

YEARS

**THE FATE AND TRANSPORT OF INORGANIC CONTAMINANTS IN
NEW JERSEY SOILS**

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ABSTRACT

Equilibrium batch measurements were made for the adsorption of four metals, Cd(II), Pb(II), Cr(III) and Cr(VI) to 15 New Jersey soils. The soils were characterized in terms of surface properties and composition, particularly organic matter and metal oxides. The adsorption of all metals followed the Langmuir relation. For cationic species the adsorption increased with increasing pH between pH 3 and 10 while for Cr(VI), an anionic species, the adsorption decreased with increasing pH. At constant pH and metal concentration, greater adsorption was observed for soils with higher organic matter content.

To better understand the mechanism of adsorption, the experimental results for Cd(II) were tested in two simplified models. A partition coefficient model was used to relate the adsorption results for different soils at fixed pH values with soil properties using formation constants between cadmium and soil components: organic matter, iron oxide, aluminum oxide and manganese oxide. Partition coefficients obtained from experimental data were correlated with those calculated using a formation constant between cadmium and organic matter alone ($R^2 = 0.982$). As expected, this model was not successful when used to model measurements at the soil natural pH because of competition of protons with metal for available sites. The results of the partition

coefficient model were used to obtain soil quality standards which insure the drinking water standard will not be exceeded in the ground water in contact with a selected soil at fixed pH.

A surface complex model was used to describe the pH dependence of cadmium adsorption to soil organic matter. Alkalimetric titration data for each soil were analyzed with a discrete multi-monoprotic acid model. The soils were all negatively charged through most of the range of the adsorption measurements. A single pK_a obtained from the titration was found to be related to organic matter content. This pK_a was used to calculate surface speciation of negatively charged sites. Speciation of cadmium and its hydroxy complexes was calculated from literature equilibrium constants. Stability constants between cadmium species and negatively charged surface sites were used to fit the experimental pH dependent adsorption measurements.

To validate the adsorption partition values, column desorption studies were carried out as a function of flow rate and metal loading. Samples were collected at each of several column flow rates. These data were treated by a double extrapolation technique to evaluate the partition coefficient obtained under desorption conditions. The apparent partition coefficient increases with increasing column velocity and duration of flow. For each flow rate, the results were extrapolated to that for zero time. These zero time partition coefficients were then extrapolated to zero flow. The zero time, zero flow desorption results were compared to those for the batch adsorption equilibrium. The partition coefficient obtained for batch adsorption provided a good estimate of the value obtained for desorption of the cadmium contaminant in the dynamic system. The slope of the regression of column K_d versus batch K_d values was greater than 0.90.

Chapter 1

INTRODUCTION

Adsorption reactions are common processes in water and wastewater treatment and the transport of chemical species in the aquatic system (Huang et al., 1987). The rapid increase in the disposal of municipal and industrial waste in landfill sites and the application of sewage sludge to land, has resulted in additional significant pollution of the environment. Contaminants from industrial and automobile emissions may also be introduced via the atmosphere. Metal levels in the atmosphere, soil, and aquatic systems have been elevated as a result.

The possible contamination of groundwater supplies by metals is a major environmental concern. The chemistry of soil and aquifer materials is critical in regulating the concentrations of metals present in groundwater. Soils are potentially large reservoirs for metals. Metals are retained by soils through interaction with soil constituents including hydrous metal oxides and humic materials. The concentration of hydrogen ions is key to the partitioning of metal ions between soils and water. The adsorption of toxic metals by soil minimizes toxic potential because the concentrations of metals in the water phase are reduced. However, the accumulation of pollutants in soil may result in soil contamination problems with consequent long-term effects on

groundwater. Therefore, assessment of soil contamination has become increasingly important over the past several years.

Förstner (1987) pointed out that soil contamination can have two different meanings. One is the slow but steady degradation of soil quality by the inputs of chemicals from various sources; the other is the massive pollution of certain areas mainly by the dumping or leakage of industrial waste materials. Contaminated soil in the former case usually relates to adverse effects in foodstuff and in the latter meaning is primarily connected with groundwater problems.

The loss of groundwater resources is increasingly troublesome. A United States Library of Congress Report from 1980 lists 1360 well closings in a 30-year span due to contamination (Förstner, 1987). There is a significant effect of heavy metal pollution (about 40 % of the cases) on the loss of ground water resources.

The growing application of chromium and cadmium compounds in manufacturing purposes, particularly in the aircraft and metal products industries during the Second World War, created new problems of industrial waste disposal. Cadmium and chromium are widely used in the aircraft industry for plating and anodizing purposes in order to enhance the corrosion resistance of aluminum and other metals. The U.S. Army and Navy specifications required that chromic acid be used on aircraft parts (Davis and Lieber, 1951). During wartime production, the anodizing solution tanks were dumped as often as every half year, and an average size plant used one hundred pounds of chromic acid per day for anodizing.

The possibility of chromate contamination of water supplies stems mainly from two industrial applications: the use of chromates or dichromates as corrosion

preventatives in cooling water systems and the use of chromic acid electrolyte for chromium plating of metals. The first incidence of chromium in a water supply was reported in June 1942 at the Liberty Aircraft plant in South Farmingdale in Nassau County, New York. The next indication of ground water pollution by chromium in the same county was found in July, 1943, at the Grumman Aircraft plant in Bethpage. The plant employees complained of a yellow discoloration in the water flowing from the drinking fountains of the plant. This area possesses unique characteristics from an environmental engineering point of view because of its complete dependence upon groundwater as a source of supply.

In the spring of 1945, the Nassau-Suffolk Water Superintendents Conference conducted a forum at which one of the topics considered was that of potential hazards to ground water. The problem of chromium contamination was discussed and, as a result, the New York City Department of Water Supply, Gas and Electricity installed a series of test wells south of the Liberty Aircraft Plant. New York City was concerned with the South Farmingdale area since the city obtains water from the Massapequa Ponds and infiltration gallery. These installations are located due south of Liberty and in direct line of normal ground water travel. The test wells which were placed parallel to the flow of ground water were drilled only to sufficient depth to penetrate the top of the ground water table. There was no hexavalent chromium detected in water from the test wells at that time. These wells were resampled by the Nassau County Health Department in April, 1948. Three of the six wells sampled were found to contain water containing hexavalent chromium. The concentrations present ranged from 1.4 to 6.0 ppm, the higher concentrations being found in samples from wells closer to the plant. All known private wells in this area were sampled and, of the 14 wells sampled, water from only

one well was found to contain hexavalent chromium (1.0 ppm) (Lieber and Welsch, 1954).

Another example of chromate contamination of water supply occurred at Douglas, Michigan, in 1947. A metal products factory in this city had done a great amount of chrome plating for a period of years, during which the disposal of waste electrolyte had created a serious problem. It could not be emptied into either Lake Michigan or adjacent streams without endangering fish life and running up against the federal government or the Michigan Stream Control Commission. Finally it was dumped into an adjoining abandoned gravel pit. The gravel contained considerable limestone, which would neutralize the acidity of the waste. A thousand feet from this waste pit was a group of six 30-ft wells from which Douglas obtained the bulk of its water supply. When water from these wells took on a yellow tinge, chemical analysis showed it to contain 11 ppm of hexavalent chromium, which made it necessary to abandon these wells as a source of water supply (Muehlberger, 1950).

Cadmium plating was used to replace zinc and tin as a rust-resistant coating for steel because of the metal shortages during World War II. Where food containers were "tinned" with cadmium, many cases of acute cadmium poisoning developed. A continuation of the study showed the presence of cadmium, a heavier and more toxic metal than chromium in the groundwater. Cadmium is utilized on a large scale in industrial plating operations. An analysis of the water in a recharge at an aircraft company established presence of 1.2 ppm of cadmium. A survey conducted on private shallow wells in the area disclosed that two of them, in operation at the time of the investigation, contained 0.6 ppm and 0.34 ppm cadmium, respectively (Lieber and Welsch, 1954). The discharge of plating wastes into ground waters created a hazardous

situation in parts of Long Island. Every effort should be made to prohibit such disposal unless the wastes have been treated to remove toxic and deleterious substances. Many years may have to elapse before the effects of rainfall and groundwater dilution will eliminate this contaminant from the ground water. It is, however, possible to follow cadmium travel in the ground water. Areas in the direct line of cadmium-contaminated ground water flow are potentially poor locations for wells intended to supply potable water.

There are a number of routes of human exposure to contaminants in soil: leaching to groundwater, runoff to surface water, uptake by animals used for human food, uptake by agricultural crops, direct dermal exposure, ingestion, inhalation of fugitive dusts. All significant routes of exposure must be considered when performing a risk assessment or in the development of a standard.

Metal adsorption by soil is highly pH dependent (Kuo and Baker, 1980, Harter, 1983, Elliott et al., 1986). Christensen (1989) correlated cadmium sorption with various soil parameters. He determined the distribution coefficients for 63 Danish agricultural soils and found that the distribution coefficients correlated very well with soil pH ($r^2=0.72$). Soil organic matter content, as a second parameter, improved the correlation ($r^2=0.79$).

Metallic ions from soil solution are attracted to chemically active surface sites of fine-grained particles. The relative proportions of ions attracted to these various sites depends on the degree of acidity or alkalinity of the soil or aquifer material, on its mineralogical composition, and on its content of organic matter.

Metallic ions may be adsorbed by particles either by ion exchange, involving the formation of relatively weak outer sphere complexes, or by ligand exchange involving the formation of strongly bound inner sphere complexes. The extent of metal adsorption depends on the charges on the adsorbing surface and the metallic cation and on the intrinsic formation constants for the complexation reactions.

Sorption results can be used to determine the maximum concentration of the metal that will not result in violation of the drinking water standard. The migration of inorganic materials through the unsaturated zone to groundwater is controlled by sorption to the soil, a highly pH-dependent process, and the hydrological regime.

The maximum level of metal in soil for which the equilibrium soluble metal does not violate the Drinking Water Standard can be computed, at any pH, from the measured partition coefficient for any metal and soil.

Lee et al. (1992) developed a methodology for the calculation of the maximum level of metal in soil for which the equilibrium soluble metal does not violate the Drinking Water Standard. These metal criteria can be used as soil standards which will be protective of groundwater quality. Soil standards applicable to the prediction of groundwater contamination by inorganic materials must take into account mechanisms important in the partitioning of metals between the soil and water.

The aims of this study are to experimentally measure metal adsorption to representative New Jersey soils and to obtain a rational understanding of the sorption process. The soil will be characterized in terms of physical and chemical properties. To achieve these, we will fit the data using models for soil surface characteristics and metal speciations.

To determine which surface properties are important, a conditional partition coefficient model will be used. Partition coefficients, measured at fixed pH and at the natural soil pH, will be regressed against the soil characteristics.

Since pH values of groundwater may vary from site to site, it is desirable to be able to predict the pH dependence of metal adsorption. A surface complexation model will be used to achieve this task.

The test of the models will focus on the success in fitting the adsorption data for cadmium. The use of the results in determining soil criteria for cadmium will be demonstrated.

Chapter 2

LITERATURE REVIEW

2.1 Sources and Toxicity of Heavy Metals

A major source of heavy metals is from industrial discharge. However, heavy metals may also be deposited into the environment by other sources, such as domestic water supplies, residential wastewater, surface run off, atmospheric precipitation, and groundwater inflow and infiltration.

The significance of heavy metals in the environment is seen from their extremely toxic effect to human beings, animals, and plants. The toxicity of a metal or metal compound has been defined as its intrinsic capacity to cause injury, including potential carcinogenic, mutagenic, and teratogenic effects (National Academy of Sciences, 1977). Listed below are the heavy metals chosen for this study and their possible sources.

Cadmium: The major users of cadmium are considered to be the electroplating and coating industry which accounted for approximately 34% of the total use in the United States in 1981 (Anon, 1985). Cadmium is also used for the production of metallurgical alloys, petrochemicals, batteries, fungicides, photography, pigments for paints, inorganic chemicals, shampoo, hair dyes and organic chemicals. Animal studies of acute cadmium poisoning have shown that it is toxic to all tissues, causing growth

retardation, hypertension, tumor formation, hepatic (liver) dysfunction, poor lactation, and lowered hematocrit levels (Luckey and Benugopal, 1977). Itai-itai disease, which was first found in 1947, was discovered in 1968 to be caused by cadmium-containing water supplies (Kobayashi, 1978). The absorption of ingested cadmium is generally low in humans, ranging from 4.7 - 7%, but may increase in cases where dietary calcium is low (Fielder, et al., 1983; Duffus, 1980). When absorbed, cadmium has a tendency to remain in man and accumulates mainly in the liver and kidneys with the concentration being directly related to the oral dose administered (Ragan, 1983).

Chromium: The major users of chromium are metallurgical, refractory and chemical industries. Chromium is also used in the production of textiles, pesticides, detergents fertilizers and in the dyeing of mordants. The major oxidation states of chromium are Cr(III) and Cr(VI). Cr(III) is less toxic than Cr(VI) and is relatively immobile in the aqueous environment because of its strong adsorption onto soils (Amacher and Baker, 1982). On the contrary, Cr(VI) is relatively mobile in aqueous environment, because Cr(VI) is not as strongly adsorbed to soils as Cr(III). Unlike Cr(III) which is cationic and can form an insoluble chromium hydroxide solid with hydroxide ion, Cr(VI) exists in aqueous solution as a complex anion. Chromium metal is biologically inert and does not produce toxic or other harmful effects in man or laboratory animals. Compounds of Cr(III) have no established mammalian toxicity. However, it is known that in an excessive concentration, trivalent chromium, in an aquatic environment, inhibits the growth of certain algae and can result in the death of shellfish or fish. The chief health problems associated with chromium are related to Cr(VI) compounds, which are irritant and corrosive and may be absorbed by ingestion,

through the skin, and by inhalation. Acute systemic poisoning is rare and usually may result from absorption through the skin.

Lead: Lead is used in various industries for the production of batteries, gasoline, paints, pigments and insecticides. In 1983 approximately 50% of all lead has been used in battery manufacturing and 25% of lead has been used in the cable sheathing industry in the United States. Another major source of lead is from plumbing systems. Lead is also used in pigments, ammunition, solder, cable covering, and anti-knock additives for gasoline (Anon, 1985). Lead-contaminated drinking water often was found in areas where lead piping was used. Acute lead poisoning in adults results in anemia, renal damage, and sometimes encephalopathy. Symptoms in children include irritability, loss of appetite, occasional vomiting, intermittent abdominal pain, and constipation. Any amount of lead intake more than 0.8 mg/l results in clinical lead poisoning (Lester, 1987; Goyer and Mushak, 1977). Lead-contaminated drinking water from pipes in Scotland resulted in miscarriage, fetal death, and abnormal births (Wilson, 1966).

2.2 Soil Characteristics

Depending on environmental conditions the soil particle size distribution may range from colloidal particles of less than 0.1 μm in diameter to large sand and gravel particles of several millimeters in diameter. However, the small clay and silt size particles are most likely to be involved in the sorption process because these have the largest specific surface areas (Hart, 1982).

Soil is a complex mixture of a number of solid phases that may include clay silica, metal oxides such as iron, manganese, aluminum oxides, and organic matter (Hart, 1982). Förstner (1987) indicated that solid phases which interact with dissolved constituents in natural waters consist of a variety of components including clay minerals, quartz, feldspars and organic solids. These components are usually “coated” with hydrous manganese and iron oxides and organic substances (Jenne, 1977).

Oxides: The most frequently observed iron oxides in soils are goethite (α -FeOOH), hematite (α -Fe₂O₃), maghemite (γ -Fe₂O₃), lepidocrocite (γ -FeOOH), and amorphous iron oxide, which has been considered to be microcrystalline goethite and is perhaps best described by the formula FeO_{n/2}(OH)_{3-n} with variable water (Jenne, 1977). However, in aquatic environments, amorphous iron oxide is a major form. Jenne (1977) indicated that there are several causes for the amorphous nature of these precipitates. Rapid precipitation is an important factor. Amorphous ferric oxides are thermodynamically metastable.

Many forms of manganese oxides are present in soil. An extensive list of the types of manganese oxides which have been found has been compiled by McKenzie (1989). Manganese oxides in soil are often reported to be amorphous (McKeague et al., 1968). Jenne (1977), in a review of trace element sorption, indicated that although manganese oxides may precipitate less rapidly than iron oxides, isomorphic substitution is much more extensive and the oxidation state of the manganese is highly variable. So, manganese oxides tend to be more amorphous than those of iron. Förstner (1987) reported that amorphous manganese oxides are also formed on clay substrates.

Organic matter: The organic matter in soils is referred to as humic substance. (made up of humic acids, fulvic acids, and humin) and biochemicals (made up of lipids amino acids or proteins, and carbohydrates). The organic matter content and its molecular nature in soils vary with various factors such as climate, drainage area, and chemical, biological, and geological characteristics of surrounding environments. The study of interactions of metals and organic matter in soils has concentrated on the structures and functional groups of these organic materials.

2.3 Surface Charge of Soils

Because soil particles commonly are electrically charged, ions in the soil solution are attracted to their surfaces. The charge on soil colloids results from (1) isomorphic substitution or crystal lattice defects in the internal structure of the mineral; (2) dissolution of ions from the surface of soils; and (3) ionization of active organic functional groups (Sparks, 1986). Structural charges, σ_{str} , are constant charges associated with the surfaces of the phyllosilicate clay minerals, whereas pH-dependent, variable charges, σ_{H} , are associated with reactions of protons in oxide and (oxy)hydroxide minerals and with certain functional groups, e.g., carboxylic and phenolic, of humic substances (Sposito, 1984). The total intrinsic charge, σ_{int} , on soil particles is made up of the charge density of constant charge plus the charge density of variable charge:

$$\sigma_{\text{int}} = \sigma_{\text{str}} + \sigma_{\text{H}} \quad (2.1)$$

2.3.1 Isomorphous Substitution

The permanent structural charge on soil colloidal particles results from ion substitution or site vacancies in the crystal structure. Generally a lower valence element substitutes for one with a higher valence. For example, when Al^{3+} substitutes for tetrahedral Si(IV) or when Mg^{2+} or Fe^{2+} substitutes for octahedral Al^{3+} , there is a deficiency of positive charge in the crystal lattice. This results in such clay colloids having a permanent negative charge.

2.3.2 Surface Ion Dissociation

Surface charges also develop as a result of adsorption of H^+ or OH^- or as a result of dissolution of surface sites. The magnitude and sign of the charge depends on the pH of the soil which distinguishes them from the permanent structural charges in clay minerals. Many minerals in soils undergo this type of surface charge formation process. The most notable of these are the oxides and/or the hydroxides of Al, Fe, Mn, and Ti.

A common surface group which reacts with protons is hydroxide. A surface hydroxide, $\equiv\text{S-OH}^0$, can undergo two protolysis reactions:



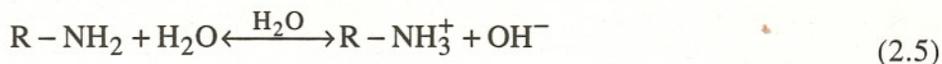
The charged sites on constant-charge and variable-charge surfaces are important for the retention of metals. Metallic counter ions can neutralize the intrinsic charges on the surfaces of soil particles by forming either outer sphere or inner sphere complexes.

2.3.3 Ionization of Active Organic Functional Groups

Ionization is confined mainly to the organic fraction which produces active positive or negative functional groups. For example:



or



The charge is dependent on the dissociation constant of each functional group and pH. The humic fraction of the soil organic matter is not a single compound in the manner indicated by the above equations. Rather it contains a large number of components whose acid-base behavior can be described in terms of a Gaussian distribution of sites. Tipping et al. (1990) have successfully modeled the heterogeneity of proton dissociation reactions for a humic acid using molecular size and carboxylate group information together with adjustable, intrinsic acid dissociation constants.

2.4 Mechanism of Interaction Between Metal Ions and Soil Particles

2.4.1 Adsorption

2.4.1.1 Theory of Adsorption Behavior

In a solid-liquid solution, adsorption is a process in which the molecules or particular components move from one phase (liquid) to another (solid phase) (Weber, 1972). The adsorption equilibrium can be visualized by the distribution relationship between a liquid and solid phase.

The aqueous concentration of an inorganic contaminant in contact with a soil can be predicted from appropriate thermodynamic measurements. Trace elements present in the solid phase are the result of adsorption to components of the soil. The aqueous phase concentration of the trace element, Me, is related to the mass of adsorbed metal (x) per unit mass of soil (m). A number of adsorption isotherms, including empirical Freundlich model and semi-empirical Langmuir model, have been developed to relate the solution and adsorbed concentrations (Hiemenz, 1986; Kinniburgh, 1986; Travis and Etnier, 1981). The most commonly used equation is the Langmuir equation

$$\Gamma = \frac{x}{m} = \frac{\Gamma_m K[\text{Me}]}{1 + K[\text{Me}]} \quad (2.6)$$

where

Γ = the amount metal adsorbed ($\mu\text{g/g}$)

$[\text{Me}]$ = the equilibrium concentration of metal (mg/L)

Γ_m = monolayer coverage ($\mu\text{g/g}$)

K = Langmuir constant (L/mg).

At low concentrations of metal the equation can be simplified to a linear adsorption isotherm

$$\Gamma = \frac{x}{m} = K_d[\text{Me}] \quad (2.7)$$

where

K_d = the partition coefficient.

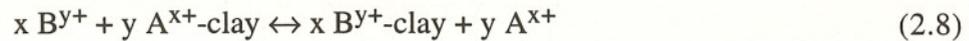
The basic limitation of these relationships is that they do not account for changes in the extent of adsorption which occur when the aqueous phase composition is altered in pH, ionic strength, or concentration of chemicals which form complexes with the metal. Neither do they provide a means to relate soil properties to the extent of adsorption. Nonetheless, these adsorption isotherms are important, particularly in defining the maximum amount of metal which can be bound by a given soil.

Additional information is needed to relate soluble metal concentrations to adsorption if the metal undergoes significant chemical reaction or complexation in the solution phase (Evans, 1989; Sposito, 1985; Stumm and Morgan, 1981; Lindsay, 1979; Sposito, 1981). Important inorganic ligands forming complexes with metal cations include hydroxide and chloride ions. The computation of solution speciation, which has been reviewed by Jenne (1979), is generally accomplished by use of chemical equilibrium computer programs such as MINEQL (Westall et al., 1976) or MINTEQA (Brown and Allison, 1987).

2.4.1.2 Cation Exchange Reactions

Cation exchange involves a weak association between the adsorbed ion and the soil particle in which the cations do not form covalent bonds with the surface. In these outer sphere complexes the cations retain their water of hydration. Because the association is weak, the adsorbed ions are easily exchanged by other cations.

The extent of cation exchange reactions can be estimated from a knowledge of the cation exchange capacity of the soil (Sposito, 1984). The negative charge at constant-charge surfaces generally is much greater than that at variable-charge surfaces. The typical reaction is described by the ion exchange equation. For B^{y+}/A^{x+} exchange:



The exchange constant can be written

$$K_{\text{ex}} = \frac{(m_A)^y (N_B)^x}{(m_B)^x (N_A)^y} \quad (2.9)$$

where m_A and m_B represent the molarity of the metals in the solution phase and N_A and N_B represent the fraction of clay exchange sites occupied by these ions. K_{ex} should remain relatively constant with changing ionic strength if the exchange cations behave as an "ideal solution" in the clay phase (Sposito, 1981).

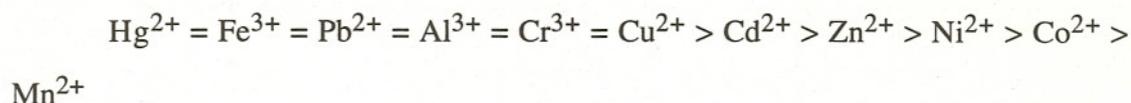
The selectivity for cations at the charged surface is dependent on the charge and hydration properties of the cation. Adsorption of monovalent cations onto constant-charge surfaces follows the order:



This order of selectivity follows the increase in hydrated radii that occurs from Cs to Li. Metals with small ionic radii have larger hydrated radii and an increased polarizing power of the cation (Kinniburgh et al., 1976; Kinniburgh and Jackson, 1981).

2.4.1.3 Adsorption by Organic Matter

Humic and fulvic acids have the greatest importance for complexation by the organic fraction. Humic and fulvic acids make up the majority of organic matter containing reduced carbon in natural water and in the earth's crust (Williams, 1990). The extent of metal retention by various humic and fulvic acid fractions separated from soil has been the subject of numerous studies (Kinniburgh and Jackson, 1981; Bruggnewert and Kamphorst, 1979). Some typical results (Schnitzer and Khan, 1978) are presented below, the extent of retention decreasing from left to right:



The mechanisms of metal binding on organic matter involves not only the process of ion exchange between H^+ and metal ions on acidic functional groups, but also inner-sphere complexation and precipitation reactions. Metals and soil organic matter can form inner sphere complexes by association between cations and coordinating functional groups found in humic substances, in which the functional groups behave like complex organic ligands. Donor atoms generally are the more electronegative nonmetallic elements. These elements usually are contained within basic

groups, such as -NH_2 (amino), =O (carbonyl), -OH (alcohol), and -S- (thioether); or within acidic groups, such as -COOH (carboxyl), -OH (enolic or phenolic), and -SH (thiol) (Stevenson, 1981). From the Pearson classification of Lewis acids and bases, sulfur-containing ligands are particularly strong, soft Lewis bases that can form strong complexes with soft Lewis acids; thus, sulfhydryl groups in soil organics could have very high preferences for trace levels of Cd^{2+} and Pb^{2+} . In contrast, a "hard acid" like Ca^{2+} would bind ligands in the order $\text{O} > \text{N} > \text{S}$. Thus, Ca^{2+} could compete successfully with Cd^{2+} for the abundant carboxylate ligands in soils.

Within the past half-dozen years there have been significant advances in the description of the binding of protons and metals by fulvic acids. Fulvic acids are important materials affecting the transport and toxicity of metals in natural water (Saar and Weber, 1982). These materials have a variety of functional groups capable of binding metal ions (Stevenson, 1981). The titration data can be described by fitting to models with a series of discrete ligands (Fish et al., 1986) or a Gaussian distribution of binding sites (Perdue and Lytle, 1983). The discrete ligand approach is the more commonly used. Usually the computer program FITEQL (Westall, 1982) is used to obtain a set of conditional constants based on a non-linear, least-squares fit of the titration data. Both methods provide adequate description of the data (Dzombak et al., 1986).

One approach to the mathematical description of binding by such multiligand systems is by a continuous affinity spectrum (Hunston, 1975; Thakur et al., 1980). These procedures calculate the probability of finding a binding constant within a given pK range. Shuman et al. (1983) applied this to humic acid and Unger and Allen (1988) applied it to metal binding by sediment. There are a number of mathematical methods to

obtain the distribution function (Nederlof et al., 1988). In the recent application of the approach to soils (Riemsdijk et al. 1987; Wit et al., 1988), the intrinsic affinity distribution, in which electrolyte effects are considered, has been determined. The drawback of these affinity spectrum approaches is that a binding distribution, as opposed to a series of discrete equilibrium constants, is obtained. The results are not readily amenable for incorporation into the commonly used equilibrium models.

Another approach to describing the titration behavior of heterogeneous systems is discrete affinity spectrum analysis (Tobler and Engel, 1983) which has recently been applied to the analysis of environmental materials. This approach has the advantage of providing a series of discrete equilibrium constants to define binding and thus the constants obtained can easily be incorporated into chemical speciation computer programs.

2.4.1.4 Adsorption on Mineral Surfaces

Through a ligand exchange process, most anions and many metallic cations can form inner sphere complexes with charged mineral surfaces. Metal oxides, hydroxides, and aluminosilicates provide surface sites for chemisorption of heavy metal. The specific adsorption of inner sphere complexes involves the formation of covalent bonds, so the adsorbed species are not readily displaced.

Most of the soil cations, such as Na^+ , K^+ , Ca^{2+} , and Mg^{2+} are weakly held by soils as exchangeable ions. However, many cations can form inner sphere complexes with variable-charge soil surfaces and therefore are strongly held. This specific

adsorption of metallic ions occurs most readily for metals that hydrolyze in water. Such metals include most of the transition elements and the rare earths, in addition to other ions, such as Hg^{2+} , and Pb^{2+} . The adsorption reaction generally involves the formation of an inner sphere complex between the hydroxo-metal complex and the negatively charged deprotonated surface of oxides, hydroxides, and oxyhydroxides of Al, Mn, and Fe (Evans, 1989). Upon hydration, the solid surface develops a hydroxy group which can be described as a Brönsted acid (Huang et al., 1987).



The corresponding conditional stability constants are

$$K_{\text{cond},a1} = \frac{[\equiv \text{S} - \text{OH}^0] \{ \text{H}^+ \}}{[\equiv \text{S} - \text{OH}_2^+]} \quad (2.12)$$

$$K_{\text{cond},a2} = \frac{[\equiv \text{S} - \text{O}^-] \{ \text{H}^+ \}}{[\equiv \text{S} - \text{OH}^0]} \quad (2.13)$$

where the brackets, [], indicate concentration and the braces, { }, indicate the activity of the chemical species.

As the surface undergoes ionization, for instance during a titration with base, the surface becomes progressively more negatively charged and it becomes more difficult to remove subsequent protons. Thus, the conditional stability constant varies with the charge on the surface. It is possible to incorporate a Boltzman, or electrostatic, factor to convert this conditional constant into an intrinsic constant which does not vary with pH

(Huang, 1981; Stumm and Morgan, 1981; Sposito, 1984; Hiemenz, 1986; Schindler and Stumm, 1987). The intrinsic constant, K^{int} , is given by the relationship:

$$K^{\text{cond}} = K^{\text{int}}[-\psi_0 F / RT] \quad (2.14)$$

where ψ_0 is the electrical potential at the surface, F is the Faraday constant, R is the molar gas constant and T is the absolute temperature.

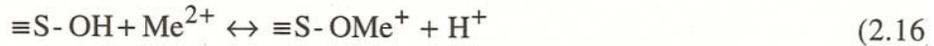
The surface potential is proportional to the surface charge, σ_0 (Sposito, 1984; Hiemenz, 1986; Schindler and Stumm, 1987; Westall, 1987; Singh and Uehara, 1986):

$$\sigma_0 = \kappa \psi_0 \quad (2.15)$$

The surface charge is directly determined from the proton or hydroxide consumption by the solid phase in an acid or base titration (Hohl et al., 1980; Huang 1981).

The electrical double layer theory of Equation 2.14 can be extended to account for the adsorption of ions at planes other than at the surface. The triple layer model of surface complexation requires an additional potential at the Stern layer (James and Parks 1982). The zeta potential, which is the potential at the plane of shear, is subject to easy instrumental measurement and is a good approximation of the Stern potential (Hiemenz 1986).

Metal sorption is highly pH dependent. Protons and metal ions compete with each other for available surface binding sites on a soil. For a divalent metal ion, Me^{2+}



for which the conditional stability constant is

$$K_{\text{cond}} = \frac{[\equiv\text{S-OMe}^+]\{\text{H}^+\}}{[\equiv\text{S-OH}]\{\text{Me}^{2+}\}} \quad (2.17)$$

This conditional constant is related to an intrinsic constant in a similar fashion to that in Equation 2.14. An analogous reaction to Equation 2.16 can be written for the binding of the metal ion to two soil surface sites with the concurrent release of two, rather than one, protons. The binding of the hydrolyzed metal complex, MeOH^+ , to $\equiv\text{S-O}^-$ to give $\equiv\text{S-OMeOH}$ with no release of protons can also be described. If one is to be able to predict the adsorption of a metal at any pH, other than the pH for which there is direct experimentally measured data, it is essential to have the acid base equilibrium constants of Equations 2.12 and 2.13.

The adsorption of anions, such as chromate, can be described in an analogous fashion to that of metal cations (Parfitt 1978; Mott 1981). Binding of the monovalent anion, L^- , by the surface is represented by the reaction



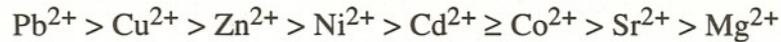
The retention of metals as oxyanions, including HVO_4^{2-} , MoO_4^{2-} , CrO_4^{2-} , and WO_4^{2-} , through ligand exchange processes, can be described in an analogous fashion to that of metal cations (Stevenson, 1981).

Again, an intrinsic stability constant describes the pH dependence of the reaction:

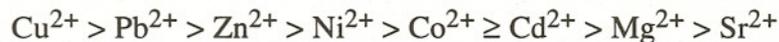
$$K^{\text{int}} = \frac{[\equiv \text{S-L}]\{\text{OH}^-\}}{[\equiv \text{S-OH}]\{\text{L}^-\}} \times (\psi_0 F / RT) \quad (2.19)$$

Mn oxides have a high adsorption capacity and adsorption affinity for metals. Significant amounts of Co, Cu, Zn, Ni, Pb, Ag, and Cd in soils have been reported to be associated with manganese oxides (Taylor, 1968; Suarez and Langmuir, 1976) although the concentration of manganese oxide in soil is generally only about 10^{-4} - 10^{-3} g/g dry weight.

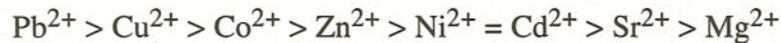
Metal affinities for amorphous Fe hydroxides have been reported to follow the order (Kinniburgh et al., 1976):



with Al hydroxide producing a somewhat different sequence



Metal affinity for the silanol groups of silica follows the order (Dugger et al., 1964; Schindler, 1976):



Many surface complexation models have been developed to describe the adsorption of metal ions onto solid surfaces. They are the constant capacitance model

(Stumm et al., 1980), the triple-layer model (Davis et al., 1978b), the Stern model (Bowden et al., 1977), the generalized two-layer model (Dzombak and Morel, 1990), and the one-pK model (Van Riemsdijk et al., 1986). The major advancement of the surface complexation models is that they consider surface charge, resulting from protonation and dissociation reactions as well as from surface complexation reactions of reactive surface hydroxyl groups at mineral surfaces. The sign and magnitude of the mineral surface charge are dependent on the pH and the ionic strength of the electrolyte solution.

The extent of metal ion adsorption is greatly affected by pH. This is attributed to the fact that both the surface acidity and the hydrolysis of the metal ions are pH-dependent.

2.4.2 Precipitation and Dissolution

The concentrations of many heavy metals in industrial and municipal wastes applied to soils is generally several orders of magnitude higher than their concentrations in nature. When such wastes are added to soil, precipitation of the metals as secondary minerals may occur. Among the most important of these precipitates are the oxides, oxyhydroxides, hydroxides, and carbonates; phosphates and silicates probably are of lesser importance (Lindsay, 1979).

The extent of dissolution of a mineral, M_xL_m , in water, and conversely its precipitation, can be described by its solubility product, K_{so} , the product of the activity of its constituent ions in solution:



At equilibrium, assuming the activity of the solid phase to be unity

$$K_{so} = \{M^{m+}\}^x \{L^{x-}\}^m \quad (2.21)$$

where L is a ligand that complexes with metals.

Metals that might be expected to occur as hydroxides under some soil conditions include Fe^{3+} , Al^{3+} , Cu^{2+} , Fe^{2+} , Zn^{2+} , and Cd^{2+} . With the exception of most of the alkali and alkaline earth metals, almost all metals hydrolyze in water, the extent of hydrolysis increasing with increasing pH. The hydroxo-complexes of some metals, especially Al and Fe, are extremely important for controlling the behavior of these metals in soils.

By contrast with hydroxides and oxyhydroxides, the extent of precipitation of metallic carbonates and sulfides in soils is controlled not only by the solubility products of the individual carbonates and sulfides, but also by the partial pressure of gaseous carbon dioxide and hydrogen sulfide, respectively. This occurs because the content of the carbonate, CO_3^{2-} , and of sulfide, S^{2-} , anions is controlled by the amount of CO_2 , or H_2S dissolved in the soil water. Metals that might be expected to precipitate as carbonates in soil include Ca^{2+} , Sr^{2+} , Ba^{2+} , Fe^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} . Metals that might be expected to occur as sulfides under reducing conditions include Ag^+ , Ni^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , and Fe^{3+} .

2.4.3 Redox Reactions

Changes in oxidation state have a dramatic impact on the solubility of transition metals and thereby modify their toxicity. Generally, heavy metals are less soluble in their higher oxidation states. The ability of Mn oxides (and to a lesser extent Fe oxides) to directly oxidize metals or to catalyze metal oxidation by O_2 could provide a mechanism for lowering trace metal solubility. Reduction of Fe(III), Mn(III, IV), Co(III), and Ni(III) (hydro)oxide minerals greatly increases the solubility. In contrast, reduction of Cr(VI) to Cr(III) by reductive organic matter dramatically decreases mobility and toxicity. It is difficult to distinguish the processes of metal chemisorption, coprecipitation, and electron transfer on Mn oxides as all have the effect of strongly scavenging heavy metals from solution.

Oxidized Mn in soil has been correlated to the tendency of soils to oxidize Cr^{3+} to chromate (Bartlett and James, 1979). In natural aerated waters, the oxidation of Cr(III) to Cr(VI) by O_2 , is greatly accelerated in the presence of Mn^{2+} (Osaki et al. , 1980). Oxidation of Cr^{3+} in soil and water may have the same chemical mechanism, which involves the autooxidation of Mn followed by catalysis of Cr oxidation. Because the chromate anion is generally more soluble than Cr^{3+} in soils, and much more toxic to animals, oxidation increases the environmental hazard of this element.

2.5 Factors Influencing the Sorption of Metals by Soil

The metal binding by soils is influenced by many factors including composition of soil, particle concentration and size, solution pH, competitive sorbates, ionic strength, complexation agents, and temperature.

2.5.1 The Properties of the Adsorbent

2.5.1.1 Composition of Soil

The composition of soil is a prime factor influencing metal binding by soil. Jenne (1968) indicated that the quantity of amorphous oxides of Fe and Mn and reactive particulate organic carbon primarily determine the sorption potential of a soil for metals. Davis (1984) also reported the predominant components of fine-grained soils which bind trace metals include the hydrous oxides of iron, aluminum and manganese aluminosilicate minerals, and organic matter.

2.5.1.2 Particle Size and Concentration

The reaction of metal binding by soil is also affected by particle size and concentration. DiToro et al. (1986) reported that reversible partitioning appears to be strongly affected by particle concentration. The partition coefficient for nickel and cobalt sorption to clay and quartz decreases with increasing particle concentration. Hart (1982) pointed out that very small colloidal particles, as well as the smaller clay and silt size particulates, are most likely involved in the sorption reaction because of their large surface areas.

2.5.2 The Properties of the Medium

2.5.2.1 Solution pH

Solution pH is a master factor influencing metal binding by soil because the complexation reaction occurs on a hydroxylated mineral surface that also contains weakly acidic organic material (humic substances). The strong pH dependency of sorption also reflects on the surface charge properties of adsorbent, as well as the species of the adsorbing ions. These will be discussed in Chapter 5.

2.5.2.2 Competitive Sorbates

Competitive sorption is the second most important way in which dissolved solutes affect the uptake of trace metals (Jenne and Zachara, 1984).

Balistreri and Murray (1982) showed that Cu, Pb, Cd, and Zn adsorption on goethite in seawater at pH 8 was slightly affected by competition with Ca and Mg ions. An interesting point with respect to competition between trace metals and Ca ion for binding sites is the apparent stability constants for surface complexes of trace metals with the iron oxyhydroxide are several orders of magnitude greater than are those of Ca with iron oxyhydroxide. This behavior can be contrasted with the stability constants of these metals with organic matter, with the exception of Cu(II). Ca-organic complexes are only slightly weaker than complexes formed by Zn(II) and Cd(II) (Balistreri and Murray, 1982). Competition for binding sites by Ca and Mg ions may be more significant for organic matter than for oxide surfaces.

2.5.2.3 Ionic Strength

Ionic strength affects metal ion activities in solution, and surface charge and double-layer capacitance of the hydrated particles. Consequently, it will influence the binding of metal by soil.

2.5.2.4 Complexation Agents

Complexation reactions will affect the uptake of metal by soil in an aquatic environment. In general, complexation with inorganic ligands other than the hydroxyl ion decreases sorption. However, Jenne and Zachara (1984) reported that exceptions may exist. For example, adsorption of Cu onto goethite is increased in the presence of Cl^- because of the postulated adsorption of CuCl^+ complexes. Complexation with organic ligands having more than one functional group can increase adsorption of complexed metals because the other functional groups bond to the surface of the solids (Davis and Leckie, 1978a).

2.5.2.5 Redox Reaction

The redox conditions of aquatic and soil systems will affect the uptake of redox-sensitive elements. Cr(VI) can be reduced to Cr(III) by reactions involving dissolved organic matter or S^{2-} (Jenne and Zachara, 1984). Cr(III) is strongly sorbed by soil (Mayer and Schick, 1981).

2.5.2.6 Temperature

In pure chemical systems, temperature influences on sorption are predictable since sorption is normally an exothermic process. Thus, sorption is favored by lower temperatures. Browman and Chesters (1975) reported that in general, this predictability holds for soil and sediment systems.

2.6 Soil Quality Standards

Humans, animals, and plants require a number of trace elements in their nutrition. A number of these elements which are required at low concentrations are detrimental to health at higher concentrations. Because water may contain potentially harmful concentrations of trace elements from natural or anthropogenic sources, drinking water criteria and standards have been established. The U.S. EPA Maximum Contaminant Levels (MCL) established under the Safe Drinking Water Act (U.S. Environmental Protection Agency, 1984a) are listed in Table 4.7.

The uncontrolled discharge of heavy metals is common and has resulted in contamination of numerous sites (U.S. Environmental Protection Agency, 1984b). A review of contaminants at Superfund sites indicates that toxic heavy metals are frequently encountered at elevated levels. Ellis et al. (1985) reported frequency of occurrence of metals at uncontrolled hazardous waste sites. The occurrence of toxic heavy metals at the sites surveyed was lead (15 percent), chromium (11 percent), cadmium (8 percent), and copper (7 percent). In addition to lead, six other inorganics

were among the twenty most commonly reported substances. In order of the frequency of their occurrence, these are zinc, cadmium, arsenic, chromium, copper, and mercury.

Metal concentrations at uncontrolled sites extend to quite high values compared to those that are normally encountered. In a study of six U.S. Army installations (Kesari et al., 1987), metal concentration ranges in soils were 0.05 - 453 mg/kg for cadmium; 1.2 - 3,000 mg/kg for chromium; and 1.2 - 4,940 mg/kg for lead. At a former battery recycling plant, the soil contained over 50,000 mg lead/kg (Evangelista and Zownir, 1988). Only recently have soil quality standards begun to be established. A major impetus for these standards has been the need to establish target levels for the cleanup of contaminated sites.

Soil adsorption behavior is the criterion on which to establish a standard based upon a maximum permissible concentration in groundwater. Based on this methodology, clean-up of contaminated sites requires a target such as that provided by standards. The data provided from this research will permit the establishment of these standards for a variety of types of New Jersey soils and will incorporate the influence of pH which is the most important factor in regulating the sorption of metals. A possible methodology will given in Section 4.4.

