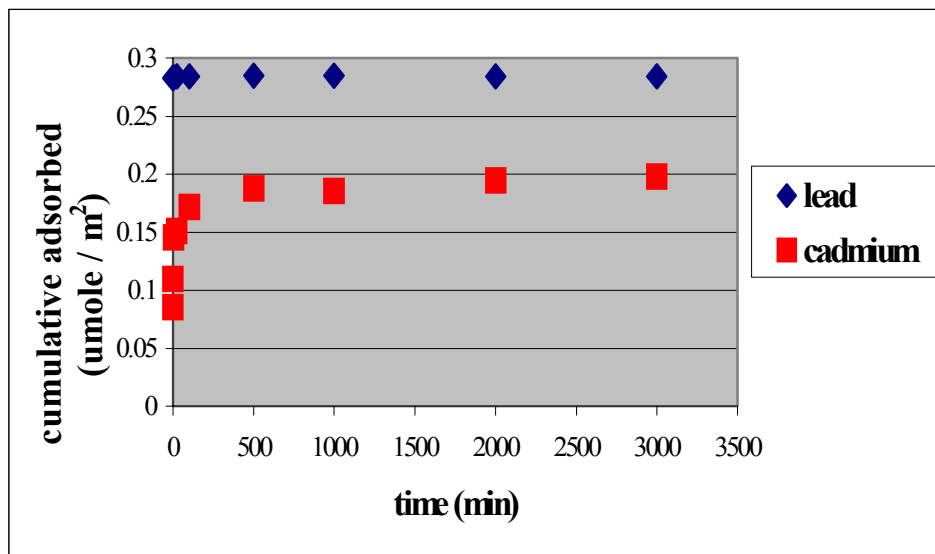
In contrast cadmium showed a slow continuous increase in the amount of adsorption over a 20-week period. Other researchers examining trace metal adsorption on Fe-oxides (Bruemmer et al.,1988) obtained similar results. Furthermore, a greater quantity of Pb^{2+} was sorbed to the goethite surface (0.1978 µmole/m^2) compared to Cd^{2+} (0.1797 µmole/m^2). The difference in the quantity and rates of Pb^{2+} and Cd^{2+} adsorption to goethite may be attributable to the different affinities of the trace metals for the goethite surface and the type of surface complex formed. Additionally, recent spectroscopic evidence has demonstrated that both Cd^{2+} and Pb^{2+} form inner-sphere surface complexes on Fe-oxide surfaces (Spandini et al., 1994; Bargar et al., 1997). However, Pb^{2+} is adsorbed as a hydrolyzed species while Cd^{2+} is not. Research has shown that goethite particles contain defect structures and micropores related to synthesis conditions and procedures (Schwertmann et al., 1985). Diffusion of cations into dead-end or micropores created by these defects may explain the slow metal sorption over time (Backes et al., 1995). One would expect that diffusion of Pb^{2+} as $Pb(OH)^{+}$ would be extremely slow compared to Cd^{2+} which may be responsible for the difference in long-term adsorption (Eick, 1999).

Chapter 5. Trace metal desorption from goethite in the presence of three extracting solutions

MATERIAL AND METHODS

A miscible displacement technique (Fig 5.1) was used to perform desorption experiments for short and long-term adsorption experiments. Miscible displacement techniques have several advantages over traditional batch techniques but they are not without problems. Problems include preferential flow of extracting solutions though oxides on the filter, metal contained in the entrained solution after adsorption, and dilution of the incoming desorption solution by the initial reaction solution resulting in concentration changes not associated with adsorption/desorption (Sparks, 1989). These problems can result in the measurement of diffusion-controlled kinetics rather than chemical kinetics. In this study many of the above problems were minimized because of the small quantity of goethite used on the filter and the low concentration of the metal in the entrained adsorption solution. Advantages of the miscible displacement technique include: 1) trace metal and goethite solutions have a greater exposure to extracting solutions than in a static system; 2) desorbed species are removed with the extracting solution, which reduces the possibility of desorbed species reabsorbing to constituent surfaces; and 3) the measurement of diffusion-controlled kinetics by miscible displacement may better represent trace metal adsorption/desorption under natural soil conditions (Sparks, 1989). We recognize that the miscible displacement technique often measures transport or diffusion controlled kinetics. This is acceptable for our studies because the objective of our studies was to determine the influence of residence time and not determine true chemical rate constants. Furthermore, the miscible displacement technique was chosen because it may better represent desorption behavior under natural conditions.

FIGURE 5.1 MISCIBLE DISPLACEMENT SYSTEM USED FOR DESORPTION STUDIES

Desorption experiments were conducted using 2 x 10^{-3} M oxalate, 2 x 10^{-3} M salicylate, and 0.05 M NaNO$_3$ at pH 4.5. A pH of 4.5 was chosen for the desorption experiments because at the low surface loading preliminary experiments indicated that trace metal desorption was below instrumental detection limits until pH of the desorption solution was <5.0. Furthermore, studies examining residence time effects have primarily focused on pH values > 6.0 (Backes et al.,1995; McLaren et al.,1998; Eick et al.,1999). Sodium nitrate was chosen as an extracting solution as a comparison with organic acids. Inorganic cations such as sodium are often used as extracting solutions for hydrous metal oxide and trace metal interactions (Naidu and Harter, 1998). Oxalate and salicylate were chosen because they are common plant and microbial exudates, and because of their differing chemical properties (Stevenson, 1994). All solutions were made from analytical grade reagents and distilled doubly de-ionized water. Desorption studies were conducted with 30 ml aliquots (0.15 g goethite) from short and long-term adsorption experiments. Aliquots were injected into a pre-weighed 47 mm Nuclepore™ filter holder, containing a 0.45 μm Gelman™ cellulose ester filter. The final weight of the filter was measured to determine the final volume of the entrained solution. The metal concentration of the background solution was measured to determine both the total trace metal sorbed and the entrained concentration. The entrained concentration was subsequently subtracted from the first fraction collected to determine the quantity of induced trace metal desorbed.

Both trace metals were desorbed from the surface by continuous piston-pumping (Fluid Metering Model RHSY) with 0.05 M NaNO$_3$, 2 x 10^{-3} M oxalate, and 2 x 10^{-3} M salicylate solutions adjusted to pH 4.5 at 298 °K. Samples were collected every five minutes for 8 hr at a constant flow rate of 3-ml min^{-1} using an Isco Cygnet™ 100 fraction collector. Between each desorption run all tubing was washed with copious amounts of dilute HNO$_3$ (0.01 M) followed by distilled doubly de-ionized water. Samples were acidified to a pH < 2 with 8 M HNO$_3$ sealed, stored, and refrigerated prior to analysis. Trace metals were measured from all fractions until they were below the limit of quantification (using either ICP-AES or AA Graphite furnace). Desorption studies were run in duplicate.

Experimental data from short and long-term desorption were fitted with a single first order rate equation, two first order rate equations, and a parabolic diffusion model. The parabolic diffusion model from Hodges and Johnson (1987) was used to model the reaction as transport limiting:

$$F_d = kt^{1/2} \qquad\qquad (5.1)$$

where F_d is the fraction of metal desorbed (1-P$_{bt}$ / P$_{b0}$), $t^{1/2}$ is the square root of time in seconds, and k is the diffusion rate coefficient (s^{-1}). If the reaction is diffusion controlled then a graph of F_d versus $t^{1/2}$ should be linear with a slope of k. The single first order rate equation from Sparks et al., (1980) was used to model the data as a single or two first order reactions:

$$\ln (Me_t / Me_0) = -k_d (t) \qquad\qquad (5.2)$$

where Me_t was the amount of metal sorbed at desorption time t (μmole m^{-2}), Me_0 was the amount of metal sorbed at time 0 (μmole m^{-2}), t is time (s), and k_d is the apparent desorption coefficient (s^{-1}). If the reaction is first order, a graph of ln (Me_t / Me_0) vs. t should yield a straight line of slope -k$_d$. Two first order rate equations were optimized by dividing the data sets consistent with an apparent rate change (Table 5.5, 5.6), and fitting both data sets to the first order rate equation developed by Sparks et al (1980). Optimized time ranges were 25-150 min and 155-480 min. Testing for significant differences in rate coefficients and cumulative quantity of metal desorbed between short and long-term desorption experiments was done using the Tukey-Kramer (Sall and Lehman, 1996) multiple comparison procedure at the 0.05 level experiment wise. The statistical analysis was performed using JMP IN Version 3.2 for Windows, SAS Institute Inc (Sall and Lehman, 1996).

INFLUENCE OF EXTRACTING SOLUTIONS ON DESORPTION

Similar to previous studies examining trace metal desorption from oxide surfaces, Pb^{2+} and Cd^{2+} desorption kinetics were slow compared to the sorption reaction and not completely reversible during an eight hour desorption period for all of the experiments, except short-term Cd^{2+} in the presence of salicylate. (Table 5.1, 5.3) (Ainsworth et al., 1994; Eick et al., 1999; McBride, 1994; Backes et al., 1995; McLaren et al., 1998). For all experiments, except long term Pb^{2+} desorption, the quantity of metal desorbed from the goethite followed the order salicylate > NaNO$_3$ > oxalate. In the case of long term Pb^{2+} desorption the quantity of metal desorbed followed the order oxalate > NaNO$_3$ > salicylate. The quantity of metal desorbed over the eight hour period at pH 4.5 ranged from 65.4 to 100 % (Tables 5.1 and 5.2). Previous research examining Pb^{2+} and Cd^{2+} desorption from goethite in the presence of NaNO$_3$ at near neutral pH values have observed a smaller percentage of the metal removed from the oxide surface (Eick et al., 1999; Backes et al., 1995). For example, Eick et al. (1999) examined Pb^{2+} desorption from goethite at a pH value of 6 over a range of surface coverage. The greatest percentage of Pb^{2+} removed from the goethite surface was 62 %. Similar results were obtained for Naidu and Harter (1998) who examined Cd^{2+} extractability from soils in the presence of various organic acids. It has been widely observed that trace metal cation desorption from oxide surface is more nearly reversible at low compared to high pH values (McBride, 1994). This has been attributed to changes in the type of surface complex, surface precipitation, and increases in net negative charge as pH is increased.

Based on the adsorption study and the affinity of the cation for the goethite surface one would expect to observe a greater quantity of Cd^{2+} desorbed in the presence of all extracting solutions compared to Pb^{2+}. However this was not the case. Salicylate desorbed more Cd^{2+} compared to Pb^{2+} while oxalate desorbed more Pb^{2+} than Cd^{2+} for both long and short term adsorption experiments. Sodium nitrate was more effective at desorbing Pb^{2+} for short term adsorption experiments compared to Cd^{2+}. However, the order was reversed for long term. Differences in the effectiveness of the extracting

solutions for desorbing Cd^{2+} and Pb^{2+} may be related to the desorption mechanism as well as the influence of residence time on the adsorption mechanism.

TABLE 5.1 QUANTITY OF CADMIUM SORBED BY GOETHITE AND PROPORTION DESORBED AFTER 8 HOURS

Sorption period	pH	Extracting solution	Initial Cd conc. (M)	Cd sorbed (μmol m^{-2})	Desorbed (%)
7 days	4.5	NaNO$_3$	1 x 10^{-4}	.176	85.15
20 weeks	4.5	NaNO$_3$	1 x 10^{-4}	.180	81.69
7 days	4.5	Oxalate	1 x 10^{-4}	.176	73.68
20 weeks	4.5	Oxalate	1 x 10^{-4}	.180	65.39
7 days	4.5	Salicylate	1 x 10^{-4}	.176	100
20 weeks	4.5	Salicylate	1 x 10^{-4}	.180	93.33

TABLE 5.2 QUANTITY OF LEAD SORBED BY GOETHITE AND PROPORTION DESORBED AFTER 8 HOURS

Sorption period	pH	Extracting Solution	Initial Pb conc. (M)	Pb sorbed (μmol m^{-2})	Desorbed (%)
7 days	4.5	NaNO$_3$	1 x 10^{-4}	.198	86.49
20 weeks	4.5	NaNO$_3$	1 x 10^{-4}	.198	79.82
7 days	4.5	Oxalate	1 x 10^{-4}	.198	80.32
20 weeks	4.5	Oxalate	1 x 10^{-4}	.198	82.96
7 days	4.5	Salicylate	1 x 10^{-4}	.198	90.90
20 weeks	4.5	Salicylate	1 x 10^{-4}	.198	73.39

The greater effectiveness of salicylate compared to oxalate in desorbing Cd^{2+} and Pb^{2+} from the goethite surface may be related to the dissociation of the acid functional group (Table 5.3) and their affinity for the goethite surface. Oxalate is an aliphatic dicarboxylate anion (Figure 5.2) while salicylate is a phenolic monocarboxylate anion (Figure 5.3)
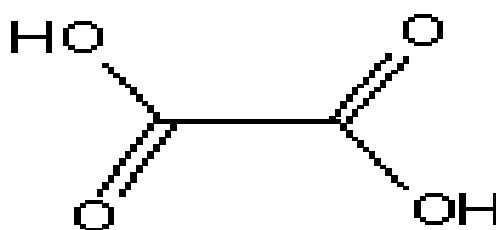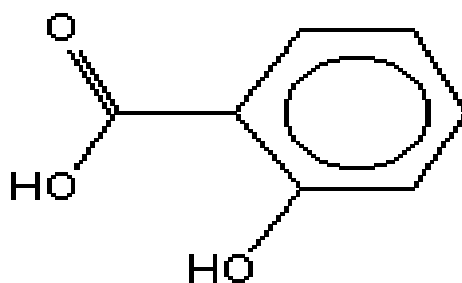
FIGURE 5.2 OXALATE STRUCTURE

FIGURE 5.3 SALICYLATE STRUCTURE

At a pH of 4.5 one of oxalate's carboxylate functional groups will be fully deprotonated while approximately 50% of the second functional group will be deprotonated. In contrast only the carboxylate functional group of salicylate will be deprotonated. In the case of oxalate it may enhance the binding of Cd^{2+} and Pb^{2+} through the formation of bridging complexes (Figure 5.4-5.5) compared to salicylate (Table 5.4).

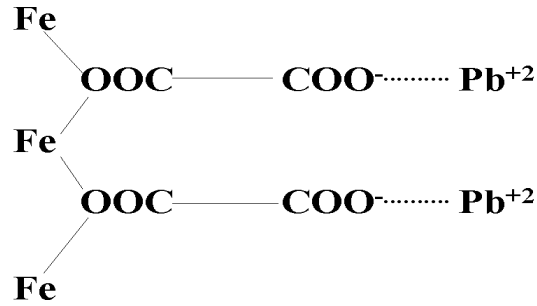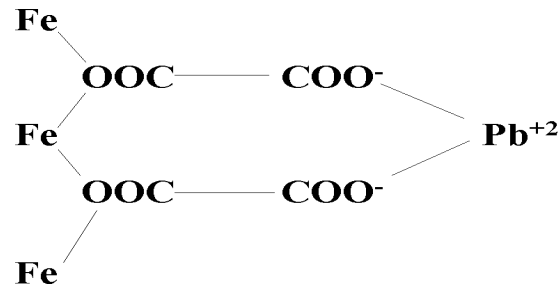FIGURE 5.4 POSSIBLE MONODENTATE OXALATE BRIDGING COMPLEX WITH PB^{2+}

Fe

OOC————COO⁻·········· Pb⁺²

Fe

OOC————COO⁻·········· Pb⁺²

Fe

FIGURE 5.5 POSSIBLE BIDENTATE OXALATE BRIDGING COMPLEX WITH PB^{2+}

Fe

OOC———— COO⁻

Fe

Pb⁺²

OOC———— COO⁻

Fe

The greater effectiveness of $NaNO_3$ for removing Cd^{2+} and Pb^{2+} compared to oxalate occurs because oxalate may form bridging complexes with trace metals and the oxide surface. Furthermore, oxalate has a greater affinity for the goethite surface compared to salicylate (Figure 4.3). This stronger affinity is also reflected in the greater dissolution of the goethite surface in the presence of oxalate compared to salicylate (Table 5.3). At low pH values oxide surfaces are positively charged and the adsorption of ligands with high affinities for oxide surfaces may lead to charge reversals (Eick et al., 1999). This charge reversal could enhance trace metal sorption especially at pH values where the goethite surface has a low affinity for Pb^{2+} and Cd^{2+}. Similar results were observed for Cd^{2+} extraction from soils in the presence of various organic ligands. (Naidu and Harter, 1998). Therefore in natural systems the presence of both organic an inorganic ligands may increase trace metal cation affinity for oxide surfaces.