Chapter 3

ADSORPTION BEHAVIOR OF HEAVY METALS ONTO NEW JERSEY SOILS

3.1 Introduction

The fate of heavy metals in the aquatic environment is governed by many physical, chemical, and biochemical interactions between the metals and their surrounding entities (Huang and Hao, 1989). The adsorption of soluble metals onto soils appears to be an important process that affects soluble metal concentration in a heterogeneous system (Krauskopf, 1956).

The general goal of this study is to obtain a practical set of values that will enable correlation of the soil-water partitioning of each of the four contaminants, Cd(II), Pb(II), Cr(III), and Cr(VI) to each of the fifteen New Jersey soils. These values will be used to model the adsorption process in Chapter 4 and 5.

3.2 Materials and Methods

3.2.1 Soil Pretreatment

The fifteen soil samples collected by the New Jersey Department of Environmental Control and Energy for this study represent a distribution of the major soil types present in New Jersey. These are Birdsboro silt loam, Boonton loam (Bergen County), Boonton loam (Union County), Downer loamy sand, Dunellen sandy loam, fill material dredged from Delaware River, Freehold sandy loam (A horizon), Freehold sandy loam (B horizon), Hazen gravelly loam, Lakewood sand, Penn silt loam, Rockaway stony loam, Sassafras sandy loam, Washington loam, and Whippany silty clay loam. Composite soil samples were taken to a depth of 1 to 2 feet, unless underlying rock prevented this. Rock was encountered only a few inches below the surface for the Boonton and Rockaway soil.

The soils were air dried and agglomerates were broken by hand and by using a wooden mallet. Those particles larger than 2 mm were removed by sieving. The fraction of materials larger than 2 mm was recorded (Table 3.1) so that results could be related to the native soil. All further tests were performed on the less than 2 mm size fraction of the soils. The material having particle size larger than 2 mm does not materially contribute to the sorption of metals by the soils and cannot be reproducibly included in the small samples used in most procedures.

3.2.2 Soil Sample Characterization Analysis

3.2.2.1 Soil pH

This measurement determines the degree of acidity or alkalinity in soil materials suspended in deionized water and 0.01 M calcium chloride solution (Storer, 1991) (Table 3.2). Measurements in CaCl_2 indicate the presence of exchangeable cations that may change the acidity or alkalinity after hydrolysis. Therefore, both liquids are required to fully define the character of the soil pH.

Both methods begin with an air dried, sieved soil. For both methods, weigh out 10 g of soil and place the soil into 20 mL glass vial and add approximately 10 mL of distilled water or 0.01 M calcium chloride solution. Mix thoroughly and let the sample stand for 1 hr or overnight. An ORION combination pH electrode and a Cole Parmer Digiphase pH meter were used for measurements. Meters are calibrated using pH 4 and pH 7 buffer solutions. The pH values of both buffer solutions are rechecked after each 5 measurements. If the measured values are not within ± 0.1 pH units of the accepted value, the data for the previously measured samples are rejected. Following the quality check, the pH meter is restandardized using the two buffer solutions.

3.2.2.2 Particle Size Distribution

Particle size distributions (Table 3.2) were determined by the University of Delaware Soil Testing Laboratory. A hydrometer method was used to determine the size distribution (Sims and Heckendorn, 1991a).

3.2.2.3 Soil Cation Exchange Capacity and Organic Matter

Soil cation exchange capacity and organic matter were determined by the University of Delaware Soil Testing Laboratory. The cation exchange capacity was measured at the soil pH (Sims and Heckendorn, 1991b). The percent organic matter content was measured using the Walkley-Black Wet Combustion Method (Sims and Heckendorn, 1991c). The soil effective cation exchange capacity and organic matter for all soil samples studied are shown in Table 3.3.

3.2.2.4 Soil Metal Oxides

The amount of three metal oxides, Al_2O_3 , Fe_2O_3 , and MnO_2 in the soils was determined by three different extraction methods: (1) perchloric - nitric acid digestion (Hesse, 1972), (2) sodium citrate - bicarbonate - dithionite extraction (Mehra and Jackson, 1960), and (3) acid ammonium oxalate extraction (Iyengar et al., 1981). After extraction, the free metal was measured by a Perkin Elmer 5000 Atomic Absorption Spectrophotometer (Tables 3.4-3.6).

3.2.2.5 Surface Area Measurement

Surface area was measured by sorption of N_2 gas (with He carrier gas) onto the soil using a Quantasorb Model QS-7 sorption system (Quantachrome Corp.) for fifteen New Jersey soils.

The results were evaluated using a linearized form of the BET equation:

$$\frac{1}{X\left(\frac{P_0}{P} - 1\right)} = \frac{C - 1}{X_m C} \frac{P}{P_0} + \frac{1}{X_m C} \quad (3.1)$$

where

P = partial pressure of N_2 (mm Hg),

P_0 = saturated vapor pressure of N_2 (mm Hg),

X = mass of N_2 sorbed (g),

X_m = mass of a monolayer of sorbed N_2 (g),

C = a constant.

The specific surface area of the solid, A_{sp} can be calculated from:

$$A_{sp} = \frac{X_m N A_{cs}}{M_{N_2} W_s} \quad (3.2)$$

where

N = Avogadro's number (6.02×10^{23}),

A_{cs} = cross-sectional area of N_2 ($1.62 \times 10^{-15} \text{ cm}^2$),

M_{N_2} = molecular weight of N_2 (14 g), and

W_s = mass of sample (g).

3.2.3 Adsorption Experiments

Batch equilibration studies were conducted for cadmium(II), lead(II), chromium(VI), and chromium(VI) for the fifteen New Jersey soils. The experimental protocol is diagrammed in Figure 3.1. The soil samples were 1.00 ± 0.01 g per 100 mL solution. Ionic strength was maintained at 0.01N with NaNO_3 . We added cadmium, lead, and chromium nitrate and potassium chromate at concentrations of 1×10^{-5} and 1×10^{-4} M. Fifteen pH values covering the range from 3 to 10 were used and the temperature was maintained at room temperature (25 ± 2 °C). The pH values of the samples were adjusted by adding NaOH or HNO_3 , as required. Samples were shaken at 150 rpm for 24 hours. The pH values were measured again after 24 hours shaking. These values were taken to be the reaction values. The samples were then filtered through 25 mm diameter, $0.45 \mu\text{m}$ membrane filters.

The cadmium and lead concentration in the filtered solution were determined by atomic absorption spectrophotometry using a Perkin Elmer 5000 Atomic Absorption Spectrophotometer.

The procedures for both trivalent and hexavalent chromium determination follow those of ASTM D 1687-86, Standard Test Methods for Chromium in Water (Storer 1990). The hexavalent chromium concentration in the filtered solution was determined by reddish-purple color complex developed between 1,5-diphenylcarbohydrazide and chromate ions in an acid solution. Absorbance was then measured at 540 nm with a Bausch & Lomb Spectronic 21 UVD spectrophotometer using a 1 cm cuvette. The minimum detectable concentration was 1×10^{-7} M (or 0.005 mg/L as Cr). In the acidic solution, both HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ can be detected by this method. Total chromium was

determined by oxidizing the chromium with permanganate followed by analysis of hexavalent chromium. Trivalent chromium was then determined by difference. The procedures for oxidizing chromium with permanganate are: (1) Put 20 mL filtered sample solutions in 30 mL centrifuge tubes and add 1 mL of 5×10^{-3} M KMnO_4 to each tube; (2) Mix well and heat them at 80-90°C for 10-15 minutes in a water bath; (3) Take out samples from water bath; (4) If purple or pink color exists, add 1 mL of 2×10^{-2} M sodium azide (NaN_3) then heat 1 to 5 minutes until the color disappears; (5) Cool down for analysis of hexavalent chromium.

The instruments were calibrated prior to sample analysis. Samples were analyzed in groups of 16, representing a single initial metal concentration. The sixteen samples were the 15 which had been equilibrated at different pH values and the initial metal solution to which no soil was added. At the end of each group of samples, a standard was reanalyzed. If the absorbance displayed for the standard deviated by more than 10% from the initial value, the instruments were restandardized and the entire set of samples was reanalyzed.

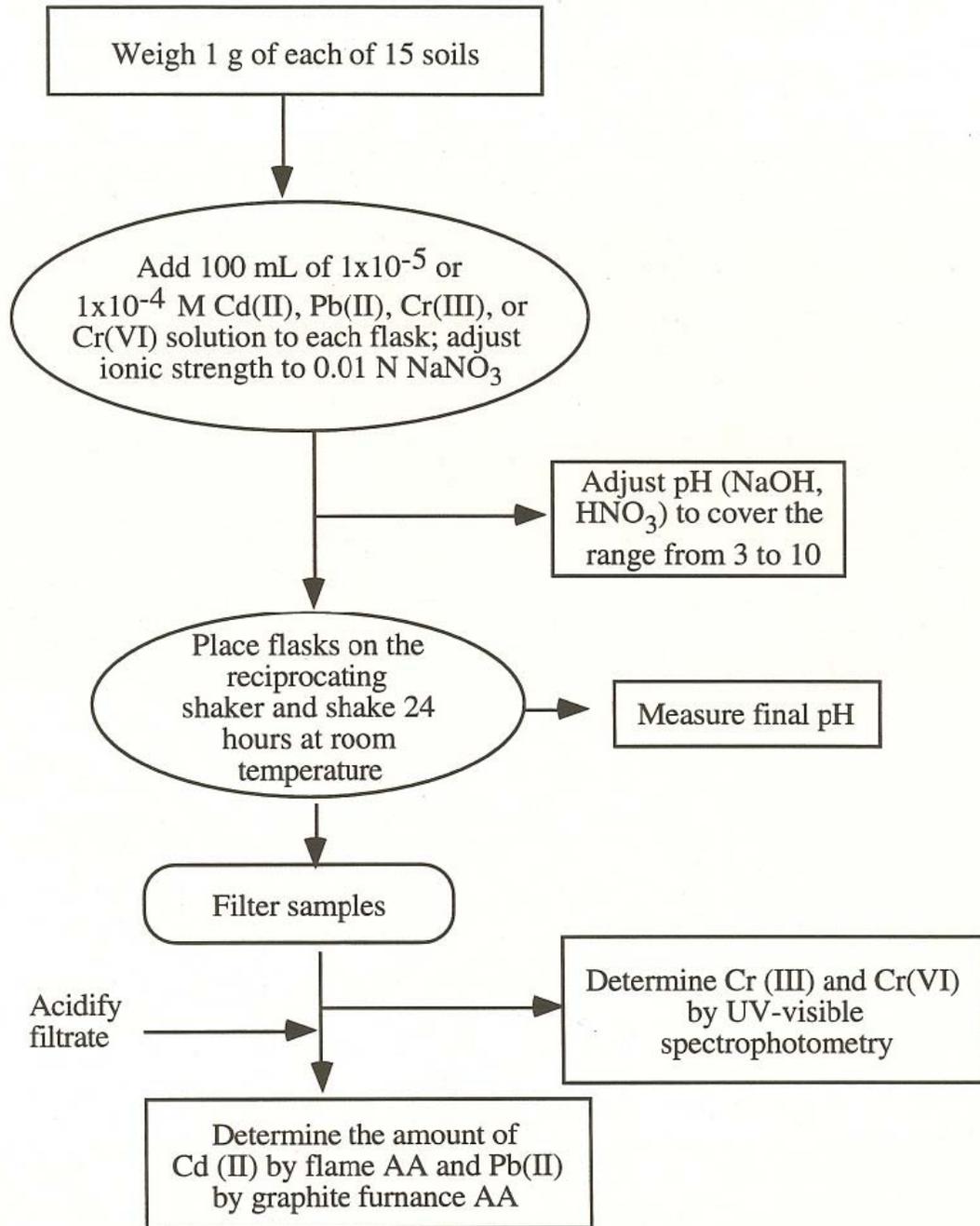


Figure 3.1 Flow chart for the batch experimental protocol.

3.2.4 Adsorption Isotherms

Air dried, sieved soil samples, 1.0 gram, were immersed in 100 mL of 0.01 M NaNO_3 . The pH was adjusted in order to approach the desired pHs, 4.0, 5.5, and 7.0 for cadmium and 4.5 and 6.0 for the other metals. The temperature was maintained at room temperature (25 ± 2 °C). The initial metal concentrations ranged from 1.0×10^{-6} to 5×10^{-3} moles/L, and the equilibration time was 24 hours. After 24 hours, the pH was readjusted to the initial value and the samples were filtered through 0.45 μm membrane filters. It was found that the changes in pH after 24 hours were small (all these adjustments were within ± 0.3 pH). The amount of adsorbed metal was calculated as the difference between the amount added initially and that remaining in solution.

The metal concentration of the liquid phase was analyzed using the same method stated in Section 3.2.3. Replicate tests were conducted for the lowest and the highest metal concentrations to determine the precision.

3.3 Results and Discussion

3.3.1 Soil Sample Characterization Analysis

The basic physical and chemical properties of the New Jersey soils are listed in Table 3.1-Table 3.6.

3.3.1.1 Particle Size Distribution

Particle size distribution is a widely used soil characteristic. Soil particles have diverse composition and structure, and generally differ from one another in both size and shape. They may be organic or inorganic, crystalline or amorphous. The hydrometer method for our study is only for inorganic particles. Soil particles with finer size may provide larger surface area and more adsorption sites for binding heavy metals. The percentages of sand, silt and clay for all soil samples studied are shown in Table 3.2. Clay mineralogy was not studied.

3.3.1.2 Soil pH

We determined the pH of the soils in 0.01 M CaCl_2 in addition to their pH in water. Because the calcium ion can replace the aluminum of soil, the soil pH values obtained in the calcium chloride solution are slightly lower than those measured in water (Peech, 1965). The pH measured in 0.01 M CaCl_2 is about 0.5 pH unit lower than that measured in water (Table 3.2). Released aluminum ions or other cations may undergo hydrolysis generating protons. Soil pH values are useful in determining the solubility of minerals, predicting the mobility of ions in the soil, and assessing the viability of the soil-plant environment. Higher pH values for some soils indicate the presence of alkaline material in the soil that might have a stronger buffering capacity (Foth, 1984a).

Table 3.1 The fraction of material larger than 2 mm.

Soil Name	< 2 mm	> 2 mm*	> 2 mm*
	(g)	(g)	(%)
Birdsboro silt loam	20203.0	10555.5	34.32
Boonton loam (Bergen County)	16571.0	3745.5	18.44
Boonton loam (Union County)	20611.6	9034.6	30.47
Downer loamy sand	16115.5	13132.0	44.90
Dunellen sandy loam	24062.0	6129.0	20.30
Fill materials from Del. River	38273.5	770.0	1.97
Freehold sandy loam (B horizon)	29394.5	2242.0	7.09
Freehold sandy loam (A horizon)	32294.5	2518.0	7.23
Hazen gravelly loam	21928.2	8262.8	27.37
Lakewood sand	18777.5	137.6	0.7
Penn silt loam	21666.5	3372.2	15.6
Rockaway stony loam	15188.5	5902.0	27.98
Sassafras sandy loam	25501.7	761.2	3.0
Washington loam	14807.9	4379.4	29.6
Whippany silty clay loam	18370.8	3946.3	21.5

* includes aggregates

Table 3.2 Analysis of particle size distribution, and soil pH

Soil Name	Particle Size Distribution			pH*	
	Sand %	Silt %	Clay %	In water	In CaCl ₂
Birdsboro silt loam	50	32	18	5.69	5.24
Boonton loam (Bergen County)	60	27	13	5.12	4.31
Boonton loam (Union County)	49	35	16	5.14	4.70
Downer loamy sand	87	5	8	4.74	3.74
Dunellen sandy loam	56	30	14	5.57	4.93
Fill materials from Del. River	85	5	10	4.77	4.09
Freehold sandy loam (B horizon)	37	42	21	6.44	5.72
Freehold sandy loam (A horizon)	92	2	6	5.22	4.87
Hazen gravelly loam	39	38	23	6.02	5.77
Lakewood sand	91	3	6	4.18	3.65
Penn silt loam	25	48	27	4.67	4.13
Rockaway stony loam	54	30	16	4.69	4.23
Sassafras sandy loam	45	37	18	5.78	5.31
Washington loam	20	49	31	6.03	5.80
Whippany silty clay loam	49	16	37	6.17	5.72

* soil pH was determined after 30 min. stirring, and then 1 hour standing.

3.3.1.3 Soil Organic Matter

Almost all soil properties, including adsorption and soil structure stabilities, are dependent upon organic matter (Foth 1984b). The soil organic matter is one of the main substances onto which metals bind. The soils with higher organic carbon content are expected to have a stronger adsorption capacity. Organic matter is determined indirectly, either by analysis for organic carbon or by determining the extent of reduction of a strong oxidizing agent (Broadbent 1965). The latter method (the Walkley - Black method) was employed for determining the soil organic matter. The organic matter content ranged from 0.2 to 8.6 percent in fifteen soils (Table 3.3). Substantial organic matter content is expected in surface soils. Organic matter is generally associated more closely with the smaller particles, particularly clay, and this is supported by comparison of Table 3.3 with Table 3.2. Organic matter coating clay minerals has been found to have an important influence on binding capacity for polar and nonpolar compounds (Oepen et al. 1991).

3.3.1.4 Soil Effective Cation Exchange Capacity

Cation exchange in soils is a reversible interchange reaction between a cation in a solution and another cation on the surface of soils. All soil components take part in cation exchange reactions; however, cation exchange in soil is mainly affected by the amount and kind of organic matter and clay and is a function of pH (Foth, 1984b). Cation exchange capacity is defined as the sum of the total exchangeable cations of a soil. Both exchangeable bases and acidity were determined. The acidity is amount of hydrogen at natural soil pH. The effective cation exchange capacity is the cation

exchange capacity that is determined with unbuffered salt solutions at the soil's natural pH. The effective cation exchange capacity ranged from 0.8 to 9.3 (meq/100 g) in fifteen soils (Table 3.3).

3.3.1.5 Metal Oxides

As mentioned in Section 3.2.2.5, three different extraction methods were used to determine the quantities of three metal oxides. Each extraction method is designed to extract a different fraction of the metal oxides present in the soils. The oxalate method can only extract amorphous oxide. The CBD method extracts amorphous and some crystalline oxides. The acid method can extract all available oxides. Metal oxides provide surface sites for chemisorption of heavy metals. The adsorption reaction generally involves the formation of an inner sphere complex between the hydroxo-metal complex and the negatively charged deprotonated surface of oxides, hydroxides, and oxyhydroxides of Al, Mn, and Fe. The fraction of Fe, Al, and Mn oxides present in the soils from each extraction method was shown in Table 3.4-3.6

Table 3.3 Analysis of soil cation exchange capacity, and soil organic matter.

Soil Name	K	Mg	Ca	ECEC	Organic
					Matter (%)
Birdsboro silt loam	0.47	1.37	3.30	5.30	2.2
Boonton loam (Bergen County)	0.017	0.60	2.59	4.20	5.3
Boonton loam (Union County)	0.19	0.42	1.58	4.20	8.6
Downer loamy sand	0.21	0.43	1.10	2.30	0.8
Dunellen sandy loam	0.13	1.06	2.71	4.20	1.9
Fill materials from Del. River	0.21	0.43	1.10	2.30	1.2
Freehold sandy loam (B horizon)	0.33	0.91	2.84	4.30	2.4
Freehold sandy loam (A horizon)	0.07	0.21	0.46	0.80	0.2
Hazen gravelly loam	0.81	1.90	6.53	9.30	3.1
Lakewood sand	0.01	0.02	0.05	0.90	0.5
Penn silt loam	0.14	0.42	1.25	3.80	1.3
Rockaway stony loam	0.15	0.14	0.59	2.70	4.9
Sassafras sandy loam	0.14	0.69	2.06	3.10	0.6
Washington loam	0.65	1.63	6.59	8.90	2.9
Whippany silty clay loam	0.05	2.52	6.87	9.50	2.3

Table 3.4 Total Fe, Al, and Mn oxides extracted by perchloric - nitric acids.

Soil	Fe ₂ O ₃	Al ₂ O ₃	MnO ₂
Name	(%)		
Birdsboro silt loam	4.723	3.697	0.077
Boonton loam (Bergen County)	3.859	4.541	0.057
Boonton loam (Union County)	2.834	3.866	0.243
Downer loamy sand	0.753	4.878	0.018
Dunellen sandy loam	4.915	4.710	0.062
Fill materials from Del. River	2.065	1.165	0.042
Freehold sandy loam (B horizon)	3.538	3.697	0.037
Freehold sandy loam (A horizon)	1.553	2.009	0.028
Hazen gravelly loam	4.307	4.372	0.116
Lakewood sand	0.657	0.321	0.008
Penn silt loam	4.851	6.397	0.077
Rockaway stony loam	3.538	5.047	0.096
Sassafras sandy loam	2.674	3.191	0.018
Washington loam	5.556	7.072	0.136
Whippany silty clay loam	3.282	5.047	0.023

Table 3.5 Amorphous and crystalline Fe, Al, and Mn oxides extracted by sodium dithionite - citrate - bicarbonate.

Soil Name	Fe ₂ O ₃	Al ₂ O ₃ (%)	MnO ₂
Birdsboro silt loam	1.600	0.744	0.119
Boonton loam (Bergen County)	2.080	0.661	0.076
Boonton loam (Union County)	2.027	2.027	0.195
Downer loamy sand	0.641	0.250	0.014
Dunellen sandy loam	1.281	0.562	0.057
Fill materials from Del. River	2.559	0.118	0.077
Freehold sandy loam (B horizon)	1.813	0.382	0.053
Freehold sandy loam (A horizon)	1.281	0.053	0.017
Hazen gravelly loam	1.493	0.958	0.189
Lakewood sand	1.600	0.201	0.016
Penn silt loam	1.654	0.546	0.142
Rockaway stony loam	3.839	1.731	0.179
Sassafras sandy loam	1.973	0.365	0.032
Washington loam	1.813	0.415	0.236
Whippany silty clay loam	1.494	0.184	0.025

Table 3.6 Amorphous Fe, Al, and Mn oxides extracted by ammonium oxalate.

Soil Type	Fe ₂ O ₃	Al ₂ O ₃ (%)	MnO ₂
Birdsboro silt loam	1.035	0.714	0.025
Boonton loam (Bergen County)	1.563	1.321	0.013
Boonton loam (Union County)	0.773	1.447	0.065
Downer loamy sand	0.076	0.120	0.0003
Dunellen sandy loam	0.435	0.355	0.011
Fill material from Del. River	0.578	0.105	0.012
Freehold sandy loam (B horizon)	0.519	0.442	0.009
Freehold sandy loam (A horizon)	0.178	0.052	0.001
Hazen gravelly loam	1.117	0.574	0.034
Lakewood sand	0.344	0.096	0.0002
Penn silt loam	0.743	0.593	0.022
Rockaway stony loam	0.832	1.181	0.028
Sassafras sandy loam	0.699	0.461	0.005
Washington loam	0.900	0.684	0.038
Whippany silty clay loam	0.736	0.388	0.004

3.3.1.6 Surface Area of Soils

The specific surface area of soils is essential as it is required in the calculation of surface charge. The value of specific surface area ranged from 1.2 to 11.6 m²/g for my soil samples (Table 3.7).

3.3.2 Metal Adsorption

Batch equilibration studies for the adsorption of cadmium, lead, trivalent and hexavalent chromium were conducted at the concentrations of 1x10⁻⁴ and 1x10⁻⁵ M at 15 values of pH, covering the range 3 to 10, for the fifteen New Jersey soils.

3.3.2.1 Effect of pH

The most important factor in controlling the partitioning of a metal to soil is the solution pH (Allen and Huang, 1990). Results of adsorption experiments indicate that metal adsorption is highly pH dependent. The amount of Cd(II), Pb(II), and Cr(III) adsorbed increases with increasing pH (Figure 3.2 and Appendix A). However, adsorption of hexavalent chromium is maximal at low pH and decreases with increasing pH, a trend which is opposite of that for the cationic metal adsorption (Figure 3.2 and Appendix A). In general, the percentage of cationic metal adsorbed increases as pH increases, sharply reaches close to 100 % at a specific pH value, then remains constant over a wide pH region. At the same initial concentration added (same surface loading),

the pH at which adsorption density increases abruptly generally, in my study, followed the order: Cr(III) < Pb(II) < Cd(II).

The high dependence on pH for metal adsorption can be explained by the fact that pH will affect the surface charge of the adsorbent and the degree of ionization and the speciation of adsorbate (Elliott and Huang 1981). This will be considered in more detail in Chapter 5.

3.3.2.2 Effect of Soil Properties

The soils vary in their metal binding strength. Among all soil properties in this study (other than pH), organic content appears to be the most important parameter correlating to metal sorption. The range of adsorption is illustrated by comparison of the Boonton loam (Union County) which displayed the greatest extent of metal adsorption of all the soils (Figures 3.3-3.6) with Freehold sandy loam (A horizon) which has the least metal adsorption capacity (Figures 3.3-3.6). The difference may be attributed to the fact that Boonton loam (Union County) had the highest percentage organic matter and Freehold sandy loam (A horizon) had the lowest (Table 3.3). A detailed analysis of cadmium adsorption and soil composition will be presented in Chapter 4.

Table 3.7 BET specific surface area of soils.

Soil	A _{sp} (surface area)
Name	(m ² /g)
Birdsboro silt loam	7.06
Boonton loam (Bergen County)	7.20
Boonton loam (Union County)	6.45
Downer loamy sand	1.15
Dunellen sandy loam	5.21
Fill materials from Del. River	2.37
Freehold sandy loam (B horizon)	9.01
Freehold sandy loam (A horizon)	2.04
Hazen gravelly loam	5.90
Lakewood sand	1.10
Penn silt loam	8.04
Rockaway stony loam	8.62
Sassafras sandy loam	5.31
Washington loam	11.59
Whippany silty clay loam	5.98

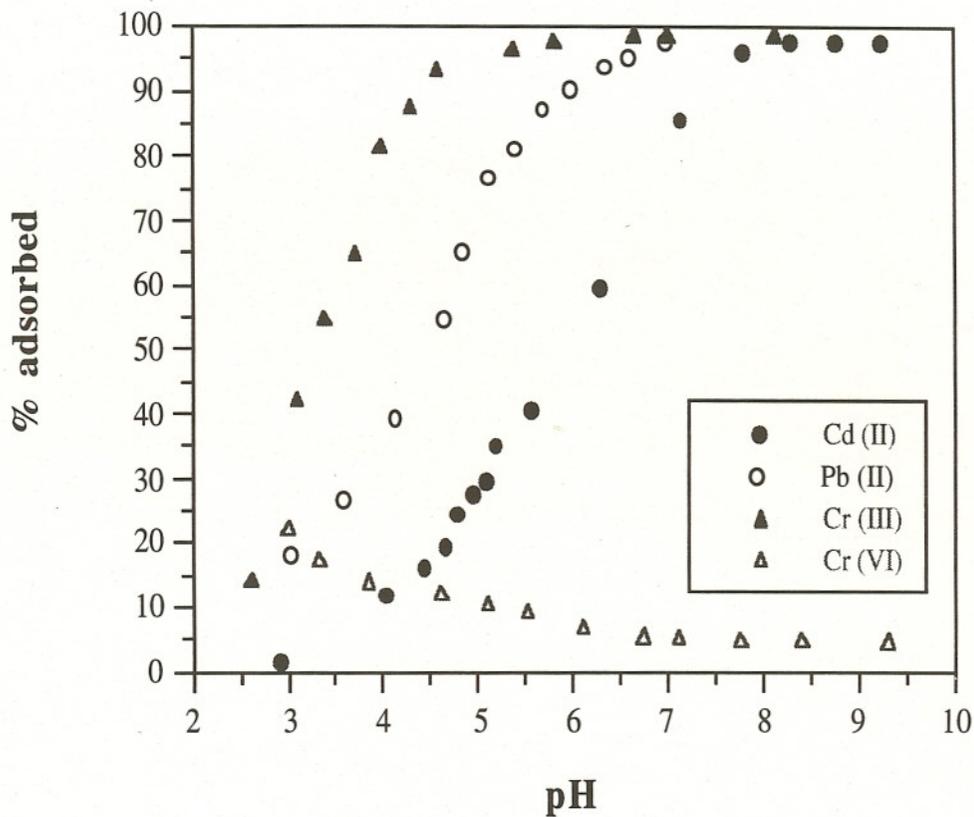


Figure 3.2 Adsorption of 1×10^{-4} M cadmium, lead, trivalent and hexavalent chromium onto Penn silt loam. Soil:water = 1 g/100 mL; I = 0.01 M NaNO_3 ; T = 25 °C.

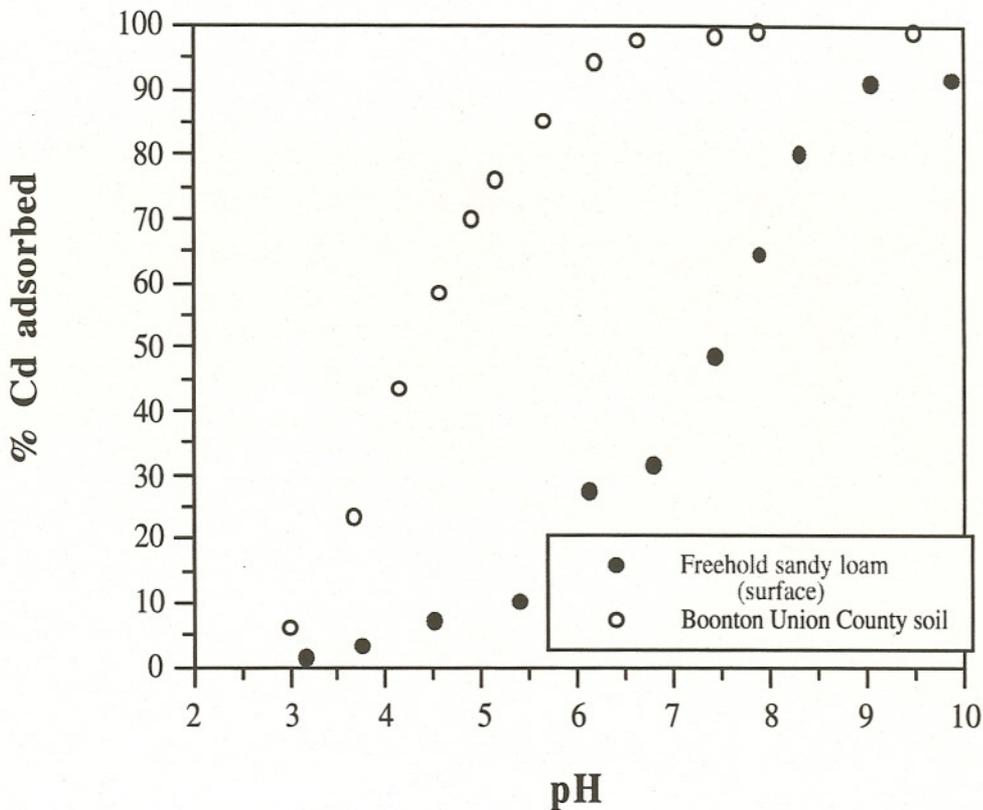


Figure 3.3 Adsorption of 1×10^{-4} M cadmium onto Freehold sandy loam (A horizon) and Boonton loam (Union County); the soils with the least and greatest adsorption. Soil:water = 1 g/100 mL; I = 0.01 M NaNO_3 ; T = 25 °C.

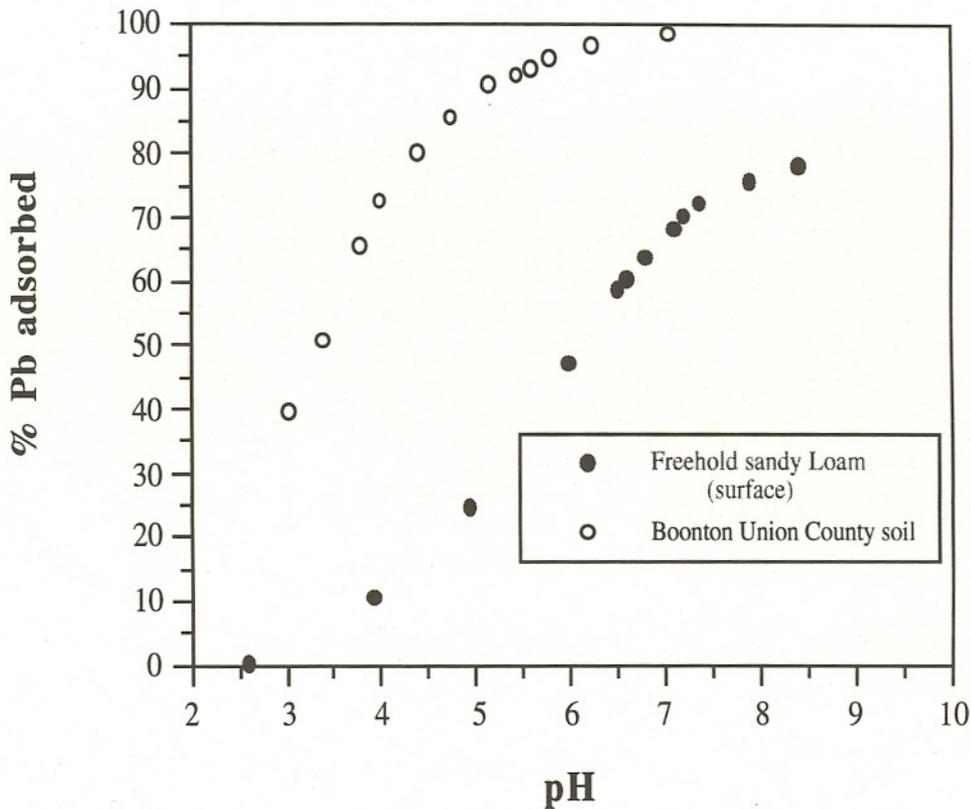


Figure 3.4 Adsorption of 1×10^{-4} M lead onto Freehold sandy loam (A horizon) and Boonton loam (Union County); the soils with the least and greatest adsorption. Soil:water = 1 g/100 mL; I = 0.01 M NaNO_3 ; T = 25 °C.

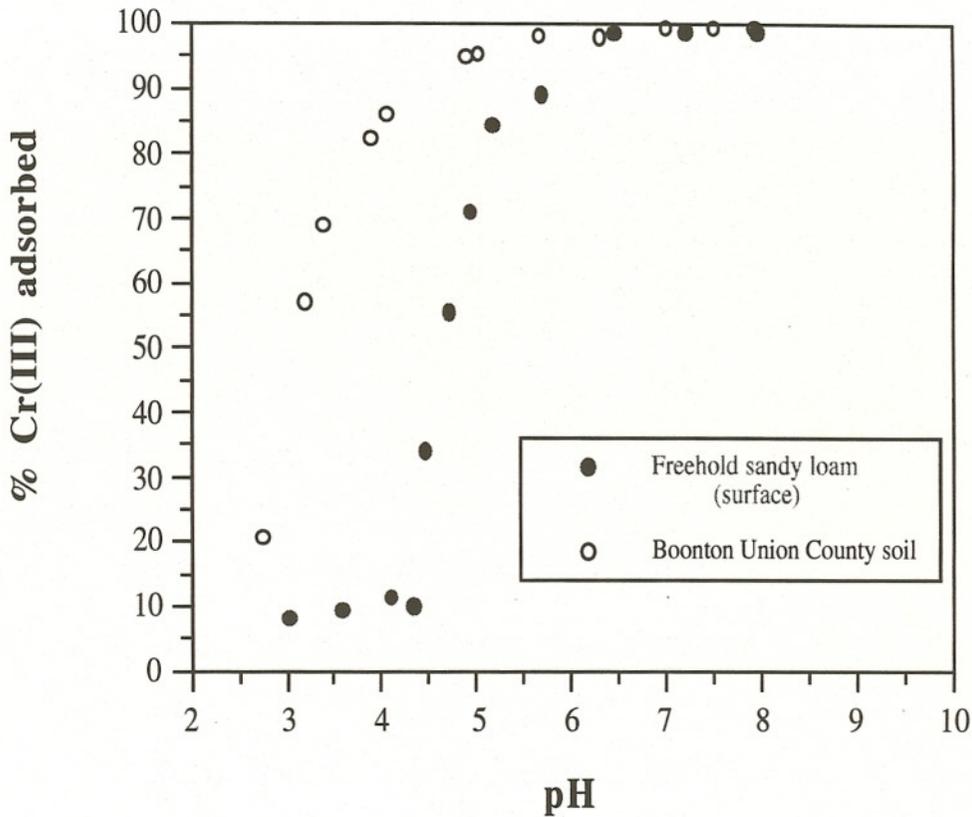


Figure 3.5 Adsorption of 1×10^{-4} M trivalent chromium onto Freehold sandy loam (A horizon) and Boonton loam (Union County); the soils with the least and greatest adsorption. Soil:water = 1 g/100 mL; I = 0.01 M NaNO_3 ; T = 25 $^{\circ}\text{C}$.

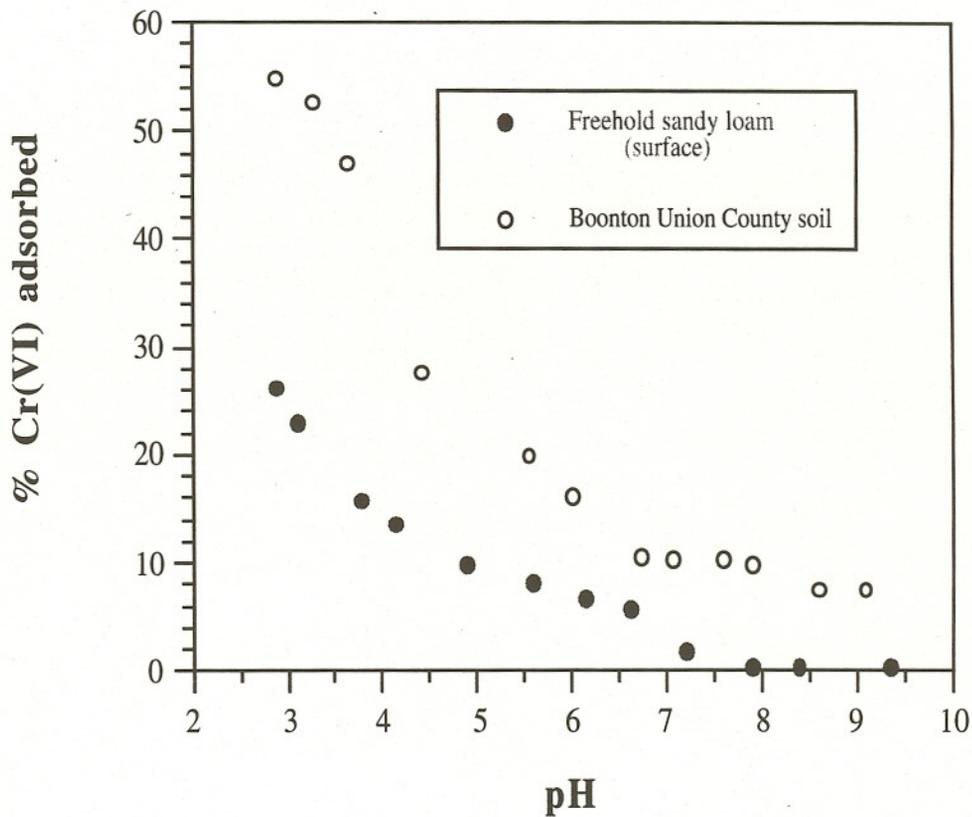


Figure 3.6 Adsorption of 1×10^{-4} M hexavalent chromium onto Freehold sandy loam (A horizon) and Boonton loam (Union County); the soils with the least and greatest adsorption. Soil:water = 1 g/100 mL; I = 0.01 M NaNO_3 ; T = 25°C

3.3.3 Adsorption Isotherms

The adsorption of metal to soils can be characterized by an adsorption isotherm which is a plot of adsorption quantity against aqueous equilibrium concentration of metal at fixed temperature, pH, and applied pressure. The adsorption isotherms allow the partition coefficient data to be extrapolated to high metal loading data. This permits the results to be used in situations where the metal concentration is much greater than that which was present in the adsorption experiments. From these results, we can also determine the maximum capacity of the soil to bind metal. This information is directly useful in the establishment of soil standards.

The adsorption data (Figures 3.7-3.10) were fitted to Langmuir adsorption isotherms using nonlinear regression. The form of the isotherm equation used was:

$$C_s = \frac{\Gamma_m \times K \times C_w}{1 + K \times C_w} \quad (3.2)$$

where

C_s = the sorbed concentration of metal ($\mu\text{g/g}$)

C_w = the equilibrium concentration of metal in solution (mg/L)

Γ_m = maximum sorbed concentration of metal ($\mu\text{g/g}$)

K = Langmuir constant (L/mg)

A nonlinear-program (Wilkinson, 1992) was applied to perform the regression. The isotherm parameters are given in Tables 3.8-11.

From the parameters shown in Table 3.8, at the same pH, the saturated adsorption quantities Γ_m for the New Jersey soils vary widely. For example, at pH 7.0 the Boonton loam (Union County) has the greatest maximum adsorption quantity, 6469 ($\mu\text{g/g}$), and the Freehold sandy loam (A horizon) has the smallest maximum adsorption quantity, 714 ($\mu\text{g/g}$). A similar result can be observed from the Langmuir equation Γ_m values for other metals, as shown in Tables 3.9-3.11.

The strong pH dependence of adsorption reflects the hydrolysis or protonation of the sorbing ions. For example, for aqueous cadmium ion, the hydrolysis product, $\text{Cd}(\text{OH})^+$, was favored to sorb onto MnO_2 at high pH (Fu et al., 1991). More importantly, the variable surface charge of the sorbent is governed by the acidity of surface groups. The solution pH affects the surface species, i.e., the concentration of protonated sites in the sorbent. The higher the pH, the higher the concentration of protonated sites. The negatively charged site species were favored to sorb positively charged Cd(II) ions. As pH increases, the net proton charge of a soil particle will change and the electrostatic attraction of a soil sorbent for cadmium will be enhanced.

In addition to the ionization of surface binding sites, which has a strong effect on the sorption of metals to soils, the displacement of the equilibrium of surface complexation reactions and the competition between H_3O^+ and Al^{3+} ions for negatively charged sites are also important factors influencing metal cation sorption onto soil particles.

The values of Γ_m at high pH differ greatly from those at low pH for the same soil, such as the Boonton loam (Union County), at same ionic strength, as shown in Tables 3.8-3.11. The comparisons of the adsorption isotherms at different pH values

are shown in Figures 3.7-3.10 and Appendix B. The sorption quantities at higher pH are higher than that at lower pH for each soil tested at the same equilibrium aqueous metal concentration and same ionic strength for all metals (Figures 3.7-3.10). The application of a surface complexation model to explain this will be presented in Chapter 5.