TABLE 5.3 AMOUNT OF IRON DESORBED AFTER 8 HOURS

Experiment	Extracting solution	Fe range (ppm)
Short term Pb	NaNO$_3$	< 0.0109 - below detection
Long term Pb	NaNO$_3$	< 0.0109 - below detection
Short term Pb	Salicylate	< 0.008 - below detection
Long term Pb	Salicylate	< 0.008 - below detection
Short term Pb	Oxalate	0.518 - 0.0204
Long term Pb	Oxalate	0.3271 - 0.0362
Short term Cd	NaNO$_3$	below detection
Short term Cd	Salicylate	0.0357- below detection
Short term Cd	Oxalate	0.839 -0.0632

* no data was collected for long-term Cd experiments

TABLE 5.4 STABILITY CONSTANT OF TRACE METAL-LIGAND COMPLEXES

Ligand	Nature of complex	Log stability constant	Nature of complex	pK$_a$
Oxalate	Cd oxalate	3.89 [a]	H$_2$L	1.23[a]
	Cd (oxalate)$_2^{-2}$	4.1 [a]		4.19[a]
	Cd (oxalate)$_3^{-4}$	5.1 [a]		
	Pb oxalate	4.2 [b]		
	Pb (oxalate)$_2^{-2}$	6.33 [b]		
Salicylate	Cd salicylate$^+$	5.55 [a]	H$_2$L	2.97[a]
	CdH salicylate^{2+}	1.9 [a]		13.4[a]

[a] Naidu and Harter
[b] NIST Standard Reference Database 46 Version 3.0

FIGURE 5.6 SHORT AND LONG-TERM CADMIUM DESORPTION WITH SODIUM NITRATE
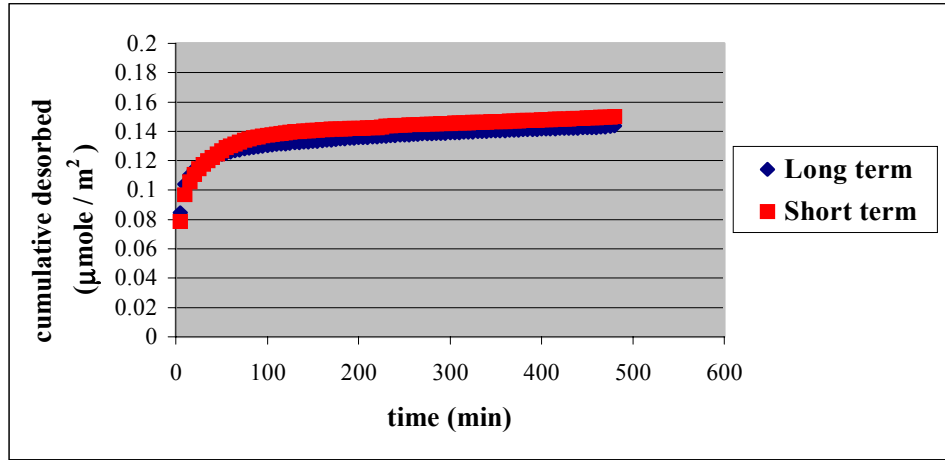

FIGURE 5.7   SHORT AND LONG-TERM CADMIUM DESORPTION WITH SALICYLATE
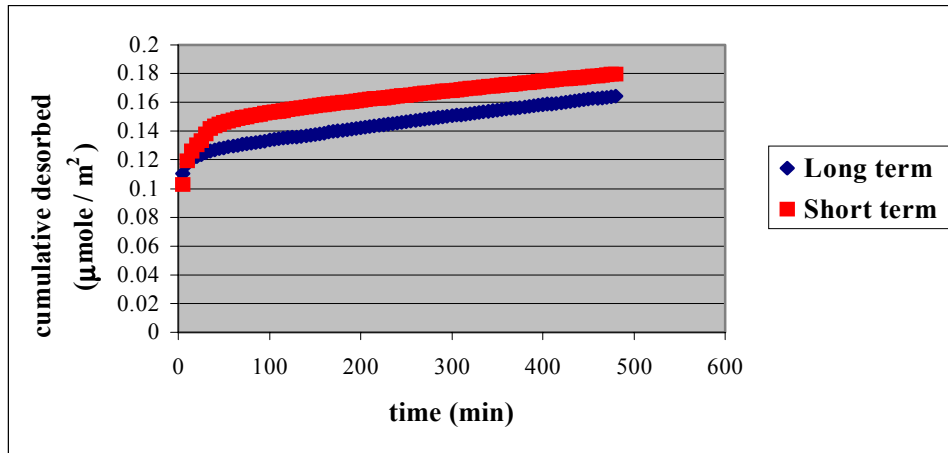

FIGURE 5.8 SHORT AND LONG-TERM CADMIUM DESORPTION WITH OXALATE
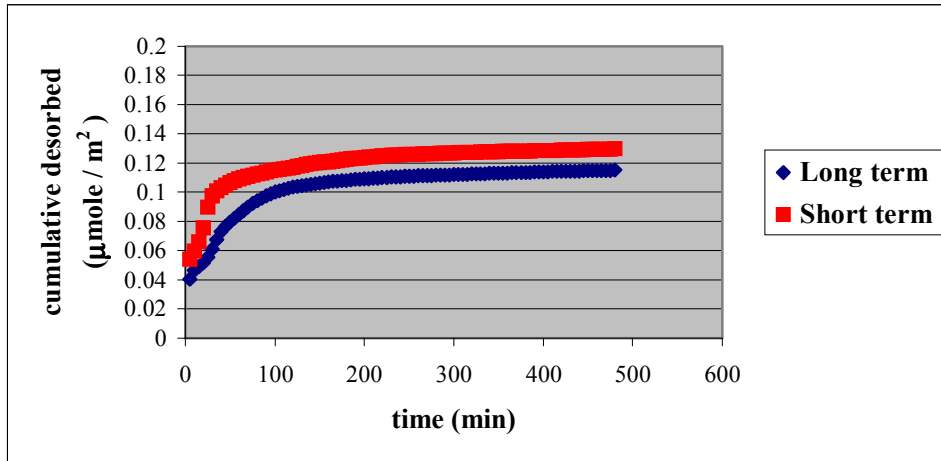
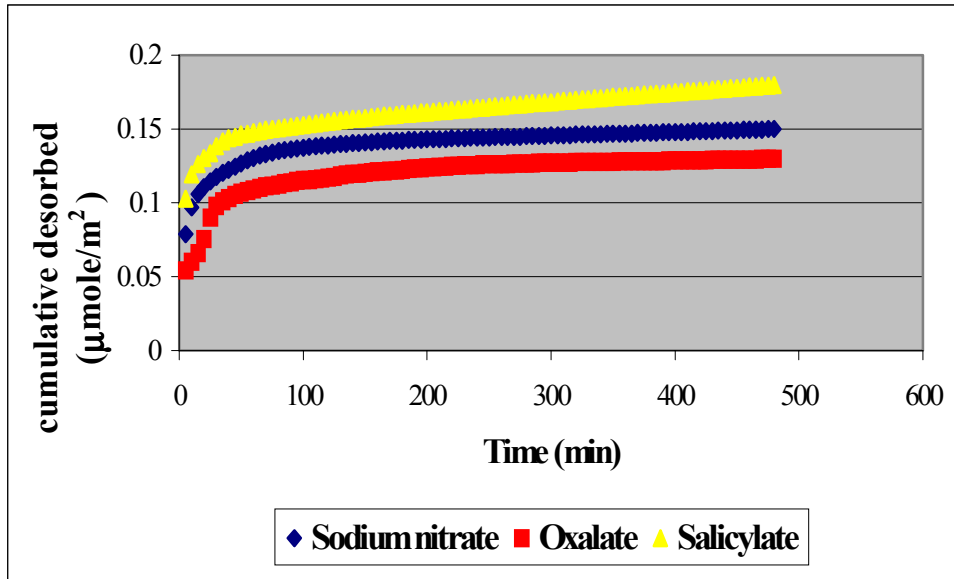FIGURE 5.9 SHORT TERM CADMIUM DESORPTION WITH DIFFERENT EXTRACTING SOLUTIONS

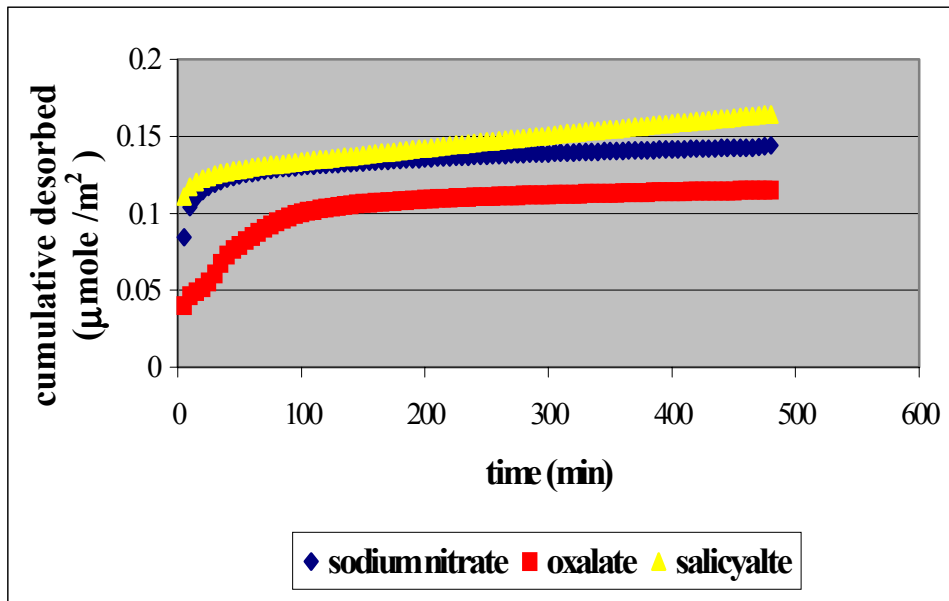FIGURE 5.10 LONG-TERM CADMIUM DESORPTION WITH DIFFERENT EXTRACTING SOLUTIONS

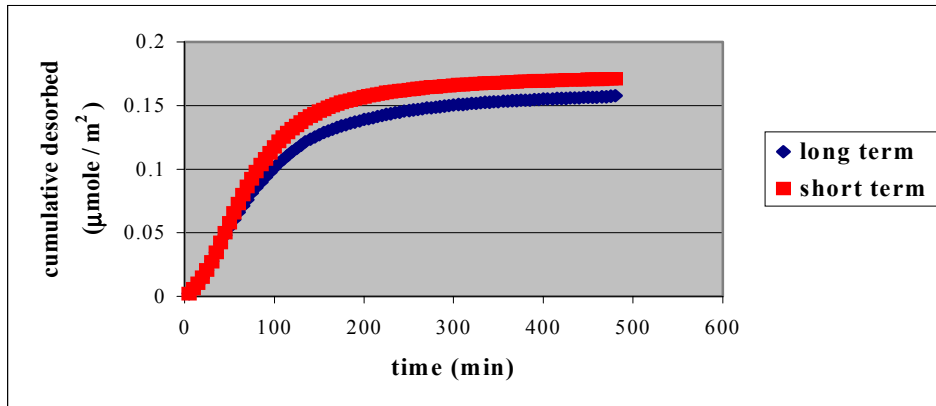FIGURE 5.11 SHORTAND LONG-TERM LEAD DESORPTION WITH SODIUM NITRATE

FIGURE 5.12 SHORT AND LONG TERM LEAD DESORPTION WITH SALICYLATE
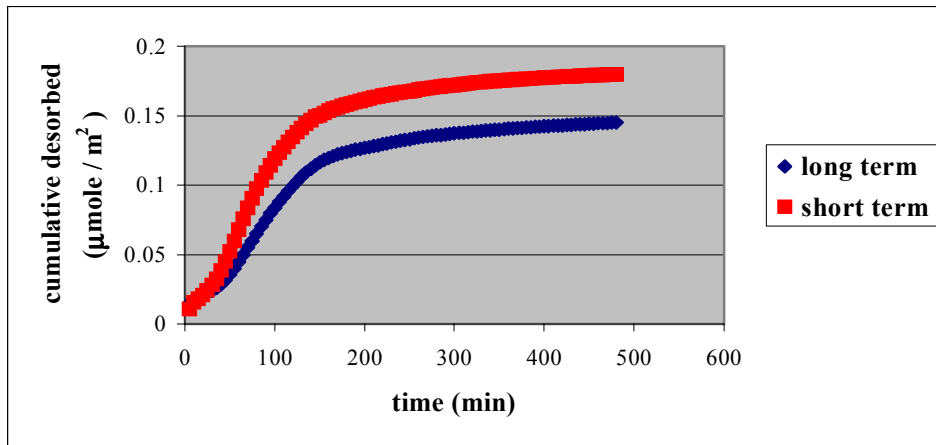

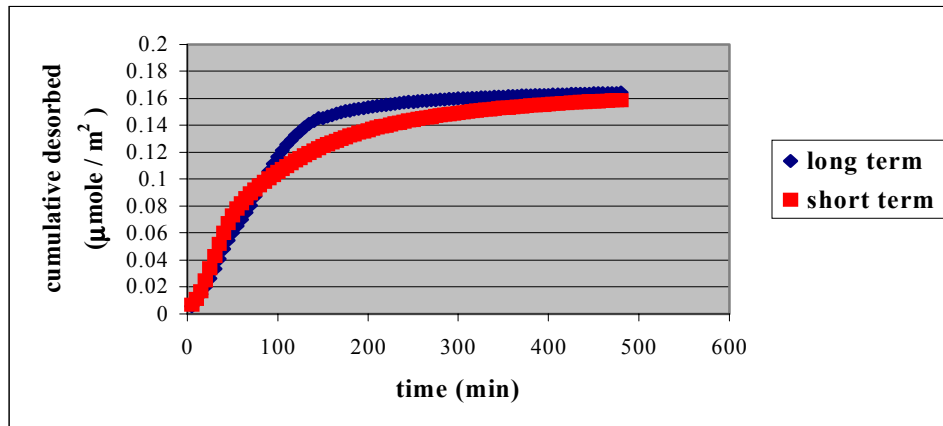FIGURE 5.13 SHORT AND LONG TERM LEAD DESORPTION WITH OXALATE

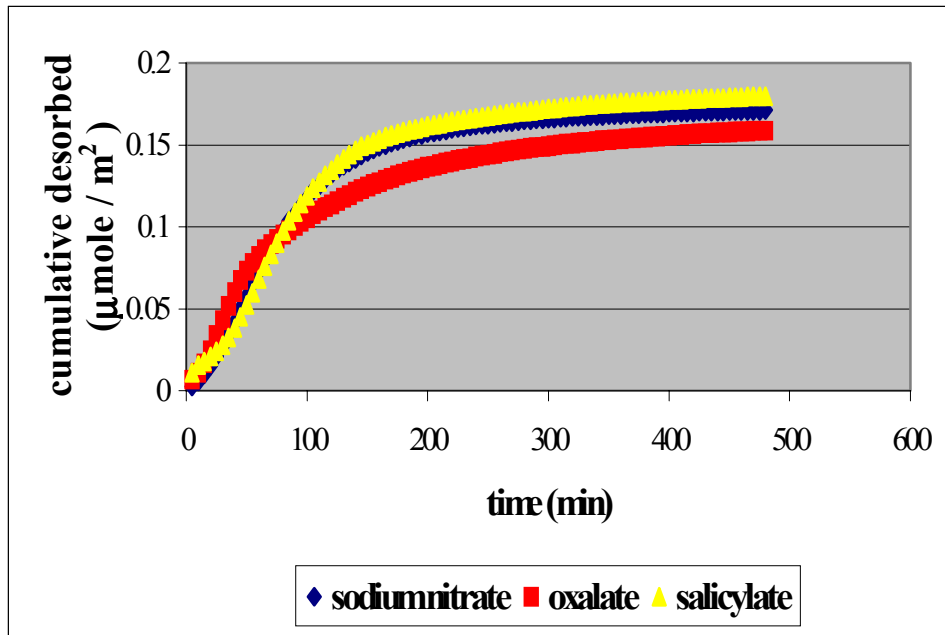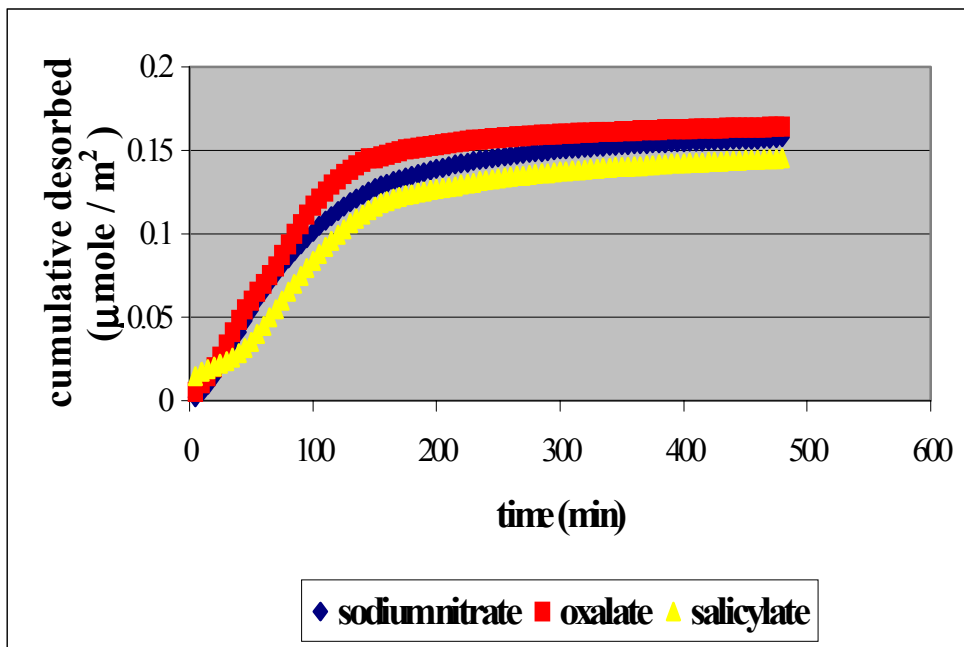FIGURE 5.14 SHORT TERM LEAD DESORPTION USING DIFFERENT EXTRACTING SOLUTIONS