The Freundlich equation is frequently used to treat adsorption onto a heterogeneous surface composed of different classes of adsorption sites, with adsorption on each class of site following the Langmuir isotherm (Weber, 1972). The Freundlich equation is

$$C_s = K_f C_w^{1/n} \quad (3.3)$$

where C_s and C_w have been defined previously and K_f and $1/n$ are experimentally determined. The equation can be linearized by taking the logarithm of both sides of the equation. This gives

$$\log C_s = \log K_f + \frac{1}{n} \log C_w \quad (3.4)$$

It should be noted that the Freundlich isotherm does not predict an adsorption maximum. Values of the Freundlich constants and graphs are presented in Appendix C. These adsorption studies were designed to achieve saturation as is shown in the Langmuir isotherms presented in Appendix B. Consequently, many of the Freundlich isotherms presented in Appendix C deviate from linearity.

Table 3.8 Langmuir constants for the adsorption of cadmium on fifteen New Jersey soils at three pH values. Soil:water = 1 g/100 mL; I = 0.01 M NaNO₃; T = 25 °C.

Soil Name	pH 4.0		pH 5.5		pH 7.0	
	Γ_m	K	Γ_m	K	Γ_m	K
	($\mu\text{g/g}$)	(L/mg)	($\mu\text{g/g}$)	(L/mg)	($\mu\text{g/g}$)	(L/mg)
Birdsboro silt loam	1123	0.016	4113	0.027	3300	0.310
Boonton loam (Bergen County)	930	0.043	2718	0.121	3977	0.357
Boonton loam (Union County)	1864	0.037	6285	0.049	6469	0.847
Downer loamy sand	2644	0.002	1208	0.075	2580	0.120
Dunellen sandy loam	1123	0.017	3021	0.040	2897	0.245
Fill materials from Del. River	886	0.014	1987	0.054	2161	0.210
Freehold sandy loam (B horizon)	942	0.004	2286	0.115	3170	0.277
Freehold sandy loam (A horizon)	293	0.019	740	0.030	714	0.171
Hazen gravelly loam	1973	0.014	5110	0.050	4333	0.602
Lakewood sand	161	0.034	323	0.215	826	0.378
Penn silt loam	154	0.175	1174	0.095	1524	0.549
Rockaway stony loam	1180	0.012	3370	0.048	3939	0.210
Sassafras sandy loam	116	0.289	984	0.081	1124	0.297
Washington loam	826	0.119	3038	0.075	2050	1.550
Whippany silty clay loam	1273	0.075	1418	0.358	1968	0.821

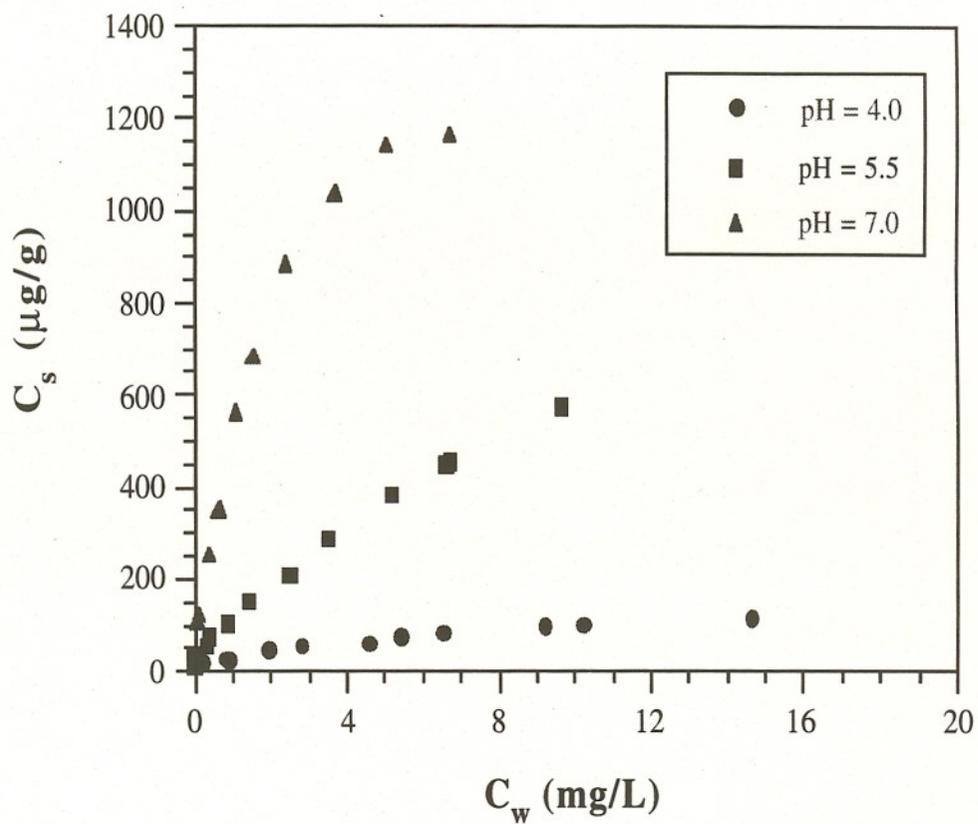


Figure 3.7 Adsorption isotherms of cadmium at three pH values for Penn silt loam. Soil:water = 1 g/100 mL; I = 0.01 M NaNO_3 ; T = 25 °C.

Table 3.9 Langmuir constants for the adsorption of lead on fifteen New Jersey soils at two pH values. Soil:water = 1 g/100 mL; I = 0.01 M NaNO₃; T = 25 °C.

Soil Name	pH 4.5		pH 6.0	
	Γ_m	K	Γ_m	K
	($\mu\text{g/g}$)	(L/mg)	($\mu\text{g/g}$)	(L/mg)
Birdsboro silt loam	6914	0.113	15747	0.003
Boonton loam (Bergen County)	7529	0.048	18073	0.018
Boonton loam (Union County)	9127	0.065	24720	0.030
Downer loamy sand	2017	0.019	7822	0.016
Dunellen sandy loam	4586	0.108	16502	0.016
Fill materials from Del. River	3455	0.061	10013	0.016
Freehold sandy loam (B horizon)	4415	0.118	13572	0.018
Freehold sandy loam (A horizon)	677	0.093	4421	0.060
Hazen gravelly loam	10785	0.178	16303	0.233
Lakewood sand	850	0.032	4335	0.139
Penn silt loam	7067	0.015	15374	0.008
Rockaway stony loam	3711	0.045	26184	0.008
Sassafras sandy loam	3118	0.09	12825	0.043
Washington loam	9692	0.177	16991	0.096
Whippany silty clay loam	9025	0.127	18531	0.039

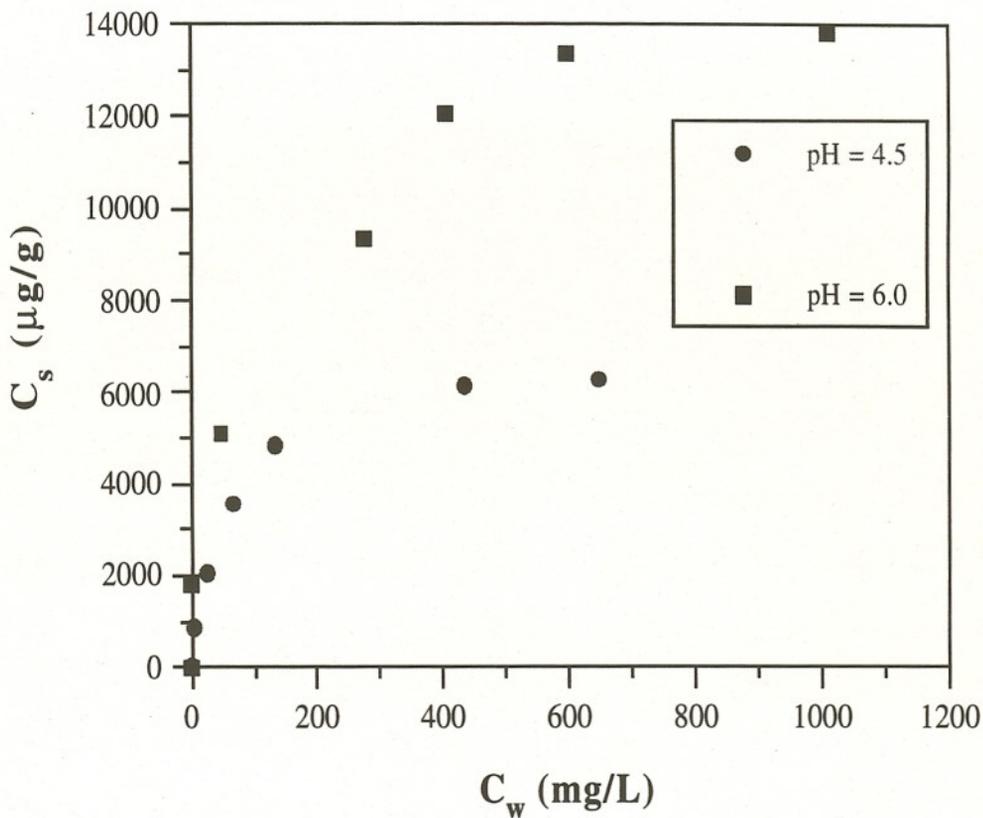


Figure 3.8 Adsorption isotherms of lead at two pH values for Penn silt loam Soil:water = 1 g/100 mL; I = 0.01 M NaNO₃; T = 25 °C.

Table 3.10 Langmuir constants for the adsorption of trivalent chromium on fifteen New Jersey soils at two pH values. Soil:water = 1 g/100 mL; I = 0.01 M NaNO₃; T = 25 °C.

Soil Name	pH 4.5		pH 6.0	
	Γ_m	K	Γ_m	K
	($\mu\text{g/g}$)	(L/mg)	($\mu\text{g/g}$)	(L/mg)
Birdsboro silt loam	2803	0.122	5435	0.086
Boonton loam (Bergen County)	3855	0.428	6707	0.050
Boonton loam (Union County)	3270	0.111	6962	0.114
Downer loamy sand	924	0.022	3220	0.025
Dunellen sandy loam	2879	0.053	6801	0.029
Fill materials from Del. River	1702	0.047	3635	0.039
Freehold sandy loam (B horizon)	2154	0.101	5498	0.034
Freehold sandy loam (A horizon)	170	0.370	1919	0.078
Hazen gravelly loam	4044	0.108	5570	0.428
Lakewood sand	239	0.093	4781	0.011
Penn silt loam	2932	0.028	6613	0.019
Rockaway stony loam	2743	0.026	8717	0.021
Sassafras sandy loam	1342	0.107	5777	0.073
Washington loam	3357	0.264	5109	0.749
Whippany silty clay loam	4350	0.037	6758	0.046

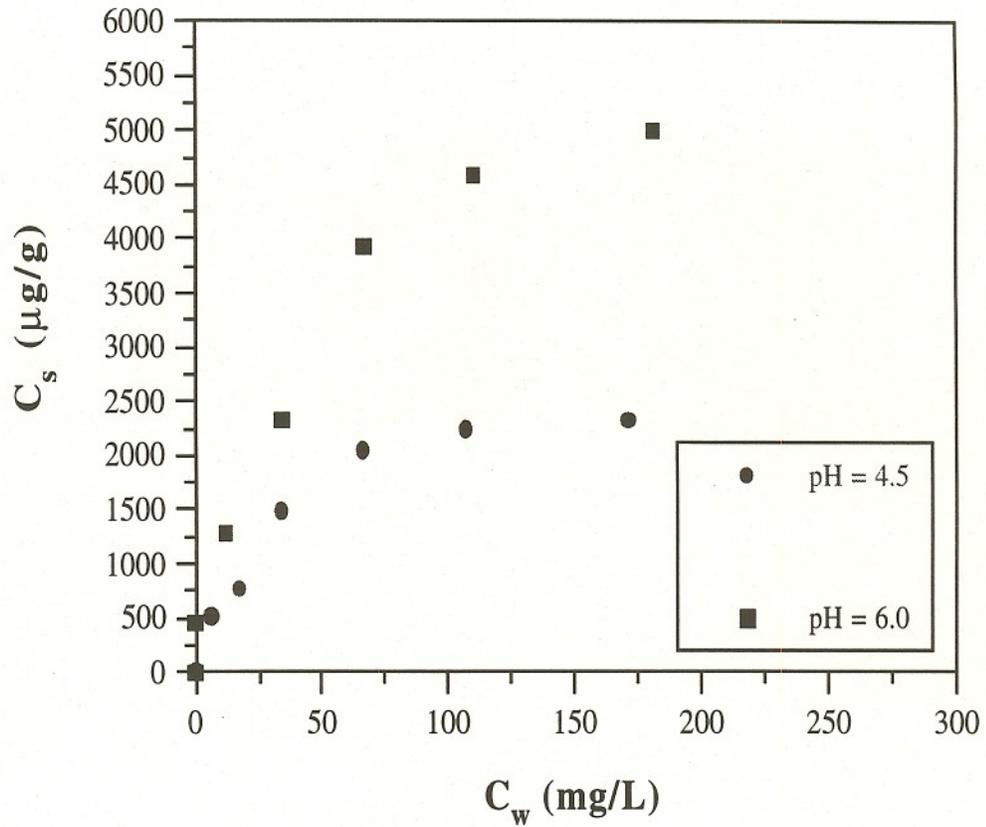


Figure 3.9 Adsorption isotherms of trivalent chromium at two pH values for Penn silt loam. Soil:water = 1 g/100 mL; I = 0.01 M NaNO_3 ; T = 25 °C.

Table 3.11 Langmuir constants for the adsorption of hexavalent chromium on fifteen New Jersey soils at two pH values. Soil:water = 1 g/100 mL; I = 0.01 M NaNO₃; T = 25 °C.

Soil Name	pH 4.5		pH 6.0	
	Γ_m	K	Γ_m	K
	($\mu\text{g/g}$)	(L/mg)	($\mu\text{g/g}$)	(L/mg)
Birdsboro silt loam	151	0.208	104	0.117
Boonton loam (Bergen County)	825	0.048	564	0.016
Boonton loam (Union County)	718	0.089	584	0.035
Downer loamy sand	290	0.090	227	0.066
Dunellen sandy loam	364	0.069	210	0.039
Fill materials from Del. River	325	0.059	130	0.133
Freehold sandy loam (B horizon)	318	0.073	169	0.091
Freehold sandy loam (A horizon)	125	0.240	54	0.634
Hazen gravelly loam	289	0.097	133	0.063
Lakewood sand	153	0.221	96	0.230
Penn silt loam	147	0.163	118	0.178
Rockaway stony loam	483	0.101	341	0.054
Sassafras sandy loam	313	0.073	146	0.085
Washington loam	334	0.053	112	0.092
Whippany silty clay loam	304	0.128	95	0.167

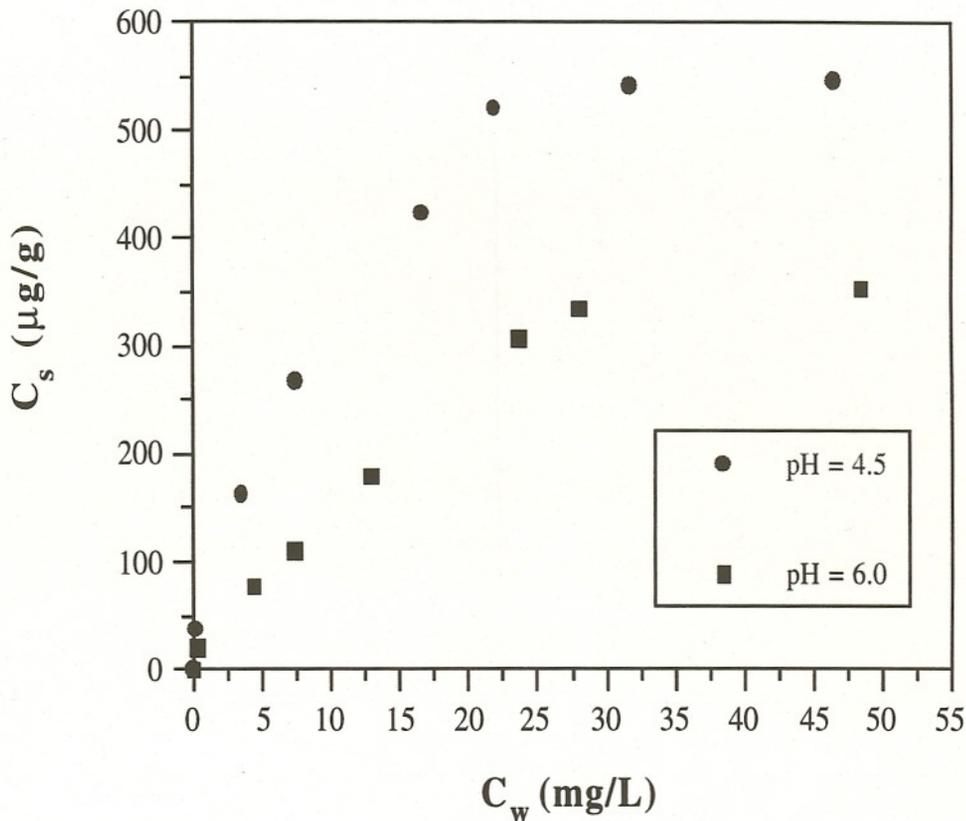


Figure 3.10 Adsorption isotherms of hexavalent chromium at two pH values for Penn silt loam. Soil:water = 1 g/100 mL; I = 0.01 M NaNO_3 ; T = 25 °C.

PREDICTION OF CONDITIONAL PARTITION COEFFICIENTS AND APPLICATION TO SOIL QUALITY CRITERIA

4.1 Introduction

In view of the variety of soils, the mechanism of interaction between metal ions and natural soil particles is complicated. Much of the work relating to trace metal sorption by surfaces in natural systems has involved the use of well defined "model surfaces such as clay, aluminum oxides, iron oxides, and manganese oxides. These substances are present in soils and including them is necessary to develop an understanding of mechanisms for the adsorption of metals.

As mentioned in Chapter 2, the most important factor in controlling the partitioning of a metal to soil is the solution pH. Different soils exhibit different absorption ability, as is shown in Figures 3.3-3.6 which compare the adsorption of Boonton loam (Union County) and Freehold sandy loam (A horizon) for cadmium, lead, trivalent, and hexavalent chromium.

The binding of metals by soluble complexing agents is similarly highly dependent on pH. Knowledge of only the stability constant for metal reactions with the

complexing agent is insufficient to permit one to calculate the free metal ion concentration. For example, the concentration of free copper in a solution containing Cu-EDTA increases 25-fold as the pH is decreased from 7 to 6 (Ringbom 1963). To predict the extent of reaction of copper with EDTA, it is necessary to also have equilibrium constants for the reaction of EDTA with protons. The same situation is true for soil solid phase reactions. Proton and metal species compete with each other for available surface binding sites on a soil. Thus, it is also necessary that equilibrium constants for reaction of the soil solid phase with protons be available. In the absence of such information, which can be obtained from acid-base titration of soil solid, it would be necessary to measure the extent of adsorption at each pH of interest! In this chapter measurements at fixed pH will be analyzed to distinguish the contributions of soil components to adsorption.

4.2 Model Development

Based upon the adsorptive equilibrium concept, a model for the sorption of metal by soil surface substances at fixed pH was developed. A preliminary statistical analysis of the variation of metal adsorption with measured soil properties was made. A general diagram illustrating this model is shown in Figure 4.1. Clay content and surface area showed less relationship with adsorption. Based on this analysis, the major adsorbing sites for binding M^{+2} are considered to be Fe_2O_3 , Al_2O_3 , Mn_2O_3 , and organic matter. The model uses fixed ionic strength and fixed initial metal concentration.

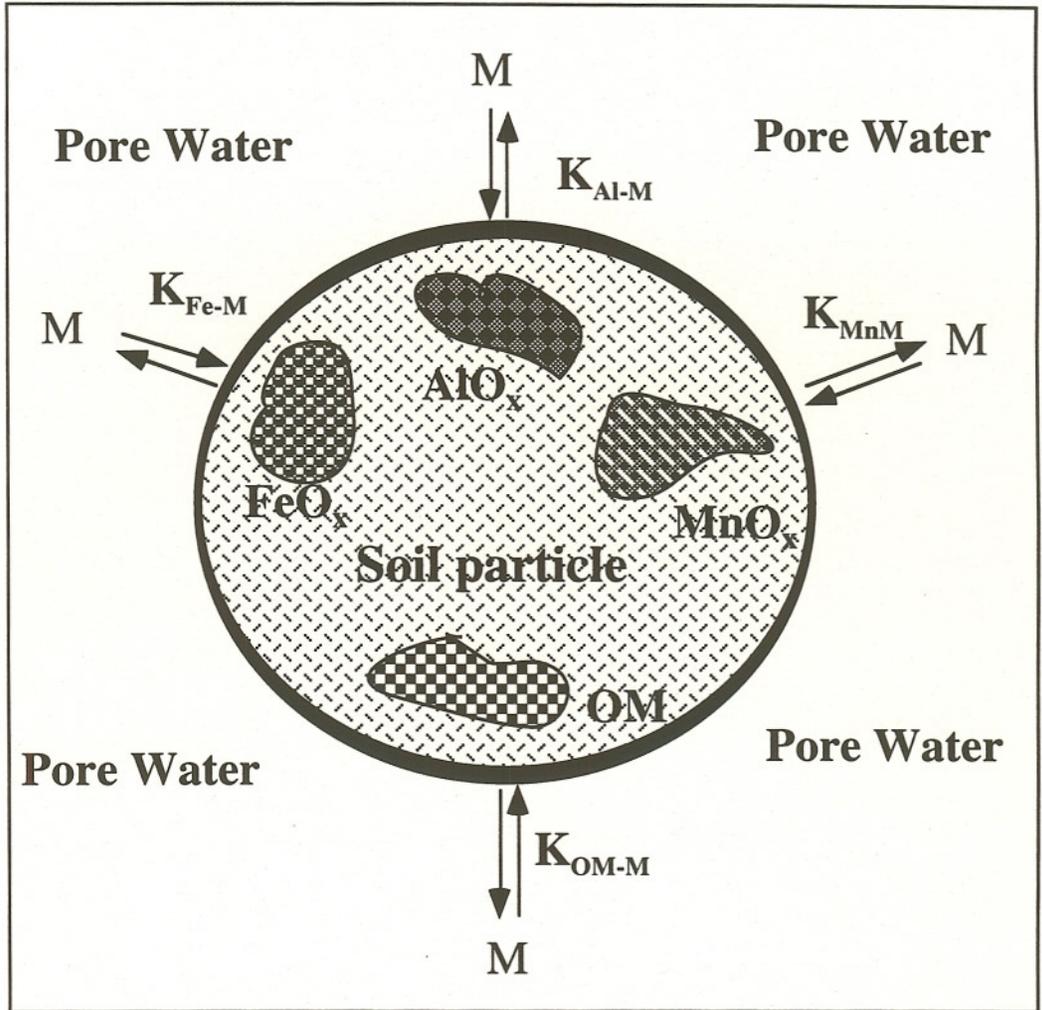


Figure 4.1 Diagram for metal sorption onto different phases of soil. ($K_{\text{Fe-M}}$, $K_{\text{Al-M}}$, $K_{\text{Mn-M}}$, and $K_{\text{OM-M}}$ are the conditional formation constants for sorption of the metal onto iron oxide, aluminum oxide, manganese oxide, and organic matter, respectively).

A typical reaction between metal and a sorption phase can be written as Equation

4.1:



$$K_{S-M} = \frac{[S - M]}{[S][M]} \quad (4.2)$$

K is the conditional stability constant of this reaction. For each individual sorption phase in the model, the reactions following Equation 4.2, can be expressed as 4.3-4.6:

$$[FeO_x - M] = K_{FeO_x - M} [M][FeO_x] \quad (4.3)$$

$$[AlO_x - M] = K_{AlO_x - M} [M][AlO_x] \quad (4.4)$$

$$[MnO_x - M] = K_{MnO_x - M} [M][MnO_x] \quad (4.5)$$

$$[OM - M] = K_{OM - M} [M][OM] \quad (4.6)$$

where $[FeO_x]$, $[AlO_x]$, $[MnO_x]$, and $[OM]$ represent the quantities of available amorphous iron oxide, aluminum oxide, manganese oxide and organic matter, respectively.

$[FeO_x - M]$, $[AlO_x - M]$, $[MnO_x - M]$, and $[OM - M]$ are the quantities of the metal sorbed by the iron oxide, aluminum oxide, manganese oxide and organic matter,

respectively. $K_{\text{FeO}_x\text{-M}}$, $K_{\text{AlO}_x\text{-M}}$, $K_{\text{MnO}_x\text{-M}}$, and $K_{\text{OM-M}}$ are the corresponding conditional formation constants. The total quantities of the metal sorbed by the soil particle, $[\text{S-M}]$, are the sum of the quantities of the metal sorbed by the individual sorption phases as is expressed in Equation 4.7:

$$[\text{S-M}] = [\text{FeO}_x\text{-M}] + [\text{AlO}_x\text{-M}] + [\text{MnO}_x\text{-M}] + [\text{OM-M}] \quad (4.7)$$

Equilibrium free metal concentration present in solution, then can be obtained by combining Equations 4.3 to 4.6 with Equation 4.7 to give Equation 4.8:

$$[\text{M}] =$$

$$\frac{[\text{S-M}]}{\left\{ K_{\text{FeO}_x\text{-M}}[\text{FeO}_x] + K_{\text{AlO}_x\text{-M}}[\text{AlO}_x] + K_{\text{MnO}_x\text{-M}}[\text{MnO}_x] + K_{\text{OM-M}}[\text{OM}] \right\}} \quad (4.8)$$

Rearranging Equation 4.7

$$\frac{[\text{M}]}{[\text{S-M}]} = \frac{1}{\sum_{\text{sites}} K_{\text{S}_i\text{-M}}[\text{S}]_i} = \frac{1}{K_d} \quad (4.9)$$

Therefore the partition coefficient,

$$K_d = \sum_{\text{sites}} K_{\text{S}_i\text{-M}}[\text{S}]_i \quad (4.10)$$

where $[\text{S}]_i$ is site concentration of a particular class of sites.

4.3 Results and Discussion

The model in Section 4.2 is applied to the experimental adsorption data for cadmium presented in Chapter 3. For each of the fifteen soils the concentration of adsorbed cadmium is computed from a mass balance. This concentration is divided by the measured soluble cadmium to obtain experimental partition coefficients at each fixed pH and at the soil natural pH (Equation 4.9). These partition coefficients were regressed against site concentrations for the component considered: organic matter, iron oxide, aluminum oxide, and manganese oxide (Table 3.3 and Table 3.6) using Equation 4.10 to obtain conditional formation constants for each phase. Separate regression was done omitting one or more sorption phases. The conditional formation constants for cadmium with organic matter as a function of pH are given in Table 4.1. These formation constants were then used to calculate predicted partition coefficients. These were compared with the experimental partition coefficients in Tables 4.3-4.6 and Figures 4.2-4.6. The success of the model including different components can be evaluated by the goodness of fit values, R^2 , for regression of experimental partition coefficients against partition coefficients calculated from the conditional formation constants (Table 4.2).

Comparisons of the results predicted by the model for different pH values with the experimental data for fifteen soils are shown in Table 4.3-4.6. The single component that gives the best correlation is organic matter. A small improvement is obtained by including aluminum while only slight improvement is obtained with three components (organic matter, aluminum and manganese) (Table 4.2). The results show that, at each fixed pH, this model fits the experimental data very well by considering organic matter as the only sorption phase (Table 4.3-4.5).

This model did not predict the metal sorption at soil natural pH (Table 4.6, Figure 4.5), as expected. Because the proton can compete for available surface binding sites with metal, different soil natural pH values result in a different proton concentration that will significantly affect the metal binding onto soil. The partition model considered here must be expanded by considering surface complex formation. This will be treated in Chapter 5.

The present study was conducted with a large initial concentration of cadmium. Therefore, we were concerned that the coefficients that were determined might not be applicable to the lower concentrations present in most field situations. As a check, we compared our batch K_d values to the results for the large field study of Anderson and Christensen (1988) who obtained their partition coefficients at the pH of the soils and with the naturally occurring concentrations of cadmium. The K_d values for our soils are comparable although our soluble cadmium concentrations are much greater (Figure 4.7). The strong dependency of partition coefficient on pH is shown in this figure.

Table 4.1 Conditional formation constants for cadmium at four different pH values by considering only organic matter in the model. Correlations determined for 1×10^{-4} M added cadmium.

Component	Conditional formation constants (mL/g organic matter)				
	Considered	pH = 4.0	pH = 5.0	pH = 6.0	Soil natural pH
K_{Cd-OM}		6.41	26.04	136.54	30.63

Table 4.2 Comparison of R^2 for regression of experimental partition coefficients against predicted values obtained from conditional formation constants. The regressions were performed at four different pH values by considering single, double, and triple components in the model (Equation 4.10). Correlations determined for 1×10^{-4} M added cadmium.

Component	R^2				
	Considered	pH = 4.0	pH = 5.0	pH = 6.0	Soil natural pH
OM ¹		0.928	0.958	0.966	0.104
Fe		0.275	0.357	0.263	0.087
Al		0.722	0.789	0.720	0.040
Mn		0.705	0.684	0.593	0.105
OM & Al		0.931	0.968	0.973	0.149
OM, Al & Mn		0.958	0.973	0.975	0.172

¹ Organic matter content

Table 4.3 Comparison of observed (experimental) and predicted partition coefficient for cadmium at pH 4.0 by considering single, double, and triple components in the model. Correlations determined for 1×10^{-4} M added cadmium.

Soil ¹ Number	Observed K_d (mL/g)	Predicted K_d (mL/g)					
		OM ²	Fe	Al	Mn	OM & Al	OM, Al & Mn
1	7.7	7.2	19.6	16.6	10.7	6.3	5.7
2	3.6	6.6	12.3	6.2	7.4	7.0	6.1
3	9.7	11.7	20.5	20.4	22.6	10.8	12.9
4	28.9	18.1	23.8	23.0	33.8	17.5	22.0
5	22.2	22.0	20.4	14.5	10.0	22.8	19.8
6	4.6	4.7	8.8	4.9	7.9	5.0	4.7
7	16.6	18.8	15.9	16.1	13.5	19.1	17.6
8	30.0	34.8	22.4	37.2	26.8	34.1	32.8
9	11.8	11.1	17.1	6.4	15.6	11.9	12.8
10	6.0	8.5	6.7	6.9	7.4	9.0	7.8
11	61.0	58.5	21.2	44.8	52.7	59.2	61.8
12	20.2	15.5	14.2	13.6	14.9	15.9	15.5
13	14.5	17.5	26.6	23.8	24.7	16.7	18.3
14	25.4	23.2	28.3	19.8	31.0	23.6	26.6
15	33.0	37.3	37.5	41.2	16.3	36.4	31.1

¹Soil number: 1: Sassafras sandy loam; 2: Lakewood sand; 3: Penn silt loam; 4: Whippany silty clay loam; 5: Washington loam; 6: Freehold sandy loam (A horizon); 7: Freehold sandy loam (B horizon); 8: Rockaway stony loam; 9: Fill materials from Del. River; 10: Downer loamy sand; 11: Boonton loam (Union County); 12: Dunellen sandy loam; 13: Birdsboro silt loam; 14: Hazen gravelly loam; 15: Boonton loam (Bergen County).

²Organic matter content.

Table 4.4 Comparison of observed (experimental) and predicted partition coefficient for cadmium at pH 5.0 by considering single, double, and triple components in the model. Correlations determined for 1×10^{-4} M added cadmium.

Soil ¹ Number	Observed K_d (mL/g)	Predicted K_d (mL/g)					
		OM ²	Fe	Al	Mn	OM & Al	OM, Al & Mn
1	27.9	33.0	83.4	70.7	48.3	33.8	31.8
2	13.5	30.4	49.8	27.1	35.0	29.9	27.4
3	61.4	51.2	87.5	86.5	95.1	52.0	58.1
4	92.5	77.2	102.4	97.4	139.3	77.8	90.5
5	99.9	92.9	86.9	62.0	45.5	92.0	83.3
6	9.4	22.5	34.2	21.8	37.2	22.2	21.2
7	90.2	79.8	66.4	68.5	59.3	79.5	75.1
8	130.8	144.9	95.9	156.9	111.7	145.6	141.9
9	43.0	48.6	71.9	28.2	67.6	47.8	50.6
10	30.0	38.2	24.5	30.0	35.3	37.7	34.2
11	239.5	241.3	90.4	188.7	213.7	240.6	248.1
12	68.9	66.8	58.4	58.1	64.8	66.5	65.2
13	90.9	74.6	115.1	101.0	103.4	75.3	80.0
14	116.4	98.1	122.9	84.3	128.2	97.8	106.3
15	140.7	155.4	165.0	173.6	70.3	156.2	141.1

¹Soil number: 1: Sassafras sandy loam; 2: Lakewood sand; 3: Penn silt loam; 4: Whippany silty clay loam; 5: Washington loam; 6: Freehold sandy loam (A horizon); 7: Freehold sandy loam (B horizon); 8: Rockaway stony loam; 9: Fill materials from Del. River; 10: Downer loamy sand; 11: Boonton loam (Union County); 12: Dunellen sandy loam; 13: Birdsboro silt loam; 14: Hazen gravelly loam; 15: Boonton loam (Bergen County).

²Organic matter content.

Table 4.5 Comparison of observed (experimental) and predicted partition coefficient for cadmium at pH 6.0 by considering single, double, and triple components in the model. Correlations determined for 1×10^{-4} M added cadmium.

Soil ¹ Number	Observed K_d (mL/g)	Predicted K_d (mL/g)					
		OM ²	Fe	Al	Mn	OM & Al	OM, Al & Mn
1	77.8	59.6	324.2	261.0	153.3	24.7	21.2
2	39.8	46.0	174.0	43.1	89.0	61.7	57.1
3	115.1	155.2	342.8	339.8	381.3	119.2	129.9
4	317.8	291.8	409.3	394.2	595.9	268.5	291.2
5	414.5	373.7	339.9	217.5	139.9	409.3	393.8
6	24.9	5.0	103.8	16.9	99.7	19.4	17.6
7	399.7	305.4	248.1	249.7	207.0	320.1	312.2
8	591.1	646.8	380.5	690.9	461.8	618.7	612.0
9	115.5	141.6	273.0	48.5	247.2	174.2	179.1
10	84.1	86.9	60.6	57.5	90.3	107.0	100.7
11	1180.8	1152	355.5	849.7	957.9	1181.4	1194.8
12	184.6	237.1	212.5	197.8	233.8	251.5	249.3
13	187.0	278.1	466.4	412.1	421.5	247.9	256.2
14	515.3	401.0	501.1	328.5	542.2	414.7	429.9
15	633.4	701.4	689.8	774.4	260.6	663.2	636.4

¹Soil number: 1: Sassafra sandy loam; 2: Lakewood sand; 3: Penn silt loam; 4: Whippany silty clay loam; 5: Washington loam; 6: Freehold sandy loam (A horizon); 7: Freehold sandy loam (B horizon); 8: Rockaway stony loam; 9: Fill materials from Del. River; 10: Downer loamy sand; 11: Boonton loam (Union County); 12: Dunellen sandy loam; 13: Birdsboro silt loam; 14: Hazen gravelly loam; 15: Boonton loam (Bergen County).

²Organic matter content.

Table 4.6

Comparison of observed (experimental) and predicted partition coefficient for cadmium at natural soil pH by considering single, double, and triple components in the model. Correlations determined for 1×10^{-4} M added cadmium.

Soil ¹ Number	Soil pH	Observed K _d (mL/g)	Predicted K _d (mL/g)					
			OM ²	Fe	Al	Mn	OM & Al	OM, Al & Mn
1	5.78	62.8	131.0	190.0	180.1	141.1	74.1	65.4
2	4.18	4.5	127.9	131.0	145.2	122.7	153.6	141.7
3	4.67	26.1	152.4	197.3	192.8	206.5	93.8	121.1
4	6.17	366.0	182.9	223.4	201.5	268.0	145.1	202.8
5	6.03	321.0	201.2	196.1	173.2	137.3	259.2	219.9
6	5.22	11.5	118.8	103.4	141.0	125.7	142.2	137.6
7	6.44	711.1	186.0	160.1	178.3	156.5	209.9	189.9
8	4.69	55.2	262.3	212.1	249.0	229.5	216.6	199.7
9	4.77	33.2	149.3	169.9	146.1	168.0	202.5	215.0
10	4.74	21.6	137.1	86.5	147.5	123.1	169.8	153.7
11	5.14	290.4	375.4	202.3	274.4	371.8	423.3	457.3
12	5.57	121.6	170.7	146.1	170.0	164.2	194.1	188.4
13	5.69	132.6	179.9	245.8	204.3	218.0	130.7	151.9
14	6.02	533.5	207.4	259.4	190.9	252.6	229.6	268.4
15	5.12	165.8	274.6	333.5	262.4	171.9	212.5	144.2

¹Soil number: 1: Sassafras sandy loam; 2: Lakewood sand; 3: Penn silt loam; 4: Whippany silty clay loam; 5: Washington loam; 6: Freehold sandy loam (A horizon); 7: Freehold sandy loam (B horizon); 8: Rockaway stony loam; 9: Fill materials from Del. River; 10: Downer loamy sand; 11: Boonton loam (Union County); 12: Dunellen sandy loam; 13: Birdsboro silt loam; 14: Hazen gravelly loam; 15: Boonton loam (Bergen County).

²Organic matter content.

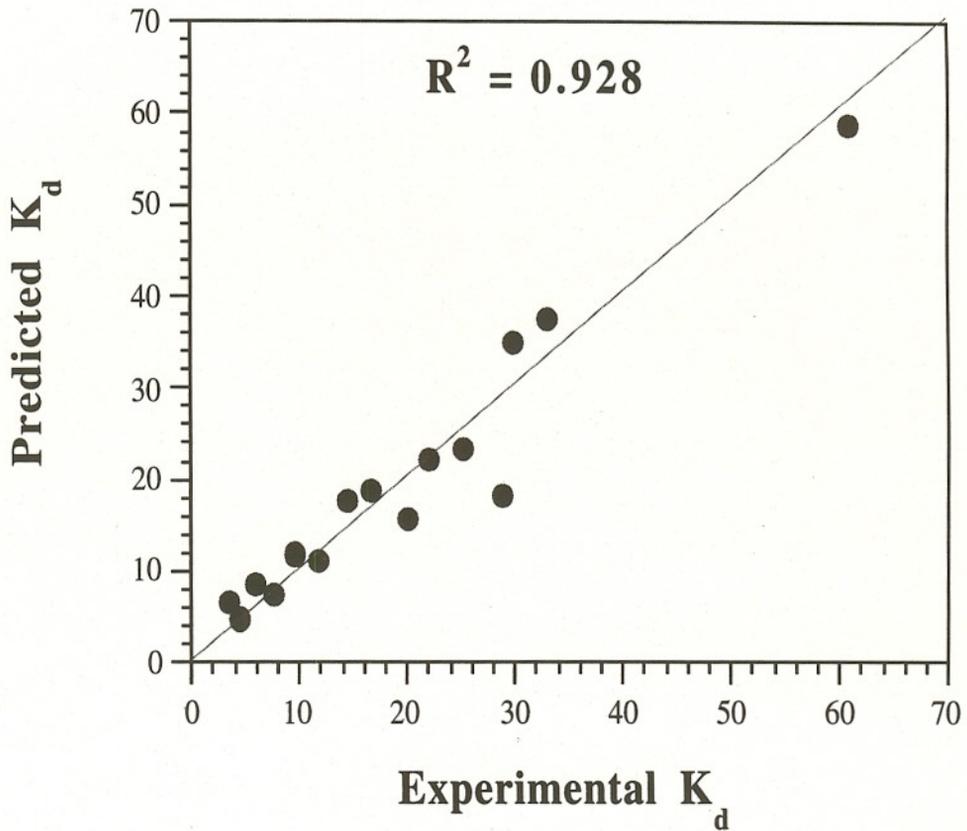


Figure 4.2. Correlation between experimental and predicted partition coefficient (mL/g) by considering organic matter only at $\text{pH } 4.0 \pm 0.05$. 1×10^{-4} M cadmium; soil:water = 1 g/100 mL; $I = 0.01$ M NaNO_3 ; $T = 25$ °C.

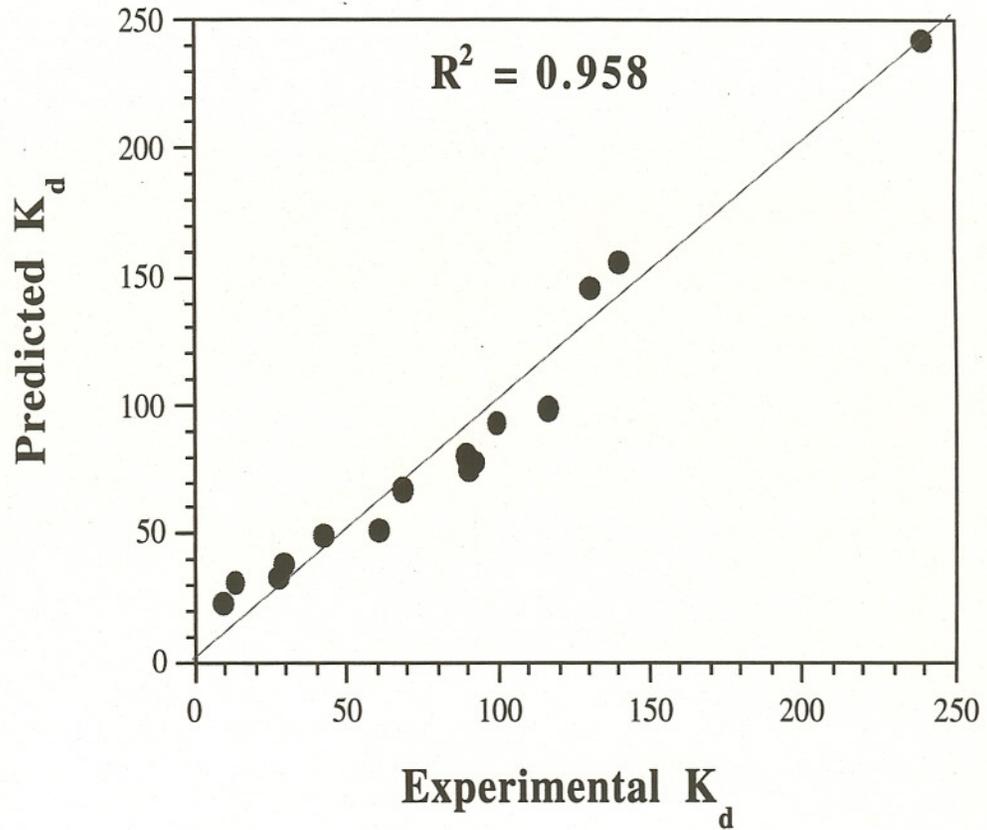


Figure 4.3. Correlation between experimental and predicted partition coefficient (mL/g) by considering organic matter only at $\text{pH } 5.0 \pm 0.05$. 1×10^{-4} M cadmium; soil:water = 1 g/100 mL; $I = 0.01$ M NaNO_3 ; $T = 25^\circ\text{C}$.

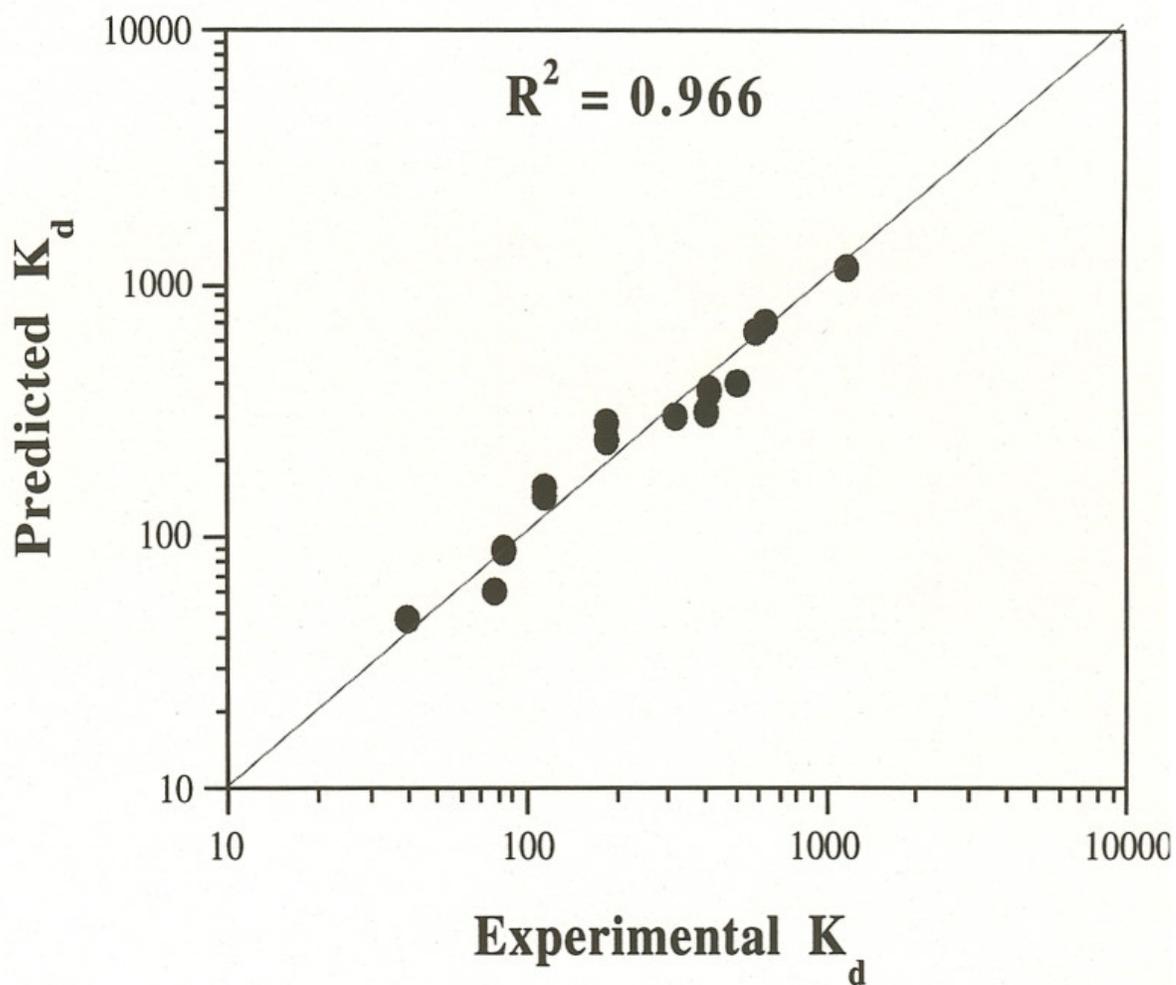


Figure 4.4. Correlation between experimental and predicted partition coefficient (mL/g by considering organic matter only at pH 6.0 ± 0.05 . 1×10^{-4} M cadmium; soil:water = 1 g/100 mL; I = 0.01 M NaNO_3 ; T = 25 °C.

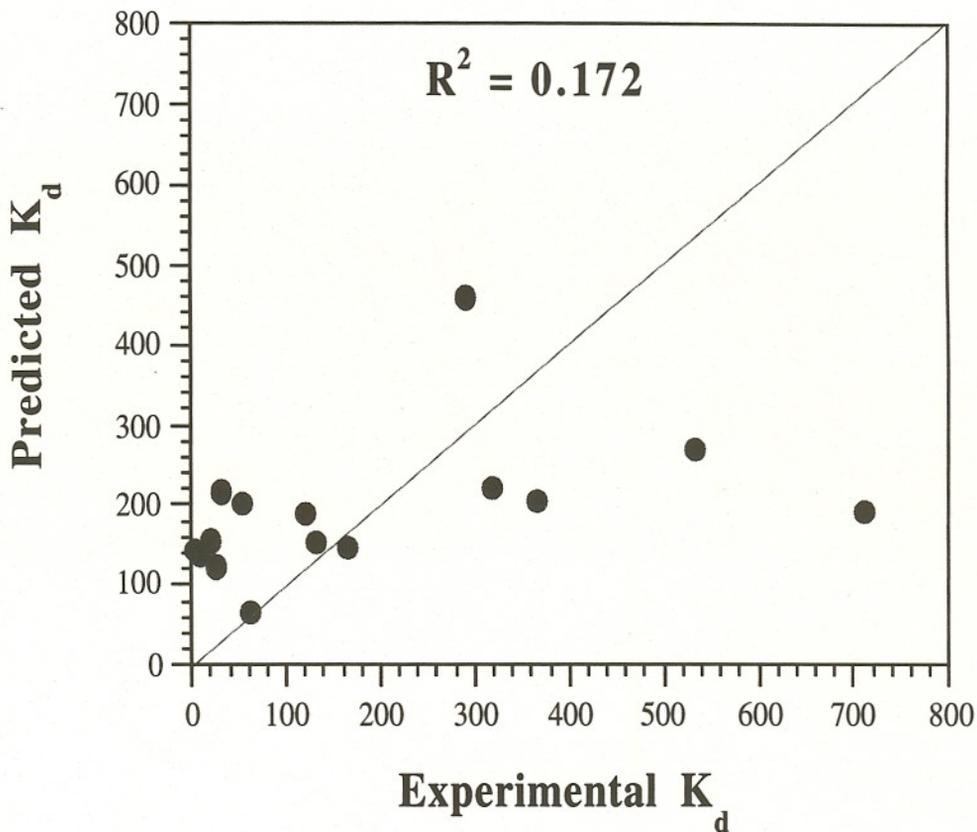


Figure 4.5. Correlation between experimental and predicted partition coefficient (mL/g) by considering three sorption components at soil natural pH. 1×10^{-4} M cadmium; soil:water = 1 g/100 mL; I = 0.01 M NaNO_3 ; T = 25 °C.

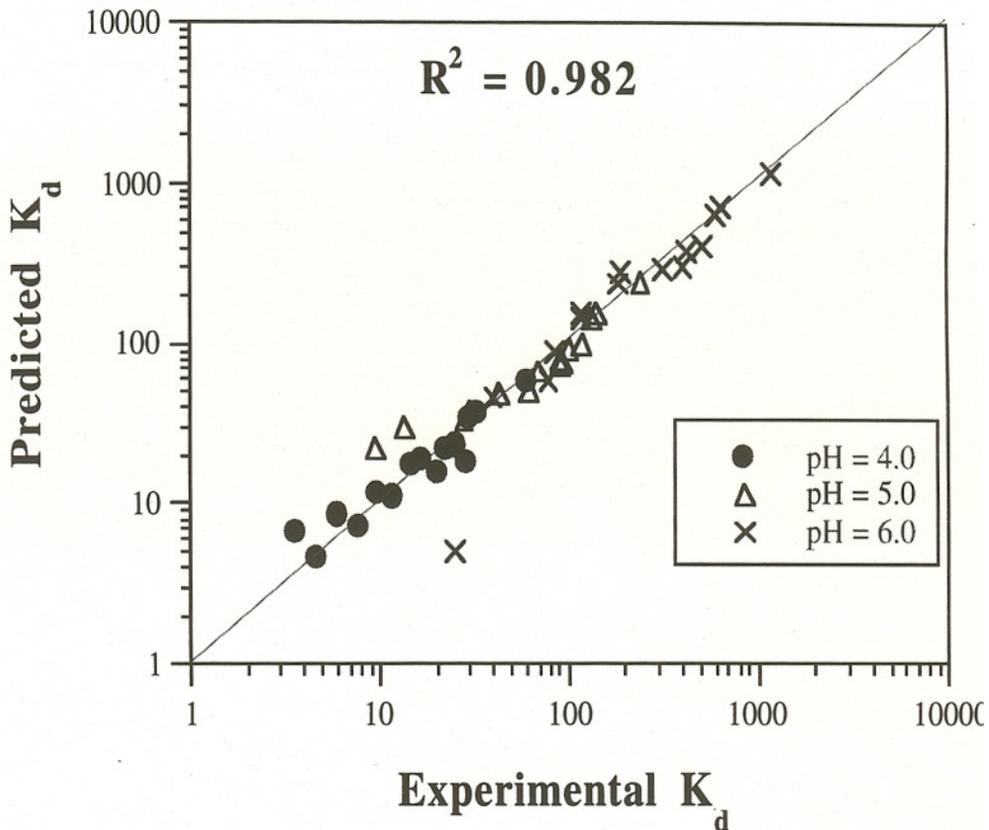


Figure 4.6. Correlation between experimental and predicted partition coefficient (mL/g) by considering organic matter only at three pH values. 1×10^{-4} M cadmium; soil:water = 1 g/100 mL; I = 0.01 M NaNO_3 ; T = 25 °C.

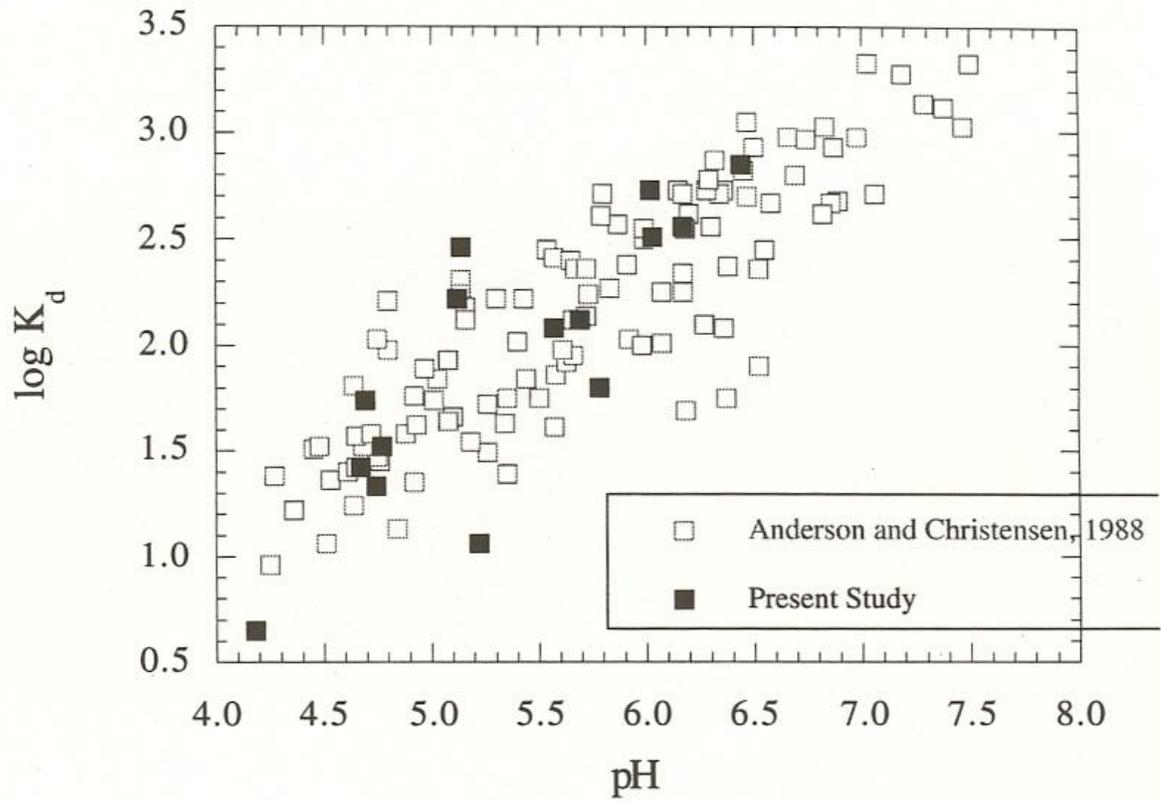


Figure 4.7 Relation of cadmium partition coefficients on soil to pH for the present study and that of Anderson and Christensen (1988).

4.4 Application to Soil Quality Standards

4.4.1 Maximum Permissible Level of Metal in Soil

4.4.1.1 Introduction

A methodology for the development of the maximum level of metal in soil for which the equilibrium soluble metal does not violate the Drinking Water Standard has been developed (Lee et al., 1992). These metal criteria can be used as soil standards that will be protective of groundwater quality.

The partitioning of trace metals is highly dependent on the nature of the soil and on the solution pH as demonstrated by the analysis in Section 4.3. The maximum level of metal in soil for which the equilibrium soluble metal does not violate the Drinking Water Standard can be computed, at any pH, from the measured partition coefficient for any metal and soil.

Although partition coefficients can be obtained easily by adsorption measurements, the conditions are very different from those found in the field and the results may not be directly related to clean-up criteria. Under field conditions the soil is subjected to a hydraulic gradient and metals in the groundwater flowing through the soil need not to be in equilibrium with the adsorbed metal. In that case equilibrium adsorption measurements might overestimate the groundwater concentrations. Column measurements allow approximation of flow conditions. If similar partition coefficients are found from batch and column methods one can utilize partition coefficients obtained directly from batch methods.

4.4.1.2 Methodology

Criteria for soil remediation are based on specific soil types and the effect of pH on metal sorption because the partitioning of trace metals is highly dependent on the solution pH (Kuo and Baker 1980; Harter 1983; Elliott et al. 1986) and the chemical nature of the soil. As the pH decreases, the amount of adsorbed cationic metal decreases (Figures 3.2-3.5). Consequently, for a given soil, the concentration of cationic metal in soil that would be protective of groundwater quality would be lower as the pH decreases. However, an opposite trend is true for hexavalent chromium.

The maximum soil concentration, C_s , in $\mu\text{g/g}$, is established by multiplying the Drinking Water Standard, DWS, in $\mu\text{g/L}$, by the partition coefficient, K_d :

$$C_s = K_d \times \text{DWS} \quad (4.11)$$

The partition coefficient is defined from adsorption data:

$$K_d = \frac{[M]_s}{[M]_w} \quad (4.12)$$

where

$[M]_s$ is the concentration of metal sorbed to the soil, $\mu\text{g/g}$, and

$[M]_w$ is the concentration of metal in the water, $\mu\text{g/L}$.

The partition coefficients of cadmium and lead for Penn silt loam are shown in Figure 4.8. These partition coefficients were converted into field conditions because the soil:water ratio in field conditions is different from that used in the laboratory. Both the metal contained on the soil particles themselves, and that in the associated water, were considered. The following Soil Quality Criteria, SoilQC, in mg/kg, that will not result in a violation of the drinking water standard is obtained:

$$\text{SoilQC} = \text{DWS} \left\{ K_d + \frac{n \times p}{D_s \times (1 - n)} \right\} \quad (4.13)$$

where n is the soil porosity, p is the degree of water saturation in the soil and D_s is the density of the soil particles (typically 2.65 g/cm^3).

4.4.1.3 Results and Discussion

Because partition coefficients can be obtained easily by batch adsorption measurements, it is desirable to utilize them, if similar partition coefficients can be obtained from batch and column methods. As is shown in Chapter 6, the partition coefficients (K_d) from batch measurements are very close to those obtained from column flow processes using a double extrapolation technique. Therefore, the batch equilibrium methods provide a good estimate of the value obtained for desorption of cadmium contaminant in the dynamic systems.

Values of the SoilQC for cadmium and lead were calculated using the values of observed K_d in Tables 4.3- 4.6 and the Standards of National Interim Primary Drinking

Water Regulations (NIPDWR) from Table 4.7 in Equation 4.11. The values range from 0.05 to 7.11 mg/kg for cadmium and 1.24 to 99.1 mg/kg for lead at the natural pH's of the soils (Table 4.8). The values of the SoilQC for cadmium can be compared to those that have been proposed or are in use as standards. Wu et al. (1991) reported proposed maximum allowable concentration of cadmium in the soils of a number of countries (Table 4.9). Comparison of Table 4.8 and Table 4.9 indicates that the proposed standards may be inadequate for some soils. The proposed standard for China would be unnecessarily low for Birdsboro silt loam at the soil pH but would not protect groundwater in contact with sandy soils such as Downer loamy sand and Freehold sandy loam (A horizon). The USSR standard would fail to protect groundwater in most of the New Jersey soils at their natural pH values.

This approach presented here offers the ability to provide SoilQC values for varying environmental soil pH conditions that could result from acid rain or from soil treatment.

The data in Tables 4.3-4.5 were used to calculate pH-dependent SoilQC's for fifteen soils. For example, the SoilQC value for cadmium in the Boonton loam (Union County) at its native pH of 5.14 was 2.91 mg/kg. If the pH were raised to 6 the SQC would be approximately 11.8 mg/kg and if the pH were lowered to pH 4, the SoilQC would have to be lowered to approximately 0.61 mg/kg (Table 4.8). At any pH, lead could have a higher soil concentration than cadmium without causing a violation of the Drinking Water Standard (Table 4.8 and Figure 4.9) because (1) lead has stronger adsorption ability than cadmium and (2) lead has a higher Drinking Water Standard.

Table 4.7 The U.S. EPA Maximum Contaminant Levels (MCL) under the Federal Safe Drinking Water Act.

Heavy Metals	NIPDWR ¹	NPDWR ²		NSDWR ³	
	MCL ⁴	MCL (mg/L)		SMCL (mg/L)	
	(mg/L)	PM ⁵	PR ⁶	PM	PR
Antimony		{0.01/0.05}			0.05
Asenic	0.05				
Barium	1.0		5		
Cadmium	0.01		0.05		
Chromium	0.05		0.1		
Copper			1.3	1	
Iron				0.3	
Lead	0.05		0.005		
Mercury	0.002		0.002		
Nickel			{0.1}		
Zinc			5		

¹ NIPDWR: National Interim Primary Drinking Water Regulations

² NPDWR: National Primary Drinking Water Regulations

³ NSDWR: National Secondary Drinking Water Regulations

⁴ MCL: Maximum Contaminant Levels

⁵ PM: Promulgated criteria

⁶ PR: Proposed/planned for proposal criteria, not yet promulgated

Table 4.8 Maximum permissible level of cadmium and lead (mg/kg) for fifteen New Jersey soils at different pH values. Determined for 1×10^{-4} M added cadmium or lead.

Soil Name	pH 4.0		pH 5.0		pH 6.0		Soil pH	
	Cd	Pb	Cd	Pb	Cd	Pb	Cd	Pb
Birdsboro silt loam	0.15	5.13	0.91	16.0	1.87	47.6	1.33	32.3
Boonton loam (Bergen County)	0.33	10.4	1.41	30.0	6.34	97.1	1.66	35.3
Boonton loam (Union County)	0.61	13.1	2.40	35.7	11.8	99.1	2.91	44.5
Downer loamy sand	0.06	1.71	0.30	3.60	0.84	10.8	0.22	2.84
Dunellen sandy loam	0.20	4.12	0.69	12.7	1.85	46.0	1.22	31.2
Fill materials from Del. River	0.12	2.37	0.43	7.57	1.16	20.1	0.33	5.60
Freehold sandy loam (B horizon)	0.17	5.95	0.90	27.2	4.00	74.4	7.11	123
Freehold sandy loam (A horizon)	0.05	0.66	0.10	1.77	0.25	4.53	0.12	2.40
Hazen gravelly loam	0.26	10.8	1.17	30.2	5.15	91.2	5.34	108
Lakewood sand	0.04	1.08	0.14	2.71	0.40	7.80	0.05	1.24
Penn silt loam	0.10	2.72	0.62	11.0	1.15	37.0	0.26	5.45
Rockaway stony loam	0.30	5.13	1.31	15.3	5.91	44.0	0.55	12.6
Sassafras sandy loam	0.08	1.54	0.28	3.38	0.78	22.0	0.63	12.4
Washington loam	0.22	6.48	1.00	23.9	4.15	77.0	3.21	85.9
Whippany silty clay loam	0.29	7.45	0.93	17.5	3.18	74.4	3.66	99.1

Table 4.9 Maximum allowable concentrations of cadmium in soils (Wu et al. 1991).

Country	Maximum Cadmium
	(mg/kg)
China	0.30
EEC	1-3
Canada	1.6
Scotland	1.6
France	2
F.R. Germany	3
Italy	3
England	3.5
USSR	5

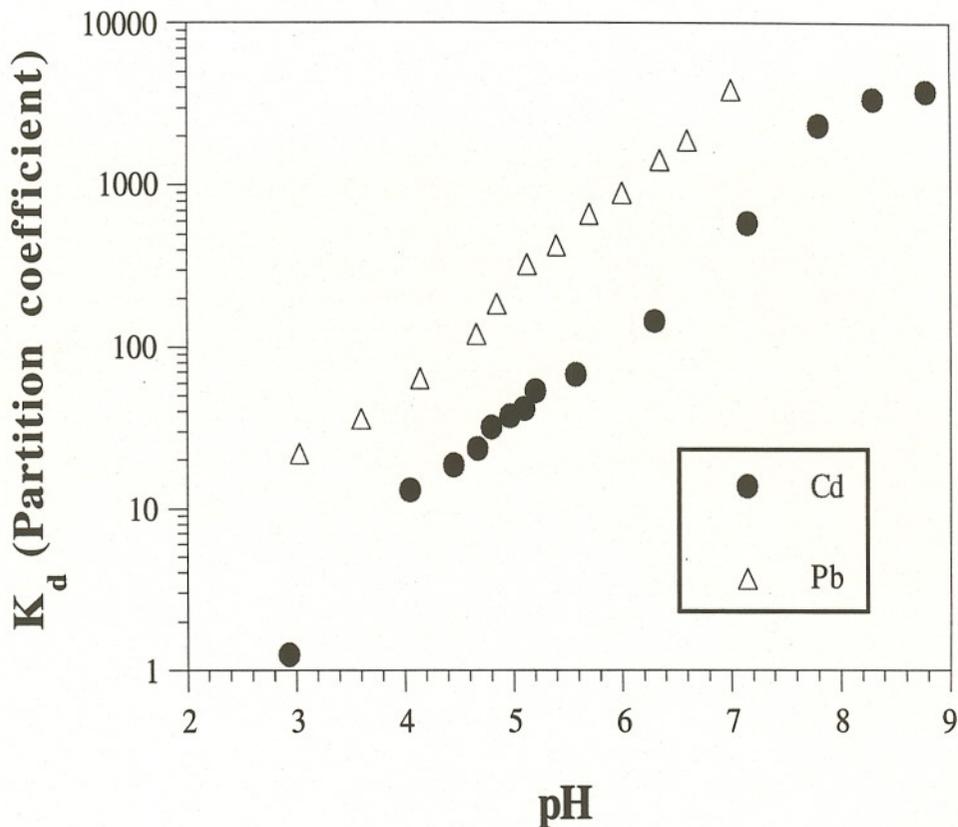


Figure 4.8 Partition coefficient (mL/g) for the adsorption of 1×10^{-4} M cadmium or lead onto Penn silt loam. Soil:water = 1 g/100 mL; I = 0.01 M NaNO₃; T = 25 °C.

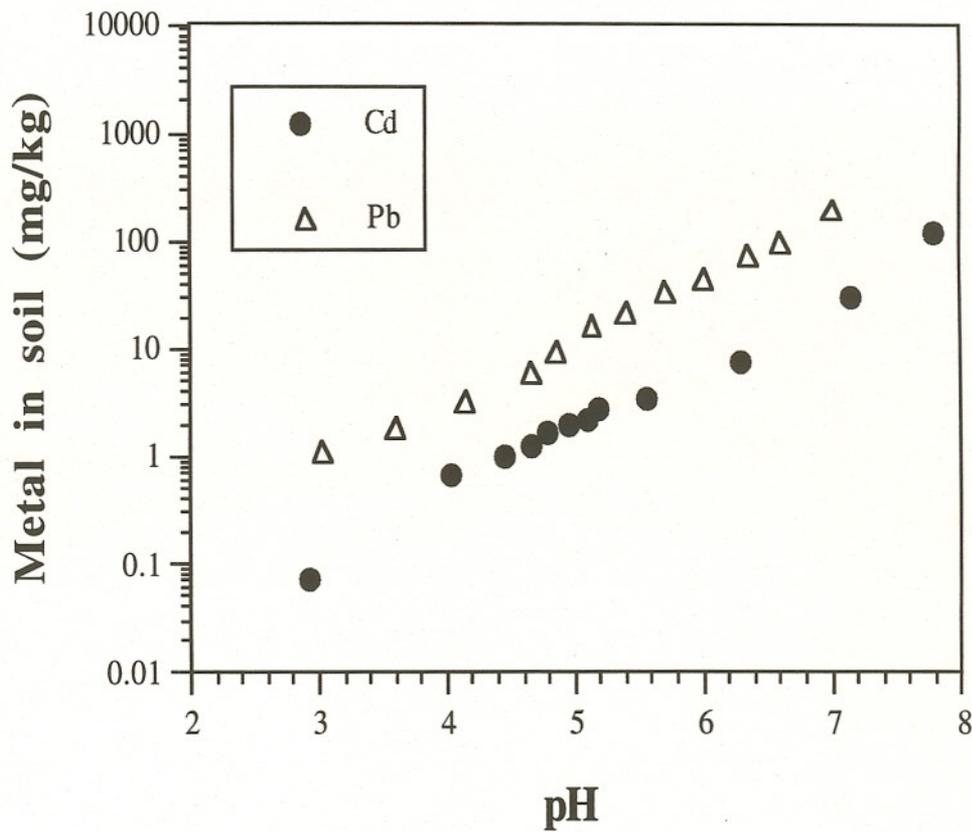


Figure 4.8 Maximum permissible level of cadmium and lead for Penn silt loam for 1×10^{-4} M initial concentration.

Chapter 5

FORMATION OF SURFACE COMPLEXES BETWEEN HEAVY METALS AND SOILS

5.1 Introduction

While the partition model presented in Chapter 4 accounted well for the adsorption of cadmium at fixed pH, it was poor in accounting for adsorption at the natural pH. The mechanism of adsorption must be considered in more detail. Adsorption occurs as a result of many binding mechanisms. Because most solids in aquatic solutions are electrically charged, the adsorption of ionic species may occur through electrostatic attraction. There are many adsorption binding forces other than electrostatic attraction such as covalent binding, van der Waals, and hydrogen bonding between the adsorbate and the solid. When the contributions of these binding forces to the adsorption energy is large, adsorption is said to be specific (Park, 1975). Specific and electrostatic adsorption may occur simultaneously depending on the conditions between the adsorbate and the solid in aquatic solution.

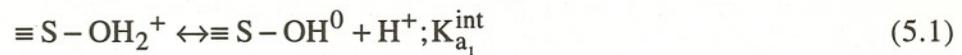
There have been a number of studies on chemical modeling to describe the adsorption of metal ions onto a solid surface as well as the reaction at the interfacial region between the oxide solid and the aqueous solution. Several adsorption models

have been developed to interpret and predict the adsorption behavior of metal ions from dilute aqueous solutions. Some models emphasize the importance of the electrical double layer structure and physical interaction in controlling the distribution of metal ions in the solution; others stress the specific chemical or coordinative interactions of metals with surface sites. These models include: 1) the Gouy-Chapman Stern-Grahame model which accounts mostly for electrostatic adsorption and considers the coulombic attraction between metal ions and the hydrous solid surface; 2) the ion exchange model wherein protons are replaced by metals upon the adsorption of metal ions on the solid surface; 3) the surface complex formation model which emphasizes the specific adsorption of metal ions on the deprotonated surface (Huang and Stumm, 1973); 4) the surface ionization and complexation model proposed by Davis et al. (1978c) which considers both the electrostatic and the chemical interactions simultaneously; and 5) the James and Healy model which includes hydration energy in addition to coulombic and chemical energy as free energy of adsorption (James and Healy, 1972). In this research, the adsorption behavior of Cd(II), Pb(II), Cr(III), and Cr(VI) onto soil surfaces was investigated and, for the sake of simplicity, the surface complex formation model was selected to describe the adsorption behavior of Cd(II). This model requires knowledge of surface acidity and metal speciation. The surface acidity of the heterogeneous soil surface will be calculated by choosing discrete constants for deprotonation that best represent experimental titration data over the pH region of experimental interest. Metal speciation will be calculated from hydrolysis equilibria for Cd(II) available in the literature.

5.2 Surface Acidity

Surface acidity can be defined as the acid strength and the acid capacity or the total number of the surface ionizable groups, N_t (Huang et al., 1987). A weak acid is one which has a weak proton donating tendency. A higher free energy is required to transfer protons from the acid to the aqueous solution. As discussed in Section 2.4.1.4, after ionic dissolution, the soil surface develops charged groups, and they can be considered as Brönsted acids and bases. The functional groups of a soil are considered to have the nature of a weak acid.

The difficulty of determining the microscopic constants mounts rapidly as the number of acid functional groups increases. A number of methods for treating these was considered in Section 2.4.1.3. To simplify the process for this study, among all acidity constants calculated by the discrete affinity spectrum program (Brassard et al., 1990), the constant that provides the best fit to the adsorption data is chosen as the average intrinsic constant for the method of potentiometric titration developed by Huang and Stumm (1973). If $\equiv\text{S-OH}_2^+$, $\equiv\text{S-OH}^0$ and $\equiv\text{S-O}^-$ represent the positive, neutral and negative states, respectively, of the functional groups for metal oxide surfaces, they can be related by:



If the concentration of each component involved in the reaction is measured at the immediate proximity of the charged surface, the equilibrium constants can be represented by equations:

$$K_{a_1}^{\text{int}} = \frac{\{\equiv\text{S}-\text{OH}^0\}\{\text{H}^+\}}{\{\equiv\text{S}-\text{OH}_2^+\}} \quad (5.3)$$

$$K_{a_2}^{\text{int}} = \frac{\{\equiv\text{S}-\text{O}^-\}\{\text{H}^+\}}{\{\equiv\text{S}-\text{OH}^0\}} \quad (5.4)$$

$$N_t = \{\equiv\text{S}-\text{OH}_2^+\} + \{\equiv\text{S}-\text{OH}^0\} + \{\equiv\text{S}-\text{O}^-\} \quad (5.5)$$

The point where positive surface charge equals negative surface charge is defined as the zero point of charge. The pH value of this point is called pH_{zpc} .

From Equation 5.1 and 5.2,

$$\text{pH}_{\text{zpc}} = \frac{1}{2}(\text{p}K_{a_1}^{\text{int}} + \text{p}K_{a_2}^{\text{int}}) \quad (5.6)$$

For $\text{pH} < \text{pH}_{\text{zpc}}$, equilibria 5.1 and 5.2 tend to go to the left and the surface of the soil is positively charged. Since $\{\equiv\text{S}-\text{O}^-\}$ is insignificant, the surface is predominated by the $\{\equiv\text{S}-\text{OH}_2^+\}$ and the $\{\equiv\text{S}-\text{OH}^0\}$ groups.

For $\text{pH} > \text{pH}_{\text{zpc}}$, equilibria 5.1 and 5.2 tend to go to the right, therefore $\{\equiv\text{S}-\text{OH}_2^+\}$ becomes insignificant, $\{\equiv\text{S}-\text{O}^-\}$ and $\{\equiv\text{S}-\text{OH}^0\}$ are the predominant groups.

By applying the equilibrium constants of Equations 5.3 and 5.4, the speciation of surface acidity can be obtained from the following equations:

$$\alpha_+ = \frac{\{H^+\}^2}{\{H^+\}^2 + K_{a1}^{int}\{H^+\} + K_{a1}^{int}K_{a2}^{int}} \quad (5.7)$$

$$\alpha_0 = \frac{K_{a1}^{int}\{H^+\}}{\{H^+\}^2 + K_{a1}^{int}\{H^+\} + K_{a1}^{int}K_{a2}^{int}} \quad (5.8)$$

$$\alpha_- = \frac{K_{a1}^{int}K_{a2}^{int}}{\{H^+\}^2 + K_{a1}^{int}\{H^+\} + K_{a1}^{int}K_{a2}^{int}} \quad (5.9)$$

where α_+ , α_0 , and α_- are the fractions of the positive, neutral and negative groups, respectively.

Adsorption to organic matter shares with metal oxide adsorption, the predominance of oxygen as the electron donor (Leckie, 1988). Similar relationships can be considered for the functional groups of organic matter but generally only two states, charged and neutral, need to be considered for each group. For example, an organic acid has neutral state, RCOOH and negative state, RCOO⁻. Organic matter in soil consists of a mixture of polymeric species having many other functional groups such as amino groups with a neutral state RNH₂ and a positive state, RNH₃⁺. Hence the organic matter is in effect polyprotic but the ionizations given by K_{a1}^{int} and K_{a2}^{int} arise from different chemical groups rather than from three states of the same group as in the case of metal oxides. Because soil is heterogeneous, containing many RCOOH and RNH₂ groups, single values for K_{a1}^{int} and K_{a2}^{int} are not expected. To simplify treatment of surface charge discrete values are chosen that fit the experimental titration properties in the desired pH range. By choosing one acidity constant from the range of acidity

constants for organic matter the method used for metal oxide adsorption can be extended to organic matter. The thermodynamic description in terms of empirical stability constants is identical for organic and metal oxide surface system.

5.3 Aqueous Metal Speciation

The adsorption of metal ions at the solid/aqueous solution interface is generally not only governed by the "free" metal ion, but also the more strongly absorbed hydroxo, sulfato, carbonate, and other metal complex species (Stumm and Bilinski, 1972). It has been suggested that all metal hydrolysis species, M^{2+} , MOH^+ , $M(OH)_2$, $M(OH)_3$, and $M(OH)_4^-$, should be considered in the adsorption of metal ions (Huang and Elliott, 1981; Corapcioglu, 1982). Thus, knowing the metal species which occur in soil systems and understanding their adsorption behavior onto solid/liquid interfaces becomes very important.

The free metal ions in solutions are actually aquo complexes, the water itself is a ligand that binds metal, and every complexation reaction in water is effectively a ligand-exchange reaction (Morel, 1983). The hydrolysis equilibria of metals can be described as:



The equilibrium stability constants, β_j , for the reaction are defined as:

$$\beta_j = \frac{\{M(OH)_j^{x-j}\}}{\{M^{x+}\} \{OH^-\}^j} \quad (5.11)$$

where $\{ \}$ stands for the activity of the dissolved species. The activity of an ion can be calculated as follows:

$$\{M^{x+}\} = [M^{x+}] \times \gamma_{M^{x+}} \quad (5.12)$$

where $[M^{x+}]$ is the concentration of metal ion, and $\gamma_{M^{x+}}$ is the activity coefficient. $\gamma_{M^{x+}}$ can be obtained from ion strength (I), temperature, and other parameters.

The total soluble metal concentration M_T , in the absence of other complex agents such as Cl^- , CO_3^{2-} , can be expressed as a total free metal concentration M^{x+} , plus the sum of soluble hydroxo complexes:

$$M_T = [M^{x+}] + \sum [M(OH)_j^{x-j}] \quad (5.13)$$

The metal species present in water are primarily governed by pH. At any specific pH value, the fraction of any metal species present $M(OH)_j^{x-j}$, can be obtained by:

$$\alpha_j = \frac{\{M(OH)_j^{x-j}\}}{\{M_T\}} \quad (5.14)$$

Among heavy metals, Pb(II), Cd(II), Cr(III), Cr(VI) were selected in this study. Tables 5.1-5.2 list the equilibrium constants of various metal hydroxy species (Martell and Smith, 1977). The speciations of each metal hydroxy species as a function of pH are shown in Figures 5.1 to 5.4.

Table 5.1 Equilibrium constants for Cd(II) and Pb(II) hydroxy species.

Equilibria	log K		Sources for log K at I = 0
	Cd ²⁺	Pb ³⁺	
$M^{2+} + OH^- = MOH^+$	4.27	6.67	Martell and Smith, 1977
$M^{2+} + 2OH^- = M(OH)_2$	8.26	11.46	
$M^{2+} + 3OH^- = M(OH)_3$	8.61	14.46	
$M^{2+} + 4OH^- = M(OH)_4^{2-}$	9.07		

Table 5.2 Equilibrium constants for Cr(III) and Cr(VI) hydroxy species.

Equilibria	log K	Sources
$Cr^{3+} + H_2O = Cr(OH)^{2+} + H^+$	-4.00	for log K at I = 0
$Cr^{3+} + 2H_2O = Cr(OH)_2^+ + 2H^+$	-9.65	Baes and Mesmer, 1976
$Cr^{3+} + 3H_2O = Cr(OH)_3 + 3H^+$	-12.00	
$Cr^{3+} + 4H_2O = Cr(OH)_4^- + 4H^+$	-27.40	

Equilibria	log K	Sources
$H_2CrO_4(aq) = HCrO_4^- + H^+$	0.20	for log K at I = 0 M
$HCrO_4^- = CrO_4^{2-} + H^+$	-6.51	Martell and Smith, 1977
$2HCrO_4^- = Cr_2O_7^{2-} + H_2O$	1.53	

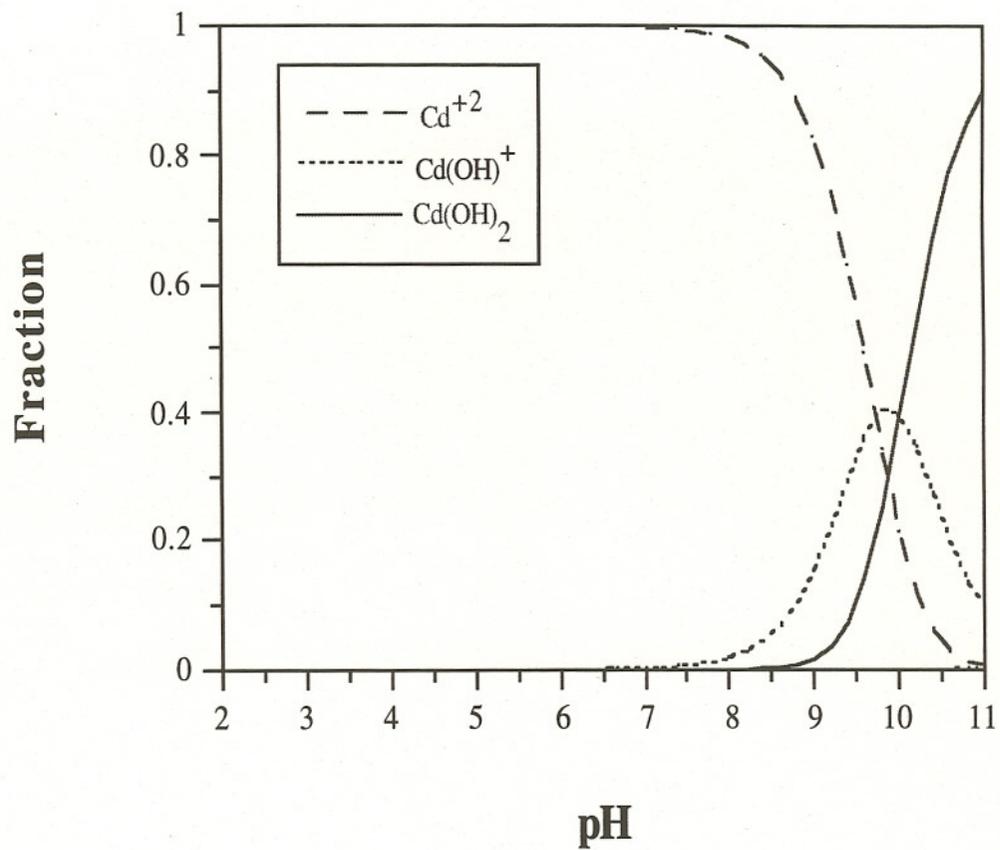


Figure 5.1 Speciation diagram for Cd(II).

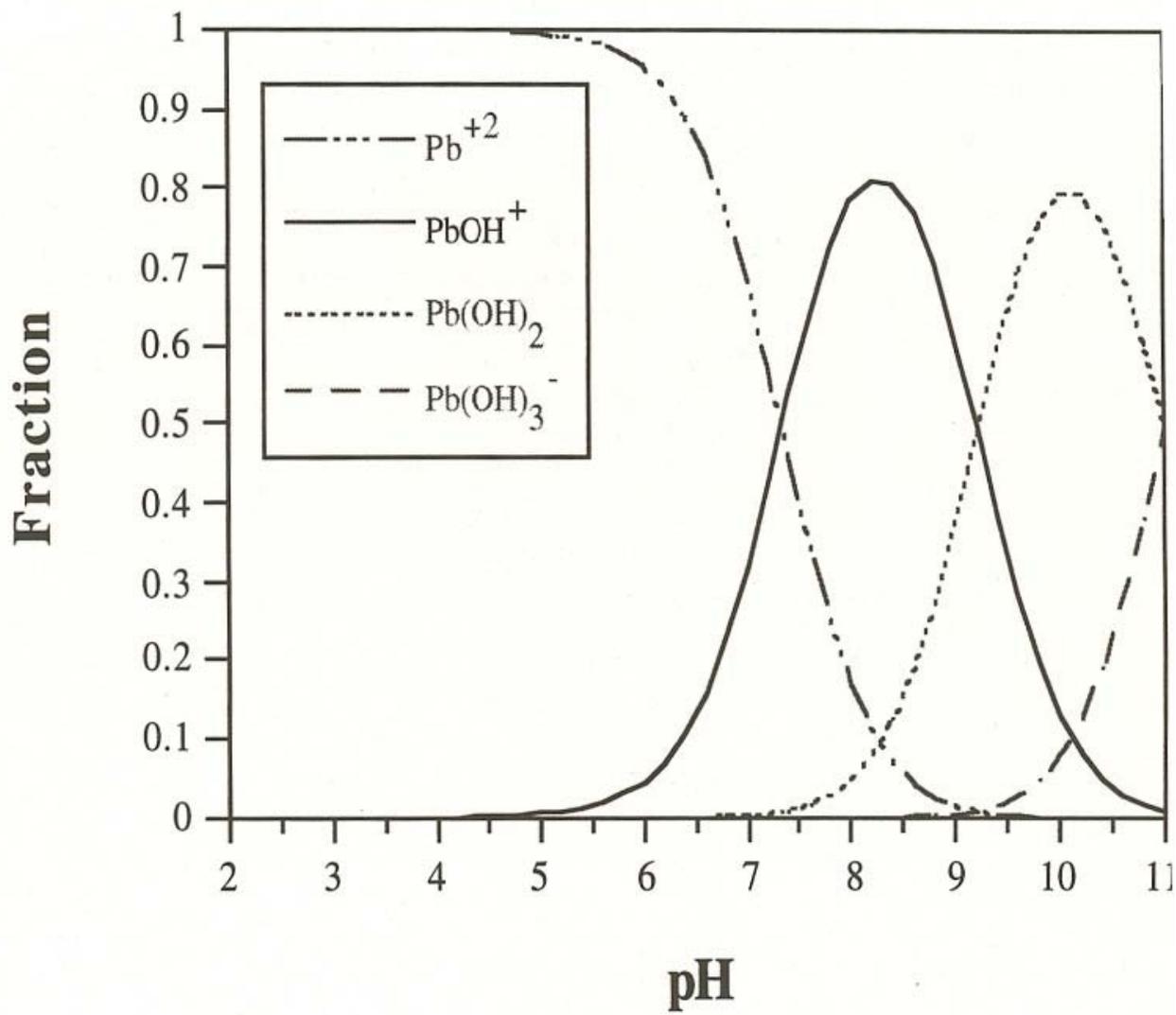


Figure 5.2 Speciation diagram for Pb(II).