FIGURE 5.15 LONG-TERM LEAD DESORPTION WITH DIFFERENT EXTRACTING SOLUTIONS

Kinetic modeling and residence time effects

Two first order equations best described the desorption of Cd^{2+} and Pb^{2+} from goethite for all extracting solutions (Figures 5.16-5.23). Similar results were obtained by Backes et al., (1995) who used two first order equations to describe the desorption of Cd^{2+} and Co^{2+} from Fe- and Mn-oxides. Correlation of determination, R^2 values, ranged from 0.904-0.998 with the highest correlation observed in Pb^{2+} experiments in the presence of salicylate (Table 5.5-5.6). Deviations in linearity were greatest for oxalate experiments and were most pronounced at the beginning of the desorption run (Figures 5.16 – 5.23). Similar non-linearity during the beginning of the desorption experiment has been observed by others which may be inherent in the miscible displacement technique (Eick et al., 1999; Sparks and Jardine, 1984). However, one must be aware that linearity with respect to first order equations only gives an indication of apparent rate coefficients that may in fact be composed of several chemical and diffusion reactions (McLaren et al., 1998). The parabolic diffusion equation and a single first order equation were also applied to the desorption data but resulted in less robust fits. Similar to previous studies examining the kinetics of trace metal desorption from oxide minerals the rate coefficients for short-term experiments were greater than long-term experiments, except for oxalate (Backes et al., 1995, McLaren et al., 1998, Eick et al., 1999). In the case of oxalate there was an increase in the first desorption rate coefficient *(k₁)* with increases in sorption period for both Cd^{2+} and Pb^{2+}. However statistical analyses indicated that these differences were not significant (Table 5.7).

TABLE 5.5 DESORPTION RATE COEFFICIENTS AND CORRELATION OF DETERMINATION DESCRIBING CADMIUM
DESORPTION FROM GOETHITE USING TWO FIRST ORDER EQUATIONS

Sorption period	Extracting solution	k_1	R^2	k_2	R^2
7 days	NaNO₃	-3.9 x 10^{-3} s^{-1}	.905	-8.0 x 10^{-4} s^{-1}	.998
20 weeks	NaNO₃	-2.1 x 10^{-3} s^{-1}	.925	-7.0 x 10^{-4} s^{-1}	.990
7 days	Oxalate	-2.6 x 10^{-3} s^{-1}	.904	-4.0 x 10^{-4} s^{-1}	.911
20 weeks	Oxalate	-4.0 x 10^{-3} s^{-1}	.916	-3.0 x 10^{-4} s^{-1}	.926
7 days	Salicylate	-4.6 x 10^{-3} s^{-1}	.944	-6.3 x 10^{-3} s^{-1}	.934
20 weeks	Salicylate	-2.2 x 10^{-3} s^{-1}	.990	-3.0 x 10^{-3} s^{-1}	.990

TABLE 5.6 DESORPTION RATE COEFFICIENTS AND CORRELATION OF DETERMINATION DESCRIBING LEAD
DESORPTION FROM GOETHITE USING TWO FIRST ORDER EQUATIONS

Sorption period	Extracting solution	k_1	R^2	k_2	R^2
7 days	NaNO$_3$	-1.02×10^{-2} s^{-1}	.997	-1.7×10^{-3} s^{-1}	.910
20 weeks	NaNO$_3$	-7.5×10^{-3} s^{-1}	.996	-1.5×10^{-3} s^{-1}	.923
7 days	Oxalate	-6.0×10^{-3} s^{-1}	.973	-1.8×10^{-3} s^{-1}	.957
20 weeks	Oxalate	-1.02×10^{-2} s^{-1}	.995	-1.1×10^{-3} s^{-1}	.916
7 days	Salicylate	-1.12×10^{-2} s^{-1}	.997	-2.7×10^{-3} s^{-1}	.968
20 weeks	Salicylate	-6.7×10^{-3} s^{-1}	.992	-1.2×10^{-3} s^{-1}	.950

Although our results show a decrease in all rate coefficients (expect k_1 for oxalate) with increased residence time statistical analysis indicates that these results are not significantly different (Table 5.7). Similar to other researchers we believe that Pb^{2+} and Cd^{2+} are sequestered by the goethite surface with an increase in residence time, however, we believe this effect may be less pronounced at pH 4.5.). We believe that raw and transformed data (Figure 5.6-5.8, 5.11-5.12) indicate desorption values are diverging as functions of aging time, but longer periods of desorption , and increases in the number of repetitions may be necessary for this effect to be statistically significant. The effectiveness of salicylate at removing trace metals combined with the high affinity of Pb^{2+} to the goethite surface over time may be responsible for the significant residence time effect between short and long term desorption (Table 5. 7)

TABLE 5.7 MEAN PERCENT LEAD AND CADMIUM DESORBED FOR SHORT AND LONG-TERM EXPERMENTS IN THE PRESESENCE OF THREE EXTRACTING SOLUTIONS

Metal	Solution	Long Term	Short Term
		Mean Percent desorbed	Mean Percent desorbed
Cadmium	NaNO3	81.69[a]	85.15 [a]
	Oxalate	65.39 [a]	73.68 [a]
	Salicylate	93.3 [a]	100.0 [a]
Lead	NaNO3	79.82 [a]	86.49 [a]
	Oxalate	82.96 [a]	80.32 [a]
	Salicylate	73.39 [a]	90.90[b]

* Means followed by the same superscript are not statistically significant at the α=0.50 level experiment wise using Tukey's HSD procedure.

FIGURE 5. 16 FIRST ORDER RATE EQUATION (K_1) PLOT OF SHORT TERM CADMIUM DESORPTION WITH
DIFFERENT EXTRACTING SOLUTIONS

FIGURE 5.17 FIRST ORDER RATE EQUATION (K_2) PLOT OF SHORT TERM CADMIUM DESORPTION WITH
DIFFERENT EXTRACTING SOLUTIONS

FIGURE 5.18 FIRST ORDER RATE EQUATION (K_1) PLOT OF LONG-TERM CADMIUM DESORPTION WITH DIFFERENT EXTRACTING SOLUTIONS

FIGURE 5.19 FIRST ORDER RATE EQUATION (K_2) PLOT OF LONG-TERM CADMIUM DESORPTION WITH DIFFERENT EXTRACTING SOLUTIONS

FIGURE 5.20 FIRST ORDER RATE EQUATION (K_1) PLOT OF SHORT TERM LEAD DESORPTION WITH DIFFERENT EXTRACTING SOLUTIONS
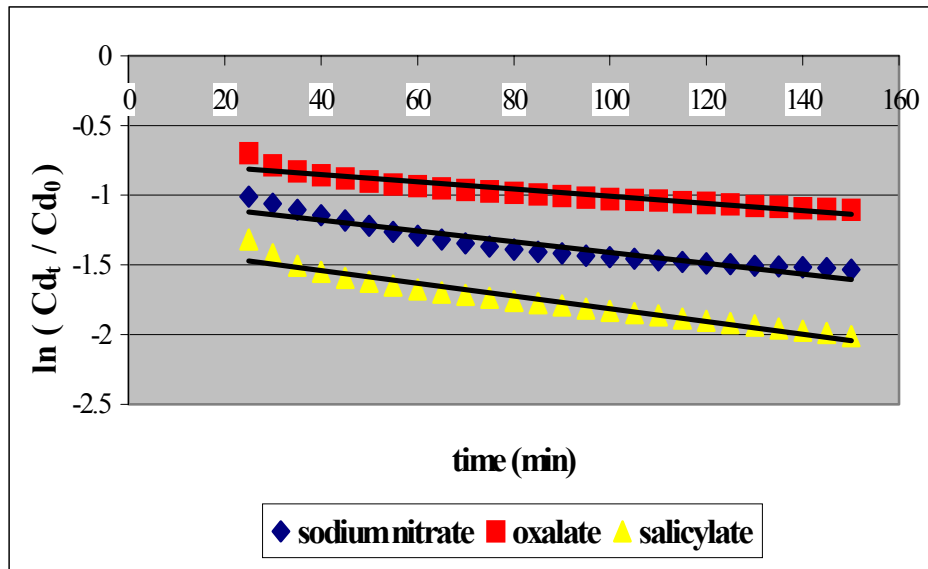