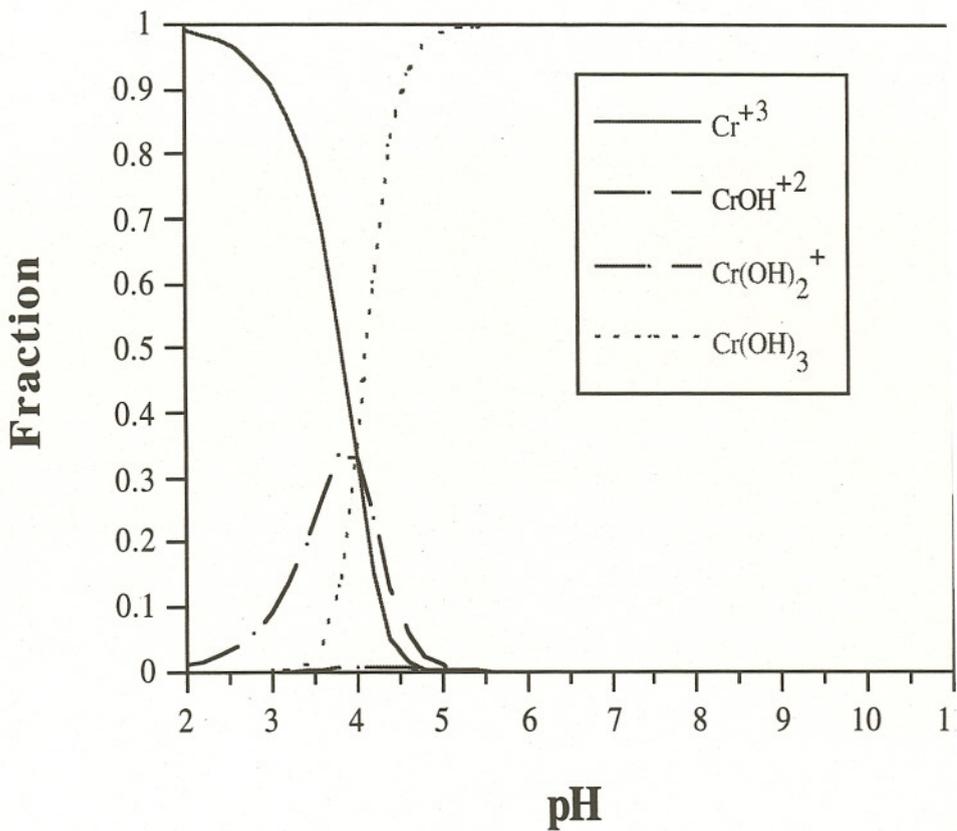


Figure 5.3 Speciation diagram for Cr(III).

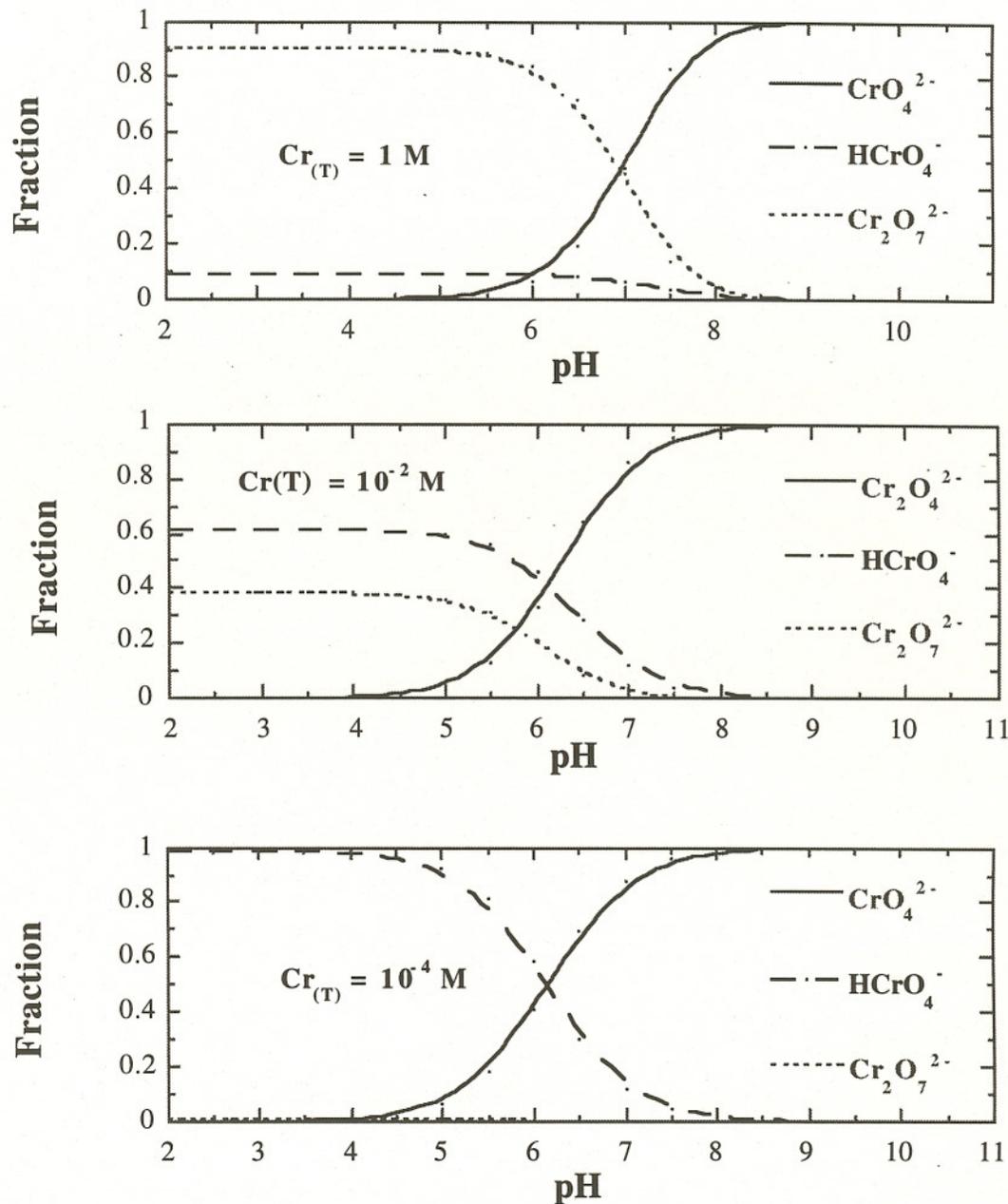
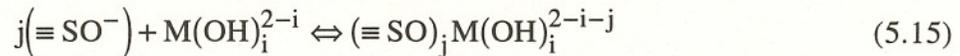


Figure 5.4 Speciation diagram for Cr(VI).

5.4 Surface Complex Formation

According to the concept of the complex formation model, a series of possible reactions between the metal species, M^{2+} , MOH^+ , $M(OH)_2$, $M(OH)_3^-$, and $M(OH)_4^{2-}$ with the surface functional groups at the surface of a soil sample can be expressed by a general equation:



for which the intrinsic stability constant

$$K_{ji}^{int} = \frac{\{(\equiv SO)_j M(OH)_i^{2-i-j}\}}{\{\equiv SO^-\}^j \{M(OH)_i^{2-i}\}} \quad (5.16)$$

can be converted to conditional constant in the double layer model by the inclusion of a Boltzman factor:

$$K_{ji}^{con} = K_{ji}^{int} \exp\left\{\frac{-j\psi_0}{RT}\right\} \quad (5.17)$$

where ψ_0 is the potential at the surface and can be determined from the surface charge (Equation 2.15).

The total adsorption density Γ_t was set to equal the sum of the adsorption densities of each individual adsorbed species, i.e. $\Gamma_{M^{2+}}$, $\Gamma_{M(OH)^+}$, $\Gamma_{M(OH)_2}$, and $\Gamma_{M(OH)_3^-}$ in the following equation:

$$\Gamma_t = \Gamma_{M^{2+}} + \Gamma_{MOH^+} + \Gamma_{M(OH)_2} + \Gamma_{M(OH)_3^-} \quad (5.18)$$

Γ_t can be obtained from an adsorption experiment. The concentrations of the surface functional groups $\equiv S-OH_2^+$, $\equiv S-OH^0$ and $\equiv S-O^-$ can be determined from the total number of available sites, N_t , using the following formulas

$$\{\equiv S-OH_2^+\} = \{N_t - \Gamma_t\} \alpha_+ \quad (5.19)$$

$$\{\equiv S-OH^0\} = \{N_t - \Gamma_t\} \alpha_0 \quad (5.20)$$

$$\{\equiv S-O^-\} = \{N_t - \Gamma_t\} \alpha_- \quad (5.21)$$

From Equation 5.16, the stability constant between a single negative surface group, $\{\equiv S-O^-\}$, and metal species, M^{2+} , MOH^+ , $M(OH)_2$, can be expressed as :

$$K_1 = \frac{\{\equiv S-O^-M^{2+}\}}{\{\equiv S-O^-\}\{M^{2+}\}} \quad (5.22)$$

$$K_2 = \frac{\{\equiv S-O^-M(OH)^+\}}{\{\equiv S-O^-\}\{M(OH)^+\}} \quad (5.23)$$

$$K_3 = \frac{\{\equiv S-O^-M(OH)_2\}}{\{\equiv S-O^-\}\{M(OH)_2\}} \quad (5.24)$$

and

$$K_4 = \frac{\{\equiv S-O^-M(OH)_3^-\}}{\{\equiv S-O^-\}\{M(OH)_3^-\}} \quad (5.25)$$

Similar equations can be formulated for $\{\equiv\text{S-OH}_2^+\}$ and $\{\equiv\text{S-OH}^0\}$ groups. Not all reactions between metal species and surface functional groups will occur at a given pH. To calculate the stability constants K_1 , K_2 , K_3 , and K_4 at a given pH, the concentration of each metal species in solution at a given pH must be determined first according to Equation 5.14. For example, the concentration of a bare metal species is determined by :

$$[\text{M}^{2+}] = [\text{M}_t - \Gamma_t] \alpha_{\text{M}^{2+}} \quad (5.26)$$

where $\alpha_{\text{M}^{2+}}$ represents the fraction of the first metal species, $[\text{M}^{2+}]$, which can be obtained from the metal speciation calculation. For a negative surface $\{\text{SO}^-\}$, for example:

$$\Gamma_{\text{M}^{2+}} = \{\equiv\text{S-O}^-\text{M}^{2+}\} = K_1 \{\equiv\text{S-O}^-\} \{\text{M}^{2+}\} \quad (5.27)$$

$$\Gamma_{\text{MOH}^+} = \{\equiv\text{S-O}^-\text{MOH}^+\} = K_2 \{\equiv\text{S-O}^-\} \{\text{MOH}^+\} \quad (5.28)$$

$$\Gamma_{\text{M(OH)}_2} = \{\equiv\text{S-O}^-\text{M(OH)}_2\} = K_3 \{\equiv\text{S-O}^-\} \{\text{M(OH)}_2\} \quad (5.29)$$

$$\Gamma_{\text{M(OH)}_3^-} = \{\equiv\text{S-O}^-\text{M(OH)}_3^-\} = K_4 \{\equiv\text{S-O}^-\} \{\text{M(OH)}_3^-\} \quad (5.30)$$

Substituting Equations 5.27-5.30 into Equation 5.18:

$$\Gamma_t = K_1 \{ \equiv S - O^- \} \{ M^{2+} \} + K_2 \{ \equiv S - O^- \} \{ MOH^+ \} + K_3 \{ \equiv S - O^- \} \{ M(OH)_2 \} + K_4 \{ \equiv S - O^- \} \{ M(OH)_3^- \} \quad (5.31)$$

5.4.1 Application of Surface Complex Model to Heterogeneous Soils

To apply this model to the adsorption data the equations may be simplified. As will be shown in Section 5.5.2 the soils are negatively charged over most of the pH region covered by experiments. Hence only a single site density is needed; $\{ \equiv S - O^- \}$. This site density was obtained by equating N_t with the site density represented by a single acidity constant in an alkalimetric titration. The fraction of negatively charged sites α_- (Equation 5.9) is obtained from the acidity constant and the experimental pH_{zpc} (Equation 5.6). The speciation diagram for Cd(II) in Figure 5.1 indicates $Cd(OH)_3^-$ is negligible below pH 11. Thus the equilibrium described by K_4 in Equation 5.31 may be neglected. Equation 5.31 becomes

$$\Gamma_t = K_1 \{ \equiv S - O^- \} \{ M^{2+} \} + K_2 \{ \equiv S - O^- \} \{ MOH^+ \} + K_3 \{ \equiv S - O^- \} \{ M(OH)_2 \} \quad (5.32)$$

For each pH the experimental data for adsorption, Γ_t , surface site concentration calculated from Equation 5.21, and surface speciation (Figure 5.1) is used in Equation 5.32. A nonlinear-program (Wilkinson, 1992) is utilized to calculate the stability constants K_1, K_2, K_3 that provide the optimum fit to all the data. This simplified model was tested by fitting experimental adsorption data for Cd(II) for the 15 soils chosen in this study.

5.5 Surface Charge of Soil Particles

In order to apply the surface complex model, it is necessary to know the surface charge and convert intrinsic stability constants to conditional constants. Two methods for measuring electrical properties of particulates are zeta potential and alkalimetric titration.

5.5.1 Zeta Potential Measurements

The soil zeta potential was determined by measuring electrophoretic mobility of the particles. The soil sample was 0.5 ± 0.01 g per 200 mL solution at three different ionic strengths (0.001 M, 0.01 M, 0.1 M). The pH values were adjusted from 3 to 10 by adding HNO_3 or NaOH . About 25 ml of sample was injected into an electrophoresis chamber which includes two compartments and a connecting chamber. The sign of particle charge was determined by the direction of movement. The magnitude of zeta potential was related to the speed of particle movement. The zeta potential was calculated by the Helmholtz - Smoluchowski equation as follows:

$$\mu = \frac{\epsilon E \zeta}{4\pi\eta} \quad (5.33)$$

where

μ = electrophoretic mobility ($\mu\text{m/s}$),

ϵ = dielectric constant of electrolyte solution,

E = applied electric field strength (volt/cm),

ζ = zeta potential (volt), and

η = viscosity of the electrolyte solution (poise).

The intrinsic constants and total available sites of soils can be obtained from alkalimetric titration or zeta potential measurements. The results of zeta potential measurements were not used in calculating the surface charge because of scatter in the data and the lack of a common intersection point from measurements at three different ionic strengths. An alkalimetric titration was used to obtain surface charge.

5.5.2 Alkalimetric Titrations of Soils

5.5.2.1 Experimental

Air dried, sieved soil samples, 1 gram, were suspended in 100 mL of 0.001, 0.01, or 0.1 M NaNO_3 . The hydration time for the soil suspension was at least 96 hours. The titrations were conducted with NaOH as the titrant. An automatic titration system was used in this study (Tanager Scientific Systems, Inc., Ancaster, Ontario). It consisted of a double wall reaction cell, a constant temperature circulating water bath, a microburette, a pH meter, a pH electrode, and a microcomputer.

The sample was bubbled with N_2 to eliminate the effect of CO_2 . The sample pH was adjusted to about 3 by adding a measured volume of 0.1 M HNO_3 . Then, the suspension was titrated with 0.1 M NaOH solution which was free from CO_2 . The titrant was automatically added in increments of 0.010 mL until the pH increased from 3

to approximately 10. The blank titrations were done by titrating 100 mL of supernatant following the same procedure as for the titration of soil suspension.

5.5.2.2 Results

The most important property affecting sorption to a particular soil is the pH. The titration behavior is affected by the ionic strength of the solution. To evaluate protonation constants it is necessary to perform titrations at a series of ionic strengths. Titrations for the suspensions of each soil in 0.001, 0.01 and 0.1 M NaNO₃ were performed from pH 3 to 10 with my automated titration system. The titration data were evaluated by the discrete affinity spectrum program (Brassard et al., 1990) to provide the conditional stability constants and the concentration of each of the sites (Tables 5.3-5.5).

The net surface charge was calculated as the difference between titrations with base for samples containing soil and those with only supernatant. The following equation was used to calculate the surface charge density:

$$\sigma = \frac{C\Delta VF}{WS} \times 0.1 \quad (5.34)$$

where

σ = surface charge density ($\mu\text{C}/\text{cm}^2$),

C = base concentration (mmoles/mL),

ΔV = difference of base consumed for titrating samples containing soil and those supernatant at the same pH (mL),

F = Faraday constant, 96500 (Coulomb/mole),

W = soil sample dry weight (g),

S = soil particle specific surface area (m^2/g), and

0.1 = units conversion factor.

The variation with pH of the net surface charge densities of Penn silt loam, as an example, at three ionic strengths, is illustrated in Figure 5.5. These results indicate that the surface of soil particle is negatively charged over a wide pH range. Comparing the surface charge density among them, the surface charge varies from soil to soil at the same pH (Appendix D). Since variable charge results from the protonation of soil particles, it should have a zero charge point where a positive charge is equal to negative charge. The pH value of the point where net surface charge equals zero is called pH_{ZPC} . The pH_{ZPC} values vary from 2.8 to 3.6 (Table 5.6). Thus, at the natural soil pH all of the soils are negatively charged. The variation of surface charge of soil particulates with pH illustrates that these charged sites result from the ionization or hydrolysis of active surface phases. The proton charges probably arise from the hydrolysis of metal oxide and from the ionization of weak organic acids, such as carboxylic or phenolic functional groups present in the humic acid and fulvic acid structures. As a result, it is impossible to identify the contribution of individual components on the soil surface to the surface charge.

Table 5.3 Acidity constants and site densities for soils (T = 25 °C; I = 0.1 M NaNO₃).

Soil Name	pK _{a1}	pK _{a2}	pK _{a3}	pK _{a4}	C ₁	C ₂	C ₃	C ₄
					(μmoles/g)			
Birdsboro silt loam	3.98	5.72	7.36	9.00	126	172	112	271
Boonton loam (Bergen County)	3.71	7.02	8.32	9.66	304	105	192	281
Boonton loam (Union County)	3.64	6.02	6.75	8.98	521	312	234	507
Downer loamy sand	4.49	5.84	7.05	9.36	33	54	52	131
Dunellen sandy loam	4.12	6.58	8.10	8.68	98	87	45	120
Fill materials from Del. River	4.25	5.68	6.75	8.95	39.5	40	34	63
Freehold sandy loam (B horizon)	4.76	6.56	7.20	9.60	18	28	18	129
Freehold sandy loam (A horizon)	4.20	6.95	8.31	9.21	135	42	151	96
Hazen gravelly loam	3.97	6.41	7.35	9.53	177	134	122	212
Lakewood sand	4.43	5.52	7.40	9.05	27	28	38	69
Penn silt loam	4.53	6.37	7.65	9.60	45	45	39	77
Rockaway stony loam	4.28	6.15	7.31	9.41	315	88	71	115
Sassafras sandy loam	4.61	5.13	6.40	8.80	31	36	12	131
Washington loam	4.15	6.45	7.18	8.60	175	94	39	125
Whippany silty clay loam	4.28	6.83	8.25	9.45	143	61	88	248

Table 5.4 Acidity constants and site densities for soils (T = 25 °C; I = 0.01 M NaNO₃).

Soil Name	pK _{a1}	pK _{a2}	pK _{a3}	pK _{a4}	C ₁	C ₂	C ₃	C ₄
Birdsboro silt loam	4.30	5.90	7.60	9.30	105	143	128	273
Boonton loam (Bergen County)	3.90	6.70	8.10	9.60	252	78	134	237
Boonton loam (Union County)	3.80	5.70	6.90	9.10	410	270	241	516
Downer loamy sand	4.26	6.10	7.40	9.50	38	29	66	141
Dunellen sandy loam	4.45	6.80	8.20	8.90	90	65	58	124
Fill materials from Del. River	4.33	5.90	7.20	9.20	57	38	34	73
Freehold sandy loam (B horizon)	4.46	6.20	7.80	9.10	10	24	21	76
Freehold sandy loam (A horizon)	4.10	7.10	8.20	9.20	114	36	134	87
Hazen gravelly loam	4.12	6.30	7.10	9.50	148	106	95	203
Lakewood sand	4.30	5.90	7.10	9.10	24	16	34	73
Penn silt loam	4.48	6.00	7.50	9.50	62	43	38	82
Rockaway stony loam	4.12	5.80	6.90	9.50	233	98	88	187
Sassafras sandy loam	4.54	5.60	6.60	9.20	29	26	23	113
Washington loam	4.30	6.20	7.60	8.70	138	70	63	134
Whippany silty clay loam	4.20	6.90	8.30	9.30	110	57	73	198

Table 5.5 Acidity constants and site densities for soils (T = 25 °C; I = 0.001 M NaNO₃).

Soil Name	pK _{a1}	pK _{a2}	pK _{a3}	pK _{a4}	C ₁	C ₂	C ₃	C ₄
Birdsboro silt loam	3.70	5.82	7.56	9.10	87	99	105	281
Boonton loam (Bergen County)	3.76	6.81	7.91	9.71	209	49	182	233
Boonton loam (Union County)	3.62	5.87	6.80	9.12	389	235	256	486
Downer loamy sand	4.13	6.56	7.65	9.55	26	30	64	120
Dunellen sandy loam	3.85	5.98	7.90	8.60	75	35	39	133
Fill materials from Del. River	4.58	6.70	7.35	9.35	45	58	18	56
Freehold sandy loam (B horizon)	4.51	6.24	7.72	8.90	9	18	16	48
Freehold sandy loam (A horizon)	3.98	7.32	8.26	9.25	65	12	126	69
Hazen gravelly loam	3.78	6.63	6.98	9.63	126	115	104	204
Lakewood sand	4.19	6.15	6.80	9.30	12	15	27	96
Penn silt loam	4.10	5.80	7.03	9.17	32	31	28	67
Rockaway stony loam	3.78	5.32	7.26	9.15	125	173	96	132
Sassafras sandy loam	4.43	6.05	6.80	9.60	10	18	35	111
Washington loam	4.20	6.13	7.45	8.90	128	68	59	157
Whippany silty clay loam	3.87	6.78	7.90	9.20	85	69	58	145

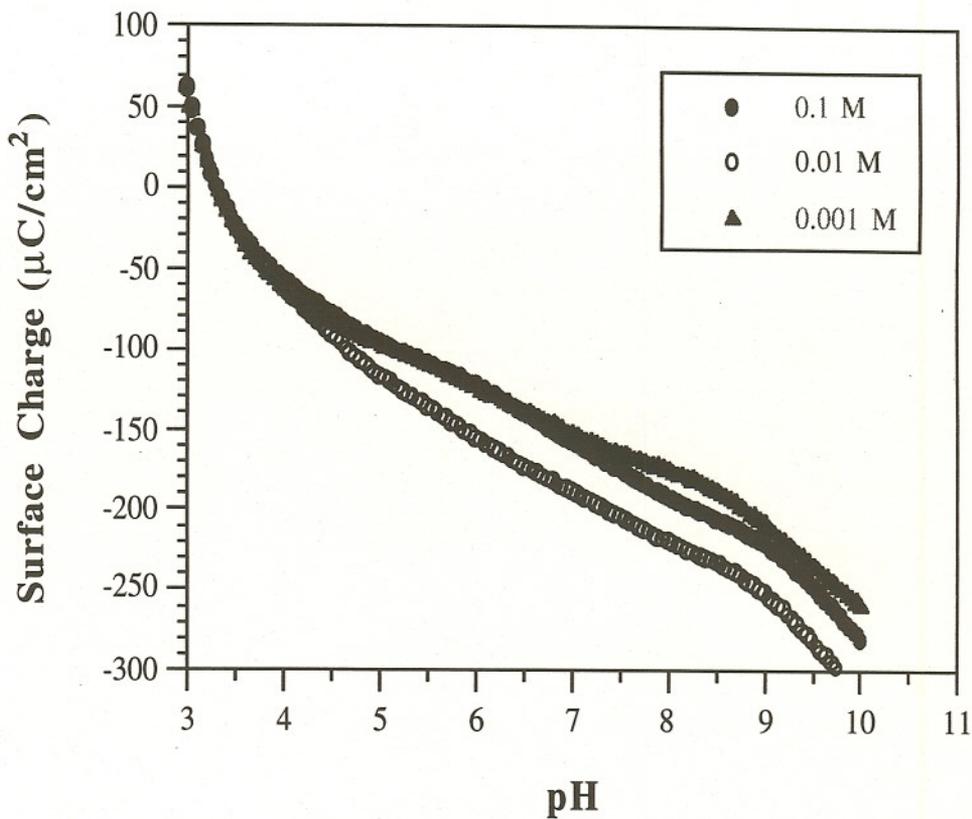


Figure 5.5 Variation of surface charge density of Penn silt loam with pH at three ionic strengths.

5.6 Results and Discussion

5.6.1 Surface Acidity

As described in Section 5.2, all acidity constants calculated by the discret affinity spectrum program were tested by applying a simplified surface complexation model (Section 5.4.1) to obtain the intrinsic constants of soils. Site density varies with organic matter content (Figures 5.6-5.8) while acidity constants show little variation (Figures 5.9-5.11). The sites with pK_{a1} have good correlation between site density C_1 , and soil organic content (Figures 5.6 -5.8). From results in Chapter 4, adsorption is correlated with organic matter content. Thus, organic matter content and pK_{a1} should be correlated although pK_{a1} could be an average of several contributions. It is also possible to eliminate higher pK_a groups, due to the very low pH_{zpc} of the soils studied compared with the range of the adsorption measurements. We expected that adsorption will be explainable in terms of pK_{a1} and C_1 .

The pH_{zpc} obtained from alkalimetric titration is the pH at which the surface charge arising from all components is zero. Since the soils are heterogeneous the pK_a 's obtained may not correspond to hydrolysis states of the same "site." Formally pK_{a1} which is a transition from neutral to negative surface charge is equated with pK_{a2}^{int} in the metal-oxide model which is the basis for Equation 5.6. From Equation 5.6, pK_{a1}^{int} is equated to $(2pH_{zpc} - pK_{a2}^{int})$. The intrinsic constants obtained in this way are listed in Table 5.6. Speciations are shown in Figure 5.12 and Appendix E.

Under the experimental conditions cadmium adsorption is complete between pH 6-7, and is not affected by ionizations of any groups at higher pH. This suggests that hydrolysis products of aluminum oxide ($pK_{a2}^{int} = 10$) and iron oxide ($pK_{a2}^{int} = 8.8$) do

not contribute to the binding of Cd^{2+} . Complexes between these and $\text{Cd}(\text{OH})^+$ or $\text{Cd}(\text{OH})_2$ cannot be ruled out.

The intrinsic constants and surface properties for different soils are listed in Table 5.6. The total number of negatively charged sites, N_t , obtained by equating with C_1 varies from 24 to 410 $\mu\text{mole/g}$. As noted this number is correlated with organic matter content (Figure 5.7) but does not show a correlation with total surface area (Table 5.6).

5.6.2 Stability Constants

The stability constants for the reaction between cadmium and the fifteen different soils were calculated according to the surface complex formation model. The concentration of negatively charged surface sites at each pH was calculated from the site densities and values of $\text{pK}_{a1}^{\text{int}}$ and $\text{pK}_{a2}^{\text{int}}$ given in Table 5.6 and cadmium speciation as presented in Figure 5.1. Adsorption data (Figure 3.2 and Appendix A) were regressed against species concentrations using Equation 5.32 to obtain stability constants given in Table 5.7. The speciation patterns of the various surface complexes were calculated from the stability constants obtained by regression, the surface site concentrations and Cd(II) speciation. Predicted adsorption for all species is compared with experimental Cd(II) adsorption in Figures 5.13-5.27. The results indicate that free metal was primarily responsible for the adsorption of cadmium over a wide pH range.

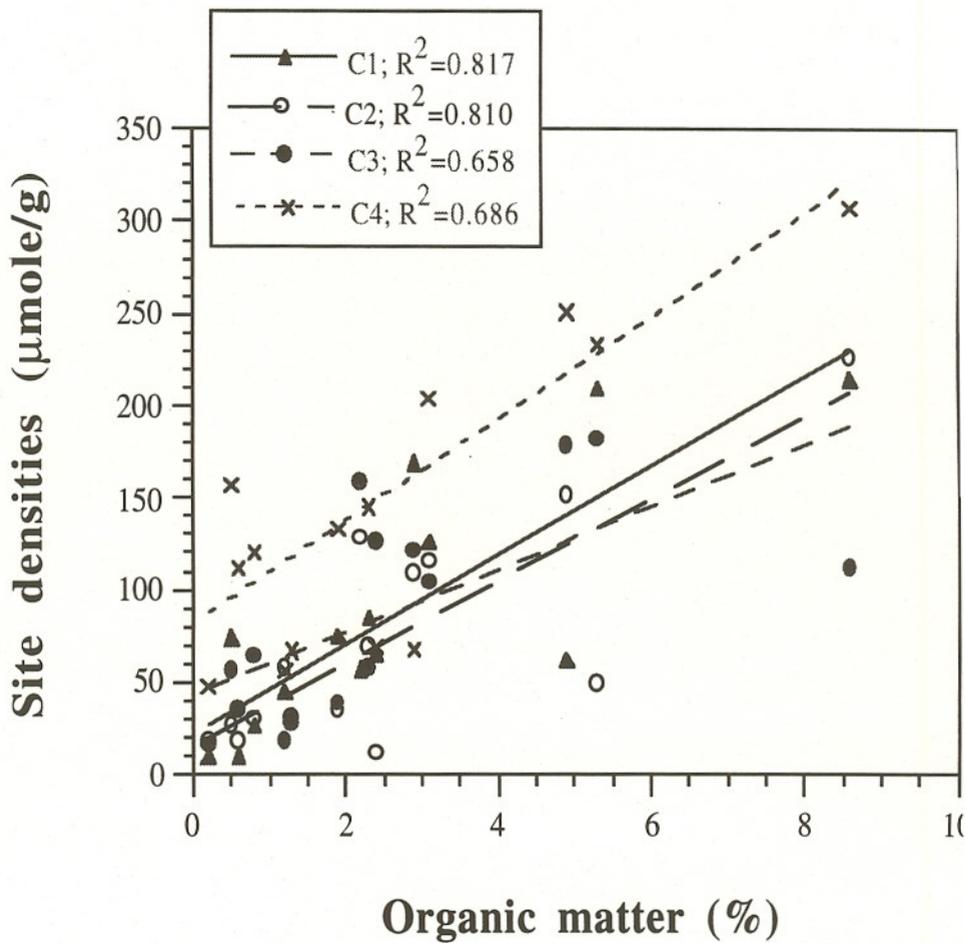


Figure 5.6 Site density as a function of soil organic content. $I = 0.001 \text{ M NaNO}_3$.

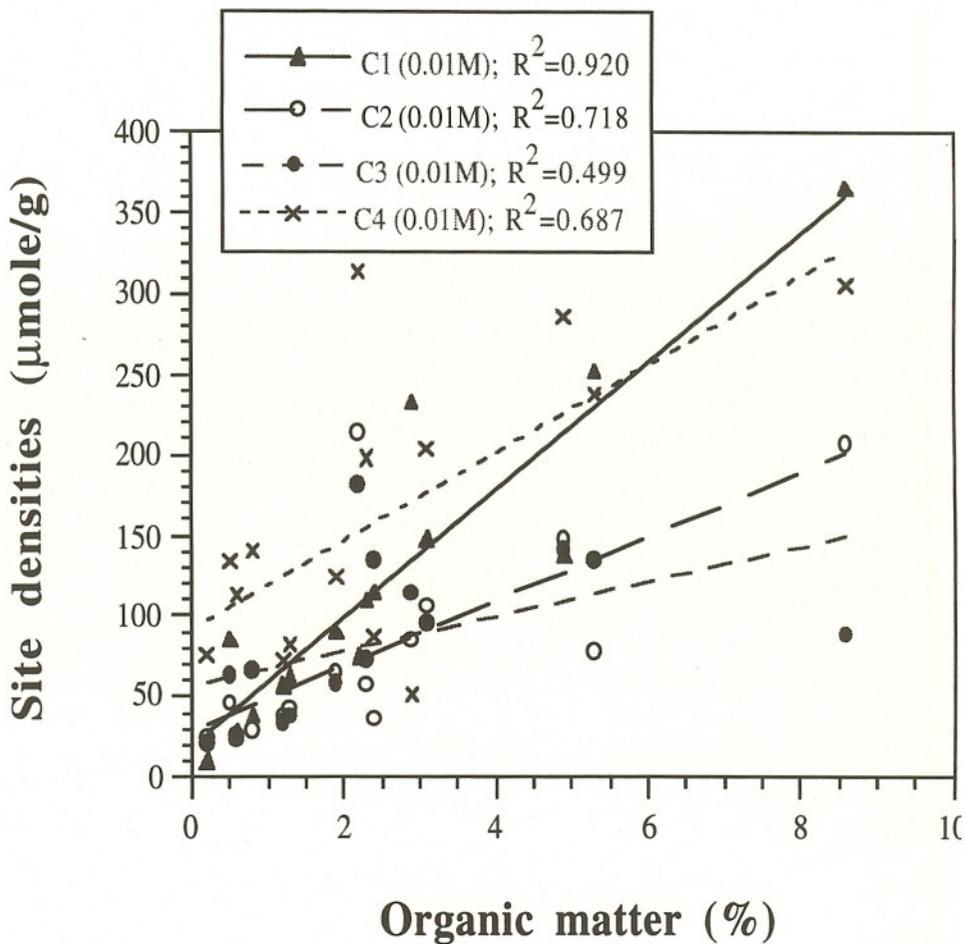


Figure 5.7 Site density as a function of soil organic content. $I = 0.01 \text{ M NaNO}_3$.

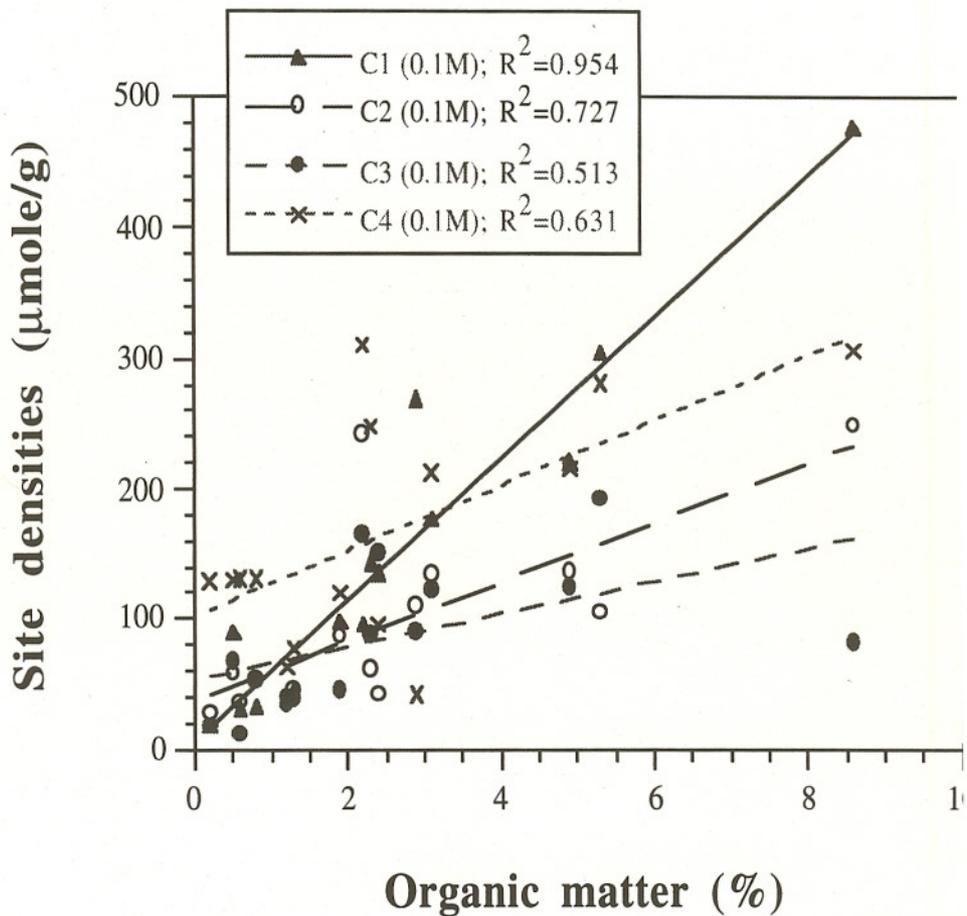


Figure 5.8 Site density as a function of soil organic content. $I = 0.1 \text{ M NaNO}_3$.

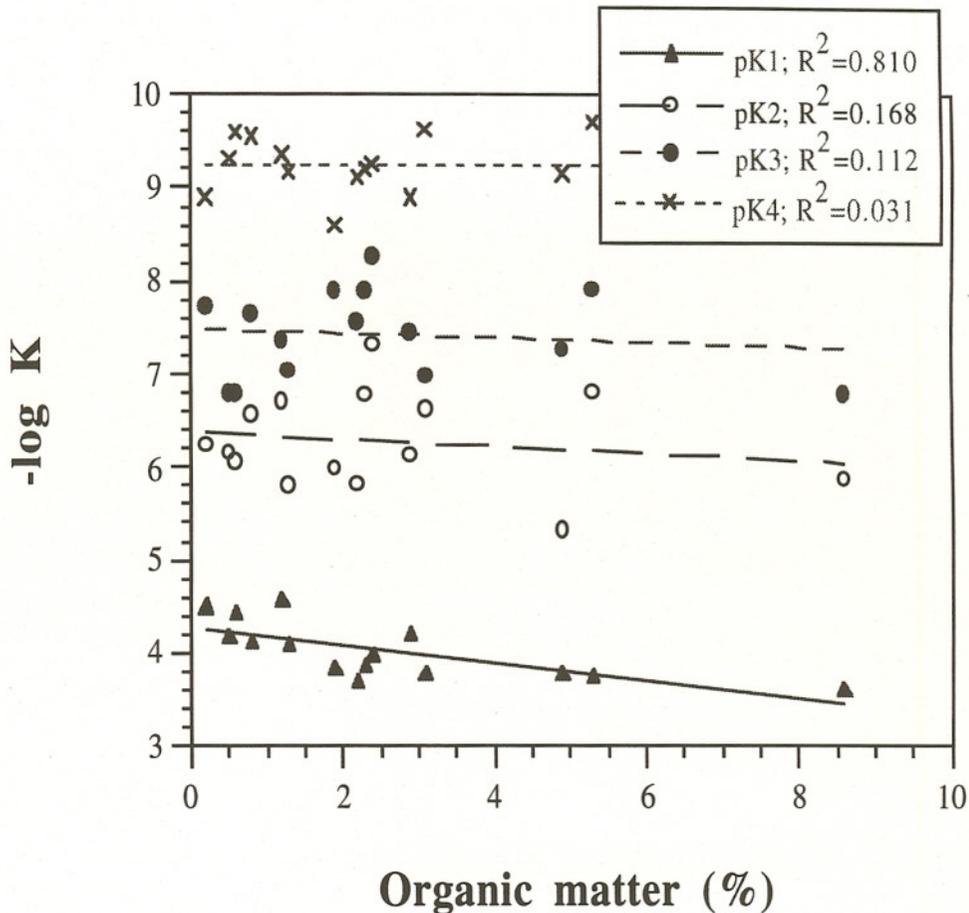


Figure 5.9 Surface acidity constants as a function of soil organic content. $I = 0.00$ M NaNO_3 .

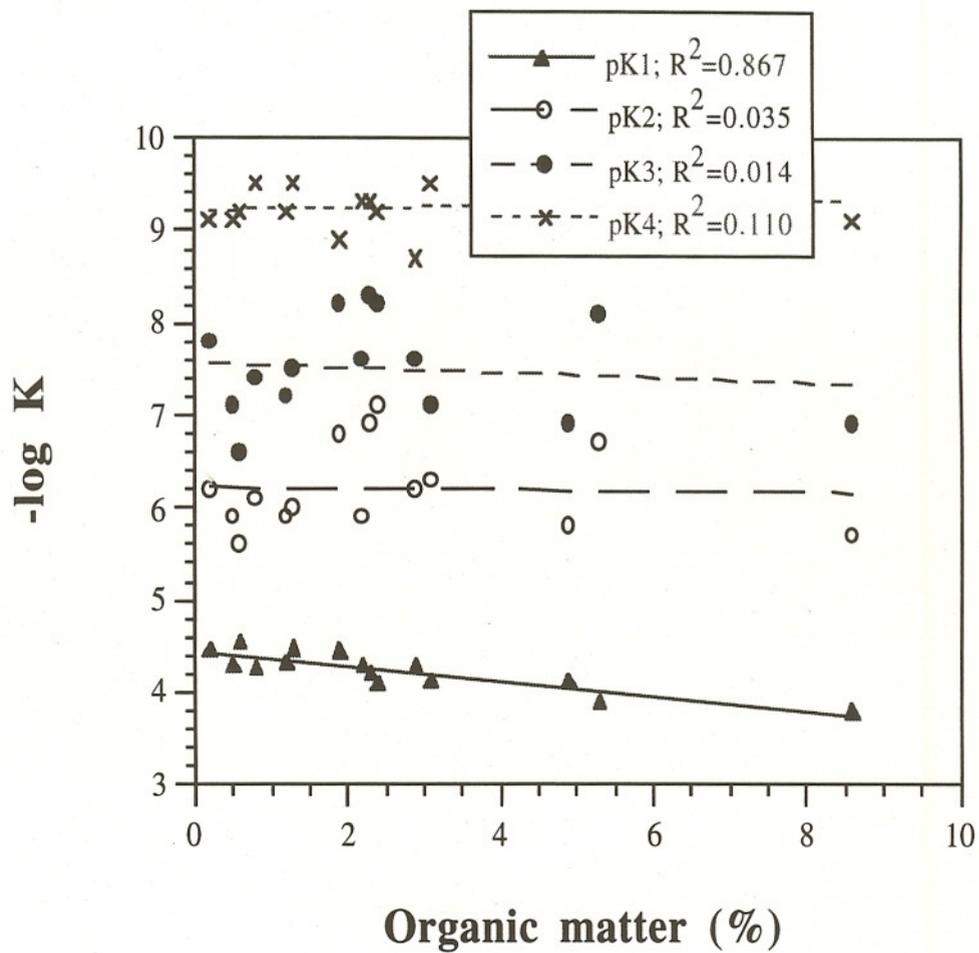


Figure 5.10 Surface acidity constants as a function of soil organic content. $I = 0.01$ M NaNO_3 .

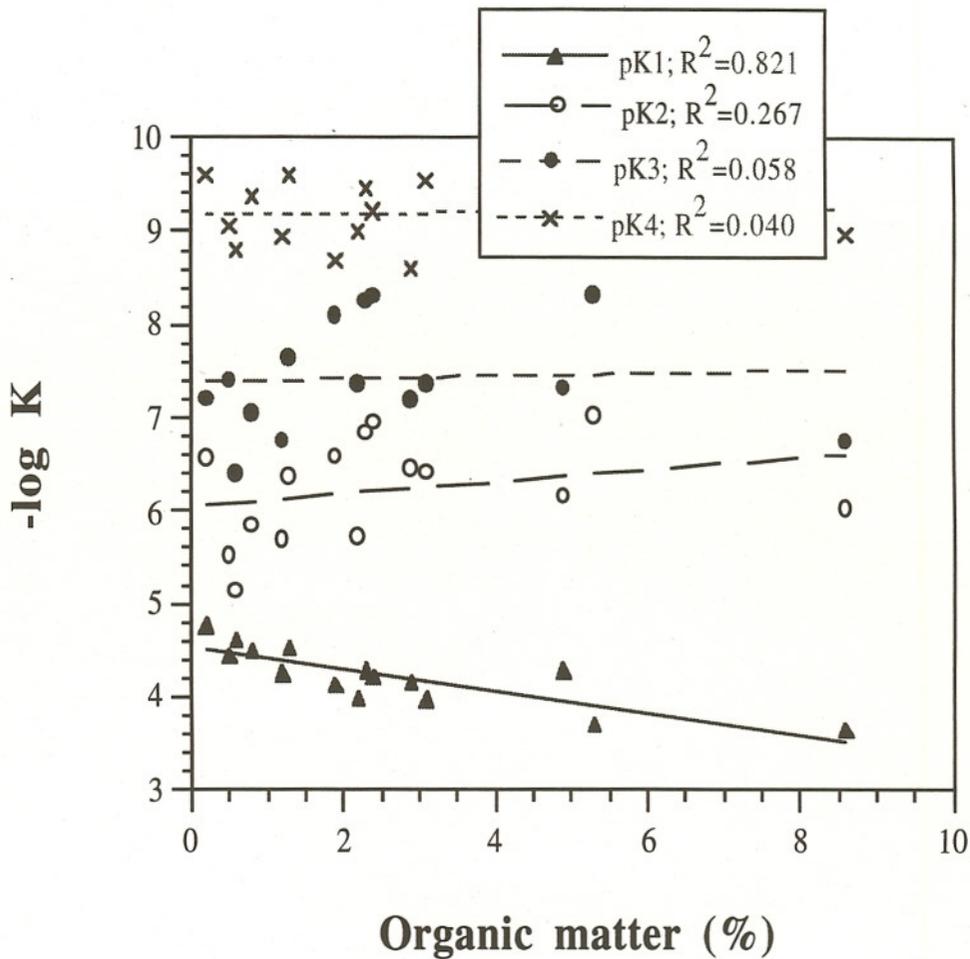


Figure 5.11 Surface acidity constants as a function of soil organic content. $I = 0.1 \text{ M NaNO}_3$.

Table 5.6 Surface acidity of soils.

Soil Name	N_t^1 ($\mu\text{moles/g}$)	pH_{zpc}	$\text{pK}_{\text{al}}^{\text{int}}$	$\text{pK}_{\text{a2}}^{\text{int}}$	A_{sp}^2 (m^2/g)
Birdsboro silt loam	105	3.40	2.50	4.30	7.06
Boonton loam (Bergen County)	252	3.00	2.10	3.90	7.20
Boonton loam (Union County)	410	2.80	1.80	3.80	6.45
Downer loamy sand	38	3.40	2.54	4.26	1.15
Dunellen sandy loam	90	3.20	1.95	4.45	5.21
Fill materials from Del. River	57	3.20	2.07	4.33	2.37
Freehold sandy loam (B horizon)	10	3.60	2.74	4.46	9.01
Freehold sandy loam (A horizon)	114	2.90	1.70	4.10	2.04
Hazen gravelly loam	148	3.10	2.08	4.12	5.90
Lakewood sand	24	3.60	2.90	4.30	1.10
Penn silt loam	62	3.30	2.12	4.48	8.04
Rockaway stony loam	233	2.80	1.48	4.12	8.62
Sassafras sandy loam	29	3.40	2.26	4.54	5.31
Washington loam	138	2.85	1.40	4.30	11.59
Whippany silty clay loam	110	3.00	1.80	4.20	5.98

¹ Equated with C_1 obtained at 0.01 M NaNO_3 .

² From Table 3.7, Chapter 3.

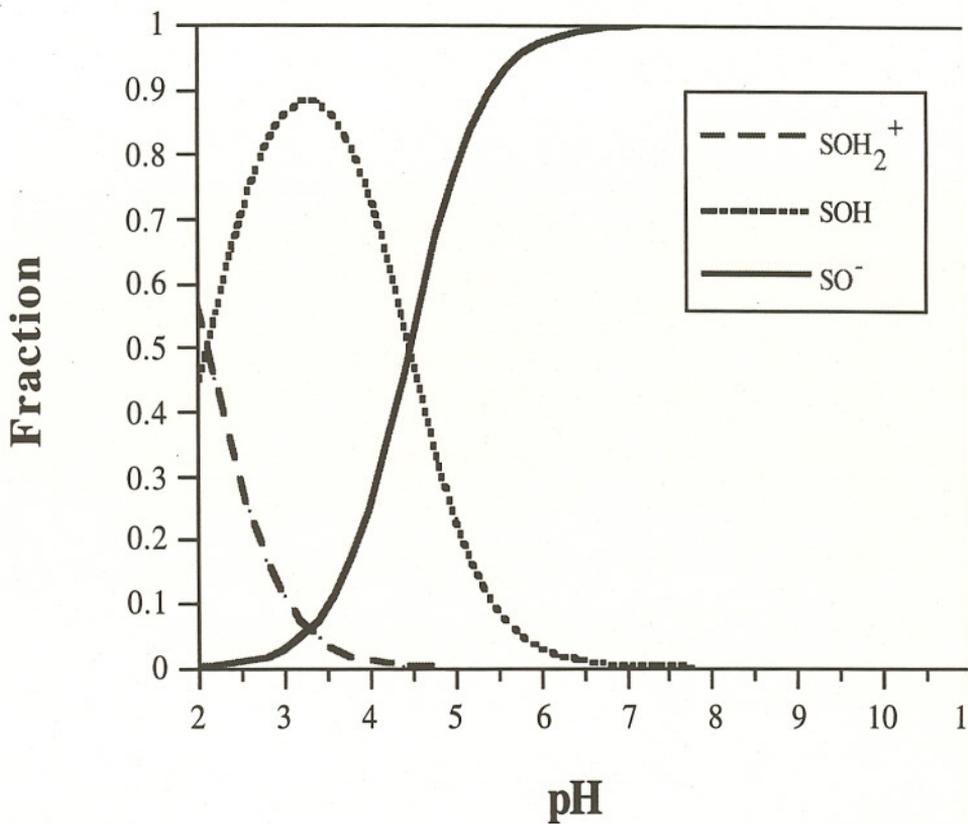


Figure 5.12 Speciation of surface acidity for Penn silt loam.

5.7 Discussion

The simplified surface complexation model (Equation 5.32) was applied to determine the stability constants of cadmium adsorbed onto soils. This model takes into account all metal hydrolysis species as adsorbates in an adsorption process and provides a simple method to predict the distribution of the metal species adsorbed at various pH values. Free cadmium was identified as the most important species up to pH 9.

The surface acidity constants of soils were determined by the alkalimetric titration method. Four stability constants for the protonation of the soil surfaces were determined. From these, the "intrinsic constants" for one site were obtained. The intrinsic acidity constants pK_{a2}^{int} ranged from 3.80 to 4.54, the pH_{zpc} ranged from 2.80 to 3.60 and the derived acidity constants pK_{a1}^{int} ranged from 1.40 to 2.90 for the 15 different soils (Table 5.6). The surface acidity measurements also gave site charge densities which vary from soil to soil with a strong correlation between C_1 , corresponding to acidity constant pK_1 , with soil organic matter (Figure 5.7).

While alkalimetric titration indicates soil surfaces have 4 discrete pK_a values, only one, pK_{a1} , corresponding to a transition from neutral to negatively charged surface site, is used to obtain pK_{a2}^{int} . In addition to pK_{a2}^{int} , pH_{zpc} is needed to adequately model the adsorption data for $pH > 5$ (Figures 5.13-5.27). Since the site charge density corresponding to this transition is correlated with organic matter, this is consistent with the results of the analysis in Chapter 4 that adsorption is primarily accounted for by organic matter content.

Above 2% organic matter the stability constants, $\log K_1$ for Cd^{2+} and soils is almost constant ranging from 4.68 to 5.12 among soils with an average value of 4.88

(Figure 5.28). This constancy suggests that adsorption of Cd^{2+} to soil organic matter may result in a complex that is similar for all soils. Thus, further characterization of soil organic matter is unnecessary for the purpose of predicting adsorption. The variation in stability constant below this organic matter content may be related to contributions from inorganic components which have not been included in the simplified model.

For most soils the simplified model (Equation 5.32), which uses only a single experimentally determined pK_a , gives a good fit above this pK_a . For some soils, for example Rockaway stony loam, the percent adsorbed is greater than predicted at low pH. This adsorption could be due to contributions from neutral or positive surface sites which were neglected in the simplified model. Adsorption could also arise from physical processes which were not considered. The simplified model in general is good for data above pH 5.

To apply this model to predict cadmium adsorption on a new soil, measurements of organic matter content, and pH_{zpc} for this soil are needed. From the organic content the regression in Figure 5.7 is used to predict the site density, $N_t = C_1$, and the regression in Figure 5.10 is used to predict acidity constant $\text{pK}_{a1} = \text{pK}_{a2}^{\text{int}}$. The second constant, $\text{pK}_{a2}^{\text{int}}$, needed to obtain surface site concentration is calculated from pH_{zpc} (Equation 5.6) and site concentration from Equation 5.9 and 5.21. Cd(II) speciation is obtained from Equations 5.13-5.14 with constants given in Table 5.1. Above 2% organic matter content an average stability constant between Cd^{2+} and soil is used: $\log K_1 = 4.88$. The first term in Equation 5.32 is then used to calculate the sorbed cadmium.

Table 5.7 Stability constants of surface complexes with soils and organic content of soils. 1×10^{-4} M Cd; soil:water = 1 g/100 mL; I = 0.01 M NaNO₃; T = 25 °C.

Soil Name	OM ¹ (%)	log K ₁ ²	log K ₂ ²	log K ₃ ²
Birdsboro silt loam	2.2	4.76	5.56	6.34
Boonton loam (Bergen County)	5.3	4.83	5.68	6.02
Boonton loam (Union County)	8.6	5.12	6.31	7.21
Downer loamy sand	0.8	4.21	5.83	6.87
Dunellen sandy loam	1.9	4.83	6.01	7.12
Fill materials from Del. River	1.2	4.73	5.21	6.23
Freehold sandy loam (B horizon)	0.2	3.85	5.32	5.88
Freehold sandy loam (A horizon)	2.4	4.68	6.33	6.54
Hazen gravelly loam	3.1	4.75	5.26	6.89
Lakewood sand	0.5	4.02	5.84	6.37
Penn silt loam	1.3	4.88	5.78	5.96
Rockaway stony loam	4.9	4.95	5.98	7.12
Sassafras sandy loam	0.6	4.14	6.12	7.06
Washington loam	2.9	5.01	5.87	6.35
Whippany silty clay loam	2.3	4.92	5.64	5.88

¹ Organic matter content

² K₁, K₂, and K₃ are stability constants of surface complexes between soil sites, SO⁻, and Cd⁺², CdOH⁺, and Cd(OH)₂, respectively.

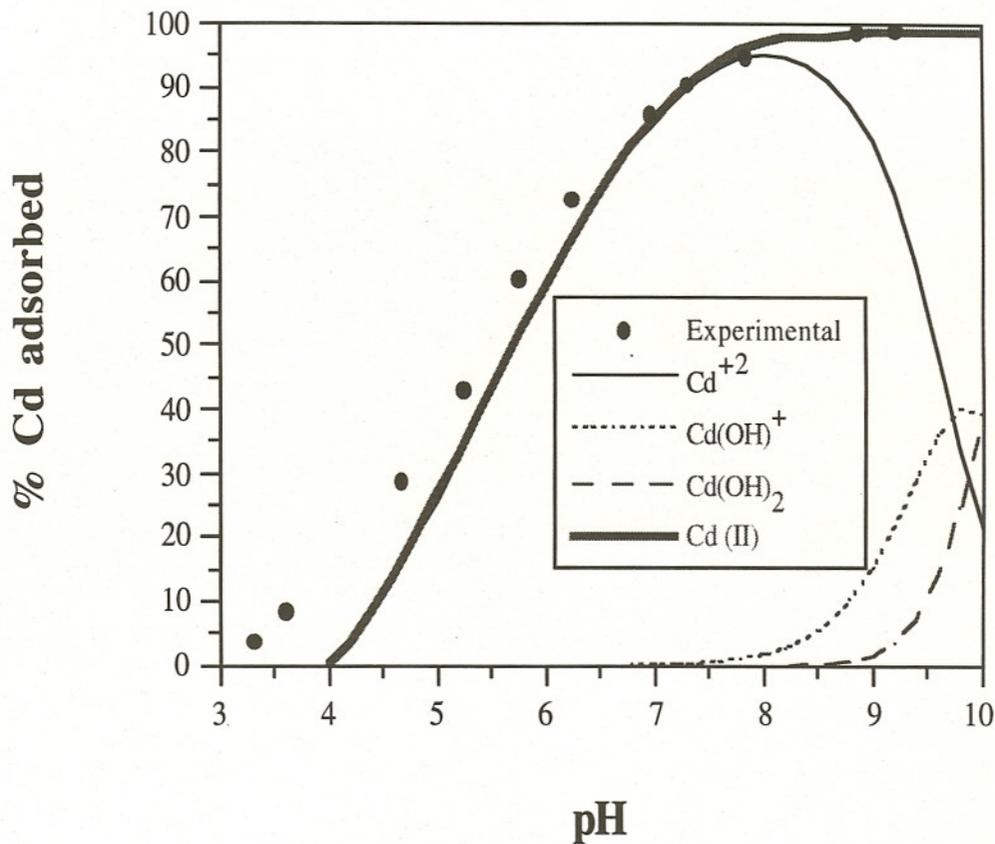


Figure 5.13 The surface complexation model fit for Cd(II) adsorption onto Birdsboro silt loam. Soil:water = 1 g/100 mL; I = 0.01 M NaNO₃; T = 25 °C.

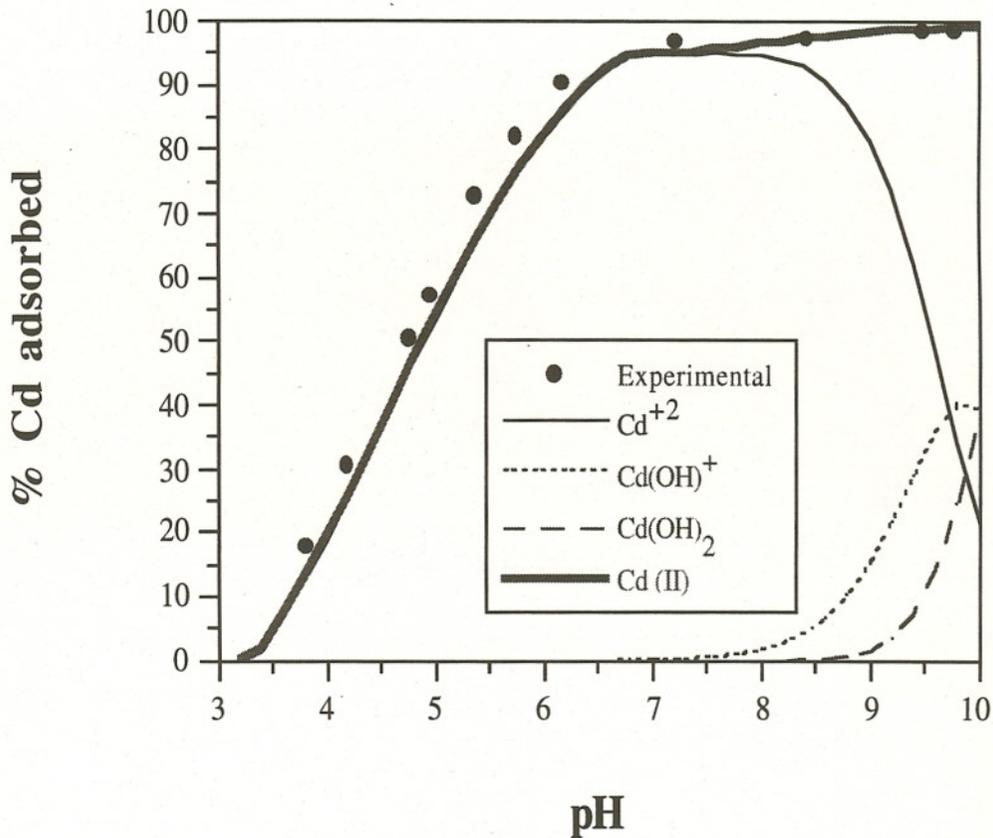


Figure 5.14 The surface complexation model fit for Cd(II) adsorption onto Boonton loam (Bergen County). Soil:water = 1 g/100 mL; I = 0.01 M NaNO₃; T = 25 °C.

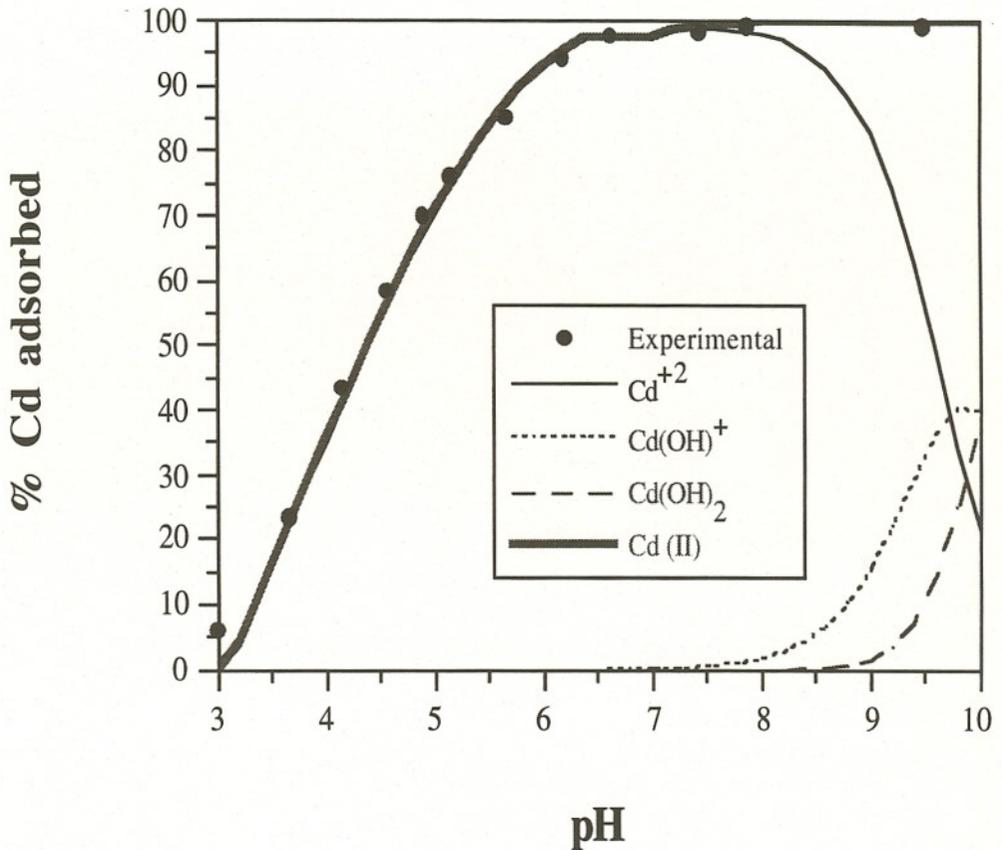


Figure 5.15 The surface complexation model fit for Cd(II) adsorption onto Boontloam (Union County). Soil:water = 1 g/100 mL; I = 0.01 M NaNO₃; T = 25 °C.

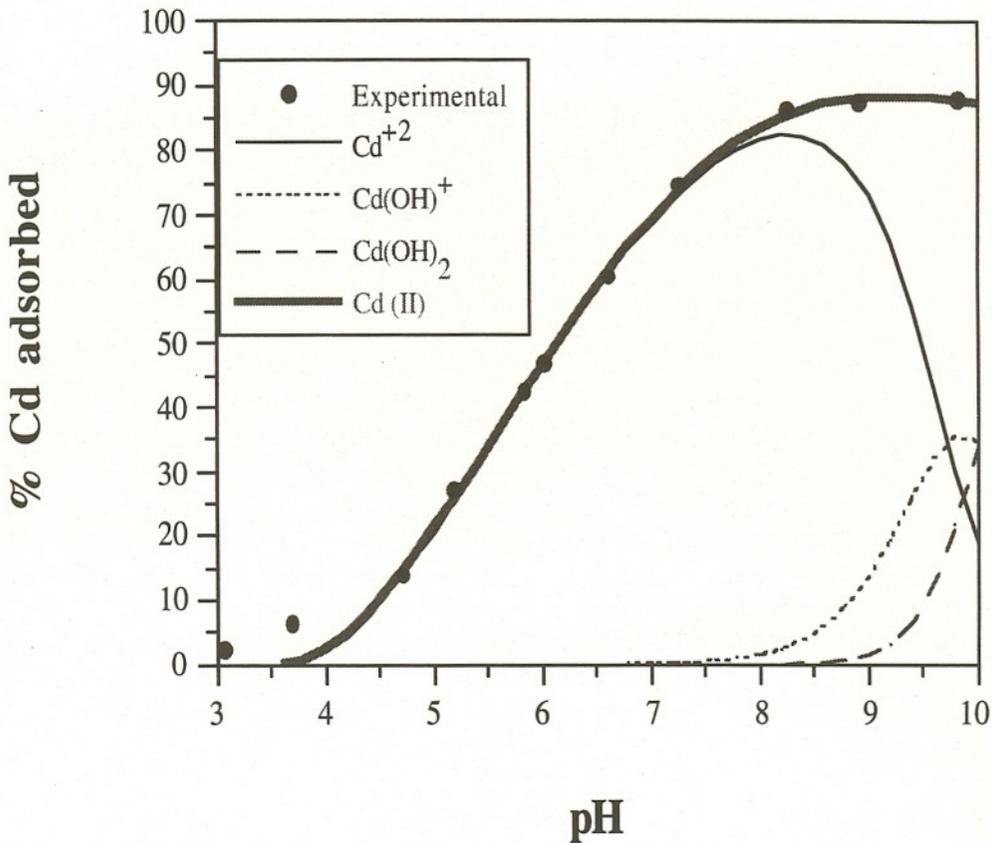


Figure 5.16 The surface complexation model fit for Cd(II) adsorption onto Downe loamy sand. Soil:water = 1 g/100 mL; I = 0.01 M NaNO₃; T = 25 °C.

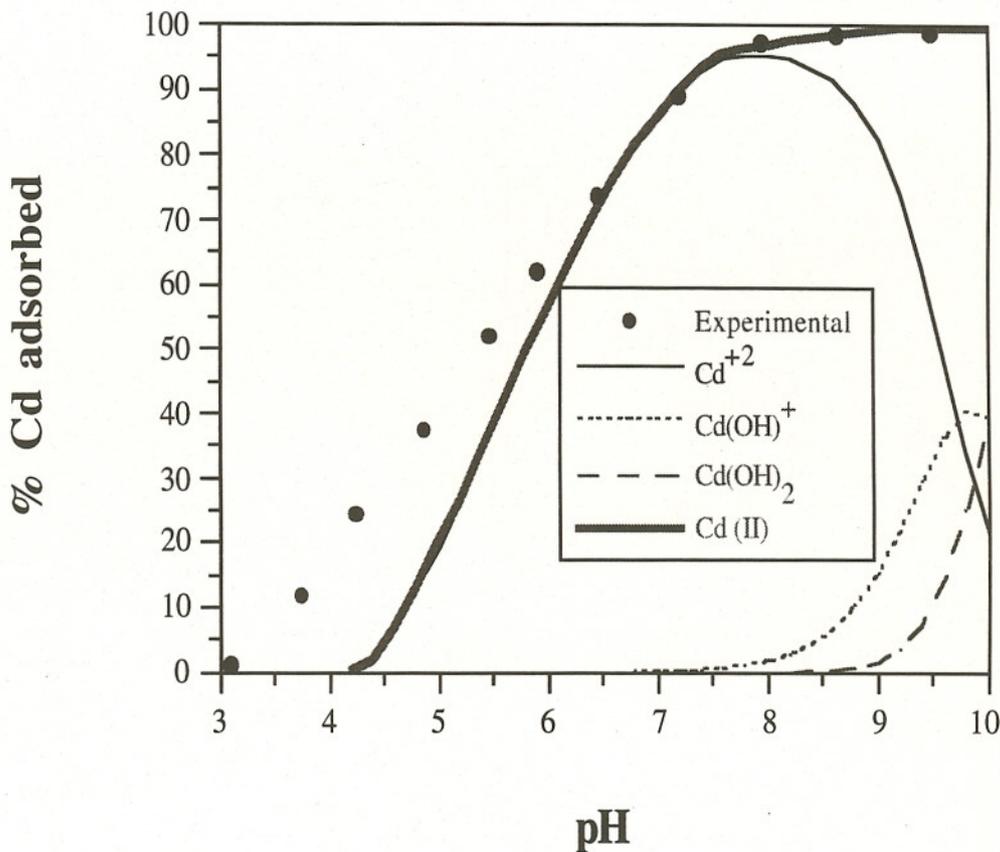


Figure 5.17 The surface complexation model fit for Cd(II) adsorption onto Duneller stony loam. Soil:water = 1 g/100 mL; I = 0.01 M NaNO₃; T = 25 °C.

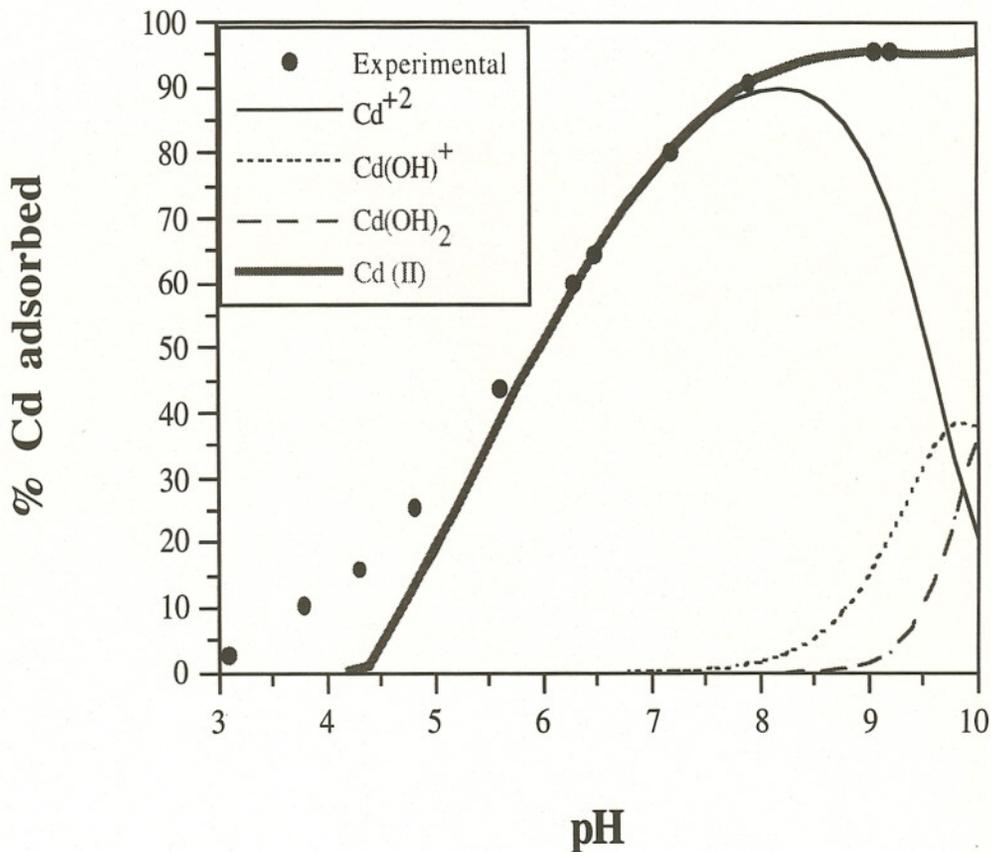


Figure 5.18 The surface complexation model fit for Cd(II) adsorption onto fill material dredged from Delaware River. Soil:water = 1 g/100 mL; I = 0.01 M NaNO₃; T = 25 °C.

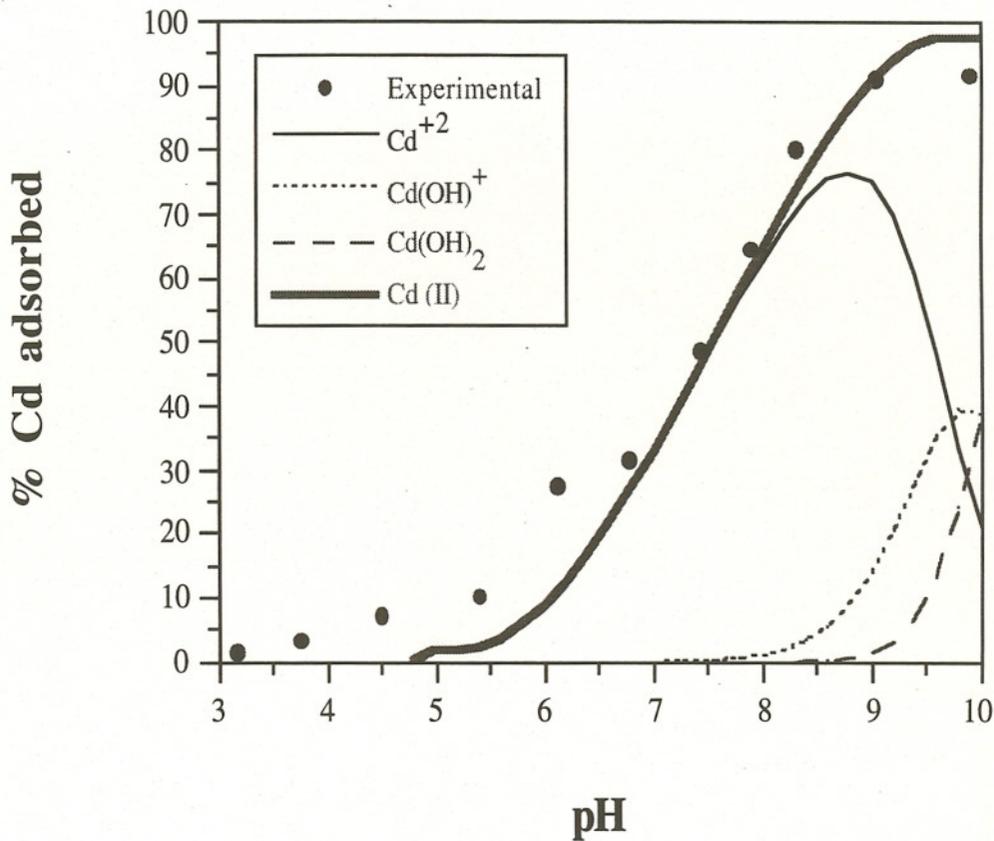


Figure 5.19 The surface complexation model fit for Cd(II) adsorption onto Freehold stony loam (A horizon). Soil:water = 1 g/100 mL; I = 0.01 M NaNO₃; T = 25 °C.

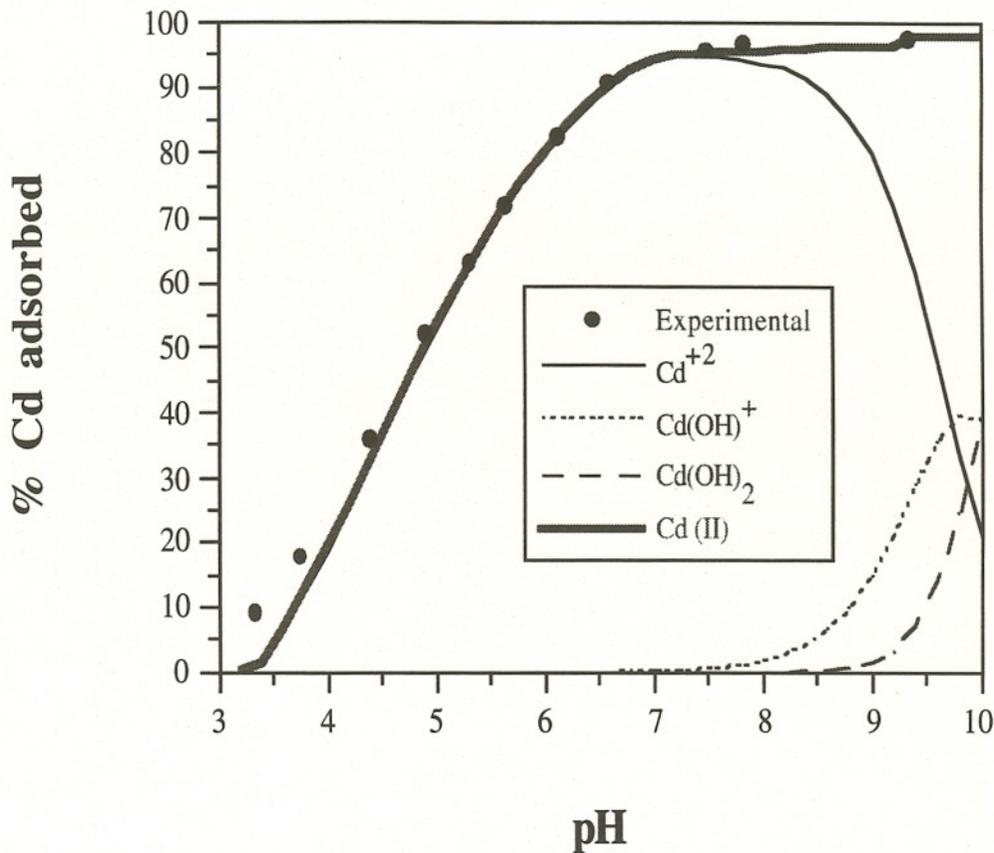


Figure 5.20 The surface complexation model fit for Cd(II) adsorption onto Freehold stony loam (B horizon). Soil:water = 1 g/100 mL; I = 0.01 M NaNO₃; T = 25 °C.

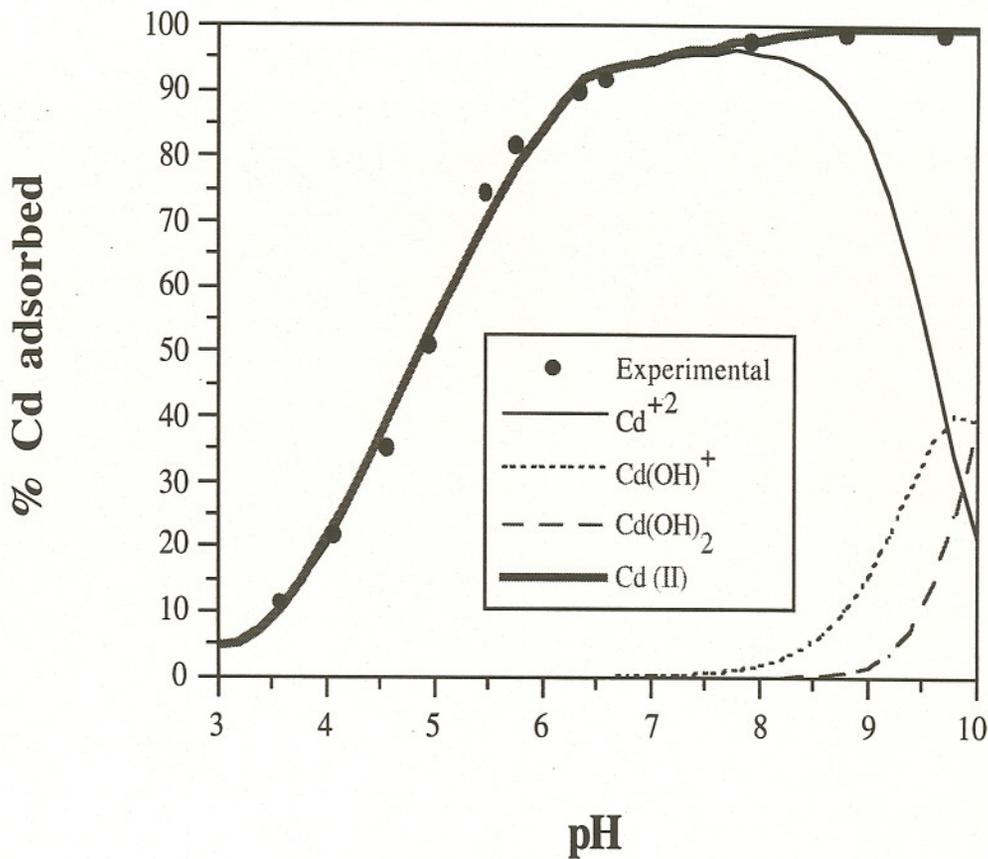


Figure 5.21 The surface complexation model fit for Cd(II) adsorption onto Hazen gravelly loam. Soil:water = 1 g/100 mL; I = 0.01 M NaNO₃; T = 25 °C.

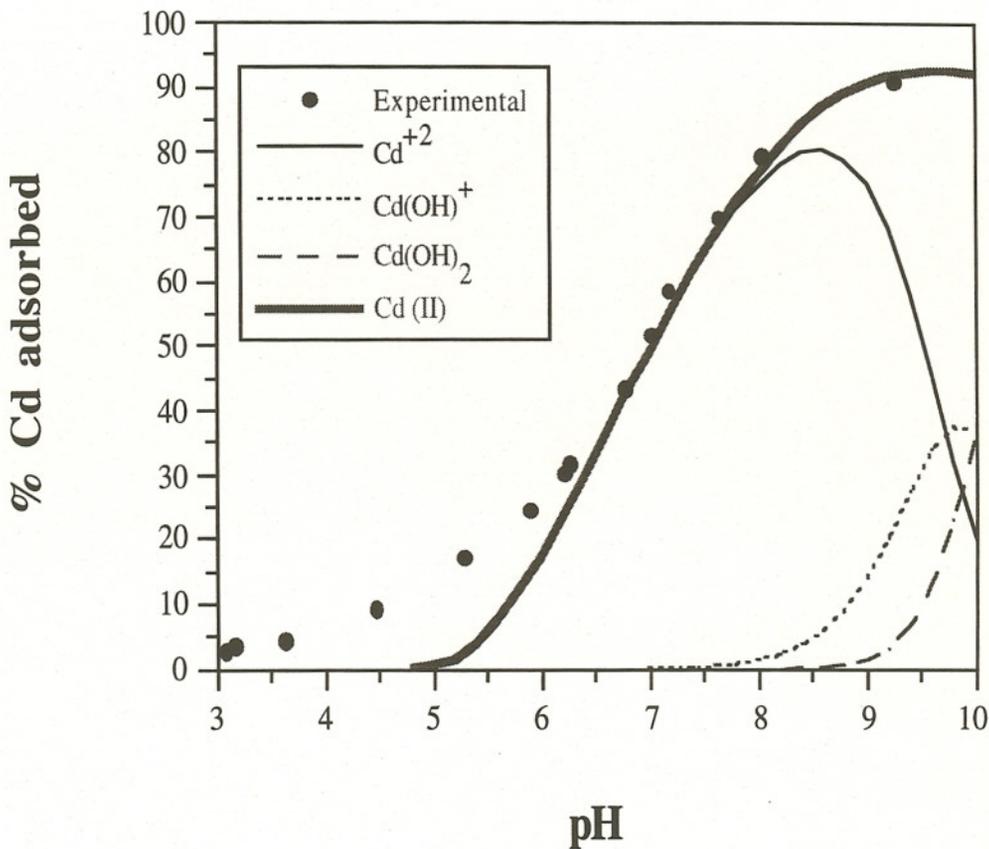


Figure 5.22 The surface complexation model fit for Cd(II) adsorption onto Lakewood sand. Soil:water = 1 g/100 mL; I = 0.01 M NaNO₃; T = 25 °C.