FIGURE 5.21 FIRST ORDER RATE EQUATION (K_2) PLOTS OF SHORT TERM LEAD DESORPTION WITH DIFFERRENT EXTRACTING SOLUTIONS.
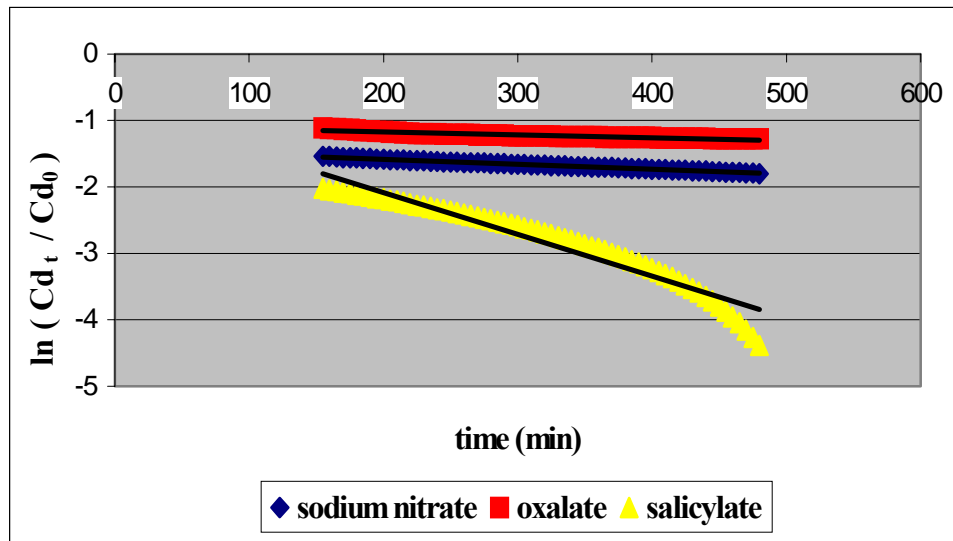
FIGURE 5.22 FIRST ORDER RATE EQUATION (K_1) PLOT OF LONG-TERM LEAD DESORPTION WITH DIFFERENT EXTRACTING SOLUTIONS
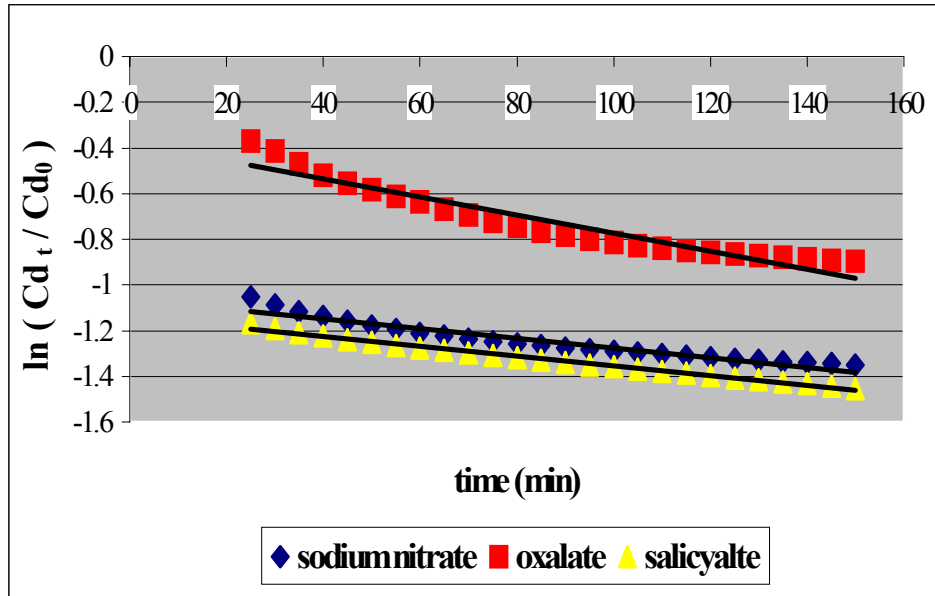