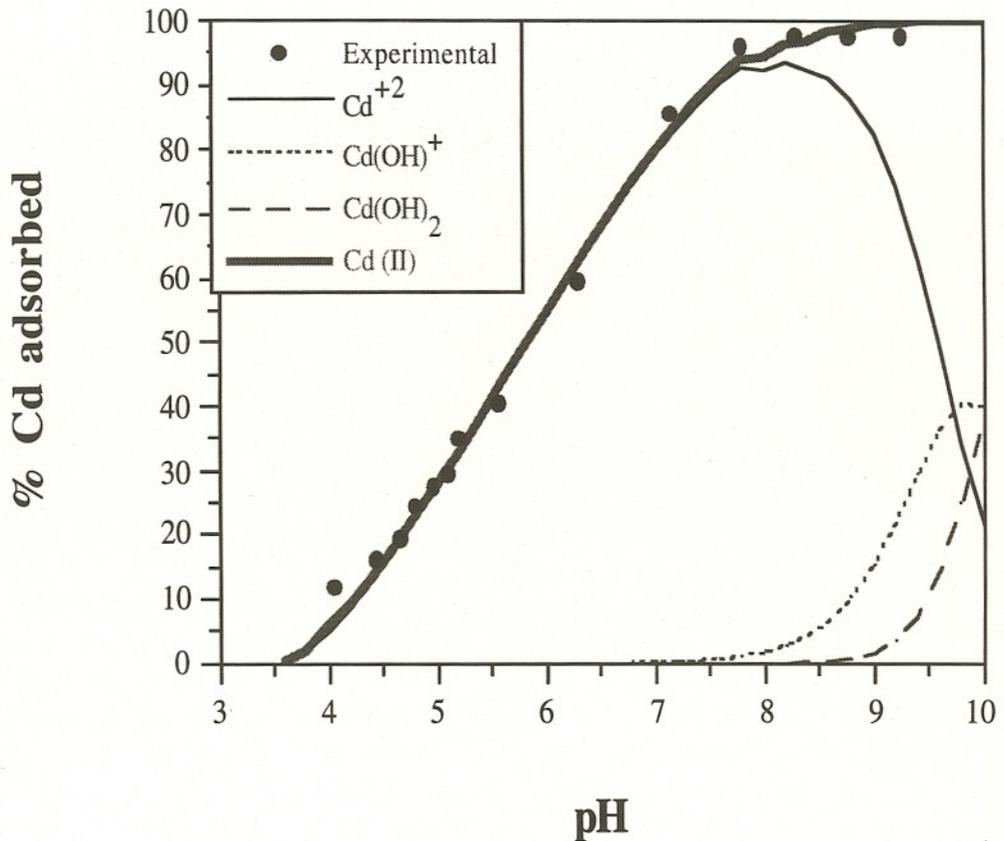


Figure 5.23 The surface complexation model fit for Cd(II) adsorption onto Penn sil loam. Soil:water = 1 g/100 mL; I = 0.01 M NaNO₃; T = 25 °C.

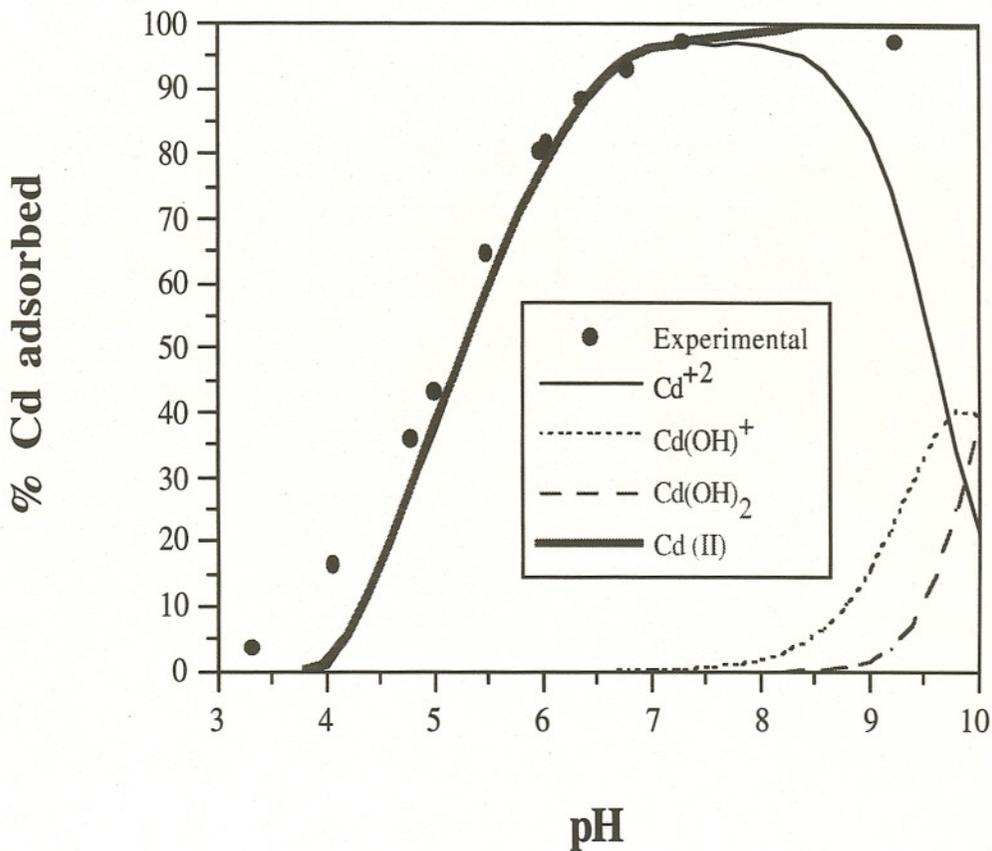


Figure 5.24 The surface complexation model fit for Cd(II) adsorption onto Rockaway stony loam. Soil:water = 1 g/100 mL; I = 0.01 M NaNO₃; T = 25 °C.

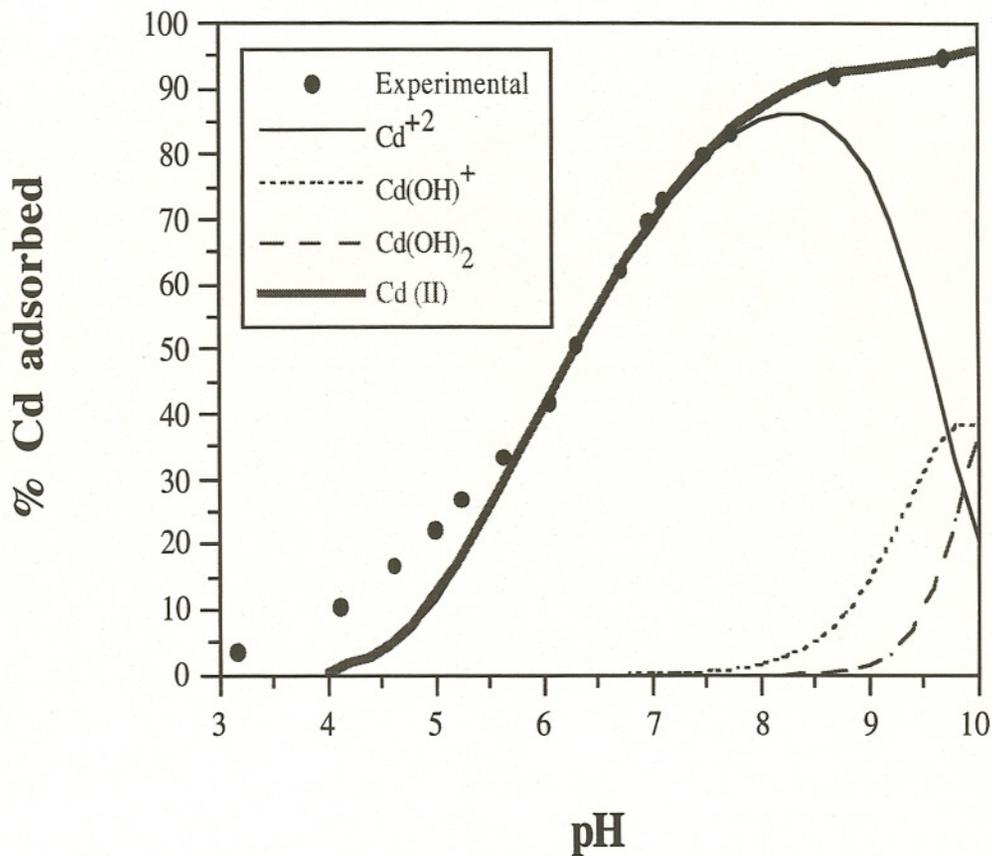


Figure 5.25 The surface complexation model fit for Cd(II) adsorption onto Sassafras stony loam. Soil:water = 1 g/100 mL; I = 0.01 M NaNO_3 ; T = 25 °C.

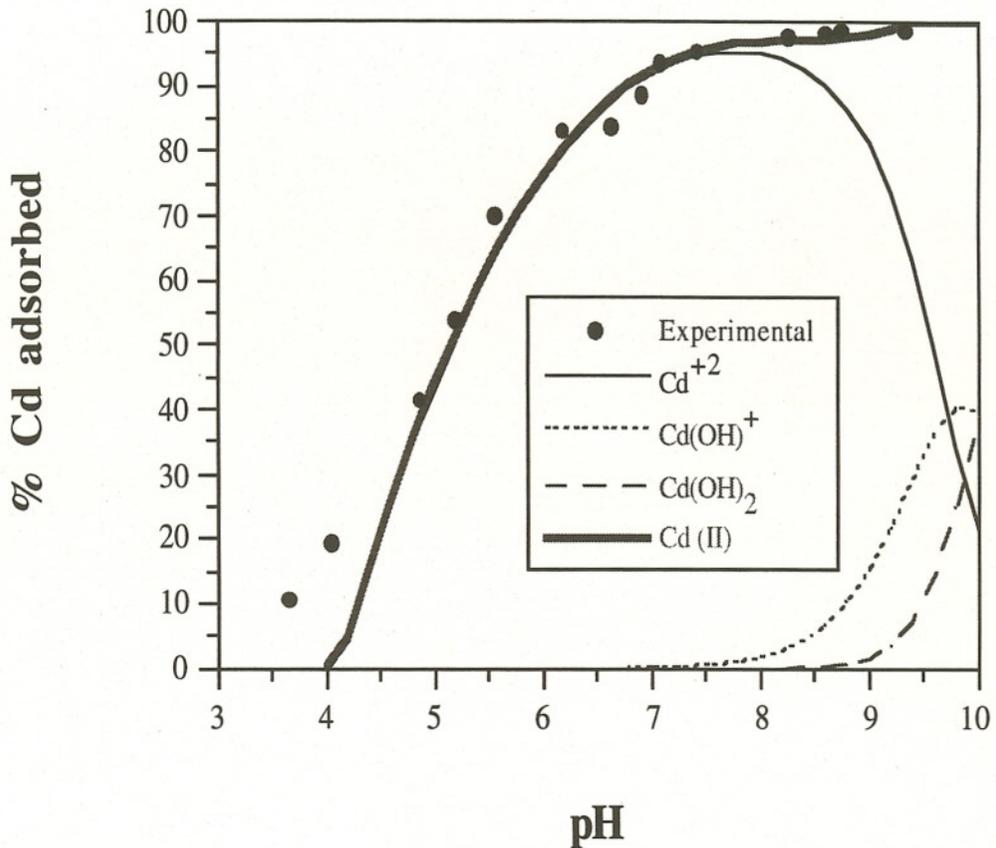


Figure 5.26 The surface complexation model fit for Cd(II) adsorption onto Washington loam. Soil:water = 1 g/100 mL; I = 0.01 M NaNO₃; T = 25 °C.

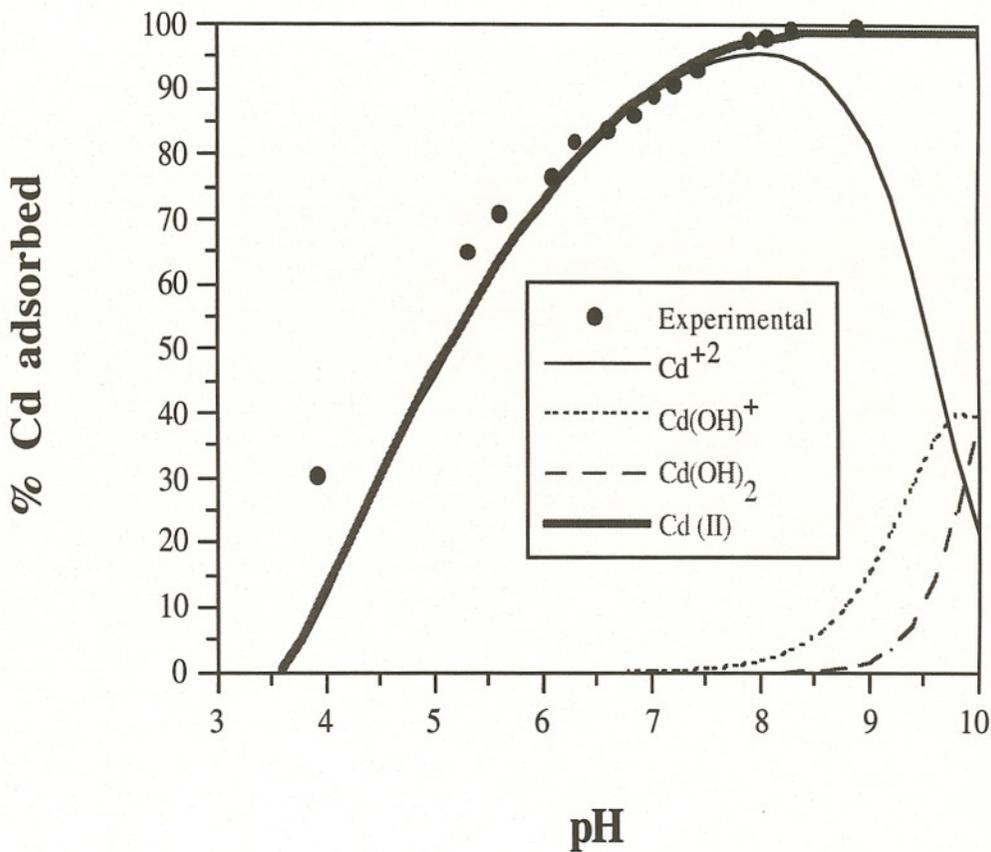


Figure 5.27 The surface complexation model fit for Cd(II) adsorption onto Whippany silty clay loam. Soil:water = 1 g/100 mL; I = 0.01 M NaNO₃; T = 25 °C.

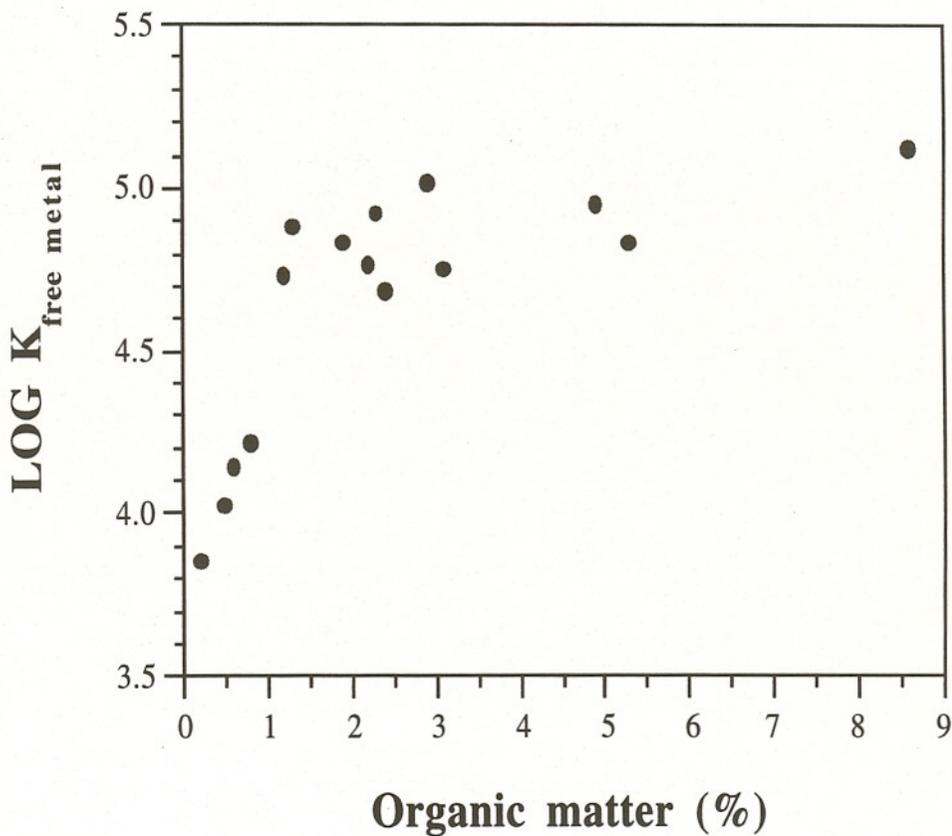


Figure 5.28 The stability constants between free cadmium and soils as a function of soil organic matter content. Soil:water = 1 g/100 mL; I = 0.01 M NaNO_3 ; T = 25 °C.

DETERMINATION OF SOIL PARTITION COEFFICIENTS FOR CD BY DESORPTION AND COMPARISON TO ADSORPTION MEASUREMENTS

6.1 Introduction

Partitioning of contaminants onto soil is usually studied in batch experiments conducted in shake-flasks that provide characteristic coefficients of adsorption. However, the conditions in these experiments are very different from those found in the field where the soil is stationary and the question frequently is the prediction of desorption behavior. Environment conditions, such as chemicals loading and water flow rate, change the rate and extent of chemical reaction on soils.

Comparisons between batch and column measurements for assessing adsorption-desorption of organic chemicals have been published by Green et al. (1971) and Jackson et al. (1984). They concluded: (1) that because the batch method is simpler and more reproducible, it will probably remain the most-used method for measuring equilibrium adsorption/desorption, whereas, (2) the column method is more realistic in simulating field conditions. Johnson and Farmer (1993) have also shown that batch and flow column methods give similar results for the retention and release of some organic

contaminants in soils. For the flow method, the column was packed uniformly with soil and then chemicals were continuously introduced at a fixed flow rate until equilibrium was achieved. The flow data were treated by three methods: (1) direct extraction of the soil, (2) the difference method, and (3) the retardation factor method to evaluate the distribution of organics between soil and water phases. For the difference method, the quantity of pesticide sorbed was the difference between the quantities added to the columns and the quantities of solute in the effluent. For the retardation method, the retardation factor was determined by dividing the volume of effluent required to leach 50% of the column. For the direct extraction of the soil method, the amount of adsorbed pesticide was extracted by organic solvents. The partition coefficients were obtained from traditional batch and flow column methods by linear and nonlinear Freundlich sorption isotherm measurements.

In this study we investigated the desorption behavior of cadmium from five of the characterized soils. Desorption was studied as a function of cadmium loading onto the soil and on the flow rate of water through the soil column. The partition coefficients determined for the desorption of cadmium from the soils were compared to those determined for the adsorption.

6.2 Materials and Methods

The soils used in this part of the study were Boonton loam (Union County), Downer loamy sand, fill material dredged from the Delaware River, Freehold sandy loam (A horizon), and Rockaway stony loam. For the batch equilibration studies, 1.00 ± 0.01 g samples of each soil were immersed in 100 mL of 0.01 N NaNO_3 . Cadmium nitrate was added at initial concentrations of 5×10^{-5} , 1×10^{-4} , or 5×10^{-4} M in the soil

suspension. Ten samples of each soil were prepared for each initial cadmium concentration. The pH values were adjusted to cover the range from 3 to 9 by adding NaOH or HNO₃ after an initial shaking for a half hour in an attempt to avoid precipitation of cadmium at high pH. Samples were shaken at 150 strokes on a reciprocating shaker (Lab-Line Instruments, Melrose Park, IL) for 24 hours at room temperature of 25 ± 2 °C. The pH values were determined and, if necessary, adjusted at 1, 2, 4, 8, 16, and 22 hours. After 24 hours of shaking, we determined the final pH value of each sample and used these as the adsorption reaction values. The samples were then filtered through 0.45 µm polypropylene fiber membrane filters (Gelman Sciences, Ann Arbor, MI). The cadmium concentrations of the filtrate were analyzed by using atomic absorption spectrophotometry (Perkin-Elmer Zeeman Model 5000). The difference between the amount of metal remaining in the solution and the amount initially present in the solution was taken as the amount of metal adsorbed by soil.

Samples for the column desorption experiments were prepared by adding 500 g soil per 50 L of 0.01 N NaNO₃ in a 80 L container. Cadmium nitrate was added at a concentration of 5×10^{-5} , 1×10^{-4} , or 5×10^{-4} M. The suspension, at natural soil pH, was stirred at 150 rpm for 24 hours at room temperature (25 ± 2 °C). After 24 hours, we measured the pH of the suspension. A 10 mL aliquot was filtered through a 0.45 µm polypropylene fiber membrane filter (Gelman Sciences, Ann Arbor, MI) and the cadmium concentration of the filtrate was analyzed by atomic absorption spectrophotometry.

The suspension was allowed to settle for four hours to separate liquids and solid phases. To reduce the loss of fine-grain solids from the supernatant, we passed the supernatant through a 65 µm filter twice prior to discarding, then the remaining solids

on the filter were replaced into the container with the remaining slurry. Six plexiglass columns 5 cm in diameter by 15 cm in length were packed identically with the soil slurry that had been equilibrated with cadmium. The soil slurry was packed into each of the plexiglass columns by adding small increments while gently tapping the sides of the column. The increments were added until the soil height was 3 cm.

A multichannel peristaltic pump was used to apply a 0.01 N NaNO_3 solution to elute the columns. Six flow rates ranging from 0.5 to 13 mL/min that reflected various rainfall intensities and field conditions (unsaturation or saturation) were employed.

For the column experiments, the natural soil pH was used and the column effluent were collected as 100 mL samples. The column effluents were completely mixed and then 10 mL aliquots were acidified by adding 0.1 N HNO_3 . Samples were analyzed by atomic absorption spectrophotometry (Perkin-Elmer Zeeman Model 5000) to determine the concentration of cadmium.

6.3 Results and Discussion

6.3.1 Batch Equilibration

We determined concentration of the added cadmium that remained in solution after the 24-hour equilibration for each soil at each of the ten pH values and at each of the three initial concentrations of cadmium. We assumed that the difference between the cadmium added and that remaining in solution at the end of the 24 hours was sorbed to the soil. We converted these partitioning data to partition coefficients (K_d). The K_d values for the 5×10^{-5} , 1×10^{-4} , and 5×10^{-4} M initial concentration are shown in Figures 6.1, 6.2, and 6.3, respectively. We used these sets of data to estimate the K_d

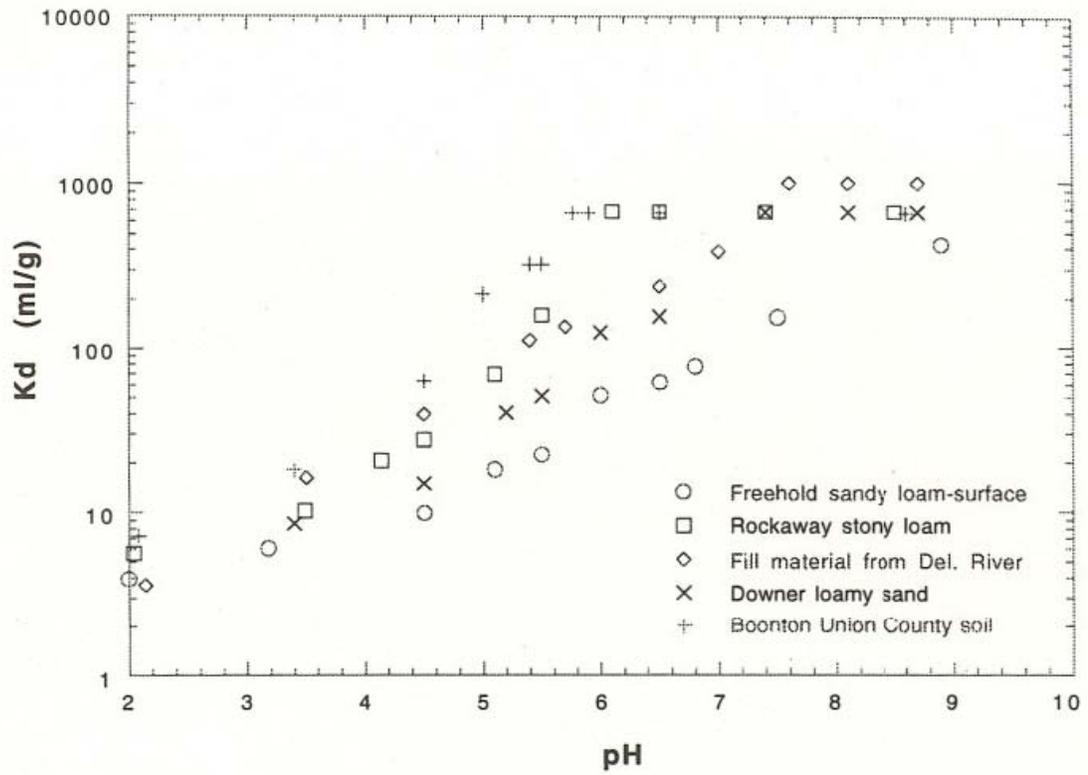


Figure 6.1. Partition coefficient (K_d) for 5×10^{-5} M cadmium. Soil:water = 1 g/100 mL; I = 0.01 M NaNO_3 ; T = 25 °C.

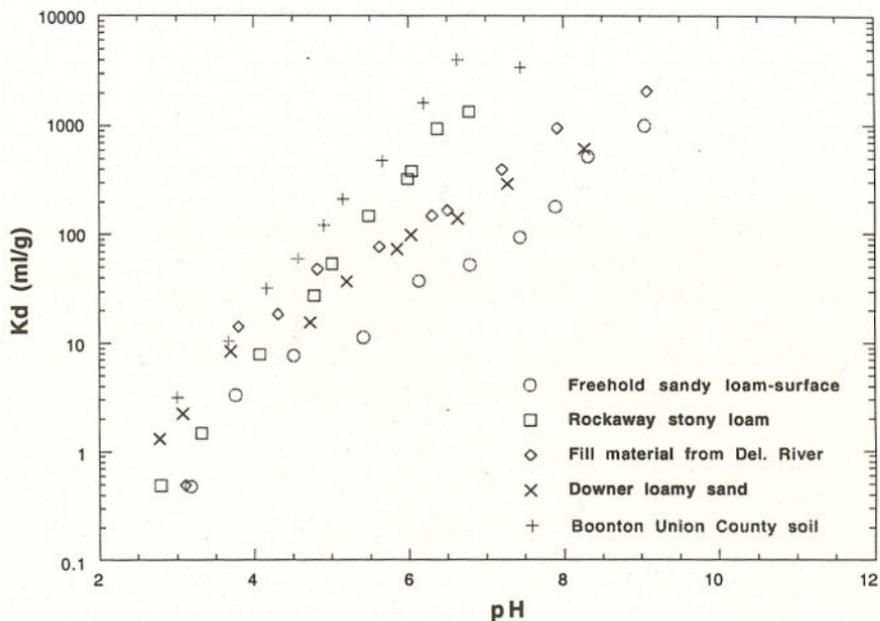


Figure 6.2. Partition coefficient (K_d) for 1×10^{-4} M cadmium. Soil:water = 1 g/100 mL; $I = 0.01$ M NaNO_3 ; $T = 25^\circ\text{C}$.

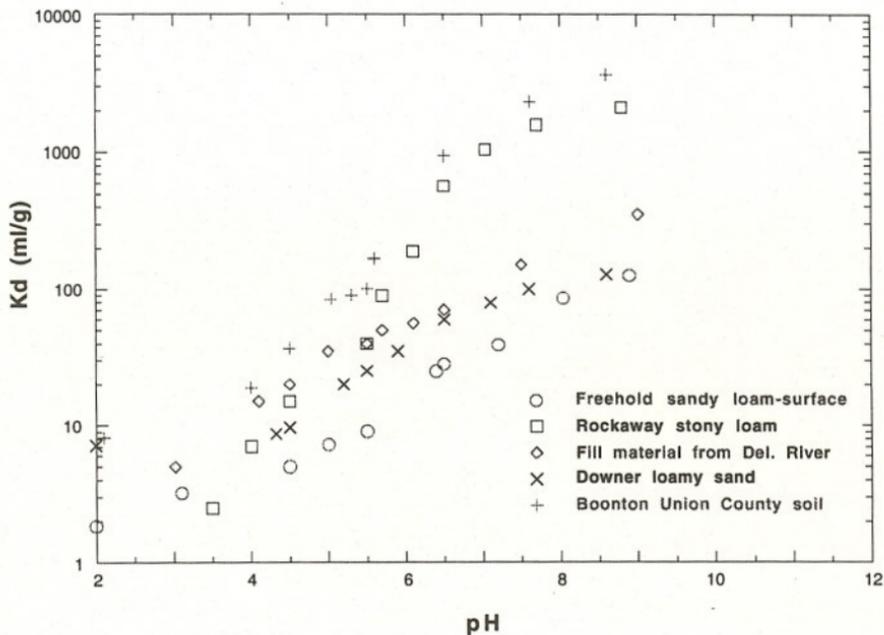


Figure 6.3. Partition coefficient (K_d) for 5×10^{-4} M cadmium. Soil:water = 1 g/100 mL; I = 0.01 M NaNO_3 ; T = 25 °C.

values that would have been obtained for batch equilibration of samples at the same pH as in the column measurements. We compared our batch K_d values to the results for the large field study of Anderson and Christensen (1988) who obtained their partition coefficients at the pH of the soils and with the naturally occurring concentrations of cadmium. The K_d values for our soils are comparable although our soluble cadmium concentrations are much greater (Figure 6.4). The strong dependency of partition coefficient on pH is shown in this figure.

6.3.2 Column Desorption

Desorption studies were carried out as a function of flow rate and initial cadmium concentration for the five New Jersey soils. An example of the two-part curve that was found for desorbed concentration vs. cumulative leaching volume is shown in Figure 6.5. (Curves for all experiments are shown in Appendix F). The first part of the curve is the portion with a steep decline in effluent concentration of cadmium (C_w) due to the flushing of the residual cadmium solution from pore water, the second part has a slower decline in C_w due to the desorption from the solids. The rate of release of cadmium from soil is dependent on transport and chemical processes. Sparks (1989) stated that effects of transport phenomena and chemical reactions are often experimentally inseparable. Apparent rate laws, including both chemical kinetics and transport-controlled processes, have usually been employed to treat these desorption data in dynamic systems. Skopp and Warrick (1974) stated that the apparent rate depends on water flux or other physical processes, and also usually assumes that either first- or zero-order kinetics is operational. Zero-order (linear) and first-order (exponential) kinetics were used as two boundary conditions to treat the desorption part of our data:

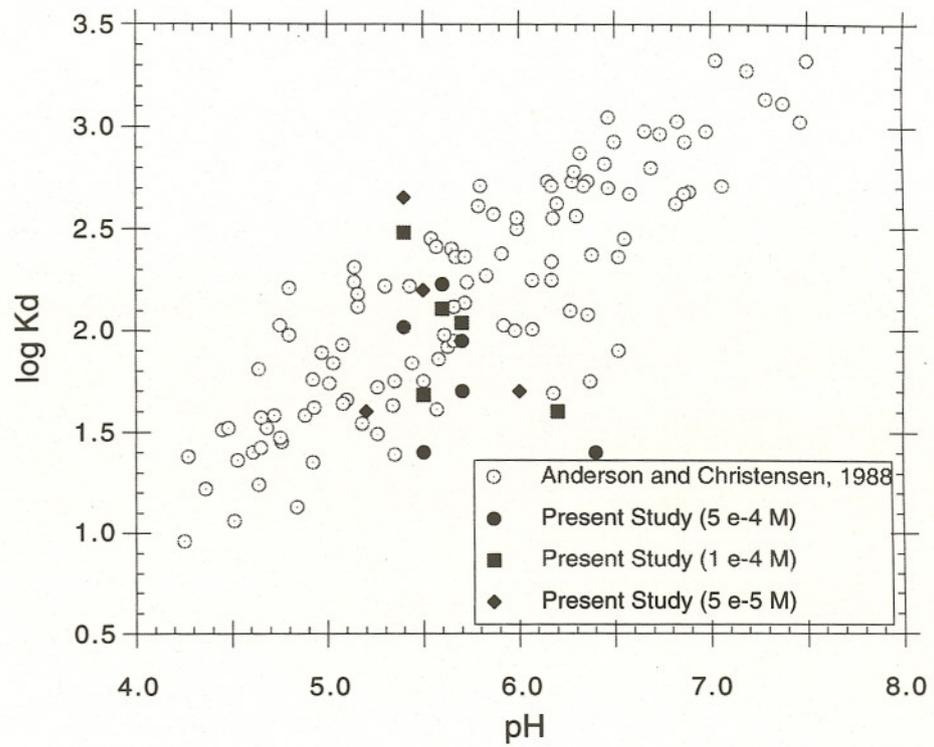


Figure 6.4. Relation of cadmium partition coefficients on soil to pH for the present study and that of Anderson and Christensen (1988).

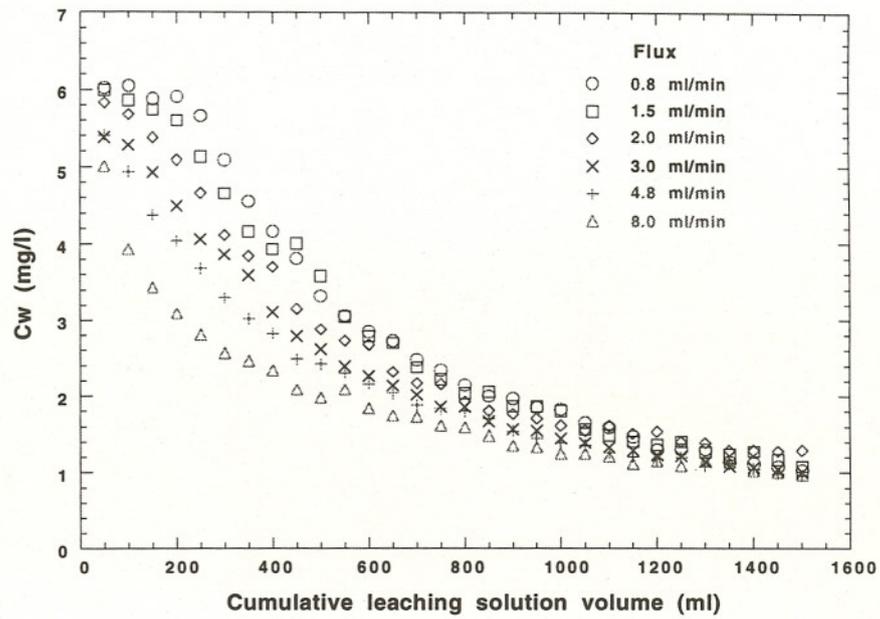


Figure 6.5. Desorption of cadmium at six fluxes from Rockaway stony loam equilibrated with 1×10^{-4} M cadmium; soil:water = 1 g/100 mL; I = 0.01 M NaNO₃; T = 25 °C.

Linear -

$$C_w = C_w^{\circ} - (k V) \quad (6.1)$$

Exponential -

$$C_w = C_w^{\circ} \exp(-k V) \quad (6.2)$$

where

C_w is the desorbed quantity of cadmium at volume V (mL),

C_w° is the apparent desorbed quantity of cadmium at zero volume (mL),

k is the rate coefficient (mg/L^2 for zero order or $1/L$ for first order), and

V is the cumulative volume (mL) which is proportional to time.

Results are shown in Figures 6.6 and 6.7 for the Downer loamy sand that had been equilibrated with 5×10^{-4} M cadmium. For each flow rate, the data were extrapolated to zero cumulative volume (zero time) using Equation 6.1 or 6.2, as appropriate, to obtain the zero-volume desorption concentration of cadmium (C_w°) for the initial volume of water passed through the column. The value of C_w° is a function of flow rate; as the flow rate increased, the desorbed cadmium concentration decreased.

Because the first part of the flushing of the residual cadmium solution cannot be clearly distinguished from the second part of curve (Figure 6.5), we investigated the effect of the choice of the volume range of the second part for the data analysis. Several initial volumes ranging from 300 to 600 mL were used as the starting point of the second part of the curve. The choice had only a slight effect on the value of C_w° .

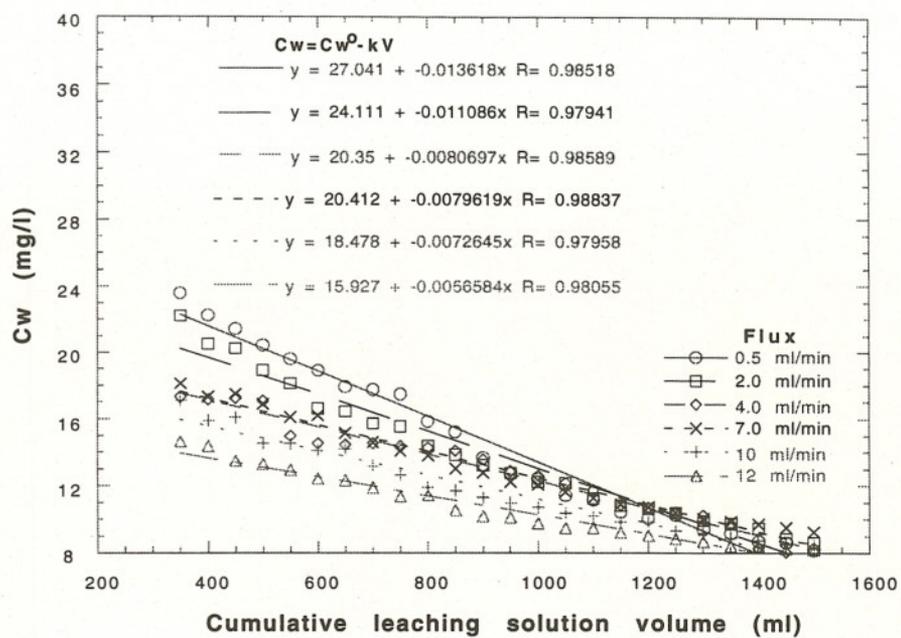


Figure 6.6. Linear extrapolation (zero order kinetics) for desorption of cadmium at six fluxes from Downer loamy sand that had been equilibrated with 5×10^{-4} M cadmium.

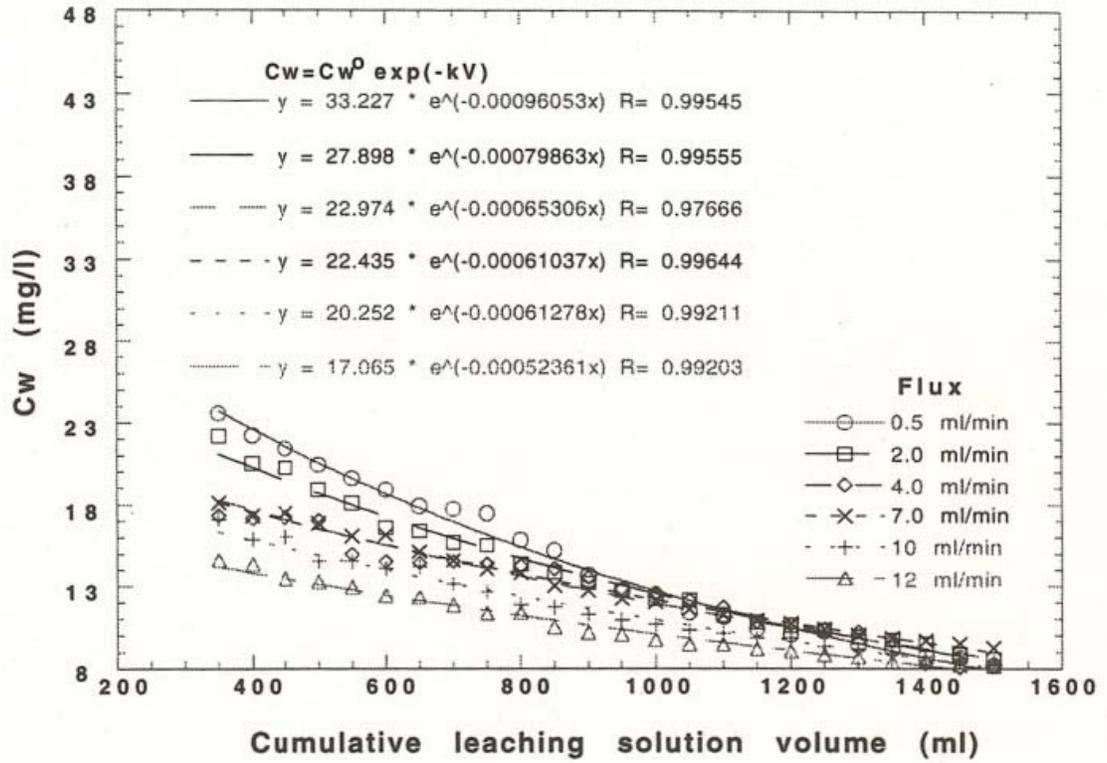


Figure 6.7. Exponential extrapolation (first order kinetics) for desorption of cadmium at six fluxes from Downer loamy sand that had been equilibrated with 5×10^{-4} M cadmium.

The zero-volume desorption concentrations of cadmium (C_w^0) were converted into apparent zero-volume partition coefficients (K_d^0) that are also a function of flow rate. The value of K_d^0 is determined by:

$$K_d^0 = \frac{C_s}{C_w^0} \quad (6.3)$$

where

C_s is the cadmium concentration in the soil ($\mu\text{g/g}$) as determined from the batch equilibrium, and

C_w^0 is the zero-volume desorption concentration of cadmium.

The apparent zero-volume partition coefficients were determined for the six different fluxes. The apparent zero-volume partition coefficients (K_d^0) increased with increasing flow velocity (Figure 6.8). The higher the K_d^0 value, the higher the amount of cadmium still bound by soil, because the higher flow velocity provided less contact time between the leaching solution and the soil, resulting in a lower desorption cadmium for a given volume of eluent.

In the second step of extrapolation, the zero-volume apparent partition coefficients were then extrapolated to zero flow rate. This procedure is shown in Figures 6.9 -6-23. The zero-volume, zero-flow rate desorption results were compared to those for the batch adsorption equilibrium at the same pH. A plot of the column desorption versus batch partition coefficients is shown in Figure 6.24 and the results are summarized in Table 6.1. The K_d value for the linear extrapolation is always greater than that for the K_d value from the exponential extrapolation. The slope for the linear relationship between the column desorption and batch equilibrium partition coefficients

for linear (slope = 0.93) and exponential (slope = 0.90) extrapolations are both near unity. Therefore, the equilibrium obtained for batch adsorption provides a good estimate of the value obtained for desorption of the cadmium contaminant in the dynamic systems.

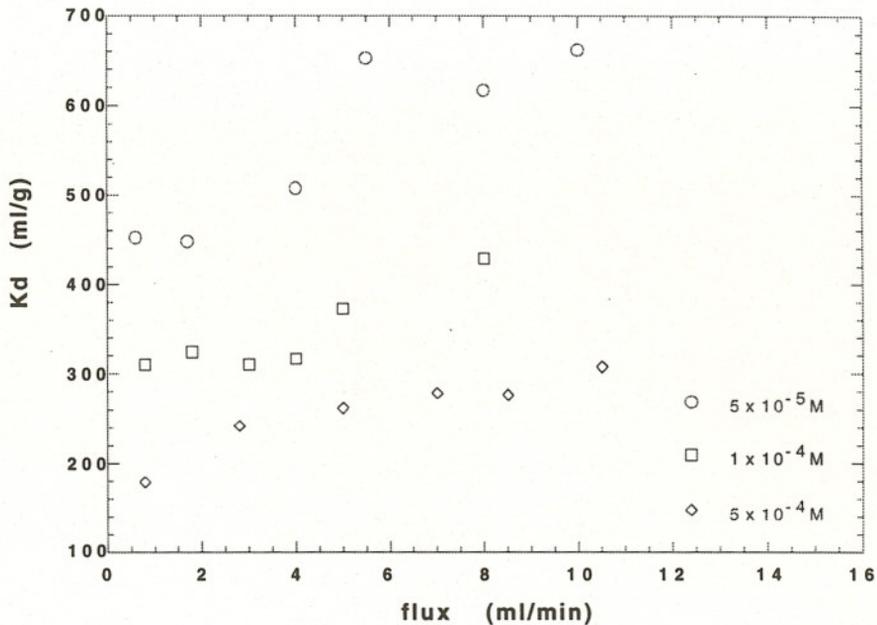


Figure 6.8. Comparison of partition coefficients for three initial cadmium concentrations using the linear extrapolation method for Boonton loan (Union County).

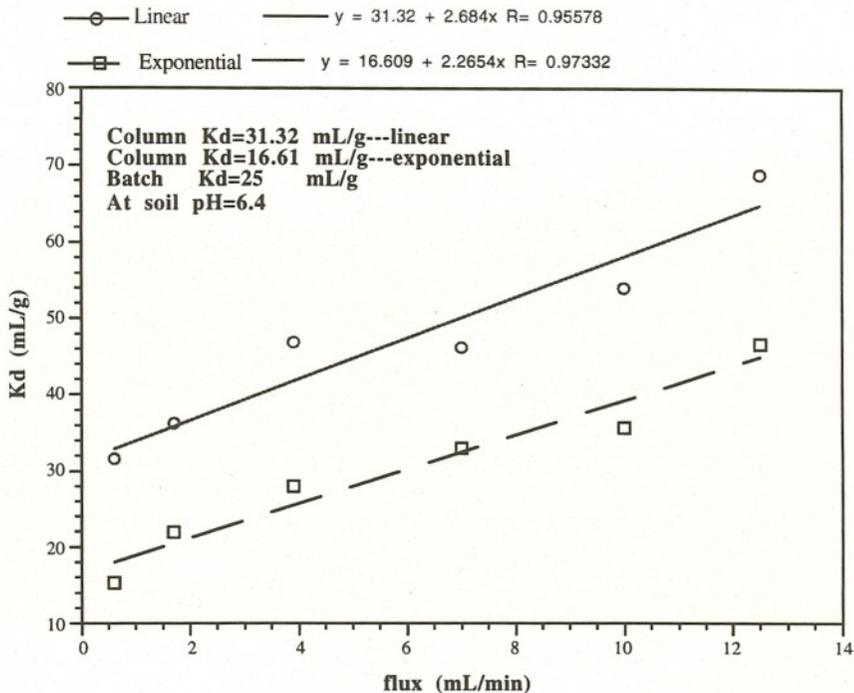


Figure 6.9 Dependence of zero-flow, apparent partition coefficients on flux. Results are for Freehold sandy loam (A horizon) that had been equilibrated with 5×10^{-4} M cadmium. Results are shown for both linear and exponential extrapolation from 300 mL cumulative leaching volume as the starting point of the second part of the curve.

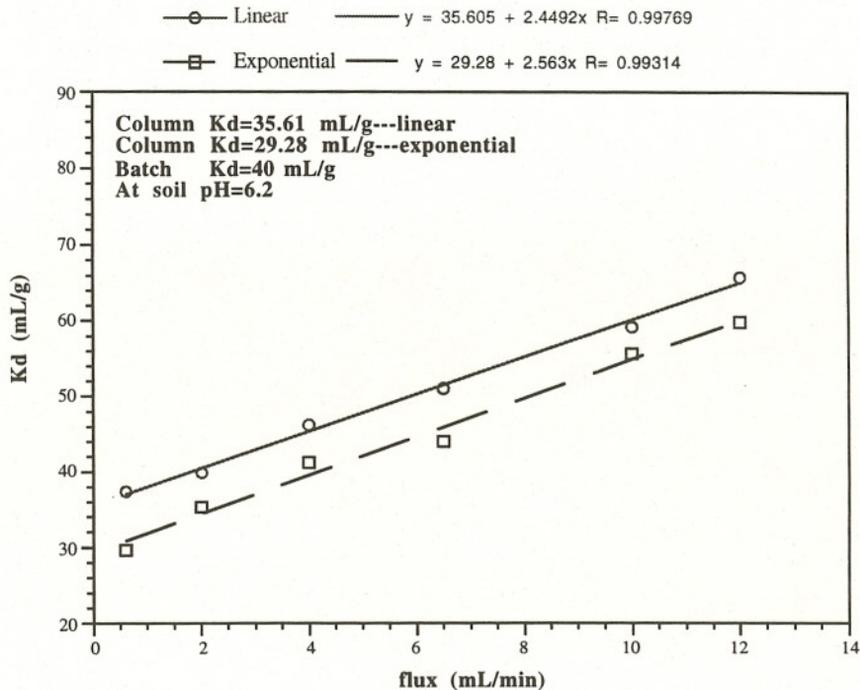


Figure 6.10 Dependence of zero-flow, apparent partition coefficients on flux. Results are for Freehold sandy loam (A horizon) that had been equilibrated with 1×10^{-4} M cadmium. Results are shown for both linear and exponential extrapolation from 300 mL cumulative leaching volume as the starting point of the second part of the curve.

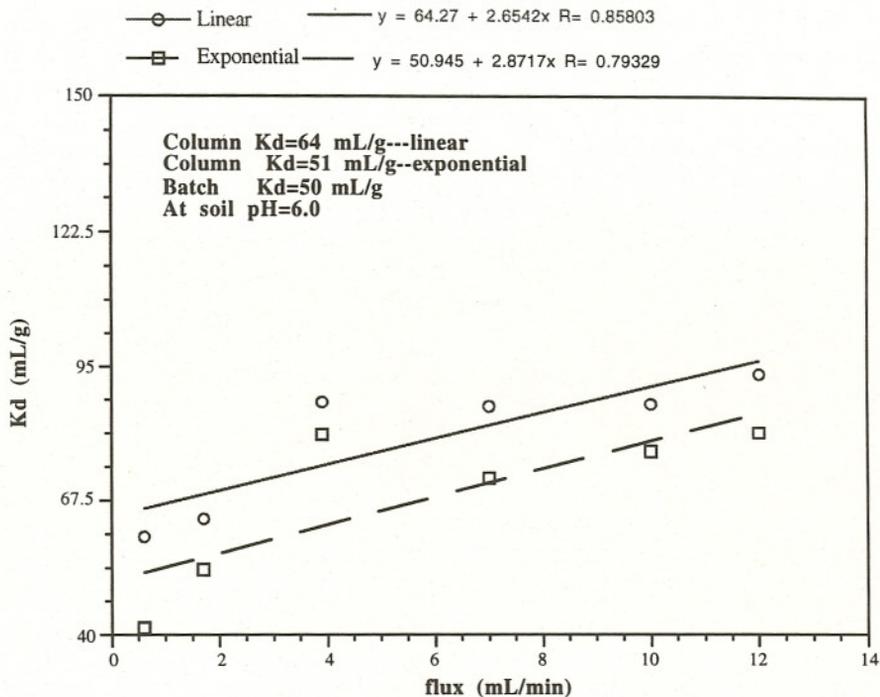


Figure 6.11 Dependence of zero-flow, apparent partition coefficients on flux. Results are for Freehold sandy loam (A horizon) that had been equilibrated with 5×10^{-5} M cadmium. Results are shown for both linear and exponential extrapolation from 300 mL cumulative leaching volume as the starting point of the second part of the curve.

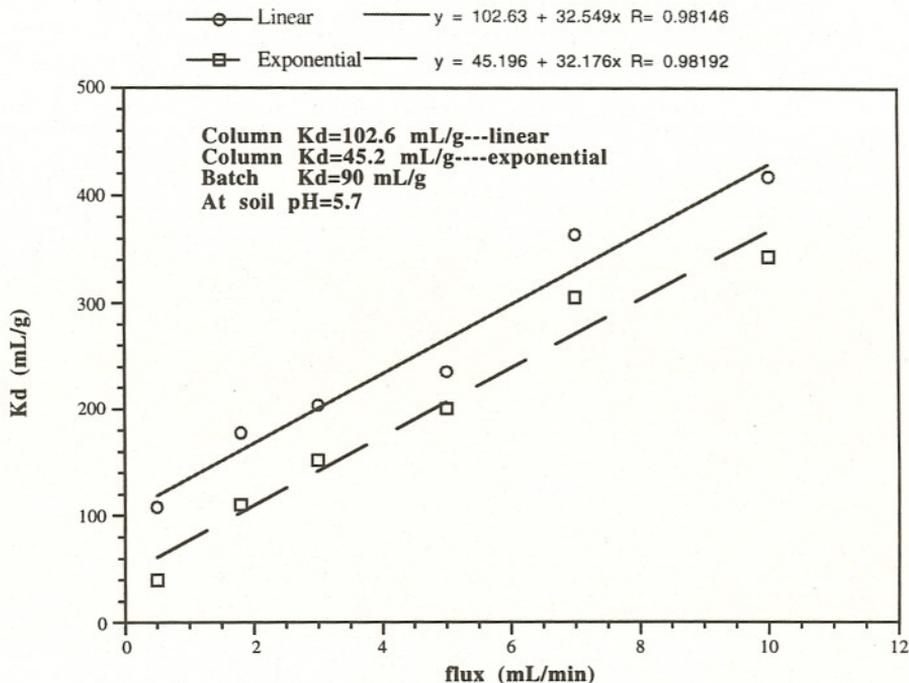


Figure 6.12 Dependence of zero-flow, apparent partition coefficients on flux. Results are for Rockaway stony loam that had been equilibrated with 5×10^{-4} M cadmium. Results are shown for both linear and exponential extrapolation from 500 mL cumulative leaching volume as the starting point of the second part of the curve.

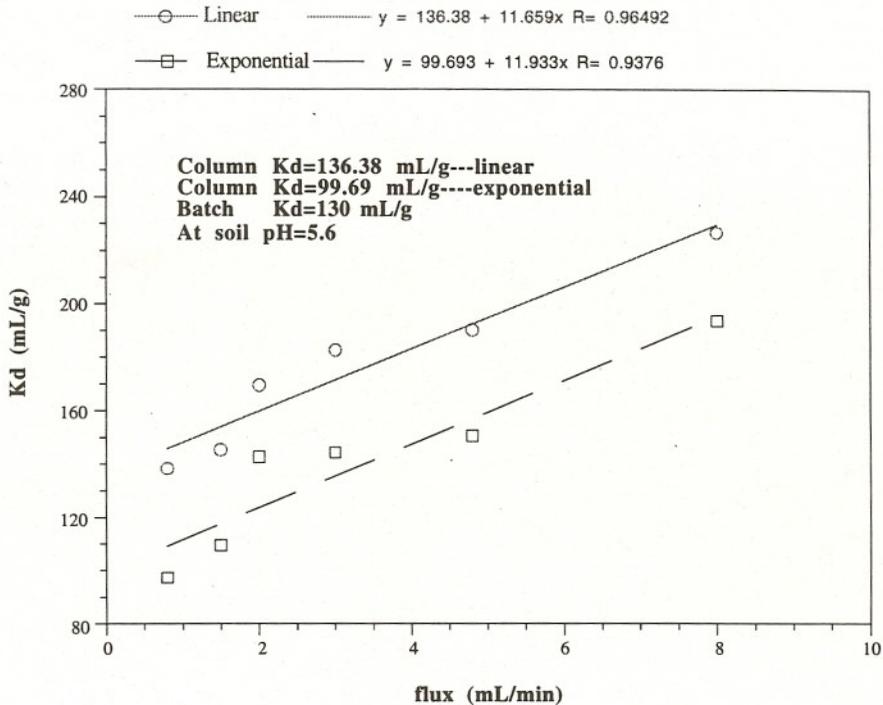


Figure 6.13 Dependence of zero-flow, apparent partition coefficients on flux. Results are for Rockaway stony loam that had been equilibrated with 1×10^{-4} M cadmium. Results are shown for both linear and exponential extrapolation from 500 mL cumulative leaching volume as the starting point of the second part of the curve.

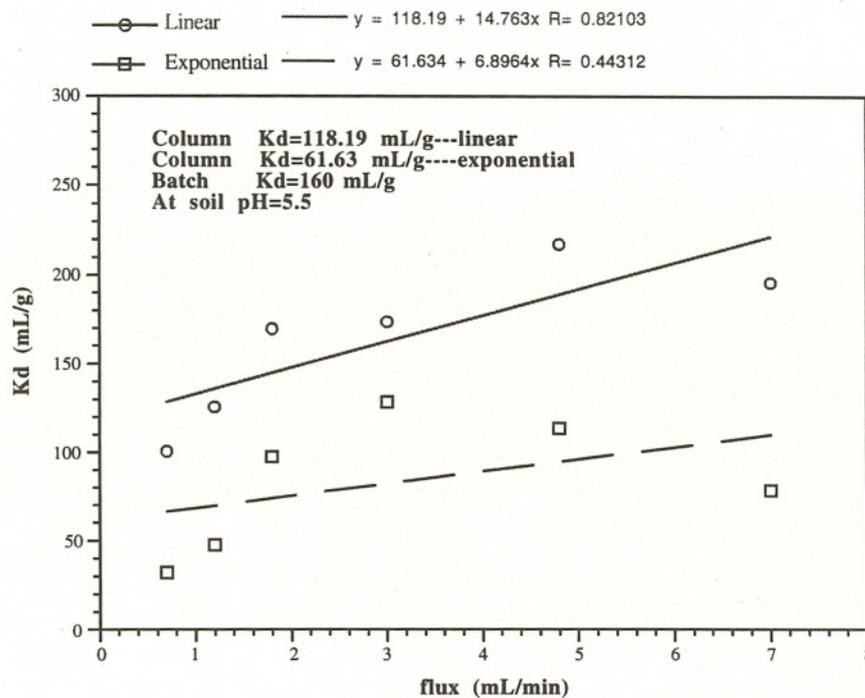


Figure 6.14 Dependence of zero-flow, apparent partition coefficients on flux. Results are for Rockaway stony loam that had been equilibrated with 5×10^{-4} M cadmium. Results are shown for both linear and exponential extrapolation from 500 mL cumulative leaching volume as the starting point of the second part of the curve.

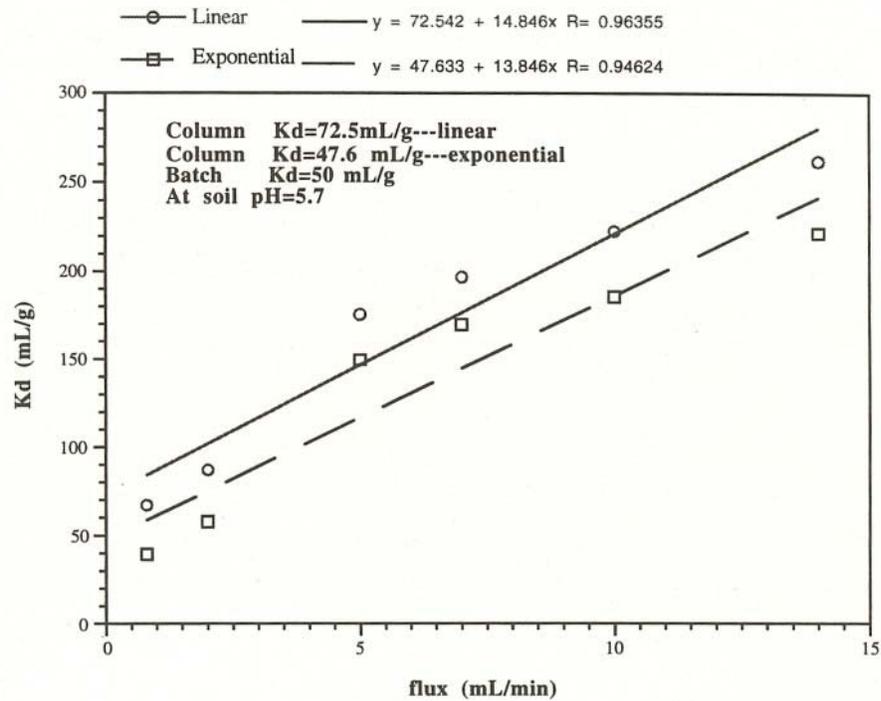


Figure 6.15 Dependence of zero-flow, apparent partition coefficients on flux. Results are for fill material from the Delaware River that had been equilibrated with 5×10^{-4} M cadmium. Results are shown for both linear and exponential extrapolation from 400 mL cumulative leaching volume as the starting point of the second part of the curve.

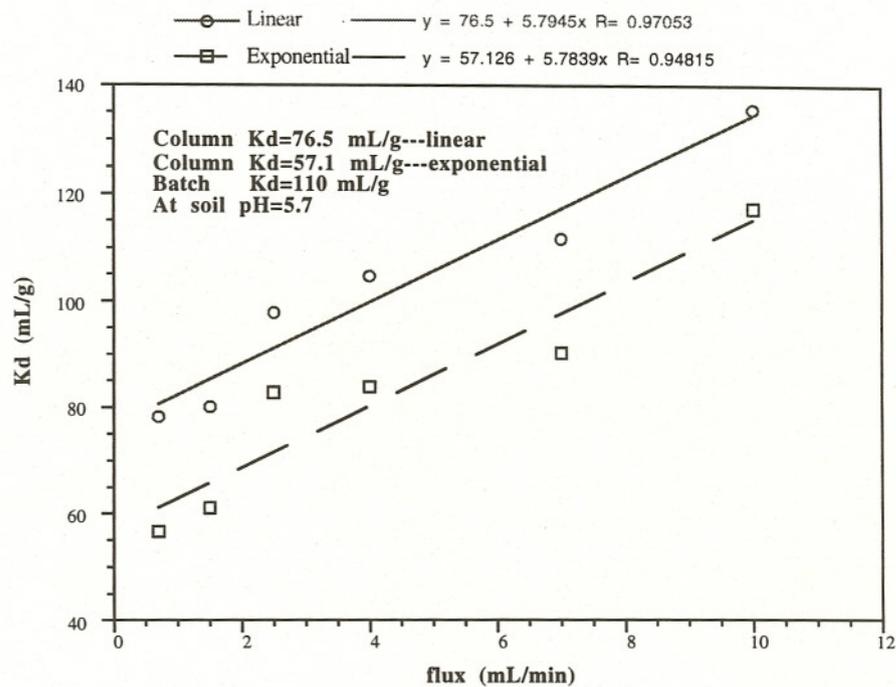


Figure 6.16 Dependence of zero-flow, apparent partition coefficients on flux. Results are for fill material from the Delaware River that had been equilibrated with 1×10^{-4} M cadmium. Results are shown for both linear and exponential extrapolation from 400 mL cumulative leaching volume as the starting point of the second part of the curve.

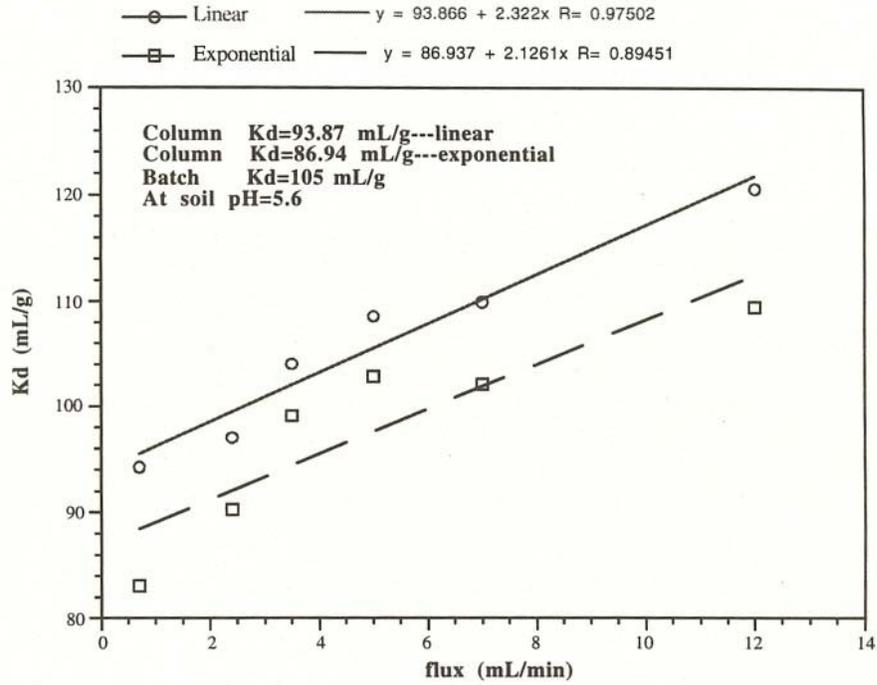


Figure 6.17 Dependence of zero-flow, apparent partition coefficients on flux. Results are for fill material from the Delaware River that had been equilibrated with 5×10^{-5} M cadmium. Results are shown for both linear and exponential extrapolation from 400 mL cumulative leaching volume as the starting point of the second part of the curve.

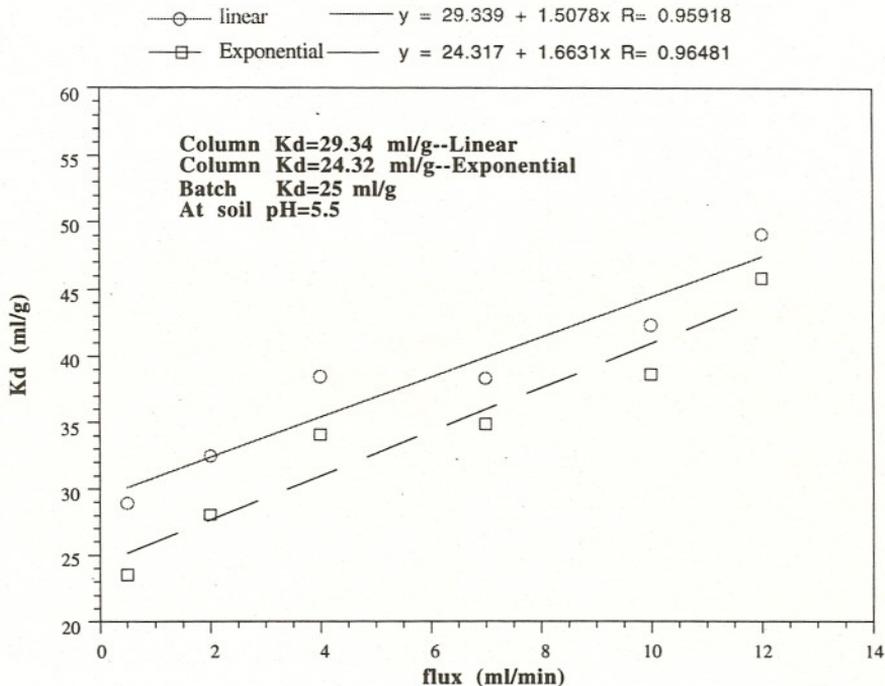


Figure 6.18 Dependence of zero-flow, apparent partition coefficients on flux. Results are for Downer loamy sand that had been equilibrated with 5×10^{-4} M cadmium. Results are shown for both linear and exponential extrapolation from 300 mL cumulative leaching volume as the starting point of the second part of the curve.

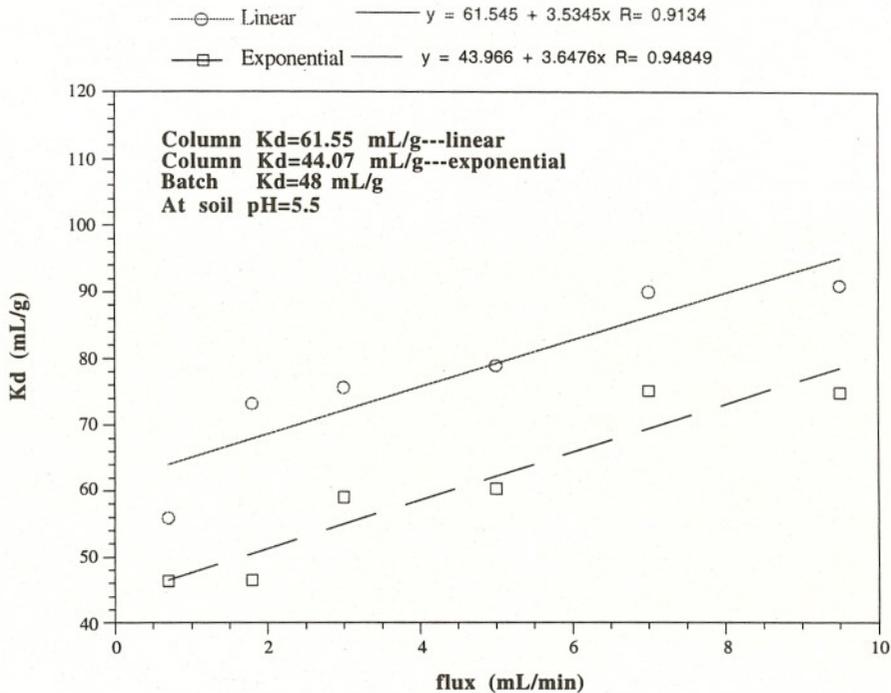


Figure 6.19 Dependence of zero-flow, apparent partition coefficients on flux. Results are for Downer loamy sand that had been equilibrated with 1×10^{-4} M cadmium. Results are shown for both linear and exponential extrapolation from 300 mL cumulative leaching volume as the starting point of the second part of the curve.

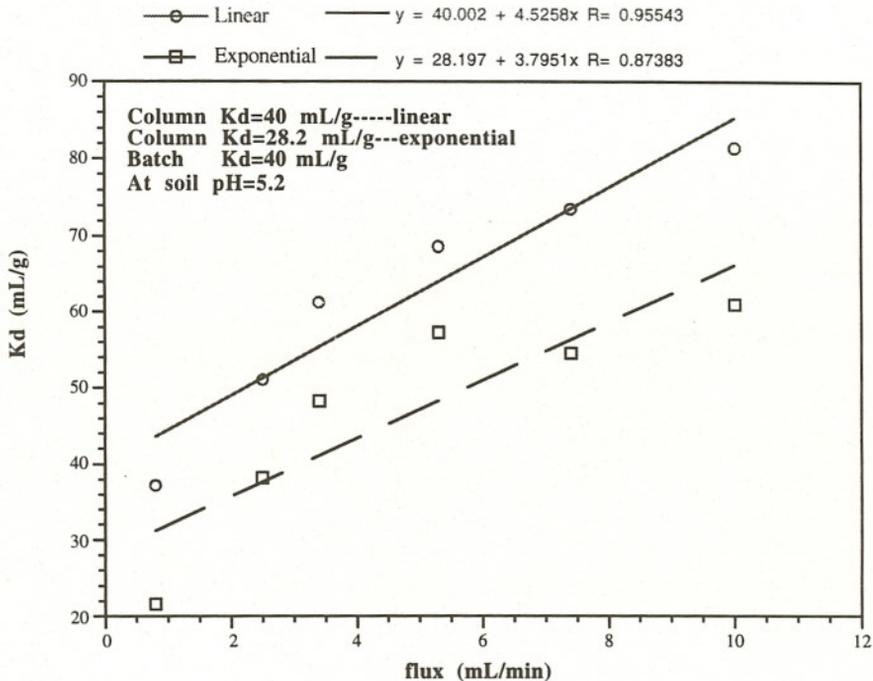


Figure 6.20 Dependence of zero-flow, apparent partition coefficients on flux. Results are for Downer loamy sand that had been equilibrated with 5×10^{-5} M cadmium. Results are shown for both linear and exponential extrapolation from 300 mL cumulative leaching volume as the starting point of the second part of the curve.

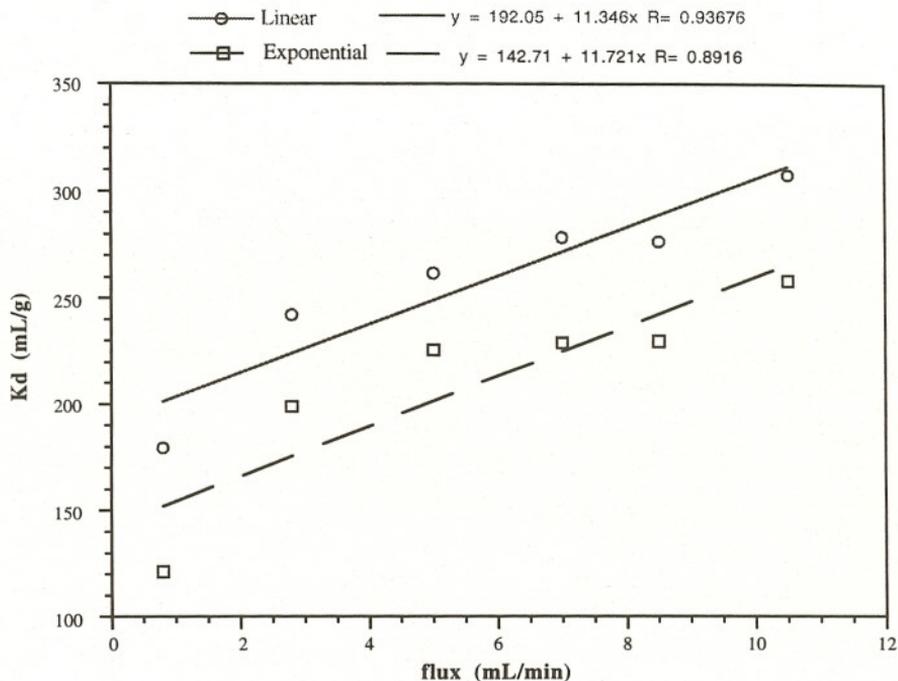


Figure 6.21 Dependence of zero-flow, apparent partition coefficients on flux. Results are for Boonton loam (Union County) that had been equilibrated with 5×10^{-4} M cadmium. Results are shown for both linear and exponential extrapolation from 500 mL cumulative leaching volume as the starting point of the second part of the curve.

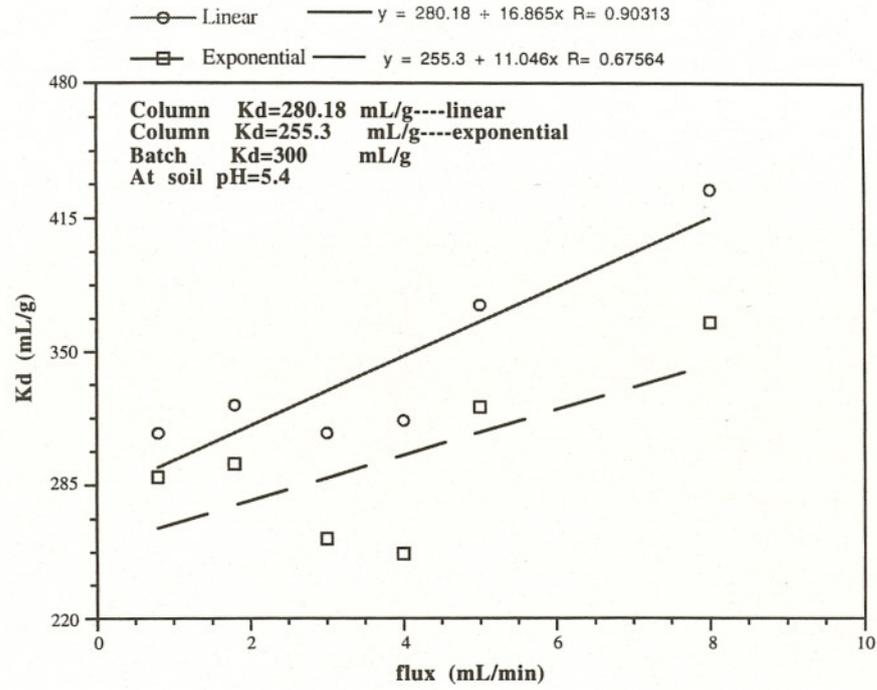


Figure 6.22 Dependence of zero-flow, apparent partition coefficients on flux. Results are for Boonton loam (Union County) that had been equilibrated with 5×10^{-4} M cadmium. Results are shown for both linear and exponential extrapolation from 500 mL cumulative leaching volume as the starting point of the second part of the curve.

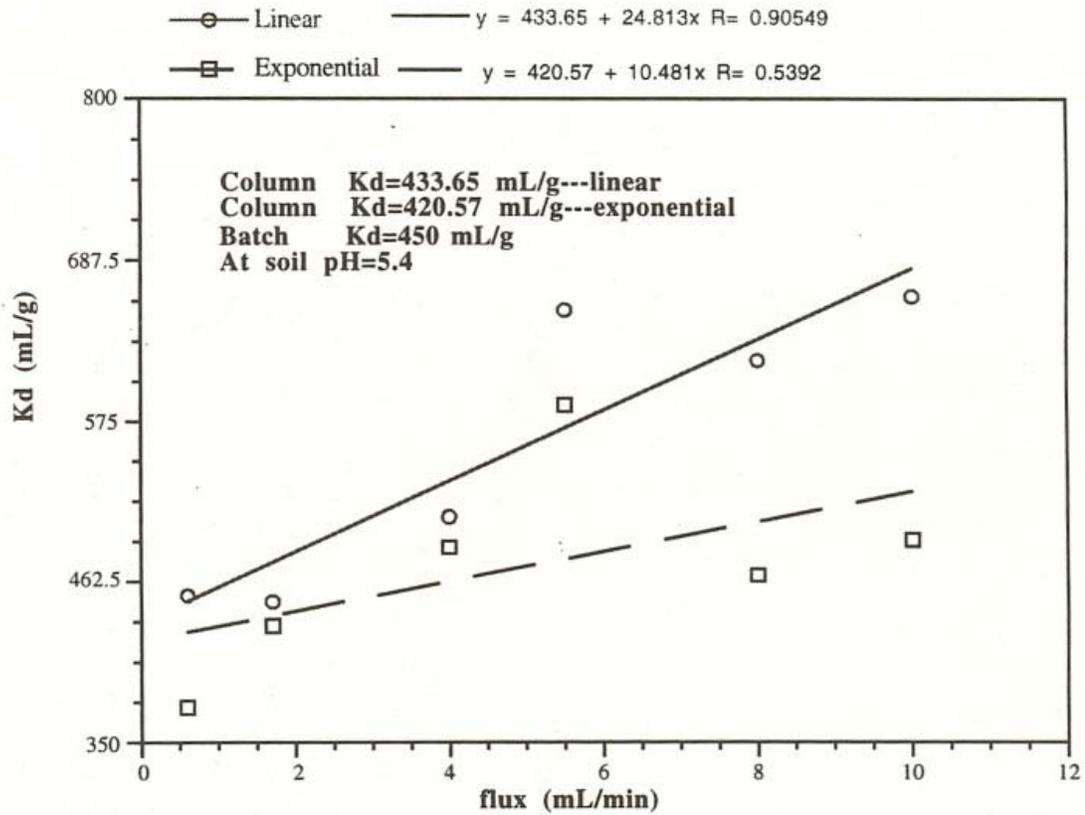


Figure 6.23 Dependence of zero-flow, apparent partition coefficients on flux. Results are for Boonton loam (Union County) that had been equilibrated with 5×10^{-5} M cadmium. Results are shown for both linear and exponential extrapolation from 500 mL cumulative leaching volume as the starting point of the second part of the curve.

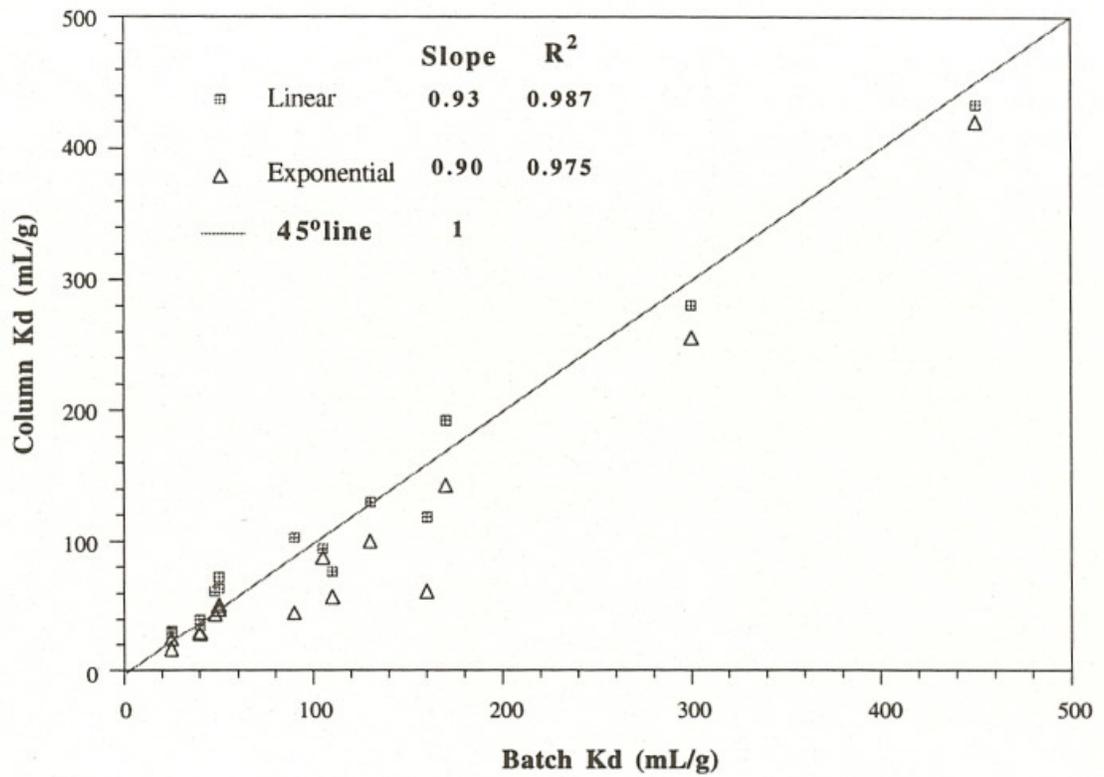


Figure 6.24 Correlation of cadmium partition coefficients from batch and column measurements.

Table 6.1 Summary of partition coefficients from batch and column flow measurements

Soil Name	Cd	Batch Kd	Column Kd (mL/g)		Volume*	pH
	(mol/L)	(mL/g)	Linear	Exponential	(mL)	
Freehold sandy loam (A horizon)	5×10^{-4}	25	31.32	16.61	300	6.4
	1×10^{-4}	40	35.61	29.28	300	6.2
	5×10^{-5}	50	64.27	50.94	300	6.0
Rockaway stony loam	5×10^{-4}	90	102.60	45.20	500	5.7
	1×10^{-4}	130	136.68	99.69	500	5.6
	5×10^{-5}	160	118.19	61.63	500	5.5
Fill material from Delaware R.	5×10^{-4}	50	72.54	47.60	400	5.7
	1×10^{-4}	110	76.50	57.13	400	5.7
	5×10^{-5}	105	93.67	86.94	400	5.6
Downer loamy sand	5×10^{-4}	25	29.34	24.32	300	5.5
	1×10^{-4}	48	61.55	44.07	300	5.5
	5×10^{-5}	40	40.00	28.20	300	5.2
Boonton loam (Union County)	5×10^{-4}	170	192.05	142.71	500	5.4
	1×10^{-4}	300	280.18	255.30	500	5.4
	5×10^{-5}	450	433.65	420.57	500	5.4

* Starting volume for the second part of the curve used for extrapolation

Chapter 7

CONCLUSIONS

This research was conceived as a basic study on the sorption of metal onto soils. The emphasis was on the rational understanding of the process.

A model for the sorption of metal by soil surface substances at fixed pH was developed. The results show that the conditional partition coefficients were highly correlated to the organic matter content at a fixed pH, i.e., the same proton concentration.

A methodology for the development of the maximum level of metal in soil for which the equilibrium soluble metal does not violate the Drinking Water Standard was developed. This methodology uses the results of the fixed pH sorption model. These metal criteria can be used as soil standards which will be protective of groundwater quality.

The major experiments designed to evaluate the sorption process included the alkalimetric titration of soil; metal sorption isotherms; and the effect of pH on adsorption. Important outcomes of the investigation are summarized in the following.

(1) Surface Acidity and Charge of Soil

The surface acidity of soils was determined by the alkalimetric titration method. The titration data were analyzed with a discrete multi-monoprotic acid model and a linear optimization programming technique to obtain the acidity constants and concentrations of ionizable sites. Microscopically, the surface of soil particles has ionizable groups which dissociate protons. The variation of surface charge results from the extent of this dissociation. The variable surface charge of soil varies with pH and increases with increasing pH. The values of pH_{zpc} ranged from 2.8 to 3.6. Due to the low pH_{zpc} values, soil particles are negatively charged over a wide pH range.

(2) The Modeling of Metal Adsorbed by Soil

The sorption of metal onto soil is hypothesized to occur by specific chemical reaction of metal ions with the charged functional groups. The surface complexation model that considers all metal hydrolysis species as adsorbates in an adsorption process was used to determine the stability constants of cadmium adsorbed onto soils. This model incorporates the effect of pH and can satisfactorily model the pH dependent sorption. Up to pH 9, free cadmium has the greatest contribution to the adsorbed complex.

(3) The Effect of pH on Sorption

Solution pH markedly affects the sorption of metal onto soils because of the high pH dependence of both the surface acidity and the hydration of the metal.

Typically, sorption of cationic metals by soil increased from near nil to near 100% as pH increased through a critical range 1-2 units wide.

(4) Soil Properties Significant for Metal Adsorption

At fixed pH, correlation analysis indicated organic matter content provides the most significant contribution to cadmium adsorption. The pK_a value from alkalimetric titration which is incorporated in the model that fits pH dependent adsorption is also well correlated with organic matter. As expected, the stability constant for free cadmium with soil is also correlated with organic matter. Additional contributions from hydrous metal oxides, particularly aluminum, are indicated.

(5) Relationship of Desorption to Adsorption Partition Coefficients

A double extrapolation method was developed to allow the results of metal desorption from soil under dynamic, column conditions to be related to adsorption values. For each flow rate, the results are extrapolated to that for zero time. These zero time partition coefficients are then extrapolated to zero flow. The zero time, zero flow desorption results are comparable to those for the batch adsorption equilibrium.

Despite the complex nature of soil, this research has successfully employed the surface complex formation model which has previously been used to describe the adsorption behavior of heavy metals on pure solid surfaces. The range of soil types chosen covered the spectrum of New Jersey soils. The success of the model indicates that it should be applicable to a similar range of soils in other locations. Modifications might be required for soils that are extremely alkaline with consequent high values of

pH_{zpc} . Clearly metal oxide components must be considered more extensively for soil with very low organic content. The methodology used here with identification of major contributions to surface acidity and of aqueous metal species should be generally applicable. The major contribution from this research will result in an improved description of the heavy metal adsorption process in any heterogeneous materials.

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