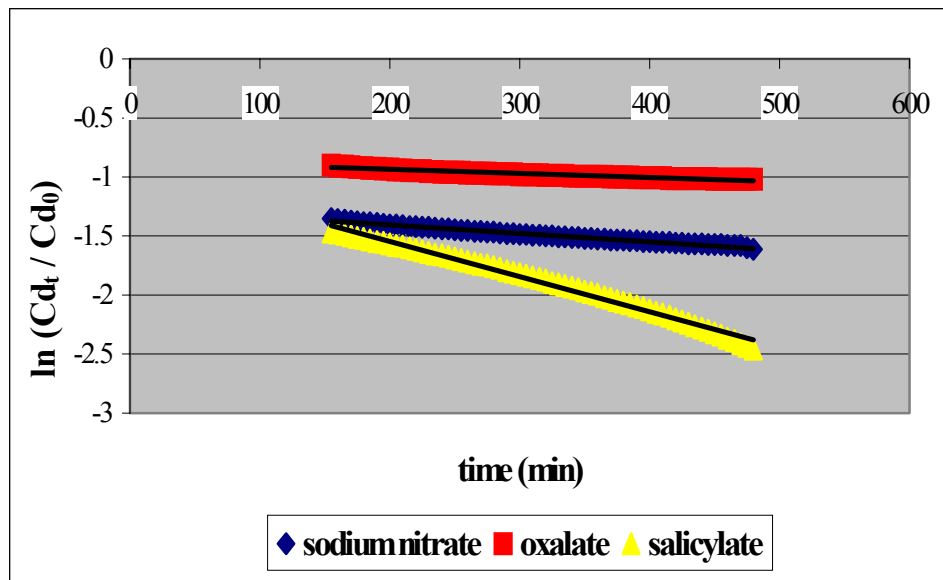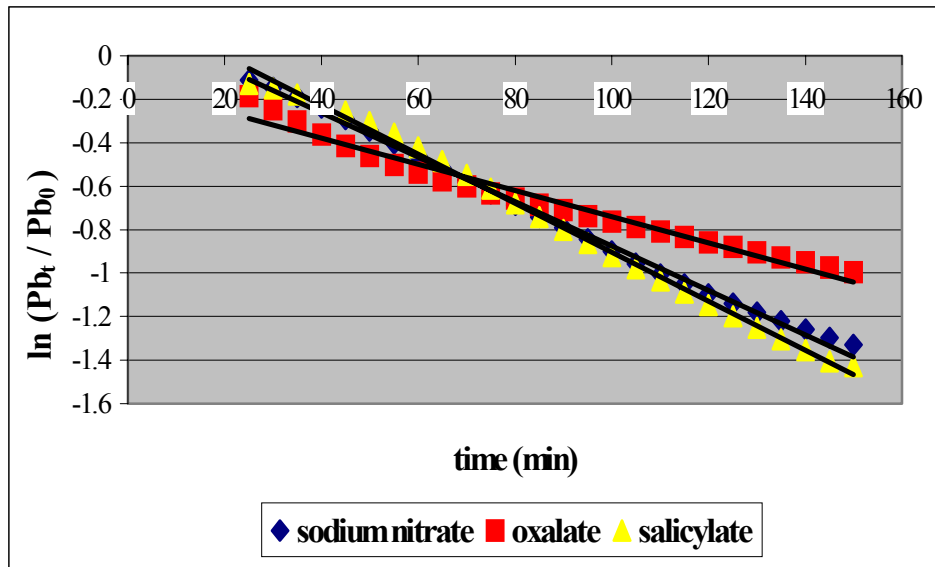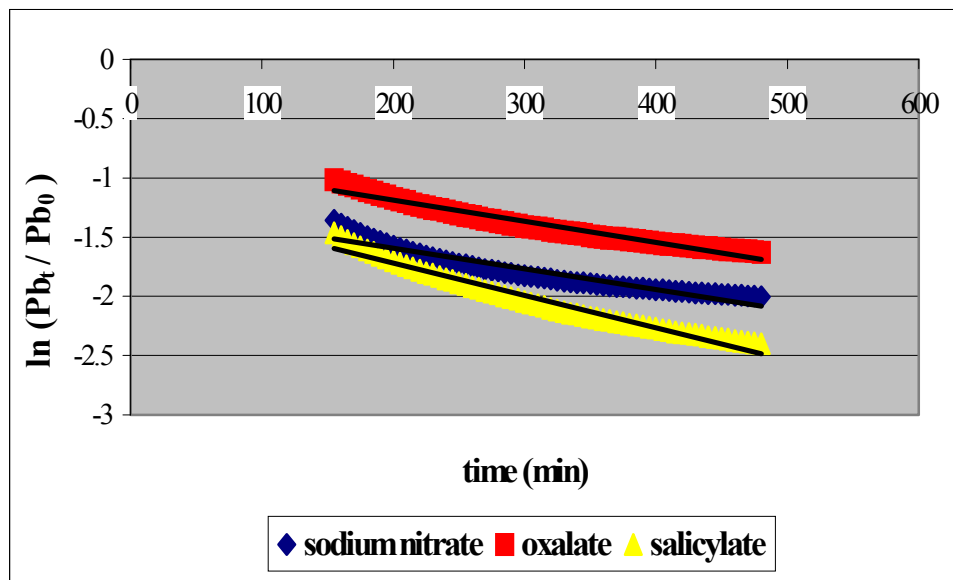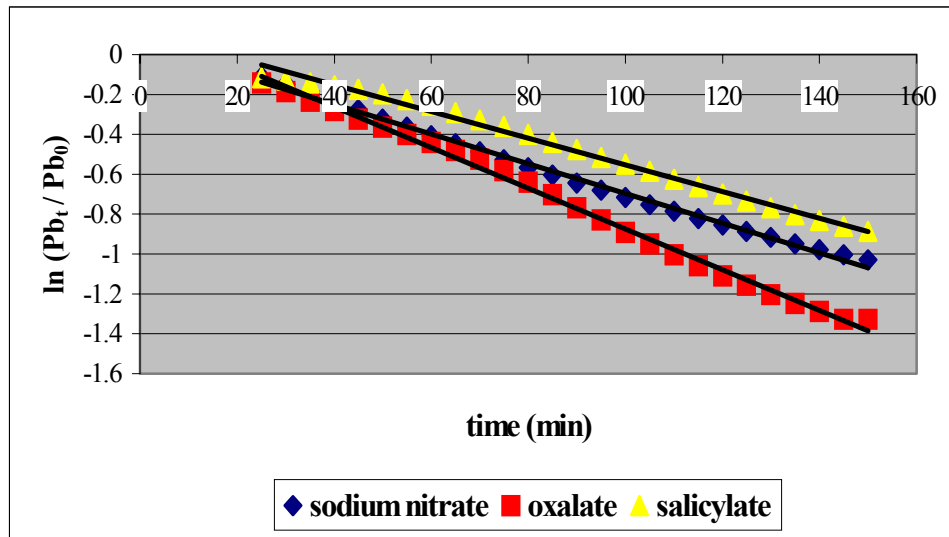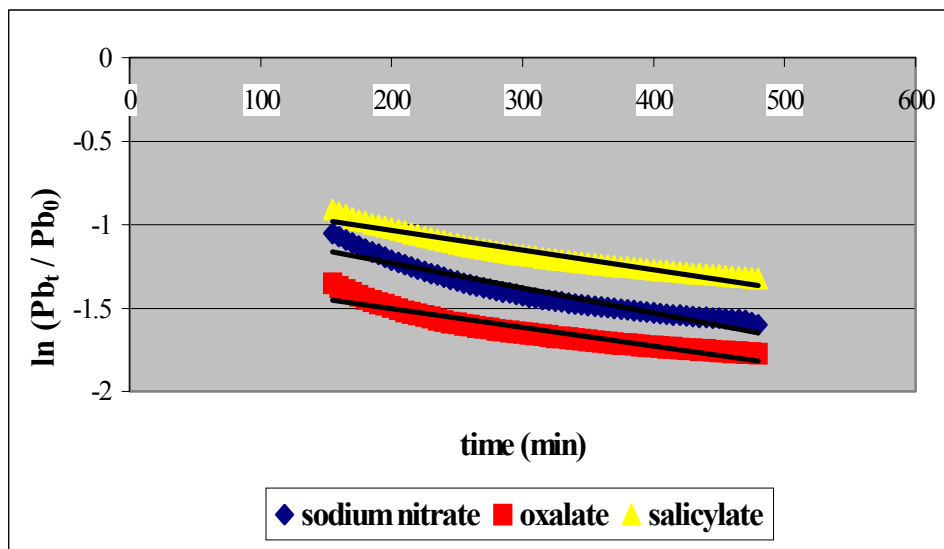FIGURE 5.23 FIRST ORDER RATE EQUATION (K_2) PLOT OF LONG-TERM LEAD DESORPTION WITH DIFFERENT EXTRACTING SOLUTIONS

Chapter 6. Summary and Conclusions

A voluminous amount of research has examined the adsorption of trace metal cations on soil constituent surfaces. However, less research has examined desorption. It is generally understood that the desorption reaction will ultimately control trace element bioavailability in natural systems. Moreover, recent research has demonstrated that the desorption of trace metals from mineral surfaces becomes more difficult with time. There have been many proposed mechanisms for this residence time effect but it still remains poorly understood. Additionally, most studies have examined the effect of residence time on the desorption of trace elements from mineral surfaces at near neutral pH values. In natural environments trace elements may be associated with mineral surfaces for indefinite periods of time. Therefore, it is imperative to understand the influence of residence time and other environmental factors that will control trace element bioavailability. Accordingly, the objectives of this research were to examine the influence of residence time and organic acids on the desorption kinetics of Pb^{2+} and Cd^{2+} from goethite. This study provides a better understanding of the factors controlling the desorption kinetics of trace metals at the liquid/solid interface of iron oxides.

Lead and cadmium exhibited different sorption behavior in both the quantity and rate of metal sorbed. The quantity of lead sorbed was greater than cadmium in both short and long-term experiments. Also the rate at which lead sorbed to goethite was faster than cadmium overall. It is believed that the difference in the quantity and rate of Pb^{2+} and Cd^{2+} adsorption to goethite is attributable to their differing affinities for the goethite surface which is related to the hydrolysis constant of the metal and the type of surface complex formed.

For all experiments (except long-term Pb^{2+}) the quantity of metal desorbed from goethite followed the order salicylate > $NaNO_3$ > oxalate. This was related to the affinity of the organic acid for the goethite surface and its functional group composition. Oxalate may form bridging complexes between the goethite surface and trace metal cation resulting in enhanced retention. Furthermore, oxalate can induce changes in surface charge properties upon adsorption resulting in enhanced metal retention. This explains the greater desorption of Pb^{2+} and Cd^{2+} in the presence of Na^+ compared to oxalate. Based on the adsorption study one would expect to observe a greater quantity of Cd^{2+} desorbed in the presence of all extracting solutions. However, we did not see any observable desorption trend related to trace metal sorption. This may be associated with the desorption mechanism of the different trace metals as well as the influence of residence time on the adsorption mechanism.

Two first order equations best described the desorption kinetics of Cd^{2+} and Pb^{2+} from goethite for all extracting solutions compared to parabolic diffusion, and single first order reactions. Correlation of determination, R^2 values, were greater than 0.910 for all desorption experiments. Experimental and kinetic results show a decrease in the rate and quantity of trace metals desorbed with increased residence time (except for oxalate experiments), but statistical analyses indicate that these differences were not significant for all experiments except Pb^{2+} and salicylate. It is proposed that residence time effects are less pronounced at pH 4.5 because of the lower affinity of the metal for the oxide surface.

My research suggests that residence time effects observed by researchers at near neutral pH values may be less prominent as the pH of the aqueous environment is reduced. This information is extremely important because the effectiveness of monitored natural attenuation may be reduced by pH fluctuations that can occur in natural soil environments. Furthermore, the presence and ability of organic acids to desorb trace metals from oxide surfaces may also reduce these effectiveness of the processes. Further research is necessary to thoroughly understand interactions of trace metals, organic acids, and residence time and the role they play on trace element availability in soils.

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Zaoski, R.G., and R.G. Burau. 1978. A technique for studying the kinetics of adsorption in suspensions. Soil Sci. Soc. Am. J. 42, 372-374.

Curriculum Vitae

Leslie James Glover II

5408 Creek Ridge Lane Apt Y*** Raleigh, NC 27607
email: ljg_2@hotmail.com   webpage: http://www.angelfire.com/vt/ljg2
Home: (919) 395 6600   Office: (919) 549 4052

PROFFESIONAL OBJECTIVE

To pursue a doctoral degree in Environmental Sciences and to obtain a position within a progressive organization, where my education and experience can be effectively utilized.

EDUCATION

Virginia Polytechnic Institute and State University. Blacksburg, Virginia. September 1997- December 1999, May 2000. Master of Science in Environmental Soil Chemistry.

Alabama Agricultural and Mechanical University. Normal, AL 35762 August 1992-May 1997. Graduated Cum Laude: Bachelor of Science in Environmental Science.

Pine Bluff High School. Pine Bluff, Arkansas. September 1990-May 1992. Graduated with Honors**.**

WORK HISTORY

Biological Science Technician USDA Forest Service. Southern Research Station. Research Triangle Park, North Carolina. February 2000 - present. Contact Dr. Kirk Johnsen (919) 549 4000.

- Developing experimental techniques for soil extractions using Supercritical Fluid Extraction, and Soil Fractionation
- Utilizing Suprex Carbon Fat Analyzer, Leco Carbon Fat Analyzer
- Supply technical support for ongoing research projects such as environmental carbon sequestration, and measuring labile carbon pools.

Graduate Assistant Virginia Polytechnic Institute and State University. Blacksburg, Virginia. September 1997-December 1999. Contact Dr. Matthew Eick (540) 231 8943.

- Performed adsorption/desorption experiments with trace metals
- Performed analysis on experimental and statistical data
- Utilized Atomic Adsorption, Thermogravimetic Analysis, pH STAT Titrino, Graphite Furnace Atomic Adsorption, pH meters, conductivity bridge, x-ray diffraction techniques, SAS software, Macintosh O/S, Microsoft O/S
- Synthesized hydrous metal oxides
- Instructor for Basic Soils Laboratory (two years)

Soil Scientist GS-470-07 USDA Forest Service -Hiawatha National Forest. St. Ignace Ranger District, St. Ignace, Michigan. July 1997- present. Contact Don Howlett (906) 786 4062 ext. 334.

- Newly hired Ecosystems resource team member.

Tissue Culture Lab Assistant Alabama Agricultural and Mechanical University- Normal, Alabama 35762. May 1997 and May 1992-August 1992. Contact Dr. Govind Sharma (205) 851 5462.

- Performed callus initiation for *Triticale* and *Avena* embryos
- Tested the efficiency of two hormone nutrient agars for *Triticale* callus production
- Assisted in the initial analysis for the productivity of various plant hormone agars used for plant regeneration on *Triticale* and *Avena callus*
- Performed dissection of hypocotyl, immature, and mature embryos of *Triticale* and *Avena*
- Created stock and auxin solution for experimentation

Student Trainee/ (Soil Scientist) - GS-0499-05 USDA Forest Service- Hiawatha National Forest. 2727 North Lincoln Rd., Escanaba, MI 49829, May 1996-August 1996. Contact Don Howlett (906) 786 4062 ext. 334

- Assisted in the ongoing Ecological Classification and Inventory Mapping project in which I integrated various ecological disciplines i.e. soils , vegetation, and hydrology from aerial photo interpretations and plot taking
- Assisted in collecting data to support the correlation between Ecological Land Type polygons and soil survey polygons
- Supervised a Youth Conservation Corps group from Green Bay, Wisconsin
- Took active part of the USDA Region Nine African American Strategy Group

Student Trainee/ (Forestry) - GS- 0499-04,03 USDA Forest Service - Hiawatha National Forest 2727 North Lincoln Rd., Escanaba, Michigan 49829, May 1993-August 1995. Contact Don Howlett or Kirsten Seleen (906) 786 4062.

- Worked in conjunction with the forest fisheries technician on a fish repopulating project as well as a walleye hatchery project
- Helped to delineate cool water streams in the Upper Peninsula of Michigan as a means of identifying trout streams that were viable for recreational use
- Helped the Forest Landscape Ecologist to establish boundaries for ecological land types for the Eastern Unit of the Hiawatha National Forest

Chemistry Lab Assistant Minority Biomedical Research Support Program, Pine Bluff, Arkansas 71601. May 1991-August 1991. Contact Dr. William Willingham (870) 541 6899.
- Performed Thin Layer Chromatography and High Performance Liquid Chromatography on food mutagens and carcinogen known as "Aflatoxins."
- Performed analysis on the chemical make-up of the Aflatoxins G1 and B1
- Utilized UV spectrometer to analyze the affinity of the Aflatoxins to the liquid phase of the 'Chromatography apparatus
- Awarded outstanding student of the program for seminar presenting the initial findings for the Aflatoxins research

Other Employment
- Bath and Body Works- sales representative. 782 New River Rd. NW, Christiansburg, Virginia 24073. November 1997- January 1998.
- University of Arkansas Pine Bluff Research Farm- research aide. 1200 University, Pine Bluff, Arkansas 71601. June 1997- August 1997
- Hibbett Sporting Goods- sales manager and sales representative. Memorial Pkwy Square, Huntsville, Alabama 35805. February 1994- October 1996

TEACHING ASSIGNMENTS

Basic Soils Laboratory. Virginia Polytechnic Institute and State University – Blacksburg, Virginia. Fall 1999, Spring 1999 and Fall 1998.
- Lecturing classes
- Laboratory preparation
- Responsible for administering and grading of homework, tests, quizzes and assigning of final grades
- Conducted soils related field trips

PRESENTATIONS

Influence of Residence Time and Organic Acids on Trace Metal Desorption from Goethite. 91st Annual ASA,CSA, SSSA Meetings - Salt Lake City, Utah. November 1999.

Analysis of Mineral Components from a Pretreated Nipe Subsoil by X-ray Diffraction, Thermal Analysis, Cation Exchange Capacity and Specific Surface Area. Virginia Polytechnic Institute and State University – Blacksburg, Virginia. May 3, 1999.

Effects of Auxins on Callus Proliferation and Plant Regeneration in *Avena* Tissue. Virginia Polytechnic Institute and State University – Blacksburg, Virginia. November 9, 1998.

Landfills. Webpage creation and presentation. Virginia Polytechnic Institute and State University - Blacksburg, Virginia. April 24, 1998.

Importance of Chlorine Deficiency in Northern Alabama. Alabama Agricultural and Mechanical University - Normal, Alabama. April 30, 1997.

Comparative Study of Auxins on Mature and Immature *Avena Sativa* and *Triticale* callus. Undergraduate research seminar. Alabama Agricultural and Mechanical University - Normal, Alabama. November 22, 1996

PROFESSIONAL AND CERTIFIED TRAINING

CPR and First Aid; by the American Red Cross. Southern Research Station, Research Triangle Park, NC. March 7-8, 2000

Lotus Notes Applications. Southern Research Station, Raleigh, NC. March 20-21, 2000

Fire Management and Fire Fighting. USDA Forest Service - Hiawatha National Forest 2727 North Lincoln Rd., Escanaba, MI. May, 1995

Hardwood and Old Growth Management. USDA Forest Service - Hiawatha National Forest 2727 North Lincoln Rd., Escanaba, MI. Summer 1994

Insect and Disease Control Management. USDA Forest Service - Hiawatha National Forest 2727 North Lincoln Rd., Escanaba, MI. Summer 1994

Best Management Practices USDA Forest Service - Hiawatha National Forest 2727 North Lincoln Rd., Escanaba, MI. Summer 1994

EXTRACURRICULR PROGRAMS

Minorities in Agriculture, Natural Resources and Related Sciences ; National Conference (Digital Portfolio Workshop Presenter) Roanoke, VA. April 8-10, 1999

State Council of Higher Education ; Regional Conference for Potential Graduate Students (Panelist and Closing Remarks) sponsored by Office of Academic Enrichment Programs at Virginia Polytechnic Institute and State University - Blacksburg, VA. March 20, 1999.

"Considering Graduate School" (Panelist) sponsored by the Career Services at Virginia Polytechnic Institute and State University – Blacksburg, VA. October 13, 1998.
College of Agriculture and Life Sciences Summer Internship Program (Events coordinator) Virginia Polytechnic Institute and State University - Blacksburg, VA. Summer 1998 and 1999.

Student tutorial project sponsored by Minorities in Agriculture, Natural Sciences, and Related Sciences. Christiansburg High School - Christiansburg, Virginia. November 1997

Big Brother Big Sisters program Harrison Home for orphans. Coalition on at Risk Minority Males. Huntsville, Alabama. January - May 1997

AWARDS

Phyllis G. and Reginald Nelson IV Scholarship Recipient (1998-99)
USDA Apprenticeship Scholarship Recipient (1992-1996)
Dean's List 1993-1997
President's List 1992.
Alabama A&M Tennis Team 1995-1997 (Captain 1997)

AFFILIATIONS

Soil Science Society of America
Graduate Student Assembly at Virginia Tech (Delegate)
Black Graduate Student Organization at Virginia Tech (President 1998-99)
Crop, Soil and Environmental Science Graduate Organization (Vice Pres. 1998-99)
National Black Graduate Student Association (Judicial Commission 1998-99)
Minorities in Agriculture, Natural Resources and Related Sciences
Pan African Alliance